Octahedral Complexes of Nickel(II) and Copper(II) with Triethylenetetra-amine

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The preparation and the physical properties of complexes of the type [Ni(trien)(en)]X_2 (trien = triethylenetetra-amine; en = ethylenediamine; X = Cl, Br, I, SCN, NO_3, AcO, ClO_4, and BPh_4 and [Cu(trien)(en)]X_2 (X = ClO_4 and BPh_4) are reported. The results indicate that both in solution and in the solid state the compounds are octahedral and that in solution the racemic mixture is present.

PREVIOUSLY we have described the preparation and properties of some polyamine–copper(II) complexes, including those of the potentially tetradentate compound, triethylenetetra-amine (trien, 1,4,7,10-tetra-azadecane).[1-4] Here we report the characterization of a series of complexes of general formula [Ni(trien)(en)]X_2 (en = ethylenediamine; X = Cl, Br, I, SCN, NO_3, AcO, ClO_4, and BPh_4) and [Cu(trien)(en)]X_2 (X = ClO_4 and BPh_4). Our aim was to establish the stereochemistry of these compounds both in solution and in the solid state; in particular we wished to establish if any of the primary amine groups was weakly co-ordinated as in Cu(dien)$_2$-Br_2,H_2O[5] [dien = 1,4,7-triazaheptane(diethylenetriamine)] or even non-co-ordinated as in Cu(dpt)$_2$(ClO_4)$_2$ and Zn(dpt)$_2$(ClO_4)$_2$ [6] [dpt = 1,5,9-triazanonane (3,3′-diaminodipropylamine)]. Two of the above quoted compounds [Ni(trien)(en)]Cl_2,H_2O and [Ni(trien)(en)](ClO_4)$_2$ have been previously reported but not extensively studied.

EXPERIMENTAL

Triethylenetetra-amine *purum*, ethylenediamine *purum*, $NiCl_2$,$6H_2O$, $NiSO_4$,$7H_2O$, Ni(OAc)$_2$,$4H_2O$, Ni(NO_3)$_2$,$6H_2O$, $CuCl_2$,$2H_2O$, and $NaBPh_4$ were commercially available. Cu(ClO_4)$_2$,$6H_2O$, Ni(ClO_4)$_2$,$6H_2O$, $NiBr_2$, NiI_2, and Ba(SCN)$_2$ were prepared according to literature methods.

Preparation of Complexes.—All complexes, with exception of tetraphenylborates, were prepared by the following method.

To a hot solution of the appropriate metal salt (0·05 mol) in ethanol (150 ml), a solution of trien (0·054 mol, 8 g) in ethanol (25 ml) and one of en (0·054 mol, 4 g) in the same solvent were slowly added. Isopropyl alcohol was added

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[1] R. Barbucci, G. Cialdi, P. Paoletti, and G. Ponticelli, *J. Chem. Soc.* (*A*), 1969, 1775.

[2] R. Barbucci, P. Paoletti, and G. Ponticelli, *J. Chem. Soc.* (*A*), 1971, 1637.

[3] G. Ponticelli and A. Diaz, *Ann. Chim.*, 1971, **61**, 46.

[4] G. Ponticelli, *Inorg. Chim. Acta*, 1971, **5**, 461.

[5] F. S. Stephens, *J. Chem. Soc.* (*A*), 1969, 2233.

[6] N. F. Curtis, R. W. Hay, and Y. M. Curtis, *J. Chem. Soc.* (*A*), 1968, 182.

to the concentrated solution in order to promote crystallization.

All the complexes were recrystallized by adding isopropyl alcohol to a filtered ethanol solution and were dried at 90—100 °C *in vacuo*.

The tetraphenylborate derivatives were obtained by adding, dropwise, en (11 mmol) to a hot solution of 10 mmol of $NiCl_2,6H_2O$ or $CuCl_2,2H_2O$; a hot aqueous solution of $NaBPh_4$ (20 mmol) was then added. The compounds formed were washed many times with water and dried for several days *in vacuo*. The compounds were analysed for nickel or copper electrolytically; and for C, H, and N with a Perkin-Elmer 240 Analyser.

Elrctronic Spectra.—Absorption spectra in methanol were recorded in the range 7000—32,500 cm^{-1} at room temperature using a Beckman DK2A spectrophotometer (4 cm silica cells for Ni and 1 cm silica cells for Cu compounds). The diffuse reflectance spectra were obtained by Venanzi's method.[7]

Infrared Spectra.—The compounds were examined in the range 4000—400 cm^{-1} recording the spectra as Nujol mulls between KBr plates with a Perkin-Elmer 457 spectrophotometer, with exception of tetraphenylborate derivatives which were studied between 4000—200 cm^{-1}.

