

***trans*-Dioxocyclam (1,4,8,11-tetraaza-cyclotetradecane-2,9-dione) dihydrate and its Ni<sup>II</sup> complex**Timothy J. Hubin,<sup>a</sup> Nickolay Tyryshkin,<sup>a</sup> Nathaniel W. Alcock<sup>b\*</sup> and Daryle H. Busch<sup>a†</sup><sup>a</sup>Department of Chemistry, University of Kansas, Lawrence, KS 66045, USA, and<sup>b</sup>Department of Chemistry, University of Warwick, Coventry CV4 7AL, England

Correspondence e-mail: msrbb@csv.warwick.ac.uk

Received 31 October 2000

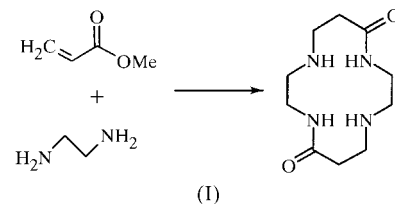
Accepted 14 December 2000

The crystal structures are reported of *trans*-dioxocyclam dihydrate, C<sub>10</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>·2H<sub>2</sub>O, a structural isomer of the well known *cis*-dioxocyclam, and of its novel Ni complex, (1,4,8,11-tetraazacyclotetradecane-2,9-dionato-*k*<sup>4</sup>N)nickel(II) dihydrate, [Ni(C<sub>10</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>)·2H<sub>2</sub>O], the first example of a transition metal complex of this ligand. Both molecules lie on crystallographic centres of inversion. The free ligand has two of its N atoms turned outwards from the ring and hydrogen bonded to water molecules. A major conformational change takes place in the complex in which the ligand binds in a *trans* tetradentate fashion, as suggested by the electronic spectrum. The nickel(II) ion is low spin, although the electronic spectrum of the complex in water indicates an equilibrium mixture of low-spin and high-spin species. The irreversible electrochemical oxidation of [NiL<sup>1</sup>] (L<sup>1</sup> is deprotonated *trans*-dioxocyclam, C<sub>10</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>) in water occurs at a potential of 0.964 V [*versus* SHE (standard hydrogen electrode)], which is very similar to that for the Ni-*cis*-dioxocyclam complex.

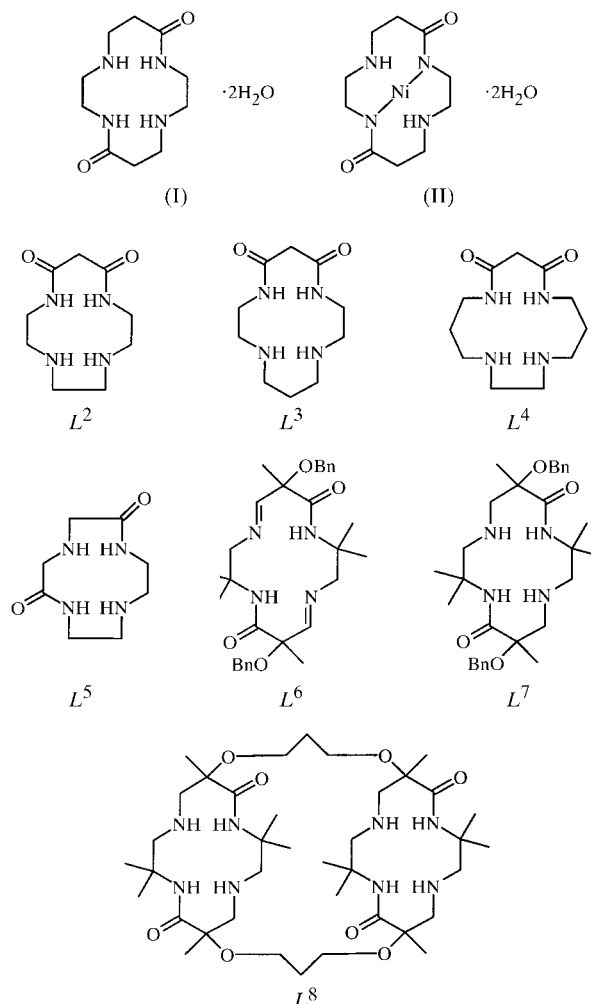
**Comment**

Macrocyclic ligands containing amide groups have recently been extensively exploited for transition metal coordination because they share the properties of oligopeptides and the more common polyamine macrocycles (Kimura, 1986). These ligands have proved particularly significant as transition metal oxidation catalysts, because the inherent negative charge of the bound deprotonated forms can stabilize high oxidation states of transition metal ions (*e.g.* Collins *et al.*, 1992). Our own studies concerned with the design of aqueous transition metal oxidation catalysts have focused on the use of intramolecularly cross-bridged tetraaza-macrocycles to produce kinetically stable complexes (Hubin *et al.*, 1998, 2000). The *trans*-dioxocyclam ligand, 1,4,8,11-tetraazacyclotetradecane-

