CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE E INORGANICA,
UNIVERSITA' DI FIRENZE, FLORENCE, ITALY

Five-Coordinated High-Spin Complexes of Bivalent Cobalt, Nickel, and Copper with Tris(2-dimethylaminoethyl)amine

BY M. CIAMPOLINI AND N. NARDI

Received August 3, 1965

The quadridentate ligand tris(2-dimethylaminoethyl)amine (trenMe) forms high-spin, five-coordinated complexes with cobalt(II), nickel(II), and copper(II) of the type [M(trenMe)X]X (where X = Cl, Br, I, NO_3, ClO_4), which probably have a trigonal bipyramidal structure. The solid and solution spectra in the range 5000–30,000 cm.$^{-1}$ are reported. The stereochemistry of some known complexes of cobalt(II) and copper(II) with the parent ligand tris(2-aminoethyl)amine is revised in the light of the present results.

Introduction

Not many five-coordinated complexes of the first row transition metals are known. Those of cobalt(II)[1] and nickel(II)[2] which contain phosphorus or arsenic ligands are all low spin. The first examples of high-spin, five-coordinated complexes of cobalt(II)[3,4] and nickel(II)[3,5] were, however, described and characterized only very recently. The structures of these complexes were established firmly by X-ray methods.[6,7] The donor atoms in the high-spin complexes are oxygen and nitrogen.

We have now undertaken a systematic investigation of the bivalent 3d transition metal ions with particular interest in high-spin compounds. Ligands suitable for this purpose have to fulfill two main conditions: (a) the donor atoms must possess strong coordinating ability and little tendency to form π bonds with the metal ions and (b) the ligand must be bulky and polydentate in order that crowding around the metal ion should prevent a six-coordinated configuration being attained.

In this communication we report the results of a study of the complexes formed by the potentially quadridentate ligand $N[CH_2CH_2N(CH_3)_2]_3$, tris(2-dimethylaminoethyl)amine with bivalent cobalt, nickel, and copper. This ligand is a hexamethyl derivative of tris(2-aminoethyl)amine (tren) and is abbreviated trenMe.

Experimental Section

Materials.—All solvents were of reagent grade quality. Nitroethane was washed with 5% aqueous sodium bicarbonate, dried with Drierite, and fractionally distilled (b.p. 113°). Chloroform was washed six times with water, dried for 24 hr. over phosphorus pentoxide, and distilled from potassium carbonate under nitrogen.

Synthesis of trenMe.—$[N(CH_2CH_2NH_3)]Cl_3$ was prepared by a modification of Ristempart's synthesis.[8,9] A mixture of 62 g. of this hydrochloride, 30 ml. of water, 200 ml. of 85% formic acid, and 170 ml. of 30% formaldehyde was heated at 120° until the evolution of carbon dioxide had practically stopped (*ca.* 6 hr.). All the volatile fractions were then removed by vacuum distillation. The solid residue which probably contains trenMe·3HCl was not characterized; when it was treated with 400 ml. of 10% sodium hydroxide, an oily layer formed which was extracted into ether. The ethereal extract was dried over potassium hydroxide. After removal of the ether the compound tris(2-dimethylaminoethyl)amine distilled as a colorless oil, b.p. 70–71° (0.5 mm.); yield 57 g. (91%).

Anal. Calcd. for $C_{12}H_{30}N_4$: N, 24.32. Found: N, 24.40.

Preparation of Complexes.—All complexes were prepared by the same general method. To a hot solution of 5 mmoles of the appropriate metal salt in 20 ml. of absolute ethanol was added slowly a solution of 5 mmoles (1.25 g.) of the ligand in 10 ml. of ethanol. The nitrate and perchlorate complexes separated from the reaction mixture as crystalline solids; petroleum ether was added to the concentrated solutions of the halides in order to promote crystallization. All complexes were recrystallized by dissolving them in chloroform or nitroethane and adding petroleum ether to the filtered solution. The crystals were collected by filtration and dried in a stream of nitrogen. All compounds are hygroscopic.

