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Mixed Ligand Complexes of 3,3'-diaminodipropylamine and Ethylenediamine or 1,3-diaminopropane with Copper(II)

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Preparations of new mixed ligand complexes of 3,3'–diaminodipropylamine (dpt) and ethylenediamine (en) or 1,3–diaminopropane (tn) with copper(II) of the type $[Cu(dpt)(L)]X_2$ *(where L is en, tn; X is* Cl^-, Br^-, I^-, ClO_4^-*) are described and their infrared, electronic spectra and magnetic susceptibilities are reported. The metal seems to be five-coordinate with a pyramidal square configuration.*

Introduction

Gert G. Schlessinger[1] studied a series of Co^{III} complexes of the following types:

$$[Co(A)(B)(NO_2)](NO_2)_2, [Co(B)_2(NO_2)_2](NO_2) \text{ and } [Co(A)(B)(Cl)]\ Cl_2$$

where A is diethylenetriamine(den); dipropylenetriamine(dpn); 3,3'–diaminodipropylamine(dpt); N,Nbis-(3–aminopropyl)methylamine(Medpt); and B stands for ethylenediamine (en); 1,3–diaminopropane(tn); 1, 2–diaminopropane(pn). This author has found that the amines, Medpt and dpt, show a normal tridenticity in only two of the mentioned complexes. Infact, these ligands seems to be mono or bi-dentate in the majority of cases. The odd behavior of these two ligands, as the author has pointed out, requires further studies.

N.F. Curtis and co-workers[2] isolated mononuclear and polynuclear compounds of dpt. The I.R. spectra of mononuclear $Cu(dpt)_2(ClO_4)_2$ and $Zn(dpt)_2(ClO_4)_2$ show a structure with non-co-ordinate primary amine groups.

Nasanen *et al.*[3] determined the stability constants of mixed copper(II) complexes of en, tn, pn, N,N'–diethylenediamine from pH titration data at 25°C.

It is known that six membered dpt chelate rings are less stable than five membered den chelate rings[4] and the stability of these dpt five-coordinated complexes in aqueous solution increases in the order:[5]

$$Mn < Fe \cong Ni < Co < Zn < Cu$$

On the other hand, the ligand strengths of the amines studied by Schlessinger[1] are in approssimate accord with the steric strain energy requirements:

$$den \geqslant dpn > pn \geqslant en > tn > dpt > Medpt$$

We have prepared a series of complexes of general formula $[Cu(dpt)(L)]X_2$ where L is en or tn and X stands for Cl^-, Br^-, I^-, and ClO_4^- in order to study the influence of the anion and the ligands on the stereochemistry and the denticity of dpt in our copper(II) complexes.

Experimental Section

Materials. Ethylenediamine, 1,3–diaminopropane and 3,3'–diaminodipropylamine were commercially available as $CuCl_2 . 2H_2O$, $CuSO_4 . 5H_2O$ and KI. $Ba(SCN)_2$, $Cu(ClO_2)_4 . 6H_2O$ and $CuBr_2$ were prepared according to literature methods.

$[Cu(dpt)(L)]Cl_2$, $[Cu(dpt)(L)]Br_2$, and $[Cu(dpt)(L)](ClO_4)_2$. 3,3'–diaminodipropylamine (13 mmoles) and ethylenediamine or 1,3–diaminopropane (13 mmoles) were added to a hot methanolic solution of 10 mmoles of $CuCl_2 . 2H_2O$ (or $CuBr_2$ or $Cu(ClO_4)_2 . 6H_2O$) and the mixture was heated for 5 min. The complex obtained, on cooling the filtrate, was crystallised from methanol and dried in a vacuum oven at 110°C.

$[Cu(dpt)(L)]I_2$. 3,3'–diaminodipropylamine (26 mmoles) and ethylenediamine or 1,3–diaminopropane (26 mmoles) were added to $CuCl_2 . 2H_2O$ dissolved in an hot ethanol-water mixture. A warm solution of KI (40 mmoles) was then added. The addiction of isopropylic alcohol to the cooled mixture produced a precipitate. The product crystallised three times from ethanol-isopropylic alcohol, was dried in a vacuum oven at 90°C.

