

COORDINATION COMPLEXES OF CAFFEIC AND FERULIC ACIDS WITH
Cu(II), Ni(II), Co(II) AND Fe(III)

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SUMMARY

Complexes of caffeic and ferulic acids with Cu(II), Ni(II), Co(II) and Fe(III) were prepared in the solid state: $K_2[Cu_2(cafH)_2Cl_2] \cdot 2CH_3OH$, $K_2[Co_2(cafH)_2Cl_2]$, $K_2[Ni_2(cafH)_2Cl_2] \cdot 2CH_3OH$, $Fe_2(cafH)_2Cl_2 \cdot 2H_2O$, $K_2[Cu_2(fer)_2Cl_2]$, $K_2[Co(fer)_2]$, $K_2[Ni_2(fer)_2Cl_2] \cdot 2CH_3OH$, $Fe_2(fer)_2Cl_2$. Spectroscopic, magnetic and thermogravimetric results indicate bis(μ -chloro) tetrahedral binuclear structures with a catechol-type of coordination.

Key words: caffeic, ferulic acid complexes, catechol-type coordination.

INTRODUCTION

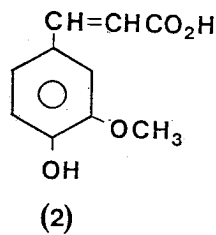
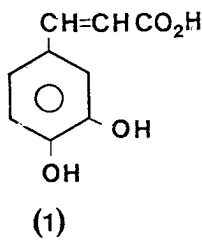
3-(3,4-dihydroxyphenyl)-propenoic acid (caffeic acid, abbr. $cafH_2$)¹ and 3-(4-hydroxy-3-methoxyphenyl)-propenoic acid (ferulic acid, abbr. $ferH_2$)² are early recognized as constituents of different plants and seeds¹.

Both acids can be found in the soil lignins as degradative products of vegetation, contributing by consequence to the availability of several biotrace metal cations from the soil to the plants¹.

Ferulic acid is a precursor of aryl tetralin lignans related to anticancer active compounds as the podophyloto-

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xin and its methylated derivatives³. Also the antiviral activity of caffeic acid was lately investigated⁴.



Phenolic hydroxyl-containing ligands, which are known to be present in the root exudates, may participate in the transport processes of metal ions from the surrounding soil to the plant roots^{4b}. Of special interest are trans - 3-(3,4-dihydroxyphenyl)propenoic acid (caffeic acid), which is believed to participate in the transport and in the reduction of iron(III) to iron(II) in the soil environment, and chlorogenic acid [1,3,4,5-tetrahydroxycyclohexanecarboxylic acid 3-(3,4-dihydroxycinnamate)], which is a precursor of caffeic acid. Complexes of 3,4-dihydroxyphenyl derivatives e.g. copper(II) complexes of chlorogenic acid and related compounds^{4c} have been investigated by pH-metric and spectroscopic methods. Preparation of coordination complexes of 3,4-dihydroxyphenylpropionic acid with copper(II), nickel(II), cobalt(II) and iron(III) was achieved^{5a}. Cupric complexes with 3,4-dihydroxybenzoic acid^{5b} have been studied where the bidentate catechol part of the ligand studied predominates as the binding site for metal ion although the carboxyl group may also participate in the metal ion binding leading to creation of the dinuclear species. More con-

centrated solutions yield a trimeric complex molecule (Cu_3A_2) with one metal ion bound to four phenolate oxygens and two others bound to the respective carboxylates. Phenolic ligands are also important as the constituents of more complicated humic and fulvic acids, which are the main ligands taking part in the transport and accumulation of the nutrient ions^{5c}.

Considering the chemical and biological importance of catechol-like coordination complexes⁵, the preparation in the solid state, the characterization and the study of the physicochemical properties of several complexes of the above ligands with Cu(II), Ni(II), Co(II) and Fe(III) was undertaken.

