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Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Complexes with an Open-chain Pentadentate Nitrogen Ligand[a]

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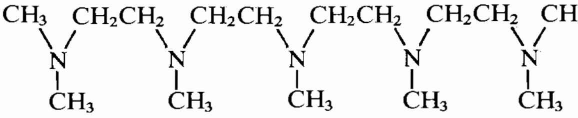
The open-chain, potentially pentadentate, ligand 1,11-bis(dimethylamino)-3,6,9-trimethyl-3,6,9-triazaundecane (Me$_7$tetren) forms a series of metal complexes having the general formula [M(Me$_7$tetren)]Y$_2$ (Y = I, M = Co, Ni; Y = ClO$_4$, M = Co, Ni, Cu, Zn). On the basis of their physical properties, it is suggested that all these compounds contains isostructural five-coordinate [M(Me$_7$tetren)]$^{2+}$ cations, the ligand acting as pentadentate. These complexes react in solution with thiocyanate ion to give mono- and, with exception of copper(II), di-thiocyanato five-and six-co-ordinate derivatives. Mono-thiocyanato derivatives of cobalt(II), nickel(II) and zinc(II) have been isolated as tetraphenylborate salts. Cobalt(II) and nickel (II) di-thiocyanato derivatives have been also isolated. Results are discussed in terms of the steric requirements of the ligand and electronic properties of the metal ions.

Introduction

The co-ordination behaviour of multidentate ligands is often closely related to the structural geometry of the ligand itself.[1] The influence of this factor is often minimised in open-chain ligands, because of their large flexibility. In this case the full co-ordination of donor atoms and the ligand arrangement around the metal ion mainly depend both on the nature of the metal and on some peculiar features of the ligand, *i.e.* the nature of donor atoms, their steric crowding and bridging links.

Neutral open-chain pentadentate ligands are known to form hexa-co-ordinate pseudo-octahedral 3*d* metal complexes of general formula [MLX]$^+$ (where X is an ionic or neutral monodentate ligand) the ligand being fully co-ordinate in a number of different configurations.[2,3]

Bearing in mind that more critical co-ordination conditions can be reached by increasing the steric crowding on the donor atoms, the ligand 1,11-bis (dimethylamino)-3,6,9-trimethyl-3,6,9-triazaundecane (Me$_7$tetren)(I)



$CH_3N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_3$

(I) Me$_7$tetren

was considered and used to form cobalt(II), nickel(II), copper(II) and zinc(II) complexes. The synthesis and characterization of some metal complexes are reported here.

Results

Three series of complexes having general formulae M(Me$_7$tetren)Y$_2$ (Y = I, M = Co, Ni; Y = ClO$_4$, M = Co, Ni, Cu, Zn), M(Me$_7$tetren)(NCS)BPh$_4$ (M = Co, Ni, Zn) and M(Me$_7$tetren)(NCS)$_2$ (M = Co, Ni), have been obtained. Analytical data for these complexes are reported in Table I.

All the di-perchlorate metal complexes show practically identical X-ray powder patterns.

With exception of the di-perchlorate and di-iodo derivatives, all the complexes are soluble in common polar organic solvents. The first complexes are soluble in aceton–methanol 50% (v/v) mixtures, the di-iodo derivatives being decomposed by the above solvents.

Conductometric measurements (see Table II) indicate that di-perchlorate and di-iodo complexes complexes behave as uni–divalent electrolytes while the monothiocyanate tetraphenylborate salts are uni–univalent electrolytes. Di-thiocyanato derivatives are practically non-electrolytes.

Electronic spectra in the range 5–25 kK have been recorded both in the solid state and in solution. Spec-

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TABLE I. Analytical Data for the Complexes.