2,9-dione (L<sup>1</sup>H<sub>2</sub>), has recently been shown to be effectively *trans* diprotected for bridging reactions that produce cross-bridged ligands (Denat *et al.*, 1997); cross-bridging such a bis(amide) ligand might produce exceptional kinetic stability, as well as stabilization of high-valent transition metal complexes. We have begun to explore the coordination



chemistry of unbridged L<sup>1</sup>H<sub>2</sub> in order to compare this with cross-bridged analogues. The ligand L<sup>1</sup>H<sub>2</sub> (see reaction scheme below) is a structural isomer of the extensively studied *cis*-dioxocyclam, L<sup>3</sup>, one of a family (L<sup>2</sup>–L<sup>5</sup>) of dioxomacrocycles studied by Kimura (see scheme). Although the synthesis of L<sup>1</sup> is quite simple, by a Michael addition between ethylenediamine and methyl acrylate (Tomalia & Wilson, 1985), and the ligand has been known for 15 years, no work on its transition metal complexes has been published. However,



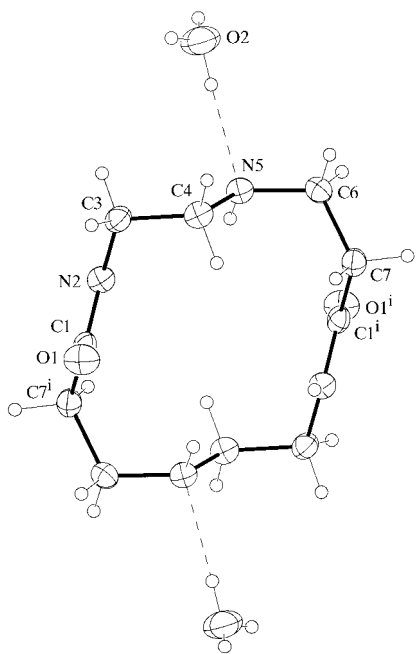
some substituted analogues (L<sup>6</sup>–L<sup>8</sup>) of the same *trans*-dioxo configuration have been synthesized by a different method,

† Additional corresponding author.

and their Ni<sup>II</sup> complexes have been reported (Betschart & Hegedus, 1992; Dumas *et al.*, 1995). We report here the crystal structures of *L*<sup>1</sup>H<sub>2</sub>·H<sub>2</sub>O, (I), and the corresponding Ni<sup>II</sup> complex, [NiL<sup>1</sup>]<sup>+</sup>·2H<sub>2</sub>O, (II).

The molecular structure of (I) is shown in Fig. 1. The asymmetric unit contains one lattice water molecule, which is hydrogen bonded to the secondary amine N atom [O2···N5 2.843 (3) Å] and to a second water molecule [O2···O2(−*x*, −*y*, 2 − *z*) 2.805 (3) Å]; because these atoms are related by a centre of inversion, their H atoms are disordered. The ligand molecules are also linked by hydrogen bonds between the amide O atom and a symmetry-related amide N atom [O1···N2(1 + *x*, *y*, *z*) 2.848 (3) Å].

Complexation of Ni<sup>2+</sup> with *L*<sup>1</sup>H<sub>2</sub> to form (II) was achieved by the *in situ* deprotonation of the two amide N atoms with KH in dimethylformamide (DMF) to produce amidate donors, followed by the addition of anhydrous NiCl<sub>2</sub> to the DMF solution. The crystal structure of (II) is shown in Fig. 2. The Ni<sup>II</sup> ion has square-planar geometry at the centre of the bis(amidate) macrocycle. Thus, a major conformational change occurs as the ligand binds the metal ion, directing all nitrogen lone pairs into the centre of the ring and placing the four N atoms essentially coplanar with Ni<sup>II</sup>. The N—Ni—N angles where the N atoms are separated by an ethylene chain are smaller by about 8° than those where they are separated by a propylene chain [86.1 (2) *versus* 93.9 (2)°]. The result is a compression of the square plane into a slightly rectangular geometry. The Ni—N<sub>amidate</sub> bonds are slightly shorter than the Ni—N<sub>amine</sub> bonds, at 1.892 (5) and 1.902 (5) Å, respectively, as might be expected due to the increased charge attraction between the amidate N atoms and the cation. This bond-

