1025. *Transition-metal Complexes with Aliphatic Schiff Bases. Part VII.*[1] *Compounds Formed by the Reaction of Copper*(II) *and Nickel*(II) *Dipropylenetriamine Complexes with Acetone*

By N. F. Curtis and D. A. House

Copper(II) and nickel(II) perchlorate complexes of dipropylenetriamine react readily with acetone to form complexes in which the metal ion is co-ordinated to one dipropylenetriamine residue with both primary amine groups replaced by *N*-isopropylidene Schiff-base groups. The compounds crystallise as hydroxide perchlorates, and conductivity measurements in acetonitrile show that the hydroxide is not dissociated. The magnetic moment of the copper compound is below the " spin only " value for one unpaired electron, indicating copper–copper interactions, probably with a dimeric structure. The magnetic moment and metal-ion spectrum of the nickel compound are normal for triplet ground state nickel(II) with other than tetrahedral symmetry. The compounds crystallise as methanol adducts, the copper adduct having an even lower magnetic moment. The metal-ion absorption spectra of the copper compounds show two distinct maxima. Dimeric five-co-ordinate structures with di-hydroxo-bridges are postulated for the compounds.

PREVIOUS Papers in this Series have described the preparation and properties of several copper(II) and nickel(II) di- and poly-amine complexes and the preparation, properties,

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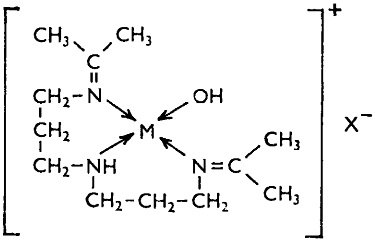
[1] Part VI, D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, 1964, **86**, 1331.

and structures of the Schiff-base complexes resulting from the condensation of these with aliphatic carbonyl compounds.[2,3]

This Paper describes the preparation of some copper(II) and nickel(II) complexes of the tridentate polyamine ligand, dipropylenetriamine (dpt), {di-(3-aminopropyl)amine, $NH_2{\cdot}[CH_2]_3{\cdot}NH{\cdot}[CH_2]_3{\cdot}NH_2$}, and the preparation, properties, and possible structure of the Schiff-base complexes formed by the reaction of these with acetone. Other compounds formed by the amine will be described later.[8]

The nickel(II) complexes $[Ni(dpt)_2](ClO_4)_2$ and $[Ni(dpt)_2](BF_4)_2$ were obtained as pale mauve, well crystallised compounds, by addition of the stoicheiometric amounts of the ligand to the hydrated nickel(II) salt dissolved in ethanol. Addition of two mol. of dipropylenetriamine to one of copper(II) perchlorate heptahydrate in ethanol gave the dinuclear complex $[Cu_2(dpt)_3](ClO_4)_4$, analogous to the complex $[Cu_2(dien)_3]I_4$ formed from the tridentate ligand diethylenetriamine.[4]

The compound $[Ni(dpt)_2](ClO_4)_2$ is not readily soluble in acetone, but if the acetone suspension is set aside at room temperature for several days, or is refluxed for a few hours, a sea-green, crystalline compound, (I), is formed. $[Ni(dpt)_2](BF_4)_2$ reacts similarly to give a similar product, (Ia). No crystalline products were formed by the reaction of bis(dipropylenetriamine)nickel(II) nitrate or chloride with acetone. The bright blue dinuclear copper(II) dipropylenetriamine complex, as the perchlorate, is readily soluble in acetone, and after about 30 min. at room temperature, sea-green crystals (II) are deposited. No crystalline product was formed with the fluoroborate analogue.



M = (I) Ni(II),(II) Cu(II

X^- = (a) BF_4^-, (b) ClO_4^-

Analysis gives the formulæ $MC_{12}H_{26}N_3O(ClO_4)$, M = Ni and Cu for (I) and (II), respectively and $NiC_{12}H_{26}N_3O(BF_4)$ for (Ia). Evidence supporting the formulation shown is given below.