Compound	Colour	% C		% H		% N		% Metal	
		calcd.	found	calcd.	found	calcd.	found	calcd.	found
$[Co(Me_7tetren)](ClO_4)_2$	violet	33.04	33.0	6.84	6.7	12.84	12.7	10.81	10.4
$[Co(Me_7tetren)]I_2$	purple	30.02	30.0	6.22	6.4	11.67	11.5	9.82	9.9
$[Co(Me_7tetren)(NCS)]BPh_4$	blue	66.38	65.7	7.94	7.9	11.61	11.5	8.14	7.9
$[Co(Me_7tetren)(NCS)_2]$	violet	44.14	43.9	8.06	7.9	21.20	21.0	12.74	12.4
$[Ni(Me_7tetren)](ClO_4)_2$	pale green	33.05	32.9	6.84	6.7	12.85	12.7	10.75	10.6
$[Ni(Me_7tetren)]I_2$	pale green	30.03	30.5	6.22	6.3	11.67	11.9	9.79	9.6
$[Ni(Me_7tetren)(NCS)]BPh_4$	green	66.40	65.9	7.94	8,0	11.61	11.4	8.11	7.9
$[Ni(Me_7tetren)(NCS)_2]$	green	44.16	43.8	8.07	8.1	21.21	20.9	12.70	12.5
$[Cu(Me_7tetren)](ClO_4)_2$	blue-green	32.76	32.3	6.78	6.6	12.73	12.6	11.55	11.4
$[Zn(Me_7tetren)](ClO_4)_2$	white	32.65	32.8	6.76	6.8	12.69	12.4	11.85	11.7
$[Zn(Me_7tetren)(NCS)]BPh_4$	white	65.81	66.0	7.87	8.0	11.51	11.3	8.96	9.0

trophotometric data are reported in Table II. The striking similarity, for any given metal between the reflectance and absorption ligand field spectra, indicates that the structures of the chromophores are probably the same in both solid and in solution.

Cobalt(II), nickel(II) and copper(II) complexes are all paramagnetic, the magnetic moment falling in the usual high-spin range for these metals (Table II).

Discussion

Di-perchlorate and Di-iodide Metal Complexes

Owing to the strict similarity of solid and solution electronic spectra and the uni–divalent conductometric behaviour of di-iodide and di-perchlorate metal complexes, they can be formulated as $[M(Me_7tetren)]Y_2$ ($Y = I, ClO_4$). The lack of any splitting of the ν_3 and ν_4 (at *ca.* 1100 and 625 cm^{-1}) active infrared absorption bands, is consistent with un-co-ordinated ClO_4^- ion.[4]

No absorption band is present in the i.r. range 2780–2820 cm^{-1} where (C–H) stretchings of free $N(CH_3)$ groups are usually expected.[5] This suggests that all five nitrogen donor atoms of the ligand are bound to the metal ion.

Moreover electronic spectra of the cobalt(II) and nickel(II) complexes are identical for iodide and perchlorate derivatives and show the typical pattern of the well known five-co-ordinate chromophores having a distorted trigonal bipyramidal stereochemistry (Fig. 1, Table II).[6,7] The orbital contribution to the magnetic moments is that usually found for compounds having this structure.

On the basis of the X-ray powder patterns, the same structure can be proposed also for the copper(II) and zinc(II) complexes. The spectra of the copper(II) one, which show a single broad band at 13.8 kK, is, although not diagnostic, quite consistent with this structure.[8]

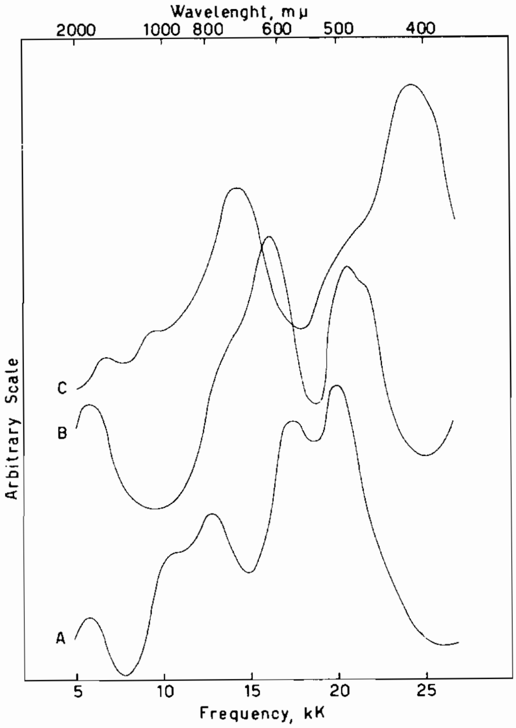

Figure 1. Reflectance spectra of: (A) $[Co(Me_7tetren)](ClO_4)_2$, (B) $[CoMe_7tetren)NCS]BPh_4$, (C) $[Ni(Me_7tetren)](ClO_4)_2$.

