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ΣΗΜΕΙΩΣΗ: Την επιμέλεια του τεύχους είχε η Επιτροπή Εκδόσεων
(Απόφαση της 438/30/8.11.89 Δ.Ε. της Ε.Ε.Χ.)

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ANALYSIS OF HARD AND SOFT GREEK CHEESES PRODUCED IN EPIROS.

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SUMMARY

Results are reported on the analysis of eleven different varieties of Greek cheeses produced in the region of Epiros. Cheeses were analyzed for % fat, % protein, % moisture, macro elements (potassium, sodium, calcium, magnesium, phosphorus) as well as trace elements (copper, iron and zinc).

Variations in values of moisture, fat and protein were generally small with the exception of those of moisture and fat for Feta, Myzithra and Metsovella cheeses. Values of the above determinations are in accordance with the literature, with the exception of those for Kaseri cheese.

Values for Na and Ca showed significant variations. Values for K were generally lower while Mg and P values were in agreement with those published.

Values for Cu, Fe, Zn generally differed from respective published values while those for Fe and Zn showed significant variations.

Present results stress the need for standardization of several cheeses analysed.

Key words: Cheese analysis, fat, moisture, protein, elements.

INTRODUCTION

Cheese is the most important dairy product and is being produced in several hundreds of varieties today. Approximately 15% of the world production of milk is being used in cheese making. In 1979 world production of cheese reached 10,483,000 tons, production of cheese in the E.E.C. reached 3,256,000 tons, and production of cheese in Greece reached 165,000 tons¹.

In Greece the largest amount of cheese produced comes from goat's and sheep's milk. In 1980, 78% of sheep's milk went into cheese making and gave 97,929 tons of cheese, 67% of goat's milk gave 41,407 tons of cheese and the 26% of cow's milk gave 20,800 tons of cheese. During the

same year Greece imported 12,342 tons of cheese and exported 1,687 tons². Greece holds the first place in cheese consumption per capita (approx. 17 Kg/year) in the world, with France holding second place by a slight margin.

A large portion of the cheeses being produced in Greece comes from small, low capacity, family owned plants (approximately 200, only in Epiros) which do not have modern facilities or quality control inspection and therefore constantly face product standardization problems and occasionally even public health related problems.

The literature contains several reports on the composition of cheeses²⁻⁷.

This paper in which eleven different cheese varieties of Epiros were analyzed, has the objective to supply information on the composition of various Greek cheeses of Epiros, towards both a more effective quality control, and a better standardization of cheese products in relation to the export of Greek cheeses to countries of the E.E.C.

EXPERIMENTAL

The cheeses analyzed, were donated by the "DODONI" plant, the Tositsa foundation and various local manufacturers. All cheeses were produced between February and June 1984, to account for possible variations in the composition of milk from which they were made, and were all ripe at the time of analysis. Samples were collected from various parts of the cheese body using a cheese sampling knife and all were mixed to give the final sample.

In all samples, moisture, fat, protein and the elements: potassium, sodium, calcium, magnesium, phosphorus, copper, iron and zinc were determined. All samples were kept away from metal containers and spatulas to avoid iron and zinc contamination.

Duplicate -3 sample- analysis was carried out for each type of cheese. Classical methods of analysis were used to determine moisture, fat and protein⁸.

Fat and protein were calculated on a "as is" basis. Sodium and potassium were determined flame photometrically⁹ using a Coleman Model 21 flame photometer by the following procedure: After wet digestion using dilute nitric acid the sodium and potassium content was measured flame

photometrically.

The rest of the metals were determined by atomic absorption spectrophotometry⁹ using a Perkin Elmer model 560 A.A.S. by the following procedure: After wet digestion using concentrated sulfuric and nitric acid the residue was dissolved in dilute acid. The solution was sprayed into the flame of the A.A.S. instrument and the absorption of the metal was measured at the appropriate wavelength.

Phosphorus was determined spectrophotometrically⁹ using a Hitachi model 102 spectrophotometer by the following procedure: After wet digestion using concentrated sulfuric acid and concentrated nitric acid, during which all the phosphorus is converted to orthophosphoric acid, the phosphorus content was measured colorimetrically after reaction with ammonium molybdate and hydrazine in acid solution.

RESULTS AND DISCUSSION

In order to compare present data with that in the literature it is important to state the source of the milk used for the production of each cheese variety, as well as the type of each cheese produced to enable comparison to well known foreign cheeses. This information is given in Table I.

The cheese samples were of different production period and different supplier. Intercomparison of data is therefore difficult. Comparison of present data of cheeses to that of the same type of foreign cheeses is also difficult due to different milk sources and different cheese manufacturing practices.

Despite the above problems comparison was attempted both for standardization purposes of domestic cheeses as well as the establishment of a relationship between domestic and foreign cheeses of the same type.

Results for moisture, fat and protein are given in Table II.

Graviera, Kefalograviera and Metsovella cheeses are discussed together since they are similar. The values for Graviera and Kefalograviera generally agree with those in the literature^{2,7}. Metsovella is clearly a domestic cheese and references for comparison are not available. This cheese showed a relatively large variation in moisture and fat content a problem that should be overcome. All three of the above cheeses as compared to the Gruyere variety² show a higher moisture and lower protein

TABLE I: Cheese Varieties Analysed, their Milk Source and Types of International Cheese to which they are Similar.

Cheese variety	Source of milk	Type
Graviera (hard)	ewe's + possibly cow's	Gruyère
Kefalograviera (hard)	ewe's + possibly cow's	Gruyère
Metsovella* (hard)	cow's	Gruyère
Kefalotyri (hard)	ewe's + possibly cow's	Romano
Vlachotyri* (hard)	cow's	Romano
Pastorella* (hard)	cow's	Parmesan
"Dodoni type"*(hard)	ewe's + cow's	Tilsit, Brick
Kaseri (hard)	ewe's + possibly cow's	Provolone
Metsovone* (hard+smoked)	cow's	Parenica (Pasta Fillata)
Feta (soft - in brine)	ewe's + possibly cow's	Domiaty
Myzithra (whey cheese)	whey of hard cheeses+0-10 % milk	Ricotta

* Trade names

TABLE II: Moisture, Fat and Protein Content of Cheese Varieties Analyzed (g/100g product, on "as is" basis).

Cheese variety	% Moisture		% Fat		% Protein	
	Ave.	Range	Ave.	Range	Ave.	Range
Graviera	34.49 ± 0.55*	33.87 - 35.20	30.02 ± 1.3	27.55 - 31.50	26.52 ± 1.2	24.75 - 28.26
Kefalograviera	35.30 ± 1.0	34.00 - 37.00	32.18 ± 1.0	31.00 - 34.00	25.29 ± 0.7	24.20 - 26.09
Kefalotyri	36.88 ± 0.5	36.50 - 37.12	30.23 ± 0.9	28.93 - 31.50	25.91 ± 0.7	24.40 - 26.03
"DODONI" type	36.76 ± 0.6	36.00 - 37.80	30.66 ± 0.9	29.00 - 31.50	22.66 ± 1.9	19.05 - 24.95
Vlahotyri	38.83 ± 0.3	38.49 - 39.18	28.84 ± 0.03	28.81 - 28.88	24.67 ± 0.5	23.78 - 25.57
Pastorella	37.77 ± 0.3	37.43 - 38.12	29.06 ± 0.3	28.64 - 29.48	25.98 ± 0.3	25.49 - 26.48
Metsovella	38.15 ± 1.5	35.51 - 40.79	28.70 ± 1.7	26.27 - 31.14	26.47 ± 0.08	26.33 - 26.61
Metsovone	35.29 ± 1.5	32.83 - 37.76	29.82 ± 1.0	27.98 - 31.67	26.94 ± 0.3	26.64 - 27.25
Kaseri	45.63 ± 0.7	44.70 - 46.56	24.02 ± 0.3	23.49 - 24.56	25.35 ± 0.3	24.94 - 25.76
Feta	52.29 ± 2.8	47.00 - 55.60	25.01 ± 2.5	21.50 - 28.00	16.45 ± 1.0	15.12 - 17.99
Myzithra	68.95 ± 3.47	65.36 - 75.50	18.20 ± 3.8	12.00 - 23.09	9.00 ± 0.2	8.70 - 9.30

* Errors given are standard deviation of the mean for n=3 (n=pairs of samples analyzed)

content while fat content is of the same level.

Kefalotyri shows a somewhat higher moisture and protein content as compared to literature data² while no references are available for Vlachotyri which is also a local cheese similar to Kefalotyri. Both cheeses, as compared to the Romano variety² show a slightly higher moisture and fat content but a lower protein content.

There are also no references for Pastorella which is a local cheese. As compared to Parmesan² it shows a somewhat higher moisture and fat content but a lower protein content.

The "Dodoni type" cheese (special variety) as compared to the similar cheese Graviera⁷ shows a somewhat higher moisture and lower protein content, while in relation to the Brick type shows a somewhat lower moisture and higher protein content.

Kaseri values for moisture and fat were higher and lower respectively to those in the literature². Values for the Metsovone variety are in accordance with other references². This cheese variety is very similar in composition to the also smoked Parenica variety².

Feta values for moisture and fat generally agree with published data. Protein values are however lower than respective ones in the literature^{2,7}. It also shows lower protein content as compared to the Domiat type².

Feta values for moisture, fat and protein show a relatively large variation which can possibly be attributed to its different suppliers (cheese plants).

Myzithra showed large variations in moisture and fat content, high fat and low protein content as compared to the literature^{2,7}. In relation to Ricotta² its moisture content is approximately the same while its fat is significantly higher and its protein lower.

Variations in moisture and fat content of Myzithra can be explained by the addition /or not of milk or cream to the whey (raw material for Myzithra production).

It can be generally observed that for several of the cheeses analyzed, protein content was lower while moisture content was higher than expected. These variations stress the need for better standardization practices.

Results for Na, Ca, Mg and P are given in Table III.

TABLE III: Macro-element Content of Cheese Varieties Analyzed (mg/100g product, on "as is" basis).

Cheese variety	Na		K	
	Ave.	Range	Ave.	Range
Graviera	506.8 ± 168.9*	260.3 - 742.5	58.5 ± 21.2	31.2 - 87.4
Kefalograviera	861.2 ± 111.5	656.6 - 988.2	43.9 ± 15.3	28.1 - 62.7
Kefalotyri	982.3 ± 201.4	627.8 - 1350.2	54.8 ± 10.8	36.9 - 67.9
"DODONI" type	502.1 ± 142.8	363.0 - 749.6	54.4 ± 8.5	38.9 - 63.9
Vlahotyri	1147.4 ± 138.3	944.7 - 1350.0	52.4 ± 2.5	49.5 - 55.2
Pastorella	800.0 ± 90.5	690.0 - 909.9	37.1 ± 0.8	36.0 - 38.2
Metsovella	774.8 ± 115.2	609.5 - 940.0	72.9 ± 12.1	56.9 - 88.8
Metsovone	904.5 ± 2.7	900.5 - 908.5	52.2 ± 0.21	52.0 - 52.5
Kaseri	357.5 ± 82.7	243.4 - 471.5	40.3 ± 10.5	27.0 - 53.6
Feta	690.6 ± 171.6	482.3 - 1041.0	38.6 ± 11.8	17.9 - 51.4
Myzithra	107.8 ± 55.4	50.4 - 208.6	71.7 ± 25.2	33.0 - 94.9

* Errors given are the standard deviation of the mean for n=3 (n=pairs of samples analyzed)

TABLE III (cont'd): Macro-element Content of Cheese Varieties Analyzed (mg/100g product, on "as is" basis)

Cheese variety	Ca		Mg		P	
	Ave.	Range	Ave.	Range	Ave.	Range
Graviera	490.3 ± 218.4*	211.0 - 875.6	41.8 ± 10.2	27.0 - 52.4	488.3 ± 119.8	286.1 - 629.2
Kefalograviera	500.9 ± 71.7	401.9 - 619.2	41.1 ± 2.6	38.3 - 45.2	516.6 ± 33.4	468.1 - 575.8
Kefalotyri	563.5 ± 75.0	455.8 - 657.9	48.9 ± 2.5	46.1 - 53.7	551.3 ± 8.7	538.1 - 564.4
"DODONI" type	416.9 ± 162.5	242.5 - 720.4	32.9 ± 2.7	28.9 - 36.1	484.1 ± 52.8	424.2 - 571.8
Vlahotyri	638.5 ± 101.4	477.0 - 800.0	42.4 ± 3.1	36.2 - 48.7	508.1 ± 16.9	486.0 - 530.2
Pastorella	369.9 ± 53.8	299.7 - 440.0	30.1 ± 0.4	29.8 - 30.4	448.6 ± 5.4	440.7 - 456.6
Metsovella	491.6 ± 65.2	380.0 - 603.3	37.3 ± 0.8	36.4 - 38.3	487.1 ± 23.5	453.9 - 520.3
Metsovone	334.0 ± 2.7	330.0 - 338.0	27.6 ± 0.4	28.6 - 27.6	443.5 ± 6.8	433.9 - 453.1
Kaseri	441.5 ± 83.1	318.0 - 564.9	38.7 ± 0.8	37.6 - 39.8	533.2 ± 11.8	515.9 - 550.6
Feta	163.9 ± 55.5	74.5 - 216.6	11.8 ± 2.4	8.9 - 14.7	212.2 ± 35.1	175.1 - 273.0
Myzithra	59.9 ± 4.1	52.0 - 64.0	11.9 ± 3.6	5.6 - 14.8	107.0 ± 34.8	56.2 - 154.3

*Errors given are the standard deviation of the mean for n=3 (n=pairs of samples analyzed)

It is dangerous to attempt comparison of Na content values because the amount of NaCl being used varies significantly from batch to batch due to lack of method of standardization. This is supported by variations in Na values between cheeses of the same variety (except Metsovone).

Na content is generally lower in cheeses analyzed compared to the literature^{2,7} indicative of a consumer preference to less salted cheeses.

Values for Ca also vary, depending on the amount of CaCl₂ being used in cheese production.

Values for K are generally lower than those mentioned in the literature⁶ and can be attributed to the following two reasons a) to the different method of analysis, flame photometry vs. atomic absorption b) to possible use of potassium sorbate (allowed preservative) which can be responsible for change in K content.

Values for Mg and P are in general agreement with those in the literature⁶.

Results for Cu, Fe and Zn are given in Table IV.

Values generally differ than those in the literature⁶. Zn and Fe values are generally lower than published values⁶ showing in many cases significant variations. Cu values are higher than those in the literature⁶, but show no significant variations.

The above can be attributed to the variety of milk sources used in cheese production, to the differences in cheese production methods as well as to differences in animal feeds.

It is concluded that present data comprise a valuable reference source for nutrition aware consumers, as well as for cheese manufacturers in their effort to achieve a better quality product through standardization, in view of large Greek cheese exports to countries on the European Economic Community.

