

Template synthesis and spectroscopic studies of 13-membered oxotetraaza macrocyclic complexes

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A new series of 13-membered tetraaza macrocyclic complexes has been prepared by the template condensation of triethylenetetraamine with ethyl acetoacetate or methyl acetoacetate in a 1:1 molar ratio. All the complexes are stable in atmosphere and soluble in DMSO and DMF. The complexes have been characterized on the basis of analytical, IR, ¹H NMR, EPR, UV-vis, spectra, magnetic susceptibility and conductivity data. An octahedral geometry around the metal ion is suggested for manganese, cobalt, and zinc complexes, while a square-planar geometry is proposed for copper and nickel complexes.

Shakir and coworkers have reported^{1,2} transition metal complexes of polyamide macrocycles prepared through metal ion controlled condensation reactions. The metal ion directs the reaction preferentially towards cyclic rather than oligomeric or polymeric products³⁻⁵. The present study is in continuation of our previous work on macrocycles bearing different number of amide groups^{1,6,7}. Herein we report synthesis and characterization of a new series of macrocyclic complexes of the types [MLX₂] [M = Mn(II), Co(II), and Zn(II)] and [ML]X₂ [M = Ni(II) and Cu(II)].

Experimental

The metal salts, MX₂·2H₂O (M = Co and Ni; X = Cl or NO₃), MnX₂·4H₂O, CuX₂·2H₂O (X = Cl or NO₂), ZnCl₂ and Zn(NO₃)₂·6H₂O were commercially available pure samples (BDH). The chemicals methyl acetoacetate, ethyl acetoacetate and triethylene tetraamine (E. Merck) were used as received. The solvents were dried before use.

Synthesis of dichloro/nitrato (2-oxo-4-methyl-1,5,8,11-tetraazacyclotrideca-4-ene) metal (II) and

(2-oxo-4-methyl-1,5,8,11-tetraazacyclotrideca-4-ene)metal (II) dichloride/dinitrate

The respective metal salt (0.01 mol) and triethylenetetraamine (0.01 mol) were dissolved in MeOH in a round bottomed flask and the mixture was stirred magnetically for about 30 min. To the above solution, ethyl acetoacetate or methyl acetoacetate (0.01 mol) was added and contents were stirred for an additional period of 6 h. The resulting solid product was removed by filtration, washed with MeOH and dried *in vacuo*. Elemental analyses data were obtained from the microanalytical laboratory of our Institute. The IR spectra (4000-400 cm⁻¹) were recorded (KBr discs) on a PE 1320 IR spectrophotometer. ¹H-NMR spectra were recorded in d₆-DMSO using a JEOL PMX 60 NMR spectrometer with Me₄Si as an internal standard. Metals and chloride were estimated volumetrically⁸ and gravimetrically⁹, respectively. The electronic spectra of complexes in DMSO were recorded on a Pye-Unicam 8800 spectrophotometer at room temperature. EPR spectra were recorded on a JEOL JES RE2X EPR spectrometer. Magnetic susceptibility measurements were made using a Faraday balance at 300 K. The electrical conductivities (10⁻³ M solution in DMSO) were obtained on a Systronic conductivity bridge type 302 equilibrated at 25°C.

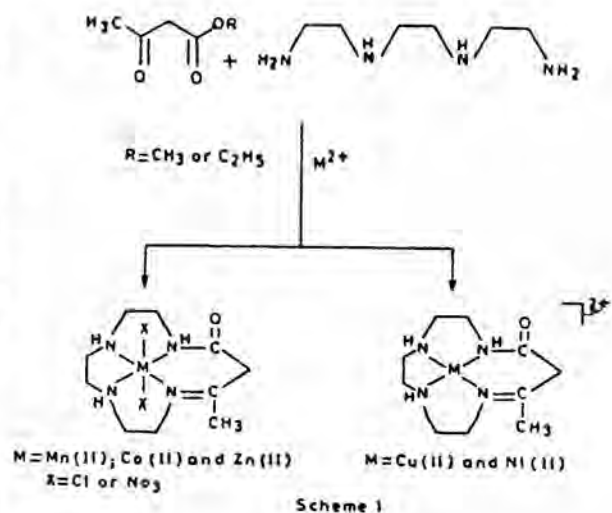


Table 1 — Melting point, colour, elemental analysis, molar conductance, magnetic moment and electronic spectral data of the compounds

