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Intermediate Products of the Reaction of (4,4,9,9-Tetramethyl-5,8-diazadodecane-2,11-dione dihydrazone)nickel(II) with Butane-2,3-dione; the Structure of *cis*-Aqua(3,4,7,9,9,14,14,16-octamethyl-1,2,5,6,10,13-hexaazacyclohexadeca-1(16),4,6-trien-3-ol)nickel(II) Perchlorate Trihydrate

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Abstract

Intermediate products have been isolated from the reaction of (4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione dihydrazone)nickel(II) perchlorate with butane-2,3-dione which finally yields the macrocyclic product (3,4,7,9,9,14,14,16-octamethyl-1,2,5,6,10,13-hexaazacyclohexadeca-2,4,6,16-tetraene)nickel(II) perchlorate, [Ni(omht)] $(ClO_4)_2$. An initial violet product is assigned a structure with the macrocyclic ligand 3-acetyl-3,6,8,8,13,13,15-heptamethyl-1,2,4,5,9,12-hexaazacyclopentadeca-5,15-diene. In water this converts into an equilibrium mixture of the tautomeric cations blue *cis*-aqua(3,4,7,9,9,14,14,16-octamethyl-1,2,5,6,10,13-hexaazacyclohexadeca-1(16),4,6-trien-3-ol)nickel(II), *cis*-$[Ni(L^2)(H_2O)]^{2+}$, and orange (3,6,8,-8,13,13-hexamethyl-4,5,9,12-tetraazahexadeca-3,5-diene-2,15-dione 15-hydrazone)nickel(II), $[Ni(L^3)]^{2+}$. The rates at 25°C of the forward and reverse reactions of this tautomerism, and of the slower conversion of the equilibrium mixture to [Ni(omht)] $(ClO_4)_2$, are reported. The structure of *cis*-$[Ni(L^2)(H_2O)](ClO_4)_2.3H_2O$ has been determined by X-ray diffractometry (monoclinic, space group $P2_1/n$, a 9·694(8), b 19·218(14), c 16·652(9) Å, β 94·88(1)°, R 0·079 for 3254 reflections). This has Ni^{II} in octahedral coordination by secondary amine nitrogen atoms 10 and 13, hydrazone nitrogen atoms 1 and 6, and the carbinolamine oxygen substituent at position 3 of the pentadentate macrocyclic ligand L^2, with a water molecule coordinated *cis* to the hydroxy group. Compounds of the tautomeric cations $[Ni(L^2)]^{2+}$ and $[Ni(L^3)]^{2+}$ with coordinated thiocyanate, azide, nitrite, oxalate and acetate are described.

Introduction

There have been a number of reports of the formation of compounds of aza macrocycles with 1,2-dinitrogen functions (hydrazine, hydrazone or diazine groups), generally by reaction of hydrazine (or substituted hydrazines) with carbonyl compounds in the presence of metal ions.[1] One such compound is [Ni(omht)] $(ClO_4)_2$ (omht = 3,4,7,9,9,14,14,16-octamethyl-1,2,5,6,10,13-hexaazacyclohexadeca-2,4,6,16-tetraene), which is formed by the reaction of the dihydrazone compound [Ni(amhy)] $(ClO_4)_2$ (amhy = 4,4,9,9-tetramethyl-

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[1] Melson, G. A., (Ed.) 'Coordination Chemistry of Macrocyclic Ligands' (Plenum Press: New York 1979).

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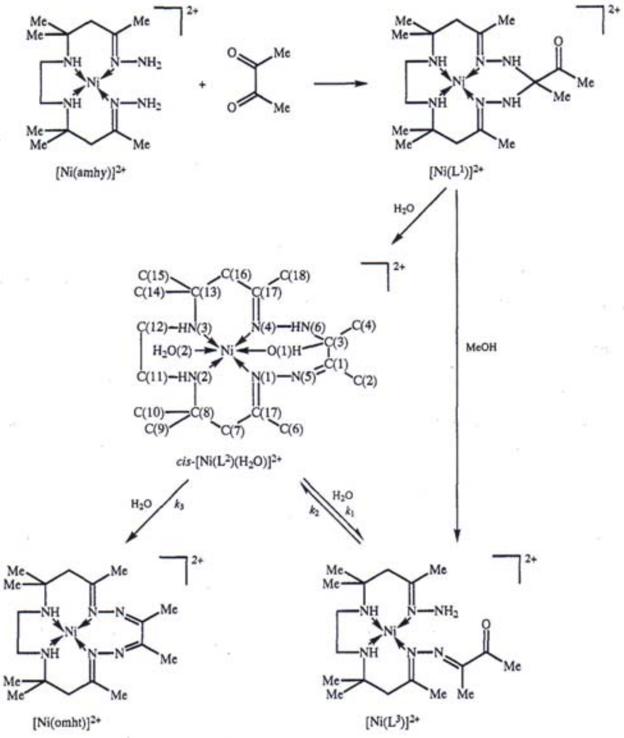
5,8-diazadodecane-2,11-dione dihydrazone)[2] with biacetyl (butane-2,3-dione), see Scheme 1. The preparation of [Ni(omht)] $(ClO_4)_2$, the 3,4-diphenyl homologue, the Cu^{II} analogue, and several triplet ground state, octahedrally coordinated Ni^{II} derivatives has been described.[3] The structures of square planar, singlet ground state [Ni(omht)] $(ClO_4)_2$ and of the octahedral triplet ground state μ-oxalato compound *cis*-$[\{Ni(omht)\}_2(C_2O_4)](ClO_4)_2.2H_2O$, which has the macrocycle in



Scheme 1. Reactions of $[Ni(amhy)]^{2+}$ with biacetyl. The cation *cis*-$[Ni(L^2)(H_2O)]^{2+}$ is shown in stylized form for clarity, with the atomic numbering used in the structural study for *cis*-$[NiL^2(H_2O)](ClO_4)_2.3H_2O$ shown; see Fig. 1 for the structure. k_1, k_2 and k_3 refer to measured rate constants. The cation $[Ni(L^1)]^{2+}$ was isolated for triplet ground state solvated compounds.

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[2] Curtis, N. F., *Inorg. Chim. Acta*, 1982, **59**, 171.

[3] Curtis, N. F., *Aust. J. Chem.*, 1988, **41**, 1665.

folded coordination, have been reported.[4] The kinetics of the hydrolysis in hydrochloric acid of [Ni(omht)]$^{2+}$ and of [Cu(omht)]$^{2+}$ have been measured.[3]

Compounds of a 15-membered diazine macrocycle related to omht have been described,[5] and the structure of one of these compounds reported.[6] Non-macrocyclic ligand compounds formed by reaction of [Ni(amhy)]$^{2+}$ with pentane-2,4-dione (acetylacetone) have been described.[7] [Ni(amhy)]$^{2+}$ and [Cu(amhy)]$^{2+}$ react with aliphatic aldehydes and ketones to form hexaaza macrocyclic ligand compounds with *gem* dihydrazine functions. The structure of one such compound, formed by reaction of [Cu(amhy)]$^{2+}$ with cyclohexanone, has been described[8] (see also p. 300 of ref. 1).