Analyses. Cu contents were determined electrolitically; halogens by the Volhards method; C,H,N, were analysed with a Perkin-Elmer 240 Analyser.

Physical measurements. Absorption spectra were recorded in the range 8000-25000 cm^{-1} at room tem-

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Table I. Physical and analytical data of $[Cu(dpt)(L)]X_2$ complexes.

			N	C	H	N	C	H	% Metal		μ_{eff}(°C) [a]
Compound	Colour	Mp, °C		Found			Calcd.		Calcd.	Found	(B.M.)
$[Cu(dpt)(en)]Cl_2$	Blue green	184	21.5	29.5	7.7	21.4	29.4	7.6	19.5	19.8	1.70 (24.8)
$[Cu(dpt)(en)]Br_2$	Pale blue	180	16.9	23.2	6.1	16.6	22.9	6.1	15.3	15.3	1.78 (24.8)
$[Cu(dpt)(en)]I_2$	Light blue	183	13.8	18.9	4.9	13.6	18.8	4.8	12.5	12.5	1.74 (25.0)
$[Cu(dpt)(en)](ClO_4)_2$	Light blue	200	15.4	21.2	5.5	15.3	20.9	5.5	14.0	13.9	1.83 (24.7)
$[Cu(dpt)(tn)]Cl_2 . H_2O$	Blue	168	19.6	30.2	7.6	19.3	29.9	7.5	17.8	17.7	1.70 (24.8)
$[Cu(dpt)(tn)]Br_2$	Blue	135	16.3	25.2	6.0	16.1	25.2	5.8	14.8	15.1	1.71 (24.8)
$[Cu(dpt)(tn)]I_2$	Light blue	156	13.4	20.7	5.2	13.1	20.5	5.5	12.2	12.0	1.75 (25.0)
$[Cu(dpt)(tn)](ClO_4)_2$	Green blue	186	15.0	23.1	5.8	14.9	23.1	5.7	13.6	13.5	1.71 (24.8)

[a] Diamagnetic corrections were calculated from Pascal's constants (B.N. Figgis, J. Lewis, Modern Coordination Chemistry, pag. 403 (1960).

Table II. Infrared spectra of $[Cu(dpt)(L)]X_2$ complexes in KBr plates, 4000 to 450 cm^{-1}; in CsI plates 450 to 200 cm^{-1}.

$[Cu(dpt)(en)]Cl_2$	3320 m, 3180 w, 3140 m, 2725 m, 1590 s, 1290 m, 1255 m, 1155 s, 1095 w, 1070 m, 1040 m, 1015 m, 965 w, 915 s, 880 m, 820 w, 800 m, 770 sh, 520 m, 485 m, 435 w.
$[Cu(dpt)(en)]Br_2$	3318 m, 3260 sh, 3210 m, 3140 m, 2720 w, 1600 vs, 1290 s, 1255 s, 1225 s, 1160 s, 1065 s, 1040 s, 1015 vs, 960 m, 950 w, 915 s, 875 s, 820 m, 800 s, 650 w, 585 w, 515 s, 433 s.
$[Cu(dpt)(en)]I_2$	3320 sh, 3220 sh, 3195 m, 3130 s, 2720 m, 1580 m, 1310 m, 1220 m, 1155 m, 1070 m, 1040 m, 980 m, 890 w, 805 w, 545 w, 510 m, 428 w.
$[Cu(dpt)(en)](ClO_4)_2$	3340 m, 3280 m, 3185 m, 2730 m, 1600 s, 1300 vw, 1150 m, 1078 br, 975 w, 920 w. 890 w, 865 w, 815 vw, 770 sh, 620 s, 510 m, 428 w.
$[Cu(dpt)(tn)]Cl_2 . H_2O$	3380 m, 3340 sh, 3240 sh, 3210 w, 3125 m, 2725 w, 1650 m, 1585 s, 1330 m, 1320 w, 1298 w, 1280 m, 1250 m, 1225 s, 1160 vs, 1110 m, 1098 w, 1070 w, 1045 vs, 950 w, 915 s, 900 s, 800 m, 660 m, 625 m, 560 w, 510 w, 480 m.
$[Cu(dpt)(tn)]Br_2$	3345 w, 3200 m, 3125 m, 2730 m, 1590 s, 1320 w, 1260 w, 1225 m, 1155 m, 1110 w, 1070 m, 1030 w, 1015 w, 980 w, 955 w, 925 m, 900 m, 870 w, 815 w, 790 m, 660 w, 500 m, 440 vw.
$[Cu(dpt)(tn)]I_2$	3340 sh, 3210 m, 3130 m, 2720 vw, 1580 s, 1290 w. 1255 m, 1220 m, 1155 s, 1095 m ,1070 m, 1060 m, 1050 w, 905 w, 895 w, 870 sh, 795 m, 690 w, 650 w, 618 w, 495 w, 450 vw.
$[Cu(dpt)(tn)]ClO_4)_2$	3320 s, 3280 s, 3180 m, 2730 m, 1600 s, 1300 vw, 1158 w, 1078 br, 975 w, 920 w, 898 m; 870 vw, 800 w, 765 w, 625 s, 545 w, 498 m, 428 vw.

