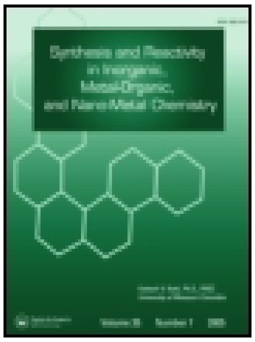

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PREPARATION AND CHARACTERIZATION OF SOME METAL CHELATES OF 5-AMINO-1-(ARYL)-IMIDAZOLE-4-CARBOXAMIDE

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ABSTRACT

Cu(II), Cr(III), VO(II) and Mn(II) chelates of 5-amino-1-(aryl)imidazole-4-carboxamide, aryl = C_6H_5-, -$C_6H_4CH_3$, and -$C_6H_4OCH_3$ were prepared and characterized by microchemical analyses, infrared and electronic spectra and thermogravimetric analyses. IR spectra showed that the ligands behave in a bidentate manner. Also, octahedral structures are proposed for the Cr(III) and Mn(II) chelates, whereas square-planar and square-pyramidal structures are proposed for the Cu(II) and oxovanadium(IV) chelates, respectively.

INTRODUCTION

The chemistry of imidazoles has been of considerable biological significance. Some of them have been reported to show interesting antifungal and antibacterial properties[1-3]. Moreover, many imidazole derivatives have been reported to be used in the synthesis of copolymers[4,5], as ligands to metals, in anisotropic conductors[6-8] and as electron acceptors in charge-transfer solids[9,10].

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Therefore, in the present work, the synthesis and characterization of some new imidazole metal chelates were carried out for their expected interesting use.

EXPERIMENTAL

Materials

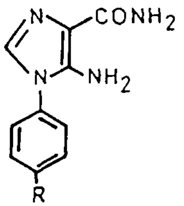
All materials used were of reagent grade (BDH, Merck or Fluka) products. The preparation of the ligands[11] used followed the procedure described in the literature. The ligands have the general structural formula shown in Fig. 1.

Synthesis and Analysis of the Metal Chelates

Metal chelates of the above ligands were prepared by mixing 25 mL of an ethanol-water (1:1) solution of the transition metal salts (0.1 mol) [$CuCl_2.2H_2O$, $CrCl_3.6H_2O$, $VOSO_4.H_2O$ and $MnCl_2.4H_2O$] with an ethanolic solution (50 mL) of the ligand (0.2 mol), followed by heating under reflux for a time depending on the transition metal salt used. The solid chelates precipitates which formed on refluxing were filtered, washed with ethanol, then with diethyl ether and dried in a desiccator over anhydrous calcium chloride.

Physical Measurements

The UV-Visible electronic spectra of the chelates were measured using a Shimadzu UV-240 UV-Visible recording spectrophotometer. The IR spectra of the ligands and their metal chelates were measured using KBr discs with a Jasco FT/IR 300E Fourier transform infrared spectrophotometer covering the range 200-4000 cm^{-1}. Thermogravimetric analysis of the investigated chelates was carried out using a DTA-7 and TGA-7 Perkin-Elmer-7 series thermal analysis system. The mass losses were measured from room temperature up to $800^{\circ}C$ at a heating rate of 10° C min^{-1}. The elemental analyses of carbon, hydrogen, nitrogen, sulphur and chlorine were performed at the Microanalytical Laboratory, Faculty of Science, Cairo University, Egypt. The metal ion (M) contents of the chelates were determined[12,13] after wet decomposition of the chelates according to the previously reported method[14].



R = H, L^1; R = CH_3, L^2; R = OCH_3, L^3.

Fig. 1. Structure of the Ligands.

Table I. Elemental Analyses of Metal Chelates of the Ligands L^1, L^2 and L^3.

