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COMPLEXES OF HYRAZONES DERIVED FROM 1,4-DIFORMYL- AND 1,4-DIACETYLBENZENES WITH TRANSITION METAL ACETATES

DAVID NICHOLLS

Donnan Laboratories, The University, Liverpool, L69 3BX, England.

JOHN MARKOPOULOS

Department of Chemistry, University of Athens, Inorganic Chemistry Laboratory, Panepistimiopolis, Kouponia, Athens - 15701, Greece.

OLGA MARKOPOULOU*

Organic Chemistry Laboratory, National Technical University of Athens, Zografou Campus, Athens - 15773, Greece.

SUMMARY

With the ligands 1,4-diformylbenzene bishydrazone (DFBH) and 1,4-diacetylbenzene bishydrazone (DABH), the metal acetates of Cd(II), Hg(II) and Cu(II) form complexes of the type $M(CH_3COO)_2(DFBH)$ or $M(CH_3COO)_2(DABH)$. The coordination atom is probably N^1 of the DFBH or DABH and the structures are probably polymeric, six coordinated with both bridging acetates and hydrazone ligands. With Zn(II) and Ni(II) if the ratio is 2:1 (excess of metal acetates), the isolated complexes are similar to the complexes which have been mentioned above, but if the ratio is 1:2 (excess of ligand), the isolated products have the formulae $M(CH_3COO)(OH)(DFBH)$ or $M(CH_3COO)(OH)(DABH)$. With rhodium(II) acetate, new ligands $C_8H_8N_3$ (starting from DFBH) and $C_{10}H_{12}N_3$ (starting from DABH) arose, and octahedral hydroxo complexes of these ligands have been isolated. Finally, with cobalt(II) acetate, the DFBH ligand forms a complex of the type $Co(CH_3COO)_2(DFBH)$ which is probably six coordinated. However with DABH if the ratio is 2:1 (excess of metal acetate), a new azine ligand $C_{10}H_{10}N_2$ is formed and the isolated complex has the type $Co(CH_3COO)_2(C_{10}H_{10}N_2)$; when the ratio is 1:2 (excess of ligand) the only isolated product is the azine.

Key words: Synthesis, Hydrazones, Transition metal acetates, 1,4-Diformylbenzene, 1,4-Diacetylbenzene, Complexes.

INTRODUCTION

Ligands with N-N bonds have been much studied in recent years because of their relationship to the problem of conversion of dinitrogen to

ammonia or hydrazine. The interest in the study of hydrazones has been growing, due to their use in biological systems[1], analytical chemistry[2] and in nonlinear optics (NLO)[3]. In recent years systematic investigation of the coordination chemistry of bishydrazones as chelating agents have been carried out and many complexes of the bishydrazones of 1,2-dicarbonyl compounds have been characterized[4,5]. In our earlier paper[6] we have reported the preparation of the new ligands 1,4-diformylbenzene bishydrazone (DFBH) and 1,4-diacetylbenzene bishydrazone (DABH) (Fig. 1) and the reactions of these ligands with anhydrous transition metal (II) halides and pseudohalides.
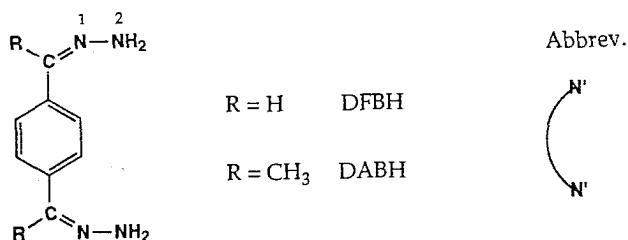

$$R = H \quad \text{DFBH}$$

$$R = CH_3 \quad \text{DABH}$$

Abbrev.

Figure 1

We obtained and characterized complexes of types MX_2(DFBH) where M = Co, Ni, Mn, Zn or Cd, X = Cl and M = Co or Ni, X = SCN and M = Ni, X = Br; MX_2(DFBH) where M = Co,Ni,Zn,Cd or Hg, X = Cl and M = Ni or Mn, X = Br; MX_2(DABH)$_2$ where M = Co,Ni or Zn, X = Cl or Br and M = Co or Ni, X = Cl,Br or SCN and finally MX_2(DABH)$_3$ where M = Co, X = Br or SCN and M = Ni, X = Cl or SCN and M = Zn, X = Cl, Br or SCN.

We report here the preparation and the study of complexes of DFBH and DABH with transition metal(II) acetates of the type $M(CH_3COO)_2 \cdot 2H_2O$ where M = Zn or Cd; $M(CH_3COO)_2 \cdot 4H_2O$ where M = Co or Ni; $Rh(CH_3COO)_2 \cdot aq$, $Cu(CH_3COO)_2 \cdot H_2O$ and $Hg(CH_3COO)_2$.

EXPERIMENTAL

The preparation of the ligands 1,4-diformylbenzene bishydrazone (DFBH) and 1,4-diacetylbenzene bishydrazone (DABH) as well as their characterization was described previously[6]. Here we have further characterized the ligands by their proton-decoupled ^{13}C NMR spectra in DMSO-d_6. The ligand DFBH showed three magnetically different types of carbon, giving

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Key words: Synthesis, Hydrazones, Transition metal acetates, 1,4-Diformylbenzene, 1,4-Diacetylbenzene, Complexes.

INTRODUCTION

    Ligands with N-N bonds have been much studied in recent years because of their relationship to the problem of conversion of dinitrogen to

rise to three peaks at δ = 129,4 ppm (unsubstituted benzene carbon atoms),
δ = 139,4 ppm (substituted benzene carbon atoms) and δ = 142,1 ppm (C =
NNH_2 carbon atoms)[7,8,9]. The DABH showed four magnetically different ty-
pes of carbon at δ = 15,3 ppm (CH_3, carbon atoms), δ = 142,4 ppm (substi-
tuted benzene carbon atoms) and δ = 146,0 ppm ($C=NNH_2$ carbon atoms)[7,8,9].
The metal (II) acetate salts were purchased from FLUKA and were used
without further purification. The preparation of complexes of DFBH and
DABH was straightforward. The metal (II) salt and the ligand (DFBH) were
dissolved in hot absolute ethanol, the solutions mixed and the mixture
allowed to stand for several hours, for complete precipitation. The mix-
ture was filtered and the precipitate washed with hot ethanol and ether
before being dried in vacuo. For the complexes of DABH the metal (II)
salt was dissolved in hot ethanol and the ligand dissolved in hot metha-
nol (a better solvent than ethanol for this ligand); the solutions were
mixed and the mixture allowed to stand for several hours. The mixture was
filtered and the precipitate washed with hot ethanol, hot methanol and
ether before being dried in vacuo. All reactions were carried out using
reaction ratios of 2:1 and 1:2 {metal(II) salt: ligand}. The reactions
between cobalt(II) acetate and DABH, rhodium(II) acetate and DFBH or DABH
were carried out under nitrogen atmosphere. The reaction of cobalt(II)
acetate with two moles of DABH yields only a yellow precipitate contain-
ing no cobalt. Found: C% 75.30, H% 6.87, N% 17.20; $C_{10}N_{10}N_2$ requires C%
75.92, H% 6.37, N% 17.71. The isolated products were insoluble in common
solvents; so it was impossible to obtain an NMR spectrum.

RESULTS AND DISCUSSION

The complexes prepared in this work are listed in Tables 1 and 2 with
their analytical data, colours and magnetic moments. Some important i.r.
bands in the complexes are listed in Tables 3 and 4 and finally the elec-
tronic spectra (diffuse-reflectance) of complexes are listed in Tables 5
and 6.

The complexes of DFBH (Table 1) of formula $M(CH_3COO)_2(DFBH)$ where
M = Cd(II), Hg(II), Co(II), Cu(II) arise in the reactions of the acetate
salts with ethanolic solutions of the ligand and their formulation is in-
dependent of the ratio of the reactants used. The i.r. spectra (Table 3)
of the complexes are all similar and clearly show the presence of the
coordinated formylhydrazone ligand. The very small shifts in $\nu(NH_2)$ modes

TABLE 1: Complexes derived from 1,4-diformylbenzene bishydrazone (DFBH). Analytical data[a], colours and magnetic moments.

Complex	C	H	N	Metal	μ_{eff}(BM 20°C)	Colour
$Cd(CH_3COO)_2(DFBH)$	36.75 (36.70)	4.29 (4.11)	14.48 (14.27)		Diam	Yellow
$Hg(CH_3COO)_2(DFBH)$	30.08 (29.97)	3.42 (3.35)	11.37 (11.65)		Diam	Olive green
$Co(CH_3COO)_2(DFBH)$	42.36 (42.49)	4.67 (4.75)	16.69 (16.52)		4.93	Yellow
$Cu(CH_3COO)_2(DFBH)$	41.80 (41.92)	4.53 (4.69)	16.12 (16.29)		1.92	Olive green
$Zn(CH_3COO)_2(DFBH)$ ·	41.16 (41.70)	4.27 (4.66)	16.54 (16.21)		Diam	Yellow
$Zn(CH_3COO)(OH)(DFBH)$	40.02 (39.56)	4.23 (4.65)	18.79 (18.45)		Diam	Yellow
$Ni(CH_3COO)_2(DFBH)$	42.80 (42.52)	4.83 (4.76)	16.84 (16.53)		Diam	Yellow
$Ni(CH_3COO)(OH)(DFBH)$	42.54 (42.75)	5.20 (5.02)	19.73 (19.94)		Diam	Yellow
$Rh(C_8H_8N_3)(OH)_3 \cdot \frac{1}{2}H_2O$	31.45 (31.08)	3.91 (3.91)	13.26 (14.59)	33.85 (33.31)	Diam	Yellow

(a) Theoretical values in parenthesis

TABLE 2: Complexes derived from 1,4-diacetylbenzene bishydrazone (DABH). Analytical data[a], colours and magnetic moments.

Complex	C	H	N	Metal	μ_{eff}(BM 20°C)	Colour
$Cd(CH_3COO)_2(DABH)$	40.05 (39.97)	4.68 (4.79)	13.57 (13.32)		Diam	Yellow
$Hg(CH_3COO)_2(DABH)$	33.42 (33.04)	3.56 (3.96)	11.10 (11.01)		Diam	Olive green
$Co(CH_3COO)_2(C_{10}H_{10}N_2)$	49.73 (50.16)	4.80 (4.81)	8.14 (8.36)	17.71 (17.58)	4.97	Yellow
$Cu(CH_3COO)_2(DABH)$	45.37 (45.22)	5.26 (5.42)	15.18 (15.07)		1.95	Olive green
$Zn(CH_3COO)_2(DABH)$	45.07 (45.00)	5.23 (5.39)	14.78 (14.99)		Diam	Yellow
$Zn(CH_3COO)(OH)(DABH)$	43.12 (43.46)	5.93 (5.47)	17.14 (16.89)		Diam	Yellow
$Ni(CH_3COO)_2(DABH)$	45.97 (45.81)	5.53 (5.49)	15.04 (15.26)		Diam	Yellow
$Ni(CH_3COO)(OH)(DABH)$	46.63 (46.96)	6.13 (5.91)	18.52 (18.26)		Diam	Yellow
$Rh(C_{10}H_{12}N_3)(OH)_3 \cdot \frac{1}{2}H_2O$	34.97 (35.16)	4.39 (4.78)	12.07 (12.46)	30.92 (30.54)	Diam	Pink

[a] Theoretical values in parenthesis.

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TABLE 3: Diagnostic i.r. bands (cm^{-1}) in complexes derived from the bishydrazone of 1,4-diformylbenzene (DFBH)

Complex	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\delta_s(NH_2)$	$\nu(C=N)$	$\nu(N-N)$	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\Delta(\nu_{as}-\nu_s)$
DFBH	3350	3180	1625	1580	1110			
Cd(CH$_3$COO)$_2$(DFBH)	3300	3160	1620	1590	1150	1545	1410	135
Hg(CH$_3$COO)$_2$(DFBH)	3360	3150	1625	1595	1165	1535	1405	130
Co(CH$_3$COO)$_2$(DFBH)	3360	3180	1615	1590	1160	1550	1405	145
Cu(CH$_3$COO)$_2$(DFBH)	3330	3140	1615	1600	1160	1550	1405	145
Zn(CH$_3$COO)$_2$(DFBH)	3330	3180	1620	1595	1160	1550	1410	140
Zn(CH$_3$COO)(OH)(DFBH)	3330	3170	1620	1595	1170	1545	1408	137
Ni(CH$_3$COO)$_2$(DFBH)	3365	3170	1615	1580	1160	1535	1415	120
Ni(CH$_3$COO)(OH)(DFBH)	3350	3160	1610	1590	1150	1570	1415	155
Rh(C$_8$H$_8$N$_3$)(OH)$_3$·$\frac{1}{2}$H$_2$O	3320	3170	1620	1590	1140			

TABLE 4: Diagnostic i.r. bands (cm^{-1}) in complexes derived from the bishydrazone of 1,4-diacetylbenzene (DABH)

Complex	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\delta_s(NH_2)$	$\nu(C=N)$	$\nu(N-N)$	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\Delta(\nu_{as}-\nu_s)$
DABH	3340	3190	1640	1585	1110			
$Cd(CH_3COO)_2(DABH)$	3340	3210	1635	1595	1120	1545	1395	150
$Hg(CH_3COO)_2(DABH)$	3340	3200	1630	1590	1120	1545	1395	150
$Cu(CH_3COO)_2(DABH)$	3360	3170	1635	1590	1115	1545	1395	150
$Zn(CH_3COO)_2(DABH)$	3340	3180	1660	1595	1140	1545	1400	145
$Zn(CH_3COO)(OH)(DABH)$	3340	3210	1640	1595	1120	1545	1400	145
$Ni(CH_3COO)_2(DABH)$	3400	3160	1640	1595	1115	1550	1400	150
$Ni(CH_3COO)(OH)(DABH)$	3340	3210	1620	1595	1120	1545	1400	145
$Co(CH_3COO)_2(C_{10}H_{10}N_2)$				1590	1115	1555	1395	160
$Rh(C_{10}H_{12}N_3)(OH)_3\cdot\frac{1}{2}H_2O$	3330	3180	1625	1590	1120			

TABLE 5: Electronic spectra data $(cm^{-1} \times 10^3)$ and possible assignments in complexes derived from the bishydra zone of 1,4-diformylbenzene (DFBH).

$Co(CH_3COO)_2(DFBH)$	$^4T_{1g} \longrightarrow {}^4T_{2g}$ 8.8	$^4T_{1g} \longrightarrow {}^4A_{2g}$ 16.0	$^4T_{1g} \longrightarrow {}^4T_{1g}(P)$ 19.0
$Cu(CH_3COO)_2(DFBH)$	$^2E_g \longrightarrow {}^2T_{2g}$ 14.00 br		
$Ni(CH_3COO)_2(DFBH)$	$^3A_{2g} \longrightarrow {}^3T_{2g}$ 8.00	$^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ 14.00	$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ 20.00
$Rh(C_8H_8N_3)(OH)_3 \cdot \frac{1}{2}H_2O$	$^1A_{1g} \longrightarrow {}^1T_{1g}$ 18.5	obscured	

TABLE 6: Electronic spectra data $(cm^{-1} \times 10^3)$, and possible assignments in complexes derived from the bishydrazone of 1,4-diacylbenzene (DABH).

