782. *Amine–Oxalate Compounds of Nickel*(II). *Part II.*[1] *Solution Equilibria.*

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The interactions with the oxalate ion in aqueous solution of the bisethylenediamine, diethylenetriamine, triethylenetetramine, and some Schiff base–amine complexes of nickel(II) have been studied by the variation method. For the polyamine complexes there is evidence for the formation of binuclear, oxalate-bridged species in solution with nickel : oxalate ratios less than unity. The formation constant for the interaction of the 4,6,6-trimethyl-3,7-diazanon-3-ene-1,9-diaminenickel(II) ion with the oxalate ion has been determined spectrophotometrically.

FOR the complex ions bisethylenediaminenickel(II), triethylenetetraminenickel(II), 4,6,6-trimethyl-3,7-diazanon-3-ene-1,9-diaminenickel(II) (I), and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienenickel(II) (II), crystalline derivatives of composition [Nickel complex] hemioxalate perchlorate have been prepared.[1] With diethylenetriamine, compounds of composition [Diethylenetriamine-X-nickel] hemioxalate perchlorate, where X represents water, ammonia, or a variety of monodentate amines, have been formed.[1] The present paper describes a spectrophotometric study undertaken to determine whether dimeric species occurred in solutions containing these complex nickel cations and oxalate ions.

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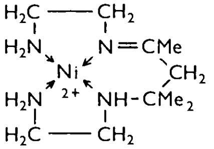
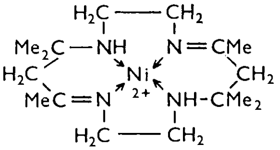
[1] Part I, Curtis, preceding paper.

The equilibria in aqueous solution of systems containing nickel(II) ions, ethylenediamine, and oxalate ions have been studied spectrophotometrically, and by pH titration techniques by Watters and De Witt,[2] whose results indicate the formation of the species [Ni en_2 ox]^0, [Ni en ox_2]$^{2-}$, and [Ni en ox]^0 at different concentration ranges (en = ethylenediamine, ox = oxalate ion). Values for the equilibrium constants for the system were calculated.

(I)





(II)

RESULTS

When a soluble oxalate is added to an aqueous solution of bisethylenediamine-, diethylenetriamine-, or triethylenetetramine-nickel(II) ions, the blue colour of the solution deepens. Spectrophotometric study shows little change in the position of the bands, but increased molar absorbance (Table). Addition of an oxalate to an aqueous solution of the Schiff base–amine nickel complex ion (I) causes the orange colour of the solution to become fainter; there is a decrease in the intensity of the 434 mμ band, characteristic of the ion (I),[3] and appearance of three weaker bands, characteristic of octahedral, triplet, nickel(II) species. The spectrum of ion (I) in saturated sodium oxalate solution is shown in Fig. 1. No change in the absorption spectrum of an aqueous solution of the cyclic Schiff base–amine nickel complex ion (II) occurred on the addition of oxalate.

Variation Method.—The interaction of the complex nickel ions with oxalate ions in aqueous solution was studied by the Job variation method.[4] The results (Fig. 2) for the diethylenetriaminenickel(II) and triethylenetetraminenickel(II) ions show a maximum at nickel to oxalate ratios of 2 : 1, indicating the formation of the species [Ni_2 $dien_2$ ox]$^{2+}$ and [Ni_2 $trien_2$ ox]$^{2+}$ (dien = diethylenetriamine, trien = triethylenetetramine). The species [Ni dien ox]^0 and [Ni trien ox]^0 could also be formed, but with smaller formation constant or, as seems more probable by analogy with the ethylenediamine case, with molar absorbance similar to that of the first species. With the bisethylenediaminenickel(II) ion the results show a broad maximum between nickel : oxalate ratios of 2 : 1 and 1 : 1, indicating the formation of both [Ni_2 en_4 ox]$^{2+}$ and [Ni en_2 ox]^0. The former species was not observed by Watters and De Witt, who performed the variation measurements in the presence of an excess of oxalate, varying the nickel : ethylenediamine ratio.[2] For the ion (I), the results indicate the formation of a single oxalate adduct, with nickel : oxalate ratio of 1 : 1. The curvature of the plot near the maximum indicates a small value for the formation constant.

Absorption spectra in aqueous solution.

