68. 1:1 Metal Complexes of Bivalent Cobalt, Nickel, Copper, Zink, and Cadmium with the Tripodal Ligand Tris[2-(dimethylamino)ethyl]amine: Their Stabilities and the X-Ray Crystal Structure of Its Copper(II) Complex Sulfate

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The complex formation by Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} with tris[2-(dimethylamino)ethyl]amine ($N(CH_2CH_2NMe_2)_3$, Me_6tren) was investigated at 25° and at an ionic strength of 1, using VIS spectroscopy and potentiometric measurements. The stability constants of these complexes are compared with those of tris(2-aminoethyl)amine ($N(CH_2CH_2NH_2)_3$, tren), obtained under the same conditions. The values of the constants for Me_6tren are much lower than those for tren, due to the bulky Me substituents. The values of the constants can be correlated with the ability of the individual metal ions to adopt coordination number 5. This appears to be easier for Cu^{2+} and Co^{2+} than for Cd^{2+} and Zn^{2+} and is very difficult for Ni^{2+}. The 1:1 complexes $[ML(H_2O)]^{2+}$ are monoprotonic acids whose pK_s values are similar or lower than those of the corresponding aquametal ions. The X-ray crystal structure of the copper(II) complex $[Cu(SO_4)(Me_6tren)] \cdot 8H_2O$ reveals pentacoordination at the central ion. The UV/VIS spectra of the aqueous solutions of the Co^{2+}, Ni^{2+}, and Cu^{2+} 1:1 complexes confirm that the same coordination number is present also in these complexes.

Introduction. – Substitution of H-atoms bound to N-atoms by Me groups in N-donors has received considerable attention because of its influence on the stability [1–4] and configuration of the complexes formed by these ligands [5]. Among them tris[2-(dimethylamino)ethyl]amine (Me_6tren) is of particular interest because of its ability to form uncommon five-coordinated complexes with bivalent metal ions. Furthermore, the stabilities of the 1:1 complexes formed are unknown, as no equilibrium constants appear to have been published. Only very recently, we reported a case [6] where the metal center was palladium(II).

We now report the results of equilibrium studies with the metal ions Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, and Cd^{II}. The data were obtained for aqueous solutions in presence of $NaClO_4$ as inert salt at ionic strength 1. For comparison purposes, the values of the stability constants of tris(2-aminoethyl)amine (tren) were obtained under the same conditions. The 1:1 complexes of such tripodal amines often behave as monoprotonic acids characterized by particularly low p*K* values, also with respect to the corresponding aqua ions. Furthermore, we report the results of the X-ray crystal structure of the complex $[Cu(SO_4)(Me_6tren)] \cdot 8H_2O$ where the Cu^{2+} ion is five-coordinate in the solid state.