Further details of the reaction between [Ni(amhy)]($ClO_4)_2$ and biacetyl are now reported. Three compounds have been isolated as intermediate products of this reaction (the sequence of reactions is shown in Scheme 1), and the structure of one intermediate compound with the macrocyclic carbinolamine ligand L^2 has been determined. The structures of other compounds with carbinolamine ligands have been reported.[9] The L^2 carbinolamine cation equilibrates in water with the tautomeric cation with the non-cyclic ligand L^3, with hydrazine and with carbonyl groups. The rates are reported for the forward and reverse reactions of the tautomerism, and for the slower irreversible reaction of the equilibrium mixture to form the immine cation [Ni(omht)]$^{2+}$, in water at 25°C. The preparations and properties of these compounds, and of some thiocyanato, azido, nitrito, oxalato and acetato derivatives of the [$Ni(L^2)]^{2+}$ and [$Ni(L^3)]^{2+}$ cations are described.

Results and Discussion

Reaction of [Ni(amhy)](ClO$_4$)$_2$ with Biacetyl

Orange-red [Ni(amhy)]($ClO_4)_2$ reacts rapidly with 1 mol proportion of biacetyl in water (or methanol or ethanol) to form a blue-violet solution from which a blue-violet coloured, triplet ground state Ni^{II} compound of a ligand L^1, discussed below, crystallizes as a hydrate (or as alcohol solvates). The alcohol solvates are very soluble in water, rapidly recrystallizing as the hydrate.

The blue-violet hydrate is appreciably soluble in cold water, initially forming a blue-violet coloured solution, which slowly changes colour to 'grey-orange' over a period of hours at low to ambient temperatures. Sparingly soluble, deep-blue crystals of a triplet ground state Ni^{II} compound of a ligand L^2 form over a period of hours. These blue crystals are *sometimes* accompanied by orange crystals of a singlet ground state Ni^{II} compound of a ligand L^3, depending upon chance nucleation. These blue (and any orange) crystals then slowly redissolve and orange-red crystals of [Ni(omht)]($ClO_4)_2$ form over a period of days.

The blue compound has been structurally characterized as *cis*-aqua(3,4,7,9,9,14,14,16-octamethyl-1,2,5,6,10,13-hexaazacyclohexadeca-1(16),4,6-trien-3-ol)nickel(II) perchlorate trihydrate, *cis*-[$Ni(L^2)(H_2O)](ClO_4)_2.3H_2O$. The Ni^{II} ion is coordinated

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[4] Davis, A. R., Einstein, F. W. B., and Willis, A. C., *Acta Crystallogr., Sect. B*, 1982, **38**, 443.

[5] Curtis, N. F., and Morgan, K. R., *Aust. J. Chem.*, 1987, **40**, 1941.

[6] Einstein, F. W. B., and Jones, T. A., *Acta Crystallogr., Sect. C*, 1983, **39**, 872.

[7] Curtis, N. F., Einstein, F. W. B., and Willis, A. C., *Inorg. Chem.*, 1984, **23**, 3444.

[8] De Courcey, J. S., Ph.D. Thesis, University of Auckland, 1978.

[9] Haque, Z. P., McPartlin, M., and Tasker, P. A., *Inorg. Chem.*, 1979, **18**, 2920.

by N 1, N 6, N 10 and N 13 of the macrocycle, which is in folded coordination, and the oxygen atom of the carbinolamine hydroxy substituent at ring atom 3, and a water molecule. The structure is discussed further, below.

The blue crystals of *cis*-$[Ni(L^2)(H_2O)](ClO_4)_2.3H_2O$ are very soluble in methanol (less so in ethanol) forming a blue solution which changes colour to orange over a period of hours at ambient temperatures. Crystals of the orange L^3 compound which sometimes form in the aqueous solution slowly deposit from the solution, and the same compound crystallizes from methanol or ethanol solutions/suspensions of the compounds of L^1; these reactions all occur rapidly upon heating. The orange compound, $[Ni(L^3)](ClO_4)_2$, which is characterized by the presence of sharp bands in the infrared spectrum of $\nu(NH)$ at 3277 and 3146 cm^{-1}, $\nu(C{=}O)$ at 1719 cm^{-1} and of $\nu(C{=}N)$ at 1649 cm^{-1}, is the square-planar complex of the N_4-tetracoordinate non-macrocyclic ligand 3,6,8,8,13,13-hexamethyl-4,5,9,12-tetraazahexadeca-3,5-diene-2,15-dione 15-hydrazone. This structure for the L^3 ligand has been established by X-ray structural characterization of a derived compound β-$[Ni(L^3)(NO_2)](ClO_4).\frac{1}{2}H_2O$, described below.

The ligands L^2 and L^3 are tautomeric. In aqueous solutions *cis*-$[Ni(L^2)(H_2O)]^{2+}$ and $[Ni(L^3)]^{2+}$ interconvert to establish an equilibrium within *c*. 30 min, and this mixture converts irreversibly to $[Ni(omht)]^{2+}$ over a period of days at ambient temperatures.

The compounds of the ligands L^1, L^2 and L^3 are demetallated rapidly by acid, even by dilute acetic acid, while the macrocyclic ligand cation $[Ni(omht)]^{2+}$ is demetallated slowly (days) in acid.[3]

Attempts to react $[Cu(amhy)](ClO_4)_2$ with biacetyl to form analogues of the Ni^{II} compounds here described have been unsuccessful. However, $[Cu(L^3)](ClO_4)_2$ is readily prepared by metal-ion substitution from the Ni^{II} compound, and this is readily converted into $[Cu(omht)](ClO_4)_2$.[3]

Structure of the L^1 Ligand

The initially formed blue-violet compounds of the ligand L^1 remain structurally uncharacterized, as all attempts to prepare crystals of an L^1 compound adequate for diffraction measurements have been unsuccessful. Analysis indicates the composition $[Ni(C_{18}H_{40}N_6O_5)](ClO_4)_2$ for the hydrate, i.e. as for $[Ni(omht)]^{2+}$ plus 3 moles of water.

Some indication of a likely structure can be deduced from the spectroscopic properties. The infrared spectra of the compounds of L^1 show bands in the 'carbonyl' region at 1710s and 1660m(br) cm^{-1}. These values can be compared with those for *cis*-$[Ni(L^2)(H_2O)](ClO_4)_2.3H_2O$ which has coordinated and non-coordinated C=N groups, but no C=O groups, and absorbs at 1650 and 1620 cm^{-1}; with those of $[Ni(L^3)](ClO_4)_2$ which has both coordinated and non-coordinated C=N groups and a non-coordinated C=O group and shows strong sharp bands at 1719 and 1649 cm^{-1}; and with those of $[Ni(omht)](ClO_4)_2$ which has both coordinated and non-coordinated C=N groups and which shows a single sharp band at 1640 cm^{-1}. It appears probable that the L^1 ligand has C=O and C=N groups. Any $\nu(OH)$ absorption by a possible carbinolamine function for L^1 is masked by bands at 3650 and 3400 cm^{-1} assigned as $\nu(OH)$ of water.