Earlier work on the caffeic acid coordination is covered by the potentiometric titrations of the caffeate-metal-proton system^{6,7} and some spectroscopic (absorption, ESR) measurements on the complexes formed in solution⁸.

It is not evident however, that the complexes formed are mononuclear involving only a catechol-type of coordination⁶, or oligonuclear involving both catecholic and carboxylic coordination especially with Cu(II), playing the role of link between adjoining ligands^{7,8}.

Infering from analogous behaviour of several dihydroxy benzoic acids, the last type of coordination was proposed as more probable⁹⁻¹¹.

EXPERIMENTAL

The caffeic (dec. 223-225°C) and ferulic (m.p. 174°C) acids were obtained from Merck Co. and were used without further purification; mass spectra: m/e of the molecular ion for caffeic acid 180 (calc. 180.163), for ferulic acid 194 (calc.

194.215). The metal salts MCl_2 ($M=Cu, Ni, Co$) and $MCl_3 \cdot 6H_2O$ ($M=Fe$) used as starting materials for the preparation, were pro analysi grade from Fluka.

Upon refluxing MCl_2 or $MCl_3 \cdot 6H_2O$ with caffeic or ferulic acid in methanolic solution containing equimolecular amount of KOH with a final ratio metal ion:acid:KOH 1:2:2, solid coloured complexes (1-8, TABLE I) were obtained. Details for the preparation are given in a previous paper concerning hydrocaffeic acid¹⁴. The coloured precipitates were also washed with 80% MeOH. Elemental analysis, physicochemical and spectroscopic measurements were carried out by published methods¹²⁻¹⁴. The magnetic susceptibilities in the solid state were performed at 24°C. The $caFH_2Na \cdot H_2O$ and $ferHNa \cdot H_2O$ salts were prepared and characterized as previously¹⁴.

RESULTS AND DISCUSSION

Preparative and analytical data, colours and molar conductivity values are reported in TABLE I. The prepared complexes are either microcrystalline (2,3,4,8) or powder-like (1,5,6,7), relatively stable in atmospheric conditions (oxygen, humidity) except for the complexes 1, 5 which gave evidence of structural changes upon time (see TABLE II). All complexes have a limited solubility in DMSO, DMF and MeOH. The molar conductivities of the complexes 1,2,3,5,6,7 in both DMSO and MeOH are low for their formulation as 2:1 electrolytes. This probably arises from the existing large volume anions in the complexes¹⁵. The complexes 4 and 8 show a conductivity which increases with time and this can be attributed to the strong donor capacity of the solvent used, which leads to displacement of anionic ligands and changes the complexes to electrolytes¹⁵.

TABLE I: Preparative data, colours, analytical results and conductivity measurements for the complexes

Compound number	Complex	Final pH in the preparation	Yield %	$\%N^b$	$\%Cl^b$	$\%C^b$	$\%H^b$	Λ_{cl}^c $ohm^{-1}mol^{-1}cm^2$	Colour	
1	$K_2[Cu_2(cafH)_2Cl_2] \cdot 2CH_3OH$	5.8	55	18.52 (18.25)	10.35 (10.20)	34.26 (34.48)	2.56 (2.87)	48	88	dark brown
2	$K_2[Co_2(cafH)_2Cl_2]$	5.5	35	19.03 (18.91)	11.54 (11.40)	34.92 (34.68)	1.86 (1.93)	80	92	dark green
3	$K_2[Ni_2(cafH)_2Cl_2] \cdot 2CH_3OH$	6.0	62	17.33 (17.10)	10.18 (10.34)	34.52 (34.97)	2.87 (2.91)	77	82	dark green
4	$Fe_2(cafH)_2Cl_2 \cdot 2H_2O$	2.0	17	19.65 (19.42)	12.41 (12.36)	37.81 (37.59)	2.54 (2.78)	57	60	black
5	$K_2[Cu_2(fer)_2Cl_2]$	4.5	25	19.56 (19.24)	10.66 (10.76)	36.12 (36.36)	2.39 (2.42)	95	94	brown
6	$K_2[Co(fer)_2]$	6.2	48	11.75 (11.31)	0.00 (0.00)	45.84 (46.07)	2.98 (3.07)	74	76	violet
7	$K_2[Ni_2(fer)_2Cl_2] \cdot 2CH_3OH$	6.7	56	16.40 (16.43)	9.85 (9.94)	37.18 (36.95)	3.10 (3.36)	85	86	pale-green
8	$Fe_2(fer)_2Cl_2$	2.8	10	19.56 (19.70)	12.65 (12.53)	42.08 (42.36)	2.75 (2.82)	55	57	brownish