	Transition 1	Transition 2	Transition 3	Transition 4
Co(CH$_3$COO)$_2$(C$_{10}$H$_{10}$N$_2$)	$^4T_{1g} \rightarrow ^4T_{2g}$ 8.3	$^4T_{1g} \rightarrow ^4A_{2g}$ 15.6	$^4T_{1g} \rightarrow ^4E_g$ 17.0	$^4T_{1g} \rightarrow ^4A_{2g}$ 20.4
Cu(CH$_3$COO)$_2$(DABH)	$^2E_g \rightarrow ^2T_{2g}$ 14.7 br			
Ni(CH$_3$COO)$_2$(DABH)	$^3A_{2g} \rightarrow ^3T_{2g}$ 8.7	$^3A_{2g} \rightarrow ^1E_g$ 13.3	$^3A_{2g} \rightarrow ^3T_{1g}(F)$ 15.4	
Ni(CH$_3$COO)(OH)(DABH)	$^3A_{2g} \rightarrow ^3T_{2g}$ 10.9	$^3A_{2g} \rightarrow ^1E_g$ 13.3	$^3A_{2g} \rightarrow ^3T_{1g}(F)$ 17.5	
Rh(C$_{10}$H$_{12}$N$_3$)(OH)$_3 \cdot \frac{1}{2}$H$_2$O	$^1A_{1g} \quad ^1T_{1g}$ 18.0	$^1A_{1g} \quad ^1T_{1g}$ 22.5		

suggests that these nitrogen atoms are not involved in coordination to the metal atoms. We believe therefore that both N^1 atoms of the ligand are coordinated to the metal ions. This conclusion is further substantiated by the small upward shift of $v(C=N)$ in the complexes which is indicative of coordination by N^1 nitrogen atoms[10,11,12,13]. The i.r. spectra in the $v(COO^-)$ region (Table 3) show a separation Δ between $v_{as}(COO^-)$ and $v_s(COO^-)$ in the range 120-155 cm^{-1}. This indicates that[14,15] the acetate groups are either ionic or bonded to the metal atoms in a bridging mode. The evidence for the structure around the metal ions comes from the electronic spectra (Table 5) and magnetic moment of the cobalt (II) complex. These clearly establish a six fold coordination around the cobalt(II). We thus believe these $M(CH_3COO)_2(DFBH)$ complexes to be polymeric and six coordinated with both bridging acetates and hydrazone ligands, with a possible structure indicated below (Fig. 2).
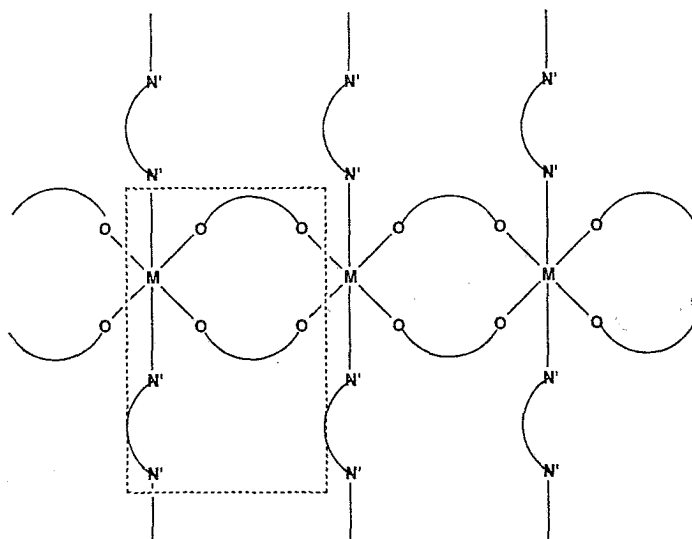

Fig 2

However it is a little surprising that the magnetic moment of the copper(II) complex shows it to be magnetically dilute. Low temperature

magnetic measurements would clarify the occurrence of antiferromagnetic interactions. The electronic spectrum shows a broad band at 14000 cm^{-1}, typical of Jahn-Teller distorted copper(II) complexes. The same results were obtained with Zn(II) and Ni(II) acetates if the reacting ratio was 2:1. When an excess of ligand is used in the reactions with Zn(II) and Ni(II) acetates, the products have the formula M(CH_3COO)(OH)(DFBH). Surprisingly the nickel(II) complex is diamagnetic; unfortunately our electronic spectrum of this complex fails to show absorption below the rising charge transfer absorption at 20000 cm^{-1}. The excess of ligand in these reactions must extract a proton from the hydrated metal acetates to give the hydroxide species. In the case of rhodium(II) acetate the addition of DFBH either with rhodium(II) acetate or the ligand in excess, results in the fission of both acetate bridges and the Rh-Rh metal bond with the formation of a rhodium(III) hydroxide complex (Table 1). The formula of the complex indicates the formation of a new ligand of empirical formula $C_8H_8N_3$. We believe that this ligand is the monoazine (Figure 3) formed by the reaction:

$$> C = N-NH_2 + H_2N-N = C < + 2Co^{2+} \rightarrow > C = N-N = C < + 2Co^{3+} + 2NH_2^-$$
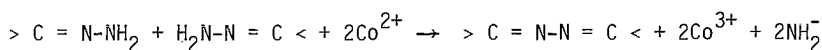
The NH_2^- species reacts with H^+ from the solvent (EtOH), to form NH_3 as shown in the overall equation:

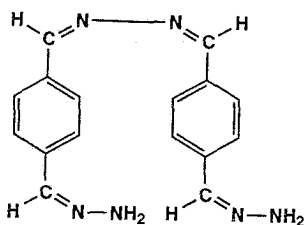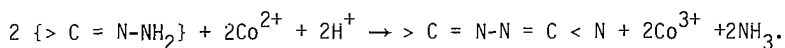$$2 \{> C = N-NH_2\} + 2Co^{2+} + 2H^+ \rightarrow > C = N-N = C < N + 2Co^{3+} + 2NH_3.$$

Figure 3

As we shall see with the acetylhydrazone ligand, the bis-azine arises in the redox reaction of the hydrazone with cobalt(II). The produced NH_3 was detected by adding drops of Nessler's reagent to the reaction filtrate after the removal of complex (immediate formation of a black precipi-

tate)[16]. The proposed production of ammonia as in the above equation accounts for the basicity of the solution and the occurrence of hydroxide group on the metal. The ammonium acetate produced is soluble in ethanol[17].

Complexes of DABH prepared (Table 2) from Cd(II), Hg(II) and Cu(II) have the formulae $M(CH_3COO)_2(DABH)$ irrespective of whether the reaction ratios of 2:1 or 1:2 (metal salt:ligand) were used. They show the same spectroscopic and magnetic properties as $M(CH_3COO)_2(DFBA)$ complexes, as indicated in Tables 2,4 and 6. We thus believe that these complexes have the same structures as those of DFBA. In contrast, complexes of DABH prepared from Zn(II) and Ni(II) have been isolated having the formulae $M(CH_3COO)_2(DABH)$ and $M(CH_3COO)(OH)(DABH)$ using reaction ratios of 2:1 and 1:2 respectively. The reaction of cobalt(II) acetate with DABH is the most interesting however. The complex isolated under a nitrogen atmosphere, when cobalt is in excess, has the formula $Co(CH_3COO)_2(C_{10}H_{10}N_2)$. This new ligand shows no $v(N-H)$ (Table 4) in the i.r. spectrum of the Co complex and is apparently the bis-azine ligand (Fig. 4).
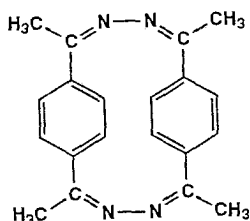
Figure 4

We thus believe oxidation of the cobalt(II) to cobalt(III) occurs and the cobalt(III) species formed (probably an ammine) is washed out from the cobalt(II) azine complex with ethanol. The electronic spectrum of the complex can be assigned to a pseudo-octahedral stereochemistry (Table 6); some splitting of $^4T_{1g}(P)$ level into ^4E_g acid $^4A_{2g}$ levels being observed. The larger effective radius of cobalt(II)[18] and the fact that Co(II) is in excess, are probable factors favouring the precipitation of a cobalt (II) complex with the cyclic ligand. If the reaction ratio is 1:2 (i.e. excess of ligand) the only isolated product has the empirical formula $C_{10}H_{10}N_2$, confirming that the Co(III) which is produced during the reaction does not form a complex with this ligand. Another explanation, in which the cylisation reaction leading to the formation of the bis-azine (Fig. 4) is that proposed by M.T. Casey et al[19], the mechanism possibly

proceeds via the metal-ion catalysed transamination (amine exchange) route (Scheme 1). Similar transamination reactions leading to the formation of macrocyclic Schiff-bases complexes have been reported by Nelson et al[20].

Both nickel(II) complexes (Tables 1,2) are diamagnetic and so may be square planar. Such complexes of nickel(II) typically have a single band in the 18000-25000 cm^{-1} region[21]; however we find lower energy bands (Table 6) which are more typical of tetragonal nickel(II) complexes and hence our assignments in the Tables. It is possible therefore that there is sufficient disparity between the positions in the spectrochemical series of the ligands CH_3COO^- and DFBH, DABH[22] that the square planar complex is insufficiently perturbed by the weak tetragonal field to cause unpairing of the electrons.

Finally, with Rh(II) irrespective of the reaction ratio, the formula of the isolated complex is $Rh(C_{10}H_{12}N_3)(OH)_3.\frac{1}{2}H_2O$. Again this complex arises from an oxidation-reduction reaction; Rh(II) is oxidized to Rh(III) and DABH is reduced to a bis-azine.

ΠΕΡΙΛΗΨΗ

"Σύμπλοκες Ενώσεις Υδραζονών που προέρχονται από 1,4-Διφορμυλο- και 1,4-Διακετυλοβενζόλιο, με οξικά άλατα στοιχείων μεταπτώσεως".
    Στην εργασία αυτή περιγράφεται η σύνθεση και η μελέτη συμπλόκων ενώσεων των οξικών αλάτων Cd(II), Hg(II), Cu(II), Zn(II), Ni(II), Rh(II) και Co(II) με την υδραζόνη του 1,4-διφορμυλοβενζολίου (DFBH) και την υδραζόνη του 1,4-διακετυλοβενζολίου (DABH). Τα προϊόντα των αντιδράσεων αυτών, είναι δυνατόν να καταταγούν στις παρακάτω κατηγορίες:
- Κατά την αντίδραση των υδραζονών με οξικά άλατα Cd(II), Hg(II) και Cu(II) σχηματίζονται ενώσεις του τύπου $M(CH_3COO)_2(DFBH)$ και $M(CH_3COO)_2$ (DABH). Η δομή των ενώσεων αυτών είναι μάλλον οκταεδρική πολυμερής,με γέφυρες οξικά ανιόντα και υδραζόνες, ενώ το πιθανό άτομο συνδέσεως είναι το N^1 της ομάδος N^1-NH_2 των υδραζονών.
- Με τα ιόντα Zn(II) και Ni(II), εάν η αναλογία αντιδράσεως είναι 2:1 (περίσσεια οξικών αλάτων), τα προϊόντα που απομονώθηκαν έχουν τους τύπους $M(CH_3COO)_2(DFBH)$ ή $M(CH_3COO)_2(DABH)$ με δομή οκταεδρική-πολυμερή, με γέφυρες οξικά ιόντα και υδραζόνες. Αν όμως η αναλογία είναι 1:2 (περίσσεια υποκαταστάτη), τα προϊόντα που απομονώθηκαν έχουν τους τύπους $M(CH_3COO)$ (OH)(DFBH) ή $M(CH_3COO)(OH)(DABH)$.
- Οι αντιδράσεις με το οξικό Rh(II) οδηγούν σε σύνθεση νέων υποκαταστατών, $C_8H_8N_3$ και $C_{10}H_{12}N_3$, αρχίζοντας από DFBH και DABH αντίστοιχα. Η δομή των συμπλόκων των νέων αυτών υποκαταστατών είναι υδροξο-οκταεδρική.
- Τέλος με οξικό Co(II) προκύπτουν διαφορετικά προϊόντα, ανάλογα με τη χρησιμοποιουμένη υδραζόνη και την αναλογία των αντιδραστηρίων.
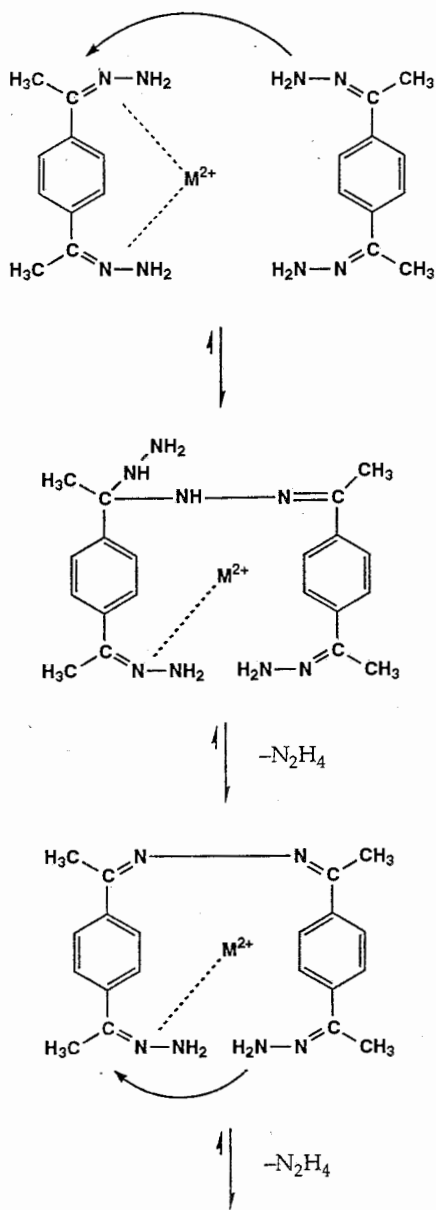
Scheme 1

bis-azine (Fig 4)

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A.IOANNOU[1] , M.DOULA[2] , A.DIMIRKOU[2] , P.PAPADOPOYLOS[2]

1 University of Athens,Department of Chemistry,Panepistimiopolis-
   Zografou,Athens 15771,Greece. .
2.. National Research Agricultural Foundation of Greece,Soil Science
   Institute of Athens.Sof.Venizelou 1,Lycovrissi 14123. Attiki Greece.

Postal address of the corresponding author: A. Ioannou 14 Thermopillon St. , Pallini,
15344 ,Greece,Fax No :01 2842 129

ABSTRACT

The present work is refering to the dielectric behaviour of solid materials.
These materials are consisted of two · phases with different electrical and
dielectrical behaviour. As result of the above , the material behaviour is different
from the behaviour of its two phases.
A variety of theories have been proposed in order to interpret this behaviour,
especially in case of static electric field with conducted and non-conducted two
phases. Maxwell-Wagner-Sillars (M.W.S.) theory is the most·common. In case of
an alternating electric field the works of Debye, Cole-Cole and others , offer a
more satisfactory solution as compared to the solutions which are given in the
case of static electric field.