The d–d spectrum of the L^1 compound in solution [CH_3CN; 852 (ϵ 10·7 l. mol^{-1} cm^{-1}) 550 nm (19·3)] was similar to that of the compound *cis*-$[Ni(L^2)(H_2O)](ClO_4)_2.3H_2O$ which has a *cis*-NiN_4O_2 chromophore [CH_3CN solution; 885 (ϵ 18·5), 546 nm (21·1)]. However, the lowest energy d–d transition ($^3T_{2g} \leftarrow {}^3A_{2g}$ of O_h) in the reflectance spectrum of the solid is a doublet ({1090, 860}, 570 nm), which indicates a large tetragonal component of the ligand field, and hence suggests a *trans* geometry. This band is singlet in the spectrum of *cis*-$[Ni(L^2)(H_2O)](ClO_4)_2.3H_2O$ (940, 569 nm). It is concluded that the aqua compound of L^1 probably has a *trans*-NiN_4O_2 chromophore in the solid state. The ν_3 band ($^3T_{1g}(P) \leftarrow {}^3A_{2g}$ transition of O_h) is generally obscured for these compounds.

Reaction of both hydrazine groups of $[Ni(amhy)](ClO_4)_2$ with *one* of the carbonyl groups of biacetyl, as observed with monofunctional carbonyl compounds (above),[1,8] (see also p. 300 of ref. 1) would give a 15-membered hexaaza macrocyclic ligand compound with 1,3-diazine function, (3-acetyl-3,6,8,8,13,13,15-heptamethyl-1,2,4,5,9,12-hexaazacyclopentadeca-5,15-diene)nickel(II) perchlorate. This structure, which is compatible with the infrared spectra of the L^1 compounds, is tentatively assumed. The L^1 compounds are formulated as aqua or alcohol solvates with octahedral triplet ground state Ni^{II} and tetradentate L^1, and, as example, the hydrate would have the diaqua cation $[Ni(L^1)(H_2O)_2]^{2+}$.

The reaction sequence of $[Ni(amhy)]^{2+}$ with biacetyl could thus be envisioned as an initial rapid reaction to form the $[Ni(L^1)]^{2+}$ cation with octahedral coordination of the Ni^{II} completed with water (or an alcohol). In water this transforms to the blue macrocyclic carbinolamine ligand cation *cis*-$[Ni(L^2)(H_2O)]^{2+}$ which exists in equilibrium with the non-macrocyclic tautomeric ligand cation $[Ni(L^3)]^{2+}$. This equilibrium mixture slowly transforms to the diazine macrocyclic ligand cation $[Ni(omht)]^{2+}$.

Solutions of *cis*-$[Ni(L^2)(H_2O)](ClO_4)_2$ in methanol, ethanol or acetone change from blue-violet to orange in colour over a period of hours as $[Ni(L^3)]^{2+}$ forms and the sparingly soluble orange perchlorate salt crystallizes from the alcohols. Blue-violet solutions of $[Ni(L^2)(H_2O)]^{2+}$ in acetonitrile ($[Ni(L^2)(MeCN)]^{2+}$?) are stable for prolonged periods. Conversion of $[Ni(L^3)]^{2+}$ into $[Ni(omht)]^{2+}$ in these non-aqueous solvents is extremely slow.

Tautomerism of cis-$[Ni(L^2)(H_2O)]^{2+}$ *and* $[Ni(L^3)]^{2+}$ *Cations*

cis-$[Ni(L^2)(H_2O)](ClO_4)_2.3H_2O$ initially forms a blue solution in water, which changes to an 'orange-grey' colour over *c.* 30 min. The bands of the spectrum of *cis*-$[Ni(L^2)(H_2O)]^{2+}$ decrease in intensity, while a band at 464 nm increases. $[Ni(L^3)](ClO_4)_2$ forms an orange solution in water which slowly changes colour as the 464 nm band of singlet ground state $[Ni(L^3)]^{2+}$ decreases in intensity, and bands of a triplet ground state Ni^{II} species increase, until the spectrum is the same as that of a solution of *cis*-$[Ni(L^2)(H_2O)](ClO_4)_2$. Rapid evaporation of aqueous solutions derived from either *cis*-$[Ni(L^2)(H_2O)](ClO_4)_2$ or $[Ni(L^3)](ClO_4)_2$ yield a mixture of the two compounds. It is reasonable to conclude that the $[Ni(L^2)]^{2+}$ and $[Ni(L^3)]^{2+}$ cations, which have tautomeric ligands, are interconverting.

The first-order rate constant k_1 at 25°C for the $[Ni(L^2)]^{2+} \rightarrow [Ni(L^3)]^{2+}$ reaction was obtained from the rate of increase in intensity of the 464 nm band of $[Ni(L^3)]^{2+}$ as $9 \cdot 5(5) \times 10^{-4}\ s^{-1}$. The first-order rate constant k_2 for the $[Ni(L^3)]^{2+} \rightarrow [Ni(L^2)]^{2+}$ reaction was obtained from the rate of decreasing intensity of the 464 nm band for a solution of $[Ni(L^3)](ClO_4)_2$ as $1 \cdot 3(2) \times 10^{-3}\ s^{-1}$ at 25°C.

The equilibrium constant for the tautomeric interconversion of the $[Ni(L^3)]^{2+}$ and $[Ni(L^2)(H_2O)]^{2+}$ cations, $[Ni(L^3)]^{2+}$ concentration divided by $[Ni(L^2)(H_2O)]^{2+}$ concentration, calculated from the ratio k_1/k_2 of the forward and reverse rate constants, is 0·7. The absorbance at 464 nm of the $[Ni(L^3)]^{2+}$ solution decreased to *c.* 0·4 of the initial value at equilibrium, corresponding to an equilibrium constant of 0·7, in agreement with the value obtained from the rate constants.

Formation of [Ni(omht)]$^{2+}$

The equilibrium mixture of the $[Ni(L^3)]^{2+}$ and $[Ni(L^2)(H_2O)]^{2+}$ cations in water slowly and irreversibly transforms to $[Ni(omht)]^{2+}$. The first-order rate constant k_3 at 25°C for the formation of $[Ni(omht)]^{2+}$ from the equilibrium mixture in water was determined spectrophotometrically as $1 \cdot 6(1) \times 10^{-6}\ s^{-1}$.

The proposed sequence of reactions in water is shown in Scheme 1.

Compounds with Coordinated Anions

Compounds of the cations $[Ni(L^2)]^{2+}$ and $[Ni(L^3)]^{2+}$ with the coordinating anions thiocyanate, nitrite, azide, oxalate and acetate were prepared, all with triplet ground state Ni^{II}. Compounds of these types of $[Ni(omht)]^{2+}$ and $[Ni(amhy)]^{2+}$ have been described, and the structures of *cis*-$[\{Ni(omht)\}_2(C_2O_4)](ClO_4)_4.2H_2O$,[2] *cis*-$[Ni(amhy)(NO_2)](ClO_4)$[6] and *trans*-$[Ni(amhy)(NCS)_2].H_2O$[6,10] have been reported.