ΠΕΡΙΛΗΨΗ

ΑΝΑΛΥΣΗ ΣΚΛΗΡΩΝ ΚΑΙ ΜΑΛΑΚΩΝ ΤΥΡΙΩΝ ΤΗΣ ΗΠΕΙΡΟΥ

Στην εργασία αυτή παρουσιάζονται τα αποτελέσματα ανάλυσης έντεκα ποικιλιών Ελληνικών τυριών της περιοχής Ηπείρου. Στα τυριά προσδιορίστηκαν το λίπος, οι πρωτεΐνες, η υγρασία, τα μακρο στοιχεία (κάλιο, νάτριο, ασβέστιο, μαγνήσιο και φωσφόρος) καθώς και τα ιχνοστοιχεία (χαλκός, σί-

TABLE IV: Trace Element Content of Cheese Varieties Analyzed ($\mu\text{g}/100\text{g}$ product, on "as is" basis)

Cheese variety	Cu		Fe		Zn	
	Ave.	Range	Ave.	Range	Ave.	Range
Graviera	669.2 \pm 85.3*	542.1 - 796.2	2209.9 \pm 670.1	1453.0 -3656.9	3892.6 \pm 912.1	2053.0-5095.5
Kefalograviera	539.2 \pm 6.8	528.8 - 549.5	2956.9 \pm 320.3	2413.5 -3449.8	3175.1 \pm 614.0	1842.8-3860.6
Kefalotyri	626.1 \pm 86.1	495.5 - 756.8	2665.5 \pm 440.6	1984.0 -3522.5	3526.1 \pm 753.8	1984.7-4530.5
"DODONI" type	540.5 \pm 71.1	426.9 - 653.8	2914.8 \pm 581.8	1835.7 -3679.8	3251.4 \pm 605.2	1993.6-4063.6
Vlahotyri	472.0 \pm 117.6	295.3 - 648.7	2046.5 \pm 382.0	1338.7 -2754.4	3785.1 \pm 30.5	3702.4-3867.8
Pastorella	571.6 \pm 58.8	488.3 - 654.9	2893.4 \pm 336.8	2451.5 -3535.2	3656.9 \pm 62.2	3446.0-3867.8
Metsovella	696.7 \pm 33.6	641.9 - 751.6	2071.8 \pm 222.3	1763.7 -2379.9	3742.1 \pm 61.8	3652.7-3831.5
Metsovone	746.5 \pm 72.0	650.0 - 842.9	2350.4 \pm 68.7	2290.8 -2410.0	4655.8 \pm 313.7	4155.0-5156.7
Kaseri	532.5 \pm 79.5	414.5 - 650.5	1920.2 \pm 631.7	926.3 -2914.1	2987.5 \pm 608.7	1971.8-4003.3
Feta	439.3 \pm 84.9	325.2 - 553.4	2648.4 \pm 752.2	1202.3 -4085.3	1894.0 \pm 642.6	1450.7-2244.1
Myzithra	398.3 \pm 67.2	293.9 - 502.8	3288.2 \pm 293.4	2705.8 -3870.5	1189.4 \pm 382.0	450.0-1687.6

*Errors given are the standard deviation of the mean for n=3 (n=pairs of samples analyzed)

δηρος και ψευδάργυρος).

Οι διακυμάνσεις στις τιμές της υγρασίας, λίπους και πρωτεϊνών ήταν γενικώς μικρές με εξαίρεση εκείνες της υγρασίας και του λίπους για τη Φέτα, τη Μυζήθρα και τη Μετσοβέλλα. Οι ευρεθείσες τιμές βρίσκονται σε συμφωνία με εκείνες της βιβλιογραφίας με εξαίρεση εκείνων για το Κασαίρι.

Οι τιμές του Na και Ca παρουσίασαν σημαντικές διακυμάνσεις. Οι τιμές του K ήταν γενικώς χαμηλότερες, ενώ οι τιμές του Mg και P ήταν παραπλήσιες εκείνων της βιβλιογραφίας.

Οι τιμές του Cu, Fe, Zn παρουσίασαν διαφορές απο εκείνες της βιβλιογραφίας, ενώ οι τιμές για τον Fe και Zn παρουσίασαν σημαντικές διακυμάνσεις.

Τα αποτελέσματα της παρούσας εργασίας ενισχύουν την άποψη της ανάγκης τυποποίησης των Ελληνικών τυριών που αναλύθηκαν.

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SHORT PAPER

DETERMINATION OF MERCURY IN SURFACE WATER AND SEDIMENT BY ATOMIC EMISSION SPECTROSCOPY

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INTRODUCTION

The problem of the environmental pollution with mercury and its determination in low concentration in a variety of samples has been discussed in a number of papers¹⁻⁵. The mercury content in waters has been determined by means of different methods: polarography, photometry, colorimetry, emission-spectroscopy, atomic-absorption and neutron-activation.

In the present paper the results from the study on the possibility to determine the mercury in water and sediment samples from the river Strimon are discussed. Two different methods are used: direct atomic emission spectroscopy (AES) and determination after pre-concentration on PbS.

EXPERIMENTAL

Apparatus and reagents

1. $1 \cdot 10^{-3} \text{ g} \cdot \text{mL}^{-1}$ standard mercury solution (Hoppcin Williams Ltd).
2. Conc. HNO_3 , p.a., (Merck)
3. 0.1 M Na_2S solution, prepared by dissolution of Na_2S p.a. (Reachim, USSR).
4. 0.1 M $\text{Pb}(\text{CH}_3\text{COO})_2$ solution, prepared by dissolution of $\text{Pb}(\text{CH}_3\text{COO})_2$, p.a. (Tchervena svezda, Bulgaria).
5. Iron chamber electrodes-fig 2.
6. Mercury evaporation system-fig 3.
7. Atomic emission spectrograph PGS-2 (Carl Zeiss, Iena, DDR).
8. ORWO WU-2 photographic plates.
9. R-09 developer.
10. Zeis D-4 rapid micrometer.

Sampling

Water and sediments were sampled from the river Strimon in the territory of Bulgaria (four points) and Greece (four points) as it is shown in fig 1. The sampling stations B-1 and B-3 are located at industrial areas, while B-2, B-4, G-1, G-2, G-3 and G-4 are not located



FIG. 1: Map showing the sampling stations along Strimon River.

nearby any industrial center; however, the sampling stations G-2 and G-3 are at places, where two tributary rivers flowing through industrial areas join the river Strimon. The samples have been collected every two months for two years 1984 and 1985.

0.5-1 l water samples were taken in polyethylene bottles. In order to decrease adsorption on the walls, the samples were acidified with HNO_3 to $\text{pH}=1$ in the moment of sampling. Before analysis the samples were filtered using $0.45\mu\text{m}$ cellulose nitrate filters.

Sediment samples were taken just below the water layer in polyethylene bottles as well. In the laboratory they were dried to $60\text{-}80^\circ\text{C}$.

Isolation and preconcentration of mercury from the water samples

Coprecipitation with PbS has been used to isolate and preconcentrate the mercury from the water samples. For this purpose simultaneously 10ml $\text{Pb}(\text{CH}_3\text{COO})_2$ and 10ml Na_2S were added. Under these conditions $0.2\text{-}0.5\text{g}$ of PbS residue was formed, which included also the water impurities. It was heated to boiling point, the clear solution was discarded and dried to 80°C . Then it was again quantitatively transferred to the iron chamber electrode and the AES measurement was carried out.

DETERMINATION OF MERCURY IN SURFACE WATER AND SEDIMENT BY ATOMIC EMISSION SPECTROSCOPY

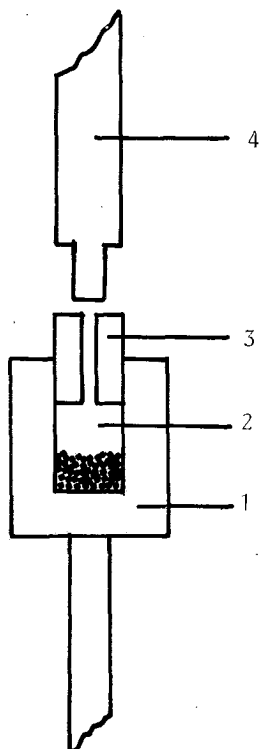


FIG. 2: *Iron chamber electrodes: 1-body, 2-chamber, 3-carbon electrode, 4-carbon counter electrode.*

Isolation and preconcentration of mercury from the sediment samples

Certain quantity of the sediment sample (1-5g) was placed into a vessel-fig 2, and was heated at 450-500°C. The mercury vapours were carried with a stream of air and retained quantitatively on PbS. The exact conditions of the experiment have been studied earlier⁶⁻⁸. PbS then was transferred to an iron chamber electrode and AES analysis has been performed.

Direct determination of mercury in sediment samples

In all sediment samples the possibility for direct AES determination has been checked. 0.2-0.4g of the sediment sample was put into the iron chamber electrode which was closed with a carbon electrode. Experimentally was proved that the procedure used⁸ for the mercury determination in soils may be used for sediment samples as well. The optimised conditions were: current intensity of the arc-12A, slitwidth-0.025mm, 102 s exposition time, registration of the spectrum on ORWO WU-2 plates, 5min development time with

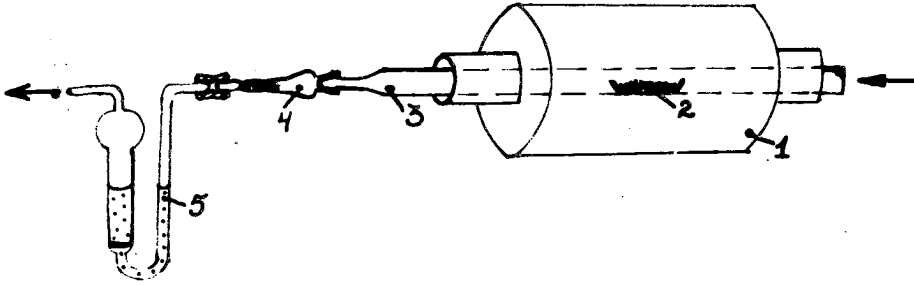


FIG. 3: System for evaporation of mercury from sediment samples and its concentration on PbS: 1-furnace, 2-vessel with sample, 3-glass tube, 4-column, containing the sorbent PbS, 5-U shaped vessel, containing solution of KI and I₂ controlling the stream of air and the completeness of the process.

R-09 developer and measurement of the 243.6nm line of mercury. The calibration curve (fig. 4.b) was obtained by analysis of soil samples containing known quantities of mercury.

AES-determination of mercury, concentrated on PbS

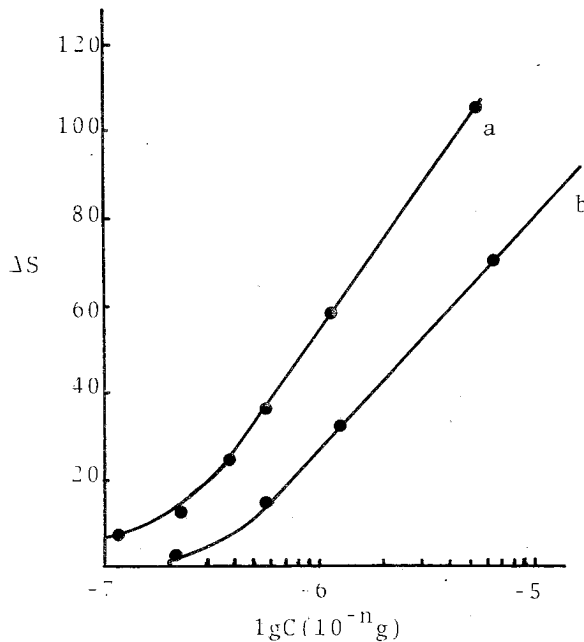


FIG. 4: Calibration curve: a. standard samples of PbS, b. standard soil samples.

DETERMINATION OF MERCURY IN SURFACE WATER AND SEDIMENT BY ATOMIC EMISSION SPECTROSCOPY

The AES determination of mercury in the PbS is performed under the same conditions as the direct determination, described in V. The calibration curve (fig. 4.a) was obtained by measuring standard PbS samples containing known quantities of mercury.

Results and Discussion

The results of the analysis are presented in Table I. In the Table the average values, $n=5$, taken throughout the whole experimental time, can be seen. It was noticed, that there was no seasonal variation of the mercury content in all of the sampling stations.

The limit of determination for the direct atomic emission spectroscopy was $0.8\mu\text{g/g}$, with relative standard deviation (RSD) 6%.

The limit of determination after preconcentration of mercury on PbS was $0.1\mu\text{g}$ of mercury, preconcentrated on 0.2-0.4g of lead sulphide, with RSD 8%.

TABLE I: Mercury content in water and sediment samples from the river Strimon.

Sampling place	Content of Mercury		
	in water ($\mu\text{g/l}$) After preconcentration	Direct AES	in sediment ($\mu\text{g/g}$) After Preconcentration
B*-1	0.4	1.5	1.4
B-2	0.5	1.8	2.0
B-3	0.3	1.1	0.9
B-4	0.2	2.2	2.0
G**1	0.5	2.7	3.0
G-2	0.1	0.7	0.8
G-3	0.3	1.8	1.5
G-4	0.2	1.3	1.5

B* sampling stations in Bulgaria

G** sampling stations in Greece

CONCLUSIONS

1. The possibility for AES determination of mercury in water as well as in sediment samples from the river Strimon after preconcentration on PbS was experimentally proved; the direct determination of mercury in sediment samples is feasible too.

2. For the first time the mercury concentration in water and sediment samples from the river Strimon has been determined.

SUMMARY

The determination of mercury in surface water and sediment samples has been studied using atomic emission spectroscopy (AES). The determination was carried out after pre-concentration of mercury on lead sulphide formed by the reaction between $\text{Pb}(\text{CH}_3\text{COO})_2$ and Na_2S added simultaneously into the sample solution. In the sediment samples the direct determination of mercury was feasible too.

The limit of determination was $0.8\mu\text{g/g}$ for the direct AES and with RSD 6%, while for the mercury preconcentrated on PbS was $0.1\mu\text{g}$ per $0.2\text{-}0.4\text{g}$ of PbS, with RSD 8%.

Keywords: Determination of mercury, Atomic emission spectroscopy, Preconcentration on lead sulphide, Surface water, Sediment.

ΠΕΡΙΛΗΨΗ

Προσδιορισμός του υδραργύρου σε επιφανειακά ύδατα και ιζήματα με ατομική φασματοσκοπία εκπομπής (AES).

Ο προσδιορισμός πραγματοποιήθηκε μετά από προσυγκέντρωση του υδραργύρου σε θειούχο μόλυβδο που σχηματίστηκε κατά την αντίδραση μεταξύ $\text{Pb}(\text{CH}_3\text{COO})_2$ και Na_2S κατά την ταυτόχρονη προσθήκη τους στο διάλυμα του δείγματος. Στα ιζήματα η απευθείας μέτρηση του υδραργύρου ήταν επίσης δυνατή.

Το όριο προσδιορισμού ήταν $0,8\mu\text{g/g}$ για την απευθείας AES και με RSD 6%, ενώ για τον υδράργγρο που είχε προσυγκεντρωθεί σε PbS ήταν $0,1\mu\text{g}$ ανά $0,2\text{-}0,4$ PbS, με RSD 8%.

Προσδιορίστηκε ο υδράργγρος σε ύδατα και ιζήματα του ποταμού Στρυμώνα τόσο σε Ελληνικές όσο και σε Βουλγαρικές περιοχές και δεν παρατηρήθηκαν σημαντικές διαφορές.

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SHORT PAPER

A MASS SPECTRAL STUDY OF SOME BIS-SCHIFF BASES

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Key words : Mass spectra, bis-Schiff bases.

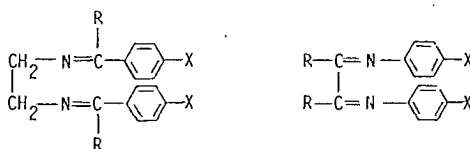
INTRODUCTION

There exist a number of reports on the mass spectra of various types of mono-Schiff bases^{1a,2} and on their versatile use for the synthesis of a great variety of heterocyclic compounds³. However, bis-Schiff bases have received no attention.

The present study was conducted as a part of a major investigation on bis-Schiff bases as photochemical precursors to important heterocycles.

RESULTS AND DISCUSSION

A consistent fragmentation pattern is observed in the mass spectra of all the compounds 1-16 (Scheme 1). In all cases scission of the molecule occurs by a process which involves cleavage of the central carbon-carbon bond. This produces two similar fragments either of which may carry the charge. In addition to these fragments that are the base peak in all cases, prominent peaks at m/z values corresponding to the molecular ions of the title compounds were observed. The relative intensities of the molecular ion peaks varied with the presence of substituents.