Spectra.—Absorption spectra were recorded in the range 5000–30,000 cm.$^{-1}$ at room temperature with a Beckman DK-2 spectrophotometer and 1-cm. silica cells. The diffuse reflectance spectra were measured using the standard Beckman reflectance attachment and magnesium oxide as the reference.

Conductivity Measurements.—The conductivity values were measured on a WTW Model LBR/B conductance bridge. Concentrations of the solutions were approximately 10^{-3} *M*.

Molecular Weight Measurements.—Molecular weights were determined in nitroethane at 37° with a Mechrolab Model 301A vapor pressure osmometer calibrated with benzil. Scale readings were made 5 min. after the drop of the solution was placed on the thermistor. The solutions were approximately 3×10^{-2} *M*. The results were reproducible to ±1%.

Magnetic Measurements.—The apparatus and the experimental technique used for the magnetic measurements were described in a previous paper.[10] The Gouy tube was calibrated with freshly distilled water and a nickel chloride solution.[11]

---

(1) G. A. Barclay and R. S. Nyholm, *Chem. Ind.* (London), 378 (1953); G. A. Barclay, *Rev. Pure Appl. Chem.*, **XX 4**, 77 (1954); A. Earnshaw, P. C. Hewlett, and L. F. Larkworthy, *Nature*, **199**, 483 (1963).

(2) G. A. Barclay and R. S. Nyholm, *Chem. Ind.* (London), 378 (1953); C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 4379 (1960); G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 415 (1960); G. A. Mair, H. M. Powell, and L. M. Venanzi, *ibid.*, 170 (1961); N. T. Barker, C. M. Harris, and E. D. McKenzie, *ibid.*, 335 (1961); R. G. Hayter, *Inorg. Chem.*, **2**, 932 (1963); G. S. Benner, W. E. Hatfield, and D. W. Meek, *ibid.*, **3**, 1544 (1964); G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965).

(3) L. Sacconi, M. Ciampolini, and G. P. Speroni, *J. Am. Chem. Soc.*, **87**, 3102 (1965).

(4) L. Sacconi, M. Ciampolini, and G. P. Speroni, *Inorg. Chem.*, **4**, 1116 (1965).

(5) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *ibid.*, **4**, 943 (1965).

(6) P. L. Orioli, M. Di Vaira, and L. Sacconi, *Chem. Commun.* (London), 103 (1965).

(7) L. Sacconi, P. L. Orioli, and M. Di Vaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965).

(8) I. Ristempart, *Ber.*, **29**, 2530 (1896).

(9) P. Paoletti, M. Ciampolini, and L. Sacconi, *J. Chem. Soc.*, 3589 (1963).

(10) L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *J. Am. Chem. Soc.*, **82**, 3487 (1960).

(11) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p. 415.

TABLE I

PROPERTIES AND ANALYSES OF THE M(II) COMPLEXES

Compound[a,b]	Color	Molar conductance, cm.^{2}/ohm M[c]		i[d]	N, %		Metal, %		Halogen, %	
		Nitrobenzene	Nitroethane		Calcd.	Found	Calcd.	Found	Calcd.	Found
[Co(trenMe)Cl]Cl	Grayish violet	32	80	1.45	15.55	15.41	16.36	16.14	19.68	19.35
[Co(trenMe)Br]Br[a]	Violet	30	83	1.60	12.47	12.53	13.12	13.04	35.58	35.28
[Co(trenMe)I]I	Violet	32	89	1.66			10.85	10.69	46.73	46.81
$[Co(trenMe)ClO_4]ClO_4$	Light green	31	93	1.47			12.07	12.10		
[Ni(trenMe)Cl]Cl[b]	Light olive	31	80	1.41	15.56	16.01	16.30	16.00	19.69	19.38
[Ni(trenMe)Br]Br	Mustard	32	77	1.47					35.60	35.31
[Ni(trenMe)I]I	Cinnamon	31	84	1.65			10.81	11.09	46.75	46.68
$[Ni(trenMe)ClO_4]ClO_4$	Light green	26	102	1.55	11.48	11.90	12.03	12.29		
$[Ni(trenMe)NO_3]NO_3$	Bluish green				20.34	20.16	14.21	14.08		
[Cu(trenMe)Br]Br	Light green	32	79	1.59			14.00	14.01	35.22	35.36
$[Cu(trenMe)ClO_4]ClO_4$	Light blue	33	103	1.59	11.37	11.65	12.89	12.84		
$[Cu(trenMe)NO_3]NO_2$	Light blue	31	83	1.46	20.11	20.14	15.21	15.04		