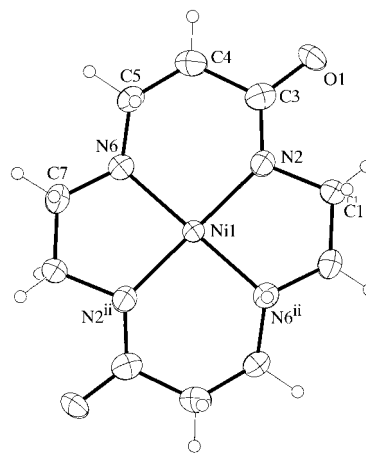


**Figure 1**  
The molecular diagram of (I) showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) −*x*, 1 − *y*, 1 − *z*].

length difference is about twice that found in the Ni<sup>II</sup> complex of the octa-*C*-substituted ligand analogue having the same size and amide placement (*L*<sup>7</sup>), where the bond distances are 1.915 Å for Ni—N<sub>amine</sub> and 1.911 Å for Ni—N<sub>amidate</sub> (Dumas *et al.*, 1995). Steric interactions between the ring substituents may account for these rather longer Ni—N bond lengths.

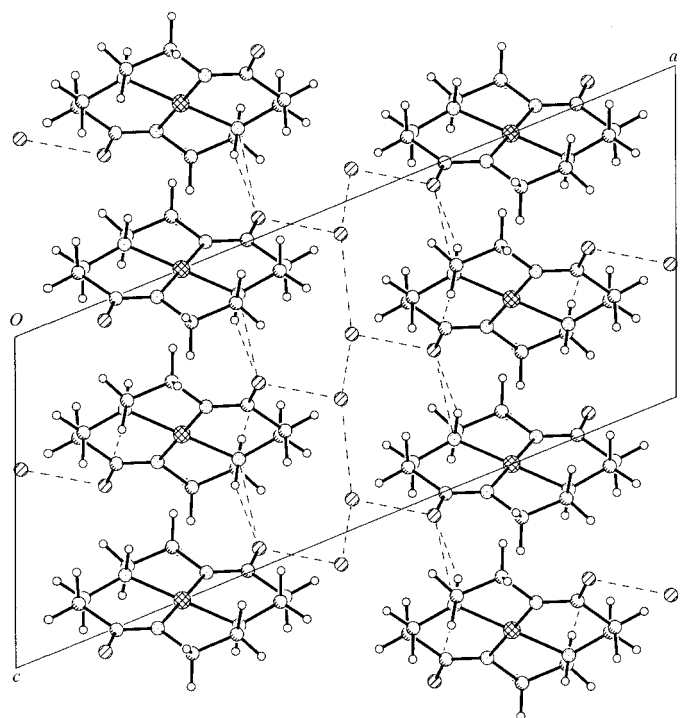
Fig. 3 shows the interesting hydrogen-bonding interactions between adjacent molecules of (II) in the solid state. In each bound ligand, one secondary amine is the hydrogen-bond donor to the carbonyl O atom of a neighbouring ligand [N6···O1(*x*, 1 − *y*, *z* − ½) 2.883 (7) Å], and the carbonyl O atom is the corresponding hydrogen-bond acceptor from a different ligand. The result is a chain of stacked planar complexes running along the *c* axis of the crystal. The chains are bridged by the lattice water molecules hydrogen bonded to the amide O atoms [O1···O2 2.780 (5) Å] and to each other [O2···O2(−*x*, 2 − *y*, *z*) 2.920 (7) and O2···O2(−*x*, *y*, −½ − *z*) 2.934 (7) Å]; as for the ligand, the H atoms, which were not located, must be disordered.