INTRODUCTION

The interfacial polarization characterizes the chemical or physical
heterogeneous solids.This polarization brought about, when mobile charge carriers
migrating under the influence of the external applied field, become trapped-
localized at the interface which exist between the two phases of solid. The

polarization is related to the charge carriers mobility, and so can exists in systems of low conductivity. The above are presented in Figure 1.

Each one of the two phases of solid is characterized by its magnitudes, such as conductivity σ , permittivity ε , and thickness d.(Fig.2a).
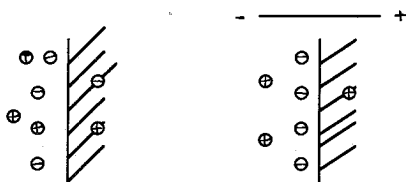
FIGURE 1. Polarization by trapping at the interface of migrating charge carriers.
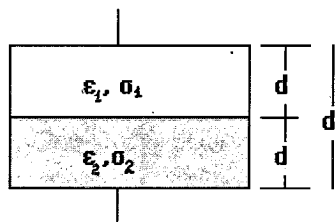
FIGURE 2a. Typical M-W-S system.
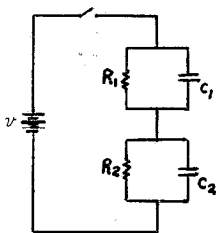
FIGURE 2b. Equivalent circuit of M-W-S system.

The solid phases may have different geometries and shapes. Could be spheres,ellipses,rods or parallel sheets. In the most cases there is not an obvious distinction between the two phases, therefore the interfacial boundary is vague.

The behaviour of a two phases system is depended on the different geometries of the disposal phase.

	conducting sheets		conducting ellipsoids
a		c	
conducting spheres		conducting cylinders	
b		d	
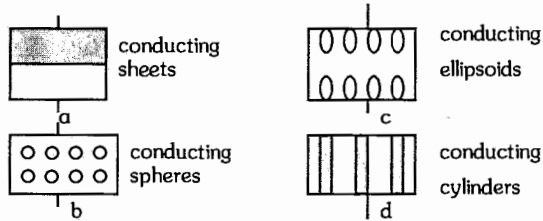
FIGURE 3. Disposal phase geometries

These geometries , which appeared at crystal solids and at amorphous or semicrystal polymers , called mesomorphic phases. [1] This is the reason , why interfacial polarization (or Maxwell-Wagner-Sillars polarization) is so essential for the study of those systems conductivity.
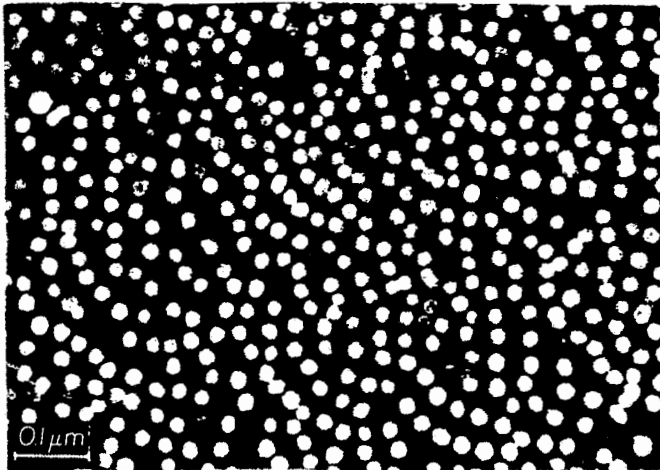
FIGURE 4. Spherical phases of boutadiene in a linear (ABA) block co-polymer (80% PS)
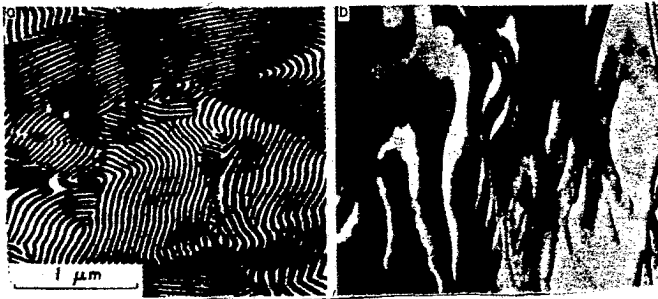
FIGURE 5. Phases of parallel sheets in linear (ABA) block co-polymer (40% PS)
a.vertical section b.plane section

A variety of theories have been developed in order the phenomenon to be
explained. This phenomenon is known as Maxwell-Wagner-Sillars phenomenon.
In practice, apart from a few specialized situations, there is not a quantitative
comparison of theoretical and experimental data. The initially formulated M.W.S.
theory , according to many theories ,which are mentioned in this work, is
regarding now rather simplified because it ignores significant parameters, which
are essential for the complete interpretation of the phenomenon and for those
systems magnitudes calculation.

DIELECTRIC PROPERTIES OF TWO PHASES SOLIDS.
a. Dielectric behaviour of non-conducted phases in static electric field.

In two phases systems occured a permittivity increment , mainly at low
frequencies.
The simplest model , which have been studied by (M.W.S.) , consider the solid as
an ensemble of isotropic ellipsoids [2,3,4] (Fig.3c) of permittivity ε_2 and volume
fraction v_2.These ellipsoids are embedded in a matrix of permittivity ε_1.
By concidering that both phases heve zero conductivity and the relation between
ε_2 and ε_1 is $\varepsilon_2 > \varepsilon_1$,then the permitivity of the system is described by the
following equation:

$$\varepsilon = \varepsilon_1 [1 + v_2(\varepsilon_2 - \varepsilon_1) \sum \frac{\cos \gamma_i}{\varepsilon_1 + A_i(1 - v_2)(\varepsilon_2 - \varepsilon_1)}] \qquad (1)$$

where γ_i (i=a,b,c) are the angles which defined the orientation of the ellipsoid axes (a,b,c) relative to the applied electric field. Ai is the depolarization ratio of the constituent ellipsoids along the i-axis. A_i is defined by:

$$A_a = \frac{abc}{2} \frac{\partial s}{(s + a^2)[(s + a^2)(s + b^2)(s + c^2)]^{1/2}} \qquad (2)$$

where s is the positive root of the equation:

$$[x^2/(a^2+u)+y^2/(b^2+u)+z^2/(c^2+u)]=1$$

where u is a point outside the ellipsoid $(x^2/a^2+y^2/b^2+z^2/c^2)=1$.
The coefficient Aa , has a value of unity for lamellae, 1/3 for spheres and tends to be zero for long thin rods.
Similar relations are available for Ab and Ac.
The orientation of the geometrics axes relative to the applied electric field leads to simple analytical relations for the system conductivity:

1. The a-axis oriented parallel to the applied electris field:

$$\cos^2\gamma_a = 1 \quad , \quad \cos^2\gamma_b = \cos^2\gamma_c = 0$$

2. The a-axis oriented perpendicular to the electric field:

$$\cos^2\gamma_a = \cos^2\gamma_b = 0 \quad , \quad \cos^2\gamma_c = 1$$

3. Random orientation of ellipsoids relative to the field:

$$\cos^2\gamma_a = \cos^2\gamma_b = \cos^2\gamma_c = 1/3$$

Systems with the a-axis parallel to the electric field, which's one phase is an esemble of rods give larger permittivity than systems of spheres and random ellipsoids.
In general, systems consisting of rods, give larger permittivity than systems with perpendicular orientation of ellipsoids or sheets.

Equation (1) which gives the permittivity of a complex system, is valid when the volume fraction is low, therefore $v_2 > 0.2$. When the volume fraction of the dispersed phase become higher , the electrostatic interactions in the domain of charge carriers become significant, thus the relation which describes the system permittivity is modified:

1. Bruggeman [5] :

$$v_2 = 1 - \frac{\varepsilon_2 - \varepsilon}{\varepsilon_2 - \varepsilon_1} \left[\frac{\varepsilon_1}{\varepsilon}\right]^{1/3} \qquad (3)$$

2. Böttcher [5] :

$$v_2 = \frac{(\varepsilon - \varepsilon_1)(2\varepsilon + \varepsilon_2)}{3\varepsilon(\varepsilon_2 - \varepsilon_1)} \qquad (4)$$

Formulae (3) and (4) have different origins:
Bruggeman used a model of regularly arranged spherical particles,and Bottcher derived his equation by discussion of the electric field inside a spherical particle.
Both formulae give approximately the same results, although their forms are different.
3) Looyenga [5] gives a more general formulae for heterogeneous mixtures, which can apply to any geometry, because of its independence from the particle's shape:

$$v_2 = \frac{\varepsilon^{1/3} - \varepsilon_1^{1/3}}{\varepsilon_2^{1/3} - \varepsilon_1^{1/3}} \qquad (5)$$

b Dielectric behaviour of cinducted phases in constant polarization.

M-W-S, by regarding at the following step that the conductivity of the two phase exists, and $\sigma_2 > \sigma_2$ give a relationship for the direct current permittivity ε_o, which appears only a real part [2,3,4].

TABLE I. Theories which have been developed in order M-W-S phenomenon to be explained.

a. Relations for low volume fraction dispersion $v_2 < 0.2$, $Xl < 1$, where l is the thickness of the layer and X the inverse of the Debye shielding radius.

Morphology	Reference	ε (eq.1) , ε_o (eq.6) , τ (eq.7)
Spheres	Wagner [4]	$Aa=1/3$: $\cos^2\gamma_a=1$, $\cos^2\gamma_b=\cos^2\gamma_c=0$
Ellipsoids (a-axis parallel)	Sillars [3]	All Aa : $\cos^2\gamma_a=1$, $\cos^2\gamma_b=\cos^2\gamma_c=0$
Ellipsoids (a-axis perpendicular)	Sillars [3]	$0 \leq Ab \leq 0.5$: $\cos^2\gamma_b=1$, $\cos^2\gamma_a=\cos^2\gamma_c=0$
Ellipsoids (random)	Fricke [11]	All Ai : $\cos^2\gamma_i=1/3$

b. Relations for concentrated dispersions for every value of v_2 and $Xl<1$: all $v_2<Xl<1$

Morphology	Reference	ε (eq.1)	ε_o	τ
Spheres	Bruggeman[5]	eq.3	$\varepsilon_o[\dfrac{3}{\sigma - \sigma_2} - \dfrac{1}{\sigma}] =$ $3[\dfrac{\varepsilon_2 - \varepsilon_1}{\sigma_2 - \sigma_1} + \dfrac{\varepsilon_2}{\sigma - \sigma_2}] - \dfrac{\varepsilon_2}{\sigma_1}$	not given
Spheres	Looyenga[5]	eq.5		

TABLE I. Theories which have been developed in order M-W-S phenomenon to be explained.
c. Modification of the relations in presence of space charge layer $v_2 < 0.05$: all Xl. Reference : Trukhan[8].

Morphology: Spheres

ε : $\varepsilon = \varepsilon_1[1 + 3v_2 \dfrac{\varepsilon_2 - \varepsilon_1}{2\varepsilon_1 + \varepsilon_2}]$

ε_o : $\varepsilon_o = \varepsilon_1\{1 + 3v_2 \text{ x } \dfrac{(Xl)^2 \text{th}(\dfrac{Xl}{2}) + \dfrac{2(2\varepsilon_2 + \varepsilon_1)}{\varepsilon_2}[2\text{th}(\dfrac{Xl}{2}) - Xl]}{(Xl)^2 \text{th}(\dfrac{Xl}{2}) + \dfrac{4(\varepsilon_2 - \varepsilon_1)}{\varepsilon_2}[2\text{th}(\dfrac{Xl}{2}) - Xl]}\}$

τ : $\tau = \dfrac{\varepsilon(2\varepsilon_1 + \varepsilon_2)}{(2\sigma_1 + \sigma_2)} \text{ x } \dfrac{(X l)^2 \text{th}(\dfrac{Xl}{2}) + 6[2\text{th}(\dfrac{Xl}{2}) - Xl]}{(X l)^2 \text{th}(\dfrac{Xl}{2}) - \dfrac{4(\varepsilon_1 - \varepsilon_2)}{\varepsilon_2}[2\text{th}(\dfrac{Xl}{2}) - Xl]}$

TABLE I. Theories which have been developed in order M-W-S phenomenon to be explained.
d. Relations for systems with surface conductivities.

Morphology	References	ε	ε_o	τ
Spheres (radius a)	O'Konski[9]	In the MWS relations of table Ia σ_2 is replaced by $\sigma_2 + \lambda_s 2/a$		eq(7)
Ellipsoids (a,b=c)	O'Konski[9]	In MWS relations of table Ia σ_2 is replaced by $\sigma_2 + K_i \lambda_s$ where $K_a = \sigma 2/b$ $K_b = K_c = \sigma 4/\pi b$		eq(7)
Spheres (radius a)	Schwarz[12]	Eq.1:Aα=1/3 $\cos^2\gamma_a = 1, \cos^2\gamma_b = \cos^2\gamma_c = 0$	$\varepsilon_\infty + \dfrac{9e^2\sigma' a v_1}{4ekT[1+(v_1/2)^2]}$	$\tau = a^2/(2n_s kT)$
Ellipsoids (a-axis parallel)	Takasima[13]	Eq.1: all Ai $\cos^2\gamma_a = 1, \cos^2\gamma_b = \cos^2\gamma_c = 0$	$\varepsilon_\infty + \dfrac{9e^2\sigma' a^2 v_1}{8ekTb[1+v_1]^2}$	$\tau = (a^2 + b^2)/2n_s kT$
Ellipsoids (random)	Takasima[13]	Eq.1: all Ai $\cos^2\gamma_a = 1/3$	$\varepsilon_\infty + \dfrac{e^2\sigma' v_1}{3kT(1+v_1)^2 \varepsilon}[\dfrac{9a^2}{8b} + 2b]$	$\tau_a = (a^2 + b^2)/2n_s kT$ τ_b —

$$\varepsilon_o = \varepsilon_1 [1 + v_2(\sigma_2 - \sigma_1) \sum \frac{\cos^2 \gamma_i}{\sigma_1 + A_i(1 - v_2)(\sigma_2 - \sigma_1)} +$$

$$+ v_2\sigma_1 \sum \frac{\cos^2 \gamma_i (\sigma_1\varepsilon_2 - \sigma_2\varepsilon_1)}{[\sigma_1 + A_i(1 - v_2)(\sigma_2 - \sigma_1)]^2} \qquad (6)$$

$$\tau = \varepsilon_k [\frac{\varepsilon_1 + A_i(1 - v_2)(\varepsilon_2 - \varepsilon_1)}{\sigma_1 + A_i(1 - v_2)(\sigma_2 - \sigma_1)}] \qquad (7)$$

where ε_k is the permittivity of free space. According to the equivalent circuit of Figure 2b the change over from one to the other condition takes place exponentially with a time constant τ.

c. Dielectric behaviour of conducted phase in an alternating electric field.

Debye studied the influence of the electric field frequency on the dielectric behaviour.
Debye proved that, when a alternating elecrric field E(t) applied to a dielectric the following equations are valid:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{1 + i\omega\tau} \qquad (8)$$

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{1 + \omega^2\tau^2} \qquad (9)$$

$$\varepsilon'' = (\varepsilon_o - \varepsilon_\infty) \frac{\omega\tau}{1 + \omega^2\tau^2} \qquad (10)$$

where ε^* is the complex permittivity of the system. If δ is the angle between the electric field Eo and electric displacement Do then the permottivity ε^* of the system may be described in terms of a complex dielectric constant.