[a] Calcd.: C, 32.09; H, 6.73. Found: C, 32.40; H, 6.66 [b] Calcd.: C, 40.03; H, 8.40. Found: C, 39.86; H, 8.52. [c] For *ca.* 10^{-3} M solutions at 25°. Reference values in nitrobenzene and nitroethane, respectively, are: $[(n\text{-}C_4H_9)_4N]Br$, 27, 70; $[(n\text{-}C_4H_9)_4N]I$, 30, 83; $[(C_2H_5)_4N]_2[Co(NCS]_4]$, 59, 147. [d] van't Hoff coefficients for *ca.* 3×10^{-2} M nitroethane solutions at 37°. Reference values, under the same conditions, are: $[(n\text{-}C_4H_9)_4N]I$, 1.62; $[(CH_3)_4N]_2[Co(NCS)_4]$, 1.94; $[(C_2H_5)_4N]_2[Co(NCS)_4]$, 1.99; $[(n\text{-}C_3H_7)_4N]_2[ZnBr_4]$, 2.30.

TABLE II

MAGNETIC DATA FOR SOME [M(trenMe)X]X COMPLEXES

Compound	State	T, °C.	$\chi_g \times 10^6$	$\chi_{Me} \times 10^6$	μ_{eff}, B.M.
[Co[trenMe)Cl]Cl	Solid	21	22.46	8312	4.45
[Co(trenMe)Br]Br	$CHCl_3$	22	18.10	8370	4.47
[Ni(trenMe)Cl]Cl	Solid	22	13.03	4912	3.42
	$CHCl_3$	21	13.08	4930	3.42
[Ni(trenMe)Br]Br	$CHCl_3$	19	10.44	4952	3.42
$[Ni(trenMe)NO_3]NO_3$	Solid	22	10.46	4540	3.28
[Cu(trenMe)Br]Br	Solid	21	2.68	1459	1.86
$[Cu(trenMe)ClO_4]ClO_4$	Solid	21	2.45	1454	1.86

Diamagnetic corrections were calculated from Pascal's constants.[12]

Results

The analytical data and characteristics of the present compounds are reported in Table I.

The compounds are soluble in nitroethane, nitrobenzene, and methanol but are insoluble in nonpolar solvents. The halides are also very soluble in chloroform. The cobalt(II) complexes are not oxidized by dry air in the solid state or in nonaqueous solution.

The room temperature magnetic moments of some representative complexes are given in Table II. The compounds are all of the high-spin type both as solids and in solution. In the case of the cobalt and copper compounds the orbital contribution to the magnetic moment is fairly small. With the nickel complexes the values of the magnetic moment are intermediate between those found in tetrahedral and octahedral compounds.