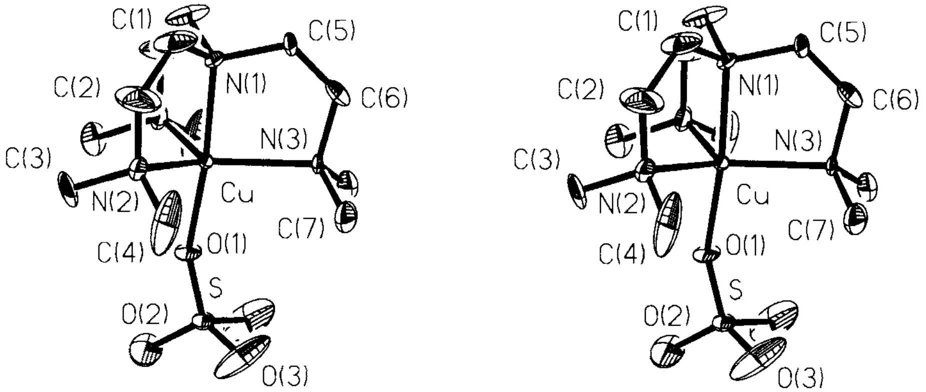

Figure. *ORTEP view of* $[Cu(SO_4)(Me_6tren)] \cdot 8H_2O$ *with 20% ellipsoids*

Experimental. – Tris[2-(dimethylamino)ethyl]amine was synthesized as described in [5] and separated from a MeOH soln. as the tris(hydroperchlorate); tris(2-aminoethyl)amine (*Fluka*, *purum*) was also isolated as tris(hydroperchlorate) (*caution*: the perchlorates might be explosive). After two recrystallizations, the substances were of the required purity for exact alkalimetric measurements of the corresponding deprotonation reactions. Metal perchlorates (*Fluka*, *purum*) were recrystallized from H_2O and their purities controlled by titration with EDTA. $NaClO_4 \cdot H_2O$, $HClO_4$, and *Titrisol* NaOH solns. (*Merck*, *p.a.*) were added to degassed, purified H_2O for the preparation of the solns. used for the alkalimetric titrations.

For the automatic pH measurements, an *Orion-SA-720* digital potentiometer and a *Metrohm-665-Dosimat* digital burette were used. The pH values of the solns. were defined using the H^+ concentrations $[H^+]$: $pH = -\log[H^+]$, in the standard state, given by the inert electrolyte in pure H_2O. Millimolar solns. of the components under study were used, *i.e.*, their concentrations were so low with respect to the ionic strenght (1M), that normally no correction of the concentration of the inert salt was needed to maintain a constant I during the titrations. The reference electrode (Hg, Hg_2Cl_2) contained 0.98M $NaClO_4$ and 0.02M NaCl, in contact with a 1M $NaClO_4$ bridge, which could be renewed. As the test soln. contained almost 1M $NaClO_4$, no large contamination and negligible residual junction potential was expected [7]. Solns. of perchloric acid ($1-4 \cdot 10^{-3}$ M) at $I = 1.00$ with

Table 1. *X-Ray Crystal Structure Determination of* $[Cu(SO_4)(Me_6tren)] \cdot 8H_2O$

Crystal data	Empirical formula	$C_{12}H_{46}CuN_4O_{12}S$
	Space group	$P2_1m$
	Unit cell dimensions	$a = 8.354(16)$ Å
		$b = 14.87(5)$ Å
		$c = 10.34(3)$ Å
		$\beta = 104.07(17)°$
	Volume	$1246(6)$ Å^3
	Z	2
	Radiation	MoK_α ($\lambda = 0.71073$ Å)
	Independent reflections	1712 ($R_{int} = 8.81\%$)
	Observed reflections	1176 ($F > 6.0\sigma(F)$)
Solution and refinement	Quantity minimized	$\Sigma w(F_o - F_c)^2$
	Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0000F^2$
	Number of parameters refined	152
	Final R indices (obs. data)	$R = 14.53\%$, $wR = 13.20\%$
	Goodness-of-fit	11.74
	Largest difference peak	1.29 eÅ^{-3}
	Largest difference hole	-1.89 eÅ^{-3}

$NaClO_4$ were used for the calibration of the cell, taking into consideration the evenutal correction for $[H^+]$ and $[OH^-]$ junction potentials. The number of experimental points was between 80 and 100. The equilibrium constants were obtained with our program KONST [8] or with SUPERQUAD [9].

The spectra were measured with a *Kontron-Uvikon-810* spectrophotometer.