^a ratio metal: acid:OH⁻ ^b theoretical values in parentheses

^c molar conductivity for ca. 10^{-3} mol.l⁻¹ solution in DMSO and CH₃OH respectively at 25 °C.

Thermogravimetric studies of the prepared complexes in the range 35-600°C show that the methanol present in 1,3,7 is completely lost between 60-70°C and is lattice-held. In 4, water is lost between 100-110°C and is also lattice-held. Complexes 1, 2, 3 decompose between 200-500°C with the same decomposition pattern possibly indicating analogous structures. Similarity in their structures is also indicated from the same thermal decomposition pattern of the complexes 5, 6, 7, which is effected in a relatively narrow temperature range between 240-320°C. Complexes 4, 8 are decomposed in higher temperatures. Complexes 1, 5 have a sudden and low temperature (200-220°C) decomposition, indicating bridged structures. All complexes were decomposed in a thermogravimetric experiment in the presence of atmospheric oxygen and gave as products metal oxides and KCl until a final temperature of 650-700°C.

The low magnetic moments of the complexes 1 and 5 are due to their binuclear structures and are typical for anti-ferromagnetic character. Their diffuse reflectance spectra clearly indicate distorted tetrahedral stereochemistry^{16,17}. The ${}^1E \leftarrow {}^1T_1$ transition expected for a d^9 system like Cu(II) in a tetrahedral environment is split to more transitions, due to Jahn-Teller effect, known also to take place in such systems¹⁸. More particularly the distortion of the tetrahedron as a flattening around the two-fold axis will result in D_{2d} symmetry, which retains the d_{yz}, d_{zx} degeneracy, splitting of both the ground and excited levels, so that either three or four transitions are expected¹⁹ namely from the ground 1B_1 to 1E , 1B_1 and 1A_1 states²⁰ as is in our case (TABLE II). The complexes 2 and 6 acquire diffuse reflectance spectra^{18,21} and magnetic moments^{22,23} close to tetrahedral structures, especially complex 6.

TABLE II: Electronic spectra and solid state magnetic moments of the complexes

Compound	Diffuse reflectance ^a						μ_{eff}^b BM
	CT		d-d				
1	22700	20800	18700	17700	15500	14200	1.30 ^c
2	21050		18900 sh	16400 sh	14800		4.75
3	21500		17500	15800 sh	14800		3.88
4	26700	23300	21500	17900 sh	16700	15000	4.97
5	25600				16100	15000	1.41
6					16400 sh	15200	4.78
7	21500		19800			14285	4.26
8	21300				15600	14700	3.50

^ain cm^{-1} . ^b at 298 K. ^cupon keeping the solids for 4-6 weeks at room temperature in a vacuum desiccator these values are increasing continuously to 2.10 BM.