The spectra of the solid compounds and of solutions in nitroethane and where possible in chloroform were all recorded; the absorption maxima and molar absorbancies are given in Table III. In all cases the solution spectra are closely similar to those of the solid compounds, which indicates that the stereochemistry of the complexes does not change appreciably on dissolution. More precisely, the nitroethane is not coordinated to the metal, though there is extensive solvolysis in water or methanol. The form of the spectra of compounds of each element does not vary significantly with changes in the anion X. Naturally small frequency shifts were found which can be correlated with the position of the anion in the spectrochemical series. The intensities of the bands mostly increase as $ClO_4 \approx NO_3 \approx Cl < Br < I$, that is, with the polarizability of the anion. It is therefore concluded that the same stereochemistry is present in all the compounds of each element studied here both in the solid state and in solution.

The complexes of trenMe with cobalt, nickel, and copper and a given anion give practically the same X-ray powder photographs. Further, for each element the powder photographs of the chloro, bromo, and iodo complexes show profound similarities. These facts point to a single stereochemistry being present in all halo complexes of all three elements.

The electrical conductivities of *ca.* 10^{-3} M solutions in nitroethane or nitrobenzene were measured at 25°. Molecular weight determinations in nitroethane at 37° were also carried out in order to obtain the van't Hoff coefficient i of these electrolytes.

Discussion

In the previous section it was concluded that all the compounds studied here have similar stereochemistries. On the other hand the conductivity values are typical of uni-univalent electrolytes based on a monomeric formula and are only a little high for bi-univalent electrolytes based on a dimeric formulation. The possibility of a dimerization is belied by the molecular weight measurements. Dimerization could occur by means of halide or nitrate bridging, but the small degree of association which was found is to be attributed to ion pair association for the following reasons: (a) The van't Hoff factor i values are 1.41–1.66 based on the monomeric formulation and obviously 2.82–3.32 for the dimeric formula. The values are to be com-

---

(12) Reference 11, p. 403.

TABLE III

THE MAXIMA AND EXTINCTION COEFFICIENTS FOR THE ELECTRONIC SPECTRA OF THE COMPLEXES

Compound	State	Absorption max., cm.$^{-1}$ (ϵ_{molar} for soln.)
$[\mathrm{Co(trenMe)Cl}]\mathrm{Cl}$	Solid	≈5700, 12,500, 15,600–16,000, 20,000
	$\mathrm{CHCl_3}$	≈5800 (32), 12,600 (30), 15,500–16,100 (87), 20,200 (118)
$[\mathrm{Co(trenMe)Br}]\mathrm{Br}$	Solid	≈5600, 12,300, 16,200, 18,900–19,600
	$\mathrm{CHCl_3}$	≈5700 (30), 12,300 (29), 15,600–16,100 (128), 19,200–19,800 (112)
$[\mathrm{Co(trenMe)I}]\mathrm{I}$	Solid	≈5400, 12,200, 16,400, 18,400–19,100
	$\mathrm{CHCl_3}$	≈5700 (37), 12,100 (16), 16,100 (198), 18,600–19,300 (99), 21,600 sh
$[\mathrm{Co(trenMe)ClO_4}]\mathrm{ClO_4}$	Solid	≈5900, 13,400, 15,600–16,300, 20,900
	$\mathrm{C_2H_5NO_2}$	≈5900 (22), 13,500 (23), 15,900–16,400 (47), 20,600 (82)
$[\mathrm{Ni(trenMe)Cl}]\mathrm{Cl}$	Solid	7100, 10,700–11,500 sh, 14,600, 20,000 sh, 23,300
	$\mathrm{CHCl_3}$	7100 (26), 10,900 (22)–11,600 (19), 14,900 (30), 20,600 sh, 23,500 (172)
$[\mathrm{Ni(trenMe)Br}]\mathrm{Br}$	Solid	7100, 10,500, 14,100, 20,000 sh, 22,700
	$\mathrm{CHCl_3}$	7100 (28), 10,500 (21)–11,400 (18), 14,500 (34), 20,000 sh, 23,000 (71)
$[\mathrm{Ni(trenMe)I}]\mathrm{I}$	Solid	7200, 10,400, 13,800, 24,300
	$\mathrm{CHCl_3}$	7100 (32), 10,300–11,100, 14,200 (38), 19,200 sh, 22,400 (218)
$[\mathrm{Ni(trenMe)ClO_4}]\mathrm{ClO_4}$	Solid	7700–8700 sh, 11,400 sh–12,300, 15,300, 24,300
	$\mathrm{C_2H_5NO_2}$	7700 (19), 11,400–12,200, 15,200 (39), 23,400 (107)
$[\mathrm{Ni(trenMe)NO_3}]\mathrm{NO_3}$	Solid	9300, 11,400 sh–12,300 sh, 15,600, 24,600
	$\mathrm{C_2H_5NO_2}$	8800 (18), 11,300–12,200 (13), 15,500 (27), 21,100 sh, 24,500 (88)
$[\mathrm{Cu(trenMe)Br}]\mathrm{Br}$	Solid	10,000, 12,800, 27,000 sh
	$\mathrm{CHCl_3}$	10,400 (450), 13,300 (209)
$[\mathrm{Cu(trenMe)ClO_4}]\mathrm{ClO_4}$	Solid	11,300, 13,500 sh
	$\mathrm{C_2H_5NO_2}$	11,200 (444), 13,800 sh
$[\mathrm{Cu(trenMe)NO_3}]\mathrm{NO_3}$	Solid	11,100, 13,800 sh
	$\mathrm{C_2H_5NO_2}$	11,200 (445), 14,300 sh, 26,700 (386)