Attempts to isolate such derivatives with $[Ni(L^1)]^{2+}$ were generally unsuccessful. Compounds of L^1 appeared to be formed initially, but as the cation $[Ni(L^1)]^{2+}$ is chemically 'fragile' and readily hydrolyses to form $[Ni(amhy)]^{2+}$ or converts into $[Ni(L^2)(H_2O)]^{2+}$ in water, or to $[Ni(L^3)]^{2+}$ in methanol, the isolated products were usually contaminated.

The L^2 compounds $[Ni(L^2)(NCS)](ClO_4).H_2O$ and $[Ni(L^2)(NO_2)](ClO_4)$ were prepared from the perchlorate. Both show absorption in the $\nu(C{=}N)$ region of the infrared [1651sh, 1634, 1618sh, including δ(HOH) of water, and 1649, 1620 cm^{-1} respectively] supportive of assignment as L^2 compounds [cf. 1650, 1620 cm^{-1} for *cis*-$[(NiL^2)(H_2O)](ClO_4)_2]$. The formation of monoanion compounds indicates that the L^2 ligand is pentadentate in these compounds, as for the aqua cation.

The $\nu(C{\equiv}N)$ infrared absorption by the thiocyanate (2097vs(sp) cm^{-1}) is indicative of coordination by this group. For the nitrite derivative the infrared spectrum in the 1100–1300 cm^{-1} region [where ν(ONO) absorption is expected] is complex but comparison with the spectra of other L^2 compounds indicates probable assignment of a band at 1329 cm^{-1} to the nitrite ion. Reported values[11] for ionic nitrite (1335w, *c.* 1250 cm^{-1}) and nitrite coordinated to Ni^{II} [*N*-nitrito (1355, 1325w cm^{-1}), *O*-nitrito (1387, 1130w cm^{-1}) and *O,O′*-chelate

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[10] Willis, A. C., Ph.D. Thesis, University of British Columbia, 1980; *Diss. Abstr. Int. B*, 1980, **42**, 210.

[11] Hitchman, M. A., and Rowbottom, G. L., *Coord. Chem. Rev.*, 1982, **42**, 55.

nitrito (1289w, 1200 cm^{-1})] are in best agreement with *N*-coordination, so a structure $[Ni(L^2)(NO_2)](ClO_4)$ is proposed. The d–d spectra of the nitrito and thiocyanato compounds in solution (and by reflectance) are indicative of *cis*-NiN_4X_2 chromophores [spectra in acetonitrile; nitrito 552 (ϵ 23), >820 nm; thiocyanato 556 (23), 926 nm (14)].

Reaction of $[Ni(L^3)](ClO_4)_2$ with sodium nitrite, thiocyanate or azide in methanol yielded salmon-pink (nitrite) or violet coloured products of formula $[Ni(L^3)(X)](ClO_4)$. These formed yellow solutions in water with spectra indicating essentially complete dissociation to the singlet ground state $[Ni(L^3)]^{2+}$ cation. The nitrite formed a 'straw' coloured solution in methanol, the spectrum indicating partial dissociation. The original $[Ni(L^3)](ClO_4)_2$ crystallized rapidly when the nitrite was dissolved in aqueous sodium perchlorate. The infrared spectra of the compounds (apart from bands assignable to the coordinated anions) were very similar, which indicated analogous structures. The 'carbonyl' region of the infrared spectrum of all three compounds showed a single strong sharp band at 1656 cm^{-1}, with only a very weak band attributable to $\nu(C{=}O)$ at 1717 cm^{-1} (plus very weak bands at 1626 $\delta(NH_2)$? and 1526 cm^{-1} ?). The major decrease in intensity of the carbonyl group band from that observed for the spectrum of $[Ni(L^3)](ClO_4)_2$ could be attributed to coordination by this group, with strong coupling between the coordinated and non-coordinated $\nu(C{=}N)$ and the $\nu(C{=}O)$ groups leading to enhancement of the 1656 cm^{-1} band and weakening of the 1717 cm^{-1} band. The lowest energy band of the d–d spectra of the three compounds in solution and by reflectance are widely separated doublets, indicative of *trans*-NiN_4X_2 chromophores [spectra in acetonitrile: nitrito 530 (ϵ 23), *c*. 720 (5), *c*. 890 nm (6); thiocyanato 542 (27); 730 (7); 1010 nm (10); azido 540 (30), 730 (11), >820 nm].

Lilac coloured $[Ni(L^3)(NCS)]ClO_4$ showed a strong sharp $\nu(C{\equiv}N)$ band at 2081 cm^{-1} in the infrared. The formation of a monothiocyanato compound from preparations with excess thiocyanate present suggests that the ligand L^3 is probably pentadentate, although alternative arrangements with μ-thiocyanato groups are possible. The azido compound appears to have an analogous structure, with a single sharp $\nu(NNN)$ band at 2049 cm^{-1}. As for the L^2 nitrite compound, bands in the infrared spectrum of $[Ni(L^3)(NO_2)](ClO_4)$ could not unambiguously be assigned to nitrite, although a band at 1267 cm^{-1} is not present for the thiocyanate, and bands at 1379 and 1267 cm^{-1} are enhanced in intensity relative to the spectrum of the thiocyanate. The 1267 cm^{-1} band is closest to the value for non-coordinated nitrite, and no pair of the bands match the values reported for chelated, unidentate *O*-coordinated or *N*-coordinated nitrite (above). In spite of this, it appears probable that the nitrite, thiocyanate and azide compounds have analogous structures with the carbonyl group of the L^3 ligand coordinated *trans* to the unidentate coordinated anions.

The 'straw' coloured solution of the α-nitrite in methanol changed to blue-violet over a period of hours at ambient temperatures, and dark blue-violet crystals formed over a period of days. Conversion was also effected by boiling a methanol solution of the α-form for *c*. 10 min, or allowing a suspension in aqueous sodium nitrite to react for a period of days. A structural study of the initially produced blue compound, β-$[Ni(L^3)(NO_2)](ClO_4).\frac{1}{2}H_2O$, showed the ligand L^3 in folded coordination, with *O,O'*-chelate coordinated nitrite[10] (see also p. 330 of ref. 1).

The infrared spectrum of this form showed strong sharp bands at 1709 cm^{-1}, assigned as $\nu(C{=}O)$, a band of similar intensity at 1622 cm^{-1}, assigned as $\nu(C{=}N)$, and a weak band at 1645 cm^{-1} assigned as $\delta(HOH)$. Unambiguous assignment of bands to nitrite was again not possible because of the other ligand bands present, but strong bands (1221, 1211 cm^{-1}) and a weaker band at 1296 cm^{-1} are in reasonable agreement with reported values for *O,O′*-chelated nitrite.[11] The spectra in acetone [570 (ϵ 24), 910 nm (13)] and by reflectance [*c*. 450sh, 580, 910 nm (more intense)] were typical of a *cis*-NiN_4O_2 chromophore. Subsequently another form with the same composition, designated γ, crystallized, and the β-form has not crystallized since then. The two forms have very similar infrared spectra, the most significant difference being the frequency and relative intensity of the carbonyl band [1709 cm^{-1}, intensity of $\nu(C{=}N)$ and $\nu(C{=}O)$ comparable for the β-form; 1700 cm^{-1}, intensity $\nu(C{=}O) > \nu(C{=}N)$ for the γ-form]. It appears probable that the forms are crystal variants.