The electronic spectrum of (II) in water shows two absorption maxima, a shoulder at λ<sub>max</sub> = 439 nm (ε = 60 M<sup>−1</sup> cm<sup>−1</sup>) and λ<sub>max</sub> = 497 nm (ε = 90 M<sup>−1</sup> cm<sup>−1</sup>). Generally, only a single absorption band is observed for low-spin square-planar Ni<sup>II</sup> complexes (Lever, 1984). In the Ni complex of the 12-membered dioxocyclam *L*<sup>5</sup>, however, a spectrum having two maxima was observed, while those of the 13-, 14- and 15-membered *cis*-dioxomacrocycles *L*<sup>2</sup>–*L*<sup>4</sup> only show the expected single absorption from 410 to 465 nm (Kodama & Kimura, 1981). These single bands, and the lowest energy band for the 12-membered ligand, have been assigned as the single absorption arising from the low-spin square-planar Ni<sup>II</sup> species and its energy is taken as the ligand field strength *Dq*<sub>xy</sub>. For the 12-membered ligand complex, the higher energy band was attributed to an octahedral structure probably having the macrocycle occupying all equatorial positions in *trans* geometry, since folding of the dioxo ligand was expected to be energetically unfavourable. Such an equilibrium between



**Figure 2**  
The molecular diagram of (II) showing the atomic numbering, with the lattice water molecules omitted. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (ii) ½ − *x*, ½ − *y*, −*z*].

square-planar and octahedral forms is common in many oxygen-free tetraaza-macrocyclic complexes (Fabrizzi, 1977), but is usually not present in dioxo ligand complexes. In complex (II), assuming a similar assignment, the square-planar band would be at 497 nm ( $Dq_{xy} = 20\,100\text{ cm}^{-1}$ ), much lower than even in the 12-membered ligand ( $Dq_{xy} = 21\,500\text{ cm}^{-1}$ ); again, an equilibrium is present with an octahedral complex (from the shoulder at 439 nm). These observations indicate that the interaction of  $L^1$  with  $\text{Ni}^{\text{II}}$  is not as strong as for the *cis*-dioxocyclam ligand  $L^3$  ( $Dq_{xy} = 21\,740\text{ cm}^{-1}$ ). The cyclic voltammogram of (II) in water shows an irreversible oxidation to  $\text{Ni}^{\text{III}}$  at  $E_{\text{ox}} = 0.964\text{ V}$  (versus SHE), with  $\Delta E \sim 450\text{ mV}$ . The  $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$   $E_{1/2}$  values for complexes of  $L^2$ – $L^5$  (*cis* oxo ligands with 12-, 13-, 14- and 15-membered rings) are:  $[\text{Ni}(L^5)]^{2+}$  0.86,  $[\text{Ni}(L^2)]^{2+}$  1.16,  $[\text{Ni}(L^3)]^{2+}$  1.04 and  $[\text{Ni}(L^4)]^{2+}$  0.86 V (Kimura, 1986). The one-electron oxidation of (II) is quite similar to the other complexes in potential, although the others have much more reversible behaviour. The origin of the electrochemical difference in behaviour is not clear, since the *cis* and *trans* dioxo complexes have the same donor atoms and geometry. Perhaps the *trans* amidate groups reduce the ability of the ring to adjust to the smaller  $\text{Ni}^{\text{III}}$  cation.



**Figure 3**  
The packing diagram for (II) viewed down the  $b$  axis. Ni atoms are cross-hatched, N atoms are stippled and O atoms are shaded.

## Experimental

The ligand  $L^1\text{H}_2$  was synthesized according to the literature procedure of Tomalia & Wilson (1985). Crystals of the dihydrate, (I), suitable for X-ray diffraction studies were grown by the slow diffusion of ether into an acetonitrile solution of the ligand. Synthesis and