A usual value for the magnetic moment of a tetrahedral weak field Ni(II) complex is 4.1 BM^{23} . The values of magnetic moments for the complexes 3 and 7 suggest tetrahedral structures. The bands at 14800 and 14285 cm^{-1} in the diffuse reflectance spectra of 3 and 7 respectively, satisfactorily account for the ${}^3T_1(\text{P}) \leftarrow {}^3T_1(\text{F})$ transition. In 3 there is a splitting due to low symmetry fields^{24,25}. The observed μ_{eff} values for the complexes 4 and 8 at room temperature are too small for high spin $S=5/2$ complexes ($\mu_{\text{eff}} = 5.9 \text{ BM}$) or too large for low spin $S=1/2$ complexes ($\mu_{\text{eff}} = 2.0 \text{ BM}$) assuming an octahedral d^5 system. An intermediate spin state ($S=3/2$) should have $\mu_{\text{eff}} = 4.0 \text{ BM}$. Both tetrahedral or octahedral complexes with A and E terms require higher values than those observed²³. The measured values can be explained either by antiferromagnetic coupling of the iron(III) in dimeric complexes²⁶, or by a spin equilibrium between high and low spin states²⁷. An alternative situation can also be proposed assuming a square pyramidal structure around iron (III) with 4A_1 electronic ground state, since a five coordinated structure is manifested by the stoichiometry of 4, or a spin-paired tetrahedral with 6A_1 ground term both with large orbital contribution²⁸. The last situation seems more probable for 4.

The bands in the diffuse reflectance spectra of the complexes 4 and 8 are weak, as it is expected since the electronic transitions of the iron(III) systems are spin forbidden. There is a considerable masking of the weak bands from the strong charge-transfer bands at $21300\text{--}26700 \text{ cm}^{-1}$. It is known that in spin equilibrium iron(III) systems the high spin form is characterized by a band at $18000\text{--}20000 \text{ cm}^{-1}$ and the low spin by another one at $14000\text{--}16000 \text{ cm}^{-1}$ ²⁹⁻³¹. Only in 4 the 17900 cm^{-1} shoulder demonstrates a high spin system,

but in both 4 and 8 the two low spin bands are present at 14700-15800 cm^{-1} . The presence of two low spin bands can be explained assuming low symmetry pseudo-tetrahedral structure in the complexes. No spectroscopic evidence has been noticed indicating presence of Fe(II) in complexes 4 and 8 owing to an oxidation-reduction mechanism sometimes found in analogous catecholic systems³¹.

In TABLE III some diagnostic ir bands of the prepared complexes are reported. The broad band at 3500 cm^{-1} exhibited by the complexes 1, 3, 7 is due to lattice methanol. The lattice water in $\text{cafH}_2\text{Na.H}_2\text{O}$, $\text{ferHNa.H}_2\text{O}$ and in 4 is shown by the broad strong bands at 3600 and 3570 cm^{-1} respectively^{33,34}.

In the spectra 1-8 the following relation is observed :

$$\Delta_{\text{Complex}} = \Delta_{\text{LNa.H}_2\text{O}}$$

where $\text{L} = \text{cafH}_2$ or ferH and Δ is the separation between $\nu_{\text{as}(\text{CO}_2)^-}$ and $\nu_{\text{s}(\text{CO}_2)^-}$. This indicates that the carboxylate group of either of caffeic or ferulic acid is not coordinated to the metal ions in all prepared complexes^{35,36}. Complexes 1, 2, 3, 4, 5, 7, 8 show a medium intensity ir band at 215-257 cm^{-1} assignable to the metal-halogen stretching mode associated with bridged structures³⁷.

The complexes 1-4 show medium intensity band at 470-485 cm^{-1} due to $\nu_{(\text{H-OH})}$ vibration whereas the complexes 5-8 show a similar medium intensity band in higher frequencies at 580-590 cm^{-1} possibly assignable to the $\nu_{(\text{H-OCH}_3)}$ stretch³⁸. All complexes exhibit a strong band at 605-667 cm^{-1} assignable to the $\nu_{(\text{H-OH})}$ stretch³⁸.