The d–d spectrum of the α-form is indicative of *trans*-NiN_4O_2 geometry, while the structural study of the β-form shows *cis*-NiN_4O_2 geometry. Planar coordination for the L^3 ligand is most likely with the coordinated secondary amine centres of opposite chirality, as observed for *trans*-$[Ni(amhy)(NCS)_2].H_2O$,[12] while the folded ligand configurations observed for β-$[Ni(L^3)(NO_2)]\,ClO_4.\frac{1}{2}H_2O$,[10] (see also p. 330 of ref. 1) *cis*-$[\{Ni(amhy)\}_2(C_2O_4)]\,(ClO_4)_2.2H_2O$[12] and *cis*-$[\{Ni(omht)_2(C_2O_4)\}]\,(ClO_4)_2.2H_2O$[4] have the same chirality for these centres. The $\alpha \rightarrow \beta/\gamma$ conversion observed for the nitrito compound therefore most probably arises from the inversion of one coordinated secondary amine centre, with coordinated carbonyl group and unidentate nitrite for the α-form and chelate nitrite for the β and γ forms.

Dinuclear Ni^{II} compounds with a variety of tetradentate amines which have bridging bidentate oxalato groups have been reported,[13] including *cis*-$[\{Ni(amhy)\}_2(C_2O_4)]\,(ClO_4)_2$[14] and *cis*-$[\{Ni(omht)\}_2(C_2O_4)]\,(ClO_4)_2.2H_2O$,[4] for which the structures have been determined. An analogous compound was prepared for $[Ni(L^3)]^{2+}$. Compounds of a variety of Ni^{II} tetraamines (and of $[Ni(amhy)]^{2+}$) with acetate functioning as a symmetrical *O,O′* chelate have also been characterized,[14] and the analogous compound *cis*-$[Ni(L^3)(CH_3CO_2)]\,(ClO_4)$ was prepared. The infrared spectra of these compounds showed the $\nu(C{=}O)$ band of L^3 at *c*. 1700 cm^{-1} with strong carboxylato bands at *c*. 1660 cm^{-1}.

Structural Determination

The structure of *cis*-aqua(3,4,7,9,9,14,14,16-octamethyl-1,2,5,6,10,13-hexaazacyclohexadeca-1(16),4,6-trien-3-ol)nickel(II) perchlorate trihydrate, *cis*-$[Ni(L^2)(H_2O)]\,(ClO_4)_2.3H_2O$, was determined by X-ray diffractometry, see the Experimental section for details. The atom numbering used for the structural study is as shown in Scheme 1. The cation of the compound is shown in Fig. 1, with dimensions shown in Tables 1 and 2. The nickel ion is in irregular *cis*-N_4O_2

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[12] Davis, A. R., Einstein, F. W. B., and Willis, A. C., *Acta Crystallogr., Sect. B*, 1982, **38**, 437.

[13] Curtis, N. F., *J. Chem. Soc. A*, 1968, 1584; Curtis, N. F., McCormick, I. R. N., and Waters, T. N., *J. Chem. Soc.*, 1973, 1537.

[14] Curtis, N. F., *J. Chem. Soc. A*, 1968, 1579; Whimp, P. O., Bailey, M. F., and Curtis, N. F., *J. Chem. Soc.*, 1970, 1956.

Table 1. Bond distances for *cis*-[Ni(L^2)(H_2O)] (ClO_4)$_2$.3H_2O

Atoms	Distance (Å)	Atoms	Distance (Å)
Ni–O(1)	2·154(4)	C(5)–C(7)	1·49(1)
Ni–O(2)	2·135(5)	C(7)–C(8)	1·54(1)
Ni–N(1)	2·053(6)	C(8)–C(9)	1·50(1)
Ni–N(2)	2·104(6)	C(8)–C(10)	1·53(1)
Ni–N(3)	2·070(6)	N(2)–C(8)	1·492(8)
Ni–N(4)	2·085(6)	N(2)–C(11)	1·504(8)
N(1)–N(5)	1·426(8)	C(11)–C(12)	1·50(1)
N(4)–N(6)	1·397(7)	N(3)–C(12)	1·43(1)
N(5)–C(1)	1·266(9)	N(3)–C(13)	1·50(1)
N(6)–C(3)	1·462(8)	C(13)–C(14)	1·52(1)
C(1)–C(2)	1·48(1)	C(13)–C(15)	1·53(1)
C(1)–C(3)	1·55(1)	C(13)–C(16)	1·50(1)
C(3)–C(4)	1·52(1)	C(16)–C(17)	1·51(1)
C(3)–O(1)	1·411(8)	C(17)–C(18)	1·48(1)
N(1)–C(5)	1·274(8)	N(4)–C(17)	1·269(8)
C(5)–C(6)	1·55(1)		

Table 2. Bond angles for *cis*-[Ni(L^2)(H_2O)] (ClO_4)$_2$.3H_2O

Atoms	Angle (degrees)	Atoms	Angle (degrees)
O(1)–Ni–O(2)	91·0(2)	N(1)–C(5)–C(6)	122·7(7)
O(1)–Ni–N(1)	74·9(2)	C(6)–C(5)–C(7)	115·3(7)
O(1)–Ni–N(2)	107·1(2)	N(1)–C(5)–C(7)	121·9(7)
O(1)–Ni–N(3)	167·3(2)	C(5)–C(7)–C(8)	116·8(6)
O(1)–Ni–N(4)	77·7(2)	C(7)–C(8)–N(2)	109·1(6)
O(2)–Ni–N(1)	163·7(2)	C(7)–C(8)–C(9)	111·6(6)
O(2)–Ni–N(2)	83·7(2)	C(7)–C(8)–C(10)	109·2(6)
O(2)–Ni–N(3)	96·5(2)	N(2)–C(8)–C(9)	106·7(6)
O(2)–Ni–N(4)	84·2(2)	N(2)–C(8)–C(10)	111·3(6)
N(1)–Ni–N(2)	92·7(2)	C(9)–C(8)–C(10)	108·9(2)
N(1)–Ni–N(3)	98·9(2)	Ni–N(2)–C(8)	118·4(4)
N(1)–Ni–N(4)	100·2(2)	Ni–N(2)–C(11)	106·3(4)
N(2)–Ni–N(3)	83·9(2)	C(8)–N(2)–C(11)	112·9(5)
N(2)–Ni–N(4)	167·0(2)	N(2)–C(11)–C(12)	112·4(6)
N(3)–Ni–N(4)	92·8(2)	N(3)–C(12)–C(11)	110·1(7)
Ni–N(1)–N(5)	118·3(4)	C(12)–N(3)–C(13)	119·4(6)
Ni–N(4)–N(6)	114·8(4)	Ni–N(3)–C(12)	103·9(4)
N(1)–N(5)–C(1)	119·9(6)	Ni–N(3)–C(13)	117·7(5)
N(4)–N(6)–C(3)	110·4(5)	N(3)–C(13)–C(14)	110·9(6)
Ni–O(1)–C(3)	106·2(4)	N(3)–C(13)–C(15)	105·6(6)
N(5)–C(1)–C(2)	114·7(7)	N(3)–C(13)–C(16)	112·6(6)
N(5)–C(1)–C(3)	128·1(7)	C(16)–C(13)–C(14)	109·1(7)
C(2)–C(1)–C(3)	117·1(7)	C(16)–C(13)–C(15)	110·5(7)
N(6)–C(3)–C(4)	107·9(5)	C(14)–C(13)–C(15)	108·0(7)
N(6)–C(3)–C(1)	103·3(6)	C(13)–C(16)–C(17)	120·0(6)
N(6)–C(3)–O(1)	111·0(5)	C(16)–C(17)–C(18)	118·4(7)
O(1)–C(3)–C(1)	110·2(6)	C(18)–C(17)–N(4)	123·3(7)
O(1)–C(3)–C(4)	110·5(6)	C(16)–C(17)–N(4)	118·3(7)
C(1)–C(3)–C(4)	113·8(6)	Ni–N(4)–C(17)	125·8(5)
Ni–N(1)–C(5)	127·1(5)	C(17)–N(4)–N(6)	116·7(6)
N(5)–N(1)–C(5)	113·5(6)		

