

781. *Amine-Oxalate Complexes of Nickel(II). Part I. Some Tetra-aminenickel(II) Oxalate Compounds: Preparation and Infrared Spectra.*

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Compounds of the type "bisethylenediaminenickel(II) hemioxalate perchlorate" have been prepared with bisethylenediamine-, diethylenetriamine-, triethylenetetramine-nickel(II), and the tetradentate Schiff base-amine complexes trimethyldiazanonediamine and hexamethyltetra-azacyclotetradecadiene-nickel(II). The compounds are all blue-violet and paramagnetic, although salts of the Schiff base-amine complexes are usually orange and diamagnetic, indicating interaction between the oxalate and the nickel ions. The infrared spectra of the oxalate ion in these compounds is similar to that observed for ionic oxalates, where the oxalate ion is planar and symmetrical, rather than that of chelate oxalato-complexes, although shifts in the position of some of the bands indicate co-ordination. It is concluded that the oxalate ion retains a symmetrical configuration, all four oxygen atoms interacting equally with nickel ions. The most probable structure is dimeric, the oxalate ion acting as a bichelate bridging group and linking two nickel tetra-amine cations. The infrared spectra of potassium bisoxalatonicckelate was found to be similar to that of the zinc and copper compounds, and at variance with the published data.

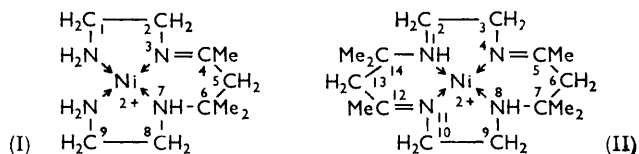
THE existence in aqueous solution of nickel(II) oxalatoethylenediamine co-ordination compounds was deduced from spectroscopic and pH titration studies by Watters and De Witt.¹ The species $[\text{Ni} 2\text{en ox}]^0$, $[\text{Ni en } 2\text{ox}]^{2-}$, and $[\text{Ni en ox}]^0$ were shown to be present at different concentration ranges (en = ethylenediamine, ox = oxalate ion).

In this paper, crystalline oxalate compounds formed by bisethylenediamine-, diethylenetriamine-, triethylenetetramine-, and the Schiff base-amine complexes 4,6,6-trimethyl-3,7-diazanon-3-ene-1,9-diamine- (I) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene-nickel(II) (II)² with nickel:oxalate ratios of 2:1 are described.

¹ Watters and De Witt, *J. Amer. Chem. Soc.*, 1960, **82**, 1333.

² Curtis, *J.*, 1960, 4409; Curtis and House, *Chem. and Ind.*, 1961, **42**, 1708; Blight and Curtis, *J.*, 1962, 3016.

Evidence for the existence of species of the same composition in solution will be presented in Part II (following paper).



Addition of a soluble oxalate to an aqueous solution of bisethylenediaminenickel(II) as the chloride, sulphate, acetate, etc., causes no precipitation, showing that the oxalate of bisethylenediaminenickel, whether co-ordinated or not, is soluble. If sodium perchlorate is added to this solution, a sparingly soluble, blue-violet crystalline precipitate is formed, of composition $\text{Ni} \cdot 2\text{en} \cdot \frac{1}{2}\text{ox} \cdot \text{ClO}_4$. Analogous compounds with nitrate or iodide replacing the perchlorate ion are similarly formed. The hemioxalate perchlorate salts of triethylenetetraminenickel(II) and the Schiff base-amine nickel complex (I) can be prepared similarly. Pale blue aquodiethylenetriaminenickel(II) hemioxalate perchlorate and nitrate can be similarly prepared, as well as a series of deep blue compounds in which ammonia or monodentate amines replace the water molecule (analytical results for these compounds are in poor agreement with stoichiometric formulæ, and exposure to air causes gradual replacement of the amine by water, the compound reverting to the pale blue aquo-compound).

The hemioxalate perchlorate of the macrocyclic Schiff base-amine complex (II) can be prepared by indirect means. This compound is more soluble in water than the simple perchlorate, and therefore cannot be crystallised from aqueous solution.

Some of the compounds crystallise from aqueous solution as hydrates. Bisethylenediaminenickel hemioxalate iodide and aquodiethylenetriaminenickel hemioxalate nitrate do not lose this water at 110° , and analyses indicate that the compounds are hemihydrates. Bisethylenediaminenickel hemioxalate perchlorate and the hemioxalate perchlorates of complexes (I) and (II) form hydrates, but the water is lost on drying in the air at room temperature.