	R	X		R	X
1	H	H	11	CH ₃	H
2	H	CH ₃	12	CH ₃	CH ₃
3	H	Cl	13	CH ₃	Cl
4	H	Br	14	Ph	H
5	H	NO ₂	15	Ph	CH ₃
6	H	N(CH ₃) ₂	16	Ph	Cl
7	CH ₃	H			
8	CH ₃	CH ₃			
9	CH ₃	Cl			
10	CH ₃	Br			

SCHEME 1 : *Bis-Schiff bases 1-16.*

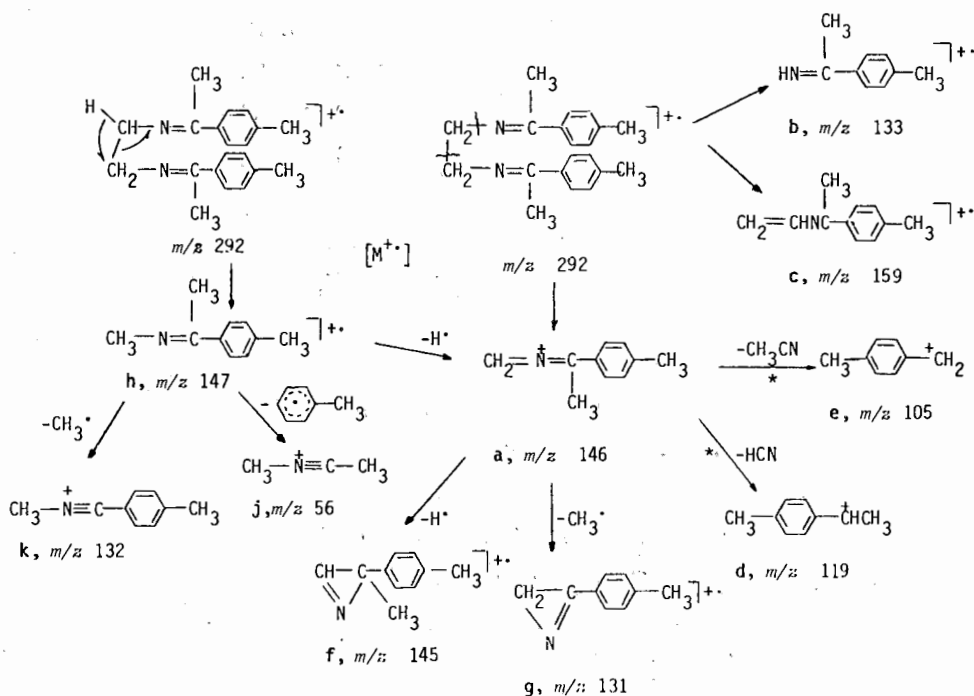
The main fragmentation pathways of the bis-Schiff bases 1-10 are delineated in Scheme 2 by the representative example of 8. Its mass spectrum is given in Figure 1.

The fragmentation pattern shown in Scheme 2 is general for the bis-Schiff bases studied, and the data for the compounds 1-10 are summarized in Table I. The fragment a in Scheme 2 arises from the cleavage of central C-C bond while the alternative breaking of the C-N bonds produces fragments b and c. Further decomposition of a leads to ions m/z 105, 119, 145 and 131. The ions at m/z 105 and 119 are confirmed by the presence of metastables at m/z 75.51 and 96.99 respectively, while the fragments at m/z 145 and 131 could be assigned the azirine-structures f and g by comparison of their fragmentation features with those reported for this ring system⁴⁻⁶

In addition to these peaks, the fragmentation pattern of this class of compounds is characterized by appearance of a prominent peak at m/z

$\left| \frac{M}{2} + 1 \right|^+$, corresponding to the Schiff base h. This fragment h is attributed to a hydrogen transfer that takes place prior to decomposition. Subsequently, loss of a hydrogen from h could be an alternative pathway for the formation of a. Further fragmentation of h is consistent with reported data^{1a} and lends support to the proposed structure.

The fragmentation of 11-16 follows the same pattern for as in 1-10. Scheme 3 illustrates the fragmentation pattern for 11-16 by the representative example of 15, while its mass spectrum is shown in Figure 2. The data for the compounds in this series are summarized in Table II. The absence of methylene groups in the bis-Schiff bases of α -diketones 11-16 simplifies their mass spectra. Furthermore it could be said that they behave essentially like their ketonic precursors, α -diketones, that are fragmented predominately between the carbonyl groups to give acylium ions^{1b}.



SCHEME 2: Fragmentation pattern of 8.

TABLE I : Fragment ions in the mass spectra of bis-Schiff bases 1-10

Compound	
1	236(10) ^a M ⁺ , 131(68), 119(25), 118(100), 117(22), 105(48), 91(40), 77(55), 70.17* [118→91] ^b , 42(7)
2	264(4) M ⁺ , 145(65), 133(27), 132(100), 131(20), 119(92), 105(95), 91(41), 83.52* [132→105], 42(8)
3 ^c	304(5) M ⁺ , 165(98), 153(23), 152(100), 151(22), 139(95), 125(97), 111(22), 100.79* [152→125], 42(7)
4 ^c	392(7) M ⁺ , 209(77), 197(20), 196(100), 195(15), 183(79), 169(82), 155(18), 145.72* [196→169], 42(7)
5	326(10) M ⁺ , 176(78), 164(22), 163(100), 162(25), 150(76), 136(85), 122(20), 113.47* [163→136], 42(9)
6	322(15) M ⁺ , 174(85), 162(15), 161(100), 160(16), 148(70), 134(45), 120(8), 111.52* [161→134], 42(10)
7	264(12) M ⁺ , 145(55), 133(15), 132(100), 131(90), 119(20), 118(34), 117(9), 105(87), 91(52), 83.52* [132→105], 77(80), 62.73* [132→91], 56(20)
8	292(33) M ⁺ , 159(47), 147(18), 146(100), 145(91), 133(23), 131(42), 119(9), 105(91), 96.99* [146→119], 91(55), 75.51* [146→105], 56(22)
9 ^c	332(8) M ⁺ , 179(4), 167(25), 166(100), 165(36), 153(8), 151(19), 139(12), 125(89), 116.39* [166→139], 111(18), 94.12* [166→125], 56(15)
10 ^c	420(10) M ⁺ , 223(10), 211(20), 210(100), 209(48), 197(21), 195(27), 183(15), 169(90), 159.47* [210→183], 155(15), 136.02* [210→169], 56(10)

^a Numbers in parentheses indicate % relative abundances

^b Numbers in brackets indicate metastable transitions

^c The values of the ion fragments refer to ³⁵Cl and ⁷⁹Br

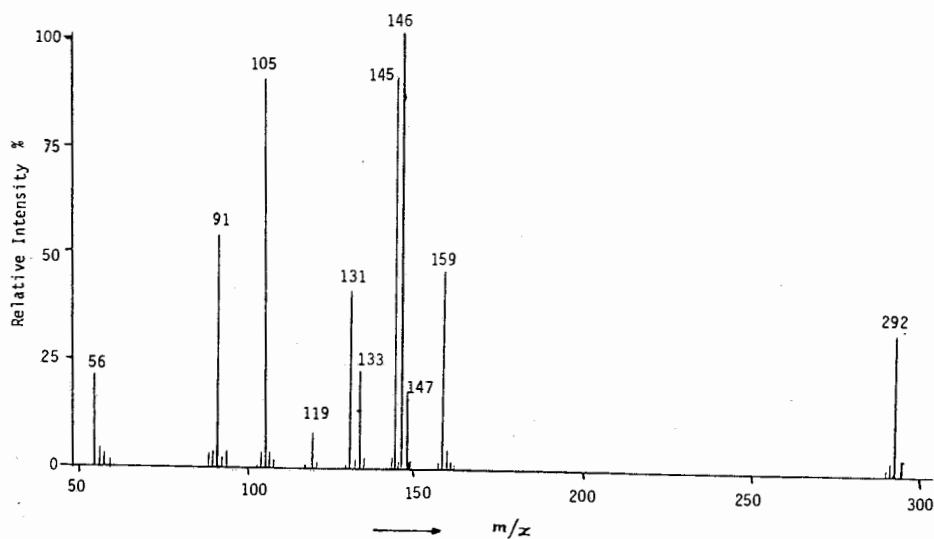


FIG. 1 : Mass spectrum of 8.

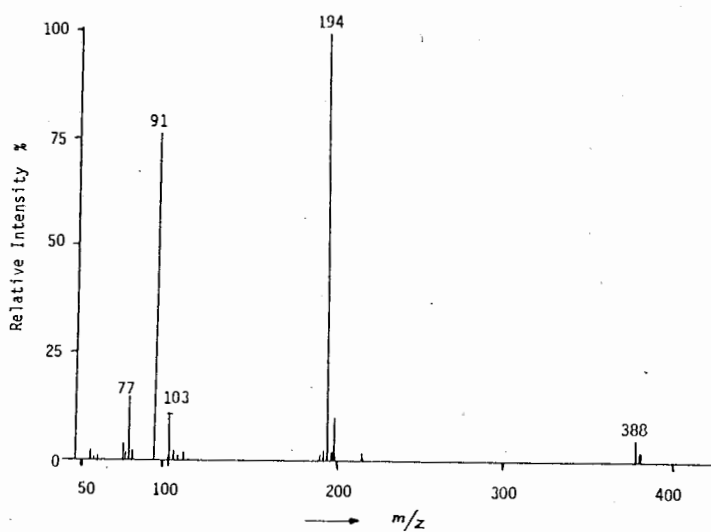
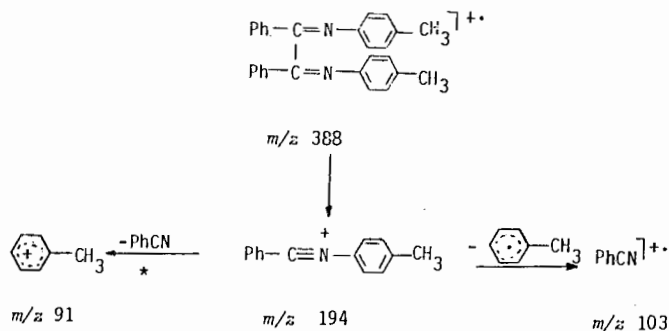


FIG. 2 : Mass spectrum of 15.



SCHEME 3 : Fragmentation pattern of 15.

TABLE II : Fragment ions in the mass spectra of bis-Schiff bases 11-16.

Compound	Fragment ions (m/z)
11	236(45) ^a M ⁺ , 118(100), 77(55), 50.24 [*] [118→117] ^b , 41(15)
12	264(40) M ⁺ , 132(100), 91(60), 62.73 [*] [132→91], 41(15)
13 ^c	304(21) M ⁺ , 152(100), 111(29), 81.05 [*] [152→111], 41(15)
14	360(14) M ⁺ , 180(100), 77(27), 32.93 [*] [180→77]
15	388(5) M ⁺ , 194(100), 103(10), 91(75), 77(15), 42.68 [*] [194→91]
16 ^c	428(3) M ⁺ , 214(100), 103(16), 111(25), 77(18), 57.57 [*] [214→111]

^a Numbers in parentheses indicate % relative abundances^b Numbers in brackets indicate metastable transitions^c The values of the ion fragments refer to ³⁵Cl

EXPERIMENTAL

M.p.s. were obtained on a hot stage apparatus and are uncorrected. The mass spectra were run at 70 eV on a RMU-6L Hitachi-Perkin-Elmer single focusing mass spectrometer using the direct insertion probe of the samples. I.r. spectra were recorded on a Perkin-Elmer 297 spectrophotometer. N.m.r. spectra were taken on a Varian Associates A-60A instrument with tetramethylsilane as an internal standard. Elemental analyses were performed on a Perkin-Elmer 240 B Analyser.

Preparation of N,N -bis-(4-substituted benzilidene- or ethylidene-)ethylenediamine 1-10.

They were synthesized in the usual manner by reaction of the appropriate aldehyde or ketone with ethylenediamine in alcohol in a 2:1 molar ratio. Purification was accomplished by recrystallization from alcohol. The bis-Schiff bases 1-7 have been reported previously⁷⁻⁹. The analytical and spectral data of the compounds 8-10 are shown in Table III.

TABLE III : Analytical and spectral data of the compounds 8-10 and 13

Compound	Yield (%)	M. p. °C	Found (%)			IR ν_{max} (nujol) cm^{-1}	¹ H NMR (CDCl ₃) δ_H
			(Required)				
			C	H	N		
8	73	121-123	81.8 (82.1)	8.45 (8.3)	9.7 (9.6)	1640 (C=N)	2.23(6H,s), 2.32(6H,s), 3.88(4H,d), 7.10(4H,d), 7.63(4H,d)
9	78	187-189	64.5 (64.9)	5.4 (5.44)	8.3 (8.4)	1630 (C=N)	2.20(6H,s), 3.85(4H,s), 7.22(4H,d), 7.63(4H,d)
10	69	153-155	51.5 (51.2)	4.35 (4.3)	6.7 (6.6)	1630 (C=N)	2.21(6H,s), 3.86(4H,s), 7.18(4H,d), 7.63(4H,d)
13	92	128-129	62.7 (63.0)	4.8 (4.6)	9.1 (9.8)	1640 (C=N)	2.17(6H,s), 6.80-7.40(8H,m)

Preparation of bis-(4-substituted-phyylimino-) diacetyl or benzil 11-16

They were prepared by reaction of the appropriate α -diketone with the proper amine in alcohol in a 12 molar ratio and recrystallized from alcohol. They have been reported previously¹⁰⁻¹² except the compound 13 for which analytical and spectral data are shown in Table III.

SUMMARY

The electron-impact mass spectra of some bis-Schiff bases are reported. Their characteristic pattern involves scission of the molecule into two fragments by cleavage of the central carbon-carbon bond. The presence of the molecular ion is prominent in all cases.

ΠΕΡΙΛΗΨΗ

Στην εργασία αυτή μελετώνται τα φάσματα μαζών ηλεκτρονικού ιονισμού μερικών βάσεων του Schiff. Χαρακτηριστικό είναι το ιόν που προκύπτει από θραύση του κεντρικού εσμού C-C του μορίου, και αποτελεί την βασική κορυφή καθώς και οι εναλλακτικές θραυσματοποιήσεις.

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SHORT PAPER

MONOHALOGENBENZOYLHYDRAZONE IV. SYNTHESE UND UNTERSUCHUNGEN VON Rh(III)-KOMPLEXEN MIT MONOHALOGENBENZOYLHYDRAZONEN DES 2-FURALDEHYDS, 2-THIOPHENALDEHYDS UND 2-PYRROLALDEHYDS ALS LIGANDEN

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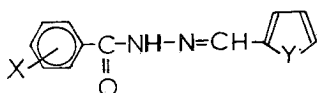
INHALTSÜBERSICHT

Eine neue Reihe von Rh(III)-Komplexen mit Benzoyl- und Chlorobenzoylhydrazonen des 2-Furaldehyds (FBH bzw. FC1BH), 2-Thiophenaldehyds (TBH bzw. TC1BH) und 2-Pyrrolaldehyds (PBH bzw. PC1BH) als Liganden wurde hergestellt und untersucht. Auf der Basis spektroskopischer Untersuchungen (IR, UV-Vis) sowie Messungen der magnetischen Suszeptibilität, der molaren Leitfähigkeiten und DTA/TG wird für die ionischen Komplexe die verzerrt oktaedrische Struktur vorgeschlagen.

Key words: Rhodium complexes, monohalogenbenzoylhydrazones, 2-furaldehyde, 2-pyrrolaldehyde, 2-thiophenaldehyde, synthesis, DTA/TG analysis.

EINLEITUNG

Bedingt durch ihre praktische Bedeutung, hat die Chemie des Rhodiums in den letzten Jahrzehnten besondere Aufmerksamkeit erfahren. Breite Anwendung finden die Komplexe des Rh(III) in der Katalyse¹, sind aber auch von besonderem Interesse für Fragen der bioanorganischen Chemie da sich diese, bekanntlich, durch eine zum Teil große bakterizide und zytostatische Wirkung auszeichnen²⁻⁴. Unter diesem Gesichtspunkt und in Fortsetzung unserer Arbeiten⁵⁻¹⁰ über das Koordinationsverhalten halogensubstituierter Benzoylhydrazone beschreiben wir in der vorliegenden Arbeit die Synthese und Untersuchung der Eigenschaften einiger Rh(III)-Komplexe mit Benzoylhydrazonen des Typs I als Liganden.



X = H, Cl

Y = O, S, NH

I

Diese Spezies haben sich als recht gute Liganden für eine Reihe von Übergangsmetallionen, u.s. für Nickel(II), Kobalt(II), Kupfer(II), Zink(II) und Titan(IV) erwiesen. Nach den bisher vorliegenden Ergebnissen bilden diese polyfunktionellen Liganden sowohl aus der Keto- als auch aus der Enolform heraus Komplexe verschiedener Zusammensetzung (1:1 bzw. 1:2), wobei in der Regel unter Koordinierung des Carbonylsauerstoffatoms und des Azomethinstickstoffatoms Fünfringchelate entstehen. Das zweite Stickstoffatom ist ebenso wie das Heteroatom des Fünfringes (O, S, N) nicht an der Koordination beteiligt. Beide zeigen auch keinen wesentlichen Einfluß auf die Koordinationseigenschaften der Hydrazone. Gleiches gilt auch für das Chloratom; seine Lage im Benzolring beeinflusst lediglich die Ausbeute der Umsetzungen. Diese steigt in allen Fällen erwartungsgemäß innerhalb der Reihe o-, m-, p-Stellung des Substituenten.