In FIG 1 and FIG 2 the titration curves for deprotonation and coordination reaction in solution of $\text{MeOH:H}_2\text{O}$ 9:1 for cafH_2 and ferH_2 respectively are reported. For the

TABLE III: Spectral IR (cm^{-1}) data for caH_3 , $\text{caH}_2\text{Na}\cdot\text{H}_2\text{O}$, ferH_2 , $\text{ferHNa}\cdot\text{H}_2\text{O}$ and the complexes 1-8

Assignments	caH_3	$\text{caH}_2\text{Na}\cdot\text{H}_2\text{O}$	ferH_2	$\text{ferHNa}\cdot\text{H}_2\text{O}$	1	2	3	4	5*	6	7	8
$\nu(\text{OH})$ alcoholic				3447sbr	3447sbr							3457sbr
$\nu(\text{OH})$ water	3600s	3600s			3600s			3567s				
$\nu(\text{OH})$ phenolic	3421m	3420m	3440m	3435m	3368m	3395m		3377m	3368m	3335m		3386m
$\nu(\text{OH})$ acid	3243, 2850		2920, 2860m									
$\nu(\text{C=O})$ acid	1663s		1690s									
ring stretching			1620, 1600		1614m	1649, 1596m	1649	1728, 1623m	1658, 1614m	1649, 1614m	1640, 1605m	1658, 1605m
vibrations	1536s		1518			1500m		1518m	1535m	1526m	1518m	1518m
$\nu_{\text{as}}(\text{COO}^-)$		1468s			1472s	1425s		1447s	1420s	1417s	1408s	1421s
$\nu_{\text{s}}(\text{COO}^-)$		1346s			1347s			1327s	1298s	1292s	1283s	1298s
$\delta(\text{OH})$ acid + $\nu(\text{C-O})$ acid		1292m			1325m, 1290m							
$\tau(\text{OH})$ acid	921m	902m	915m		900m			860s	860s	877s	877s	877s
$\nu(\text{H-OH})$								614s	614s	658s	614s	667s
$\nu(\text{H-OH})$					480m	485m		480m	470m			
$\nu(\text{H-OCH}_3)$								257m	220m	550m	575m	572m
$\nu_{\text{b}}(\text{H-Cl})$					220m	218m				215m	220m	210m

s=strong, b=bridge, m=medium, ν_{as} =antisymmetric stretching, ν_{s} =symmetric stretching

coordination reactions the titration was effected in the presence of metal cation in the ratio metal to ligand 1:2. It can be seen from the potentiometric titration curves that the precipitation of the complexes occurs at relatively low pH's before the ionization of all carboxylic and phenolic protons of the acid ligands takes place. This behaviour of cafH_3 and ferH_3 resembles the complexing ability of 3,4-dihydroxybenzoic acid which coordinates to metal ions with a catecholic type of binding¹⁹.

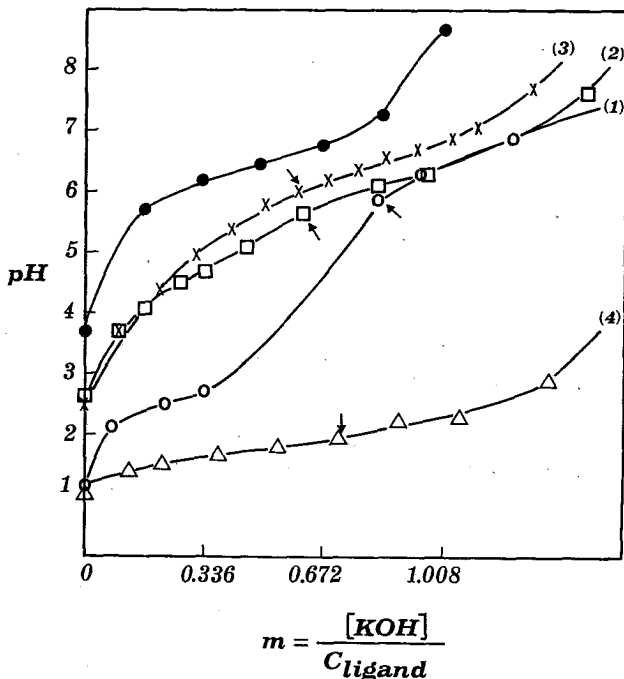


FIG.1.: Potentiometric titration curves of the caffeic acid and the metal ions in a MeOH:H₂O solution (9:1).