Chelates	F.Wt.	M.p. or (d.p.) °C	Yield in %	%C Found (Calc.)	%H Found (Calc.)	%N Found (Calc.)	%Cl Found (Calc.)	%S Found (Calc.)	%M Found (Calc.)
$[Cu(L^1)_2]Cl_2.0.5H_2O$ $CuC_{20}H_{21}N_8O_{2.5}Cl_2$	547.6	(236)	65	43.88 (43.83)	3.78 (3.84)	20.41 (20.45)	12.95 (12.97)	-- --	11.55 (11.61)
$[Cr(L^1)_2.Cl_2]Cl.3H_2O$ $CrC_{20}H_{26}N_8O_5Cl_3$	616.5	271	62	38.88 (38.93)	4.15 (4.22)	18.25 (18.17)	17.16 (17.27)	-- --	8.33 (8.43)
$[VO(L^1)_2]SO_4..3H_2O$ $VC_{20}H_{26}N_8O_{10}S$	621.0	(301)	70	38.59 (38.65)	4.08 (4.19)	18.15 (18.04)	-- --	5.10 (5.15)	8.15 (8.21)
$[Mn(L^1)_2Cl_2].0.5H_2O$ $MnC_{20}H_{21}N_8O_{2.5}Cl_2$	539.0	251	60	44.62 (44.53)	3.95 (3.90)	20.66 (20.78)	13.14 (13.17)	-- --	10.15 (10.20)
$[Cu(L^2)_2]Cl_2.H_2O$ $CuC_{22}H_{26}N_8O_3Cl_2$	584.6	(248)	63	45.24 (45.16)	4.37 (4.45)	19.25 (19.16)	12.03 (12.15)	-- --	10.91 (10.87)
$[Cr(L^2)_2Cl_2]Cl.H_2O$ $CrC_{22}H_{26}N_8O_3Cl_3$	608.5	292	67	43.52 (43.39)	4.30 (4.27)	18.35 (18.41)	17.38 (17.50)	-- --	8.48 (8.55)
$[Cu(L^3)_2]Cl_2.2H_2O$ $CuC_{22}H_{28}N_8O_6Cl_2$	634.5	(270)	62	41.70 (41.60)	4.28 (4.41)	17.81 (17.65)	11.28 (11.19)	-- --	10.12 (10.01)
$[Cr(L^3)_2Cl_2]Cl.2H_2O$ $CrC_{22}H_{28}N_8O_6Cl_3$	658.5	300	64	40.49 (40.09)	4.18 (4.25)	17.59 (17.01)	16.12 (16.17)	-- --	8.16 (7.90)
$[VO(L^3)_2]SO_4.2H_2O$ $VC_{22}H_{28}N_8O_{11}S$	663.0	(300)	65	39.85 (39.82)	4.15 (4.22)	16.80 (16.89)	-- --	4.92 (4.83)	7.68 (7.69)
$[Mn(L^3)_2Cl_2].H_2O$ $MnC_{22}H_{26}N_8O_5Cl_2$	607.9	275	68	43.40 (43.42)	4.30 (4.28)	18.60 (18.42)	11.80 (11.68)	-- --	9.10 (9.05)

RESULTS AND DISCUSSION

The elemental analysis data of the solid chelates, listed in Table I, show that there is good agreement between the results obtained and those calculated according to the proposed formulae of these chelates. These results also show that the ligands L^1, L^2 and L^3 gave chelates with the stoichiometric 1:2 M: L ratio. The formation of the complexes can be represented by the following general equations:

$$2L^{1\text{-}3} + M(Cl)_{2\ \mathrm{or}\ 3}.xH_2O + yH_2O \longrightarrow M(L^{1\text{-}3})_2(Cl)_{2\ \mathrm{or}\ 3}.(x+y)H_2O$$

$$2L^{1,3} + VOSO_4.H_2O + (1\text{-}2)H_2O \longrightarrow VO(L^{1,3})_2SO_4.(2\text{-}3)H_2O$$

Infrared Spectra

The most important IR bands of the ligands and their metal chelates are listed in Table II.

The broad band at 3280-3460 cm^{-1} in the IR spectra of all chelates, assigned to $\upsilon(OH)$, suggests the presence of water molecules[15]. The amide (I) band at 1670 cm^{-1} in the IR spectra of all ligands is either shifted to lower frequency (1650-1660 cm^{-1}) in all copper and manganese chelates and Cr-L^2 and L^3 chelates, weakened in case of the VO-L^3 chelate, or split in case of the Cr-L^1 and VO-L^1 chelates, indicating the participation of the carbonyl group in chelation.

The weakness or shifting of the amide II bands to lower frequencies in all the studied chelates support the involvement of the amide carbonyl group in chelate formation.

The IR spectra of the studied chelates revealed two different modes of chelation. The presence of a $\upsilon(C=N)$ band[16] at nearly the same position as that in their parent ligands, or its shifting to higher wave numbers in case of the Cu-L^1,

Table II. IR Frequencies of the Bands (cm^{-1}) of the Ligands L^1, L^2 and L^3 and their Chelates and their Assignments.