Compound	M.P. (°C)	Colour	Found(Calc.)(%)					Molar Conductivity ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)	μ_{eff} (B.M.)	λ_{max} (cm^{-1})
			C	H	N	M	Cl			
[MnLCl ₂]	>340	Sardine brown	35.8 (35.5)	6.0 (6.2)	17.0 (16.6)	16.8 (16.3)	21.4 (21.0)	25	5.81	22,950 19,950
[MnL(NO ₃) ₂]	>340	Cherry blossom	30.5 (30.7)	5.8 (5.4)	21.2 (21.5)	14.2 (14.0)	-	29	5.80	23,350 19,250
[CoLCl ₂]	250	Brown	35.5 (35.1)	6.4 (6.1)	16.8 (16.4)	17.3 (17.2)	20.5 (20.8)	34	4.54	22,000 13,900
[CoL(NO ₃) ₂]	210	Reddish brown	30.5 (30.4)	5.6 (5.1)	21.1 (21.3)	15.2 (14.9)	-	30	4.60	22,400 14,250
[NiL]Cl ₂	320	Light grey	35.3 (35.1)	6.6 (6.1)	16.2 (16.4)	17.5 (17.1)	20.4 (20.8)	95	-	20,100 15,400
[NiL](NO ₃) ₂	260	Bright grey	30.6 (30.4)	5.5 (5.1)	21.0 (21.3)	15.2 (14.9)	-	101	-	19,800 16,000
[CuL]Cl ₂	240	Blue	35.0 (34.6)	5.3 (5.8)	16.0 (16.1)	18.5 (18.3)	20.9 (20.5)	115	1.78	21,450 16,000
[CuL](NO ₃) ₂	250	Light blue	30.5 (30.0)	5.2 (5.0)	21.5 (21.0)	16.1 (16.0)	-	100	1.75	21,600 12,600
[ZnLCl ₂]	260	Off-white	34.7 (34.4)	6.2 (6.0)	16.5 (16.1)	18.4 (18.8)	20.5 (20.4)	33	-	-
[ZnL(NO ₃) ₂]	270	White	30.2 (29.9)	5.5 (5.2)	20.7 (20.9)	16.1 (16.3)	-	28	-	-

Results and discussion

The template reaction of triethylenetetraamine with methyl acetoacetate or ethyl acetoacetate resulted in the formation of the macrocyclic complexes, [MLX₂] [M=Mn(II), Co(II) and Zn(II)] [ML]X₂ [M=Cu(II) and Ni(II)] as shown in Scheme 1 which clearly indicates that the C₂H₅O or CH₃O group of the alkyl acetoacetate moiety has been condensed. These compounds show poor solubility in polar solvents and methyl cyanide. They are freely soluble in dimethyl sulphoxide and warm dimethylformamide. The results of analytical data (Table 1) suggest their 1:1 (metal to ligand) stoichiometry. The molar conductivity values for all the complexes except nickel and copper complexes in DMSO solution show them to be non-electrolytes¹⁰ while those of nickel and copper complexes suggest their 1:2 electrolytic¹¹ nature in DMSO.

The IR spectra of all the complexes exhibit a single sharp band in the region 3250-3270 cm^{-1} which may be assigned¹¹ to coordinated NH stretching vibration. This information together with the appearance of four bands in the regions 1680-1710, 1530-1570, 1250-1270 and 650-680 cm^{-1} assignable¹² to amide-I $\nu(\text{C}=\text{O})$; amide-II ($\nu(\text{C}-\text{N} +$

$\delta \text{ N-H}$); amide-III ($\delta \text{ N-H}$) and amide-IV $\phi(\text{C}=\text{O})$ bands, respectively, suggest the formation of proposed macrocyclic framework. The absorption bands appearing in the regions 2880-2930 and 1410-1460 cm^{-1} in all the complexes may reasonably be assigned¹³ to the CH stretching and CH bending vibrational modes, respectively. This result has been further confirmed by the appearance of a strong, medium intensity band at ~1620 cm^{-1} assigned¹⁴ to the coordinated imine, $\nu(\text{C}=\text{N})$. Bands in the regions 1230-1245, 1000-1030, 850-875 cm^{-1} for the nitrate complexes indicate the presence of the monodentate coordinated nitrate group¹⁵.

The ¹H-NMR spectra of zinc(II) macrocyclic complexes show multiplet at around 8.56 ppm which can be assigned¹⁶ to amide (NH-C=O) proton. A sharp signal observed at 2.52 ppm for the macrocyclic complexes correspond to imine methyl (CH₃-C=N-) proton¹⁷. A multiplet appearing at 3.50 ppm may be ascribed¹⁸ to the methylene proton of amine linkage (CH₂-N=C). A singlet was observed at 2.15 ppm which may be assigned¹⁹ to methylene (C-CH₂-C) proton of alkyl acetoacetate moiety. Furthermore, a multiplet appears in the region 6.25-6.40 ppm which can be assigned²⁰ to

secondary amino (C-NH-C) protons of the triethylene tetraamine moiety.

The EPR spectra of poly-crystalline copper(II) macrocyclic complexes were recorded at room temperature and their $g_{||}$ and g_{\perp} values were calculated. The non-occurrence of hyperfine splitting may be attributed to the strong dipolar and exchange interactions between copper(II) ions in the unit cell. The calculated $g_{||}$ and g_{\perp} values were found to be 2.23 and 2.09 respectively, which are characteristic²¹ of square-planar copper(II) complexes. This suggests that the unpaired electron is present in the $d_{x^2-y^2}$ orbital as $g_{||} > g_{\perp} > 2.02$ (ref. 22). In an axial symmetry the g values are related by the expression $G=(g_{||}-2)/(g_{\perp}-2)$ which measure the exchange interaction between copper centers in the unit cell. The calculated G values are found to be 2.55 ($G < 4$) indicating^{23,24} considerable exchange interaction between copper centres.

The electronic spectral and magnetic moment data are consistent^{25,26} with the proposed structure.

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