Methanol Adducts.—The nickel(II) and copper(II) dipropylenetriamine–acetone condensation products readily give emerald-green methanol solutions from which emerald-green adducts slowly crystallise. The nickel(II) derivatives lose methanol on drying, re-forming the original blue compounds, but the copper(II) derivative is more stable. On exposure to the atmosphere for several days, or on gentle heating for several hours, the methanol is lost, the colour changing from green to blue. Under vacuum over phosphorus pentoxide, some methanol is lost rapidly, the colour remaining green; thereafter, the remaining methanol is lost extremely slowly (weeks). The much more rapid loss of methanol on exposure to the atmosphere suggests that atmospheric moisture may be involved in the reaction mechanism. Consistent values for the loss in weight could not be obtained; for example, the sample used for the susceptibility measurement as an example, lost 8·4% in weight on exposure to the air for 3 days or on heating at 90° for 5 hours, and lost 3·08% in vacuum over phosphorus pentoxide in 3 days. ($-CH_3OH = 7{\cdot}6\%$, $-1{\cdot}5CH_3OH = 10{\cdot}9\%$).

Properties in Solution.—Compounds (I), (Ia), and (II) are sparingly soluble in acetone,

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[2] N. F. Curtis, *J.*, 1960, 4409; M. M. Blight and N. F. Curtis, *J.*, 1962, 1204, 3016; D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, 1962, **84**, 3248; N. F. Curtis and D. A. House, *Chem. and Ind.*, 1961, 1708.

[3] D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, 1964, **86**, 223.

[4] F. G. Mann, *J.*, 1934, 466.

more soluble in acetonitrile, dimethylformamide, dimethyl sulphoxide, nitromethane, and dichloromethane, to give blue-green solutions. The compound (Ia) is usually more soluble than compound (I) (the spectra of the solutions are discussed below). The conductivities of the solutions in acetonitrile are characteristic of 1 : 1 electrolytes showing that the OH^- is not appreciably dissociated in this solvent (see Experimental section). Compounds (I) and (II) are sparingly soluble in water, to give a strongly basic solution (pH 10·6). Related compounds [1-3] formed by the condensation of other copper(II) and nickel(II) amine complexes with acetone all give neutral solutions, thus indicating that the basicity is due to partial dissociation of the hydroxide ion. When suspensions of compounds (I) and (II) in water were titrated with standard acid, the solids dissolved as the acid was added and the end point (pH 7) corresponded to an equivalent weight equal to the formula weight. The compounds (I) and (II) dissolved readily in dilute mineral acid to form sea-green solutions, which slowly decomposed, yielding acetone (identified as the 2,4-dinitrophenylhydrazone), dipropylenetriamine, and the metal(II) ion. [$t_{\frac{1}{2}}$ for the decomposition reaction in 0·1M-hydrochloric acid was about 30 min. for compound (I), of the order of seconds for compound (II).]

Attempts to determine molecular weight by boiling-point elevation in acetonitrile were unsuccessful, the compounds being insufficiently soluble.

Infrared Spectra (see Experimental section).—The bands due to NH_2 stretch and deformation of the simple dipropylenetriamine complexes are absent from the spectra of the acetone condensation products, indicating removal of these groups by reaction with the acetone. This is supported by the appearance of a strong band near 1660 cm.$^{-1}$, assigned to co-ordinated N:C stretch for analogous compounds.[1-3] The NH stretch bands of the dipropylenetriamine complexes are enhanced for the acetone condensation products. The spectra of these compounds also show strong, sharp bands near 3650 cm.$^{-1}$, assigned to the co-ordinated OH^- ion {being similar in appearance and frequency to the OH band for $[Co(NH_3)_5OH](ClO_4)_2$ at 3595 cm.$^{-1}$, and other hydroxo-compounds}.[5]

The spectrum of the methanol adduct of compound (II) is very similar to that of compound (II) itself, but shows an additional sharp OH stretch band, assigned to the methanol OH group. The C:N band remains of approximately the same intensity, but is split into a doublet.