Table III. Principal infrared bands of $[Cu(dpt)(L)]X_2$ complexes.

Compound	$\nu(OH)$	Sym. $\nu(NH_2)$	Asym. $\nu(NH_2)$	$\nu(NH)$	$\delta(HOH)$	$\delta(NH_2)$	a.str. ClO_4^-	Sym.str. ClO_4^-	a.bend. ClO_4^-
$[Cu(dpt)(en)]Cl_2$		3320 m	3260 sh	3180 w, 3140 m		1590 s			
$[Cu(dpt)(en)]Br_2$		3318 m	3260 sh 3210 m	3140 m		1600 vs			
$[Cu(dpt)(en)]I_2$		3320 sh	3220 sh	3195 m 3130 s		1580 m			
$[Cu(dpt)(en)](ClO_4)_2$		3340 m	3280 m	3185 m		1600 s	1078 br	920 w	620 s
$[Cu(dpt)(tn)]Cl_2 . H_2O$	3380 m	3340 sh	3240 sh 3210 w	3125 m	1650 m	1585 m			
$[Cu(dpt)(tn)]Br_2$		3345 w	3200 m	3125 m		1590 s			
$[Cu(dpt)(tn)]I_2$		3340 sh	3210 m	3130 m		1580 s			
$[Cu(dpt)(tn)](ClO_4)_2$		3320 s	3280 s	3180 m		1600 s	1075 br	920w	625 s

perature with a Beckman DK2-A Spectrophotometer with 1 cm silica cells. The reflectance spectra were obtained by a method analogous to that reported by Venanzi.[6]

The I.R. spectra from 450 at 4000 cm^{-1} were recorded on Nujol mulls between KBr plates with a Perkin-Elmer Model 457 Spectrophotometer. In the range 200-450 cm^{-1} the spectra were further studied between thin polyethylene sheets with a Perkin-Elmer Model 225; atmospheric water was removed from the spectrophotometer housing a stream of dry nitrogen.

Molar conductivities were measured at 25 ± 0.1°C with a WTW Model LBR/B conductance bridge. The concentrations of the solution were of the order 10^{-3} M in CH_3OH.

Magnetic measurements were obtained for solid samples by the Gouy method using a Gouy tube that was calibrated with freshly distilled water and $[Ni(en)_3]S_2O_3$.

Results and Discussion

The analytical data and the physical properties of these compounds are reported in Table I. The complexes obtained are all crystalline and intensely coloured; they are very soluble in methanol and ethanol, and slightly soluble in butylic and isopropylic alcohol. The magnetic moments at room temperature are those typical of Cu^{II} complexes.

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Table IV. Electronic spectra and molar conductances of $[Cu(dpt)(L)]X_2$ complexes.

