Transition-metal Complexes of *NNN'N''N'''N'''*-Hexamethyl-3,6-diazaoctane-1,8-diamine. Part I. Nickel(II) and Copper(II) Compounds

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A series of compounds have been prepared of general formula M(trien)X_2 (trien = *NNN'N''N'''N'''*-hexamethyl-3,6-diazaoctane-1,8-diamine) for M = Ni^{II}, X = Cl, Br, NO_3, SCN, ClO_4, or BPh_4; for M = Cu^{II}, X = Br, SCN, $\frac{1}{2}SO_4$, ClO_4, BPh_4. The i.r. and electronic spectra, the magnetic moments, and the conductivities of the compounds have been recorded and used to elucidate their structure; nickel compounds with X = Cl, Br, NO_3, and SCN are octahedral, with X = ClO_4 and BPh_4 square planar; copper compounds are five-co-ordinate with exception for X = ClO_4 and BPh_4.

TRIETHYLENETETRA-AMINE (3,6-DIAZAOCTANE-1,8-DIAMINE) forms four-, five-, and six-co-ordinate complexes.[1-5] It seemed therefore of interest to synthesise *NNN'N''N'''N'''*-hexamethyl-3,6-diazoctane-1,8-diamine in order to see whether this bulkier ligand, forms compounds having a different stereochemistry.

EXPERIMENTAL

Synthesis of NNN'N''N'''N'''*-Hexamethyl-*3,6-*diazaoctane-*1,8-*diamine* (*trien*).—This compound was prepared by methylation of the parent amine with a mixture of formic acid and formaldehyde.[2] The amine distilled at 120 °C/0·2 mmHg, n_D 1·463 (Found: C, 62·2; H, 12·8; N, 24·3. Calc. for $C_{12}H_{30}N_4$: C, 62·6; H, 13·0; N, 24·3%).

Preparation of Trien Complexes.—All complexes, with the exception of M(trien)$(BPh_4)_2$ were prepared by the same general method. A solution of trien (12 mmol) in methanol (50 ml) was mixed with a hot methanolic solution (50 ml) of the appropriate metal salt (11 mmol). Acetone (20 ml) or isopropyl alcohol was added to the solution in order to promote crystallization. The complex, so obtained, was recrystallized from methanol and dried *in vacuo* at 70—80 °C.

Preparation of M(trien)$(BPh_4)_2$.—The tetraphenylborates were obtained by dropwise addition of trien (6 mmol) to hot aqueous $NiCl_2,6H_2O$ (or $CuCl_2,2H_2O$) (5 mmol); hot aqueous Na[BPh_4] (10 mmol) was then added dropwise to the mixture.

Analyses for the complexes, all of which were satisfactory, are deposited with the N.L.L. as Supplementary Publication no. 20361 (4 pp).†

Physical Measurements.—Absorption spectra were recorded in the range 8000—30,000 cm^{-1} at room temperature with a Beckman DK 2A Spectrophotometer with 1- and 4-cm long silica cells for the copper and nickel compounds, respectively.

The reflectance spectra were obtained by a method analogous to that reported by Venanzi and his co-workers.[6] The i.r. spectra in the range 4000—450 cm^{-1} were recorded for Nujol or hexachlorobutadiene mulls between KBr plates with a Perkin-Elmer model 457 spectrophotometer. In the range 450—200 cm^{-1} the spectra were further studied between thin polyethylene sheets with a Perkin-Elmer spectrophotometer model 225; atmospheric water was removed from the spectrophotometer housing with a stream of dry nitrogen. Details of the spectra are deposited with the N.L.L. as Supplementary Publication No. 20361 (4 pp.).†

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† For details of Supplementary Publications see Notice to Authors No. 7, in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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Molar conductivities were measured at 25 ± 0·1 °C with a W.T.W. model LBR/B conductance bridge. The concentrations of the solution were 10^{-3}M in MeOH and $EtNO_2$. Magnetic measurements were carried out by Gouy's method and the molecular susceptibilities were corrected for the diamagnetism of the component atoms by using Pascal's constants.[7] The Gouy tube was calibrated with distilled water and $[Ni(en)_3]S_2O_3$.

RESULTS AND DISCUSSION

All the compounds are crystalline, except the tetraphenylborates which were powders. Generally, they are soluble in MeOH, EtOH, and $EtNO_2$, less soluble in higher alcohols, and insoluble in nonpolar solvents; however, $Ni(trien)Cl_2,2{\cdot}5H_2O$ is only sparingly soluble in MeOH and $Ni(trien)(ClO_4)_2,2H_2O$ is insoluble in common organic solvents. Further, the tetraphenylborate salts are soluble in MeOH and sparingly soluble in $EtNO_2$.