pared with those of reference electrolytes in the same concentration range: 1.56–1.62 for the 1:1 electrolytes but only 1.91–2.30 for the 1:2 electrolytes. (b) The values of i for the perchlorate ion are practically the same as those for the other compounds. The perchlorate ion is unlikely to behave as a bridging ligand.

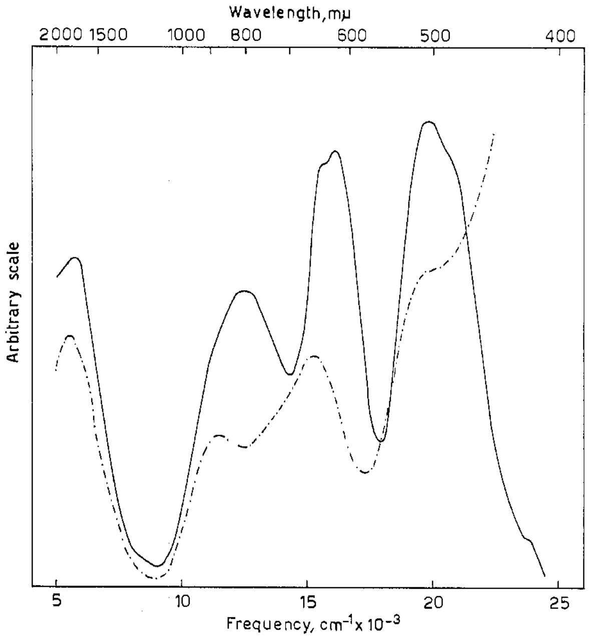

Figure 1.—Reflectance spectra of $[\mathrm{Co(trenMe)Cl}]\mathrm{Cl}$ (solid line) and bis(N-methylsalicylaldimino)cobalt(II) (dotted line).