octahedral coordination. A 16-membered hexaaza macrocyclic ligand, related to omht by the formal addition of water across one hydrazone function of omht to form the carbinolamine, is coordinated by four nitrogen atoms and the carbinolamine oxygen. The macrocycle is in folded coordination, with a water molecule coordinated *cis* to the carbinolamine oxygen. A seven-membered bis-diazine chelate ring is present, as for the omht compounds [N(1)–Ni–N(4), 100°] but the coordinated pendant carbinolamine oxygen creates new constrained six-membered [O(1)–Ni–N(1), 75°] and five-membered [O(1)–Ni–N(4), 78°] chelate rings. The Ni–N distances to the secondary amine nitrogens [N(2), 2·10; N(3), 2·07 Å] are marginally longer than to the hydrazone nitrogens [N(1), 2·05; N(4), 2·09 Å], while the Ni–O distances to the water oxygen (2·14 Å) and hydroxy oxygen (2·15 Å) are similar. The C–N distances to the carbon atoms C(1) and C(3) of the biacetyl residue [C(1)–N(5), 1·27; C(3)–N(6), 1·46 Å], together with the angles about these atoms, clearly indicate the presence of the hydrazone and carbinolamine functions, respectively. The macrocycle conformation is related to that present for *cis*-$[\{Ni(omht)\}_2(C_2O_4)](ClO_4)_2.2H_2O$, with the macrocycle folded along N(2)–Ni–N(4) (167°) and with the same helicity for the coordinated secondary amine centres N(1) and N(2), which are rendered inequivalent by the presence of the carbinolamine function.

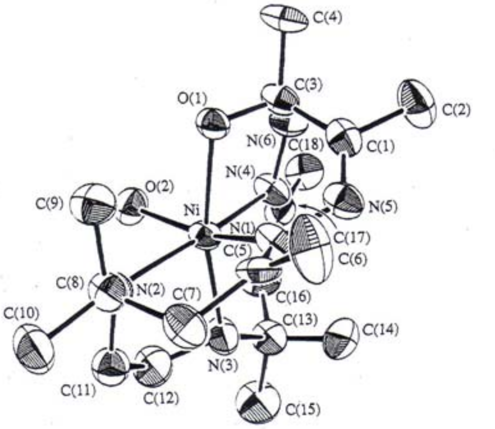

Fig. 1. ORTEP drawing of the complex cation of *cis*-aqua(3,4,7,9,9,14,14,16-octamethyl-1,2,5,6,10,13-hexaazacyclooctadeca-1(16),4,6-trien-3-ol)nickel(II) perchlorate trihydrate, *cis*-$[Ni(L^2)(H_2O)]^{2+}$. Atom numbering is as shown in Scheme 1.

Experimental

The compound $[Ni(amhy)](ClO_4)_2$ was prepared as previously described.[2] The yields of the L^1, L^2 and L^3 compounds were essentially quantitative.

Infrared spectra were measured with a Digilab FTS40 instrument. Magnetic susceptibilities were measured by using a Sherwood susceptibility balance with $Hg[Co(NCS)_4]$ as calibrant.

This preparation was repeated a number of times, but success appears to depend upon the failure of $[Ni(L^3)](ClO_4)_2$ to nucleate. The crystallization of the L^2 product effectively continuously displaces the $L^2 \rightleftharpoons L^3$ equilibrium in favour of L^2. Should $[Ni(L^3)](ClO_4)_2$ nucleate, then a mixture of the blue L^2 and orange L^3 compounds is obtained. These can be separated by recrystallization from methanol/water, as described above.

(3,4,7,9,9,14,14,16-Octamethyl-1,2,5,6,10,13-hexaazacyclohexadeca-1(16),4,6-trien-3-ol)-(thiocyanato)nickel(II) *Perchlorate Hydrate,* $[Ni(L^2)(NCS)](ClO_4).H_2O$

Cold solutions of *cis*-$[Ni(L^2)(H_2O)](ClO_4)_2.3H_2O$ (0·5 g) and sodium thiocyanate (0·2 g) in methanol were mixed and propan-2-ol was added. The blue-violet *product* was filtered off and washed with ethanol. Effective magnetic moment at 23°C, 3·2 μ_B (Found: C, 38·8; H, 6·9; N, 16·2. $C_{18}H_{38}ClN_7NiO_6$ requires C, 38·9; H, 6·5; N, 16·7%).

Nitrito(3,4,7,9,9,14,14,16-octamethyl-1,2,5,6,10,13-hexaazacyclohexadeca-1(16),4,6-trien-3-ol)nickel(II) *Perchlorate,* $[Ni(L^2)(NO_2)](ClO_4)$

A cold concentrated methanol solution of *cis*-$[Ni(L^2)(H_2O)](ClO_4)_2.3H_2O$ was added to a small volume of water containing excess of sodium nitrite. The blue-violet *product* was filtered off and washed well with ethanol (Found: C, 38·7; H, 6·7; N, 17·6. $C_{18}H_{36}ClN_7NiO_7$ requires C, 38·7; H, 6·9; N, 17·5%).

(3,6,8,8,13,13-Hexamethyl-4,5,9,12-tetraazahexadeca-3,5-diene-2,15-dione 15-hydrazone)nickel(II) *Perchlorate,* $[Ni(L^3)](ClO_4)_2$

The methanol solvate of $[Ni(L^1)](ClO_4)_2$, obtained from the first preparation, was dissolved in warm methanol (10 g in 50 ml), and the solution was filtered and allowed to react for *c.* 1 day, while the orange product crystallized. The crystals were filtered off and washed with propan-2-ol. The *compound* was recrystallized from hot methanol, or by dissolving in acetonitrile plus a few drops of water, and adding propan-2-ol (Found: C, 35·7; H, 5·6; N, 13·7; Ni, 9·5. $C_{18}H_{36}Cl_2N_6NiO_9$ requires C, 35·4; H, 5·9; N, 13·8; Ni, 9·6%).