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \qquad (11)$$

ε' and ε'' are defined:

$$\varepsilon' = (Do/Eo)\cos\delta \, , \quad \varepsilon'' = (Do/Eo)\sin\delta$$

Friction causes dielectric loss, which expressed by ε''. The tangement of δ angle , called losses tangment , is given : $\tan\delta = \varepsilon'' / \varepsilon'$

$\tan\delta$ expresses the amount of energy which alternated to heat per period, to the stored amount of energy in the dielectric. It is an "adsorption conductivity" of dielectric. ε_∞ is value of permittivity for optical frequencies and called oprical permittivity. This constant is characterised only from real term.

In optical frequencies the orientation of dipols prevent from the internal friction of medium. As it mentioned before ε_0 is the static permittivity which is characterized from real term too. In this case the molecular electric dipole moments are parallel to the electric field, ω is the circular frequency of the applied field, τ is a characteristic constant which called relaxation time of dipols. τ is defined as the requisite time to become the polarization the $1/e$ of the initial value when the external field was removed.

According to Debye theory the above equations are valid also in an axial isotropic phase disposal.

The inferences from those equations are:

a. ε' is depended on ε_0 and ε_∞ .

b. For high and low frequencies , ε'' vs ω presents a maximum value at a characteristic frequency , ω_0 when the following equation is valid:

$$\omega_0\tau = 1$$

Equation (12) gives the relaxation time.

Equations (9) and (10) are expressed in Figure 6.

The experimental data often posses this same type of logarithmic symmetry but with the important differences that the frequency range of dispersion is broader and the adsorption smaller in maximum value.

According to Cole-Cole[6] more representative diagrams are those which have ε' and ε'' as axis.
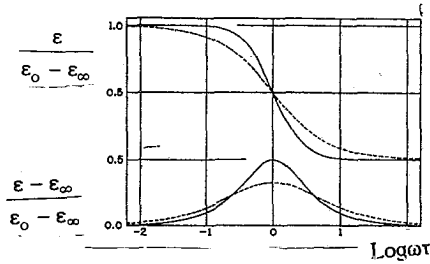
FIGURE 6. Real and imaginary parts of the dielectric constant plotted against frequency.The solid curves are for the Debye equation, and dashed curves indicate the type of behaviour frequently found experimentally.

This representation is a semicircle with its center on the real (ε) axis and intercepts at ε_0 and ε_∞ on this axis.

$$(\varepsilon - \frac{\varepsilon_0 + \varepsilon_\infty}{2})^2 + (\varepsilon)^2 = [\frac{1}{2}(\varepsilon_0 - \varepsilon_\infty)]^2 \qquad \text{(Curve 1, Fig.7)}$$

In general cases the diagram e' vs e'' is a circle arc and its center doesn't lie on the real axis (7).

In this case is valid (6):

$$\text{Cole-Cole}: \quad \frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + (i\omega\tau)^{1-a}} \qquad (13) \quad \text{(curve 3)}$$

where a is a constant and ε^* the complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$.

$$\text{Cole-Davidson}: \quad \frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{(1 + i\omega\tau)^a} \qquad (14) \quad \text{(curve 2)}$$

The Havriliak-Negami relation combines these two:

Havriliak-Negami : $\dfrac{\varepsilon^{*}-\varepsilon_{\infty}}{\varepsilon_{o}-\varepsilon_{\infty}} = \dfrac{1}{[1 + (i\omega\tau)^{1-\alpha}]^{\beta}}$ (15)

where β is constant.

FIGURE 7. Diagram of real and imaginary permittivity.
1. Ideal Debye relaxation 2. Cole-Davinson skewed-arc relaxation. 3.Cole-Cole symmetric relaxation with semicircle centredepressed from Co to C.

The maximum value of adsorption depends on the different geometries of dispersed phases. (Fig.8).

a.Sheets
b.Shperes
c.Ellipsoids
d.Cylinders
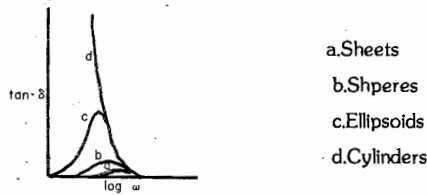
FIGURE 8. Dependence tanδ on phase geometry.

From Fig.8 it is clear that the dielectric dispertion and the maximum value of tanδ are increased as the particles' shape changes from sheet to cylinder.

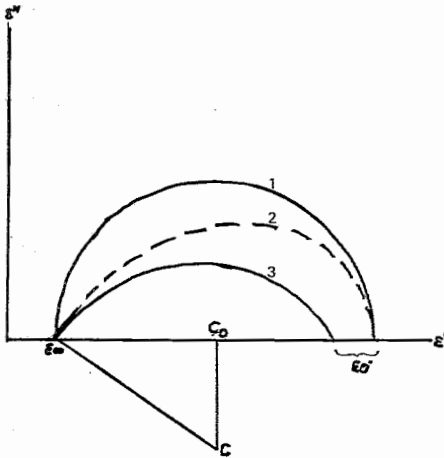In the simplest M-W-S models the interfacial polarization is assumed to arise from charges located on an infinitely thin layer surrounding the dispersed phase.In practice , the layer may have a finite thickness (l) of the order of the Dedye-shielding-radius which is defined:

$$X^{-1} = (\frac{\varepsilon_k \varepsilon_2 kT}{2e^2 n})^{1/2} \qquad (16)$$

where ε_k is the permittivity of free space , n is the charge carrier density, e is the charge on an electron, ε_2 is the dielectric constant of material two (Fig.2a), k the Boltzmann constant and T the absolute temperature.

According to Trukhan[8] M-W-S polarization depends wholly on the accumulation of charges on the boundary surfaces and completely ignores the space charge. That happens for high concentrations of charge carriers in the system or, more accurately when the Debye shielding radius is sufficiently small compared with the size of the system. In a lamellar system he did not made the assumption that the field layer is uniform and that charges were presented only on the interfaces (as M-W-S assumed) he gave the following equation for the conductivity of the layer:

$$\sigma = e\ n^+ (x,t)\ u^+ + e\ n^- (x,t)\ u^- \qquad (17)$$

where n^+, n^- are the charge carrier concentrations of both signs, u^+, u^- are the charge carrier mobilities,x is the distance along axis and t is the time.

Thus the conductivity is a not a constant but it is a function of X and is no longer a characteristic of the material only,but also depends from the charge carriers mobilities and the frequency of its oscillations.

In case that the disposal phase is homogeneous spheres,the terms which express the behaviour of the system are presented at the Table I ;where l is the diameter or the thichness of interfacial layer.

d. Influence of the surface conductivity

The diffuse region between the two phases has different properties from either of pure phases. The conductivity [9] σ_s is much hogher than the pure phases conductivities σ_1, σ_2. (Fig.9)
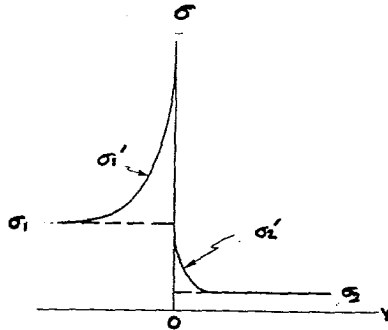
FIGURE 9. Variation of surface conductivity at the interface.

There are two models which explain the properties of such a system.
Both involve the surface conductivity,which in the first is independent of frequency and in the second exhibits a frequency dependence. In the first case the surface conductivity is given by:

$$\lambda_s = \sum n_i n_s q_i \qquad (18)$$

where n_i is the charge carrier density at the surface , n_s is the mobility of the charge q_i.
In the more general [9] case , carriers will not necessarily be restricted to a surface,but may be transported through the bulk media aswell. Furhter more,their concentrations will be functions of position with respect to the surface.When the region of conductivity variation is thin compared to the dimesions of the particles the local conductivity at each point may be regarded as the sum of a bulk value. Then the surface conductivity may be written as the sum of λ_s defined above,

and λ_s, the contribution to be evaluated from the excess conductivity due to the ion atmosphere.The relaxation behaviour is obtained by replacing σ_2 in the simple model by $(\sigma_2+k\lambda_s)$, where k is depended on both the shape and size of the dispersed phase.

Espesstally for spheres of radius a, $k_a=2/a$, while for long thin rods $(a>>b=c)$ the constant has three terms $k_a=2/a$, $k_b=k_c=4/\pi b$. The other theory assumes that the surface conductivity depends on the field frequency   because the strong electrostatic interaction between the charge carriers motion the relaxation time is reduced and the dielectric constant is increased by $(1+2xn_s/n)$ where n_s is the charge carrier density in the interface , and n is the bulk charge carrier density and X the inverse of the Debye shielding radius.Relations of the above theories are shown in Table I [10].

MWS POLARIZATION IN POLYMERS.

Polymer systems which have been studied , appear interfacial polarization. Solid polymers have high absorption , e>100 at frequencies lower than 1Hz and at enviroment temperature.

The problem which arises while solid polymers are studied, is that there are not systems with obvious distinctioned phases. It is also difficult for solid polymers their morphology to be defined.

In general , permittivity increment in those systems is higher than the increment which can be calculated according to M-W-S theory. For ellipsoid disposal phase there is a more quantitative comparison of theoretical and experimental data.

ΜΕΣΕΠΙΦΑΝΕΙΑΚΗ ΠΟΛΩΣΗ ΣΤΕΡΕΩΝ

ΠΕΡΙΛΗΨΗ

Στην εργασία αυτή γίνεται μελέτη της διηλεκτρικής συπμεριφοράς υλικών σε στερεά κατάσταση.Τα υλικά αυτά αποτελούνται από δύο φάσεις (περιοχές) που παρουσιάζουν διαφορετική ηλεκτρική-διηλεκτρική συμπεριφορά. Αποτέλεσμα αυτού είναι η συμπεριφορά του υλικού να διφέρει από αυτή των φάσεών του. Για την αντιμετώπιση του προβλήματος αυτού έχουν αναπτυχθεί διάφορες θεωρίες,κυρίως στην περίπτωση του στατικού ηλεκτρικού πεδίου με αγώγιμες ή

μη αγώγιμες τις δύο φάσεις.Πιο γνωστή είναι η θεωρία των Maxwell-Wagner-Sillars.

Στην περίπτωση του εναλλασόμενου ηλεκτρικού πεδίου οι εργασίες των Debye, Cole-Cole και άλλων, δίδουν αρκετά καλή λύση στο πρόβλημα σε σύγκριση με τις λύσεις που δίνονται στην περίπτωση του στατικού ηλεκτρικού πεδίου.

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A NEW SERIES OF DIETHYLENETRIAMINE AND TRIETHYLENETETRAMINE DITHIOCAR-
BAMATES AND THEIR COMPLEXES

C.A. BOLOS* and G.E. MANOUSSAKIS

*Aristotle University of Thessaloniki, Faculty of Chemistry, Laboratory
of Inorganic Chemistry, POB 135, Thessaloniki 54006, Greece.*

SUMMARY

New nickel, copper and zinc complexes of diethylenetriamine(dien) di-
thiocarbamate (dtc) of the types $Cu(diendtcHCl)$, $NiCl(diendtcHCl)$ and
$Zn(diendtcHCl)_2$ ($diendtc=H_2NCH_2CH_2\overset{+}{N}H_2CH_2CH_2NHCS_2^-$) and of triethylenetetra-
mine(trien)bisdtc with the general formula trienbisdtcM(trienbisdtc=
$^-S_2CHNCH_2CH_2\overset{+}{N}H_2CH_2CH_2\overset{+}{N}H_2CH_2CH_2NHCS_2^-$; M=Ni,Cu,Zn), have been prepared by
the reaction of the respective dithiocarbamate zwitterions with metal
salts. The dien and trien zwitterions were isolated by the reaction of
dien and trien with carbon disulphide. The dien zwitterion reaction with
aromatic aldehydes gave Schiff bases. The ligands and their complexes ha-
ve been characterized and studied by elemental analysis, IR and UV - Vis
spectroscopy as well as by conductivity and magnetic susceptibility mea-
surements.
The fungitoxicity of selected ligands and complexes against fungi
Camarosporium Dalmatica is discussed.

Key words : Copper(I), Copper(II), Nickel(II) and Zinc(II) complexes. Di-
thiocarbamates of Dien and Trien. IR, UV-Vis studies. Polyamines.

INTRODUCTION

The complexing ability of dithiocarbamates derived from primary and
secondary monoamines and diamines has received considerable attention[1-7].
Conversely the synthesis or complexing behaviour of dithiocarbamates, de-
rived from polyamines, have scarcely been studied[8].

We report here on the synthesis of dithiocarbamates coupled to die-
thylenetriamine(diendtc) and triethylenetetramine(trienbisdtc), the con-
densation reaction of diendtc with various aldehydes, the complexation

with several transition metals and the fungitoxicity of a selected   number of ligands, their Schiff bases and complexes.

EXPERIMENTAL

i. Reagents and Techniques

All chemicals were reagent grade, used without purification. Elemental analyses were carried out with a Perkin-Elmer 240 Elemental Analyser. The metal concentrations were determined by volumetric titration, after treating the complexes with a 1:1 mixture of nitric and sulphuric acids and chlorine by Volhard's method.

The IR spectra were recorded in the region 4000-200 cm^{-1} with   a Perkin-Elmer 467 Spectrophotometer with KBr discs.

The electronic spectra were measured with a Perkin-Elmer Hitachi 200 spectrophotometer in the 200-800 nm region. Conductivity measurements were carried out with an Industrial Instrument, Inc. Model RC   216 B_2 Conductivity bridge.

Magnetic susceptibility measurements were carried out by the Faraday method at room temperature, using Hg $Co(SCN)_4$ as the calibrant.

ii. Synthesis of ligands

Reaction of diethylenetriamine with carbon disulphide

Diethylenetriamine (10 cm^3, 0.1 mol) dissolved in methanol (50 cm^3) was added dropwise to a solution of carbon disulphide (6 cm^3, 0.1 mol) in methanol (150 cm^3) at -5^oC. The mixture was stirred for 2 h   and   the white solid diendtc was separated by filtration, washed with methanol and ether and dried under vacuum.

Reaction of triethylenetetramine with carbon disulphide

Triethylenetetramine (14.6 cm^3, 0.1 mol) dissolved in methanol   (50 cm^3) was added dropwise to a solution of carbon disulphide (12 cm^3,   0.2 mol) in methanol (200 cm^3) at -5^oC. The reaction mixture was stirred for 2 h and the white solid trienbisdtc was separated by filtration, washed with methanol and ether and dried under vacuum.

Reaction of diethylenetriaminedithiocarbamate with aldehydes

The diendtc Schiff bases have been prepared as follows : Benzaldehy-
de, substituted benzaldehydes or pyridine-2 - aldehyde (10 mmol)   was
added dropwise to a solution of diendtc (10 mmol) in water (50 cm^3). The
mixture was stirred for 1 h. Filtration gave a solid which was   washed
with water, methanol and ether and dried under vacuum. Table I lists the
analytical results, yields and other physical data for   the   prepared
compounds.

iii. Synthesis of Complexes

Reaction of diendtc with metal salts

To a suspension of diendtc (20 mmol) in methanol (20 cm^3), a soluti-
on of nickel(II) chloride hexahydrate (copper(II) chloride dihydrate or
zinc(II) chloride (10 mmol)) in methanol (20 cm^3) was added and the mix-
ture was stirred at room temperature. After 1 h the mixture was   filte-
red, the solids obtained washed with methanol and ether and dried under
     vacuum. Only from the nickel solution, a green solid precipitated from
the filtrate when ether was slowly added. The solid was isolated by fil-
tration and dried under vacuum.

