1153. *Transition-metal Complexes of Triethylenetetramine. Part II.*[1] *Some Nickel*(II) *and Copper*(II) *Derivatives*

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The preparations of the triethylenetetramine derivatives $[Ni_2(trien)_3](ClO_4)_4$, $[Ni\ trien\ en](ClO_4)_2$, $[Ni\ trien\ en]Cl_2,H_2O$, $[Ni\ trien(py)_2](ClO_4)_2$, $[Ni\ trien\ py\ H_2O]Cl_2$, $[Ni\ trien](ClO_4)_2$ and $[Cu\ trien](ClO_4)_2$ (trien = triethylenetetramine, en = ethylenediamine, py = pyridine) are described. Orange, diamagnetic $[Ni\ trien](ClO_4)_2$ and $[Cu\ trien](ClO_4)_2$ are isostructural. The other nickel compounds have $\mu_{eff} \sim 3$ B.M. Absorption spectra are reported.

Nickel(II) and copper(II) complexes of triethylenetetramine, $(NH_2\text{-}[CH_2]_2\cdot NH\cdot CH_2)_2$, are usually very soluble, and few crystalline derivatives have been described. Salts of the binuclear hexamine $[Ni_2(trien)_3]^{4+}$, as the chloride, nitrate, and chloroplatinate were described by Jonassen and Douglas,[2] who reported that they were unable to isolate any derivatives of the ion $[Ni\ trien]^{2+}$. Jørgensen[3] studied the solution spectra of the ion

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[1] Part I, D. A. House and N. F. Curtis, *J.*, 1963, 3149.

[2] H. B. Jonassen and B. E. Douglas, *J. Amer. Chem. Soc.*, 1949, **71**, 4094.

[3] C. K. Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 399.

$[\text{Ni trien}]^{2+}$ and complexes such as $[\text{Ni trien L}_2]^{2+}$, L = NH_3, $\frac{1}{2}$ en, etc. He reported that addition of thiocyanate caused the precipitation of $[\text{Ni trien}](SCN)_2$ and addition of $AgBrI^-$ caused precipitation of $[\text{Ni trien}](AgBrI)_2$. He was unable to obtain $[\text{Ni trien}](ClO_4)_2$ crystalline. In Part I the complexes $[\text{M trien}]ZnCl_4,H_2O$ and $[\text{M trien}]ZnCl_4$ [M = Ni(II) or Cu(II)] were described, the nickel(II) hydrate having a triplet ground-state and the anhydrous salt having a singlet ground-state.[1] These are the only reported compounds containing the ion $[\text{Cu trien}]^{2+}$. Curtis described the compound $[Ni_2(\text{trien})_2C_2O_4](ClO_4)_2$, for which a binuclear oxalato-bridged structure was proposed.[4]

Commercial triethylenetetramine contains much amine impurity, which can be conveniently removed by recrystallisation of appropriate metal complex salts. Nickel(II) triethylenetetramine chloride derivatives can be prepared from $[Ni_2(\text{trien})_3]Cl_4,2H_2O$ and the perchlorate derivatives from $[Ni_2(\text{trien})_3](ClO_4)_4$, both of which can be readily obtained pure. Mono-(trien) derivatives can be prepared by reaction of equimolar amounts of the appropriate $[Ni_2(\text{trien})_3]^{4+}$ and $[Ni(H_2O)_6]^{2+}$ salts in a suitable solvent.

Anhydrous $[\text{Ni trien}](ClO_4)_2$ was isolated as an orange hygroscopic diamagnetic solid by the evaporation of an aqueous solution of $[\text{Ni trien}(H_2O)_2](ClO_4)_2$ and trituration of the resultant gum[3] with propan-2-ol. (The anhydrous salt resembles $[Ni(\text{en})_2](ClO_4)_2$, which can be prepared by dehydration of the dihydrate, by heating, desiccation, or trituration with propan-2-ol. The triethylenetetramine compound forms a brown gum on exposure to the atmosphere, whereas the ethylenediamine compound reforms the crystalline hydrate.) Very hygroscopic crystalline adducts were obtained with ethanol (orange $[\text{Ni trien}](ClO_4)_2$ slowly recrystallising as the pale blue adduct when left under absolute ethanol) and with dimethyl sulphoxide (blue crystals separated from a hot saturated solution of the perchlorate in propan-2-ol containing a little dimethyl sulphoxide).