Maxima for the C–H stretching mode of the $N{-}CH_3$ groups, fall in the range 2990—2760 cm^{-1} for trien and generally in the range 3020—2840 cm^{-1} for the complexes. Trien shows bands at 2970, 2940, 2850, 2815, and 2760 cm^{-1}. According to Baldwin and Leigh [8] the spectrum of an organic base containing the $N{-}CH_3$ groups, shows strong or medium bands between 2820—2760 cm^{-1}, which are characteristic of the C–H stretching vibrations of the $N{-}CH_3$ group, provided that the lone-pair electrons of the nitrogen atom is not involved in a bond. On co-ordination these bands disappear. Indeed the compounds $M(trien)X_2$ show bands in the range 3020—2840 cm^{-1} and generally no bands between 2820—2760 cm^{-1}.

The bands which occur in the perchlorate of nickel and copper derivatives are typical for the non-bonded perchlorate group.[9]

The medium absorption bands, ν(OH) and δ(HOH), in $Ni(trien)(ClO_4)_2,2H_2O$ and $Cu(trien)SO_4,H_2O$ respectively confirm the presence of unco-ordinated water; the water is lost at 110 °C *in vacuo*. The i.r. spectra of $Ni(trien)Cl_2,2{\cdot}5H_2O$, $Ni(trien)Br_2,4H_2O$, and $Ni(trien)(NO_3)_2,H_2O$ show clearly the presence of water. At 110 °C *in vacuo* $Ni(trien)Cl_2,2{\cdot}5H_2O$ loses only 1·5 water molecules, whereas $Ni(trien)Br_2,4H_2O$ loses 3 water molecules; in $Ni(trien)(NO_3)_2,H_2O$ no loss of weight is found, before the compound decomposes. This suggests that the three compounds have one water molecule directly co-ordinated to the metal. Furthermore, the molar conductivity values typical for 1·1 electrolytes (Table) lead to the following formulation: $[Ni(trien)(H_2O)Cl]Cl,1{\cdot}5H_2O$, $[Ni(trien)(H_2O)Br]Br,3H_2O$, and $[Ni(trien)(H_2O)(NO_3)](NO_3)$.

In the thiocyanate copper derivative the absorption band of ν(C–N) is respectively attributed to an *N*-bonded and to a free SCN group.[10] In $Ni(trien)(NCS)_2$ both thiocyanate groups are co-ordinated through nitrogen, a conclusion which is consistent with molar conductivity values [2] (Table). The complex $[Ni(trien)(H_2O)(NO_3)]NO_3$ shows bands typical of a compound, in which monodentate NO_3 and ionic NO_3 are present.[11] In $Cu(trien)SO_4,H_2O$ the polyatomic anion SO_4 is monodentate.[12] In the far-i.r. region, the complexes $M(trien)X_2$ (for $M = Ni^{II}$, X = Cl, Br, NO_3 and for $M = Cu^{II}$, X = Br,$\frac{1}{2}SO_4$) show the typical M–X or M–O bands expected, which usually fall in the range 290—200 cm^{-1}.[13] The thiocyanate compounds show the metal–nitrogen stretching mode involving the nitrogen of the thiocyanate group in the range 250—290 cm^{-1}.[14]

Nickel Complexes.—The magnetic moments at room temperature in the range 2·85—3·05 B.M. are normal values for high-spin nickel paramagnetic complexes. The complexes $[Ni(trien)](ClO_4)_2,2H_2O$ and $[Ni(trien)](BPh_4)_2$ are diamagnetic. The complexes $[Ni(trien)(H_2O)Cl]Cl,1{\cdot}5H_2O$, $[Ni(trien)(H_2O)Br]Br,3H_2O$, $[Ni(trien)(NCS)_2]$, and $[Ni(trien)(H_2O)(NO_3)]NO_3$ exhibit in the solid state and solution state electronic spectra with maxima generally at 8800—9100, 15,200—16,000, and 24,000—25,400 cm^{-1}. The shape of these spectra is typical of octahedral compounds. The values of the frequencies of the first and second band maxima lie between 1·5 and 1·7 (ref. 15) (Table). The $[Ni(trien)](ClO_4)_2,2H_2O$ and $[Ni(trien)](BPh_4)_2$ complexes in the solid state show a large band at 20,000 cm^{-1}, characteristic of square-planar species.[16] The tetraphenylborate derivative shows absorption at 9900, 16,000, and 25,650 cm^{-1}. In solution, therefore, the complex becomes octahedral probably by co-ordination with two molecules of the solvent.[1,9] The molar conductivity values are low for a 1 : 2 electrolyte (Table); this fact seems likely to be due to the low mobility of the large tetraphenylborate ion in solution.[9]

Copper Complexes.—The magnetic moments in the range 1·70—1·90 B.M. are normal values for copper(II) complexes. From the visible spectra and conductivity values it appears that the bromide copper compound is five-co-ordinate, and may be formulated as [Cu(trien)Br]Br. The wavelength of the maximum in the reflectance spectra is comparable with those found for other copper–amine compounds to which a trigonal-bipyramidal structure has been assigned.[17] In contrast the spectrum of $[Cu(trien)SO_4],H_2O$ in the solid state is similar to those of square pyramidal copper–amine compounds.[18] The $[Cu(trien)](ClO_4)_2$ square planar and [Cu(trien)(NCS)](SCN) five-co-ordinate trigonal-bipyramidal complex have been already reported [2] (Table).