Conductivity Measurements.—Molar conductivity were measured at $25 \pm 0{\cdot}1$ °C with a WTW model LBR/B conductance bridge.

Polarimetric Measurements.—Polarimetric measurements were carried out at room temperature on aqueous or methanol solutions in the concentration range 10^{-4}—10^{-8}M with the aid of a Lippich Polarimeter, Galileo model MN 602, equipped with 200 mm cells.

RESULTS AND DISCUSSION

Physical and analytical data for compounds $[M(trien)(en)]X_2$ are in Table 1. Attempts to prepare $[Cu(trien)(en)]_2$, (X = Br, I and SCN) led to the formation of five-co-ordinated $[Cu(trien)X]X$ compounds;[8] attempts to obtain solid complexes where X = Cl, AcO, and NO_3 failed because of high solubilities.

Solid compounds are, in general, crystalline, soluble in methanol and ethanol; slightly soluble in isopropyl alcohol and nitromethane and insoluble, except the tetraphenylborate derivatives, in other common solvents. Tetraphenylborates are soluble in acetone, nitrobenzene, acetonitrile and nitroethane and insoluble in water. Acetate and thiocyanate derivatives are hygroscopic.

The molar conductivity values in methanol at 25 °C for 10^{-3}M-solutions fall in the range expected for 1 : 2 electrolytes, as can be deduced by the value of reference compounds in the same solvent at the same concentration.

This fact seems to suggest a co-ordination number of six for copper and nickel ions. These complexes therefore should be formulated as $[M(trien)(en)]X_2$. Conclusive evidence concerning the co-ordination number and the stereochemistry of these complexes are obtained by i.r. and electronic spectra.

The assignments for the stretching and deformation vibration of the i.r. bands of the amino-groups are reported in Table 2. All amino-groups of ligands seem to be directly co-ordinated to the metal as observed in the case of $Ni(dpt)(L)X_2$ complexes[9] (where L = en or 1,3-diaminopropane) because of the negative shifts of $\nu(NH_2)$ and $\nu(NH)$ on passing from the free ligands to the complexes.

In $[Ni(trien)(en)](NO_3)_2$ as in the spectra of many nitrate compounds, there are several bands in the region 2500—1700 cm^{-1}. These weak absorptions could be interpreted as the $(\nu_1 + \nu_3)$ combination, 2390 cm^{-1} and 1760 cm^{-1}, the $(\nu_1 + \nu_4)$ combination.[10]

The i.r. data in Table 2 show that the thiocyanate, nitrate, acetate, perchlorate, and tetraphenylborate groups are present as free anions. Absorption spectra (Table 3) of $[Ni(trien)(en)]X_2$ in methanol have a shape similar to that found in the solid state, except for a shoulder at 12,500 cm^{-1}. This fact indicates that the stereochemistry of the complexes does not change appreciably on dissolution. The electronic spectra of $[Ni(trien)(en)]X_2$ complexes are typical of octahedral compounds[11] and show the characteristic bands. These bands in an O_h symmetry can be assigned to the transition $\nu_1 = {}^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$; $\nu_2 = {}^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$; $\nu_3 = {}^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$, while the shoulder could be assigned to the ${}^3A_2(F) \longrightarrow {}^1E_g(D)$. From these data, D_q values, B', β, and $\frac{\nu_2}{\nu_1}$ values were calculated (Table 4). These results are consistent with an octahedral environment and are in agreement with those obtained by Farago *et al.*[11]

Of the copper compounds only $[Cu(trien)(en)](ClO_4)_2$ and $[Cu(trien)(en)](BPh_4)_2$ were isolated. The fact that the anions are not co-ordinated, and the presence of two free positions makes possible the bonding of ethylenediamine. The failure to prepare $[Cu(trien)(en)]X_2$ compounds, where X = Br, I, or SCN is possibly due to the higher stability of five-co-ordinate complexes of the type $[Cu(trien)X]X$.[8,12] The electronic spectra of $[Cu(trien)(en)](BPh_4)_2$ and of $[Cu(trien)(en)](ClO_4)_2$ have a band with a maximum at 16,550 and 17,500 cm^{-1} respectively (see Figure). These spectra are similar to those of octahedral complexes such as $Cu[N$-(2-hydroxyethyl)ethylenediamine$]_2(NO_3)_2$ and $[Cu(NN'$-diethylethylenediamine$)_2(H_2O)_2]Br_2$.[13]

CONCLUSIONS

We conclude that $[Ni(trien)(en)]X_2$ compounds are octahedral. From the i.r. and electronic spectra and conductivity measurements on the $[Cu(trien)(en)]X_2$ compounds an octahedral stereochemistry is suggested.