Compound		Electronic spectra (kK) [a]	Molar conductance [c] $cm^2 . ohm^{-1} mol^{-1}$
$[Cu(dpt)(en)]Cl_2$	solid	14.1, ~ 11.0 sh [b]	
	CH_3OH	15.3(123), ~ 12.1 sh	120
$[Cu(dpt)(en)]Br_2$	solid	13.8, ~ 12.0 sh	
	CH_3OH	15.0(142), ~ 11.8 sh	129
$[Cu(dpt)(en)]I_2$	solid	14.4, ~ 11.4 sh	
	CH_3OH	15.0(165), ~ 11.4 sh	137
$[Cu(dpt)(en)](ClO_4)_2$	solid	15.4, ~ 11.4 sh	
	CH_3OH	14.8(130), ~ 12.5 sh	159
$[Cu(dpt)(tn)]Cl_2 . H_2O$	solid	14.6, ~ 12.3 sh	
	CH_3OH	15.4(161), ~ 12.8 sh	120
$[Cu(dpt)(tn)]Br_2$	solid	15.0, ~ 13.7 sh	
	CH_3OH	15.7(166)	113
$[Cu(dpt)(tn)]I_2$	solid	14.3, ~ 11.1 sh	
	CH_3OH	14.8(175), ~ 13.6 sh	128
$[Cu(dpt)(tn)](ClO_4)_2$	solid	14.0, ~ 11.5 sh	
	CH_3OH	14.1(132), ~ 11.5 sh	162

[a] The values in parenthesis are the molar extinction coefficents. [b] sh, shoulder. [c] For *ca.* 10^{-3} *M* solutions at 25°C. Reference values in CH_3OH are: $[(C_2H_5)_4]N$ I, 103; $[(C_4H_9)_4]N$ Br, 88; NaCl, 95; for 1 : 1 electrolytes and $BaCl_2$, 126 and $Ba(ClO_4)_2$, 160 for 1:2 electrolytes.

The conductivity values are typical of uni-bivalent electrolytes, as can be deduced by the value of the reference electrolyte in the same solvent and in the same concentration range (Table IV). This fact seems to suggest a coordination number five for the copper ion. These complexes therefore, should be formulated as $[Cu(dpt)(L)]X_2$.

Conclusive evidences concernieng the coordination number and the stereochemistry of these compounds are obtained by infrared and electronic spectra data.

The infrared bands are listed in Table II. The infrared transition bands assigned to the stretching and deformation of the amino-groups, those due to the perchlorate group vibration and to the H_2O bands are listed in Table III. The single band (occasionally a doublet) at 3340-3320 cm^{-1} can be assigned to sym-

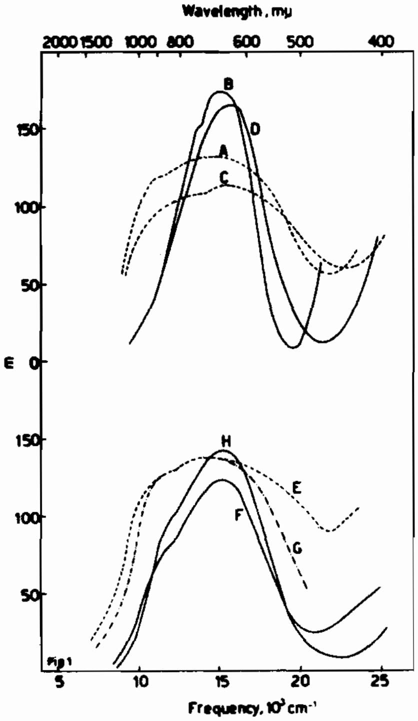

Figure 1. Reflectance spectra of:
$[Cu(dpt)(tn)]I_2$ (A); $[Cu(dpt)(tn)]Br_2$ (C); $[Cu(dpt)(en)]Cl_2$ (E); $[Cu(dpt)(en)]Br_2$ (G);

and absorption spectra of:
$[Cu(dpt)(tn)I]_2$ (B); $[Cu(dpt)(tn)]Br_2$ (D); $[Cu(dpt)(en)]Cl_2$ (F); $[Cu(dpt)(en)]Br_2$ (H) in methanolic solution.