Solution	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε
Ni en_2^{2+}	920	6·7	570	5·5	352	8·7
Ni en_2^{2+} plus oxalate *	915	7·9	565	10·2	—†	—
Ni $dien^{2+}$	935	9·5	590	5·4	363	8·5
Ni $dien^{2+}$ plus oxalate	950	10·7	585	8·8	—†	—
Ni $trien^{2+}$	910	12·3	565	6·2	355	10·0
Ni $trien^{2+}$ plus oxalate	900	15·7	557	14·4	—†	—

* An excess of solid sodium oxalate was added to the 0·06M-solution of the nickel ammine. † Obscured by absorption of the oxalate ion.

Spectrophotometric Determination of Formation Constants.—(*a*) 4,6,6-*Trimethyl*-3,7-*diazanon*-3-*ene*-1,9-*diaminenickel*(II), (I) *with oxalate ion.* Solutions of 0·005M (I) $(ClO_4)_2$, and sodium oxalate varying from 0 to 0·15M were prepared, the total ionic concentration being kept constant

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[2] Watters and De Witt, *J. Amer. Chem. Soc.*, 1960, **82**, 1333.
[3] Blight and Curtis, *J.*, 1962, 1204.
[4] Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437.

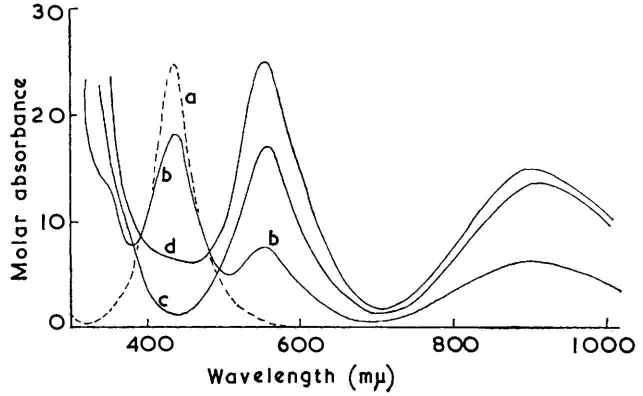

FIG. 1. Absorption spectra.
(a) The ion (I) in water ($\times \frac{1}{3}$).
(b) The ion (I) in saturated aqueous sodium oxalate.
(c) The hemioxalate perchlorate of (I) in dimethylformamide.
(d) The hemioxalate perchlorate of (II) in dimethylformamide.

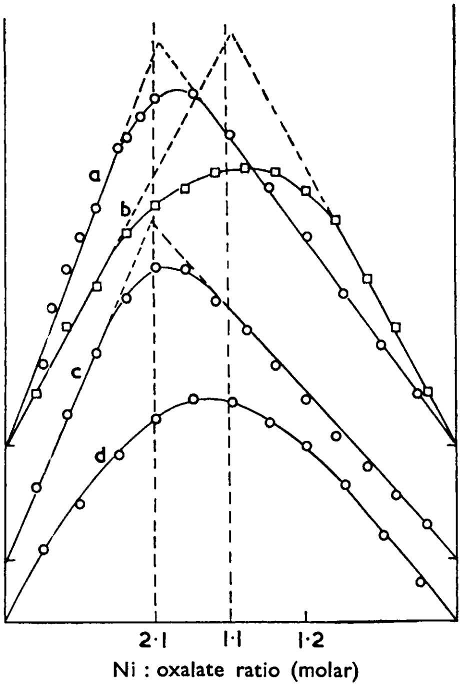

FIG. 2. Job variation plots.
(a) Triethylenetetraminenickel(II), 570 mμ.
(b) 4,6,6-Trimethyl-3,7-diazanon-3-ene-1,9-diaminenickel(II) (I), 434 mμ.
(c) Diethylenetriaminenickel(II), 590 mμ.
(d) Bisethylenediaminenickel(II), 570 mμ.

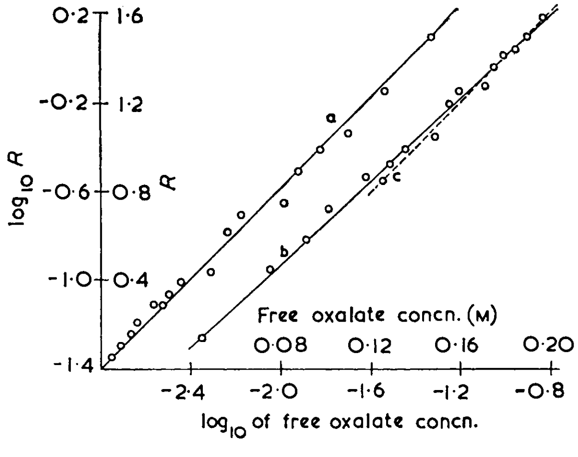

FIG. 3.
(a) Plot of R against free oxalate concentration.
(b and c) Plots of $\log_{10} R$ against $\log_{10}$ (free oxalate concentration).