A concentrated (*ca.* 1M) clear soln. of the complex $[Cu(SO_4)(Me_6tren)]\cdot H_2O$ was prepared by mixing a weighed amount of the amine with the equimolar quantity of $CuSO_4\cdot 5H_2O$ (*Merck*) in H_2O. Crystals were obtained by slow evaporation. Only at extremely high concentrations, crystals began to grow in a rather uncontrolled manner (the analogous Ni^{II} compound could not be obtained in crystalline form; either a glass or a more or less amorphous powder resulted). Since the crystals were unstable in air under irradiation, they were mounted in a glass capillary. The exper. conditions used for the X-ray crystal-structure determination and a summary of the data are given in *Table 1*. It is possible that the crystallographic mirror plane of the molecule actually represents a pseudosymmetry and that the true local space group is $P2_1$. Striations observed under the polarizing microscope support the hypothesis that the mirror plane is not a symmetry of the space group but a twinning plane. However, several attempts with restrained as well as uncontstrained models in $P2_1$ did not yield any improvement of the unsatisfactory situation. Therefore, the data of the average structure in $P2_1/m$ are presented.

Results and Discussion. – The stepwise logarithmic protonation constants log K_p of the two amines are reported in *Table 2*. For the same value of p, the logarithms for Me_6tren show a decrease relative to tren which goes from 0.29 for $p = 1$ to 0.56 and 0.745 for $p = 2$ and 3, respectively. This can be explained by the replacement of all the tren H-atoms bound to the N-atoms by Me groups [11][1]. The data for tren at different I are quite similar (*Table 2*), implying that, in the two ionic media, there is a partial compensation of the activity coefficient ratios of the species appearing in the appropriate protonation constants.

The two ligands tren and Me_6tren are able to form two 1:1 complexes $[ML]^{2+}$ and $[M(HL)]^{3+}$, in which four and three N-atoms, respectively, are coordinated to the metal center. The corresponding stability constants are summarized in *Table 3* where data for another terdentate ligand, the linear triethylenetetramine ($H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$, trien), are also included [12]. The stability constants for both series of complexes $[ML]^{2+}$ and $[M(HL)]^{3+}$ show that the largest values are given by tren, the only exception being those for Cu^{2+} and trien. Because of the higher basicity of trien (30.41) relative to tren (29.25) and Me_6tren (27.62), as measured by the sum of the logarithms of their stepwise protonation constants (given in parenthesis), one would expect the formation of the more stable complexes with the former ligand. The loss of stability due to steric strain is remarkable in the case of accumulation of chelate rings of the same type and, presumably, leads to a destabilization of the coordinate bonds [13]. The stability constant for Me_6tren, relative to tren, for the same metal ion, is several

Table 2. *Protonation Constants* K_p $(= [H_pL]/[H][H_{p-1}L])$ *of tren and* Me_6*tren at* $I = 1$ $(NaClO_4)$ *and 25°.* In parenthesis three times the standard deviation in the last digit(s).

Ligand	log K_1	log K_2	log K_3
Me_6tren	10.13(1)	9.32(1)	8.17(1)
tren	10.42(1)	9.88(1)	8.915(5)
tren[a])	10.39	9.84	8.79

[a]) Data for $I = 0.1$ (KCl) [10].

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[1]) The log K_p values obtained using the data given by *Clark* and *Perrin* [11] for 25° and $I \to 0$ are for tren log $K_1 = 10.15$, log $K_2 = 8.62$, and log $K_3 = 8.97$ and for Me_6tren 9.85, 9.34, and 8.70, respectively. For log K_1 – log K_3 one obtains 1.18 and 1.15 instead of the experimental values 1.5 and 2.0.

orders of magnitude lower. The lowest difference in log K_{ML} is found for Cu^{2+} (3.93), followed by Co^{2+} (4.55), Cd^{2+} (5.03), Zn^{2+} (5.25), and Ni^{2+} (7.81). This could reflect the reluctance of the central metal ion in the case of Me_6tren to give a 1:1 complex with trigonal bipyramidal structure in the 1:1 complexes. In the case of Ni^{2+}, the value of K_{ML} and $K_{M(HL)}$ have decreased so strongly that the 'natural' sequence of the values $Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ [14] is not followed. The existence of tren complexes with coordination number 5 for some of the metal ions in *Table 3* was already postulated or observed [13] [15], and the decrease of K_{ML} can be attributed to strain due to the presence of the bulky Me group, as well as to an increased endothermic dehydration of the metal ion [4]. The spectra of solutions of the pentacoordinated 1:1 complexes of Co^{2+}, Ni^{2+}, and Cu^{2+} with Me_6tren in $C_2H_5NO_2$ and $CHCl_3$ [5] are very similar to the spectra of the corresponding complexes in aqueous solution for which the coordination number (c.n.) 5 can be assumed.