characterization of (II) were carried out as follows: to  $L^1\text{H}_2$  (0.457 g, 2 mmol), stirred in dry degassed DMF (20 ml) under nitrogen, was added KH (0.156 g, 4 mmol) with stirring. The mixture was allowed to stir for 1 h at room temperature. Then  $\text{NiCl}_2$  (0.260 g, 2 mmol) was added and the reaction mixture was stirred at 323 K overnight. The mixture was cooled and filtered to give the crude product, a pale orange solid, as a mixture with KCl. This crude product was allowed to dry in the air overnight, water (100 ml) was stirred in and the mixture was allowed to settle for several hours before being filtered. The bright-orange solid obtained was the pure product, as residual DMF and the KCl contaminant remained in the aqueous filtrate (yield 0.366 g, 60%). The FAB+ mass spectra in methanol (NBA matrix) exhibited a peak at  $m/z = 285$  ( $[\text{NiL}^1]^+$ ). Elemental analysis, calculated for  $\text{C}_{10}\text{H}_{20}\text{N}_4\text{NiO}_4$ : C 39.64, H 6.65, N 18.49%; found: C 39.75, H 6.84, N 18.50%. Spectroscopic analysis:  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , p.p.m.): 2.02–2.17 ( $m$ , 4H,  $\text{CH}_2\text{C}=\text{O}$ ), 2.19–2.32 ( $m$ , 4H,  $\text{NCH}_2\text{CH}_2\text{NH}$ ), 2.39–2.54 ( $m$ , 2H,  $\text{O}=\text{CCH}_2\text{CH}_2\text{NH}$ ), 2.58–2.70 ( $m$ , 2H,  $\text{CH}_2\text{NC}=\text{O}$ ), 2.72–2.83 ( $m$ , 1H, NH), 2.90–3.02 ( $m$ , 2H,  $\text{CH}_2\text{NC}=\text{O}$ ), 3.12–3.22 ( $m$ , 1H, NH);  $^{13}\text{C}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , p.p.m.): 37.54 ( $\text{O}=\text{CCH}_2$ ), 49.52 ( $\text{CH}_2\text{NH}$ ), 49.97 ( $\text{CH}_2\text{NH}$ ), 54.52 ( $\text{CH}_2\text{NC}=\text{O}$ ), 178.82 ( $\text{C}=\text{O}$ ); IR (KBr,  $\text{cm}^{-1}$ ): 3457, 3069, 2900, 2834, 1635, 1538, 1435, 1352, 1315, 1259, 1174, 1088. The neutral product complex and the KCl produced are insoluble in DMF and can be collected by filtration; the crude product can be purified by simply washing the KCl and residual DMF away with water. The product has some solubility in water, but most reprecipitates from the aqueous wash upon standing. A final filtration and washing with water gave the analytically pure product as a monohydrate. Crystals of (II) suitable for X-ray diffraction studies were obtained by slow evaporation of the solvent from a methanol solution of the monohydrate complex, and contain an additional water of crystallization. The neutral complex has very limited solubility in most common solvents. Useful concentrations could only be obtained in water and methanol, in both of which the complex behaves as a non-electrolyte. Electrochemical experiments were performed using a Princeton Applied Research Model 175 programmer and Model 173 potentiostat using a home-made cell. A glassy carbon electrode was used as the working electrode, with a Pt-wire counter electrode and an Ag/AgCl reference electrode. The electrochemical measurements were carried out on an aqueous solution, 0.001 M in complex and 0.5 M in sodium sulfate as the supporting electrolyte.

## Compound (I)

### Crystal data

$\text{C}_{10}\text{H}_{20}\text{N}_4\text{O}_2 \cdot 2\text{H}_2\text{O}$   
 $M_r = 264.33$   
Triclinic,  $P\bar{1}$   
 $a = 4.869$  (3) Å  
 $b = 7.530$  (5) Å  
 $c = 9.150$  (5) Å  
 $\alpha = 83.037$  (10)°  
 $\beta = 88.727$  (15)°  
 $\gamma = 79.806$  (10)°  
 $V = 327.7$  (3) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.339\text{ Mg m}^{-3}$   
Mo  $K\alpha$  radiation  
Cell parameters from 1077 reflections  
 $\theta = 3\text{--}20^\circ$   
 $\mu = 0.103\text{ mm}^{-1}$   
 $T = 200$  (2) K  
Rectangular prism, colourless  
0.48 × 0.10 × 0.10 mm

### Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\text{min}} = 0.58$ ,  $T_{\text{max}} = 0.96$   
1627 measured reflections

1118 independent reflections  
825 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.018$   
 $\theta_{\text{max}} = 25^\circ$   
 $h = -5 \rightarrow 5$   
 $k = -8 \rightarrow 8$   
 $l = -10 \rightarrow 6$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.118$   
 $S = 0.967$   
 1118 reflections  
 102 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.073P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.025$   
 $\Delta\rho_{\max} = 0.18 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.24 \text{ e } \text{Å}^{-3}$