Magnetic Susceptibilities.—The magnetic susceptibilities were measured for the solids by the Gouy method, with trisethylenediaminenickel(II) thiosulphate as calibrant.³ The results (Table I) indicate that the nickel ions in all the compounds are paramagnetic, with two unpaired electrons. The complex ions (I) and (II) in most of their salts are diamagnetic

TABLE I.
Magnetic susceptibilities.

Compound	Temp. ($^\circ\text{K}$)	$10^6\chi_g$	$10^6\chi_m$	Diam. (corr.)	$10^6\chi_m'$	μ_{eff} (B.M.)
$\text{Ni en}_2 \cdot \frac{1}{2}\text{ox} \cdot \text{ClO}_4$	288	11.58	3733	155	3888	3.00
$\text{Ni dien} \cdot \text{H}_2\text{O} \cdot \frac{1}{2}\text{ox} \cdot \text{ClO}_4$...	291	10.57	3418	150	3568	2.89
$\text{Ni trien} \cdot \frac{1}{2}\text{ox} \cdot \text{ClO}_4$	292	10.52	3665	181	3846	3.01
(I) $\cdot \frac{1}{2}\text{ox} \cdot \text{ClO}_4$	291	8.13	3273	222	3495	2.86
(II) $\cdot \frac{1}{2}\text{ox} \cdot \text{ClO}_4$	291	7.03	3393	299	3694	2.94

en = Ethylenediamine; dien = diethylenetriamine; trien = triethylenetetramine; ox = oxalate ion.

Infrared Spectra.—The infrared spectra of the compounds were measured over the 4000—400 cm^{-1} region for Nujol, "Halocarbon oil," and hexachlorobutadiene mulls, in a Perkin-Elmer model 221 spectrophotometer with sodium chloride/grating and potassium bromide optics.

For comparison the spectra of sodium oxalate (representing an "ionic" oxalate of

³ Curtis, *J.*, 1961, 3147.

known structure⁴), and of potassium bisoxalatocuprate(II) dihydrate and potassium bisoxalatonickelate(II) hexahydrate (representing chelate oxalate complexes), were measured. The spectra of ionic oxalates and of many oxalate complexes have previously been reported.^{5-7, 16, 17} The results in Table 3 (other than for the platinum complex) were obtained in this investigation. They differ only slightly from those reported, except for the nickel oxalate complex which has a spectrum like those of the zinc and copper compounds, and not as previously described.⁷

The oxalate ion in sodium oxalate is planar and symmetrical with all C-O bonds of equal length (V_h symmetry).⁴ The infrared spectrum shows bands due to antisymmetric and symmetric (O-C-O) stretching at 1640 and 1335, 1316 cm^{-1} , respectively. The other components of these vibrations are infrared-inactive, but have been reported in the Raman spectrum of potassium oxalate hydrate at 1664 and 1485, 1450 cm^{-1} , respectively.^{6, 8}

When chelate oxalate complexes are formed the C-O bonds interacting with the metal ion become longer, the other two shorter (C_{2v} symmetry).⁹ In the infrared spectra the antisymmetric (O-C-O) stretching bands shift to higher frequencies (tending towards C=O values), the symmetric (O-C-O) stretching bands shift to lower frequencies (tending towards C-O values), and all vibrations become infrared-active.

The spectrum of the oxalate ion in the nickel-amine-oxalate compounds resembles that of sodium oxalate, rather than that of chelate oxalato-complexes (Tables 2 and 3). The ν_u (O-C-O) stretching vibrations occur at values close to those observed for "ionic" oxalates. The 1640 cm^{-1} band is overlaid by C-N stretching and NH_2 deformation vibrations which cause shoulders, but the band does not show the splitting observed for many oxalato-complexes. The 1485 cm^{-1} Raman band, which is infrared-inactive for the symmetrical oxalate ion but occurs strongly for the chelate oxalate complexes in the 1430-1380 cm^{-1} region, is not observed with these compounds.

TABLE 2.
Infrared spectra of the oxalate group (cm^{-1}).