(3,6,8,8,13,13-Hexamethyl-4,5,9,12-tetraazahexadeca-3,5-diene-2,15-dione 15-hydrazone)(thiocyanato)nickel(II) *Perchlorate,* $[Ni(L^3)(NCS)](ClO_4)$

This blue-violet coloured compound was formed by dissolving $[Ni(L^3)](ClO_4)_2$ in warm methanol containing 2 mol proportions of sodium thiocyanate, quickly filtering, and precipitating the blue-violet *product* with propan-2-ol. This was recrystallized from hot methanol. Effective magnetic moment at 21°C, 3·0 μ_B (Found: C, 40·1; H, 6·4; N, 17·4. $C_{19}H_{36}ClN_7NiO_5$ requires C, 40·1; H, 6·4; N, 17·2%).

Azido(3,6,8,8,13,13-hexamethyl-4,5,9,12-tetraazahexadeca-3,5-diene-2,15-dione 15-hydrazone)nickel(II) *Perchlorate,* $[Ni(L^3)(N_3)](ClO_4)$

This blue-violet *compound* was prepared as for the previous compound by substituting sodium azide for the thiocyanate salt (Found: C, 40·2; H, 6·8; N, 17·4; Ni, 9·9. $C_{19}H_{36}ClN_7NiO_5S$ requires C, 40·1; H, 6·4; N, 17·2; Ni, 10·3%).

α-(3,6,8,8,13,13-Hexamethyl-4,5,9,12-tetraazahexadeca-3,5-diene-2,15-dione 15-hydrazone)(nitrito)nickel(II) *Perchlorate,* α-$[Ni(L^3)(NO_2)](ClO_4)$

$[Ni(L^3)](ClO_4)_2$ was dissolved in hot methanol (or cold water) containing 2 mol proportions of sodium nitrite, and the solution was quickly filtered. The salmon-pink coloured α-form crystallized within minutes. This was filtered off and washed with ethanol. The *product* was recrystallized from hot acetonitrile/propan-2-ol, or quickly from hot methanol. Effective magnetic moment at 21°C, 3·0 μ_B (Found: C, 39·0; H, 6·3; Ni, 10·4. $C_{18}H_{36}ClN_7NiO_7$ requires C, 38·8; H, 6·5; Ni, 10·5%).

γ-(3,6,8,8,13,13-Hexamethyl-4,5,9,12-tetraazahexadeca-3,5-diene-2,15-dione 15-hydrazone)-(nitrito-O,O′)nickel(II) Perchlorate Hemihydrate, γ-$[Ni(L^3)(NO_2)](ClO_4).\frac{1}{2}H_2O$

The α-form (previous preparation) was suspended in methanol to give an orange-pink solution, which slowly changed to mauve over *c.* 1 day at ambient temperatures. Blue crystals of the product were filtered off when the starting material had all reacted, after *c.* 3 days, and washed with ethanol. Alternatively, the α-form was boiled in methanol for *c.* 10 min, the product crystallizing as the solution cooled. The *compound* was recrystallized from hot methanol.

This compound initially crystallized in a variant designated β for which the structure was determined (see p. 330 of ref. 1). It later crystallized in a different form, designated γ, of the same composition. The two forms have the same d–d spectra and the infrared spectra are similar but differ in detail, the most obvious difference being in the frequency and relative intensity of the ν(C=O) band, see above. Effective magnetic moment of γ-form at 21°C, 3·1 μ_B (Found for β form: C, 38·6; H, 6·5; N, 17·4. Found for γ form: C, 38·6; H, 6·5; N, 17·4. $C_{18}H_{37}ClN_7NiO_{7\cdot5}$ requires C, 38·2; H, 6·6; N, 17·3%).

μ-Oxalato-bis[(3,6,8,8,13,13-hexamethyl-4,5,9,12-tetraazahexadeca-3,5-diene-2,15-dione 15-hydrazone)nickel(II)] Perchlorate, $[\{Ni(L^3)\}_2(C_2O_4)](ClO_4)_2$

$[Ni(L^3)](ClO_4)_2$ was stirred in hot methanol and diethylammonium oxalate was added in small portions until all the orange starting material had dissolved; the sparingly soluble blue-violet product was recrystallized when the supernatant solution changed from orange to pale blue in colour. The *product* was recrystallized from hot acetonitrile/propan-2-ol (Found: C, 40·9; H, 6·7; Ni, 10·7. $C_{19}H_{36}ClN_6NiO_7$ requires C, 41·1; H, 6·5; Ni, 10·6%).

Diethylammonium oxalate was prepared by adding 0·5 mol proportion of oxalic acid to diethylamine (33% in ethanol), followed by propan-2-ol. The white crystalline product was filtered off, washed with propan-2-ol and stored in a desiccator. Preparations analogous to that described for the L^3 compound can be used to make a variety of Ni^{II} and Cu^{II} amine oxalato products.

cis-*(Acetato-O,O′)(3,6,8,8,13,13-hexamethyl-4,5,9,12-tetraazahexadeca-3,5-diene-2,15-dione 15-hydrazone)nickel(II) Perchlorate,* cis-$[Ni(L^3)(CH_3CO_2)](ClO_4)$

This very water-soluble blue-violet *compound* was prepared in ethanol as for the nitrito analogue, by substituting sodium acetate for the nitrite salt (Found: C, 42·5; H, 7·3. $C_{20}H_{39}ClN_6NiO_7$ requires C, 42·2; H, 6·9%).

Structural Study

The structure of the compound *cis*-aqua(3,4,7,9,9,14,14,16-octamethyl-1,2,5,6,10,13-hexaazacyclohexadeca-1(16),4,6-trien-3-ol)nickel(II) perchlorate trihydrate, *cis*-$[Ni(L^2)(H_2O)](ClO_4)_2.3H_2O$, was determined by X-ray diffractometry.

The compound crystallized from water as blue rhombohedral plates. A crystal of approximate dimensions 0·30 by 0·30 by 0·25 mm was used for the study. Weissenberg photographs of the $hk0$ and $hk1$ layers and precession photographs of the $h0l$, $h1l$ and $0kl$ layers established the monoclinic space group $P2_1/n$ (absences for $h0l$, $h+l = 2n+1$, and $0k0$, $k = 2n+1$). The crystal was mounted with the c^* axis approximately coincident with the axis of a Picker FACS-1 four-circle diffractometer. Twelve reflections with $2\theta > 25°$ were centred and from their positions accurate cell dimensions were calculated.