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TABLE 1

Analytical data and physical properties

Compound	Colour	M.p. (°C)	Found C	Found H	Found N	Found Metal	Required C	Required H	Required N	Required Metal	Λ [a]
$[Ni(trien)(en)]Cl_2,2H_2O$	Pale violet	242	25·0	8·3	22·7	15·7	25·8	8·1	22·6	15·8	160
$[Ni(trien)(en)]Br_2$	Pale violet	257	21·8	6·3	19·4	13·6	22·6	6·2	19·8	13·8	145
$[Ni(trien)(en)]I_2$	Lilac	268	18·0	5·0	16·0	11·1	18·5	5·0	16·2	11·3	154
$[Ni(trien)(en)](CNS)_2,H_2O$	Pink violet	269	30·2	6·5	28·3	14·8	30·1	7·1	28·1	14·7	159
$[Ni(trien)(en)](ClO_4)_2$	Violet	225	20·3	5·5	17·9	12·6	20·7	5·6	18·1	12·6	164
$[Ni(trien)(en)](AcO)_2,2H_2O$	Pink	196	35·0	8·8	20·4	14·1	34·4	8·6	20·1	14·0	139
$[Ni(trien)(en)](NO_3)_2$	Pale violet	248	24·1	6·4	28·6	15·2	24·7	6·7	28·8	15·1	160
$[Ni(trien)(en)](BPh_4)_2$	Pale pink	207	74·2	7·2	9·2		74·4	7·4	9·3		145
$[Cu(trien)(en)](ClO_4)_2$	Deep blue	156	20·4	5·4	17·8	13·4	20·5	5·6	17·9	13·6	161
$[Cu(trien)(en)](BPh_4)_2$	Light blue	138	74·0	7·3	8·9	6·9	74·0	7·3	9·2	7·0	*b*

[a] For solutions 10^{-3}M at 25 °C in methanol; in $cm^2\,\Omega^{-1}\,mol^{-1}$; reference values in the same solvent are: Et_4NI, 103; $Bu^n{}_4NBr$, 88 for 1 : 1 electrolytes; $BaCl_2$, 126; and $Ba(ClO_4)_2$ = 160 for 1 : 2 electrolytes. [b] Slightly soluble.

TABLE 2

Principal infrared bands of ligands and complexes

Compound	ν(OH) δ(HOH)	Sym. $\nu(NH_2)$	Asym. $\nu(NH_2)$	ν(NH)	$\delta(NH_2)$	Bands of polyatomic anions ν_1	ν_2	ν_3	ν_4
en		3360s	3280m	3200sh	1600vs				
trien		3350w	3280s	3200sh	1600s				
$NaBPh_4$						745vs	262w	1150m	525vw
$[Ni(trien)(en)]Cl_2,2H_2O$	3465w 1660w		3240s	3150s	1585s				
$[Ni(trien)(en)]Br_2$			3265w 3235w	3160sh	1580vs				
$[Ni(trien)(en)]I_2$			3230m	3150w	1580sh 1575s				
$[Ni(trien)(en)](NO_3)_2$		3330s	3275m	3185sh	1580s	1040s	820vs	1380br	720m
$[Ni(trien)(en)](CNS)_2,H_2O$ [a]	3410w 1660w	3220sh	3230sh	3160sh	1570m				
$[Ni(trien)(en)](ClO_4)_2$		3350s 3300s		3180m	1590vs	910vw		1090br	625vs
$[Ni(trien)(en)](AcO)_2,2H_2O$	1610m	*b*		3180w	*c*	1400br		1565br	650s
$[Ni(trien)(en)](BPh_4)_2$		3320m	3270m	3170sh	1580s	740vs	259w	1100w	510w
$[Cu(trien)(en)](ClO_4)_2$		3235m	3260sh	3170sh	1595vs	920w		1080br	625vs
$[Cu(trien)(en)](BPh_4)_2$		3210sh	3240m 3225sh	3130sh	1580s	740s	257w	1100w	530w

[a] ν(CS), 720s; ν(CN), 2050m; δ(NCS), 465vw. [b] $\nu(NH_2)$ bands are obscured by CH_3 of the acetate ion. [c] $\delta(NH_2)$ band obscured by ν_{as}(OCO).