EXPERIMENTELLES

Die Herstellung der Benzoyl- und Chlorbenzoylhydrazone erfolgt nach den in der Literatur¹¹⁻¹⁴ beschriebenen Methoden, die Schwingungsspektren der Komplexe werden an KBr-Preßlingen im Bereich 4000-250 cm^{-1} mit einem Spektrometer 467 der Firma Perkin-Elmer aufgenommen. Elektronenabsorptionsspektren werden mit Hilfe eines UV/Vis-Spektrometers 200 (Perkin-Elmer-Hitachi) registriert. Die molaren Leitfähigkeiten werden in 10^{-3} M methanolischen Lösungen mit Hilfe einer Leitfähigkeitsbrücke Modell RC 216 B2 der Firma Industrial Instruments Inc., die magnetischen Momente in der üblichen Weise nach Gouy bestimmt. Die DTA/TG-Diagramme werden mit einer Thermowaage Linseis L 81-82 bei ca. 750 Torr und einer Aufheizgeschwindigkeit von $10^{\circ}\text{C}/\text{min}$ aufgenommen. Zur Reinigungskontrolle werden die CHN-Analysen mit einem Perkin-Elmer 240 Analyzer durchgeführt; die Ergebnisse (zusammen mit der Angabe von Ausbeuten und molaren Leitfähigkeiten) sind in Tab. I zusammengefaßt.

TABELLE I. Ausbeuten, molare Leitfähigkeiten und analytische Daten der Komplexe.

Verbindung	Ausbeute (%)	Molare Leitfähigkeit ($\text{Ohm}^{-1} \text{cm}^{-2} \text{mol}^{-1}$)	Analytische Daten					
			%C		%N		%H	
			ber.	gef.	ber.	gef.	ber.	gef.
I $\text{RhCl}_2(\text{FBH})(\text{H}_2\text{O})_2 \text{Cl}$	74	80	31.36	31.44	6.09	6.24	3.07	3.22
II $\text{RhCl}_2(\text{FoClBH})(\text{H}_2\text{O})_2 \text{Cl}$	58	92	29.18	30.10	5.67	5.83	2.65	2.82
III $\text{RhCl}_2(\text{FmClBH})(\text{H}_2\text{O})_2 \text{Cl}$	65	104	29.18	29.15	5.67	5.55	2.65	2.60
IV $\text{RhCl}_2(\text{FpClBH})(\text{H}_2\text{O})_2 \text{Cl}$	72	109	29.18	30.09	5.67	5.95	2.65	2.70
V $\text{RhCl}_2(\text{TBH})(\text{H}_2\text{O})_2 \text{Cl}$	56	101	30.31	30.90	5.89	6.05	2.96	3.10
VI $\text{RhCl}_2(\text{ToClBH})(\text{H}_2\text{O})_2 \text{Cl}$	45	110	28.26	28.47	5.49	5.85	2.57	2.59
VII $\text{RhCl}_2(\text{ImClBH})(\text{H}_2\text{O})_2 \text{Cl}$	55	116	28.26	28.01	5.49	5.49	2.17	2.39
VIII $\text{RhCl}_2(\text{TpClBH})(\text{H}_2\text{O})_2 \text{Cl}$	60	97	28.26	28.14	5.49	6.15	2.57	2.39
IX $\text{RhCl}_2(\text{PBH})(\text{H}_2\text{O})_2 \text{Cl}$	82	111	31.43	33.23	9.16	10.24	3.29	3.81
X $\text{RhCl}_2(\text{PoClBH})(\text{H}_2\text{O})_2 \text{Cl}$	75	89	29.23	30.25	8.52	9.19	2.86	2.36
XI $\text{RhCl}_2(\text{PmClBH})(\text{H}_2\text{O})_2$	77	87	29.23	29.65	8.52	8.93	2.86	2.74
XII $\text{RhCl}_2(\text{PpClBH})(\text{H}_2\text{O})_2$	80	105	29.23	30.15	8.52	8.92	2.86	3.02

Synthese der Komplexe

Zur Präparation der Komplexe wird zu einer Lösung von $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in wenig Methanol die methanolische Lösung der äquimolaren Menge des Liganden langsam zugetropft und bei $50\text{-}60^\circ\text{C}$ etwa 2 Stunden gerührt, wobei die Komplexe in Form farbiger Festkörper fallen. Die Fällung kann durch Zugabe von wenig Diethylether vervollständigt werden. Die Produkte werden anschließend durch Filtration isoliert und im Vakuum getrocknet.

ERGEBNISSE UND DISKUSSION

Die Umsetzung der Hydrazone mit $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in methanolischer Lösung im Molverhältniss 1:1 liefert schon nach kurzer Zeit in guten Ausbeuten luftstabile farbige Festkörper der Zusammensetzung $\text{RhCl}_2(\text{L}) \cdot 2\text{H}_2\text{O}$. Diese sind bis 270°C unschmelzbar (oberhalb dieser Temperatur tritt in allen Fällen Zersetzung ein), unlöslich in Wasser und wenig löslich in den üblichen organischen Lösungsmitteln.

Einen ersten Hinweis auf die Struktur der Komplexe liefert die Messung ihrer magnetischen Momente. Die Verbindungen erweisen sich als diamagnetisch, ein Befund, der im Falle des vorliegenden Rh^{3+} -Ions (d^6), für eine oktaedrische Anordnung der Liganden spricht (Low-Spin-Konfiguration t_{2g}^6). Im Einklang damit zeigen die Werte der molaren Leitfähigkeit methanolischer Lösungen der Komplexe (Tab.I) das Vorhandensein von Elektrolyten des Typs 1:1 an¹⁶ und legen damit die Formulierung $[\text{RhCl}_2(\text{L})(\text{H}_2\text{O})_2] \text{Cl}$ nahe.

Schwingungsspektren

In Tab. II sind die Banden einiger charakteristischer Gruppen angegeben. Im folgenden werden diese ausgewählten Schwingungsbanden kurz diskutiert. Die Absorptionen der übrigen Gruppen liegen in den erwarteten Bereichen und sind für die Strukturaufklärung der Komplexe weniger charakteristisch.

Die sehr starke Bande der Hydrazone im Bereich $1670\text{-}1650 \text{ cm}^{-1}$ ^{9,15}, welche der Valenzschwingung der Carbonylgruppe $\nu(\text{CO})$ oder der Amidbande I zugeordnet werden kann^{15,17-21}, erscheint in den Komplexen infolge der Koordination dieser Gruppe um $25\text{-}60 \text{ cm}^{-1}$ zu tieferen Frequenzen verschoben. Eine ebenso starke Koordinationsverschiebung in gleicher Richtung erfährt die im Bereich $1625\text{-}1570 \text{ cm}^{-1}$ liegende Bande der Aminocarbonschwingung $\nu(\text{C=N})$ ²²⁻²⁵.

Die (N-N)-Valenzschwingung, die in den freien Liganden im Bereich um

900 cm^{-1} liegt, ist in den Komplexen um 10–55 cm^{-1} zu höheren Wellenzahlen (960–910 cm^{-1}) verschoben^{25,26}. Diese koordinationsbedingte Verstärkung der N-N-Bindung deutet im Zusammenhang mit der Lage der (C=O)-Va-

TABELLE II. Charakteristische IR-Banden der Rh(III)-Komplexe (KBr-Preßlinge, in cm^{-1}).

Verb.	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\nu(\text{Rh}-\text{N})$	$\nu(\text{Rh}-\text{O})$	$\nu(\text{Rh}-\text{Cl})$
I	1625	1550	940	590	410	325
II	1630	1560	960	585	430	330
III	1625	1550	930	590	420	320
IV	1625	1545	935	585	420	320
V	1605	1530	925	590	430	320
VI	1630	1580	930	590	430	320
VII	1630	1605	930	590	420	330
VIII	1600	1580	925	610	420	330
IX	1600	1545	930	590	420	330
X	1610	1590	930	590	430	335
XI	1610	1570	920	590	420	330
XII	1600	1580	910	600	440	330

lenzschwingungsbande auf eine stark ausgeprägte Ladungsdelokalisation im System $\text{O}=\text{C}=\text{NH}-\text{N}$ der Chelatkomplexe hin.

Die (Rh-N)-, (Rh-O)- und (Rh-Cl)-Valenzschwingungen²⁷⁻²⁹ erscheinen in den IR-Spektren aller Komplexe als relativ schwache Banden bei 610–585 cm^{-1} , 440–410 cm^{-1} bzw. 335–320 cm^{-1} . Die recht starke Bande bei 3420 cm^{-1} wird schließlich der $\nu(\text{O}-\text{H})$ -Schwingung des koordinierten Wassermoleküls zugeordnet.

Elektronenabsorptionsspektren

Die Daten der Elektronenabsorptionsspektren der Komplexe sind in Tab. III zusammengefaßt. Die UV/Vis-Absorptionsspektren der Liganden sind durch zwei intensive Banden im Bereich 230–273 und 304–331 nm gekennzeichnet, die als $\pi \rightarrow \pi^*$ - und $n \rightarrow \pi^*$ -Übergänge in den Gruppen C=N bzw. C=O zu interpretieren sind^{20,30,31}. In den Spektren der Komplexe sind die Maxima dieser Banden im Vergleich zu den Banden der freien Liganden stets zu höheren Frequenzen (um 5–35 nm für die erste und um 10–36 nm für die zweite Bande) verschoben. Diese Tatsache bekräftigt die Annahme einer Koordination über

das Azomethinstickstoff- und das Carbonyl-sauerstoff-Atom³². Die UV/Vis-Absorptionsspektren der Komplexe von PBH und PC1BH weisen schließlich

TABELLE III. Elektronische Spektren der Rh(III)-Komplexe bei 25°C (in Methanol).

Verbindung	Absorptionsbanden in nm (log-ε)			
I	255 (4.68)	332 (4.35)		
II	266 (4.43)	340 (4.16)		
III	235 (4.41)	324 (4.56)		
IV	245 (4.38)	335 (4.19)		
V	275 sh	340 (4.09)		
VI	273 (4.03)	328 (3.87)		
VII	270 sh	340 (4.04)		
VIII	270 (4.19)	348 (3.75)		
IX	265 sh	350 (3.91)	490 (3.83)	
X	267 (4.30)	348 (3.56)	503 (3.74)	536 sh
XI	270 sh	355 (3.86)	535 (3.99)	
XII	268 (4.39)	350 (3.42)	523 (3.50)	

recht intensive Charge-Transfer-Banden im Bereich 490–536 nm auf. Die entsprechenden Banden analoger Rh(III)-Komplexe werden von einigen Autoren^{33,34} (d-d)-Übergängen des Typs $^1A_{1g} \rightarrow ^1T_{1g}$ und $^1A_{1g} \rightarrow ^1T_{2g}$ zugeordnet, was jedoch im Falle der von uns untersuchten Komplexe auf Grund der Intensitäten nicht zutreffen kann.

DTA/TG-Messungen

Die Daten der DTA/TG-Messungen dreier repräsentativer Komplexe (IV, VIII und XII) sind in Abb. 1, 2 und 3 angegeben. Wie daraus zu entnehmen ist, läuft die Zersetzung der Komplexe in drei bzw. vier Stufen ab. In der ersten Stufe zwischen 40–150°C werden in allen Fällen zwei Wassermoleküle abgebaut. In der zweiten und dritten Stufe zwischen 210–400°C werden die beiden organischen Gruppen C_7H_5Cl und C_5H_4O bzw. C_5H_4S bzw. C_5H_5N abgegeben. Beim Komplex XII ist der getrennte Abgang dieser zwei Gruppen eindeutig erkennbar und zwar wird zuerst die C_7H_5Cl - und darauf folgend die C_5H_5N -Gruppe abgespalten. Im Falle des Komplexes VIII wird dieser Befund sogar durch die zwei dazugehörigen endothermen Peaks belegt. In der letzten ebenfalls stark endothermen Stufe zwischen 335–550°C entweichen drei Cl-Atome; charakteristisch hierfür sind drei aufeinander-

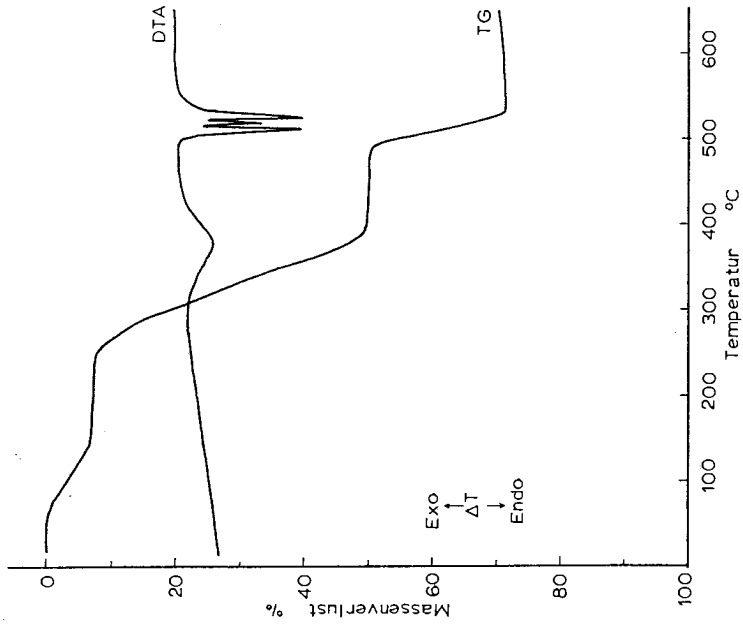


Abb. I Thermoabbau von $\text{RhCl}_3(\text{FpClBH})(\text{H}_2\text{O})_2$

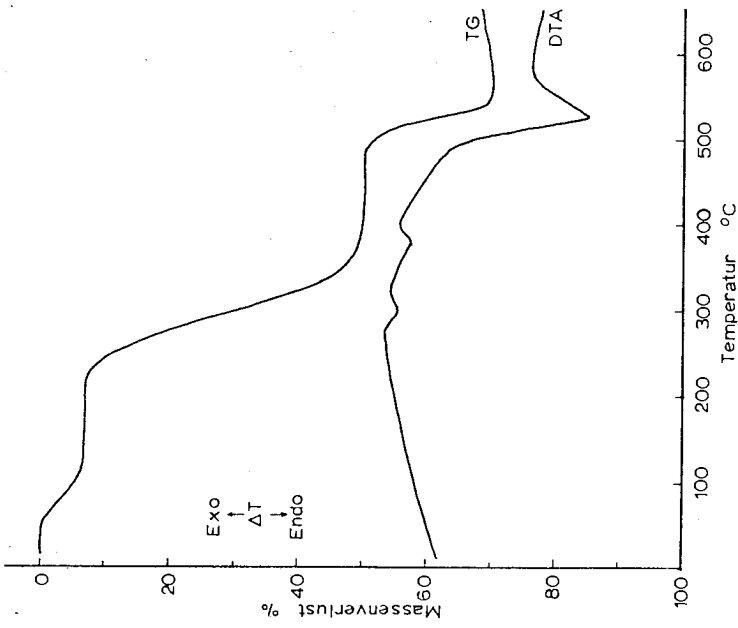
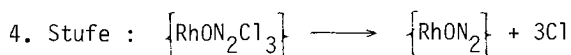


Abb. II Thermoabbau von $\text{RhCl}_3(\text{TpClBH})(\text{H}_2\text{O})_2$



Vergleicht man die IR- und UV/Vis-spektroskopischen Daten der von uns untersuchten Komplexe mit den entsprechenden Daten analoger Komplexe³⁰, so kann man auch hier die Beteiligung der Azomethin- und der Carbonyl-Gruppe der Hydrazone an der Komplexbildung als gesichert ansehen. Wie aus der Literatur bekannt ist³⁵, bildet Rh(III) mit zweizähligen Liganden oktaedrische Komplexe des Typs $[\text{RhCl}_2\text{L}(\text{H}_2\text{O})_2]\text{Cl}$. Im Falle der von uns untersuchten Komplexe wird die Annahme einer verzerrt oktaedrischen Struktur zusätzlich durch die Ergebnisse der Messungen der magnetischen Suszeptibilität bekräftigt. Welche der prinzipiell möglichen Strukturisomeren (Abb. 4, a-d) bevorzugt realisiert wird, ist aus den bisher vorliegenden Daten nicht zu erkennen.