Therefore it may be concluded that all these complexes both in solid state and solution exist as five-co-ordinate MN_5 chromophores.

Thiocyanate Derivatives

Conductometric titrations of di-perchlorate metal complexes with $[Me_4N]NCS$ in acetone–methanol 50% v/v mixtures, show a sharp break at 1:2 mole ratio for cobalt(II), nickel(II) and zinc(II) and only

TABLE II. Physical Data for the Complexes.

Compound	μ_{eff} (B.M.)[a]	Λ_M (cm^2 ohm^{-1})[b]	State	Absorption max. (kK) with ε_{molar} for soln. in parentheses[d]
$[Co(Me_7tetren)](ClO_4)$	4.62(22)	240	R	5.2vbr, 10.5, 12.6, 17.7, 20.0, 22.0sh
			MA	10.6sh, 12.6(15), 17.7(29), 20.1(35), 22.0sh
$[Co(Me_7tetren)]I_2$	4.59(28)	186	R	5.2vbr, 10.3, 12.7, 17.4, 20.0
			MA	10.6(12), 12.5sh, 16.7(43), 19.0(44)
$[Co(Me_7tetren)(NCS)]BPh_4$	4.44(22)	91	R	5.8br, 13.3sh, 15.2sh, 16.2, 20.5, 21.4sh
			MA	13.2sh, 15.6sh, 16.4(167), 20.8(100), 21.7sh
$[Co(Me_7tetren)(NCS)_2]$	4.72(22)	29	R	8.5, 16.1sh, 18.8, 20.2sh
		2.6(D)	D	8.7(9), 16.2sh, 18.9(44), 20.4sh
			MA	8.4(8), 13.3sh, 16.3(45), 18.7sh, 20.3(49)
$[Ni(Me_7tetren)](ClO_4)_2$	3.44(22)	238	R	7.0br, 9.5, 11.0sh, 14.4, 20.5sh, 24.3
			MA	7.0(9), 9.3(8), 11.0(11), 11.6sh, 14.4(40), 20.4sh, 24.3(135)
$[Ni(Me_7tetren)]I_2$	3.50(28)	195	R	6.2br, 9.5, 11.4sh, 14.1, 19.6sh, 23s
			MA	9.3(10), 11.1sh, 14.2(32), 19.8sh, 24.0(140)
$[Ni(Me_7tetren)(NCS)]BPh_4$	3.14(22)	88	R	9.3, 13.5sh, 15.5, 23.5sh, 26.0
			MA	8.9(15), 15.6(13), 25.5(32)
$[Ni(Me_7tetren)(NCS)_2]$	3.25(22)	8	R	9.3, 15.7, 24.4
		2(D)	D	8.9(23), 15.7(21), 24.3(43)
			MA	8.9(21), 15.8(19), 24.7(38)
$[Cu(Me_7tetren)](ClO_4)_2$	1.93(22)	238	R	13.8br
			MA	13.9(350)
			MA[f]	12sh, 15.1(310)
$[Zn(Me_7tetren)](ClO_4)_2$	diam. (23)	244		
$[Zn(Me_7tetren)(NCS)]BPh_4$	diam. (22)	93		

[a] Temp. (° C) in parentheses. [b] For *ca.* 10^{-3}*M* soln. in methanol–acetone 50% at 20° C. Ref. values: $[NBu_4]BPh_4$, 93; $Ba(ClO_4)_2$, 223. [c] R = diffuse reflectance, M/A = methanol–acetone 50% mixtures, D = 1,2-dichloroethane. [d] sh = shoulder, v = very, br = broad. [e] Molar conductivity in 1,2-di-chloroethane at 20° C. [f] Equimolar amount of $[Me_4N]NCS$ added.