Compound						
Ni en ₂ $\frac{1}{2}$ ox ClO ₄	1657, 50, 45	1352	1312	—	798	481
Ni en ₂ $\frac{1}{2}$ ox ClO ₄ · $\frac{1}{2}$ H ₂ O ...	1660, 53, 45	1357	1316	—	793	484
Ni en ₂ $\frac{1}{2}$ ox NO ₃	1645	(NO ₃ ⁻)	1322	—	798	486
Ni en ₂ $\frac{1}{2}$ ox I, $\frac{1}{2}$ H ₂ O	1640	1344	1310	—	785	477
Ni dien H ₂ O $\frac{1}{2}$ ox ClO ₄ ...	1657	1355	1315	—	802	485
Ni dien H ₂ O $\frac{1}{2}$ ox NO ₃ ...	1655	1367	1325	—	800	495
Ni trien $\frac{1}{2}$ ox ClO ₄	1637	1360	1310	(897?)	795	485
(I) $\frac{1}{2}$ ox ClO ₄	1640	1357	1312	—	790	484
(I) $\frac{1}{2}$ ox ClO ₄ · $\frac{1}{2}$ H ₂ O	1645	1360	1315	885	790	—*
(II) $\frac{1}{2}$ ox ClO ₄	1640	1352	1312	880	792	482
(II) $\frac{1}{2}$ ox ClO ₄ · $\frac{1}{2}$ H ₂ O	1645	1360	1320	—	790	—*

* Spectra not measured in KBr region.

The other bands observed occur at frequencies close to those observed for the copper oxalato-complex. Bands are observed in the following regions:

795 cm^{-1} . This is observed as a strong sharp band for all the compounds and corresponds to the (O-C-O) deformation vibration observed at 774 cm^{-1} for the oxalate ion and 785-825 cm^{-1} for the chelate oxalate complexes.

485 cm^{-1} . This band corresponds to that observed at 518 cm^{-1} for the oxalate ion, which is shifted to lower values in the chelate complexes. This band has been assigned to (C-C-O) deformation and to coupled (O-C-O) and ring deformations.

⁴ Jeffrey and Parry, *J. Amer. Chem. Soc.*, 1954, **76**, 5283.

⁵ Douville, Duval, and Lecompte, *Bull. Soc. chim. France*, 1942, **9**, 548; *Compt. rend.*, 1941, **212**, 697; Schmelz, Miyazawa Mizushima, Lane, and Quagliano, *Spectrochim. Acta*, 1957, **9**, 51.

⁶ Murata and Kawai, *J. Chem. Phys.*, 1956, **25**, 589.

⁷ Fujita, Nakamoto, and Kobayashi, *J. Phys. Chem.*, 1957, **61**, 1014.

⁸ Edsall, *J. Chem. Phys.*, 1937, **5**, 508.

⁹ van Nierkerk and Schoening, *Acta Cryst.*, 1951, **4**, 35, 381.

TABLE 3.
Infrared spectra of the oxalate group (cm.⁻¹).

Assignment	Na ₂ ox	Ni amine oxalate	K ₂ Ni ox ₂ ,6H ₂ O	K ₂ Cu ox ₂ ,2H ₂ O	K ₂ Pt ox ₂ ,3H ₂ O ¹⁶
ν_a (O-C-O)	[1664] *	— †	1720sh 1660sh 1630sh 1610vs	1710sh 1675vs 1650sh	1709vs 1674vs
	1640vs	1640vs			
ν_s (O-C-O)	[1485, 1450] *	— †	1433s	1425s	1388s
	1335s 1316s	1355w 1315m	1305s	1290s	1236s
δ (O-C-O)	780sh 774s	795m,sp	800sh 775s	805s,br	825s
δ (O-C-O) ¹⁶	512s	485m	506m,br	484s,br	469s
δ (C-C-O) ⁷					
ν (C-C)	[898] *	890w ‡	887w	900m	900 m
ν (M-O) ¹⁶	[545] *	— †	520w,v.br §	535m,br	575sh
δ (O-C-O) ⁷					559s
?	1420w		1365w	863w,sp	

* Raman spectrum of K₂ox,H₂O. † Bands absent. ‡ Band observed for some of the compounds. § Extremely broad band (460—580 cm.⁻¹), appearing as shoulders on both sides of the 506 cm.⁻¹ band.

885 cm.⁻¹. This band was observed for only some of the compounds. It corresponds to the (C-C) stretching vibration, infrared-inactive for the oxalate ion (Raman band, 898 cm.⁻¹) but observed for all the chelate oxalate complexes.

A band at 520—570 cm.⁻¹, which is present for the chelate oxalate complexes, is not observed with the amine-oxalate compounds.