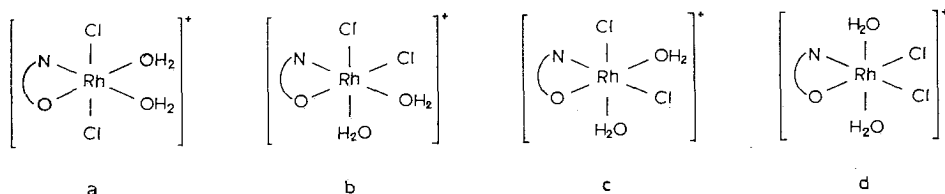


Abb. IV Mögliche Strukturisomere der $[\text{RhCl}_2\text{L}(\text{H}_2\text{O})_2]^+$ - Komplexe

Aufgrund dieses Strukturvorschlags wurde man zwar eine Aufspaltung der drei chemisch unterschiedlichen Cl-Atome bei der TG-Analyse der Komplexe in verschiedenen Stufen erwarten, was jedoch vom Experiment nicht bestätigt wird. Das anders lautende experimentelle Ergebnis findet eine mögliche Erklärung in der Annahme, daß das Cl-Ion, nach der H_2O -Abspaltung, wahrscheinlich unter gleichzeitiger Umwandlung der Struktur, koordinativ an das Zentrallatom gebunden wird. Weiterhin können, sowohl die Tatsache daß O und N Bestandteile des Rückstands der chemischen Zersetzung aller untersuchten Komplexe ist, als auch die jeweiligen Zerfallsmuster, als weitere Indizien für die Koordination der Liganden über das Carbonylsauerstoff- und das Azomethinstickstoff-Atom gelten. Aus den TG-Daten geht schließlich hervor, daß die Rh-Cl Bindung thermisch labiler ist als die Rh-O und Rh-N-Bindung, zumindest unter den Bedingungen des Experiments.

TABELLE IV. DTA/TG-Daten für einige Rhodium(II) - Komplexe.

Verbindung	Stufe	DTA-Ergebnisse	TG-Ergebnisse			
		Temperatur-Peak(°C) Endotherm(-)	Temperaturbereich(°C)	Massenverlust (%)	Abgespaltenes Fragment	Berechn. Masse (%)
$\text{RhCl}_3(\text{FpClBH})(\text{H}_2\text{O})_2$	a		50-150	7.3	$2\text{H}_2\text{O}$	7.29
	b	370(-)	250-380	42.6	$\text{C}_7\text{H}_5\text{Cl} + \text{C}_5\text{H}_4\text{O}$	41.39
	c	510(-), 515(-), 520(-)	490-525	21.6	3Cl	21.56
	Rückst.		>525	28.5	RhON_2	29.76
$\text{RhCl}_3(\text{TpClBH})(\text{H}_2\text{O})_2$	a		50-130	7.0	$2\text{H}_2\text{O}$	7.06
	b	300(-), 375(-)	220-330	42.8	$\text{C}_7\text{H}_5\text{Cl} + \text{C}_5\text{H}_4\text{S}$	43.25
	c	525(-)	490-550	20.0	3Cl	20.89
	Rückst.	570(-)	>550	30.2	RhON_2	28.80
$\text{RhCl}_3(\text{PpClBH})(\text{H}_2\text{O})_2$	a	40(-)	40-120	6.9	$2\text{H}_2\text{O}$	7.30
	b		210-230	24.5	$\text{C}_7\text{H}_5\text{Cl}$	25.26
	c	355(-)	330-355	16.5	$\text{C}_5\text{H}_5\text{N}$	16.03
	d	380(-)	355-430	22.6	3Cl	21.61
	Rückst.		>430	29.5	RhON_2	29.82

SUMMARY

MONOHALOGENOBENZOYLHYDRAZONES IV. SYNTHESIS AND STUDY OF Rh(III) COMPLEXES WITH MONOCHLOROBENZOYLHYDRAZONES OF 2-FURALDEHYDE, 2-THIOPHENALDEHYDE AND 2-PYRROLALDEHYDE AS LIGANDS.

A new series of Rh(III) complexes with benzoyl and chlorobenzoyl hydrazones of 2-furaldehyde (FBH and FC1BH), 2-thiophenylaldehyde (TBH and TC1BH) and 2-pyrrolaldehyde (PBH and PC1BH) have been synthesized and studied. According to the spectral (IR, UV-Vis) data, magnetic and conductivity measurements and DTA/TG thermal studies the distorted octahedral geometry has been proposed.

ΠΕΡΙΛΗΨΗ

ΜΟΝΟΧΛΩΡΟΒΕΝΖΟΥΛΟΥΔΡΑΖΟΝΕΣ IV. ΣΥΝΘΕΣΗ ΚΑΙ ΜΕΛΕΤΗ ΣΥΜΠΛΟΚΩΝ ΕΝΩΣΕΩΝ ΤΟΥ Rh(III) ΜΕ ΥΠΟΚΑΤΑΣΤΑΤΕΣ ΜΟΝΟΧΛΩΡΟΒΕΝΖΟΥΛΟΥΔΡΑΖΟΝΕΣ ΤΗ' 2-ΦΟΥΡΑΛΔΕΥΔΗΣ, 2-ΘΕΙΟΦΑΙΝΑΛΔΕΥΔΗΣ ΚΑΙ 2-ΠΥΡΡΟΑΛΔΕΥΔΗΣ.

Στην παρούσα εργασία περιγράφεται η σύνθεση και η μελέτη δώδεκα νέων συμπλόκων ενώσεων του Rh(III) με βενζούλο- και μονοχλωρο-βενζούλουδραζόνες της 2-φουραλδεΐδης (FBH και FC1BH), της 2-θειοφαιναλδεΐδης (TBH και TC1BH) και της 2-πυρροαλδεΐδης (PBH και PC1BH) ως υποκαταστάτες. Η παρασκευή των συμπλόκων αυτών ενώσεων, οι οποίες είναι όλες έγχρωμες (κίτρινες έως κεραμέρυθρες) γίνεται με ανάμιξη μεθανολικών διαλυμάτων $RhCl_3$ και της αντίστοιχης υδραζόνης σε μοριακή αναλογία 1:1. Η στοιχειακή ³ ανάλυση των παρασκευασθέντων συμπλόκων αντιστοιχεί στο γενικό τύπο $RhCl_3L(H_2O)_2$. Από μετρήσεις της μοριακής αγωγιμότητας συμπεραίνουμε ότι πρόκειται για ηλεκτρολύτες του τύπου 1:1. Εξάλλου το γεγονός ότι είναι διαμαγνητικά είναι ένα στοιχείο ύπαρξης οκταεδρικής συμμετρίας t_{2g} , με χαμηλού spin ηλεκτρονική διαμόρφωση του κεντρικού ιόντος Rh^{3+} . Η μελέτη των φασμάτων i.r. και uv-vis των μελετούμενων συμπλόκων οδηγεί στο συμπέρασμα ότι οι υποκαταστάτες είναι διδοντικοί συναρμοζόμενοι μέσω του καρβονυλικού οξυγόνου και του ατόμου του αζώτου της αζωμεθινικής ομάδας, ενώ ο αριθμός συναρμογής έξι συμπληρώνεται με δύο μόρια ύδατος και δύο άτομα χλωρίου. Έτσι καταλήγουμε στο συμπέρασμα ότι τα παρασκευασθέντα σύμπλοκα είναι κατιονικά, οκταεδρικά του τύπου $[RhCl_2L(H_2O)_2]^+ Cl^-$, πλην όμως τα υπάρχοντα πειραματικά δεδομένα δεν επιτρέπουν την επακριβή διάκριση μεταξύ των δυνατών ισομερών (Σχ. IV). Επίσης από τη θερμική ανάλυση DTA/TG προκύπτει ότι στο πρώτο στάδιο αποσπώνται δύο μόρια ύδατος, ακολουθεί η απόσπαση των δύο οργανικών ομάδων (C_7H_5Cl και C_5H_4X , όπου $X=S,O,NH$) και στο τελευταίο στάδιο αποσπώνται τα τρία άτομα χλωρίου, ενώ μένει ως υπόλειμμα ($RhON_2$). Τέλος διαπιστώνεται ότι ο δεσμός Rh-Cl είναι θερμικά ασταθέστερος των δεσμών Rh-O και Rh-Cl, τουλάχιστον υπό τις συνθήκες του πειράματος.

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PYRIMIDINIUM CATIONIC SURFACTANTS AS FIXING AGENTS IN THE DYEING OF COTTON FIBRES WITH DIRECT DYES

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SUMMARY

The aim of this paper is to examine the effectiveness of the application as fixing agents of eleven 1(3)-alkyl-4-amino-5-phenyl-pyrimidinium bromides (cationic surfactants) to five direct dyes on cotton fibres, as well as, to compare these cationics with a conventional one (Levogen) which is already used commercially for similar purposes.

The evaluation of the fixing was measured by the wet fastness tests. Some of the pyrimidinium cationics are believed to be of great interest, because they improve fixing of some of the most difficult dyes as are red, blue and orange. This fixation was sometimes almost excellent, even with low concentration of the cationics (1, 2%).

Key words : Cationic surfactants, 1(3)-alkyl-4-amino-5-phenyl-pyrimidinium bromides, fixing agents, dyeing of cotton fibres, direct dyes.

INTRODUCTION

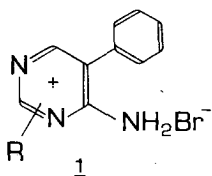
The cationic surfactants are widely used as fixing agents in fibres dyed with direct¹⁻⁵ or reactive dyes⁶.

R. Schetter¹ uses as fixing agents for cotton fibres dyed with direct dyes, among others, Levogen FWN and Solidogen FFL, which are believed to be quaternary cationic surfactants, in 4% o.w.f. depth of shade, whereas J.A.Rippon⁷ uses Glytac A 100 and Levogen RS as fibre reactive quaternary ammonium compounds in 4 and 6% o.w.f. depth of shades.

Cationic pyrimidinium surfactants are not known nevertheless as fixing agents. The only known pyrimidinium compounds in that field, are reactive quaternary compounds⁸⁻¹⁰ which are used as pretreatment agents on the cellulosic fibres.

That fact encouraged us to use the cationic surfactants 1(3)-alkyl-4-amino-5-phenyl-pyrimidinium bromides 1^{11,12} as aftertreatment agents. The

proposed cationics are easily synthesized with high yields^{11,12} from not expensive raw materials.



$$R = C_nH_{2n+1}$$

a : n = 8, b : n = 9, c : n = 10, d : n = 11,
 e : n = 12, f : n = 13, g : n = 14, h : n = 15,
 i : n = 16, j : n = 17, k : n = 18.

These pyrimidinium cationics were examined as fixing agents on dyed cotton fabrics with five direct dyes in the same depth of shade (3% o.w.f.).

The dyeinds were aftertreated with different concentrations (0.4, 1, 2, 4% o.w.f. of weight fibre) of all the above cationics, using the exhaust method.

The fixing result of the cationics was evaluated from the wet fastness of the aftertreated dyeings^{1,7,13}.

These pyrimidinium cationics have shown a satisfactory effectiveness in ISO nr 2, whereas in the perspiration fastness have sometimes shown almost excellent results.

EXPERIMENTAL

Fabrics

Greek bleached cotton fabrics commercially available were used. For all the water fastness tests the undyed fabrics were cotton and wool, both commercially available too. The fabrics were well washed with soap and rinsed before any use.

Dyestuffs

The following direct dyes of Ciba Geigy were used in the trials :

- 1) Solophenyl Rouge 3BL-C.I. Direct Red 80.
- 2) Solophenyl Brill Blue BL-C.I. Direct Blue 106.
- 3) Solophenyl Orange TGL-C.I. Direct Orange 34.
- 4) Solophenyl Gris NGL-C.I. Direct Black 113.
- 5) Solophenyl Brillant Green 2GL-C.I. Direct Green 65.

Fixing agents

Levogen FWN was used in 4% o.w.f. depth of shade. The cationic surfactants 1(a-k) were used in 0.4, 1, 2 and 4% o.w.f. depth of shades.

Dyeing process

The samples were dyed in a dyeing machine John Jeffreys Ltd Rochdale

Bambury, to the same depth of shade (3% o.w.f.) with all the above direct dyes. Liquor ratio 20:1. The temperature of the dyeing bath was gradually raised from 50 to 100°C in 0.5 h during which 20 g/l glauher salt was added and then the temperature held at 100°C for 1 h. After dyeing, the fabrics were thoroughly rinsed with cold tap water and dried at room temperature.

Aftertreatment of Dyed Fabrics

The dyed fabrics were aftertreated with the solutions of the above cationics 1(a-k) at Liquid Ratio (LR) 40:1, pH 6, in the previous dye machine over 45°C for 0.5 h. The samples were then squeezed and dried at room temperature. The fabrics dyed with red, blue and orange were aftertreated with Levogen FWN in 4% o.w.f. depth of shade.

Bleeding during this aftertreatment¹⁴ was measured spectrophotometrically using a Spectronic 20 Bausch & Lomb spectrophotometer at λ max 520, 590, 419, 590 and 640 nm for the dyes rouge 3BL, blue BL, orange TGL, gris NGL and green 2GL respectively.

Dye Fastness tests

Washing fastness was determined according to ISO nr 2 and perspiration fastness according to DRAFT PROPOSAL for ISO RECOMMENDATION. The results of fastness are summarized in Tables I-III for the dyes red, blue and orange respectively. For the perspiration tests six cationics, 1c-1h, were used as representatives.

RESULTS

Bleeding

In the aftertreatment trials bleeding was for the dyes orange red, and blue, in the absence of agent (blank) 0.0036, 0.0104 and 0.0015% respectively. In concentration 0.4% of all the cationics for the same dyes was 0-0.002, 0-0.002 and 0-0.0015% respectively, whereas in concentrations 1-4% was always 0%.

For the dyes green and grey in the absence of agent bleeding was 0.0022 and 0.0011% respectively, whereas in concentrations 1-4% of all the cationics was always 0%.

Wet fastness tests

The score of cotton staining in the ISO test for the three dyes red,

TABLE I : Fastness to Washing and Perspiration of dyeings (with Solophenyl Rouge 3BL) aftertreated with several concentrations of the cationics 1(a-k)(ISO nr 2, C=Colour Change and S=Cotton Staining).

Amount of agent % o.w.f.	None						1a		1b		1c						1d				1e															
	ISO		Perspiration				ISO	ISO	ISO	Perspiration				ISO	Perspiration			ISO	Perspiration																	
			pH 5,5		pH 8					pH 5,5		pH 8			pH 5,5		pH 8		pH 5,5		pH 8															
	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S										
0	4	1-2	4-5	1-2	4-5	1-2																														
0,4														4	3-4																					
1							4	2-3	4	2-3	4	2-3	4	2-3	4	4-5	1-2	4	4-5	1-2	4	3-4	4	4-5	3	4	4-5	2-3	4	2-3	4	4-5	3	4	4-5	2-3
2							4	2-3	4	2-3	4	2-3	4	2-3	4	4-5	2-3	4	4-5	2	4	3-4	4	4-5	4	4-5	4	4	2-3	4	4-5	4	4-5	4		
4							4	2-3	4	2-3	4	2-3	4	2-3	4	4-5	3	4	4-5	2-3	4	3-4	4	4-5	4	4-5	4	4	2-3	4	4-5	4	4-5	4		

1f				1g				1h				1i	1j	1k											
ISO		Perspiration		ISO	Perspiration		ISO	Perspiration		ISO	Perspiration		ISO	ISO	ISO										
		pH 5,5		pH 8			pH 5,5		pH 8		pH 5,5		pH 8												
C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S										
		4-5	1-2	4-5	1-2	4	2-3																		
4	2-3	4-5	4-5	4-5	4	4	2-3	4-5	1-2	4-5	1-2	4	2-3	4-5	4	4-5	3-4	4	2-3	4	2-3	4	2-3	4	2-3
4	2-3	4-5	5	4-5	4	4	2-3	4-5	3-4	4-5	3-4	4	2-3	4-5	4-5	4-5	4	4	2-3	4	2-3	4	2-3		
4	2-3	4-5	5	4-5	4	4	2-3	4-5	5	4-5	4-5	4	2-3	4-5	5	4-5	5	4	2-3	4	2-3	4	2-3		

TABLE III : Fastness to Washing and Perspiration of dyeing (with Solophenyl Orange TGL) aftertreated with several concentrations of the cationics 1(a-k)(ISO nr 2, C=Colour Change and S=Cotton Staining).