Free Ligand	Cu(II) complex	Cr(III) complex	VO(II) complex	Mn(II) complex	Assignment
L^1	L^1 Chelates				
----	3400 (b)	3380-3440 (b)	3360 (b)	3310 (b)	υ(OH)
3190 (m)	3190 (vw)	3190 (m)	3190 (m)	3180 (w)	υ(NH)
1670 (s)	1650 (m)	1670 (w) 1660 (w)	1675 (m) 1640 (sh)	1660(m)	Amide I
1610 (s)	1610 (b)	1600 (w)	1600 (m)	1620 (m)	υ(C=N)
1550 (s)	1550 (vw)	1560 (w)	1520 (w)	1550 (m)	Amide II
1510 (s)	1490 (vw)	1490 (s)	1490 (s)	1490 (w)	δ(NH_2) [a]
----	----	----	1050 (vs)	----	υ(SO_4)
----	----	----	980 (s)	----	υ(V=O)
L^2	L^2 Chelates				
----	3340 (b)	3280-3430 (b)			υ(OH)
3200 (s)	3180 (b)	3160 (m)			υ(NH)
1670 (s)	1650 (s)	1655 (s)			Amide I
1600 (s)	1600 (m)	1600 (m)			υ(C=N)
1550 (s)	1550 (vw)	1560 (m)			Amide II
1520 (s)	1520 (vw)	1520 (w)			δ(NH_2) [a]
	1490 (w)	1470 (m)			
L^3	L^3 Chelates				
----	3460 (b)	3400 (b)	3420 (w)	3340 (b)	υ(OH)
3160 (m)	3140 (s)	3160 (m)	3200 (m)	3180 (w) 3140 (w)	υ(NH)
1670 (s)	1660 (s)	1660 (s)	1670 (m)	1665 (s)	Amide I
1610 (s)	1605 (s)	1600 (w) 1580 (w)	1595 (m)	1610 (s)	υ(C=N)
1550 (m)	1520 (s)	1560 (s)	1560 (w)	1550 (s)	Amide II
1510 (m)	1490 (s)	1510 (s)	1505 (s)	1515 (m)	δ(NH_2) [a]
1490 (w)				1490 (w)	
----	----	----	1020 (s)	----	υ(SO_4)
----	----	----	980 (s)	----	υ(V=O)

[a] δ(NH_2) of the free amino group.

-L^2 and -L^3, Mn-L^1, -L^3 and Cr- L^2 chelates implies that the nitrogen atom of the C=N group remains uncoordinated. However, in case of the Cr-L^1, VO-L^1, VO-L^3 chelates, the band due to υ(C=N) of the free ligand is either weakened, split or red-shifted, indicating that the nitrogen atom of the C=N group is involved in chelation with the metal ion, showing that C=N is a coordination site in chelate formation.

In Table II, the band assigned to $\delta(NH_2)$ is either red-shifted and/or weakened in the spectra of the Cu-L^1, Mn-L^1, Cu-L^3 complexes, or split into weaker bands in the Cu-L^2, Cr-L^2 and Mn-L^3 chelates, showing that the N atom of the free amino group may take part in chelation with the metal ion. In addition, the bands at 3190, 3200 and 3160 cm^{-1} in the spectra of the free ligands L^1, L^2 and L^3, respectively, assigned to υ(NH) are either weakened, and/or red-shifted, split into weaker bands, or almost disappeared in the Cu-L^1, -L^2 and -L^3, Mn-L^1 and -L^3 and Cr-L^2 chelates (Table II), supporting the view that the N atom of the amino group is directly coordinated to the metal ion.

The new strong bands occurring at 1050 and 1020 cm^{-1} in the spectra of the VO-L^1 and L^3 chelates, respectively, which are absent in the parent ligand spectra, may be assigned to the normal modes of vibration[17]of $(SO_4)^{2-}$. Moreover, the appearance of the new strong band at 980 cm^{-1} in all oxovanadium chelates may be attributable[18] to υ(V=O).