- ↓ Complex precipitation
- L cafH_3
- 1 $\text{cafH}_3 + \text{CuCl}_2$ 2:1
- 2 $\text{cafH}_3 + \text{CoCl}_2$ 2:1
- 3 $\text{cafH}_3 + \text{NiCl}_2$ 2:1
- 4 $\text{cafH}_3 + \text{FeCl}_3$ 2:1

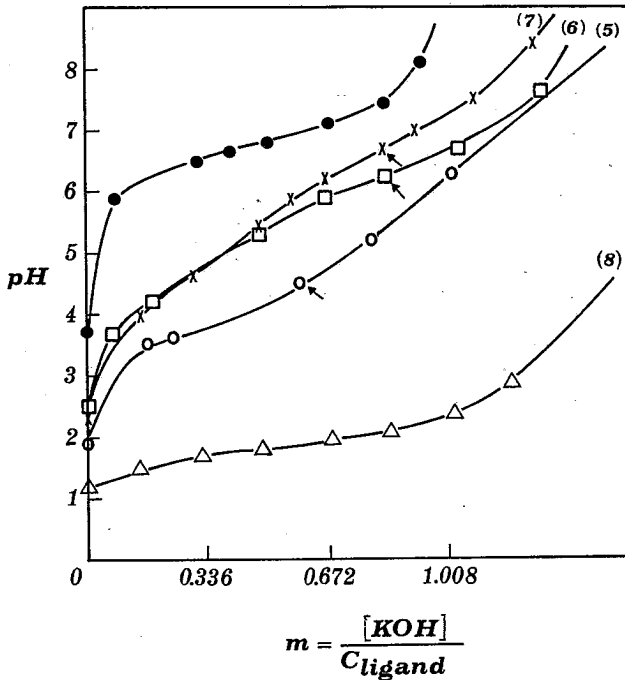


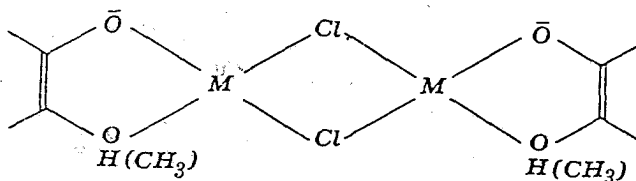
FIG.2: Potentiometric titration curves of the ferulic acid and the metal ions in a MeOH:H₂O solution (9:1).

↓ Complex precipitation

- L ferH_2
- 5 $\text{ferH}_2 + \text{CuCl}_2$ 2:1
- 6 $\text{ferH}_2 + \text{CoCl}_2$ 2:1
- 7 $\text{ferH}_2 + \text{NiCl}_2$ 2:1
- 8 $\text{ferH}_2 + \text{FeCl}_3$ 2:1

Concluding remarks

From the overall study it is therefore concluded that caffeic and ferulic acids form 1:1 complexes with Cu(II), Co(II), Ni(II) and Fe(III) regardless of the ratio of the ligand to metal cation of the preparation mixture except for the case of the Co(II) complex with ferulic acid which is formed in the ratio 1:2. An analogous situation was met with the complex of hydrocaffeic acid with Co(II)⁵. In the prepared 1:1 complexes chlorine bridged structures are formed with a catechol type of coordination 3.



3

A pseudotetrahedral or tetrahedral microsymmetry around the metal ion seems to be in prevalence. Owing to the difficulty in obtaining convenient monocrystals of the prepared complexes, their X-rays structural investigation is at present lacking.

ΠΕΡΙΛΗΨΗ

ΣΥΜΠΛΟΚΕΣ ΕΝΩΣΕΙΣ ΤΩΝ ΟΞΕΩΝ ΚΑΦΕΪΚΟΥ ΚΑΙ ΦΕΡΟΥΛΙΚΟΥ ΜΕ Cu(II), Ni(II), Co(II) ΚΑΙ Fe (III).