Crystal data: $C_{18}H_{44}Cl_2N_6NiO_{13}$; M_r 682·2; monoclinic, space group $P2_1/n$, a 9·694(8); b 19·218(14); c 16·652(9) Å; β 94·88(1)°; V 3091(0) $Å^{-3}$; $\rho_{meas.}$ 1·47(1); $\rho_{calc.}$ 1·47 g cm^{-3}; Z 4; μ 8·70 cm^{-1}; temperature 21°C. Intensity data were collected by using graphite-monochromatized Mo Kα radiation (λ 0·70926 Å) with symmetrical θ–2θ scans with a scan rate of 2°/min, in two sets, an inner sphere with $2\theta < 30°$ with a scan width of 1·4° and an outer shell of data with $30° > 2\theta > 45°$ collected with a scan width of 1·0°. A total of

4295 reflections were measured, and of these 3254 were considered to be observed, i.e. with intensity $I > 2\cdot3\sigma(I)$, where $\sigma(I) = [C_T+(t_S/t_B)^2(B_1+B_2)+(kI)^2]^{\frac{1}{2}}$, where C_T is the total count, B_1 and B_2 are the background counts at each end of the scan range, t_S is the scan time, t_B is the total background count time, k is a constant set to $0\cdot03$, and I is the net count. The measured intensities were corrected for Lorentz and polarization effects. Absorption was neglected since it was estimated to introduce a maximum error of $\pm0\cdot5\%$ in the net count.

The structure was solved by direct methods by using the inner data set only.[15] From a three-dimensional Fourier synthesis with 100 reflections with E values $>1\cdot5$, the positions of the nickel, two chlorine and ten lighter atoms were determined. Least squares refinement of these parameters and a scale factor gave a residual R-factor of $0\cdot32$, where $R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$. Several cycles of refinement and subsequent electron density difference synthesis revealed all non-hydrogen atom positions. Inclusion of the outer set of data, and with calculated hydrogen atom positions, together with anisotropic thermal motion parameters for all non-hydrogen atoms gave an R-factor of $0\cdot092$. Considerable thermal motion was evident for the oxygen atoms of both perchlorate ions. For O(11) refinement in two half-occupied positions gave a model which fitted the data better. For other oxygen atoms the pairs of positions did not refine well and gave no improved agreement with the data. Full matrix least squares refinement gave a final R-factor of $0\cdot079$ for 370 parameters. In the final refinement a weighting of $1/\sigma^2(F)$ was used, where $\sigma(F) = \sigma(I)/(L_p.2F_o)$. Atomic scattering factors used[16] included corrections for anomalous dispersion for nickel ($\Delta f' = 0\cdot285$, $\Delta f'' = 1\cdot113$) and chlorine ($\Delta f' = 0\cdot132$, $\Delta f'' = 0\cdot159$).

Table 3. Positional parameters for *cis*-[Ni(L^2)(H_2O)](ClO_4)$_2$.$3H_2O$

Cl(1) plus O(11)–O(14) and Cl(2) plus O(21)–O(24) constitute perchlorate ions, O(1) coordinated water oxygen, O(3) coordinated hydroxy oxygen and O(2), O(4) and O(5) water of crystallization oxygen atoms

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$
Ni	1695·2(9)	2412·0(4)	1569·2(5)	N(5)	4436(6)	1692(3)	1901(4)
Cl(1)	−2417(3)	4787(1)	1212(2)	N(6)	1714(6)	956(3)	998(3)
Cl(2)	2923(3)	3782(1)	4604(1)	C(1)	4050(8)	1243(4)	1374(5)
O(11)	−2720(22)	5437(9)	1387(15)	C(2)	4756(9)	559(4)	1476(6)
O(11)′	−3586(19)	5221(12)	1140(13)	C(3)	4050(8)	1243(4)	1374(5)
O(12)	−2306(8)	4426(5)	1930(6)	C(4)	3204(8)	935(4)	−89(5)
O(13)	−1148(9)	4947(5)	973(6)	C(5)	4640(8)	2863(4)	1949(4)
O(14)	−2936(11)	4338(6)	655(7)	C(6)	6220(8)	2763(4)	1916(6)
O(21)	3251(7)	3219(4)	4088(4)	C(7)	4176(8)	3595(4)	2020(5)
O(22)	4026(10)	4257(5)	4690(6)	C(8)	3068(8)	3855(4)	1375(4)
O(23)	2819(8)	3525(4)	4617(4)	C(9)	3432(8)	3671(4)	541(5)
O(24)	1707(8)	4093(4)	4323(5)	C(10)	2941(8)	4647(4)	1440(5)
O(1)	2583(5)	2015(2)	518(3)	C(11)	1059(8)	3771(4)	2214(4)
O(2)	−280(5)	2517(3)	908(3)	C(12)	232(9)	3223(4)	2593(5)
O(3)	−415(6)	3656(3)	−26(3)	C(13)	442(8)	1993(4)	3128(5)
O(4)	724(6)	3512(3)	−152(3)	C(14)	−393(10)	2244(5)	3807(5)
O(5)	1111(6)	2184(3)	−99(3)	C(15)	1700(10)	1590(4)	3507(5)
N(1)	3786(6)	2358(3)	1888(3)	C(16)	−449(8)	1531(4)	2576(5)
N(2)	1726(6)	3504(3)	1491(3)	C(17)	195(8)	1098(4)	1950(4)
N(3)	1022(7)	2594(3)	2697(4)	C(18)	−379(8)	395(4)	1766(5)
N(4)	1183(6)	1359(3)	1598(3)				

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[15] Programs used: Gabe, E. J., Larsen, A. C., Lee, F. L., and Wang, Y., 'The PDP-8e Crystal Structure System', N.R.C. Ottawa, 1979.

[16] Cromer, D. T., and Waber, J. T., 'International Tables for X-Ray Crystallography' Vol. IV (Kynoch Press: Birmingham 1974).

Atom site parameters are shown in Table 3. Structure factors, thermal parameters and a unit cell packing diagram are in an Accessory Publication (available from the Australian Journal of Chemistry, P.O. Box 89, East Melbourne, Vic. 3002).

Kinetic Measurements

The rate of conversion in water at 25°C of $[Ni(L^3)]^{2+}$ (and of $[Ni(L^2)(H_2O)]^{2+}$) to an equilibrium mixture of triplet ground state $[Ni(L^2)(H_2O)]^{2+}$ and singlet ground state $[Ni(L^3)]^{2+}$ were measured spectrophotometrically by following the rate of decreasing (or increasing) absorbance at 464 nm (characteristic of the $[Ni(L^3)]^{2+}$ cation), by using the thermostatted cell compartment of a Hewlett Packard model 8452A spectrophotometer. The rate of conversion at 25°C of this equilibrium mixture to $[Ni(omht)]^{2+}$ was measured by periodically withdrawing an aliquot of a solution kept in a thermostat bath, prepared from $[Ni(L^3)](ClO_4)_2$, and acidifying with concentrated hydrochloric acid (0·05 ml added to 2·5 ml of solution). The absorbance at 500 nm (characteristic of $[Ni(omht)]^{2+}$) was measured after 3 min with the same instrument, by which time most of the $[Ni(L^2)(H_2O)]^{2+}$ and $[Ni(L^3)]^{2+}$ cations had hydrolysed, but an insignificant proportion of $[Ni(omht)]^{2+}$ had hydrolysed.[3]