## Compound (II)

### Crystal data

$[\text{Ni}(\text{C}_{10}\text{H}_{18}\text{N}_4\text{O}_2)] \cdot 2\text{H}_2\text{O}$   
 $M_r = 321.03$   
 Monoclinic,  $C2/c$   
 $a = 20.861 (3) \text{ Å}$   
 $b = 7.3385 (10) \text{ Å}$   
 $c = 9.6130 (13) \text{ Å}$   
 $\beta = 112.205 (2)^\circ$   
 $V = 1362.5 (3) \text{ Å}^3$   
 $Z = 4$

$D_x = 1.565 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 1275 reflections  
 $\theta = 3\text{--}20^\circ$   
 $\mu = 1.441 \text{ mm}^{-1}$   
 $T = 180 (2) \text{ K}$   
 Plate, red  
 $0.40 \times 0.15 \times 0.04 \text{ mm}$

### Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction:  $\psi$  scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.67, T_{\max} = 0.96$   
 3255 measured reflections

1193 independent reflections  
 799 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.073$   
 $\theta_{\max} = 25^\circ$   
 $h = -24 \rightarrow 24$   
 $k = -6 \rightarrow 8$   
 $l = -11 \rightarrow 11$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.060$   
 $wR(F^2) = 0.153$   
 $S = 1.040$   
 1193 reflections  
 91 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.079P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.025$   
 $\Delta\rho_{\max} = 0.90 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.53 \text{ e } \text{Å}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{Å}, ^\circ$ ) for (II).

Ni1—N2	1.892 (5)	Ni1—N6	1.902 (5)
N2—Ni1—N6 <sup>i</sup>	86.1 (2)	N2—Ni1—N6	93.9 (2)

Symmetry code: (i)  $\frac{1}{2} - x, \frac{1}{2} - y, -z$ .

The water H atoms in the Ni complex could not be clearly located on difference maps and were omitted. The H atoms on N atoms for both compounds were refined freely, as were the water H atoms of (I). All other H atoms were added at calculated positions and refined using a riding model ( $\text{C—H} = 0.99 \text{ Å}$ ), including free rotation about

C—C bonds for methyl groups, and with isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the carrier atom.

For both compounds, data collection: SMART (Siemens, 1994); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

We wish to acknowledge the use of the EPSRC Chemical Database Service at Daresbury Laboratory (Fletcher *et al.*, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993). The EPSRC and Siemens plc generously supported the purchase of the SMART diffractometer. The Warwick–Kansas collaboration has been supported by NATO. Support of this work by the Procter & Gamble Company is gratefully acknowledged. TJH thanks the Madison and Lila Self Graduate Research Fellowship of the University of Kansas for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1440). Services for accessing these data are described at the back of the journal.

## References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.  
 Betschart, C. & Hegedus, L. S. (1992). *J. Am. Chem. Soc.* **114**, 5010–5017.  
 Collins, T. J., Fox, B. G., Hu, Z. G., Kostka, K. L., Münck, E., Rickard, C. E. F. & Wright, L. J. (1992). *J. Am. Chem. Soc.* **114**, 8724–8725.  
 Denat, F., Lacour, S., Brandes, S. & Guillard, R. (1997). *Tetrahedron Lett.* **38**, 4417–4420.  
 Dumas, S., Lastra, E. & Hegedus, L. S. (1995). *J. Am. Chem. Soc.* **117**, 3368–3379.  
 Fabrizzi, L. (1977). *Inorg. Chem.* **16**, 2667–2668.  
 Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.  
 Hubin, T. J., McCormick, J. M., Collinson, S. R., Alcock, N. W. & Busch, D. H. (1998). *J. Chem. Soc. Chem. Commun.* pp. 1675–1676.  
 Hubin, T. J., McCormick, J. M., Collinson, S. R., Perkins, C. M., Alcock, N. W., Raghunathan, A. & Busch, D. H. (2000). *J. Am. Chem. Soc.* **122**, 2512–2522.  
 Kimura, E. (1986). *Coord. Chem.* **15**, 1–28.  
 Kodama, M. & Kimura, E. (1981). *J. Chem. Soc. Dalton Trans.* pp. 694–700.  
 Lever, A. B. P. (1984). *Inorganic Electronic Spectroscopy*, 2nd ed. Amsterdam: Elsevier.  
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.  
 Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Siemens (1994). *SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Siemens (1995). *SAINTE*. Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Tomalia, D. A. & Wilson, L. R. (1985). US Patent 4 517 122.