The amine derivatives of $[\text{Ni trien}]^{2+}$, $[\text{Ni trien en}](ClO_4)_2$, $[\text{Ni trien en}]Cl_2,H_2O$ and $[\text{Ni trien}(\text{py})_2](ClO_4)_2$ were prepared by addition of the amine to solutions of $[\text{Ni trien}]X_2$ in ethanol. Attempts to prepare $[\text{Ni trien}(\text{py})_2]Cl_2$ by this method, were not successful, $[Ni(\text{py})_4]Cl_2$ crystallising under anhydrous conditions and a water-containing complex when water was present. The latter compound can be formulated as $[\text{Ni trien py }H_2O]Cl_2$, or as $[\text{Ni trien py Cl}]Cl,H_2O$. Co-ordination of water rather than chloride would normally be expected for nickel(II), although the compound $[Ni_2(\text{trien})_2Cl_2](ClO_4)_2$ (to be described subsequently) crystallises from methanol containing an appreciable concentration of water. The reflectance spectrum of the solid is compatable with either formulation. The bathochromic shift (~500 cm.$^{-1}$) expected if the co-ordinated water molecule in $[\text{Ni trien py }H_2O]^{2+}$ was replaced by chloride is within the range of variation observed for a particular complex nickel(II) cation of this type with different anions (see Table 1). The

TABLE 1

Reflectance spectra[a] and magnetic susceptibilities[b]

Complex	Maxima (cm.$^{-1}$ × 10^3) ν_1[c]	ν_2[c]	ν_3[c]	$\chi_g \times 10^6$ (°K)	μ_{eff} (B.M.)[d]
$[Ni_2(\text{trien})_3](ClO_4)_4$	11·8	18·8	27·4	7·79(294)	3·06
$[Ni_2(\text{trien})_3]Cl_4,2H_2O$	11·4	18·7	28·3	10·45(293)	3·10
$[\text{Ni trien en}](ClO_4)_2$	11·3	17·4	28·3	8·46(293)	3·14
$[\text{Ni trien en}]Cl_2,H_2O$	12·0	19·0	28·8	10·31(293)	3·03
$[\text{Ni trien}(\text{py})_2](ClO_4)_2$	11·0	18·2	27·6	6·81(293)	3·11
$[\text{Ni trien py }H_2O]Cl_2$	10·3	18·2	27·2	10·55(295)	3·15
$[\text{Ni trien}(H_2O)_2]^{2+}$[e]	10·2	17·3	28·2		
$[Ni_2(\text{trien})_2Cl_2](ClO_4)_2$[f]	9·4	15·9	26·4		
$[\text{Ni trien}](ClO_4)_2$				Diamagnetic	

[a] Measured using a Unicam S.P. 700 spectrophotometer, with magnesium carbonate as reference. [b] Measured by the Gouy method, using $[Ni(\text{en})_3]S_2O_3$ as calibrant (N. F. Curtis, *J.*, 1961, 3147). [c] $\nu_1 = {}^3A_{2g} \longrightarrow {}^3T_{1g}$, $\nu_2 = {}^3A_{2g} \longrightarrow {}^3T_{2g}(F)$, $\nu_3 = {}^3A_{2g} \longrightarrow {}^3T_{2g}(P)$ for O_h symmetry. [d] Calculated from $\mu_{\text{eff}} = 2{\cdot}84\,(\chi_m T)^{\frac{1}{2}}$, where χ_m is corrected for diamagnetism. [e] In aqueous solution.[3] [f] This binuclear chlorobridged complex, to be described subsequently, is quoted as an example of a triethylenetetramine-nickel compound with co-ordinated chloride.

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[4] N. F. Curtis, *J.*, 1963, 4109.

infrared spectrum assignable to the water molecule, [ν(OH) ~ 3200 cm.$^{-1}$, vbr; δ(HOH) ~ 1650 cm.$^{-1}$, br] is compatable with either co-ordination or strong hydrogen bonding.