Thus all the evidence indicates that the complexes should be formulated as $[\mathrm{M(trenMe)X}]\mathrm{X}$. The coordination number six can be excluded but a coordination number of four could be present if one nitrogen atom were not coordinated to the metal. Conclusive evidence concerning the stereochemistry of these complexes is obtained when their spectra are compared with the spectra typical of various high-spin configurations. It is found that the spectra of the trenMe complexes cannot be consistently interpreted in terms of a regular or distorted tetrahedral (or octahedral) configuration.[13] Instead there is a marked similarity with the spectra of some high-spin cobalt and nickel complexes for which a five-coordinated structure was proved by X-ray methods.[6,7] The known five-coordinated configurations are not very symmetrical, tending in the one case toward a trigonal bipyramid and in the other to a square pyramid. The spectra of the complexes $[\mathrm{M(trenMe)X}]\mathrm{X}$ (M = Co, Ni) approach more nearly the spectra of the trigonal bipyramidal compounds.[3] This is illustrated in Figure 1, where the spectrum of the trigonal bipyramidal complex bis(N-methylsalicylaldimino)cobalt(II) can be compared with that of the compound $[\mathrm{Co(trenMe)Cl}]\mathrm{Cl}$. The similarity of the two spectra is very marked up to 20,000 cm.$^{-1}$, where ligand and charge-transfer bands begin to appear. Also the spectra of the nickel complexes of trenMe are similar to the one attributed[3] to a distorted trigonal bipyramidal complex of nickel(II); the latter is obtained when the complex bis(N-methylsalicylaldimino)nickel(II) is placed in the crystal lattice of the analogous zinc compound, which is also isostructural with the cobalt compound. Because of the low concentration of the nickel complex in these solid solutions the diffuse reflectance spectra are not well resolved. However, in the region 5000–20,000 cm.$^{-1}$ two relatively strong bands are found at 7500 and 14,500 cm.$^{-1}$ with some ill-defined shoulders. The ratio of the fre-

---

(13) See, for instance: S. Buffagni and T. M. Dunn, *Nature*, **188**, 937 (1960); F. A. Cotton and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 1777 (1961); D. L. Goodgame, M. Goodgame, and F. A. Cotton, *ibid.*, **83**, 4161 (1961); C. Furlani and G. Morpurgo, *Z. physik. Chem.* (Frankfurt), **28**, 93 (1961); J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **1**, 866 (1962); C. Furlani and G. Morpurgo, *Theor. Chim. Acta*, **1**, 102 (1963).

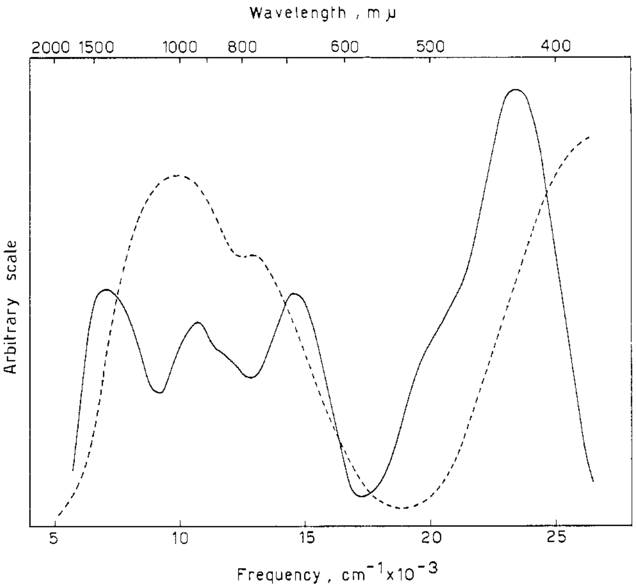

Figure 2.—Reflectance spectra of [Ni(trenMe)Cl]Cl (solid line) and [Cu(trenMe)Br]Br (dotted line).

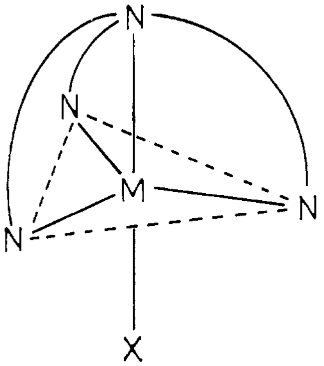

Figure 3.—Proposed structure for [M(trenMe)X]$^+$ ions.

quencies of these two bands is approximately two, just as is found with the first two intense bands in the spectra of the trenMe complexes (Figure 2, Table III).