Additional information could be obtained by considering the thermodynamic functions for the formation of the complexes in solution. Tripodal ligands can occupy only four coordination sites on the metal ion, but the presence of voluminous substituents can decrease its normal coordination number. As mentioned by *Ciampolini* and *Nardi* [5], the geometry of Me_6tren is such that the three Me_2N groups are constrained to occupy the corners of an equilateral triangle with the metal ion at its center. As no space for other ligands in the plane of the three Me_2N groups is available, octahedral or square-pyramidal structures cannot be formed. However, in solution, the coordination sites not occupied by the organic ligand can be taken by H_2O molecules. In the case of tren and

Table 3. *Stability Constants of the Complexes* $[ML]^{2+}$ (K_{ML} = [ML]/([M][L]) *and* $[M(HL)]^{3+}$ ($K_{M(HL)}$ = [M(HL)]/([M][HL]) *at* I = *1 and 25°*.
In parenthesis three times the standard deviation in the last digit(s).

Complex	Ligand L	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
$[ML]^{2+}$	Me_6tren	8.53(3)	7.14(4)	15.65(3)	9.75(4)	7.32(3)
	tren	13.08(4)	14.95(4)	19.58(3)	15.00(4)	12.35(3)
	trien[a])	11.31	14.45	20.90	12.14	11.12
$[M(HL)]^{3+}$	Me_6tren	4.28(3)	3.77(4)	9.53(4)	5.31(4)	
	tren	8.47(4)		13.22(4)		7.56(4)
	trien[a])	6.66	8.93	14.10	7.13	6.65

[a]) For $I = 1$ (KNO_3).

Table 4. *p*K *Values* (±0.05) *of the Aquametal Ions and of the 1:1 Complexes with Tripodal Tetramines, as Monoprotonic Acids*

Metal complex	*I*	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ref.
$[M(OH_2)_6]^{2+}$	var.	9.8	10.3	7.8	9.5	–	[16]
$[M(Me_6tren)H_2O]^{2+}$[a])	1	8.6	9.6	8.1	8.95	8.6	this work
$[M(tren)H_2O]^{2+}$[a])	1	9.75	> 11	9.4	10.4	10.9	this work
$[M(tpa)H_2O]^{2+}$[b])	0.1	8.54	> 11	7.4	8.03	> 11	[15]
$[M(tla)H_2O]^{2+}$[b])	0.1	9.66	> 11	8.04	7.71	9.88	[15]

[a]) Further values for $[M(tren)H_2O]^{2+}$: Co^{2+} 10.22, Cu^{2+} 9.32, and Zn^{2+} 10.26; for $[M(Me_6tren)H_2O]^{2+}$ Co^{2+} 8.80, Ni^{2+} 9.53, Cu^{2+} 8.52, and Zn^{2+} 9.00 at $I = 1$ ($NaClO_4$) and 25° [16].

[b]) tpa = tris[(pyridin-2-yl)methyl]amine; tla = tris[(6-methylpyridin-2-yl)methyl]amine.

Me_6tren, the 1:1 complexes contain at least one coordination site for a H_2O molecule which can then act as a monoprotonic acid. The pK values for the 1:1 complexes of these two tetramines are given in *Table 4* together with those for the aquametal ions and the 1:1 complexes of two tripodal tetramines containing each three pyridine N-atoms (*i.e.*, tpa = tris[(pyridin-2-yl)methyl]amine and tla = tris[(6-methylpyridin-2-yl)methyl]-amine).