In weakly co-ordinating solvents (propan-2-ol, acetone, nitromethane) [Ni trien]$(ClO_4)_2$ dissolves to form yellow solutions, the spectra showing the single band (22,200 cm.$^{-1}$, ε 80) characteristic of singlet ground-state nickel(II) amine compounds. Solutions in solvents of higher co-ordinating ability (water, methanol, dimethyl sulphoxide, dimethylformamide, pyridine) are blue-violet, the spectra showing the three weak bands characteristic of triplet ground-state nickel(II) in approximately octahedral co-ordination. When heated, these solutions reversibly change to yellow, the spectra showing the bands characteristic of both singlet and triplet ground-state forms, as observed by Jørgenson[3] for aqueous solution of the ion [Ni trien$(H_2O)_2]^{2+}$. Solutions of the triethylenetetramine pyridine derivatives on heating show the same reversible blue-yellow colour change as solutions of [Ni trien$(H_2O)]^{2+}$. The thermochroism of the solution in methanol is greater for the bispyridine perchlorate (which changes from violet to yellow on heating) than for the aquopyridine chloride (which changes from blue to blue-green). The addition of lithium chloride to the bispyridine perchlorate solution causes it to behave like the aquopyridine chloride solution in this respect, suggesting that chloride co-ordination may be occurring in the hot methanol solution. Chloride co-ordination in methanol solution is also suggested by the conductance. (Λ_m,25°, 0·937 and $1{\cdot}27 \times 10^{-3}$ M = 127 and 120 ohm^{-1}mole.$^{-1}$) which are low for a 1 : 2 electrolyte (cf. [Cu trien]$(ClO_4)_2$ Λ_m, 25°, $1{\cdot}175 \times 10^{-3}$ M = 140 ohm^{-1}mole^{-1}).

Blue-violet [Cu trien]$(ClO_4)_2$ crystallises when a slight excess of triethylenetetramine is added to a solution of copper(II) perchlorate in methanol–propan-2-ol. The salt is extremely soluble in water, methanol, acetone, etc. Attempts to prepare salts of [Cu trien]$^{2+}$ with other anions (BF_4^-, Cl^-, NO_3^-, SO_4^{2-}) were not successful because of high solubilities, and tendencies to separate as gums.

Orange, diamagnetic [Ni trien]$(ClO_4)_2$ and blue-violet [Cu trien]$(ClO_4)_2$ have *X*-ray powder diffraction patterns with all major lines in common, and hence are isostructural. The absorption spectra of the compounds (Table 2), and the diamagnetism of the nickel compound are normal for square–planar co-ordination.

TABLE 2

Absorption spectra in methanol solution [a]

	Band maximum (cm.$^{-1}$ × 10^3)	ε		Band maximum (cm.$^{-1}$ × 10^3)	ε
[Ni trien en]Cl_2,H_2O ...	28·82	10·2	[Ni trien py H_2O]Cl_2...	32·40	10·4[b]
	18·40	7·9		28·00	11·4[b]
	11·00	10·7		17·35	7·0
Ni trien py_2]$(ClO_4)_2$ ...	33·00	22·2[b]		10·40	12·0
	28·80	16·6[b]	[Ni trien]$(ClO_4)_2$[d]	22·20	80
	23·00	6·0[c]	[Cu trien]$(ClO_4)_2$	17·10	146
	17·55	8·9			
	10·60	13·1			

[a] The solution spectra of $[Ni_2(trien)_3]^{4+}$,[2] [Ni trien$(H_2O)_2]^{2+}$,[3] and various amine adducts of [Ni trien]$^{2+}$ have previously been reported. [b] These bands occurred as shoulders on the more intense pyridine bands. [c] This band, due to the singlet ground-state species, becomes the major band in acetone solution. [d] In acetone solution.

Pairs of isostructural salts $[M(en)_2]X_2$, M = Cu^{II} or Ni^{II}, X = a bulky linear anion such as $AgBrI^-$, have been reported.[5] In contrast to the triethylenetetramine case, orange diamagnetic $[Ni(en)_2](ClO_4)_2$, crystallised from propan-2-ol, and $[Cu(en)_2](ClO_4)_2$ have dissimilar *X*-ray powder diffraction patterns, and are thus apparently not isostructural.

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[5] A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J.*, **1963**, **2552**.

EXPERIMENTAL

Commercial triethylenetetramine was used without purification. All yields were greater than 80%.

Bistriethylenetetramine-μ-triethylenetetraminedinickel(II) *Perchlorate*, $[Ni_2(trien)_3](ClO_4)_4$.—Triethylenetetramine (7 ml.) was added to a solution of nickel perchlorate hexahydrate (10 g., 1 : 1·75 mole ratio) dissolved in 20 ml. of water. The solution was boiled with charcoal, filtered, and the filtrate heated to boiling, and allowed to cool slowly. (Rapid cooling causes deposition of the product as a gum.) The *product* was filtered from the cold solution, washed well with ethanol and recrystallised from hot water (Found: C, 22·5; H, 5·7; Ni, 12·3. $C_{18}H_{54}Cl_2N_{12}Ni_2O_{16}$ requires C, 22·7; H, 5·7; Ni, 12·3%).