Amount of agent % o.w.f.	None		1a		1b		1c				1d				1e									
	ISO Perspiration		ISO		ISO		ISO		Perspiration		ISO		Perspiration		ISO		Perspiration							
	pH 5,5 pH 8								pH 5,5 pH 8				pH 5,5 pH 8				pH 5,5 pH 8							
	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S		
0	4	1-2	4	1	4	1																		
0,4																								
1			4	3	4	3	4	3	4	3-4	4	3-4	4	3	4	4-5	4	4-5	4	2-3	4	4-5	4	4-5
2			4	3	4	3	4	3	4	4	4	3-4	4	3	4	4-5	4	4-5	4	2-3	4	4-5	4	4-5
4			4	3	4	3	4	3	4	4-5	4	4-5	4	3	4	5	4	5	4	2-3	4	5	4	5
		1f		1g				1h				1i		1j		1k								
		ISO Perspiration		ISO		Perspiration		ISO		Perspiration		ISO		ISO		ISO								
		pH 5,5 pH 8		pH 5,5 pH 8				pH 5,5 pH 8																
		C	S	C	S	C	S	C	S	C	S	C	S	C	S	C	S							
		4 1-2		4	1-2					4 1-2		4	3	4	3	4 3								
4		3	4	4-5	4	4-5	4	3	4	2-3	4	2-3	4	3	4	3	4 3							
4		3	4	4-5	4	4-5	4	3	4-5	5	4-5	5	4	3	4	3	4 3							
4		3	4	5	4	5	4	3	4-5	5	4-5	5	4	3	4	3	4 3							

blue and orange showed a satisfactory improvement for all the cationics (Tables I-III).

For the dyes green and grey the cotton staining of the blank was 2-3 and 3-4 respectively, whereas for all the concentrations of all the cationics was 2-3 and 4-5 respectively.

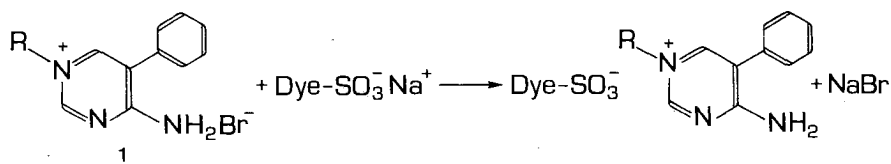
In the perspiration tests the cotton staining of the blank was for the green and grey 4-5 and 5 respectively. The score of cotton staining for all the cationics in concentrations 0.4-4% was from 4-5 to 5 for the dye green, whereas for the dye grey in the same concentrations was from 4 to 5.

Concerning the wool staining, only the dyes blue and red showed a score different than 5, that is in concentrations 0.4-2% of all the cationics the score was 4-5 for both dyes and both pH, whereas the respective blanks were 3-4 and 4-5.

DISCUSSION

The pyrimidinium cationics were effective as fixing agents in cotton fabrics dyed with direct dyes. This can be explained as follows :

The pyrimidinium cation reacts with the dye forming ionic bonds with the anionic sulfonic groups according to the equation :



Firstly, this compound 1 neutralizes the solubilising effect of the sulfonic groups of the dye making it less water soluble and so less easily washed out. Secondly, it increases the physical size of the dye molecule, so that it becomes trapped in the internal structure⁶. We consider that the phenyl group of the pyrimidine ring of the 1 reinforces that second effect, by increasing more the size of the dye molecule, compared with the sizes of the quaternary ammonium salts or pyridinium salts which are mostly used as conventional cationics.

Besides, the conventional cationics have been used many times to give antibacterial textile finishes¹⁵. The examined pyrimidinium cationic surfactants have also shown these antibacterial properties^{11,12} with more ef-

fective the compounds with 12-15 carbon atoms in the long chain, that is the compounds 1e-1f.

The effectiveness of the pyrimidinium cationics in ISO nr 2 was similar to that usually obtained with the conventional ones, whereas in perspiration fastness the results were sometimes excellent.

Table IV shows the lowest concentrations of the cationics, which the best scores (4-5 and 5) are obtained with, in the perspiration tests (optimum concentrations). It is visible that for the dye red the cationics 1f-1h gave the best scores at concentrations 2, 4 and 4% respectively, for the dye blue the cationics 1d-1h gave the best scores at concentrations 4, 2, 1, 2 and 1% respectively, whereas for the dye orange, the cationics 1c-1h at 4, 1, 1, 1, 2 and 1% respectively.

TABLE IV : Optimum concentrations of the aftertreatment agents for perspiration fastness.

Aftertreatment agent	Concentrations of the agents (%o.w.f.)		
	Rouge	Blue	Orange
1c	—	—	4
1d	—	4	1
1e	—	2	1
1f	2	1	1
1g	4	2	1
1h	4	1	1

Table V shows the scores of the perspiration fastness tests of some conventional cationics, in comparison with some pyrimidinium ones in concentrations 4% o.w.f. for the dyes red, blue and orange.

It is visible than in the same concentration 4% o.w.f. some of the pyrimidinium cationics have shown better scores, compared with the conventional ones.

TABLE V : The scores of perspiration fastness tests of some conventional cationics in comparison with some pyrimidinium ones (in concentrations 4% of the agent) for the dyes red, blue and orange.

Dyes	Levogen FWN (a)		Levogen FWN (b)		Levogen RS (c)		Pyrimidinium Cationics	
	pH		pH		pH		pH	
	5,5	8	5,5	8	5,5	8	5,5	8
	S	S	S	S	S	S	S	S
Red (a,b,c)	4-5	4-5	4	4	3-4	3-4	(1h)5	5
Blue (a,c)	4-5	4-5	-	-	5	5	(1g-1h)5	5
Orange (a,b,c)	4-5	4-5	4-5	4	4-5	4-5	(1d-1h)5	5

(a) : Our trials, Solophenyl Rouge 3BL, Solophenyl brill Blue BL, Solophenyl Orange TCL.

(b) : Schetter¹ Benzoscharlach 4BS, Siriuslichtorange 3GLD.

(c) : Rippon⁷ C.I. Direct Red 84, C.I. Direct Blue 78, C.I. Direct Orange 34.

ΠΕΡΙΛΗΨΗ

ΠΥΡΙΜΙΔΙΝΙΚΑ ΚΑΤΙΟΝΙΚΑ ΤΑΣΕΝΕΡΓΑ ΩΣ ΣΤΕΡΕΩΤΙΚΑ ΣΕ ΒΑΜΒΑΚΕΡΑ ΒΑΜΜΕΝΑ ΜΕ ΑΠΕΥΘΕΙΑΣ ΧΡΩΜΑΤΑ

Σκοπός αυτής της εργασίας είναι να μελετηθεί η βελτίωση που προκαλούν έντεκα κατιονικά τασενεργά 1(3)-αλκυλο-4-αμινο-5-φαινυλο-πυριδινό βρωμίδια στη στερέωση των χρωμάτων σε βαμβακερά υφάσματα. Τα υφάσματα βάφτηκαν με 5 διαφορετικά απευθείας χρώματα και μετακατεργάστηκαν με τα πιο πάνω τασενεργά. Η ίδια μετακατεργασία έγινε και με ένα συμβατικό κατιονικό τασενεργό, το Levogen FWN που χρησιμοποιείται ήδη ως στερεωτικό στο εμπόριο.

Το αποτέλεσμα (ή ο βαθμός) της στερέωσης του χρώματος μετρήθηκε με δοκιμές αντοχής σε υγρές κατεργασίες. Μερικά από τα πυριμιδινικά κατιονικά τασενεργά, που εξετάστηκαν παρουσιάζουν ενδιαφέρον, γιατί βελτιώνουν την αντοχή στις υγρές κατεργασίες των βαμβακερών βαμμένων με κάποια "δύσκολα" χρώματα, όπως είναι το κόκκινο, το μπλέ, το πορτοκαλλί. Η στερέωση του χρώματος ήταν για αυτά τα τασενεργά σχεδόν τέλεια, ακόμη και σε μικρές συγκεντρώσεις τους (1%, 2%).

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SYNTHESIS AND SPECTRAL STUDIES OF SOME NEW ZINC(II), LEAD(II) AND NICKEL(II) HYDROXYSUBSTITUTED DITHIOBENZOATO COMPLEXES

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SUMMARY

New Complexes of Zn(II), Pb(II) and Ni(II) with the o-, m-, p-hydroxydithiobenzoato and 2,4-dihydroxydithiobenzoato ligands have been prepared and characterized. The bonding properties and stereochemistries of these compounds are discussed in relation to their spectroscopic data (i.r. and UV-Vis). Moreover, the ability of the MS_4 chromophores to form adducts with pyridine has been also investigated.

Key Words: Dithiobenzoato complexes. EHMO-SCCC calculations. Pyridine adducts.

INTRODUCTION

It is well known that dithiocarboxylates, $RCSS^-$ (R = alkyl or aryl) behave as ligands in a similar way to that of other gem-disulfide ligands, such as dithiocarbamates, xanthates and dithiophosphates which have been studied extensively so far¹. However, their coordination compounds with bivalent and trivalent transition metal ions exhibited, in many cases, peculiar geometric, electronic and reactivity properties non-innocent to those of the other members in the series of the coordination compounds of the gem-disulfide ligands. Even, for dithiocarboxylates with different organic groups a wide range of physical²⁻⁴, spectral^{5,6} and chemical properties⁷⁻⁹ has been observed. Therefore, any investigation of new coordination compounds of the dithiocarboxylato ligands involving a variety of organic substituents would be of potential interest providing means to understand their peculiar chemistry. Along this line we report on, in the present paper, our results concerning the synthesis and study of the spectral and bonding properties of

twelve new o-, m-, p-hydroxy and 2,4-dihydroxy-substituted dithiobenzoato complexes of the bivalent metal ions, Zn(II), Pb(II) and Ni(II). The ability of these complexes to form adducts with pyridine is also discussed.

EXPERIMENTAL

Physical Measurements

Ir spectra were recorded in the 4000-250 cm^{-1} region on a Perkin-Elmer 467 spectrophotometer using KBr pellets or Nujol mulls. Electronic spectra were obtained on a Cary 17DX spectrophotometer using methanol and pyridine solutions. Conductivity measurements were carried out on a WTW conductivity meter using 10^{-3} solutions in DMF. Molecular weights were determined in chloroform solution using a Perkin-Elmer Model 115 molecular weight apparatus. Magnetic susceptibility measurements in solid state were done by the Faraday technique using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant. Melting points were determined with a Büchi apparatus and are uncorrected. The elemental analysis of carbon, nitrogen and hydrogen was performed on a Perkin-Elmer 240B Elemental Analyzer. Zinc, lead and nickel were determined according to published methods¹⁰

Starting Material

All solvents were of reagent grade and were used without further purification in synthetic work. The sodium salts of o-hydroxydithiobenzoic acid, [o-OH,dtbNa], m-hydroxydithiobenzoic acid, [m-OH,dtbNa], and p-hydroxydithiobenzoic acid, [p-OH,dtbNa], were prepared from the appropriate hydroxy-substituted benzaldehydes and ammonium disulfide according to the method described by Bost and coworkers¹¹. The 2,4-dihydroxydithiobenzoic acid, [2,4-(OH)₂,dtbH], was synthesized from resorcinol and carbon disulfide in sodium hydroxide aqueous solution¹².

Preparation of the complexes

The bis(hydroxy-substituted dithiobenzoato) zinc(II), lead(II) and nickel(II) complexes were prepared according to the following synthetic route: To a solution containing 1.0 mmol of the metal salt $[(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$, $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}]$ in 30 ml of water and 5 ml of glacial acetic acid, an alkaline aqueous solution containing 2.0 mmol of the sodium salt of the appropriate dithioacid was added slowly under continuous magnetic stirring. The solid products were filtered off, washed several times with water and dried in vacuum over P_2O_5 . Recrystalli-

sation was carried out by dissolving the solids in acetone, filtering and reprecipitating with water. The yield in this procedure were about 95%.

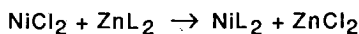
TABLE I: Analytical Data^a, Melting Points(^aC)^b and Molecular Weights for the New Complexes.

Compound	M.P.	%C	%H	%M ^c	M.W.
Zn(o-OH,dtb) ₂	113-115	42.11	2.43	16.25	418
		(41.64)	(2.50)	(16.19)	(403.9)
Zn(m-OH,dtb) ₂	118-120	41.78	2.48	16.38	423
		(41.64)	(2.50)	(16.19)	(403.9)
Zn(p-OH,dtb) ₂	197-199d	41.83	2.57	16.45	417
		(41.64)	(2.50)	(16.19)	(403.9)
Zn(2,4-(OH) ₂ ,dtb) ₂	135-138	39.22	2:28	15.52	453
		(38.59)	(2.31)	(15.00)	(453.9)
Pb(o-OH,dtb) ₂	199d	31.13	1.78	37.46	560
		(30.81)	(1.85)	(37.97)	(545.7)
Pb(m-OH,dtb) ₂	187-189d	30.37	1.93	37.53	556
		(30.81)	(1.85)	(37.97)	(545.7)
Pb(p-OH,dtb) ₂	231-233d	31.06	1.87	37.38	543
		(30.81)	(1.85)	(37.97)	(545.7)
Pb(2,4-(OH) ₂ ,dtb) ₂	>300	29.24	1.78	36.43	589
		(29.11)	(1.74)	(35.87)	(577.7)
Ni(o-OH,dtb) ₂	205d	41.98	2.42	14.80	380
		(42.33)	(2.54)	(14.78)	(397.2)
Ni(m-OH,dtb) ₂	236-238	41.86	2.58	14.85	378
		(42.33)	(2.54)	(14.78)	(397.2)
Ni(p-OH,dtb) ₂	245-248d	42.38	2.64	14.67	392
		(42.33)	(2.54)	(14.78)	(397.2)
Ni(2,4-(OH) ₂ ,dtb) ₂	228-230	39.30	2.35	13.92	440
		(39.18)	(2.35)	(13.68)	(429.2)

^a Figures in parentheses are the calculated values. ^b d = decomposition. ^c M = Zn, Pb or Ni.

RESULTS AND DISCUSSION

The hydroxy-substituted dithiobenzoato ligands readily form diamagnetic, non-electrolyte compounds with the bivalent metal ions Zn(II), Pb(II) and Ni(II) corresponding to the general formula $M^{II}L_2$. All new compounds can be prepared in almost quantitative yield by the reaction of the corresponding simple metal salts with the sodium salts of the appropriate dithio acids at room temperature. An alternative synthetic route for the Ni(II) complexes based on the metathetical reaction:



in alcoholic medium can be also used.

The twelve new compounds under investigation are listed in TABLE I along with some of their physical properties (melting points, elemental analysis and molecular weights). All compounds were isolated as microcrystalline solids, orange in colour for the Zn(II) and Pb(II) complexes and blue-violet for the Ni(II) complexes, insoluble in water, but soluble in strong alkaline aqueous solutions and in most of the common organic solvents. They are stable in the atmosphere either in the solid state or in solution. Molecular weight determinations in chloroform solutions showed the monomeric nature of all complexes and therefore the formula $M^{II}L_2$ represents correctly not only the stoichiometric composition, but also the true molecular complexity of the compounds in solutions of non-coordinated solvents.

To have an insight on the bonding mode of the hydroxysubstituted dithiobenzoato ligands and the stereochemistry of the new compounds, their IR and electronic spectral data were analysed carefully. The results are discussed in the following sections.

Infrared Spectra

The most relevant vibrational frequencies (cm^{-1}) of the new compounds along with their assignments are shown in TABLE II. All other absorption bands present in the IR spectra of the complexes were easily identified to aryl group vibrations by comparison with the spectra of substituted benzenes¹³ or phenols¹⁴. These bands will not be discussed further, for they do not provide any significant information about the coordination mode of the ligands.

TABLE II: The most Relevant IR Frequencies (cm^{-1}) of the Investigated Compounds and their Assignments (KBr discs)^a.