Reaction of trienbisdtc with metal salts

To a suspension of trienbisdtc (10mmol) in methanol (30 cm^3),   the
following amounts were added : (i) Solution of sodium hydroxide (0.8 g,
20 mmol) in water (20 cm^3), (ii) In the respective solution of trien -
bisdtc sodium salt, a solution of nickel(II) chloride hexahydrate (cop-
per(II) chloride dihydrate or zinc chloride (10 mmol)) in methanol   (20
cm^3). After 1 h, the solid was filtered and washed with water, methanol
and ether and dried under vacuum.

The analytical data and some physical properties   for the   li-
gands and complexes are given in Table I.

RESULTS AND DISCUSSION

The dithiocarbamate ligands, diendtc and trienbisdtc have been   ob-
tained at low temperature with good yields from the direct reactions of
CS$_2$ with dien and trien respectively,

(Reactions 1-2)

$$H_2NCH_2CH_2NHCH_2CH_2NH_2 + CS_2 \rightarrow H_2NCH_2CH_2\overset{+}{N}H_2CH_2CH_2NHCS_2^- \text{(diendtc)}$$

Reaction 1

$$H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2 + 2CS_2 \rightarrow {}^-S_2CNHCH_2CH_2\overset{+}{N}H_2CH_2CH_2\overset{+}{N}H_2CH_2CH_2NHCS_2^-$$

(trienbisdtc)
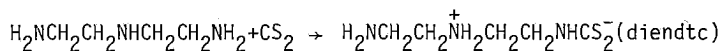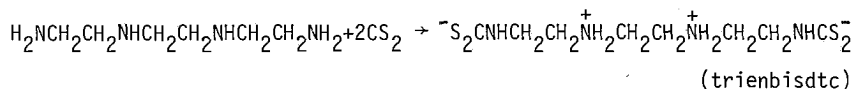
Reaction 2

For both products, the elemental analysis results agree with the pro-
posed formulations. Further support for the tentative formulae is given
by the behaviour of the compounds towards NaOH and by their infrared
spectra. Titration of diendtc and trienbisdtc with NaOH indicates   the
presence of one and two acidic groups, respectively. The ir spectra   of
both compounds show bands in the 2580 and 2700 cm^{-1} region pointing   to
zwitterionic nature of the reaction product. In the case of diendtc,   a
primary amine group has been established through its behaviour with   re-
spect to aldehydes. Thus the reaction of diendtc with benzaldehyde   or
its derivatives, readily afforded Schiff bases. Similar behaviour   was
observed with pyridinoaldehyde.
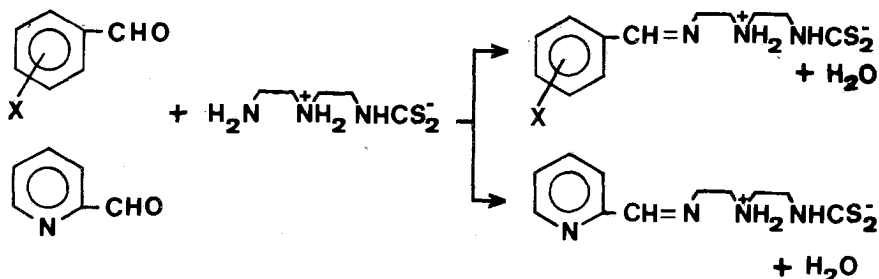
Where X = H, o-Cl, m-Cl, p-Cl , o-NO$_2$, m-NO$_2$, p-NO$_2$.

The compounds obtained from these reactions and their properties are
also listed in Table I.

The dithiocarbamate ligand diendtc reacts readily with   zinc(II),
nickel(II) and copper(II) salts, to give coordination compounds of   the
type Zn(diendtcHCl)$_2$, NiCl(diendtcHCl) and Cu(diendtcHCl). The same com-
plexes were prepared by the reaction of Schiff bases with metal salts.
This is probably due to the hydrolysis of the ligands during their   com-

plexation reaction. The acidic medium, required for the hydrolysis of the
Schiff bases, is provided by the HCl released during the preparation pro-
cedure and may follow an analogous mechanism proposed by Hine et al.[9] as
indicated below:

*Y = $CH_2NHCH_2CH_2NHCS_2M/2$
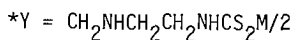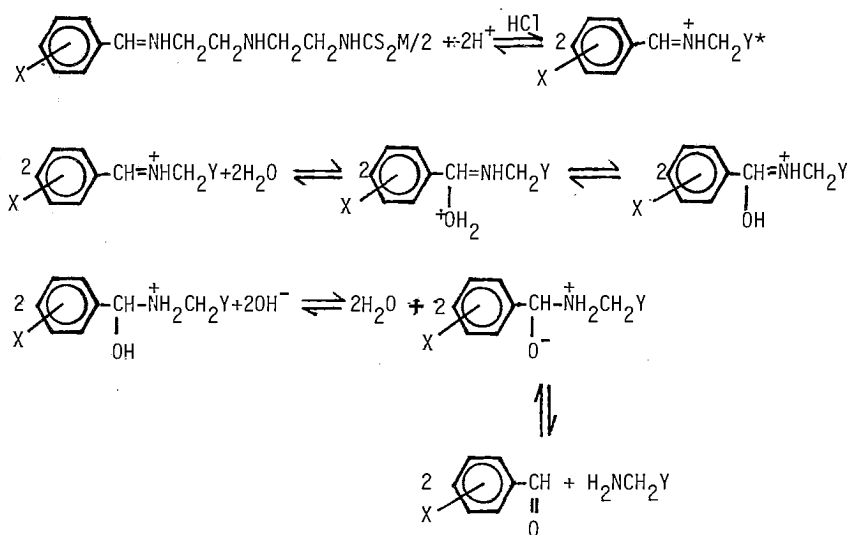
In contrast, the trienbisdtc ligand did not react directly with   the
metal salts. However, the reaction of the sodium salt of the same ligand
with the metal salts gave polymeric forms of the type trienbisdtcNa(trien
bisdtcM)$_x$trienbisdtcNa. The polymeric nature of these products is evident
from the broad bands in the IR spectra, the C,H,N and metal analyses, as
well as by their insolubility in water and in common organic solvents.
   The IR spectra data of the ligands and their metal coordination com-
pounds are presented in Table II. A strong broad band in the 2580-2700
cm^{-1} region of the ligands spectrum is assigned to the $-\overset{+}{N}H_2$ group[7,10],
indicating the formation of dien and trien dithiocarbamate zwitterions.
The thiureide band[11] at ca 1500 cm^{-1} shifts to lower wave numbers on
coordination. Further evidence for the metal chelation are the weak   to
medium intensity bands at 375-390 cm^{-1}, assigned to $v(M-S)$[16,17]. The 950-
1000 cm^{-1} region is associated with the $C \overset{...}{-} S$ stretching frequency[12-14].
The appearance of only one band in this region, indicates a symmetric bi-

Table II. IR and UV-Vis Spectra Data of the Ligands and the Complexes

| Compound | Infrared Data (cm^{-1}) | | | | | Electronic Spectra Data , λ_{max}(logε) | | | | | | Solvent | μ_{eff} |
	$v(\overset{+}{N}H_2)$	v(C=N)	v(C$\cdots$N)	v(C$\cdots$S)	v(M-S)	Band I	Band II	Band III	Band IV (nm)	Band V	Band VI		B.M.
I	2580 s-br		1520 vs	960 vs 980 vs		293(4.25)	345(3.0)					H$_2$O	
II	2580 s-br	1640 s	1480 vs	950 s 990 s		302(4.33)	347(3.1)					DMF	
III	2580 s-br	1645 s	1490 vs	960 s 980 s		300(4.27)	338(3.15)					DMF	
IV	2600 s-br	1655 vs	1499 vs	950 s 970 s		301(4.30)	345(3.05)					DMF	
V	2580 s-br	1640 m	1525 vs	960 m 990 m		302(4.29)	346(3.16)					DMF	
VI	2590 s-br	1645 m	1520 vs	960 m 985 m		301(4.38)	345(3.17)					DMF	
VII	2585 s-br	1640 m	1520 vs	960 m 990 m		299(4.30)	343(3.01)					DMF	
VIII	2580 s	1650 s	1465 vs	980 m 1000m		298(4.21)	340(3.11)					DMF	
IX			1500 vs	950 s	385 w		323(4.20)	388(3.49)	435 (3.0)	490 sh	625(1.86)	DMSO	1.50
X			1490 vs	975 m	385 s		325(4.01)	390(3.32)	435(2.60)	492 sh	630(1.48)	H$_2$O	0.73
XI			1490 vs	985 w	375 w	292 sh	359(3.24)		437(3.19)			DMSO	Dia
XII			1475 vs	970vs-br	380 w	295	340 sh					NUJOL	Dia
XIII	2700 s-br		1510 s	960 s 990 s		282	333					NUJOL	
XIV			1495 vs	975 w	390 m		335	395	435 sh	500sh	630	NUJOL	1.48
XV			1500 vs	960 w	370 w	280 sh		380	415 sh	520 sh	610	NUJOL	0.98
XVI			1475 vs	980 s-br	370 w	293 sh	330					NUJOL	Dia

Dia= Diamagnetic

dentate bonding of the dtc ligands. The ir spectra of nickel and copper compounds show only one band in this region which strongly supports bidentate dtc coordination. In the case of the zinc complexes, the broadening of this band is associated with the bidentate asymmetrical coordination of the dtc ligands[15]. In the ir spectrum of NiCl(diendtcHCl) complex the band at 320 cm^{-1} is due to v(Ni-Cl). Finally the strong band in the 1640-1650 cm^{-1} region is attributed to v(C=N), confirming the formation of diendtc Schiff bases[18-19].

The electronic spectra of the ligands and complexes, listed in Table II, show absorption bands at high energy values due to the chromophore group -NCS$_2$[20]. These bands are denoted as bands I and II. Band I at ca 300 nm is assigned to a charge transfer transition in the ligand of the $\pi^* \leftarrow \pi$ type located at S$\cdots$C$\cdots$S group[21-23]. Band II may be due to an electronic transition $\pi^* \leftarrow n$ located at the sulphur atom[24,25]. For some compounds band I is lacking suggesting the bidentate dtc coordination, while for some others compounds it appears as shoulder suggesting asymetric bidentate ligand. Band II was not observed in case XV, probably because it is overlapped by strong charge transfer bands. In the UV-Vis spectra of diendtc and trienbisdtc nickel compounds, band I is absent, while bands II, III and IV at ca 325, 390 and 435 nm can be assigned either to a charge transfer or to d-d transitions. The last two bands as well as the band at 630 nm which is also of low intensity indicate a square planar arrangement[25,26]. The μ_{eff} values of the nickel(II) compounds are in the 0,75-1,50 BM range. The non-zero μ_{eff} values do not support a tetragonal geometry for the Ni(II) complexes. They are not, however, in a range to justify any other geometry (e.g. tetrahedral, octahedral). On the other hand, a singlet-triplet equilibrium for a pseudo-square planar complex may be put forward. According to the above UV-Vis and magnetic data it is tentatively proposed that the nickel compounds have approximately a square planar geometry. The value of molar conductance of the soluble diendtcNi compound in water (280 ohm^{-1}cm^{2}mol^{-1}) indicates three ions per molecule, suggesting a plausible dimerization of the following type:
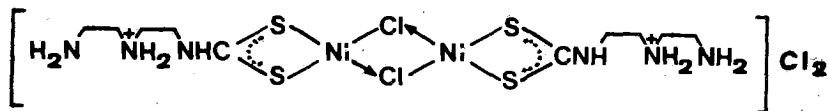
The electronic spectrum of diendtcCu complex in DMSO solution, bands
II at 359 nm and III at 437 nm can be assigned to a charge transfer
transition. The absence of any band in the visible region, as well   as
the diamagnetic character of the complex, show that the Cu oxidation
state is +1. The insolubility of the product in common organic solvents
is probably an indication that the structure is polymeric and could be
tentatively written as,
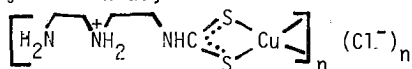
The electronic spectrum of trienbisdtcCu compound (in nujol mulls)
shows broad absorption bands at 415, 520 and 610 nm, which could be te-
ntatively assigned to d-d transitions. The low magnetic moment (0.98 BM)
indicates either inter or intramolecular magnetic exhange interactions[27]
In the electronic spectra of the $Zn(diendtcHCl)_2$ and trienbisdtcZn com-
plexes the presence of band I confirms the asymmetric bidentate bonding
of the ligands[15] as inferred from the ir spectra of the coordination
compounds.

The fungitoxicity of selected ligands and   their   metal   complexes
against *Camarosporium Damaltica* using   a culture media Potato Dextrose
Agar was studied. Preliminary results show that the fungitoxicity of so-
me of the studied ligands and compounds, is slightly higher than   the
best known fungicide zinc dimethyldithiocarbamate. The diendtc ligands
or their coordination compounds are more active than the   trienbisdtc
species and its polymeric complexes. As far as the diendtc lignad   and
its Schiff bases fungitoxicity is concerned, the latter are significant-
ly more active. However, the bases with the chlorosubstituted   aromatic
rings appear to be more active than their nitro- or substituted 2-pyri-
dine counterparts. Interestigly, the soluble nickel(II) compound of di-
endtc with the chloro-substituted Schiff bases showed comparable beha-
viour.

Περίληψη

ΝΕΑ ΣΕΙΡΑ ΔΙΘΕΙΟΚΑΡΒΑΜΙΔΙΚΩΝ ΕΝΩΣΕΩΝ ΤΗΣ ΔΙΑΙΘΥΛΕΝΟΤΡΙΑΜΙΝΗΣ,ΤΗΣ ΤΡΙΑΙΘΥ-
ΛΕΝΟΤΕΤΡΑΜΙΝΗΣ ΚΑΙ ΤΩΝ ΣΥΜΠΛΟΚΩΝ ΤΟΥΣ

Νέα διθειοκαρβαμιδικά σύμπλοκα του νικελίου, του χαλκού και του ψευ-
δαργύρου της διαιθυλενοτριαμίνης (DIEN) και της τριαιθυλενοτετραμίνης
(TRIEN) έχουν παρασκευαστεί από την αντίδραση των αντίστοιχων διθειοκαρ-
βαμιδικών εσωτερικών αλάτων των πολυαμινών με άλατα μετάλλων. Τα διθειο-
καρβαμιδικά εσωτερικά άλατα της διαιθυλενοτριαμίνης και της τριαιθυλενο-

Table I. Analytical data and some physical properties of the new diendtc, trienbisdtc ligands and their complexes.