The hydrates formed by some of the compounds show the same infrared absorption due to the oxalate ion as do the anhydrous compounds, indicating the same basic structure. However, there seems to be a slight shift of the (O-C-O) stretching vibrations to higher frequencies, and of the deformation vibrations to lower frequencies, for the hydrates compared with the anhydrous compounds. This, together with the analytical evidence indicating one water molecule per oxalate ion in the hydrates, suggests that the water is associated with the oxalate ion, as is commonly observed in "ionic" oxalates.

The infrared spectrum in the N-H stretching region for the oxalate-perchlorate compound of the complex (II) shows considerable alteration compared with the simple perchlorate salt. The single N-H band at 3173 cm.⁻¹ in the diamagnetic perchlorate becomes a doublet at 3255 and 3250 cm.⁻¹ for the paramagnetic oxalate-perchlorate (or a single band at 3250 cm.⁻¹ for the hydrate).

Discussion.—The tetra-amine complexes of nickel(II) formed by the amines studied are normally blue-violet and paramagnetic, with the nickel ion in octahedral co-ordination. Some orange, diamagnetic salts are formed, *e.g.*, the bisethylenediamine- and triethylenetetramine-nickel(II) ions as the iodomercurate and bromoiodideargentate.¹⁰ The compounds [Ni en₂,2H₂O](ClO₄)₂ and [Ni trien,2H₂O](ZnCl₄) both lose water when heated and regain it on exposure to air, changing from blue paramagnetic hydrates to orange diamagnetic anhydrous compounds.¹¹

Salts formed by the ion (I) are usually orange and diamagnetic. Exceptions observed are the blue-violet paramagnetic compounds (I) NO₂,ClO₄,¹² (I) $\frac{1}{2}$ ox,ClO₄, (I) BH₄,ClO₄,¹³ and (I) Ni(CN)₄,¹³ in all of which the infrared spectrum of the anion shows evidence of interaction with the cation. In aqueous solution the ion (I) forms blue-violet, paramagnetic

¹⁰ Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 399.

¹¹ House and Curtis, *J.*, 1963, 3149.

¹² Curtis, Thesis, University of New Zealand, 1954.

¹³ Curtis, unpublished work.

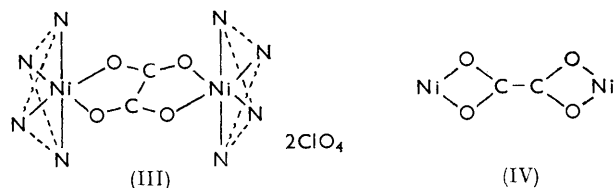
adducts with ammonia,¹⁴ with some amines (*e.g.*, ethylenediamine), with the oxalate ion (following paper), and with the cyanide ion.¹⁵

The cyclic tetradentate ion (II) shows much less tendency to form paramagnetic compounds, the only examples being the oxalate described in this paper and a cyanido-nickel derivative of complex structure (to be described subsequently). An unstable adduct formed with the cyanide ion¹⁵ is the only paramagnetic species of (II) observed in aqueous solution.

The increasing stability of the square-planar, spin-paired configuration, relative to the spin-free state with higher co-ordination number in the sequence triethylenetetramine-nickel(II), (I), (II) is probably due to π -bond stabilisation of the square-planar configuration by the co-ordinated N:C group of complexes (I) and (II). This is supported by the properties of the cyclic-tetra-amine-nickel complexes formed by reduction of the N:C groups of (II), which form mainly spin-free compounds.¹³

The formation of spin-free hemioxalates by the ions (I) and (II), therefore, indicates strong interactions between the oxalate ion and the nickel ion, supporting the evidence from the infrared spectra of the oxalate ion.

Conclusions.—The formulæ of the hemioxalates allow one oxalate ion for every two nickel ions. The magnetic susceptibility values of the oxalates formed by (I) and (II) indicate that all the nickel ions are in the triplet state and are therefore interacting with oxalate ions. The infrared spectra indicate that the oxalate ions are planar and symmetrical but interacting with the nickel ions.



The dimeric structure (III) is considered the most probable arrangement consistent with this evidence. Structure (IV) is considered less likely because of the two four-membered chelate rings, and because packing considerations are likely to cause rotation about the C-C bond whereas the infrared spectra indicate that the oxalate ion is planar.

Polymeric structures with each oxalate ion interacting with four nickel ions are considered improbable for steric reasons, especially for the large Schiff base-amine complex cations. The compounds of the ions (I) and (II) dissolve without dissociation in dimethylformamide, supporting a non-polymeric structure (these solutions are described in the following paper).