TABLE 3

Electronic spectra of the complexes

	State *					
$[Ni(trien)(en)]Cl_2,2H_2O$ [a]	S	11,300			19,250	29,250
	M	11,300 (11·3)	12,500sh		18,650 (8·7)	29,300 (11·8)
$[Ni(trien)(en)]Br_2$	S	11,750			19,600	29,950
	M	11,300 (10·8)	12,500sh		18,700 (8·4)	28,800 (10·0)
$[Ni(trien)(en)]I_2$	S	11,400			19,100	29,400
	M	11,400 (9·6)	12,500sh		18,800 (6·8)	29,100 (9·3)
$[Ni(trien)(en)](CNS)_2,H_2O$	S	11,300			19,050	29,700
	M	11,300 (11·6)	12,700sh		18,800 (8·8)	29,250 (16·5)
$[Ni(trien)(en)](NO_3)_2$	S	11,800			19,400	
	M	11,300 (10·6)	12,600sh		18,750 (7·5)	29,400 (10·2)
$[Ni(trien)(en)](ClO_4)_2$ [a]	S	11,450			19,100	29,250
	M	11,350 (10·5)	12,500sh		18,900 (7·3)	29,150 (10·0)
$[Ni(trien)(en)](AcO)_2,2H_2O$	S	11,700			20,000	31,250sh
	M	11,200 (11·0)	12,500sh		18,700 (8·7)	31,250sh
$[Ni(trien)(en)](BPh_4)_2$	S	11,600			19,500	30,300sh
	M	Insoluble				
$[Cu(trien)(en)](ClO_4)_2$	S		13,000sh	16,550		
	M			17,550 (115)		
$(Cu(trien)(en)](BPh_4)_2$ [b]	S		12,600sh	16,800		
	M					

* S = Solid, M = in MeOH.

[a] D. A. House and N. F. Curtis, *J. Chem. Soc.*, 1965, 6194, found maxima at 12,000, 19,000, and 28,800 cm^{-1} for the reflectance spectrum of $[Ni(trien)(en)]Cl_2,H_2O$; and at 11,300, 17,400, and 28,300 cm^{-1} for the reflectance spectrum of $[Ni(trien)(en)](ClO_4)_2$.
[b] Slightly soluble in CH_3OH.

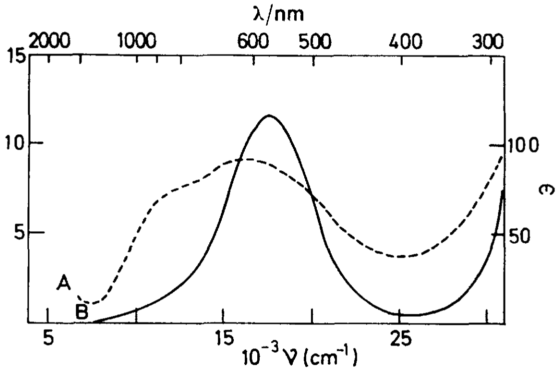
Octahedral complexes with triethylenetetra-amine and ethylenediamine ligands would have three optically active isomers. However polarimetric measurements carried out in aqueous and methanol solutions, over the concentration range 10^{-4}—10^{-8} M, showed no rotation of polarized light. We conclude that our complexes [M(trien)(en)]X_2 are racemic mixtures in solution.

TABLE 4

Ligand field parameters (cm^{-1}) of the complexes [Ni(trien)(en)]X_2 in methanolic solution

	Dq	*B'* [a]	β	ν_2/ν_1
[Ni(trien)(en)]Cl_2,$2H_2O$	1·130	935	0·90	1·65
[Ni(trien)(en)]Br_2	1·130	910	0·88	1·65
[Ni(trien)(en)]I_2	1·140	915	0·88	1·65
[Ni(trien)(en)]$(CNS)_2$,H_2O	1·130	945	0·91	1·66
[Ni(trien)(en)]$(NO_3)_2$	1·130	950	0·92	1·66
[Ni(trien)(en)]$(AcO)_2$,$2H_2O$	1·135	1·090 [b]	1·05	1·70
[Ni(trien)(en)]$(ClO_4)_2$	1·120	935	0·89	1·67
[Ni(trien)(en)]$(BPh_4)_2$ [c]		Slightly soluble		

[a] *B'* (free ion), 1041 cm^{-1} (L. Sacconi, *Transition Metal Chem.*, 1968, **4**, 199. [b] These values are higher than those generally reported for octahedral structures. [c] Solid: 1·160; 1·000; 0·96; 1·68.



A, Reflectance spectrum of [Cu(trien)(en)]$(ClO_4)_2$, and B, absorption spectrum

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