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Physical data on nickel and copper complexes

Compound	Colour*	M.p.		Absorption maxima (cm^{-1})	$\frac{\nu_2}{\nu_1}$	Λ_M[d] ($cm^2\,\Omega^{-1}\,mol^{-1}$)
$[Ni(trien)(H_2O)(Cl)](Cl),1{\cdot}5H_2O$ [a]	G	240°	Solid	8800, 15,200 25,400	1·73	
			MeOH			108
$[Ni(trien)(H_2O)(Br)]Br,3H_2O$	G	145	Solid	9000, 15,400, 25,800	1·71	
			MeOH	9000 (16·8) [b], 14,300 (26·0), 23,800 (49·2)	1·59	115
			$EtNO_2$	9000 (38·0), 14,800 (51·0), 24,400 (86), 26,100sh	1·64	50
$[Ni(trien)(NCS)_2]$	G	280	Solid	9100, 16,000, 25,000	1·76	
			MeOH	9150 (22·9), 16,000 (19·2), 25,000 (36·4)	1·75	8
			$EtNO_2$	9100 (21·0), 15,900 (18·0), 24,750 (38·2)	1·75	9
$[Ni(trien)](ClO_4)_2,2H_2O$	R	240(d)	Solid	16,000sh,[c] 20,000		
$[Ni(trien)(H_2O)(NO_3)](NO_3)$	G	230	Solid	9100, 15,650, 25,650	1·72	
			MeOH	10,000 (25·0), 16,000 (50·5), 25,750 (107·0)	1·60	89
			$EtNO_2$	9800 (24·7), 15,000 (47·0), 25,700 (99·0)	1·53	65
$[Ni(trien)](BPh_4)_2$ [e]	P	220	Solid	15,500sh, 20,000		
			MeOH	9500 (25·3), 15,800 (27·8), 25,450 (49·2)	1·66	85
			$EtNO_2$			70
$[Cu(trien)Br]Br$	G	144	Solid	14,800, 16,500sh		
			MeOH	13,800 (266), 15,000sh		83
			$EtNO_2$	13,600 (249)		65
$[Cu(trien)(NCS)](SCN)$	G	145	Solid	14,500, 16,500sh		
			MeOH	15,600 (252), 16,300sh		90
			$EtNO_2$	14,500 (257)		60
$[Cu(trien)SO_4],H_2O$	B	202	Solid	11,000sh, 15,400		
			MeOH	14,600 (194)		7
$[Cu(trien)](ClO_4)_2$	B	242	Solid	17,500		
			MeOH	17,200 (349)		170
			$EtNO_2$	17,700 (274)		107
$[Cu(trien)](BPh_4)_2$ [e]	A	98	Solid	12,300sh, 18,500		
			MeOH	16,150 (149)		80
			$EtNO_2$			65

[a] Sparingly soluble in MeOH. [b] Molar for solutions in parentheses. [c] sh = Shoulder. [d] For solutions 10^{-3}M. The reference values are: 80—115 in CH_3OH; 75—95 in $MeNO_2$; 65—95 in $EtNO_2$; 135—155 in MeCN for electrolytes 1 : 1; 120—180 in MeOH; 150—180 in $MeNO_2$; 119—147 in $EtNO_2$; 250—310 in MeCN for electrolytes 1 : 2 (W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81, and ref. 5). [e] Sparingly soluble in $EtNO_2$.

* G = Green, R = Red, P = Pink, B = Blue, A = Azure.

The electronic spectra of $[Cu(trien)](BPh_4)_2$ are typical for a square-planar compound.[2] The molar conductivity values are low for a 1 : 2 electrolyte (Table) and as for the $[Ni(trien)](BPh_4)_2$ seems due to the low mobility of the tetraphenylborate ion in solution.[9,19]

On the basis of our results for the complexes $M(trien)X_2$ we conclude that *NNN'N''N'''N'''*-hexamethyl-3,6-diazaoctane-1,8-diamine exhibits co-ordination behaviour essentially the same as that of 3,6-diazaoctane-1,8-diamine.[1-3,5,20]

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