Παρασκευάσθηκαν και απομονώθηκαν στην στερεά κατάσταση τα σύμπλοκα των οξέων καφεϊκού και φερουλικού με Cu(II), Ni(II), Co(II) και Fe(III) : $K_2[Cu_2(cafH)_2Cl_2] \cdot 2CH_3OH$, $K_2[Co_2(cafH)_2Cl_2]$, $K_2[Ni_2(cafH)_2Cl_2] \cdot 2CH_3OH$, $Fe_2(cafH)_2Cl_2 \cdot 2H_2O$, $K_2[Cu_2(fer)_2Cl_2]$, $K_2[Co(fer)_2]$, $K_2[Ni_2(fer)_2Cl_2] \cdot 2CH_3OH$, $Fe_2(fer)_2Cl_2$. Ανεξάρτητα από το λόγο μεταλλικού ιόντος: υποκαταστάτη στο μίγμα παρασκευής τα σύμπλοκα που σχηματίζονται είναι 1:1 εκτός από την περίπτωση του συμπλόκου του Co(II) με το φερουλικό οξύ που είναι 1:2. Ανάλογη συμπεριφορά αναφέρεται στην περίπτωση του συμπλόκου του υδροκαφεϊκού οξέος με το Co(II)⁵. Από τα φασματοσκοπικά, μαγνητικά και θερμοσταθμικά αποτελέσματα συμπεραίνεται ότι στα 1:1 σύμπλοκα οι δομές είναι τετραεδρικές διπυρηνικές με γέφυρες χλωρίου και με κατεχολικού τύπου σύμπλεξη.

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REFERENCES AND NOTES

1. Bate-Smith, E. C., *Chem. and Ind.*, 1457 (1954)
2. Stevenson, F., *Humus Chemistry, Genesis, Composition, Reactions*. Wiley-Interscience N. Y. 1982.
3. Jackson, D. E., and Dewick, D. M., *Phytochemistry*, 23(5), 1029 (1984)
- 4.a. Grodzinska-Zachwieja, Z., Zgorniak-Nowosielska, I., Marcisjewska, M., and Gatkienicz, A., *Acta Biol. Cracov.*, (*ser-Bot.*) 19(1), 29 (1976)
- 4.b. Olsen, R. A., Brown, J. C., Bennett, J. H., and Bloom, D., *J. Plant Nutr.* 5, 433, 1982.
- 4.c. Kiss, T., Nagy, G., Pecsí, M., Kozłowski, H., Micera, G., and Erre, L. S., *Polyhedron* 8, 2345 (1989)
- 5.a. Petrou, A.L., Koromantzou, M. V., and Tsangaris, J. M., *Trans. Met. Chem.*, 16, 48 (1991)
- 5.b. Gerega, K., Kozłowski, H., Kiss, T., Micera, G., Erre, L. S., *Inorganica Chimica Acta*, 138, 31-34 (1987)
- 5.c. Schnitzer, M. and Khan, S. U., "*Humic Substances in the Environment*", Dekker, N. Y., 1972
6. Bizri, Y., Cromer, M., Lamy, I., and Scharff, J. P., *Analisis* 13, 128 (1985)
7. Linder, P. W., and Vayé, A. *Polyhedron*, 6, 53 (1987)
8. Kiss, T., Nagy, G., Pecsí, M., Kozłowski, H., Micera, G., and Erre, L.S., *Polyhedron*, 8, 2345 (1989)
9. Cariati, F., Erre, L., Micera, G., Panzanelli, A., Gianni, G., and Sironi, A., *Inorg. Chim. Acta*, 80, 57 (1983)
10. Gerega, K., Kozłowski, H., Kiss, T., Micera, G., Erre, L.S., and Cariati, F., *Inorg. Chim. Acta*, 138, 31 (1987)
11. Kiss, T., Kozłowski, H., Micera, G., and Erre, L.S., *Polyhedron* 8, 647 (1989)
12. Kabanos, T. A., and Tsangaris, J. M., *J. Coord. Chem.*, 13, 89 (1984)
13. Rahman, A.A., Nichols, D., and Tsangaris, J. M., *J. Coord. Chem.*, 14, 327 (1986)
14. Kovala-Demertzi, D., and Tsangaris, J. M., *Inorg. Chim. Acta*, 125, L31 (1986)
15. Geary, W. J., *Coord. Chem. Rev.*, 7, 81 (1971)
16. Sacconi, L., and Ciampolini, M., *J. Chem. Soc.*, 276 (1964)
17. Gaura, R. M., Stein, P., Willett, R. D., and West, D. X., *Inorg. Chim. Acta*, 60, 213 (1982)
18. Lever, A. B. P. *Inorganic Electronic Spectroscopy*. p. 203. Elsevier Scien. Publ. 1984.
19. Furlani, C. and Morpurgo, G. *Theor. Chim. Acta* I, 102 (1963)