at 1 : 1 mole ratio for the copper(II) analogue. At 1 : 1 mole ratio only an inflection point can be detected for the former three complexes. These results can be accounted for by the existence of the following equilibria in solution

$$(1)\quad [M(Me_7tetren)]^{2+} + NCS^- \rightleftharpoons [M(Me_7tetren)(NCS)]^+ \quad (M = Co, Ni, Cu, Zn)$$

$$(2)\quad [M(Me_7tetren)(NCS)]^+ + NCS^- \rightleftharpoons [M(Me_7tetren)(NCS)_2] \quad (M = Co, Ni, Zn)$$

Calorimetric measurements support this hypothesis and indicate two distinct thermal steps for cobalt(II), nickel(II) and zinc(II) but only one step for copper (II).[10]

Some of the species stoichiometrically established in (1) and (2) were isolated in the solid state. In particular mono-thiocyanate derivatives of cobalt(II), nickel(II) and zinc(II) were isolated as tetraphenylborate salts. All attempts to prepare the copper(II) analogue were unsuccessful (see Experimental). Cobalt(II) and nickel(II) di-thiocyanato derivatives were also isolated.

Mono-thiocyanato Derivatives:
$[M(Me_7tetren)(NCS)]BPh_4$ (M = Co, Ni, Zn)

These complexes behave as uni–univalent electrolytes in solution (Table II) and their i.r. spectra show a band at 2075 cm^{-1} indicative of N-bonded non-bridging thiocyanate groups.[11] The spectra of cobalt (II) and zinc(II) complexes show a band at 2785 cm^{-1}, attributable to the ν(C–H) stretching of non-bonded $N(CH_3)$ groups.[5] In agreement with these data the electronic spectra of the nickel(II) complex are typical of a pseudo-octahedral six-co-ordinate complex (Table II), whereas those of the cobalt(II) complex indicate a five-co-ordinate trigonal bipyramidal structure (Fig. 1, Table II),[6,7] where the thiocyanate probably substitutes a terminal amino-group of the ligand.

A similar five-co-ordinate structure is proposed for the zinc complex.

A spectrophotometric titration of a solution of the five-co-ordinate [Cu(Me$_7$tetren)](ClO$_4$)$_2$ with [Me$_4$N]NCS evidences the formation of a new species, whose spectral features are also characteristic of a five-co-ordinate chromophore (Fig. 2).[6,8,12] The most simple structural hypothesis is that proposed for the [Co(Me$_7$tetren)(NCS)]$^+$ species, in which the ligand acts as tetradentate.

Di-thiocyanato Derivatives: [M(Me$_7$tetren)(NCS)$_2$] (M = Co, Ni)

These complexes are monomeric and non-electrolytes in 1,2-dichloroethane solution. Again the i.r. spectra show a band at 2780 cm^{-1} indicative of incomplete co-ordination of tertiary amino-groups.[5] Consistent with their electronic spectra, these complexes are presumably six-co-ordinate, the ligand acting as tetradentate. The fact that no splitting is observed in the band at 2070 cm^{-1} (ν(C–N) stretching) suggests the *trans* structure as the most probable for these complexes.

It is interesting to note from absorption electronic spectra and conductometric measurements in acetone–methanol 50% (v/v) mixtures (Table II) that the cobalt(II) complex (in contrast to the nickel(II) analogue) undergoes a five- / six-co-ordinate equilibrium occurring through partial detachment of NCS$^-$ ion. However, under the experimental condition used, the percentage of the five-co-ordinate species is low.

Conclusions

The results reported here indicate that the linear ligand Me$_7$tetren, containing five potential donor atoms, can act as pentadentate ligand both in trigonal bipyramidal and pseudo-octahedral co-ordination polyhedra. In the first case the ligand acts in a stereospecific way giving a series of isomorphous complexes with all the metal ions considered. We could find the latter behaviour only in the [Ni(Me$_7$tetren)(NCS)]$^+$ chromophore. In the case of cobalt(II), zinc(II) and probably copper(II) a five-co-ordinate geometry occurs, by substitution of a terminal donor atom of the ligand with a thiocyanate ion. This is probably due both to the steric requirements of the ligand, which, as shown by molecular models, is hardly able to behave as pentadentate in a pseudo-octahedral co-ordination polyhedron, and to the well known greater tendency of cobalt(II), copper(II) and zinc(II), with respect to nickel(II) to form five-co-ordinate metal complexes.