Metal-ion Absorption Spectra.—The pairs of compounds (I), (II), and their methanol adducts subjectively appear very similar in colour, although the absorption spectra of the copper(II) and nickel(II) compounds are quite dissimilar (see Table). Square-planar

Metal-ion absorption spectra (cm.$^{-1}$ × 10^{-3}, ε in parentheses)

Compound (I)	Solid *†	DMF †‡§
ν_1	7·4	7·4 (20)
ν_2	16·4	16·6 (35)
ν_3	26·4	26·8 (80) ¶

			DMSO ‡		DMF ‡	
Compound (II)	Solid ‖	Solid MeOH Adduct ‖	Fresh	Aged	Fresh	Aged
	15·6	14·8	15·4 (129)	16·0 (121)	15·2 (132)	14·7 (142)
	10·6	9·3	10·4 (50)	10·2 (40)	10·0 (39)	9·0 (58)

	CH_3CN				
Compound (II)	Fresh	Aged	$CH_3·OH$	$CH_3·NO_2$	CH_2Cl_2
	15·3 (142)	15·2 (143)	15·0	14·6 (150)	14·6
	10·3 (51)	10·2 (39)	9·6	8·8 (50)	9·2

* Reflectance spectrum, relative to $MgCO_3$. † The spectra showed a further weak band near 12,000 cm.$^{-1}$ between ν_1 and ν_2, and a weak shoulder on ν_3 near 23,000 cm.$^{-1}$. ‡ DMF = dimethylformamide, DMSO = dimethyl sulphoxide. § The spectra in other solvents ranging in co-ordinating ability from dimethylsulphoxide to dichloromethane, are very similar. ¶ The intensity of this band is enhanced by an adjacent charge transfer band. ‖ Mull spectrum in hexachlorobutadiene.

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[5] R. W. Hay and G. E. R. Hook, *Austral. J. Chem.*, 1964, **17**, 601; W. R. McWhinnie, *J.*, 1964, 2959.

copper(II) compounds normally show a single absorption band in the visible region, but the reflectance and mull spectra of the blue-green compound (II) shows two distinct bands at 15,500 and 10,200 cm.$^{-1}$ (Figure 1). The emerald-green methanol adduct has a similar spectrum, with the bands displaced to lower energies at 14,800 and 9300 cm.$^{-1}$.

Compound (II) dissolves in dimethyl sulphoxide (DMSO), dimethylformamide (DMF) and acetonitrile to form blue-green solutions, the spectra of which resemble that of the solid. When heated for a few minutes or when kept for several days, the colour (and spectra) of the solutions change in a manner characteristic of the solvent. With dimethylformamide, the solution changes from blue-green to blue; with dimethyl sulphoxide, there is little apparent change, while with acetonitrile the solution changes to green. The spectra show small changes in the positions and extinction coefficients of the bands, but the change in appearance is caused largely by changes in the charge transfer bands in the near ultra-violet region (Figure 2). With nitromethane and methanol, the initial green solution does not change when heated or stored. The very slow rate of solution in cold solvent makes the initial colour difficult to determine in dichloromethane. Spectra of the initial and final solutions in dimethylformamide, in acetonitrile and the solution in nitromethane (typical of the initially green solutions) are shown in Figure 1. Band maxima and extinction coefficients for some of the solutions are listed in the Table. The positions of the bands in the " aged " solutions varies with the co-ordinating ability of the solvent (DMSO > DMF > $CH_3{\cdot}CN > CH_3{\cdot}OH > CH_3{\cdot}NO_2 > CH_2Cl_2$), which is not the same as the order of dielectric constants, suggesting that solvent-co-ordination may be occurring.