Compound	C%	H%	N%	M%	Colour	M.P.(^{o}C)	Yield (%)	Solubility
	Found (Calculated)							
I $H_2NCH_2CH_2\overset{+}{N}H_2CH_2CH_2NHC\overset{-}{S_2}$	33.25(33.52)	7.15(7.26)	22.97(23.43)		white	111-113	90	H_2O
II o-$ClC_6H_4CH=NCH_2CH_2\overset{+}{N}H_2CH_2CH_2NHC\overset{-}{S_2}$	47.61(47.76)	5.25(5.31)	13.85(13.93)		white	95-97	23	NaOH,DMF
III m-$ClC_6H_4CH=NCH_2CH_2\overset{+}{N}H_2CH_2CH_2NHC\overset{-}{S_2}$	48.45(47.76)	5.28(5.31)	13.70(13.93)		white	105-107	32	NaOH,DMF
IV p-$ClC_6H_4CH=NCH_2CH_2\overset{+}{N}H_2CH_2CH_2NHC\overset{-}{S_2}$	47.70(47.76)	5.30(5.31)	13.80(13.93)		white	108-110	45	NaOH,DMF
V o-$NO_2C_6H_4CH=NCH_2CH_2\overset{+}{N}H_2CH_2CH_2NHC\overset{-}{S_2}$	46.11(46.15)	5.10(5.13)	17.80(17.95)		yellowish	118-121	48	NaOH,DMF
VI m-$NO_2C_6H_4CH=NCH_2CH_2\overset{+}{N}H_2CH_2CH_2NHC\overset{-}{S_2}$	45.85(46.15)	4.98(5.13)	17.69(17.95)		yellowish	109-112	30	NaOH,DMF
VII p-$NO_2C_6H_4CH=NCH_2CH_2\overset{+}{N}H_2CH_2CH_2NHC\overset{-}{S_2}$	46.20(46.15)	5.05(5.13)	17.90(17.95)		yellowish	109-111	70	NaOH,DMF
VIII $C_5H_5NCH=NCH_2CH_2\overset{+}{N}H_2CH_2CH_2NHC\overset{-}{S_2}$	49.10(49.25)	5.85(5.97)	20.81(20.90)		yellowish	102-104	25	NaOH,DMF
IX $(H_2NCH_2CH_2NHCH_2CH_2NHCS_2)NiCl \cdot HCl^a$	19.25(19.44)	4.40(4.21)	13.51(13.61)	18.95(19.02)	green	185^d	57	H_2O,CH_3OH
X $(H_2NCH_2CH_2NHCH_2CH_2NHCS_2)NiCl \cdot HCl^b$	19.12(19.44)	4.05(4.21)	13.51(13.61)	18.80(19.02)	green	90^d	10	DMSO
XI $(H_2NCH_2CH_2NHCH_2CH_2NHCS_2)Cu \cdot HCl$	21.70(21.58)	4.70(4.68)	16.95(17.12)	22.50(22.85)	brown	78^d	80	DMSO
XII $(H_2NCH_2CH_2NHCH_2CH_2NHCS_2)Zn \cdot 2HCl$	24.10(24.27)	5.20(5.26)	16.85(16.99)	13.00(13.22)	white	123^d	78	DMSO
XIII $\overset{-}{S_2}CNHCH_2CH_2\overset{+}{N}H_2CH_2CH_2NH_2CH_2CH_2NHC\overset{-}{S_2}$	32.10(32.21)	5.97(6.04)	18.60(18.70)		white	115-7	85	NaOH
XIV trienbisdtcNi	26.90(27.17)	4.63(4.56)	15.60(15.84)	14.71(14.52) 1.57(1.62)Na	green	220^d	65	Insoluble
XV trienbisdtcCu	26.10(26.45)	4.49(4.30)	15.63(15.70)	16.50(16.11) 1.39(1.16)Na	brown	145^d	60	Insoluble
XVI trienbisdtcZn	26.15(26.72)	4.31(4.45)	15.40(15.59)	16.00(16.18) 1.37(1.42)Na	white	186^d	78	Insoluble

^{a} Soluble ^{b} Insoluble ^{d} Decomposition

τετραμίνης έχουν απομονωθεί από την αντίδραση των αμινών με διθειάνθρακα. Το διθειοκαρβαμιδικό άλας της DIEN με αρωματικές αλδεΰδες έδωσε   Βάσεις του

Τα ligands και τα σύμπλοκα που παρασκευάστηκαν έχουν χαρακτηριστεί και μελετηθεί με στοιχειακή ανάλυση, φασματοσκοπικές μεθόδους (IR, UV-Vis) καθώς και με αγωγιμομετρικές και μαγνητικές μετρήσεις. Τέλος, σε προκα-. ταρκτικό στάδιο, μελετήθηκε και συζητιέται η μυκητοκτόνος δράση μερικών από τα παρασκευασθέντα ligands και σύμπλοκα.

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CHEMICAL AND MINERALOGICAL CHARACTERISTICS

OF GREEK MUDS AND PELOIDS

M. MITRAKAS AND C. SIKALIDIS

Department of Chemical Engineering, School of Engineering, Aristotle University of Thessaloniki, Thessaloniki 54006, Greece.

SUMMARY

The chemical and mineralogical characteristics of seven mud and peloid samples from thermal spring areas of Greece (Krinides, Lisbori, Lagadas, Thermi, Kyllini and Preveza), as well as from the area of Pikrolimni, were determined in order to evaluate their use for therapeutic applications. The samples were so selected to represent deposits that either currently used or can be used for these purposes. Pikrolimni and Thermi samples had a pH of 9.8 and 8.4, respectively, which suggest their potential as beautifying muds. The high montmorillonite content of Lisbori and Thermi samples is also indicative of their effective application. Preveza and Kyllini samples exhibited poor mud characteristics due to their low content of clay minerals and high content of silica. If Krinides and Lagadas deposits are to be exploited commercially they should be beneficiated with the intent to increase their clay mineral content. The study of the well-known mud from Boario and the beautifying mud Argilla Solare, both from Italy, substantiate the fact that the desirable mud characteristics are a high amount of clay minerals and low amount of free silica, feldspar and carbonates.

Key words: Mud, Peloid, Clay Minerals.

INTRODUCTION

Muds have been used empirically, nonetheless effectively, since the antiquity. However, it was not until 1931 that the International Society of Medical Hydrology established certain criteria for mud's classification and their corresponding therapeutic practices. Recent classification schemes[1] divide muds into three main categories, namely, sapropelic, peat and spring mineral (clay) muds, on the basis of their origin and physico-chemical characteristics.[1]

The properties, that make mud a prized therapeutic material different from a simple hot poultice, are acquired after a slow and complex "maturation" process[2]. The process involves long periods (months or even years) of contact of a specific clay (called peloid henceforth) with thermal mineral water in special basins. During the contact the solid clayey component of the mud is mixed with the liquid phase[3] and is progressively enriched with organic substances. The latter are produced through the profuse development of different kind of algae in the maturation basins. These algae, by their metabolic activities and products, modify the physico-chemical characteristics of the peloid until mature mud is formed[4] and also enrich it with vitamins, biostimulins and antibiotics[1,4,5], that add to the mud pharmacodynamic properties. Other mud characteristics, such as, water retentivity, heat adsorption and its retention, plasticity and viscosity[2], are also very important with respect to its therapeutic power.

Chemical analysis of muds allows interpretations of their origin and maturation and helps in their classification. It also allows the qualitative and quantitative identification of the components influencing mud's physico-chemical properties, such as the liquid phase and its dissolved salts and the solid phase with its organic and inorganic constituents. Chemical analysis also assists in evaluating the suitability of a certain peloid to produce a mud after maturation.

In many European and other countries modern pelotherapeutic units are operating under strict medical supervision and have been proven to be effective in many diseases[6,7]. Their muds have been characterised and used locally or exported to other countries among which is Greece. Very expensive muds are imported in Greece, although vast deposits, that can be commercially exploited, exist.

In this work the chemical and mineralogical characteristics of Greek spring mineral muds and peloids were determined and their deposits were surveyed, in order to be evaluated for potential use in therapeutic applications.

MATERIALS AND METHODS

Forty mud and peloid samples in total were collected, during summer 1990, from selected locations (Fig. 1) where: a) muds are widely used (Krinides, Kavala prefecture, 15 samples, Pikrolimni , Kilkis prefecture , 4 samples), b) muds exist but are not commercially exploited (Lisbori 6 samples and Thermi 4 samples of Lesbos island, Kyllini, Helia prefecture, 2 samples, Preveza, Preveza prefecture , 2 samples), and c) muds were used in the past (Lagadas, Thessaloniki prefecture, 4 samples). The results reported in the following Tables represent the analysis of one sample considered representative of each location. Samples of various imported beautifying muds, such as "Black Mud" from the Dead Sea, Israel, "Argilla Solare" from Italy, as well as matured mud from "Boario Therme" of Italy, were also examined for comparative purposes.
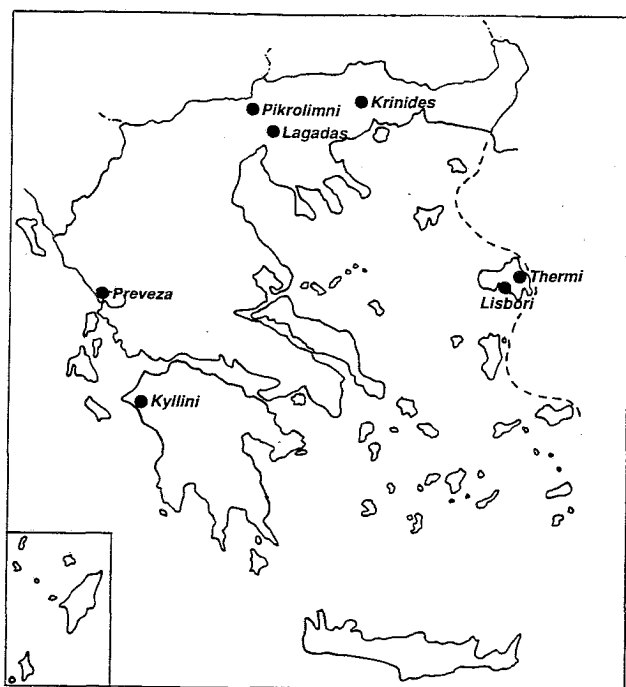
FIG. 1. Map of Greece: sample locations.

The water content of mud and peloid samples was determined by drying them at 70 °C for 48 h and the ash content by heating at 850 °C for 4 h. Organic carbon was determined by a Leco Element Analyser, model CHN 800 and the results were converted to organic matter by multiplying the carbon percentage by the factor 1.724[8]. Water soluble salts of muds and peloids were determined after extraction with distilled water (1:5), calcium and magnesium carbonates and some iron compounds after dissolution with 2N HCl acid and elemental analysis of the residue (aluminosilicates) was performed after HF-HClO$_4$-H$_2$SO$_4$ digestion. Carbonates were also determined volumetrically. Cations were determined by AAS, using a Perkin Elmer 503 instrument, and anions by anion chromatography[9], using a Wescan 215/110/01 instrument. Cation Exchange Capacity (C.E.C) was measured according to the procedure outlined by Alexiades and Jackson[10]. Amorphous SiO$_2$ was determined after its selective dissolution with 0.5N boiling NaOH[10]. The mineralogical composition of mud and peloid samples was determined by means of a Rigaku Geigerflex X-ray diffractometer (XRD) and a Rigaku Thermoflex TG-DT Analyser. The presence of montmorillonite in the samples was verified by XRD after sample saturation with ethyleneglycol.

TABLE 1. Water soluble cations and anions of mature muds

Ions	Krinides	Pikro-limni	Lisbori	Thermi	Kyllini	Black mud	Boario	Argilla Solare
				g/kg				
Na^+	1.05	67.8	2.62	3.98	0.83	34.1	2.10	1.97
K^+	0.24	0.4	0.72	0.28	0.16	2.5	1.52	0.20
Ca^{2+}	0.21	0.1	2.34	0.41	0.85	7.6	0.60	0.00
Mg^{2+}	0.06	0.1	0.35	0.06	0.13	0.8	0.11	0.04
Cl^-	1.80	63.6	2.70	6.90	0.95	50.4	2.95	0.06
HCO_3^-	0.38	10.2	0.25	0.22	2.19	19.5	0.52	1.35
SO_4^{2-}	0.48	32.5	9.60	0.55	1.40	7.1	3.28	1.30
NO_3^-	0.00	1.4	0.02	0.00	0.09	1.1	0.32	0.30
CO_3^{2-}	0.00	9.1	0.00	0.00	0.00	2.7	0.00	1.14
Sum	4.22	185.2	18.60	12.40	6.60	125.8	11.40	6.36

RESULTS AND DISCUSSION

Water soluble salts contribute to the therapeutic properties of muds through their absorption by the human skin. Soluble salts differentiation or accumulation occurs in muds during the maturation process and there for in Table 1, only the water soluble cations and anions of mature muds are presented.

The percentage of calcium and magnesium carbonates are presented in Table 2. These carbonates have an adverse effect on mud's plasticity and it is therefore preferable their content to be less than 10% by weight[11]. The HCl acid treatment dissolves also various iron compounds, such as oxides, oxy-hydroxides and sulphides. In Table 2, dissolved iron is reported as Fe_2O_3. Sulphides, particularly iron sulphide, in muds originate through the action of hydrogen sulphide on iron oxides. Hydrogen sulphide in muds is produced during the anaerobic decomposition of the organic matter or the reduction of sulphates. It may also originate from the thermal mineral water. Iron sulphide gives its characteristic black colour to the mud. When its concentration is lower than 0.1% w/w the mud is grey (Pikrolimni, Boario), whereas at higher concentrations it becomes black[1] (Krinides, Lisbori, Kyllini). Iron sulphide is considered an important mud component because it releases sulphide ions upon the action of the skin's acidic substances, which are absorbed by the skin[12] curing dermatological diseases and also various forms of arthritis because of its angiohemodynamic action.

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K^+	0.24	0.4	0.72	0.28	0.16	2.5	1.52	0.20
Ca^{2+}	0.21	0.1	2.34	0.41	0.85	7.6	0.60	0.00
Mg^{2+}	0.06	0.1	0.35	0.06	0.13	0.8	0.11	0.04
Cl^-	1.80	63.6	2.70	6.90	0.95	50.4	2.95	0.06
HCO_3^-	0.38	10.2	0.25	0.22	2.19	19.5	0.52	1.35
SO_4^{2-}	0.48	32.5	9.60	0.55	1.40	7.1	3.28	1.30
NO_3^-	0.00	1.4	0.02	0.00	0.09	1.1	0.32	0.30
CO_3^{2-}	0.00	9.1	0.00	0.00	0.00	2.7	0.00	1.14
Sum	4.22	185.2	18.60	12.40	6.60	125.8	11.40	6.36

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TABLE 2. Hydrochloric acid soluble constituents of the various muds and peloids

Origin	$CaCO_3$	$MgCO_3$	Fe_2O_3	Sum
		% w/w		
Krinides	3.1	0.4	0.7	4.2
Pikrolimni	9.2	3.5	1.8	14.5
Lisbori	4.7	0.7	1.6	7.0
Thermi	26.1	0.7	0.3	27.1
Lagadas	1.6	0.8	0.8	3.2
Preveza	3.5	0.4	0.7	4.6
Kyllini	17.1	1.0	0.6	18.7
Black mud	51.4	5.4	0.5	57.3
Boario	10.3	1.1	1.5	12.9
Argilla Solare	1.1	0.5	0.9	2.5

The main constituents (organic matter, ash and water) and physicochemical characteristics (pH, C.E.C.) of muds and peloids are presented in Table 3. For the investigation of the pharmacodynamic and other properties of the muds further studies concerning the chemical composition of their organic matter are needed. Chemical analysis of aluminosilicates is presented in Table 4, and their semiquantitative mineralogical analysis is shown in Table 5.