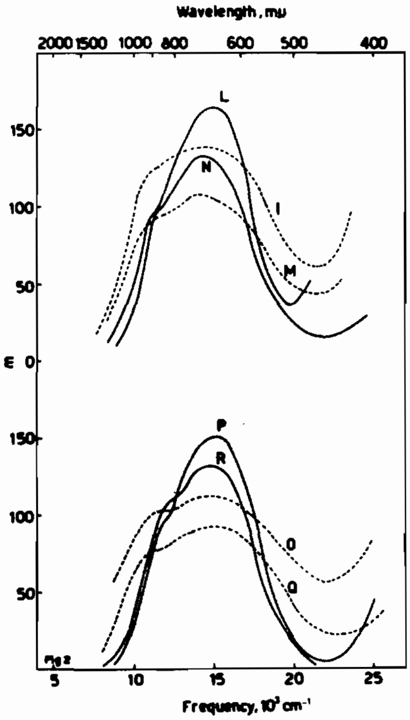

Figure 2. Reflectance spectra of:
$[Cu(dpt)(en)]I_2$ (I); $[Cu(dpt)(tn)](ClO_4)_2$ (M); $[Cu(dpt)(tn)]Cl_2 . H_2O$ (O); $[Cu(dpt)(en)](ClO_4)_2$ (Q);

and absorption spectra of:
$[Cu(dpt)(en)]I_2$ (L); $[Cu(dpt)(tn)](ClO_4)_2$ (N); $[Cu(dpt)(tn)]Cl_2 . H_2O$ (P); $[Cu(dpt)(en)](ClO_4)_2$ (R) in methanolic solution.

metric $\nu(NH_2)$; the bands in the region 3300-3200 cm^{-1} to asymmetric $\nu(NH_2)$. A single band near 3170 cm^{-1} is usually assigned to the $\nu(NH)$ stretching of a secondary amino group (possibly plus uncoupled ν-(NH) of the primary amino group), the band near 1600 cm^{-1} to $\delta(NH_2)$.[2] It appear that all amino groups of these complexes are coordinated to the metal which is therefore five-coordinate. The bands assigned to the perchlorate group are: the antisymmetric stretching at *ca.* 1078-1075 cm^{-1}, the antisymmetric bending at 620 cm^{-1} and the non-degenerate symmetrical stretching near 920 cm^{-1}. These bands are typical of compounds with free ClO_4^-.[7]

Furthermore, we can see in Table II that the complexes $[Cu(dpt)(L)]X_2$ do not show the typical Cu-halogen bands which occur at 215-291 cm^{-1}.[8]

The data of electronic spectra are shown in Table IV. The spectra of the solids have a large asymmetric band with a shoulder at lower wave number (Figures 1 and 2). These spectra have generally absorption maxima in the range 13.0-15.4 kK and the shoulder in the range 11.0-13.7 kK. This pattern is similar to that presented by the diffuse reflectance spectrum of penta-coordinate $CudpeaBr_2$, where dpea stands for bis–[2–(2–pyridil)ethyl]amine[9] (maximum at 13.3 and shoulder at 10.0 kK) and of square pyramidal $[Cu(tpt)(NCS)](CNS)$,[10] where tpt is tris(2-aminopropyl)amine (with maximum at 15.5 and shoulder at 13.0 kK). This strongly suggest that the examinated complexes are five coordinated and probably have a square pyramidal configuration. In all cases, the solution spectra are similar to those of the corresponding solid compounds. They also are similar to the solution spectrum of $[Cu(tpt)(NCS)](CNS)$,[8] which have maximum at 14.8 ($\varepsilon = 184$) and shoulder at 13.5 kK.

The close similarity between solid and solution spectra and the conductivities values clearly indicate that passing from the solution to the solid state the configuration of the complexes does not change appreciably.

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