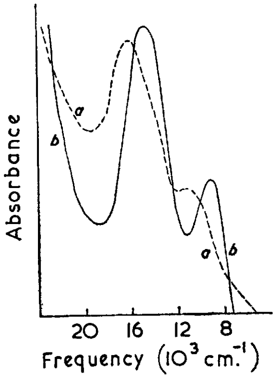

FIGURE 1. Solid spectra (hexachlorobutadiene mulls) *a*, Compound (II). *b*, Compound (II)–methanol adduct.

The spectra of the nickel(II) complexes (I) and (Ia) resemble those of typical approximately octahedral triplet ground-state nickel(II) complexes (Table and Figure 3).

X-*Ray Powder Diffraction*.—The diffraction patterns of the compounds (I) and (Ia) are very similar, indicating that they are isostructural. The diffraction pattern of compound (II) is different from that of compound (I), indicating that these compounds are not isostructural.

Magnetic Susceptibilities.—(see Experimental section). The magnetic moment observed for compound (I) ($\mu_{eff} = 2{\cdot}95$ BM) is " normal " for triplet ground-state nickel(II) compounds with other than tetrahedral configuration. The magnetic moment of the copper(II) compound (II), ($\mu_{eff} = 1{\cdot}6$ BM) is below the " spin only " value for one unpaired electron, 1·73 BM. Because of the rapid loss of methanol by the methanol adduct on exposure to the air, this compound was difficult to obtain pure, and magnetic susceptibility measurements gave variable results, all below the value observed for compound (II). The lowest value obtained ($\mu_{eff} \sim 0{\cdot}8$ BM) suggests that the pure compound may be diamagnetic.

Structure of the Schiff-base Compounds.—Previously reported Schiff-base compounds formed by condensation of acetone with copper(II) or nickel(II) amine complexes are of two types; *N*-isopropylidene compounds which hydrolyse readily, reforming acetone, and more resistant compounds with a C_6 bridging group derived from two acetone residues, which yield mesityl oxide on hydrolysis.[1-3] The compounds (I), (Ia), and (II) are readily hydrolysed by dilute acid, giving acetone, and are therefore assigned *N*-isopropylidene Schiff-base structures. Infrared spectral and conductance measurements indicate that the hydroxide ion, shown to be present by the analytical results, is co-ordinated, giving the nominally four co-ordinate formula shown.

The infrared spectrum of the methanol adduct, compared with that of compound (II), shows no reduction of intensity of the C:N stretching band, indicating that the methanol has not been added across the C:N bond as observed with the Schiff-base complex 1,2-bis-(2′-pyridylmethenamino)ethanecopper(II).[6] The methanol OH band in the infrared spectrum is sharp and in the range observed for hydrogen-bonded alcohols.[7] This, together with the splitting observed for the C:N band suggests that the methanol may be hydrogen bonded to the CN group.

The magnetic moment of compound (II) is below the " spin only " value and the moment of the methanol adduct is even lower. Copper(II) compounds with sub-normal magnetic moments, which are relatively common, have been described in a recent Review.[8] A low moment usually indicates a dimeric structure, with direct copper–copper interactions of the copper(II) acetate type and/or super-exchange through bridges (in this case hydroxy), of the acetylacetone–mono(*o*-hydroxyanil)copper(II) type. The metal-ion absorption spectra of compound (II) and its methanol adduct, with two distinct maxima, are unlike those observed for normal square-planar copper(II) complexes, which have a single band in this region [*e.g.*, Cu(en)$_2^{2+}$, or the complexes produced by the condensation of other copper amine complexes with acetone [1-3]]. An additional band has been observed in the spectrum of other copper(II) compounds with subnormal magnetic moments.[8] A five-co-ordinate, dimeric structure with two hydroxo-bridges is suggested for compound (II).