On the basis of the method of preparation, similarities in physical properties, and particularly the infrared spectrum of the oxalate ion, it is inferred that the compounds formed by the simple amines have structures entirely analogous to those formed by the Schiff base-amine complexes. With diethylenetriamine the oxygen of a water molecule, or the nitrogen of a monodentate amine replaces one of the nitrogen atoms of the bis-ethylenediamine, triethylenetetramine, or tetradentate Schiff base-amine systems.

From the similarity in position of the O-C-O stretching vibrations of the oxalate ion in "ionic" oxalates, and in the amine-oxalate compounds, and from the absence of the bands which are Raman-active for the oxalate ion but infrared-active for chelate oxalato-complexes, it is concluded that the oxalate ion in the amine-oxalate compounds retains the planar, symmetrical configuration.

The deformation vibrations, however, occur at frequencies close to those observed for the copper oxalato-complex. These vibrations would be sensitive to any reduction in

¹⁴ Burns, Thesis, University of New Zealand, 1962.

¹⁵ Howard, Thesis, University of New Zealand, 1962.

the charge carried by the oxygen atoms, and it is concluded that the total transfer of charge by co-ordination is similar in the two cases. For the chelate complexes co-ordination is by two oxygen atoms, while in the amine-oxalate compounds all four oxygen atoms must interact equally with the nickel ions.

A band at 520–570 cm^{-1} in the spectra of the chelate oxalato-complexes is not observed in those of the amine-oxalate compounds. This band has been assigned to M–O stretching,¹⁶ but possibly corresponds to a band observed at 545 cm^{-1} in the Raman spectrum of the oxalate ion, assigned to C–C–O deformation.⁷ The band would not appear in the infrared spectrum of the amine-oxalate compounds on the second assignment if the oxalate ion is symmetrical.

EXPERIMENTAL

The Schiff-base complexes (I) $(\text{ClO}_4)_2$ and (II) $(\text{ClO}_4)_2$ were prepared as previously described. The hemioxalates, other than the derivative of the ion (II), were prepared by the same general method. A concentrated solution of sodium oxalate was added to a hot aqueous solution of the appropriate nickel complex, the product separating on cooling. The compounds were recrystallised from hot water. The solutions of the nickel-amine complexes were prepared by adding the calculated quantity of the appropriate nickel salt to the recrystallised nickel hexa-amine salt (*e.g.*, a solution of bisethylenediaminenickel perchlorate was prepared by the addition of 0.5 mol. of nickel perchlorate hexahydrate to triethylenediaminenickel perchlorate hemihydrate). A slight excess of amine above the correct 1 : 1 ratio for triethylenetetramine and diethylenetriamine, or 2 : 1 ratio for ethylenediamine, is no disadvantage, but ratios below this figure cause the precipitation of insoluble oxalates. The following salts were prepared:

Bisethylenediaminenickel(II) hemioxalate perchlorate (Found: Ni, 18.2; C, 18.8; H, 5.5; ox^{2-} , 13.7. $\text{C}_5\text{H}_{16}\text{ClN}_4\text{NiO}_6$ requires Ni, 18.2; C, 18.6; H, 5.0; ox^{2-} , 13.7%); this forms a hydrate, which loses water on drying.

Bisethylenediaminenickel(II) hemioxalate nitrate (Found: Ni, 20.6; C, 21.4; H, 6.5. $\text{C}_5\text{H}_{16}\text{N}_5\text{NiO}_5$ requires Ni, 20.6; C, 21.1; H, 5.6%).

Bisethylenediaminenickel(II) hemioxalate iodide hemihydrate (does not lose water on drying at 110°) (Found: Ni, 16.5; C, 16.3; H, 5.2; I, 35.0. $\text{C}_5\text{H}_{16}\text{IN}_4\text{NiO}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ requires Ni, 16.4; C, 16.7; H, 4.8; I, 35.4%).

Aquodiethylenetriaminickel(II) hemioxalate perchlorate (Found: Ni, 18.0; C, 18.7; H, 5.3; ox^{2-} , 13.4. $\text{C}_5\text{H}_{15}\text{ClN}_3\text{NiO}_7$ requires Ni, 18.2; C, 18.6; H, 4.7; ox^{2-} , 13.6%).