Compound	$\nu(\text{OH})$	$\nu(\text{S}_2\text{C}\cdots\text{Ar})^b$	$\nu(\text{C}\cdots\text{O})$	$\nu_{\text{as}}(\text{CSS})$	$\nu_{\text{s}}(\text{CSS})$	$\nu(\text{M}\cdots\text{S})^c$
Zn(o-OH,dtb) ₂	3350m,br	1302s	1252	985w	930w	302w
Zn(m-OH,dtb) ₂	3400m,br	1290vs	1228s	1030vs	980s	328w
Zn(p-OH,dtb) ₂	3440m,br	1279s	1238vs	994vs	916s	330m
Zn(2,4-(OH) ₂ ,dtb) ₂	3380m,br	1248s	1221s	984s	930m	332w
Pb(o-OH,dtb) ₂	3350w,br	1278s	1234s	959s	914s	313w
Pb(m-OH,dtb) ₂	3380m,br	1274vs	1220m	980vs	958s	323w
Pb(p-OH,dtb) ₂	3400m,br	1270vs	1231vs	986vs	915s	350w
Pb(2,4-(OH) ₂ ,dtb) ₂	3380m,br	1250vs	1220vs	987m	967vs	310w
Ni(o-OH,dtb) ₂	3360m,br	1291vs	1215vs	974s	953s	372w
Ni(m-OH,dtb) ₂	3380m,br	1295vs	1232s	1022m	974vs	370s
Ni(p-OH,dtb) ₂	3400m,br	1298vs	1235vs	980s	950s	383m
Ni(2,4-(OH) ₂ ,dtb) ₂	3370m,br	1250vs	1225vs	981vs	935m	380w

^a vs = very strong, s = strong, m = medium, w = weak, br = broad. ^b Ar = aryl. ^c M = Zn, Pb or Ni.

The broad absorption band occurring in the 3350-3410 cm^{-1} region of the spectra was assigned to the $\nu(\text{OH})$ stretching vibration of the hydroxyl substituents. This band is shifted towards lower frequencies relative to the corresponding band of the free phenols¹⁴ as a consequence of the electron withdrawing capacity of the CSS^- moiety of the ligands. Moreover, the $\nu(\text{OH})$ band of the $\text{M}(\text{o-OH,dtb})_2$ and $\text{M}(2,4-(\text{OH})_2,\text{dtb})_2$ complexes was found at lower frequencies than the corresponding bands of all other complexes under investigation, suggesting the existence of intramolecular hydrogen bonds in these complexes.

The positions of the bands due to $\nu(\text{S}_2\text{C}\cdots\text{Ar})$ (1250-1300 cm^{-1}) and $\nu(\text{C}\cdots\text{O})$ (1220-1250 cm^{-1}) stretching vibrations¹⁵⁻¹⁸ strongly call for an extensive π -electron density delocalization over the entire nuclear framework of the molecules. Such an electron density delocalization results in a partial double bond character for both $\text{C}\cdots\text{Ar}$ and $\text{C}\cdots\text{O}$ bonds. In fact, the $\text{C}\cdots\text{Ar}$ partial bond character has been verified by an X-ray structure determination of the $\text{Ni}(\text{dtb})_2$ complex².

Of special importance in determining the bonding mode of the ligands are the bands due to the $\nu_{\text{as}}(\text{CSS})$ and $\nu_{\text{s}}(\text{CSS})$ stretching vibrations of the coordinated

CSS moiety. According to a well established criterion¹⁹ based on the magnitude of $D = [v_{as}(CSS) - v_s(CSS)]$ ($D = 200-500\text{cm}^{-1}$ for unidentate and $30-80\text{cm}^{-1}$ for bidentate dithio-ligands²⁰) there is no doubt that all ligands in the new complexes act in a bidentate fashion ($D = 20-50\text{cm}^{-1}$). Thus, for the Zn(II) and Pb(II) central atoms with d^{10} -electronic configuration one would expect tetrahedral geometries for the MS_4 chromophores, whereas for Ni(II) with d^8 -electronic configuration square planar ones. Actually these geometries have been determined by X-ray crystallography for both Zn(II) and Ni(II) dithiobenzoato complexes^{2,21}. However, X-ray structure determinations on Pb(II) complexes with sulfur containing chelate ligands^{22,23} showed that these complexes adopt the square pyramidal structure instead of the tetrahedral one. Therefore, there is no reason to exclude the square pyramidal structure of the new Pb(II) dithio-complexes as well.

Electronic Spectra

The electronic spectral bands for the ZnS_4 and PbS_4 chromophores listed in Table III repeat rather regularly the spectral pattern characterizing the free dithiobenzoato ligands⁵. The band at c.a. 40 kK was attributed to the intraligand benzenoid transitions, whereas that at c.a. 34 kK may be due to an "intramolecular charge transfer" between the aryl and the CSS group, according to the model proposed by Nagakura^{24,25}. Alternatively, such a transition involves molecular orbitals localized on the phenyl and CSS moieties respectively. The band around 20 kK, which appears as a shoulder of low intensity was attributed to an $L(\pi^*) \leftarrow L(\pi)$ transition located on the thiocarbonyl group. Finally, the remaining band near 28 kK not observed in the spectra of the free ligands could be undoubtedly assigned to an $L(\pi^*) \leftarrow M(d)$ charge transfer band.

The electronic transitions of the NiS_4 chromophores studied along with their assignments are listed in Table IV. Due to the complicated nature of the spectra - a number of overlapping intense bands in the ultraviolet and visible region - all assignments were made on the basis of a series of EHMO-SCCC molecular orbital calculations on the Ni(II) complexes²⁶. According to these calculations the bands existing in the region 31-43 kK of the spectra are attributed to intraligand transitions of the $L(\pi^*) \leftarrow L(\pi)$ type. These bands are similar to those found in the spectra of the Zn(II) and Pb(II) chromophores. The rest part of the spectra is characterized by the existence of two band envelopes. The first one occurring in the region of 26-30 kK is composed from a strong band accompanied by a shoulder of lower intensity. This band envelope includes all charge transfer transitions of the $L(\pi^*) \leftarrow M(d)$ nature and is similar to that

recorded in the spectra of the corresponding d^{10} chromophores as well of analogous d^8 MS_4 chromophores^{5,6}. The second band envelope consisting of a strong band at c.a. 19.0 kK and one or two shoulders of lower intensity exist in the spectra of all square planar d^8 MS_4 chromophores^{5,6}, but is absent from the spectra of the d^{10} MS_4 chromophores. Obviously this band envelope includes all charge transfer bands of the $M(d) \leftarrow L(\pi)$ nature in accordance with the results of the EHMO-SCCC calculations²⁶. Finally, the position and low intensity of the band at c.a. 13 kK is consistent with its assignment to a ${}^1B_{1g} \leftarrow {}^1A_g$ ligand field excitation in a ligand field of D_{2h} symmetry.

TABLE III: Electronic Spectral Data of the New Zn(II) and Pb(II) Complexes in MeOH^a.

Compound	$L(\pi^*) \leftarrow L(\pi)$	$L(\pi^*) \leftarrow L(\pi)$	$L(\pi^*) \leftarrow M(d)$	$L(\pi^*) \leftarrow n(S)$
Zn(o-OH,dtb) ₂	40.1sh(4.15)	35.1 (4.15)	28.8 (3.90)	19.8 (3.00)
Zn(m-OH,dtb) ₂	41.3 (4.26)	32.8 (4.43)	29.2 (4.30)	23.3sh(3.90)
Zn(p-OH,dtb) ₂	42.2 (4.54)	34.3sh(4.24)	28.0 (4.84)	22.7sh(3.09)
				21.3sh(2.90)
Zn(2,4-(OH) ₂ ,dtb) ₂	42.9 (4.38)	32.6 (4.19)	28.4 (4.28)	21.3sh(2.49)
				26.3sh(4.17)
Pb(o-OH,dtb) ₂	40.8sh(4.22)	34.7 (4.28)	27.5 (4.19)	20.0sh(2.60)
Pb(m-OH,dtb) ₂	40.5 (4.31)	32.8 (4.26)	27.8 (4.04)	19.7sh(2.71)
Pb(p-OH,dtb) ₂	43.0 (4.49)	34.1sh(4.13)	27.9 (4.52)	21.5sh(3.24)
				19.6sh(2.87)
Pb(2,4-(OH) ₂ ,dtb) ₂	42.8 (4.28)	32.5 (4.23)	28.3 (4.54)	19.0sh(2.46)
			29.4sh(4.44)	26.3sh(4.17)

^a $\nu/kK(\log \epsilon_{m0})$, sh = shoulder

All other expected ligand field transitions for a quadratic MS_4 chromophore could not be observed in the spectra, for they are obscured by the more intense CT and intraligand bands. However, for the Ni(m-OH,dtb)₂ and Ni(p-OH,dtb)₂ complexes the observed shoulders at 15.4 and 16.3 kK respectively, can be attributed to the second ligand field transition of the ${}^1B_{1g} \leftarrow {}^1A_g$ type. These electronic transitions predicted also by the EHMO-SCCC calculations²⁶ correspond to absorption bands of unexpectedly high intensity for ligand field transitions. However, this is not surprising considering the position of these bands very close

to that of the more intense CT bands and therefore an "intensity borrowing mechanism" provides means for their enhanced intensity.

TABLE IV: Electronic Spectral Data of the New Ni(II) Complexes^a.

Ni(o-OH,dtb) ₂	Ni(o-OH,dtb) ₂	Ni(o-OH,dtb) ₂	Ni(2,4(OH) ₂ ,dtb) ₂	Assignments
<i>MeOH solutions</i>				
13.1 (1.99)	13.1 (2.72)	13.7 (1.91)	12.9sh(2.08)	¹ B _{1g} ← ¹ A _g (D _{2h})
	15.4sh(3.04)	16.3sh(3.38)		¹ B _{3g} ← ¹ A _g (D _{2h})
18.0sh(4.07)	16.9sh(3.79)	17.5sh(3.82)		
19.2 (4.09)	18.4 (3.79)	19.1 (3.96)	19.1 (4.32)	M(d)←L(π)
22.6 (3.76)	21.4sh(3.64)	23.5sh(3.73)	20.2sh(4.27)	
27.2 (4.23)	26.8sh(4.29)	27.6 (4.55)	26.2 (4.46)	L(π*)←M(d)
30.6 (4.45)	29.9 (4.46)	30.0sh(4.15)	29.9sh(4.34)	
34.8sh(3.97)	34.0 (4.27)	35.2 (3.86)	37.0 (4.20)	L(π*)←L(π)
42.9sh(3.96)	41.7 (4.20)	38.8 (3.83)	40.8sh(4.18)	
<i>Pyridine solutions</i>				
8.9sh(0.78)	9.3sh(1.18)	9.1sh(1.22)	9.2sh(0.48)	³ E _g ← ³ B _{1g} (D _{4h})
10.5sh(1.09)	10.7 (1.46)	10.4 (1.53)	11.7sh(1.03)	³ B _{2g} ← ³ B _{1g} (D _{4h})

^a v/kK(logε_{m0}), sh = shoulder

The spectra of all new complexes were also recorded in pyridine solutions. Only for the Ni(II) complexes significant differences have been observed, suggesting a change of the nature of the NiS₄ chromophore in the pyridine donor solvent. Such a change could be attributed to adduct formation between the NiS₄ chromophore and the pyridine donor molecules. A careful analysis of the ligand field part of the electronic spectra strongly call for the formation of 1:2 adducts assumed to contain trans-[NiS₄N₂] chromophores, since they are fitted well to the spectra of pseudo-octahedral high-spin Ni(II) complexes²⁷. The spectral data for the adducts along with their assignments based on pseudo-octahedral [NiS₄N₂] chromophores of D_{4h} symmetry²⁸ are also listed in Table IV.

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SYNTHESIS AND STUDY OF METAL COMPLEXES OF N,N-DIALKYL(DI AND TRI)METHYLENE-DITHIOCARBAMATO LIGANDS

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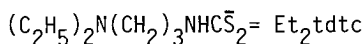
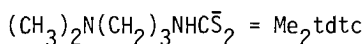
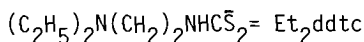
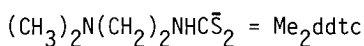
SUMMARY

Sixteen new complexes of Ni(II), Co(II), Zn(II) and Cd(II) with N,N-dimethyldimethylene-, N,N-diethyldimethylene-, N,N-dimethyltrimethylene- and N,N-diethyltrimethylene-dithiocarbamate ligands have been prepared. Elemental analyses, IR, UV-Vis spectra and magnetic measurements were used to characterize the complexes. Based on these information plausible structures are proposed. Calculations by the MNDO method have been performed on a representative ligand in an attempt to understand the bonding capacity of all four molecules.

Key words : Dialkyldimethylene dithiocarbamic acid, dialkyltrimethylene dithiocarbamic acid, metal dithiocarbamate complexes, synthesis, study, MNDO method calculation.

INTRODUCTION

Due to a well known fungicide activity various dithiocarbamate ligands and their complexes with transition metals and main group elements have received considerable attention over the last few years [1-4]. As our interest on this group of molecules continues, we report here the preparation and characterization by physical methods of a new series of sixteen complexes of Ni(II), Co(II), Zn(II) and Cd(II) with N,N-dialkyl-(di- and tri-)methylene-dithiocarbamate anions. The general formula of the ligand is $R_2N(CH_2)_nNHC\bar{S}_2$, where $R=CH_3, C_2H_5$ and $n=2,3$. The following abbreviations will be used for the four ligands:



All these compounds have similar ligation behaviour. To study their mode of coordination, the ligand Me_2tdtc , has been examined by the MNDO method.

EXPERIMENTAL

Physical Measurements

The H, C and N analyses were performed on a Perkin-Elmer 240 Elemental Analyzer. The metal determinations were carried out volumetrically by published methods [5]. Infrared spectra were recorded as KBr discs or Nujol mulls on a Perkin-Elmer 467 spectrometer in the region 4000 - 250 cm^{-1} . UV-Visible spectra were obtained by a Carry 17 DX and a Perkin-Elmer-Hitachi 200 spectrophotometer. Magnetic susceptibilities measurements at room temperature (25°C) used the Faraday technique with $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrator. Diamagnetic corrections were using Pascal's constants.

Theoretical calculation

The reported computation has been performed by using the MNDOC [6] system of programs implemented on an IBM 4381 computer. The parameters used for sulfur are those presented by Dewar and McKee [7]. An improved set was recently proposed by Dewar and Reynolds [8], but this is particularly important in case of compounds with SS bonds or molecules with the S atom in higher valence states, where d functions are, probably, necessary in the basis set and will not be adopted here.

Preparation of the Complexes

First the free acids $\text{R}_2\overset{+}{\text{N}}(\text{CH}_2)_n\text{NHCS}_2^-$ (R=Me, Et and n=2,3) were prepared by reaction of stoichiometric amounts of CS_2 and the appropriate amine, both dissolved in ether, at room temperature [9]. Then sodium salts of the anions $\text{R}_2\text{N}(\text{CH}_2)_n\text{NHCS}_2^-$ were prepared, as usually, by reaction of the free acids with sodium hydroxide in ethanol/water solution. Finally the complexes were obtained from this solution by addition of hydrated metal chlorides in stoichiometric quantities, after stirring for a period of 2 hours. The precipitates were washed with water, ethanol and ether and dried.