Experimental

Synthesis of the Ligand

The ligand was prepared by methylation of tetraethylenpentamine (Fluka Prakt.) with formaldehyde and formic acid as described by Spialter and Moshier.[13] It was freed as an insoluble oil by treatment with an excess for 30% aqueous potassium hydroxide and extracted from the resulting mixture with ether. After the evaporation of the solvent the crude ligand was dried (Na$_2$CO$_3$) and fractionally distilled under reduced pressure. The fraction distilled at 114–117°C/0.2 torr was collected, redistilled and stored over solid KOH. Calcd. for C$_{15}$H$_{37}$N$_5$: C, 65.87; H, 13.63; N, 20.48; found: C, 65.3; H, 14.0; N, 20.2.

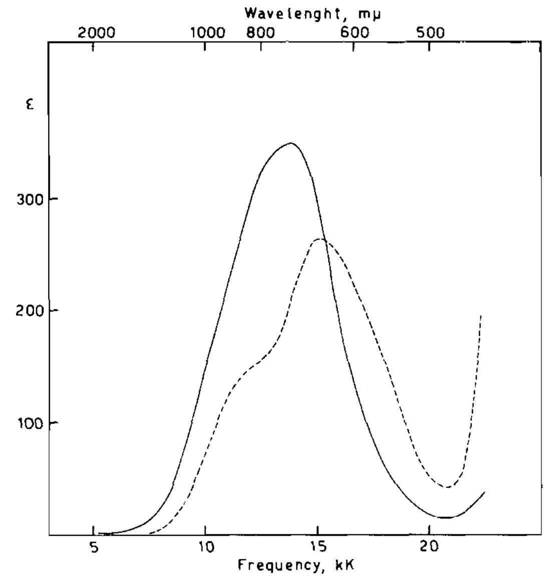

Figure 2. Absorption spectra of acetone–methanol 50% solutions of [Cu(Me$_7$tetren)](ClO$_4$)$_2$ alone (solid line) and with a stoichiometric amount of [Me$_4$N]NCS added (dotted line).

Preparation of the Complexes

Di-perchlorate metal complexes

All these complexes were obtained by the following general method: to a hot solution of the requisite metal perchlorate (2 mmol) in methanol (30 ml), a stoichiometric amount of the ligand in the same solvent was added. The complexes immediately precipitate and were recrystallized from acetone–methanol, collected onto a sintered-glass funnel and dried *in vacuo* at 70°C.

Di-iodide metal complexes

These complexes were obtained with the above procedure using absolute ethanol as solvent.

Di-thiocyanato metal complexes

These complexes were prepared by mixing a solution of di-thiocyanate metal salt (2 mmol) in butan-1-ol (30 ml) with a solution of the ligand (2 mmol) in the same solvent. Crystallization occured by adding cyclohexane.

Monothiocyanato tetraphenylborate metal complexes

These complexes were prepared by adding to a solution of di-thiocyanate metal salt (2 mmol) and of the ligand (2 mmol) in hot ethanol (30 ml), a solution of sodium tetraphenylborate (2 mmol) in acetone (30 ml). The filtered solution was concentrated until crystallization occurred. The complexes were recrystallized from acetone–ethanol or dichloromethane–ethanol, filtered and dried as described previously.

All attempts to obtain the copper(II) monothiocyanato tetraphenylborate or perchlorate derivatives by using a large variety of solvents were unsuccesfull. In every case the di-perchlorate and di-tetraphenylborate complexes were obtained. The latter compound shows physical properties very similar to the di-perchlorate compound.

Materials and Physical Measurements

All solvents were reagent grade. Conductometric, spectrophotometric and magnetic measurements were carried out as described previously.[14] Calorimetric measurements were carried out with a LKB 8700/2 titration calorimeter, using a procedure already described.[15]

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