Krinides

The natural mud of Krinides was formed by the existing thermal (29 °C) spring . It was traditionally considered to be beautifying mud and effective for musculosceletal and dermatological diseases. It is used during the summer months for group mud baths, while during the winter months it is naturally regenerated.

The fifteen samples studied, in addition to the mud itself, were collected within an area of 300m radius from the mud bath. The samples were taken at a depth of 3m, since a previous geophysical survey[13] showed that approximately at such depths clay minerals and earthly peats coexist. Chemical analyses revealed no significant variations in the composition of the samples. They contained, like the mud, 2-4 g/kg soluble ions (4.22 g/kg, Table 1), less than 10% w/w carbonates (3.5% w/w, Table 2), and 80-85% w/w aluminosilicates (82.6 w/w, Table 4). The percentage of water soluble ions of mud is considered very low, with Na^+ and Cl^- (possibly in the form NaCl) being the prevalent ions (Table 1), while Ca^{2+} and HCO_3^- found to be the main ions of the peloid samples studied (data not given). Hydrochloric acid soluble constituents are mainly $CaCO_3$ (Table 2). The dominant minerals of Krinides mud, as well as of other samples in this area, are feldspar and quartz (Table 5). The C.E.C. (15 meq/100g, Table 3) of the mud is similar to the well known muds from "Boario" and "Argilla Solare" and can be attributed to the

TABLE 3. Main constituents and physico-chemical characteristics of the various muds and
peloids

Origin	Organic matter	Ash content	Water content*	pH	C.E.C.
	% w/w				
Krinides	6.5	85.9	50	7.8	15
Pikrolimni	2.5	87.1	45	9.8	8
Lisbori	1.8	90.5	48	7.7	26
Thermi	0.5	82.2	45	8.4	19
Lagadas	1.2	92.7		7.5	12
Preveza	5.3	87.5		7.8	3
Kyllini	5.5	83.8	49	7.8	4
Black mud	1.6	72.1	40	8.5	2
Boario	1.8	88.2	50	7.5	10
Argilla Solare	0.9	89.8		10.2	18

* Water content of muds in their natural state.

presence of montmorillonite and organic matter as well. The organic matter content of the
mud was 6.5% w/w (Table 1), which is the highest value among the studied samples and is also
considerably different from the samples of the same area. This fact, as mentioned in the
Introduction, is rather due to the enrichment of the mud with organic matter during the
maturation process, which in this specific case lasts many years. The determined organic
matter content of the other samples from the area ranged between 1.5-5% w/w, a percentage
which is considered essential not only for the function of the complex biological processes[5],
but for the increase in water permeability of the clays[14] as well.

Pikrolimni

Pikrolimni lake covers an area of about 4×10^6 m² and its perimeter is about 6,600m. It is
mainly being fed by surface waters and thus the water covered area varies according to the
climatic conditions. During the summer months, when evaporation is intense, large deposits of
mud appear around its perimeter. They are traditionally used for the cure of dermatological
diseases. Four samples of this mud, collected from 4 different places in an area of about 5×10^5
m² between the villages of Pikrolimni and Xilokeratea, were studied. The composition of the
samples was the same and not considerably different from the composition of the various
samples studied from the same area in the past[15]. The amount of water soluble salts,
calculated from Table 1, consisted mainly of NaCl (105 g/kg), $NaHCO_3$ (14 g/kg), Na_2CO_3 (16
g/kg) and Na_2SO_4 (47 g/kg). The high pH of the mud (Table 3) is due to $NaHCO_3$ and Na_2CO_3,

TABLE 4. Chemical analysis of the aluminosilicates residue of the various muds and peloids

Origin	Na$_2$O	K$_2$O	CaO	MgO	Al$_2$O$_3$	Fe$_2$O$_3$	SiO$_2$	Sum
	% w/w							
Krinides	0.9	2.8	0.3	0.8	14.8	2.7	60.3	82.6
Pikrolimni	2.2	2.5	0.3	1.6	16.3	4.4	35.6	62.9
Lisbori	2.3	3.0	1.3	1.3	16.0	4.1	56.1	84.1
Thermi	1.0	1.4	0.6	0.8	11.1	4.1	46.7	65.7
Lagadas	2.5	2.9	1.1	1.7	17.7	4.8	58.2	88.9
Preveza	0.9	1.7	0.3	1.4	9.9	3.7	66.2	84.1
Kyllini	1.2	1.1	1.1	0.8	7.8	1.8	58.6	72.4
Black mud	0.9	0.9	1.6	0.4	5.3	2.0	17.1	28.1
Boario	0.5	1.6	1.1	1.6	16.6	5.2	52.8	79.4
Argilla Solare	1.4	3.2	0.2	4.2	16.9	6.5	54.5	86.9

while Na$_2$SO$_4$ are responsible for the bitter taste of the lake water and also the lake's name "Pikrolimni". The amount of soluble salts was 185.2 g/kg (Table 1), meaning that the water phase (45% w/w) is almost salt saturated. The soluble salts content of mud ranged between 150-200 g/kg, with NaCl (80-120 g/kg) being the main component, the alkaline earth carbonates content (12.7% w/w, Table 2) ranged between 8-13% w/w and that of aluminosilicates content (62.9% w/w, Table 4) ranged between 60-70% w/w. Micas and feldspar were the dominant minerals accompanied by montmorillonite and kaolinite in lower quantities (Table 5). Organic matter content (2.5% w/w, Table 3) ranged between 2-3% w/w, and its origin is probably from the decomposition of the lake greenfinch[15], such as Chlorococcum Sp., Coniochloris Sp., etc.

This mud because of its contact with the lake's water, which contains significant amount of trace elements, was found to have one order of magnitude higher concentration of biological active components, such as As (140 mg/kg), B (650 mg/kg) and Bromine (210 mg/kg), than the other samples studied. Also, because of the way of its formation the mud of Pikrolimni has a very fine texture (100%<88μm, 97%<44μm and 50%<5μm).

Lisbori

In Lisbori, of Lesbos island, located north-east of St John's thermal mineral spring a deposit of black mud was reported[16]. It was found on a depth of 5-20m within a radius of at least 200 m. From this area 6 mud samples were collected. The water soluble ions (18.6 g/kg) were presumably consist of CaSO$_4$ (8 g/kg) and NaCl (5 g/kg) as was calculated from the data of Table 1. Alkaline earth carbonates (5.4% w/w, Table 2) ranged between 5-10% w/w. The dominant mineral in the mud was montmorillonite, which accounts for the mud's good plasticity and high C.E.C. (26 meq/100g, Table 5).

TABLE 5. Semi-quantitative mineralogical analysis of the various muds and peloids

Origin	Mt	Chl	Mi	Kl	Fd	Qtz	Clc	Other
Krinides	+		+	+	+++	+++		+
Pikrolimni	+		+++	+	++		+	++
Lisbori	+++		+	+	++	++		+
Thermi	++			++	+	++	+++	+
Lagadas	+	+	++	+	+++	++		
Preveza		+	++	+	+	++++		+
Kyllini		+	+		+	++++	++	+
Black mud			+	+	+	+	++++	+++
Boario	+	+	++	++	+	++	+	
Argilla Solare	++		++	++	++	+		+

Abbreviations: Mt=montmorillonite, Chl=chlorite, Mi=micas, Kl=kaolinite, Fd=feldspars, Qtz=quartz, Clc=calcite.
Each + represents ≈10% w/w.

Thermi

Thermal mineral spring of Thermi in Lesbos results from the crossing of a group of faults having a S-N direction and of a fault having an E-W direction. These faults caused a graben in the area which was covered by unconsolidated sediments. In these sediments mud deposits were formed, at a depth of 5-20m and in a radius of about 150m around the spring[16]. The chemical analyses of the 4 mud samples collected, showed that the water soluble salts were of sea origin (Table 1). Also, they had relatively good plasticity, in spite of their high carbonates percentage (26.8% w/w, Table 2). This fact should be attributed to the nature of the dominant mineral, which is montmorillonite (Table 5). The greatest part (10% w/w) of the free SiO_2 of the mud was amorphous as was in the mud of Lisbori (12% w/w), while amorphous SiO_2 in all other mud and peloid samples studied, ranged between 1-3% w/w (data not given in Tables). Organic matter (0.5% w/w, Table 3) was the lowest among all studied samples.

Lagadas

From an area away from Lagada spa, where a mud sanatorium existed in the past, 4 peloid samples were collected from a depth of 1 m and 3 m. The samples showed a percentage of carbonates (2.4% w/w, Table 2) and organic matter (1.2% w/w, Table 3), comparatively lower to the other samples examined. The dominant minerals were feldspars, micas and quartz, accompanied by montmorillonite, chlorite and kaolinite in lower quantities (Table 5). The C.E.C. of the samples ranged between 10-15 meq/100g (12 meq/100g, Table 3).

Preveza

Around the mineral water spring of Preveza, at a depth of 0.5 m and with thickness lower than 1 m there is a soil layer rich in seaweed. From this layer, two peloid samples were collected. The samples had a high organic matter content (5.3% w/w, Table 3), but contained small quantities of water soluble salts (data not given), meaning that they are not influenced by the nearby sea. Their carbonate content was also low (3.9% w/w, Table 2). The principal mineral was quartz (Table 5) accompanied by small amounts of micas, chlorite, kaolinite and feldspars, to which the low C.E.C. (3 meq/100g, Table 3) is attributed. Except all the above mentioned poor chemical characteristics, the peloid of Preveza is located in the vicinity of an inhabited area, so its use is doubtful.

Kyllini

At the area of Kyllini spa there are small surface deposits of black mud (holes of 1 m diameter). Two mud samples were collected for a first estimation of the minerals present. Quartz and calcite (Table 5) were the dominant minerals in the mud, a fact that explains its low C.E.C. (4 meq/100g, Table 3). In any case the results can not be judged conclusive and further examination of the existing deposits is needed.

Beautifying muds

Muds are difficult to rehydrate once they have been dried[5]. This means that it is not easy for the powder of "Argilla Solare" to form mud when mixed with water. It is possible that its beautifying action is mainly due to the high pH[17], a physico-chemical characteristic to which the beautifying action of the "Black Mud" may be attributed. " Black Mud" was dominated by alkaline earth carbonates (56.8% w/w, Table 2), while its aluminosilicates content (28.1% w/w, Table 4) was the lower among the samples analysed. However, in spite the high carbonates content and the low C.E.C., "Black Mud" shows relatively good plasticity probably because of its very small particle size. Muds from Pikrolimni and Thermi possess also high pH and thus they could be used for beautifying purposes.

Boario

The mud of Boario is used at a temperature of 46 °C for the curing of musculoskeletal diseases. The two main characteristics of the "Boario" and "Argilla Solare" muds, related to their well known therapeutic properties, are their high clay mineral and low quartz, feldspar and carbonates content (Table 5).

In conclusion, since most of the Greek peloids studied contained small amount of clay minerals, the first step towards their use as muds should be their beneficiation in the direction of increasing their clay minerals content.

ΠΕΡΙΛΗΨΗ

ΧΗΜΙΚΑ ΚΑΙ ΟΡΥΚΤΟΛΟΓΙΚΑ ΧΑΡΑΚΤΗΡΙΣΤΙΚΑ ΤΩΝ ΕΛΛΗΝΙΚΩΝ ΠΗΛΩΝ ΚΑΙ ΠΗΛΟΕΙΔΩΝ

Στην εργασία αυτή προσδιορίσθηκαν τα χημικά και ορυκτολογικά χαρακτηριστικά πηλών και πηλοειδών επτά Ελληνικών περιοχών που βρίσκονται κοντά σε θερμές πηγές (Κρηνίδες, Λισβόρι, Θερμή, Λαγκαδάς, Πρέβεζα, Κυλλήνη), καθώς και από την περιοχή της Πικρολίμνης, με σκοπό να εκτιμηθεί η δυνατότητα χρησιμοποίησής τους για θεραπευτικές εφαρμογές. Συλλέχθηκαν αντιπροσωπευτικά δείγματα, τόσο από τους πηλούς που ήδη χρησιμοποιούνται, όσο και από αυτούς που θα μπορούσαν να χρησιμοποιηθούν. Το αλκαλικό pH, 9,8 και 8,4 αντίστοιχα, των δειγμάτων από την Πικρολίμνη και τη Θερμή δείχνει ότι μπορούν να χρησιμοποιηθούν και ως καλλυντικοί πηλοί. Η υψηλή περιεκτικότητα σε μοντμοριλλονίτη των δειγμάτων από το Λισβόρι και τη Θερμή είναι ενδεικτική της δυνατότητας να χρησιμοποιηθούν αποτελεσματικά ως θεραπευτικοί πηλοί. Αντίθετα, η χαμηλή περιεκτικότητα σε ορυκτά της αργίλου και η υψηλή περιεκτικότητα σε ελεύθερο χαλαζία, των δειγμάτων από την Πρέβεζα και την Κυλλήνη, δικαιολογούν τα πτωχά τους χαρακτηριστικά ως πηλοί. Η χρησιμοποίηση, για παραγωγή πηλού, των πηλοειδών Κρηνίδων και Λαγκαδά θα πρέπει να συνοδευθεί από εμπλουτισμό με σκοπό την αύξηση του ποσοστού των ορυκτών της αργίλου που περιέχουν. Η μελέτη των γνωστών πηλών "Boario" και "Argilla Solare" της Ιταλίας επιβεβαίωσε το γεγονός ότι τα επιθυμητά χαρακτηριστικά ενός πηλού είναι η υψηλή περιεκτικότητα σε ορυκτά της αργίλου και η χαμηλή περιεκτικότητα σε ελεύθερο χαλαζία, αστρίους και ανθρακικά άλατα.

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SHORT PAPER

CHEMICAL CONTROL OF DRINKING WATER

I. KAGALOY[1], I. ROUSSIS[2], and V.KATSOUGIANNOPOULOS[1]

[1]Laboratory of Hygiene, Medical School, University of Ioannina, Ioannina 45110, Greece.
[2]Laboratory of Food Chemistry, Department of Chemistry, University of Ioannina, Ioannina 45110, Greece.

SUMMARY

The physicochemical parameters NO_3^-, NO_2^-, NH_4^+, F^-, Mg, Mn, Cu, Pb, total hardness, conductivity, pH and total solids of drinking water from the distribution system of three cities (Ioannina, Preveza, Leucada) in Epirus-Greece were examined during a year.

In general, NO_3^-, NO_2^- and NH_4^+ concentrations were lower than the maximum admissible limits.

Fluoride was found to be in significant amounts (410-600, 510-620, 500-680 µg/l), sufficient for dental protection, while manganese existed in higher concentrations (40-77, 40-80, 45-80 µg/l) than the desirable limits, which was also observed for the copper content of Ioannina's drinking water (30-160 µg/l).