20. Ferguson, J., *J. Chem. Phys.*, **40**, 3406 (1964)
21. Figgis, B. N., *Introduction to Ligand Fields*. p. 29, Intern. Publ. N. Y., 1967
22. Earnshaw, A., *Introduction to Magnetochemistry*, Acad. Press. N. Y. 1968
23. Figgis, B. N., and Lewis, J. M. *Progr. Inorg. Chem.*, **6**, 429 (1964)
24. Barefield, E. K., Bush, D. H., and Nelson, S. M., *Quart. Rev.*, **22**, 457 (1969)
25. Rowley, D. A., and Drago, R. S., *Inorg. Chem.*, **7**, 795 (1968)
26. Gerloch, M., Lewis, J., Mabbs, F. E., and Richards, A., *J. Chem. Soc.*, (A), 112 (1968)
27. Elizabethathe, J. M., and Zacharias, P. S. *Polyhedron*. **6**, 969 (1987)
28. Carlin, R. L., *Science*, **227**, 4692 (1985)
29. Dose, E. V., Murphy, K. M. M., and Wilson, L. J., *Inorg. Chem.*, **15**, 2622 (1976)
30. Tweedle, M. F., and Wilson, L. J., *J. Am. Chem. Soc.*, **98**, 4824 (1976)
31. Maeda, Y., Tsutsumi, N., and Takashima, Y., *Inorg. Chem.*, **23**, 2440 (1984)
32. Xu, J., and Jordan, R. B., *Inorg. Chem.*, **27**, 4563 (1988)
33. Mikulski, C. M., Mattucci, L., Smith, Y., Tran, T. B., and Karayannis, N.M. *Inorg. Chim. Acta*, **80**, 127 (1983)
34. Gelfand, L. S., Iaconianni, F. J., Pytlewski, L. L., Specca, A. N., Mikulski, C. M., and Karayannis, N. M., *J. Inorg. Nucl. Chem.*, **42**, 377 (1980)
35. Deacon, G. B., and Phillips, R. J., *Coord. Chem. Rev.*, **33**, 227 (1980)
36. Deacon, G. B., Huber, F., and Phillips, R. J., *Inorg. Chim. Acta*, **104**, 41 (1985)
37. Nakamoto, K., *Infra Red Spectra of Inorganic and Coordination Compounds*, p. 216 Wiley-Intern. N. Y. 1970
38. Adams, D. M., *Metal-Ligand and Related Vibrations*. p. 248. St. Martin's Press. N.Y. 1968.
39. Kiss, T., Kozlowski, H., Micera, G., and Erre, L. S., *J. Coord. Chem.*, **20**, 49 (1989)

Abbreviations

Caffeic Acid	abbr. caffH ₂
Ferulic Acid	abbr. FerH ₂