The spectroscopic results therefore indicate a five-coordinated, probably trigonal-bipyramidal structure to all the trenMe complexes of cobalt and nickel (Figure 3). As noted above, the same structure can also be assigned to the copper complexes.

Stuart molecular models of the complexes were constructed and these showed that the trigonal bipyramidal structure is indeed the most likely structure to result when all four nitrogen atoms of the ligand are attached to the metal. The geometry of the ligand is such that the three dimethylamino groups are constrained to lie at the corners of an equilateral triangle which has the metal atom at the center. There is no room for another ligand in the same plane as the dimethylamino groups and in this way an octahedral or square-pyramidal structure cannot be obtained. The only coordination position available, in which there is little steric hindrance, is on the threefold axis of the triangle and this is occupied by the anion.

It is interesting to recall the results of previous work on the stereochemistry of complexes of the ligand tren, in which the terminal amino groups are, of course, less bulky than those of trenMe. At first it was held that this ligand could form only tetrahedral complexes,[14] but later it was realized it could more easily form a *cis*-octahedral complex with additional ligands as, for instance, two water molecules or the anions. Then, a thermochemical study showed that species with a coordination number less than six could be present in solution, at least with cobalt and zinc.[9] In the case of the nickel complexes with metal:ligand ratio 1:1 and various anions the spectra both in the solid state and in solution are characteristic of the octahedral configuration and were so interpreted by Jørgensen.[15] The complex [Ni(trenMe)(NCS)$_2$] was then shown to be octahedral by X-ray crystallography.[16]

The solution spectra of the copper complexes were considered by Jørgensen to be compatible with six coordination; they are different from the spectra of the trenMe complexes of copper (Figure 2), the higher frequency band being absent. The *cis*-octahedral configuration with two molecules of water thus appears to be the more likely in this case. On other hand the spectrum of the complex[17] [Cu(tren)OH]$^+$ in alkaline solution ($\epsilon_{11,900}$ 145, $\epsilon_{14,400}$ 116) is similar to those of the complexes [Cu(trenMe)X]X. This leads to the assignment of a five-coordinated configuration to the hydroxo tren complex of copper(II). Finally, for the cobalt tren complex, a probable high-spin five-coordinated structure has been postulated, on the basis of the entropy of formation on the one hand and spectral evidence on the other.[9] The close similarity of the spectra of the complex ions [Co(trenMe)X]$^+$ with that of the tren complex in aqueous solution further supports the assumption of a five-coordinated (distorted trigonal-bipyramidal) structure of the complex which should be formulated as [Co(tren)H$_2$O]$^{2+}$. The molar extinction coefficients[3] are about one-third of the values for the trenMe complexes which could indicate that not all the molecules have the same stereochemistry, the remainder being weakly absorbing species such as the octahedral species.

One may therefore conclude that the steric requirements of the amine tren are already on the borderline of compatibility for five or six coordination. The five-coordinated structure can be attained depending either on the nature of the metal ion (in the case of cobalt) or on the presence of other suitable ligands in solution, such as the hydroxide ion in the case of the copper–tren complex.

Acknowledgment.—Thanks are expressed to Professor L. Sacconi for helpful suggestions and to Mr. F. Zanobini for assistance in the preparation of the ligand. We are indebted to Dr. I. Gelsomini for microanalyses and to Mr. P. Innocenti for the metal and halogen analyses. The financial support of the Italian "Consiglio Nazionale Richerche" is gratefully acknowledged.

---

(14) F. G. Mann and W. J. Pope, *Proc. Roy. Soc.* (London), **A109**, 444 (1925).

(15) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

(16) D. Hall and M. D. Woulfe, *Proc. Chem. Soc.*, 346 (1958); S. E. Rasmussen, *J. Inorg. Nucl. Chem.*, **8**, 441 (1958).

(17) P. Paoletti and M. Ciampolini, *Ricerca Sci.*, **33** (IIA), 399 (1963).