The drinking water of all three cities was hard and Leucada's, an island, too hard, which also contained higher magnesium concentrations (26.4-43.2 mg/l).

Total solids were found to be in high concentrations (96-301, 95.5-470, 203-886 mg/l).

Key words: water control, physicochemical quality, elements.

INTRODUCTION

The quality of drinking water is critical for public health. Physicochemical along with microbiological parameters determine its suitability for drinking, while the concentration of some constituents, such as fluoride, is significant for good hygiene[1,2].

The purpose of this study is to monitor, during a year, physico-chemical parameters (NO_3^-, NO_2^-, NH_4^+, F^-, Mg, Mn, Cu, Pb, total hardness, conductivity, pH and total solids) of drinking water in the area of West Greece.

EXPERIMENTAL

The samples were collected from the distribution systems of three cities of W.Greece (Ioannina, Preveza, Leucada) in plastic or glass bottles and were stored and preserved according to the APHA[3,4].

The determination of NO_3^-, NO_2^-, and NH_4^+, was performed by the chromotropic diazotization and Nessler's method respectively [3,4]. The spadn's method was used for the determination of F^{-4}. The metals were determined by atomic absorption spectrophotometry using a Perkin Elmer model 560 AAS. Total hardness was measured by EDTA titration and total solids by drying at $103-105^{\circ}C$[3,4]. Conductivity and pH were measured using a conductivity instrument and a pH -meter respectively[3,4].

RESULTS AND DISCUSSION

The descriptive values of the examined parameters are presented on the Tables I,II,III, and in Figures 1,2,3.

TABLE I: Descriptive values of the examined parameters for Ioannina's drinking water.

n=30	NO_3^- mg/l	NO_2^- mg/l	NH_4^+ mg/l	F^- µg/l	Total hard- ness mg/l $CaCO_3$	Mg mg/l	Condu- ctivity µs	Mn µg/l	Cu µg/l	Total solids mg/l	pH
x	5.79	0.005	0.011	553.3	195.9	4.09	357.2	63.06	70.33	176.2	7.32
S	0.69	0.002	0.014	36.04	15.7	2.22	28.77	11.47	24.42	59.1	0.14
median	5.72	0.006	0.006	550.0	191.5	3.30	358.5	65.00	70.00	180.5	7.30
min	5.28	0.003	0.000	410.0	172.0	2.30	318.0	40.00	30.00	96.0	7.10
max	8.36	0.013	0.060	600.0	228.0	9.60	458.0	77.00	160.00	301.0	7.80

The values of NO_3^-, NO_2^-, and NH_4^+, of all three cities were lower than the upper limits[2]. In some cases, in the liberature, higher values of these nitrogenous indexes have been reported[5,6,7].

Fluoride was found to be in significant amounts lower than the lower recommended limits[1,2]. So it could be assumed that the fluoride level is sufficient for dental protection [1,8,9,10].

The total hardness of drinking water from Ioannina and Preveza belong to the hard category while the drinking water of Leucada was too hard. This may be due to the fact that the city of Leucada and its wells are on an island while the wells of Ioannina and Preveza are in the inland. In agreement with the above, conductivity values of Leucada's water were much higher than those of Ioannina's and Preveza's.

Magnesium level in the drinking water of Ioannina and Preveza were lower than guide level value[1,2]. The high values of Mg in the Leucada's drinking water may be due to the migration from the sea water. In every case Leucada's values of Mg were lower than the maximum admissible concentrations[1,2].

TABLE II: Descriptive values of the examined parameters for Preveza's drinking water.

n=22	NO_3^- mg/l	NO_2^- mg/l	NH_4^+ mg/l	F^- µg/l	Total hard-ness mg/l $CaCO_3$	Mg mg/l	Condu-ctivity µs	Mn µg/l	Cu µg/l	Total solids mg/l	pH
x	5.58	0.005	0.016	573.6	219.2	12.30	371.0	69.5	31.81	266.3	7.44
S	0.98	0.002	0.027	32.15	21.79	4.88	21.27	9.24	9.58	104.1	0.09
median	5.28	0.006	0.002	580.0	213.5	13.25	373.0	71.50	30.00	256.5	7.47
min	4.40	0.000	0.000	510.0	190.0	6.00	323.0	40.00	10.00	95.5	7.20
max	9.24	0.009	0.103	620.0	268.0	19.80	418.0	80.00	50.00	470.0	7.60

TABLE III: Descriptive values of the examined parameters for Leucada's drinking water.

n=24	NO_3^- mg/l	NO_2^- mg/l	NH_4^+ mg/l	F^- µg/l	Total hard-ness mg/l $CaCO_3$	Mg mg/l	Condu-ctivity µs	Mn µg/l	Cu µg/l	Total solids mg/l	pH
x	4.45	0.006	0.026	534.1	354.33	31.50	974.3	72.12	29.16	531.3	7.41
S	1.08	0.003	0.047	44.6	50.98	3.24	65.05	7.18	6.53	236.4	0.12
median	4.18	0.006	0.003	520.0	361.00	31.00	970.0	72.50	30.00	389.5	7.40
min	2.64	0.000	0.000	500.0	225.00	26.40	901.0	45.00	20.00	203.0	7.20
max	7.04	0.016	0.167	680.0	415.00	43.20	1214.0	80.00	40.00	886.0	7.61

In all examined samples manganese was found to be higher than the desirable limits but much lower than the upper limit[1,2]. In literature, manganese values have been reported, in a wide region, to be lower and higher than these reported here[11].

Preveza's and Leucada's drinking water contain copper in concentrations lower than the desirable limit while Ioannina's contain copper in concentrations higher than the desirable limit and lower than the maximum admissible limit[1,2]. A possible explanation to this could be the fact that part of the distribution system of the city of Ioannina consists of copper pipes. Copper concentrations in drinking water higher and lower than those reported here have been reported[12].
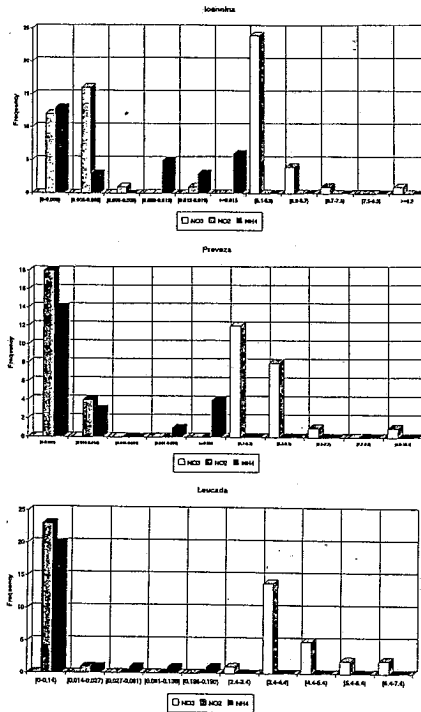

FIG.1. *Histograms of NO_3^-, NO_2^-, NH_4^+ values, of the examined drinking waters.*

In all cases Pb was in concentrations lower than the tentative limit for lead[1,2]. Values have not been reported for lead since, in all examined samples, it was in concentrations lower than the limit of instrument's sensitivity.

Total solids, generally, were found to be in high concentrations, which indicates no application of a filtration step before the entrance of water in the distribution systems.

In all cases pH was found to be in the neutral region, as expected.
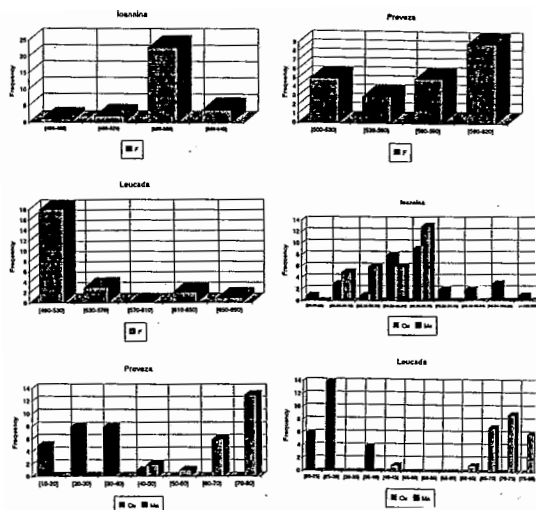
FIG.2. Histograms of F, Cu, Mn values, of the examined drinking waters.
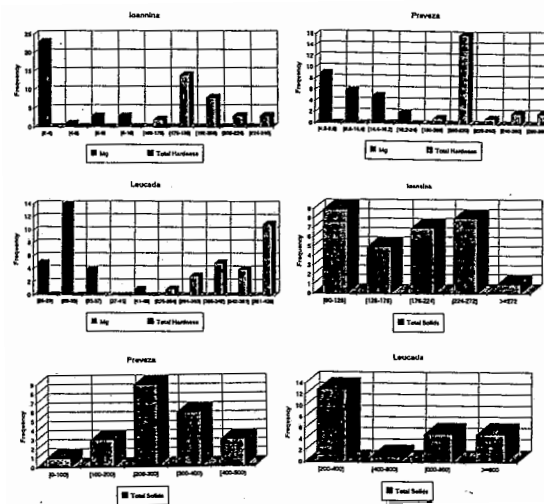

FIG. 3. Histograms of Mg, total hardness, total solids values of the examined drinking

waters.

In conclusion, it can be said that the drinking water of all three cities was of a good quality, since the examined parameters were generally below the E.C. directive standards. It is noticeable the high values of total hardness and magnesium in Leucada's drinking water. The somehow high concentration of copper in Ioannina's drinking water may give some indications for the replacing of the old parts of the distribution system.

ΠΕΡΙΛΗΨΗ

ΧΗΜΙΚΟΣ ΕΛΕΓΧΟΣ ΠΟΣΙΜΩΝ ΝΕΡΩΝ

Εξετάστηκαν, κατά την διάρκεια ενός έτους, οι φυσικοχημικές παράμετροι NO_3^-, NO_2^-, NH_4^+, F^-, Mg, Mn, Cu, Pb, ολική σκληρότητα, αγωγιμότητα, pH και ολικά στερεά των νερών των δικτύων ύδρευσης τριών πόλεων της Ηπείρου (Ιωάννινα, Πρέβεζα, Λευκάδα).

Γενικά οι τιμές των NO_3^-, NO_2^-, και NH_4^+ ήταν μικρότερες απο τα μέγιστα παραδεκτά όρια.

Το φθόριο βρέθηκε σε σημαντικές ποσότητες (410-600, 510-620, 500-680μg/l), επαρκές για την προστασία των δοντιών, ενώ το μαγγάνιο σε συγκεντρώσεις (40-77, 40-80, 45-80μg/l), υψηλότερες απο το επιθυμητό επίπεδο. Το ίδιο ίσχυε για τις τιμές του χαλκού στο νερό της πόλης των Ιωαννίνων (30-160μg/l).

Τα νερά που εξετάστηκαν ήταν σκληρά, ενώ της πόλης της Λευκάδας πολύ σκληρό, το οποίο επίσης περιείχε υψηλότερες συγκεντρώσεις μαγνησίου (26, 4-43,2mg/l).

Τα συνολικά στερεά ήταν σε σημαντικές συγκεντρώσεις(96-301,95,5-470,203-886mg/l).

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CHIMIKA CHRONIKA, *NEW SERIES*

CONTENTS

Macedonia
For 4,000 years* steeped in the history of Greece

Statue of Aristotle, Stagira.

Aristotle, the tutor of Alexander the Great, was born in Stagira in Macedonia in 384 BC. Together with Plato, he is regarded as one of the greatest philosophers the world has known. Aristotle was a true academic, concerned with Physics, Astronomy, Rhetoric, Literature, Political Science and History. His teachings laid the foundation for modern scientific thought.

The White Tower of Thessaloniki.
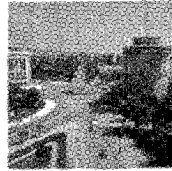
Thessaloniki, the heart of Macedonia, is a modern city with 1,000,000 inhabitants. It is strategically located at the crossroads of Europe with Asia. Having spread the Word at Philippi, the Apostle Paul continued his teachings in Thessaloniki. Its important monuments from antiquity and byzantium up to the present, provide testimony to the role that the city has played as the second capital of Hellenism.

The Bust of Alexander the Great. Acropolis Museum, Athens.

Alexander was born in 356 BC in Pella, Macedonia, established by his father Philip II, as the centre of Hellenism. Nurtured on the thoughts of his tutor, Aristotle, he rose to fame as a brilliant military leader. He influenced the course of history, rightfully earning his title as Alexander the Great. In 335 BC he became Commander in Chief of all the Greeks. By the time of his death in 323 BC he had created an enormous empire, stretching from the shores of the Adriatic to India, and from the Caucasus Mountains to Egypt. He spread the Greek spirit far and wide among nations who worshipped him as a god.

Symbol of the Greek Macedonian Dynasty from the tomb of Philip II. Archaeological Museum, Thessaloniki.
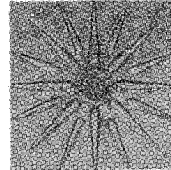
This 16 pointed star of Vergina was uncovered during the archaeological excavations at Vergina. This symbol of the Greek Macedonian Dynasty decorated the golden tomb of Philip II. The Star of Vergina, extracted from the soil of Macedonia, has since become the symbol of Hellenism.

4.000 years:* Post-Mycenaean ceramic relics found in Assiros and Mycenaean swords found in Grevena date back 4.000 years, evidence of Macedonia's role at the vortex of Greek history. Even in mythology Macedon, mythical founder of the Macedonian race, is the son of Aeolos (god of the winds). Throughout the years Macedonia contributed to the fountain of knowledge of the Ancient Greeks. In the 5th century BC Demokritos, father of Atomic Theory, lived and worked in Avdira.

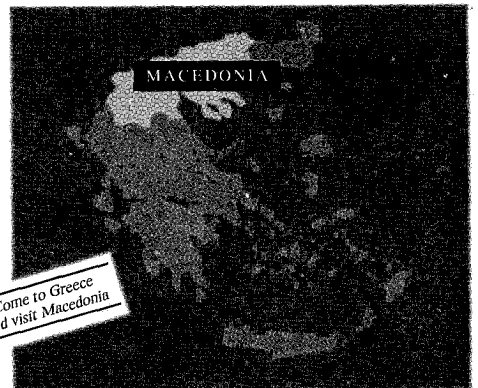The Olympian Aphrodite (3rd Century BC) Museum of Dion.

This statue of Aphrodite came to light during archaeological digs at the ancient sacred city of Dion. Dion, at the foot of Mt Olympus, was the most important spiritual site for the Northern Greeks, playing the same role in their lives as that of the oracle at Delphi.

St Dimitrios, detail of 7th Century Mosaic. Church of St. Dimitrios, Thessaloniki.
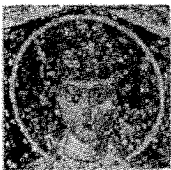
St Dimitrios, Protector of the city of Thessaloniki, was martyred in 305 AD defending Christianity. He is regarded as the Patron Saint of Thessaloniki and its saviour during difficult moments.

MACEDONIA

Come to Greece and visit Macedonia

GREECE
Chosen by the Gods