Electronic Spectra

The very weak broad bands centered at 420 and 530 nm observed in the UV-Visible spectra of the Mn-L^1 and Mn-L^3 chelates, respectively, may be assigned to the $^6A_{1g}(S) \rightarrow {}^4E_g(G) + {}^4A_{1g}(G)$ and $^6A_{1g}(S) \rightarrow {}^4T_{1g}(S)$ multiplicity-forbidden transitions, respectively, suggesting an octahedral field around the manganese ion[19].

The oxovanadium(IV) chelates VO-L^1 and -L^3, characterized by bands at

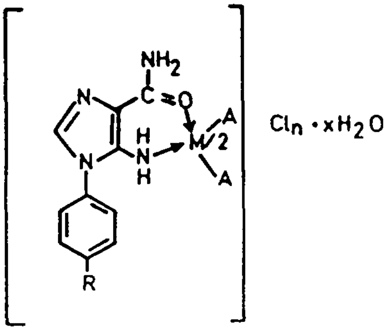
Table III. Thermogravimetric Analysis Results of the Investigated Metal Chelates of the three Ligands.

Chelate	M:L	Water of hydration Mass loss % Calc. (Found)	No. Of water molecules/ chelate molecule	Temp. (°C)	Metal Oxide Residue at 600-750 °C Calc. (Found)
$[VO(L^1)_2]SO_4.3H_2O$	1:2	8.70 (8.64)	3.0	120-180	14.65 (14.55)
$[Mn(L^1)_2Cl_2].0.5H_2O$	1:2	1.67 (1.72)	0.5	125-170	14.66 (14.88)
$[Cu(L^2)_2]Cl_2.H_2O$	1:2	3.08 (2.98)	1.0	125-160	13.61 (13.78)
$[Cr(L^2)_2Cl_2]Cl.H_2O$	1:2	2.96 (3.04)	1.0	117-165	12.49 (12.54)
$[Cu(L^3)_2]Cl_2.2H_2O$	1:2	5.67 (5.80)	2.0	130-160	12.54 (12.41)
$[Cr(L^3)_2Cl_2]Cl.2H_2O$	1:2	5.47 (5.58)	2.0	135-160	11.54 (11.66)
$[VO(L^3)_2]SO_4.2H_2O$	1:2	5.43 (4.58)	2.0	130-170	13.73 (13.89)
$[Mn(L^3)_2Cl_2].H_2O$	1:2	2.96 (2.82)	1.0	145-170	12.99 (12.97)

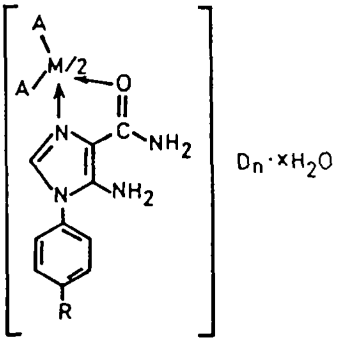
700 and 585 nm, respectively, assigned to the $^2T_{2g}\rightarrow{}^2E_g$ transition, and the charge-transfer bands at 420-320 nm, suggest that these complexes may have square-pyramidal structure[20].

The electronic spectra of the three chromium chelates with L^1, L^2 and L^3 show two absorption bands with maxima at 390-425 nm and 520-585 nm attributable to the $^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$ and $^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$ transitions, respectively, in an octahedral configuration[18].

The UV-Visible spectra of the Cu(II) chelates have two bands at 700-710 nm and 420-490 nm due to $^2B_{1g}\rightarrow{}^2A_{1g}$ and $^2B_{1g}\rightarrow{}^2E_g$ transitions, respectively, consistent with the square-planar stereochemistry[21,22].



R = H, M = Cu , A (absent), n = 2, x = 0.5 for the Cu-L^1 chelate.
R = H, M = Mn, A = Cl, n = 0, x = 0.5 for the Mn-L^1 chelate.
R = CH_3, M = Cu, A (absent), n = 2, x = 1 for the Cu-L^2 chelate.
R = CH_3, M = Cr, A = Cl, n = 1, x = 1 for the Cr-L^2 chelate.
R = OCH_3, M = Cu, A (absent), n = 2, x = 2 for the Cu-L^3 chelate.
R = OCH_3, M = Mn, A = Cl, n = 0, x = 1 for the Mn-L^3 chelate.