Aquodiethylenetriaminickel(II) hemioxalate nitrate hemihydrate (does not lose water on drying at 110°) (Found: Ni, 19.9; C, 20.8; H, 5.8; N, 19.1. $\text{C}_5\text{H}_{15}\text{N}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ requires Ni, 19.9; C, 20.4; H, 5.4; N, 19.0%).

Triethylenetetraminenickel(II) hemioxalate perchlorate (Found: Ni, 16.9; C, 24.5; H, 5.6; ox^{2-} , 12.8. $\text{C}_7\text{H}_{18}\text{ClN}_4\text{NiO}_6$ requires Ni, 16.8; C, 24.2; H, 5.2; ox^{2-} , 12.6%).

4,6,6-Trimethyl-3,7-diazanon-3-ene-1,9-diaminenickel(II) hemioxalate perchlorate. The general preparation was modified by use of 4,6,6-trimethyl-3,7-diazanon-3-ene-1,9-diaminenickel perchlorate in place of, *e.g.*, the bisethylenediamine salt. This complex, forms a blue hydrate which loses water on drying, giving the violet anhydrous salt (Found: Ni, 14.5; C, 32.6; H, 6.2; N, 13.7; ox^{2-} , 10.4. $\text{C}_{11}\text{H}_{24}\text{ClN}_4\text{O}_6$ requires Ni, 14.6; C, 32.8; H, 6.0; N, 13.9; ox^{2-} , 10.9%).

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienickel(II) hemioxalate perchlorate. A hot concentrated aqueous solution of the hexamethyltetra-azacyclotetradecadienenickel perchlorate was mixed with a hot concentrated aqueous solution of potassium oxalate (0.5 mol.), and the mixture was seeded with potassium perchlorate and allowed to cool slowly. If yellow crystals of the starting material were deposited, the solution was warmed till they redissolved. Finally the solution was set aside to stand in ice overnight and then filtered from potassium perchlorate. The filtrate was evaporated to small volume under reduced pressure, and the product precipitated by addition of acetone. The product was recrystallised by dissolution in a very small volume of hot water, filtration, and reprecipitation as the anhydrous salt by dropwise addition of acetone to the stirred solution at $\sim 40^\circ$. It crystallised

¹⁶ Fujita, Martell, and Nakamoto, *J. Chem. Phys.*, 1962, **36**, 324.

as a deep blue hydrate from hot methanol containing 5% of water, which loses water slowly in the air, forming the violet anhydrous *salt* (Found: Ni, 12.0; C, 41.8; H, 7.0; N, 11.6; ox^{2-} , 9.7. $\text{C}_{17}\text{H}_{32}\text{ClN}_4\text{NiO}_6$ requires Ni, 12.2; C, 42.3; H, 6.7; N, 11.6; ox^{2-} , 9.1%).

Because the infrared spectra observed for the bisoxalatonicelate(II) ion differ from previously reported values, the method of preparation is here described. Nickel oxalate hydrate was added to a boiling, concentrated aqueous solution of potassium oxalate until no more would dissolve. The solution was boiled for about 10 min., filtered while hot, and allowed to cool slowly; the product crystallised. While the solution was still warm, the product was separated by filtration, sucked as free from the solution as possible, and allowed to dry in the air. The product prepared in this manner is slightly contaminated with potassium oxalate. This was removed by rapid washing with small portions of ice-water, but as the product is decomposed by water, forming nickel oxalate dihydrate, the washed product is probably contaminated with nickel oxalate. No significant difference in the analytical figures or infrared spectra was noticed between the washed and the unwashed samples (Found: Ni, 13.8; ox^{2-} , 42.1. Calc. for $\text{C}_4\text{K}_2\text{NiO}_6 \cdot 6\text{H}_2\text{O}$: Ni, 14.0; ox^{2-} , 41.8%).

Analyses.—For nickel analysis the compounds were generally decomposed by heating them to fuming with perchloric acid. The compound of the very stable ion (II) was decomposed by boiling peroxydisulphate solution. Nickel was estimated gravimetrically by using dimethylglyoxime. Where the nickel-amine cation was stable to permanganate, the oxalate content was estimated by direct titration. For the compounds of triethylenetetramine and for complexes (I) and (II), where permanganate reacts with the complex cation, calcium oxalate was precipitated, filtered, and washed, and the oxalate determined by permanganate titration. Nitrogen analysis by the Dumas method tended to be erratic.

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¹⁷ Fujita, Martell, and Nakamoto, *J. Chem. Phys.*, 1962, **36**, 331.