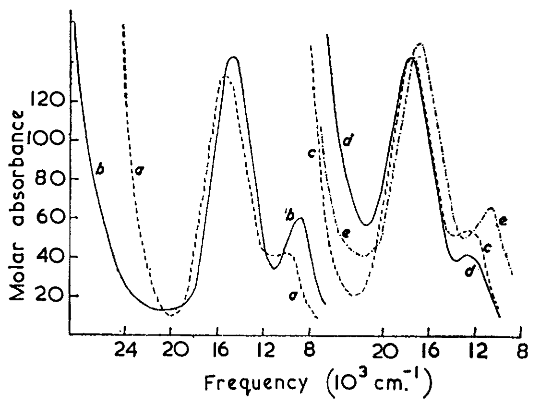

FIGURE 2. Absorption spectra of solutions of compound (II) *a*, Fresh solution in dimethylformamide. *b*, Aged solution in dimethylformamide. *c*, Fresh solution in acetonitrile. *d*, Aged solution in acetonitrile. *e*, Solution in nitromethane.

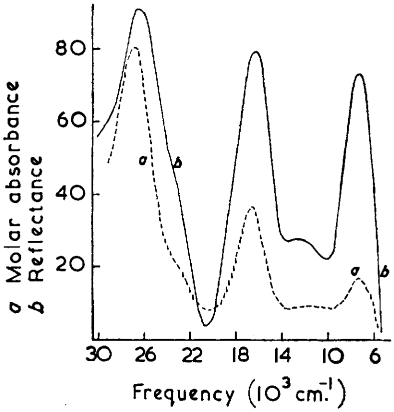

FIGURE 3. Spectra of compound (I) *a*, Solution in dimethylformamide. *b*, Reflectance spectrum (relative to magnesium carbonate).

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[6] C. M. Harris and E. D. McKenzie, *Nature*, 1962, **196**, 670.

[7] L. J. Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1962, p. 95.

[8] M. Kata, H. B. Jonassen, and C. J. Fanning, *Chem. Rev.*, 1964, **64**, 99.

Five-co-ordinate structures with both trigonal bipyramidal[9] as well as the more common square-pyramidal structures have been reported for copper(II) compounds.[10]

If monomeric, the nickel compound could be tetrahedral or square-planar. The magnetic moment of compound (I) is lower than observed for tetrahedral nickel(II) complexes,[11] although this may be due to the considerable deviation from regular tetrahedral symmetry with one secondary amine, one hydroxo and two azomethine donor groups. The absorption spectrum, in appearance, band positions, and extinction coefficients, resembles spectra of typical approximately octahedral complexes, and is quite unlike spectra reported for known tetrahedral complexes.[11] Triplet ground state, square-planar nickel(II) complexes have not been definitely established in the solid state. Solvent interaction in the axial positions would be expected to cause changes in the spectra of such complexes, but the spectra of solid compound (I), solutions in good donor solvents such as dimethyl sulphoxide, and in poor donor solvents such as dichloromethane are very similar.

In the absence of evidence to the contrary, it is suggested that compounds (I) and (Ia) are dimers, analogous to the copper compound. Five-co-ordinate structures are rare for nickel(II) compounds.[11,12] The differing number of *d* electrons for the nickel(II) and copper(II) compounds and the greater tendency of copper(II) compounds to form metal–metal interactions could cause sufficient differences in the detail of the structure to change the molecular packing arrangement, and hence the crystal structure. The fact that compounds (I), (Ia), and (II) all crystallise as methanol adducts gives additional support to analogous structures for them. Six-co-ordinate structures could only be achieved if the perchlorate or fluoroborate ions were co-ordinated, and the infrared spectra of these ions give no evidence of such interaction.

The difference between the magnetic moments of compound (II) and its methanol adduct indicates some conformational difference enhancing the copper–copper interaction for the adduct. The change in colour and spectra of solutions on heating or at room temperature suggests that this conformational change can occur in solution, the copper–copper interaction being enhanced in solvents of low co-ordinating ability.