R = H, M = Cr, A = Cl, D = Cl, n = 1, x = 3 , for the Cr–L^1 chelate.
R = H, M = VO, A (absent), D = SO_4, n = 1, x = 3 , for the VO–L^1 chelate.
R = OCH_3, M = VO, A (absent), D = SO_4, n = 1, x = 2 , for the VO–L^3 chelate.
R = OCH_3, M = Cr, A = Cl, D = Cl, n = 1, x = 2 , for the Cr-L^3 chelate.

Fig. 2. Suggested Structures of the Chelates.

Thermogravimetric Analysis

Table III shows the TG data of some of the prepared chelates: VO-L[1], -L[3], Mn-L[1], -L[3], Cu- L[2], -L[3], Cr-L[2] and L[3] complexes. The results agree with the theoretical formulae as suggested from the elemental analyses.

The first mass loss, at the temperature range of 122-190° C may be ascribed to the loss of hydrated water in the chelates. Above 190° C, the chelates begin to decompose, at first slowly and then increasingly rapid, till formation of the corresponding oxides, CuO, V_2O_5, Cr_2O_3 or Mn_2O_3 at 600-750° C.

Suggested Structure of the Complexes

From the elemental analyses and/or thermal analyses together with the spectral properties, the structural formulae in Fig. 2 may be suggested for these chelates.

REFERENCES

1. M. T. Cocco, C. Congiu, A. Plumitallo, M. L.Schivo and G. Palmieri, Farmaco, Ed. Sci., 42, 347 (1987); Chem. Abstr., 107, 55624q (1987).

2. M. T. Cocco, C. Congiu, A. Maccinoni, A. Plumitallo, M. L. Schivo and A. De Logu, Farmaco, 44, 975 (1989); Chem. Abstr., 112, 195108c (1990).

3. M. T. Cocco, C. Olla, V. Onnis, M. L. Schivo and A. De Logu, Farmaco, 47, 229 (1992); Chem. Abstr., 117, 171303q (1992).

4. R. N. MacDonald, A. Cairncross, J. B. Sieja and W. H. Sharkey, J. Polym. Sci., Polym. Chem. Ed., 12, 664 (1974).

5. K. J. Bouck and P. G. Rasmussen, Macromolecules, 26, 2077 (1993).

6. P. G. Rasmussen, J. B. Kolowich and J. C. V. Bayon, J. Am. Chem. Soc., 110, 7042 (1988).

7. P. G. Rasmussen, J. G. Andresen and J. C. Bayon, Inorg. Chim. Acta, 87, 159 (1984).

8. P. G. Rasmussen and J. C. Bayon, Inorg. Chim. Acta, 81, 115 (1984).

9. E. L. Thurber, R. P. Subrayan and P. G. Rasmussen, " Contemporary Topics in Polymer Science", Plenum Press, New York, N.Y.,Vol. 7, pp. 95 (1992).

10. E. L. Thurber and P. G. Rasmussen, J. Polym. Science, Part A, Polym. Chem. Ed., 31, 351 (1993).

11. K. A. M. El-Bayouki, M. Hammad, S. A. Osman and W. M. Basyouni, Oriental J. Chem., 2, 45 (1986).

12. F. J. Welcher, "The Analytical Uses of EDTA", Van Nostrand, USA (1958).

13. "Vogel's Text Book of Quantitative Inorganic Analysis", 4th Ed., Longman (1978).

14. A. M. G. McDonald and P. Sirichanya, Microchem. J., 14, 199 (1969).

15. K.Nakamoto,"Infrared Spectra of Inorganic and Coordination Compounds", John Wiley, New York (1970).

16. L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen, London (1975).

17. K. Nakamoto, J. Fugita, S. Tanaka and M. Kobayashi, J. Amer. Chem. Soc., 79, 4904 (1957).

18. B. B. Kaul and K. B. Pandeya, J. Inorg. Nucl. Chem., 40, 1035 (1978).

19. a) Ballhausen, "Introduction to Ligand Field Theory", McGraw Hill, New York (1962).
    b) V. Banerji and A. K. Dey, J. Indian Chem. Soc., 59, 591 (1982).

20. J. Selbin, H. Holnes and S. P. McGlyn, J. Inorg. Nucl. Chem., 25, 1359(1963).

21. B. N. Figgis, "Introduction to Ligand Field Theory", Interscience, New York, p. 316 (1967).

22. T. Tokii, Y. Muto, M. Kato, K. Imai and H. B. Jonassen, J. Inorg. Nucl. Chem., 35, 1539 (1973).

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