by the substitution of 0·3M-sodium nitrate for the oxalate. The optical density of these solutions at 434 mμ were measured. [$\lambda_{\text{max.}}$ for the ion (I) 434 mμ, $\varepsilon = 70$.][3] At this wavelength the oxalate adduct shows negligible absorption, and hence the concentration of the free ion (I) could be directly determined and the concentrations of the oxalate adduct and the free oxalate calculated.

The results of the variation study indicate that the equilibrium studied by spectrophotometric measurements at 434 mμ is of the form

$$(\text{I})^{2+} + \text{ox}^{2-} \rightleftharpoons [(\text{I})\ \text{ox}]^0$$
$$K = [(\text{I})\ \text{ox}]/[(\text{I})^{2+}][\text{ox}^{2-}] = R/[\text{ox}^{2-}].$$

A plot of the ratio R against the free oxalate ion concentration $[\text{ox}^{2-}]$ should be a straight line through the origin, of slope R. The results (Fig. 3a) are in agreement, with $K = 10{\cdot}1$ at at 19° ± 2°. Confirmation that only a 1 : 1 complex is formed over the concentration range studied is obtained from the plot of log R against log $[\text{ox}^{2-}]$, which should be a straight line, of slope 1 under these conditions. The best line, through all the points (line " b," Fig. 3) is of slope 0·94, but this overweights the values for small R and $[\text{ox}^{2-}]$ where the errors are largest. If these points are ignored, the remaining points lie close to the line " c " of slope 1·0.

(*b*) *Triethylenetetraminenickel*(II) *with oxalate ion.* A similar method was used to determine an approximate value for the formation constant of the species with nickel : oxalate ratio of 2 : 1, shown to be formed by the variation study. An accurate determination was not possible because of the limited range of oxalate concentrations over which useful measurements could be made. The large value of the formation constant caused $[\text{ox}^{2-}]$ to be very small, with consequent large uncertainties, for low total oxalate concentrations, and other species occurred for oxalate : nickel ratios above 1 : 1. The formation constant

$$K = [\text{Ni}_2\ \text{trien}_2\ \text{ox}^{2+}]/[\text{Ni trien}^{2+}]^2\ [\text{ox}^{2-}]$$

was found to be of the order of 10^5.

Solutions in Dimethylformamide.—The crystalline hemioxalate perchlorates of the ions (I) and (II) give blue-violet solutions in dimethylformamide, whose absorption spectra show the three bands characteristic of triplet nickel octahedral complexes (Fig. 1). The compound of the ion (II) shows some absorption due to the free ion (II) at 434 mμ. If this solution is heated, the colour changes reversibly to orange, the 434 mμ band increasing in intensity, the others decreasing proportionately, indicating increased dissociation. This solution becomes orange on addition of a trace of water, the spectra indicating complete dissociation. The solution of the compound of the ion (I) remains blue-violet on heating and is unaffected by addition of a small amount of water.

DISCUSSION

For nickel(II) the oxalate ion has a spectroscopic field constant similar to that of water, smaller than those of co-ordinated amines. [$[\text{Ni(H}_2\text{O)}_6]^{2+}$ has absorption bands at 1180, 650, and 395 mμ;[5] Ni ox_3^{4-} at 1105 and 668 mμ;[2] and Ni en_3^{2+} at 890, 545, and 343 mμ.[5]] Replacement of co-ordinated water molecules in aquoamine complexes of nickel by oxalate should therefore cause little change in the position of the absorption bands. When oxalate is added to solutions of diethylenetriamine- or triethylenetetramine-nickel(II) there is little change in the position of the bands, but the intensity increases until a nickel : oxalate ratio of about 2 : 1 is reached, and it then remains constant. With bisethylenediaminenickel(II) there is a large increase in intensity until a ratio of 2 : 1 is reached, and a slight further increase until the 1 : 1 value is reached. Formation of dimeric species with the polyamines as bridging groups, such as $\{\text{en}_2\text{Ni–NH}_2{\cdot}[\text{CH}_2]_2{\cdot}\text{NH}_2\text{–Ni en ox}\}^{2+}$, with five amine nitrogen atoms co-ordinated to one nickel ion, and three to the other, would be expected to cause doubling, or at least broadening, of the absorption bands, which is not observed. For the same reason, equilibrium reactions such as $[\text{Ni en}_2]^{2+} + \text{ox}^{2-} \rightleftharpoons [\text{Ni en}_3]^{2+} +$

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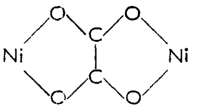
[5] Jorgensen, *Acta Chem. Scand.*, 1955, **9**, 1362.