For complexes containing ligands different from H_2O, one generally finds an increase of the pK value also with respect to the aquametal ion, with an increase of the number of bound N-atoms [17]. This is normally valid, if no change in the c.n. of the aquametal ion occurs. This behaviour is not followed if the c.n. of the central ion changes. Thus, using ligands promoting a decrease in c.n., a decrease of the pK value is favoured. The data of *Table 4* show that, in several cases, there is a decrease of the value of pK with respect to the aquametal ion, as expected for a c.n. lower than 6. This could be considered the normal case, in agreement with the interpretation of the thermodynamic data for complex formation, the spectral data, and the X-ray crystal structure of their complexes. An exception is Ni^{2+}, which mainly prefers an octahedral arrangement and is forced only with Me_6tren to form a complex with c.n. 5. This is also in agreement with the octahedral structure of the 1:1 complex found in the crystalline salts of tren [18], tpa, and tla [19]. For Cu^{2+} and Zn^{2+} with tren, the 1:1 complexes in solution could show an equilibrium between species with c.n. 6 and 5, to explain their pK values, in agreement with the other experimental data. For the larger Cd^{2+}, equilibrium data with polyamines are very scarce, and no useful spectral data can be obtained. It is very likely that only the Me_6tren complex has c.n. 5. In this context, in nature one finds only in the case of Zn^{2+} two metalloenzymes (carboxypeptidase [20] and carbonic anhydrase [21]) which are able to form tetrahedral complexes which also contain a coordinated H_2O molecule with pK values of *ca.* 7. Indeed, complexes with tridentate ligands show pK values larger than 10 [13].

Our efforts to determine the X-ray crystal structures of complexes with Me_6tren was successful only in the case of Cu^{II}. The *Figure* shows an ORTEP view of $[Cu(SO_4)(Me_6tren)]$ in which the central metal ion has the expected pentacoordination, also found in the corresponding bromide salt which was obtained from absolute MeOH

Table 5. *Comparison of Distances and Angles of the CuN_4X Cores* (X = Br [22] and O) *with e.s.d.'s*

	Distances [Å]			Angles [°]	
	X = Br	X = O		X = Br	X = O
Cu–X	2.393(3)	1.91(2)	N(1)–Cu–N(2)	84.7(5)	82.8(6)
Cu–N(1)	2.07(1)	2.03(2)	N(2)–Cu–Br(1)	95.3(4)	94.2(6)
Cu–N(2)	2.14(1)	2.18(2)	N(2)–Cu–N(2′)	119.1(6)	120.1(5)
N(1)–C(1)	1.47(2)	1.47(3)	Cu–N(1)–C(1)	108(1)	112(1)
C(1)–C(2)	1.52(2)	1.37(4)	C(1)–N(1)–C(1′)	111(1)	108(1)
C(2)–N(2)	1.49(2)	1.38(3)	N(1)–C(1)–C(2)	111(1)	114(2)
N(2)–C(3)	1.50(2)	1.41(2)	C(1)–C(2)–N(2)	108(1)	125(3)
N(2)–C(4)	1.47(2)	1.46(3)	C(2)–N(2)–C(3)	109(1)	111(2)
			C(2)–N(2)–C(4)	108(1)	110(2)
			C(3)–N(2)–C(4)	108(1)	107(2)
			Cu–N(2)–C(3)	116(1)	111(2)
			Cu–N(2)–C(4)	111(1)	111(1)
			Cu–N(2)–C(2)	104(1)	105(2)

[22]. Only the distances and the angles of the CuN_4O core are in reasonable agreement with the data of *Di Vaira* and *Orioli* [22] for the corresponding bromide salt (*Table 5*). All other distances are very much shorter due to extensive disorder (*cf. Fig.*, where 20% allipsoids instead of the usual 50% ellipsoids are shown). This disorder may further explain some of the difficulties encountered during crystallization and the high final *R* value.

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