RESULTS AND DISCUSSION

Complete elemental analyses and physical characteristics of the new

TABLE I. Analytical Data found (calc) % and some physical properties of the complexes

Compound	C	H	N	S	M	M.P.	Colour
Ni Me ₂ ddtc ₂	30.96(31.17)	5.67(5.71)	14.38(14.55)	32.92(33.25)	15.50(15.32)	115d	green
Ni Et ₂ ddtc ₂	38.54(38.09)	6.72(6.80)	12.24(12.70)	29.38(29.02)	13.41(13.38)	148d	green
Ni Me ₂ tdtc ₂	34.86(34.87)	6.43(6.30)	13.44(13.56)	30.74(30.92)	14.68(14.29)	156d	green
Ni Et ₂ tdtc ₂	40.70(40.92)	7.40(7.25)	12.20(11.94)	27.13(27.29)	12.33(12.52)	90d	green
Co Me ₂ ddtc ₂	31.42(31.17)	5.63(5.71)	14.39(14.55)	33.41(33.25)	15.18(15.32)	69d	green
Co Et ₂ ddtc ₂	38.18(38.10)	6.89(6.80)	13.04(12.70)	27.41(29.02)	13.67(13.38)	65d	dark green
Co Me ₂ tdtc ₂	34.51(34.87)	6.19(6.30)	13.78(13.56)	30.12(30.99)	14.59(14.29)	78d	dark green
Co Et ₂ tdtc ₂	40.58(40.94)	7.22(7.25)	11.52(11.94)	25.30(27.29)	12.65(12.58)	70d	dark green
Zn Me ₂ ddtc	25.86(25.28)	4.98(4.82)	12.38(12.26)	27.93(29.02)	28.27(28.52)	58d	white
Zn Et ₂ ddtc	33.25(32.76)	6.06(5.86)	11.36(10.92)	24.65(24.96)	25.31(25.50)	90d	white
Zn Me ₂ tdtc	29.88(29.71)	5.28(5.36)	11.67(11.55)	26.27(26.41)	26.83(26.27)	65d	white
Zn Et ₂ tdtc	35.42(35.51)	6.18(6.29)	10.28(10.36)	23.46(23.57)	23.98(24.19)	72d	white
Cd Me ₂ ddtc ₂ ₂	26.98(27.37)	4.98(5.02)	12.38(12.77)	29.51(29.20)	25.32(25.64)	120	white-yellow
Cd Et ₂ ddtc ₂	33.79(33.98)	6.03(6.07)	11.24(11.33)	25.67(25.90)	22.58(22.73)	98	white-yellow
Cd Me ₂ tdtc ₂	30.68(30.97)	5.38(5.57)	11.38(12.01)	27.75(27.44)	23.98(24.10)	126	white
Cd Et ₂ tdtc ₂	36.41(36.75)	6.43(6.51)	10.63(10.72)	23.95(24.50)	21.46(21.52)	90	white-yellow

complexes are given in TABLE I. The Ni(II) complexes are green, diamagnetic solids, stable in the air and soluble in common organic solvents like chloroform, dichloromethane and ethanol. The Co(II) complexes are dark green paramagnetic substances, soluble in chloroform. The Zn(II) and Cd(II) are yellowish and white respectively diamagnetic amorphous insoluble solids. It should be noted that all attempts to prepare complexes of Zn(II) in a different than 1:1 stoichiometric analogy have failed.

In order to have a preliminary idea concerning the structure of the new complexes, it seems interesting to estimate, by means of theoretical calculations, the bonding capacities in each donor atom of the free ligand anions. Thus, we tried to determine the sites responsible for the ligand bonding effects in terms of the atomic charges derived from the MNDO density matrix by means of Mulliken's population analysis, and the atomic constitution in the frontier molecular orbitals (FMOs) of the ligands.

The reported MO calculations have been performed by using the SCF-LCAO-MO method in the framework of the MNDO approximation [10]. Some attempts have also been made to derive the pertinent parameters by means of other semi-empirical methods, but these were not so successful, so we shall here report on the aforementioned results only. The initial geometries, taken from crystallographic data for the free acid [4], have been optimized for the corresponding anion by means of the Davidson-Fletcher-Powell algorithm included in the program. The final geometries are presented in TABLE II, along with some bond lengths of the free acid, which have been modified during the optimization procedure. The difference in length, between the two bonds $S(1)-C(2)=1.618 \text{ \AA}$ and $C(2)-S(3)=1.605 \text{ \AA}$ implies that they are not equivalent, with, as a result, the splitting of the IR C-S band in two components. The $C(2)-N(4)$ distance, 1.395 \AA , makes evident the double-bond character of this bond. One should also notice the reduction in the length of bonds due to the negative charge of the molecule. Finally mention has to be made that the geometrical data derived from this optimization show the general trends of the MNDO method with the characteristic underestimation of bond lengths also noted elsewhere [11].

The Figure 1 gives the atomic numbering scheme and the net atomic charges. It is also evident from this Figure that the sites of nucleophilic attack are the two sulfur atoms with their slightly inequivalent net

TABLE II. Optimized bond lengths (in Å) and angles (in degrees) of the ligand Me₂tdtc (in brackets are quoted some bond lengths of the free acid).

S(1)-C(2)	1.618	1.727	S(1)-C(2)-S(3)	125.9
C(2)-S(3)	1.605	1.699	S(3)-C(2)-N(4)	121.2
C(2)-N(4)	1.395		C(2)-N(4)-C(5)	127.5
N(4)-C(5)	1.464		N(4)-C(5)-C(6)	107.5
C(5)-C(6)	1.521		C(5)-C(6)-C(7)	116.5
C(6)-C(7)	1.508		C(6)-C(7)-N(8)	115.8
C(7)-N(8)	1.574		C(7)-N(8)-C(9)	120.9
N(8)-C(9)	1.480	1.483	C(7)-N(8)-C(10)	120.9
C(9)-C(10)	1.480	1.503	C(2)-N(4)-H(11)	116.3

atomic charges.

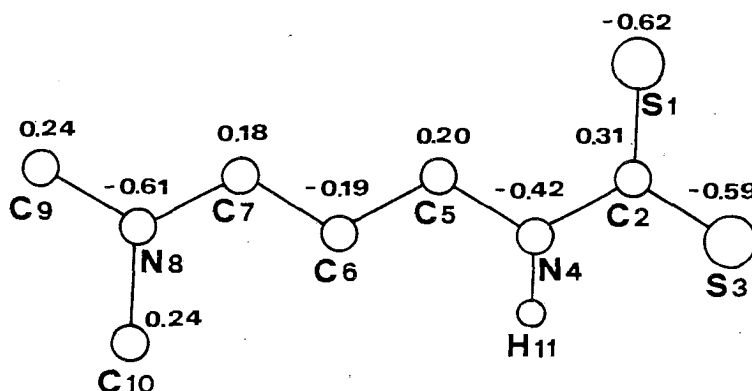


FIG. 1 : Atomic numbering scheme and MND0 atomic charges of the Me₂tdtc ligand.

The energies and atomic constitution of the frontier MOs are presented in TABLE III. We notice that the two sulfur atoms participate heavily in the HOMO eigenvector and its two neighbours in the occupied space, whereas the unoccupied NNLUMO (3rd in ascending order) extends over the whole dithiocarbamate region of the anion.

Keeping these computational results in mind, we tried to establish the bonding of the new complexes by spectroscopic methods and magnetic susceptibility measurements.

The infrared spectra of the ligands and the new complexes (TABLE IV) show medium broad bands in the region 3160-3200 cm⁻¹ assigned to the ν(N-H) stretching vibration [12]. The strong bands appearing in the re-

TABLE III. Eigenvalues (in a.u.) and atomic constitution (%) in the eigenvectors of the frontier MOs of the ligand Me_2tdtc .

MO-type	Eigenvalue	Eigenvector constitution (%)				
		S(1)	C(2)	S(3)	N(3)	$\text{Me}_2\text{NH}(\text{CH}_2)_3$
NNLUMO	5.3329	12.40	65.17	13.04	7.96	1.43
NLUMO	5.1227	0.00	0.00	0.00	1.33	98.67
LUMO	3.7418	0.00	0.00	0.00	0.00	100.00
HOMO	-4.0569	52.89	0.00	46.40	0.00	0.71
NHOMO	-4.1062	53.72	0.00	46.21	0.00	0.07
NNHOMO	-4.6744	43.25	0.00	48.38	4.92	3.45

gion $1505\text{-}1520\text{ cm}^{-1}$ are due to the stretching of the C-N bond [13-15]. In the case of the Ni(II) complexes this band is shifted to higher frequencies ($1575\text{-}1590\text{ cm}^{-1}$) showing a considerable double bond character which suggests a bidentate linkage of the dithiocarbamate group. This evidence is further supported by the stretching vibration of the C-S bond ($965\text{-}1020\text{ cm}^{-1}$). Generally, the stretching vibrations of the C-N and C-S bonds are little affected by the nature of the central atom in the complexes. An exception occurs, however, in the case of the Ni(II) compounds due, presumably, to their square planar stereochemistry [14]. Notice that the IR spectra of the ligands and their complexes remain unperturbed when we change the R group or the number of methylene groups. Finally, the metal-ligand bonding modes of the complexes appear in the usual range ($300\text{-}400\text{ cm}^{-1}$) [16].

The electronic spectra of the sodium salts of the anions in aqueous solutions exhibit a first intense UV band at ca. 40 kK ($\log \epsilon_{\text{max}} = 4.5$) and 35 kK ($\log \epsilon_{\text{max}} = 4.1$) and a second very weak forbidden band at ca. 30 kK ($\log \epsilon_{\text{max}} = 2.0$) (TABLE V). Solid state spectra exhibit also similar UV bands. These have been attributed to intraligand excitations. For the Ni(II) complexes in chloroform solution an additional band appearing at ca. 26 kK has been assigned to a charge transfer transition [17-21]. An intense band at ca. 23 kK has been assigned to an allowed L→M charge transfer transition. Another weak band starts at ca. 16 kK with a $d_{x^2-y^2} \rightarrow d_{xy}$ electronic transition [19] and finishes at ca. 20 kK with a shoulder due to a $d_{z^2} \rightarrow d_{xy}$ transition. The remaining parity and spin-forbidden d→d transitions stay practically unobserved. The absence of any band in the range $10\text{-}15\text{ kK}$ is a strong evidence against the existence of an octahedral

TABLE IV. Infrared Bands of the Ligands and their Complexes (in cm^{-1})

Compound	Vibrational assignments				
	$\nu(\text{N-H})$	$\nu(\text{C-N})$	$\nu(\text{C-S})$	$\nu(\text{CSS})$	$\nu(\text{M-S})$
Me_2ddtc	3160 s	1510 vs	1025 s 925 vs	865 m	
$\text{Ni} \text{Me}_2\text{ddtc} _2$	3150	1575	1030 930	880	390
$\text{Co} \text{Me}_2\text{ddtc} _2$	3200	1506	1054 956	870	
$\text{Zn} \text{Me}_2\text{ddtc} $	3240 br	1490 vs	1025 m 978 vs	920 m	355 m
$\text{Cd} \text{Me}_2\text{ddtc} _2$	3220 s	1510 vs	1030	850 s	388 w
Et_2ddtc	3180 s	1510 vs	1010 s 955 vs	877 m	
$\text{Ni} \text{Et}_2\text{ddtc} _2$	3170 m	1590 s	1018 m 965 vs	900 w	388 w
$\text{Co} \text{Et}_2\text{ddtc} _2$	3200 s	1508 vs	1062 s 968 s	870 w	350 vs
$\text{Zn} \text{Et}_2\text{ddtc} $	3240 br	1490 vs br	1008 m 965 vs	898 m	355 s
$\text{Cd} \text{Et}_2\text{ddtc} _2$	3200 m br	1510 vs br	965 vs br		
Me_2tdtc	3180 s	1510 vs	1012 m 958 vs	878 m	
$\text{Ni} \text{Me}_2\text{tdtc} _2$	3160 m	1580 vs	1021 w 955 m	870 w	388 s
$\text{Co} \text{Me}_2\text{tdtc} _2$	3200 br	1505 vs	1035 m 955 m	870 m	350 s
$\text{Zn} \text{Me}_2\text{tdtc} $	3240 br	1510 br	1025 m 952	878 s	365 s
$\text{Cd} \text{Me}_2\text{tdtc} _2$	3210 m br	1510 vs br	1040 m 955 vs br	840 m	365 w
Et_2tdtc	3200 s	1510 vs	1035 m 910 vs	880 m	
$\text{Ni} \text{Et}_2\text{tdtc} _2$	3160 m	1580 vs	1022 m 960 s	870 s	395 vs
$\text{Co} \text{Et}_2\text{tdtc} _2$	3200 br	1505 vs	1065 m 945 w	870 w	350 s
$\text{Zn} \text{Et}_2\text{tdtc} $	3240 br	1505 vs	1065 m		350
$\text{Cd} \text{Et}_2\text{tdtc} _2$	3200 m	1510 vs br	1035 w	855 m	370 w

TABLE V. Electronic spectra of the Ligands and their complexes (in kK).

Compound	Band 1	Band 2	Band 3	Band 4	Band 5	Band 6
Me ₂ ddtc	40.32 35.33	29.85				
Ni Me ₂ ddtc ₂	38.76	30.77	25.77	23.15	20.62 sh	15.55
Co Me ₂ ddtc ₂	40.82 37.45	31.09	27.50	25.11	20.20	15.46
Zn Me ₂ ddtc	38.02 36.00	30.67				
Cd Me ₂ ddtc ₂	38.55 35.09	30.80	27.40			
Et ₂ ddtc	40.00 34.13	29.67				
Ni Et ₂ ddtc ₂	39.22	30.86	26.18	23.42	20.62	15.62
Co Et ₂ ddtc ₂	40.82 37.45	31.25	27.55	25.00	20.20	15.50
Zn Et ₂ ddtc	40.00 35.09	30.76				
Cd Et ₂ ddtc ₂	38.46 34.48	30.85	27.03			
Me ₂ tdtc	40.32 35.33	29.67				
Ni Me ₂ tdtc ₂	39.22	30.49	26.11	23.53	20.75	15.62
Co Me ₂ tdtc ₂	40.82 37.45	31.06	27.40	25.00	20.20	15.46
Zn Me ₂ tdtc	40.00 34.48	30.96				
Cd Me ₂ tdtc ₂	39.20 34.48	30.85	27.03			
Et ₂ tdtc	40.00 35.33	29.85				
Ni Et ₂ tdtc ₂	40.82	30.77	26.11	23.53	20.62	15.50
Co Et ₂ tdtc ₂	40.82 37.45	30.96	27.55	25.32	20.20	15.43
Zn Et ₂ tdtc	39.22 35.09	30.76				
Cd Et ₂ tdtc ₂	38.46 34.60	30.95	27.40			

or tetrahedral arrangement [18]. This conclusion is further supported by the magnetic measurements. All the Ni(II) complexes reported are diamag-

netic indicating a spin singlet ground state characteristic of a square planar Ni(II) structure. The band at ca. 16kK is then attributed to the well known ($^1A_{1g} \rightarrow ^1B_{1g}$) transition of square planar complexes [22,23].

Adopting the value $F_4=80\text{cm}^{-1}$ [24] ($F_2=10F_4=800\text{cm}^{-1}$) for the Slater-Condon interelectronic repulsion parameters the experimental Δ value of Ni(II) complexes is found at 18.6kK. This value is in agreement with the position of these ligands in the spectrochemical series.

Identical absorption spectra for the Ni(II) complexes were obtained in a number of solvents, such as pyridine and acetonitrile, which is an expected feature in planar NiS_4 chromophores and indicates that axial solvent perturbations are of minor importance so that the symmetry remains unchanged.

The absorption spectra of the Co(II) complexes present the same bands. In the visible region of the spectrum the values are quite similar to those for the Ni(II) planar complexes. This fact in unison with the magnetic measurements ($\mu_{\text{eff}}=2.20-3.07$ B.M. in quite the same ranges as reported in [25]) suggests that the Co(II) complexes are also of square planar geometry.

As expected, quite similar electronic spectra are exhibited by the complexes of the d^{10} metal ions. The position of the $n \rightarrow \pi^*$ transition is practically unchanged whereas the most significant changes occur in the ultraviolet region.

One cannot say more for the Zn(II) and Cd(II) complexes. As previously noted, they are quite insoluble so only their spectra in the solid state could be studied. One can clearly distinguish one charge transfer band in the Cd(II) case, similar to the first CT band discussed earlier. This band is absent in the Zn(II) case.

ΠΕΡΙΛΗΨΗ : Σύνθεση και μελέτη των μεταλλικών συμπλόκων των N,N-διαλκυλο (δι- και τρι-)μεθυλενο-διθειοκαρβαμιδικών

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Σύμπλοκα των μετάλλων Ni(II), Co(II), Cd(II) και Zn(II) με τα N,N-διαλκυλαιθυλενο- και N,N-διαλκυλοτριμεθυλενο-διθειοκαρβαμιδικά παρασκευάζονται κατά την αντίδραση σε υδατοαλκοολικά διαλύματα των χλωριούχων αλάτων των μετάλλων με τα αντίστοιχα διθειοκαρβαμιδικά άλατα του νατρίου.

Η ταυτοποίηση των ενώσεων και η δομή τους έγινε από τη στοιχειομετρική τους ανάλυση και τα δεδομένα της φασματοσκοπικής τους μελέτης και από

τη μέτρηση της μαγνητικής επιδεκτικότητας. Για την εξήγηση του τρόπου συναρμογής έγινε επίσης και θεωρητική μελέτη με κβαντοχημικούς υπολογισμούς με τη μέθοδο MNDO.

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