[Ni en ox]^0 are excluded. It is, therefore, concluded that the species formed with a nickel : oxalate ratio of 2 : 1 is dimeric, the oxalate ion acting as the bridging group.


(A)

From a study of the infrared spectra of the crystalline nickel–amine–hemioxalate compounds described in Part I, a dimeric structure of type (A), with a symmetrical oxalate ion, was suggested. The hemioxalate species formed in solution could have this structure, or the oxalate ion could function as a bico-ordinate bridging group, with water molecules occupying the sixth co-ordination positions. Species of the latter type are not usually formed, largely because the translational-entropy change favours the normal chelate. Occurrence of the hemioxalates may thus be due to the ability of the oxalate ion to function as a tetraco-ordinate, bichelate bridging group.

In water and in dimethylformamide, the stability of the hemioxalate species decreases for the series of tetradentate complexes triethylenetetramine, (I), (II). The triethylenetetraminenickel ion normally exists in aqueous solution with the nickel ion in the triplet state (*i.e.*, paramagnetic and blue), with the visible absorption spectrum showing the three bands characteristic of octahedral nickel(II) complexes. The oxalate adducts can be formed by replacement of co-ordinated water molecules by the oxalate ion, without change in the multiplicity or co-ordination number of the nickel ion. The ions (I) and (II) normally form orange, diamagnetic solutions, their visible spectra showing the single, more intense band characteristic of the nickel(II) ion in the singlet state and square-planar co-ordination.[3] In aqueous solution the ion (I) is in equilibrium with paramagnetic species in the presence of ammonia, ethylenediamine, the oxalate ion, etc., while the ion (II) shows similar interaction only with the cyanide ion. In these cases, formation of the oxalate adduct requires a change from square-planar, singlet, to octahedral, triplet, co-ordination by the nickel ion. The decreasing tendency to form octahedrally co-ordinated compounds in the series of tetradentate complexes triethylenetetraminenickel(II), (I), and (II) is probably due to the increasing π-bond stabilisation of the singlet square-planar form for the ions (I), with one co-ordinated azomethine group, and (II), with two co-ordinated azomethine groups.[6] When a triplet species is formed, these π-bonds would be greatly weakened because of the increased Ni–N bond length caused by the presence of an electron in the $d_{x^2-y^2}$ antibonding orbital.

EXPERIMENTAL

Absorption spectra were measured on a Unicam S.P. 500 spectrophotometer. Quantitative spectrophotometric measurements were made on a Hilger Uvispek spectrophotometer.

The Schiff base–amine nickel perchlorates were prepared as previously described.[7] Solutions of bisethylenediaminenickel(II) were prepared from the solid diaquobisethylenediaminenickel perchlorate, prepared by adding 0·5 mol. of nickel perchlorate hexahydrate to recrystallised trisethylenediaminenickel perchlorate hemihydrate. The product was recrystallised by slow evaporation of an aqueous solution. Solutions of diethylenetriamine- and triethylenetetramine-nickel(II) were made by adding the calculated quantity of nickel sulphate hexahydrate (from a freshly opened bottle of " AnalaR " material in which the crystals showed no sign of exsiccation), to recrystallised bisdiethylenetriaminenickel(II) chloride hydrate,[8] or bistriethylenetetramine-μ-triethylenetetraminedinickel chloride dihydrate,[9] respectively.

Solutions for the variation method were prepared by mixing 0·06M-solutions of the nickel–amines complexes and " AnalaR " sodium oxalate. For the complex (I), 0·01M-solutions were used. All measurements were at room temperature (~19°), the measurements for each compound being performed in a single run and the solutions mixed immediately before measurement.

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[6] Blight and Curtis, *J.*, 1962, 3016.
[7] Curtis, *J.*, 1960, 4409.
[8] Breckenridge, *Canad. J. Res.*, 1948, **26**, 11.
[9] Jonassen and Douglas, *J. Amer. Chem. Soc.*, 1949, **71**, 4094; House and Curtis, *J.*, 1963, 3149.