Diethylenetriamine Analogues.—Attempts to prepare diethylenetriamine analogues of the dipropylenetriamine–acetone condensation products were not successful. There was no indication of any reaction between bis(diethylenetriamine)nickel(II) and acetone even on prolonged heating in a sealed tube. With the copper(II) complex, a colour change indicated that some reaction had occurred, but no crystalline product could be isolated.

EXPERIMENTAL

Bis(dipropylenetriamine)nickel(II) *Perchlorate*, $Ni(dpt)_2(ClO_4)_2$.—Nickel perchlorate hexahydrate (18·3 g., 0·05 mole) was dissolved in methanol (25 ml.), and the solution added slowly to a solution of dipropylene triamine (13·5 g., 0·103 mole) in ethanol (50 ml.). The pale mauve perchlorate that separated was recrystallised from hot methanol (Found: C, 27·5; H, 6·8; Ni, 11·4. $C_{12}H_{34}Cl_2N_6NiO_8$ requires C, 27·7; H, 6·6; Ni, 11·3%).

Bis(dipropylenetriamine)nickel(II) *Fluoroborate*, $Ni(dpt)_2(BF_4)_2$.—As for the previous preparation, but with nickel fluoroborate hexahydrate (16·9 g., 0·05 mole) instead of the perchlorate (Found: C, 29·3; H, 7·3; Ni, 11·9. $C_{12}H_{34}B_2F_8N_6Ni$ requires C, 29·1; H, 6·9; Ni, 11·9%).

Bis(dipropylenetriamine)-μ-(dipropylenetriame)dicopper(II) *Perchlorate*, $Cu_2(dpt)_3(ClO_4)$.—As for the first preparation, but with copper(II) perchlorate tetrahydrate (16·8 g., 0·05 mole) instead

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[9] D. E. C. Corbridge and E. G. Cox, *J.*, 1956, 594; G. A. Barclay and G. H. L. Kennard, *Nature*, 1961, **192**, 425.

[10] T. N. Waters, D. Hall, and F. J. Llewellyn, *Chem. and Ind.*, 1958, 1203; F. J. Llewellyn and T. N. Waters, *J.*, 1960, 2639; D. Hall, A. D. Rae, and T. N. Waters, *J.*, 1963, 424.

[11] J. R. Millar, " Advances in Inorganic Chemistry and Radiochemistry," H. J. Emeleus and A. G. Sharpe, ed., Academic Press, New York, 1962, p. 133.

[12] G. S. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, 1964, **4**, 1544 (and references therein); G. Dyer, J. G. Hartley, and L. M. Venazi, *J.*, 1965, 1293; L. Sacconi, P. L. Oriali, and M. Di Vaira, *J. Amer. Chem. Soc.*, 1965, **87**, 2059.

of the nickel perchlorate. The bright blue product was recrystallised from hot methanol (Found: C, 23·3; H, 5·8; Cu, 13·8. $C_{18}H_{51}Cl_4Cu_2N_9O_{16}$ requires C, 23·5; H, 5·6; Cu, 13·8%).

Hydroxo[*di*-(3-*isopropylideneaminopropyl*)*amine*]*nickel*(II) *Perchlorate*.—$Ni(dpt)_2(ClO_4)_2$ (10 g.) and acetone (50 ml.) were agitated occasionally during 3 days, during which time the starting material dissolved and a sea-green product crystallised. The supernatant liquid was then decanted and the product washed several times with acetone (yield 75%). Purification was conveniently effected by conversion into the methanol adduct. The emerald-green adduct was washed with methanol, and dried when the blue-green product re-formed. The product could be recrystallised by the addition of acetone to a filtered solution in dimethylformamide (Found: C, 37·4; H, 6·7; N, 10·6; Ni, 15·3%; Equiv. by acid titration, 384. $C_{12}H_{26}ClN_3NiO_5$ requires C, 37·3; H, 6·8; N, 10·8; Ni, 15·2%; Equiv., 387).