Triethylenetetraminenickel(II) *Perchlorate*, $[Ni\ trien](ClO_4)_2$.—The blue solution prepared by reaction of equimolar amounts of the salts $[Ni_2(trien)_3](ClO_4)_4$ (10 g.) and nickel perchlorate hexahydrate (3·48 g.) was filtered, evaporated to dryness under reduced pressure, and finally heated *in vacuo* at 100°. The resulting brown gum was triturated with dry propan-2-ol, when the orange product crystallised. Large crystals were obtained if the gum was set aside under propan-2-ol for several weeks. The very hygroscopic *product* was filtered, washed with propan-2-ol and quickly transferred to desiccator (Found: C, 17·9; H, 4·9; Ni, 14·2. $C_6H_{18}Cl_2N_4NiO_8$ requires C, 17·9; H, 4·5; Ni, 14·5%).

Ethylenediaminetriethylenetetraminenickel(II) *Perchlorate*, $[Ni\ trien\ en](ClO_4)_2$.—The reactants in the previous preparation were dissolved in methanol, an excess (2 ml.) of ethylenediamine was added, and the violet *product* precipitated by the addition of propan-2-ol. Recrystallisation was effected by extraction into methanol–propan-2-ol (Found: C, 20·1; H, 5·6; Ni, 12·8. $C_8H_{26}Cl_2N_6NiO_8$ requires C, 20·7; H, 5·6; Ni, 12·6%).

Dipyridinetriethylenetetraminenickel(II) *Perchlorate*, $[Ni\ trien(py)_2](ClO_4)_2$.—Prepared as in the preceding preparation, substituting pyridine (5 ml.) for the ethylenediamine, the *product* was recrystallised by extraction into methanol–propan-2-ol containing 1 ml. of pyridine (Found: C, 34·2; H, 5·4; Ni, 10·3. $C_{16}H_{28}Cl_2N_6NiO_8$ requires C, 34·2; H, 5·0; Ni, 10·4%).

Ethylenediaminetriethylenetetraminenickel(II) *Chloride Hydrate*, $[Ni\ trien\ en]Cl_2,H_2O$.—Equimolar quantities of the salts $[Ni_2(trien)_3]Cl_4,2H_2O$ (15·4 g.) and nickel chloride hexahydrate (5 g.) were heated together in methanol (47·5 ml.) and water (2·5 ml.) until solution was complete and ethylenediamine (2 ml.) was added. The *product* was precipitated by the slow addition of acetone, and recrystallised by extraction into methanol–propan-2-ol (Found: C, 27·0; H, 8·1; Cl, 20·0; Ni, 16·8. $C_8H_{28}Cl_2N_6NiO$ requires C, 27·1; H, 8·0; Cl, 20·0; Ni, 16·6%).

Aquopyridinetriethylenetetraminenickel(II) *Chloride*, $[Ni\ trien\ py\ H_2O]Cl_2$.—The reactants used in the previous preparation were dissolved in boiling methanol (45 ml.) and water (5 ml.), the solution was filtered, and pyridine (10 ml.) added. Propan-2-ol was added to the hot filtrate until crystallisation commenced, and the solution allowed to cool, when the *product* crystallised, was filtered off, and washed well with propan-2-ol (Found: C, 35·2; H, 7·1; Cl, 19·0; Ni, 15·7. $C_{11}H_{25}Cl_2N_5NiO$ requires C, 35·4; H, 6·8; Cl, 19·1; Ni, 15·7%).

Triethylenetetraminecopper(II) *Perchlorate*, $[Cu\ trien](ClO_4)_2$.—Copper(II) perchlorate tetrahydrate (15 g., 0·045 mole) dissolved in propan-2-ol (100 ml.) was added slowly with stirring to triethylenetetramine (7·5 g., 0·05 mole) dissolved in propan-2-ol (50 ml.). A light blue semisolid gum separated, and the propan-2-ol removed by decantation. The gum was dissolved in hot methanol (50 ml.) and the filtered solution poured into 200 ml. of hot propan-2-ol. Deep-purple crystals of the *product* separated on cooling (Found: C, 17·9; H, 5·0; Cu, 15·0. $C_6H_{18}Cl_2CuN_4O_8$ requires C, 17·6; H, 4·4; Cu, 15·5%).

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