Hydroxo[*di*-(3-*isopropylideneaminopropyl*)*amine*]*nickel*(II) *Fluoroborate*.—Prepared as for the previous preparation, but with $Ni(dpt)_2(BF_4)_2$ (Found: C, 38·3; H, 7·2; Ni, 15·7. $C_{12}H_{26}BF_4N_3NiO$ requires C, 38·6; H, 7·0; Ni, 15·8%).

Hydroxo[*di*-(3-*isopropylideneaminopropyl*)*amine*]*copper*(II) *Perchlorate*.—When a solution of $Cu_2(dpt)_3(ClO_4)_4$ in acetone was set aside for about 24 hr., the sea-green product crystallised (yield 75%). Purification was as for the nickel analogue. In this case, the emerald-green methanol adduct is more stable and the methanol was removed by heating the product at 110° (Found: C, 37·0; H, 7·0; Cu, 16·2; N, 10·1%; Equiv. by acid titration, 389. $C_{12}H_{26}ClCuN_3O_5$ requires C, 36·9; H, 6·7; Cu, 16·2; N, 10·7%; Equiv., 391).

Conductances in Acetonitrile at 25°.—Compound (I), $1{\cdot}6 \times 10^{-3}$M, $\Lambda_M = 140$ ohm^{-1} cm.^{2}. Compound (II), $2{\cdot}4 \times 10^{-3}$M, $\Lambda_M = 137$ ohm^{-1} cm.^{2}. The concentrations were calculated on the assumption of a monomeric formula. Reported conductances [13] of 1 : 1 electrolytes are $\Lambda_M \sim 150$ ohm^{-1} cm.^{2}.

Visible Spectra.—Spectra were measured with a Unicam S.P. 700 spectrophotometer. Reflectance spectra were determined with magnesium carbonate as reference.

Infrared Absorption Spectra.—Spectra were measured in mulls with a Perkin-Elmer 221 spectrophotometer. (I): ν(OH), 3645; ν(NH), 3255; ν(C:N), 1664 cm^{-1}. (Ia): ν(OH), 3660 (3640 sh); ν(NH), 3275; ν(C:N), 1662 cm^{-1}. (II): ν(OH), 3625; ν(NH), 3295, 3255; ν(C:N), 1660 cm.$^{-1}$. (II) (CH_3OH adduct): ν(OH), 3630, 3560; ν(NH), 3295, 3265; ν(C:N), 1670, 1662 cm.$^{-1}$.

Magnetic Susceptibilities.—Measured for the solids by the Gouy method with $Ni(en)_3S_2O_3$ as calibrant.[14] Magnetic moments were calculated from $\mu_{\text{eff}} = 2{\cdot}84\,(\chi_M T)^{\frac{1}{2}}$, χ_M being corrected for diamagnetism. (I): χ_g at 290°K $= 9{\cdot}07 \times 10^{-6}$; $\mu_{\text{eff}} = 2{\cdot}95$ BM. (II): χ_g at 293°K $= 2{\cdot}29 \times 10^{-6}$; $\mu_{\text{eff}} = 1{\cdot}60$ BM. (II) (CH_3OH adduct): χ_g at 291°K $\sim 0{\cdot}1 \times 10^{-6}$; $\mu_{\text{eff}} \sim 0{\cdot}8$ BM. The sample lost 8·4% in weight on exposure to the atmosphere.

X-*Ray Powder-diffraction*.—Measurements were made with a Philips diffractometer.

Analyses.—Nickel and copper were determined gravimetrically. Carbon, hydrogen, and nitrogen, analyses were by Dr. A. D. Campbell of the University of Otago.

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[13] F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, 1965, **4**, 326.

[14] N. F. Curtis, *J.*, 1961, 3147.