dihydrate and forms stacks of the '*M–L*' type (Endres, 1979). The intermolecular H-bonding network, however, is quite different: In the oxamide oxime complex the water molecules are linked by H bridges to adjacent complex molecules within a stack, leading to a ladder-like structure. In the title compound, however, the water molecules are H-bonded to the oxime O atoms of complexes of different stacks (Fig. 2). Each stack is thus linked to its four neighbours. A weaker H-bonding interaction exists between the amino group and the water molecule. Details of the distances are included in Fig. 2.

This investigation shows that the amino(methyl)-glyoxime nickel complex is similar to the oxamide oxime complex in its tendency to participate in intermolecular H bonding. Hence the complex is a promising candidate for the inclusion of other species in the crystal, possibly leading to molecular electron conductors, as is the case with oxamide oxime complexes (Endres *et al.*, 1985; Endres, 1984). Indeed, it forms a blue-black solid when co-crystallized with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ).

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Structure of Bis(isothiocyanato)(1,4,8,11-tetraazacyclotetradecane)nickel(III) Perchlorate

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Abstract. $[Ni(NCS)_2(C_{10}H_{24}N_4)]ClO_4$, $M_r = 474{\cdot}6$, triclinic, $P\bar{1}$, $a = 8{\cdot}559\,(1)$, $b = 9{\cdot}095\,(2)$, $c = 7{\cdot}517\,(1)$ Å, $\alpha = 110{\cdot}66\,(1)$, $\beta = 81{\cdot}42\,(1)$, $\gamma = 114{\cdot}95\,(1)^\circ$, $V = 496{\cdot}4\,(2)$ Å^3, $Z = 1$, $D_x = 1{\cdot}59$, $D_m = 1{\cdot}60$ Mg m^{-3}, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}7107$ Å, $\mu(\mathrm{Mo}\,K\alpha) = 1{\cdot}35$ mm^{-1}, $F(000) = 247$, room temperature, $R = 0{\cdot}041$ and $wR = 0{\cdot}053$ for 2645 observed reflections $[|F_o| > 3\sigma(F_o)]$. The Ni^{III} ion is surrounded octahedrally by a square-planar array of the four N atoms of 1,4,8,11-tetraazacyclotetradecane and by two N atoms of NCS^- ions occupying the axial positions. The macrocyclic ligand adopts the most stable conformation with two five- and two six-membered chelate rings in *gauche* and chair forms, respectively. The average in-plane Ni—N and Ni—NCS distances are 1·972 (7) and 2·081 (3) Å, respectively.

Introduction. One dominant characteristic of tetraazacycloalkane ligands (*L*) is that they often form stable compounds of metal ions in unusually high oxidation states, such as Cu^{III}, Ni^{III}, Ni^{IV}, Ag^{II}, and Ag^{III} (Busch, 1978; Haines & McAuley, 1981; Nag & Chakravorty, 1980; Olson & Vasilevskis, 1971; Barefield & Mocella, 1973; Ito, Ito & Toriumi, 1981; Yamashita & Ito, 1984). The stability of the resulting complex depends on the sizes of the metal ion and of the cavity of the macrocyclic ligand. According to this guiding principle, a series of Ni^{III} complexes containing *L*, $[NiX_2L]ClO_4$ (X = Cl and Br; L = [13]aneN_4, [14]aneN_4, [15]aneN_4, *meso*-Me_6[14]aneN_4 *etc.*)† have been prepared and characterized by means of magnetic moments, ESR, X-ray photoelectron spectra (XPS) and

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† [13]aneN_4 = 1,4,7,10-tetraazacyclotridecane, [14]aneN_4 = 1,4,8,11-tetraazacyclotetradecane, [15]aneN_4 = 1,4,8,12-tetraazacyclopentadecane, *meso*-Me_6[14]aneN_4 = (7*RS*,14*SR*)-5,5,7,12,-12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

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other physicochemical techniques (Gore & Busch, 1973; Barefield & Busch, 1970; Barefield & Mocella, 1975; Desideri, Raynor & Poon, 1977). Among such Ni^{III} complexes, X-ray structures of $[NiCl_2([14]aneN_4)]ClO_4$ (Ito, Sugimoto, Toriumi & Ito, 1981) and $[Ni(H_2PO_4)_2(meso\text{-}Me_6[14]aneN_4)]ClO_4$ (Zeigerson, Bar, Bernstein, Kirschenbaum & Meyerstein, 1982) have been reported. In this paper we describe the X-ray structure of the title compound.

Experimental. Dark-red needles of $[Ni(NCS)_2([14]aneN_4)]ClO_4$ obtained by standing aqueous solution containing $[Ni^{II}([14]aneN_4)](ClO_4)_2$, $[NH_4]_2[S_2O_8]$ and an excess of NH_4NCS in a refrigerator. Crystal 0·30 × 0·45 × 0·40 mm. D_m by flotation in $CH_2BrCH_2Br/CHCl_3$. Rigaku AFC-5 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Unit-cell dimensions by least-squares fit of 50 2θ values ($25° < 2\theta < 30°$). Intensities in the range $2\theta < 60°$ measured with θ–2θ scan technique. h −11→11, k −11→12, l 0→10. Three reference reflections monitored periodically showed no significant intensity deterioration. 3092 unique reflections measured. Intensity data corrected for Lorentz–polarization factors and for absorption. Structure solved by the conventional heavy-atom method and refined (on F) by a block-diagonal least-squares method with anisotropic thermal parameters for non-hydrogen atoms and isotropic for H from ΔF map. Scattering factors for non-hydrogen atoms taken from *International Tables for X-ray Crystallography* (1974). Weighting scheme $w = [\sigma^2_{\rm count} + (0{\cdot}015|F_o|)^2]^{-1}$ employed. $\Delta/\sigma < \frac{1}{3}$; $-0{\cdot}9 < \Delta\rho < 1{\cdot}7$ e Å^{-3}. No correction for secondary extinction. Calculations carried out on the HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with the *Universal Crystallographic Computation Program System UNICS* III (Sakurai & Kobayashi, 1979).

Discussion. Atomic parameters are listed in Table 1.* Fig. 1 shows the structure of $[Ni(NCS)_2([14]aneN_4)]^+$ and the atomic numbering system. Relevant bond distances and angles are listed in Table 2. The Ni^{III} ion is at a center of symmetry, and is octahedrally surrounded by a square-planar array of the four N atoms of the macrocyclic ligand and by two NCS^- ions occupying the axial positions, where the NCS^- group coordinates to the Ni^{III} ion through the N atom. The tetragonal coordination geometry found is consistent with that proposed on the basis of the ESR spectrum (Haines & McAuley, 1980).

The total stereochemistry of the macrocyclic ligand is the same as that of the corresponding Ni^{II} analogue, *trans*-$[Ni(NCS)_2([14]aneN_4)]$ (Ito, Kato & Ito, 1984): the two six-membered rings take the chair form and the two five-membered rings adopt the *gauche* conformation.

Table 1. *Fractional coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (Å²) *for non-hydrogen atoms*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Ni	5000	5000	5000	1·9
Cl	0	0	0	5·3
S	2420 (1)	6332 (1)	1058 (1)	4·7
N(1)	6742 (3)	7389 (3)	5733 (3)	4·0
N(2)	6841 (3)	4368 (3)	3501 (3)	3·6
N(3)	4338 (3)	5250 (3)	2599 (3)	3·4
C(1)	8204 (4)	7399 (5)	4388 (5)	6·5
C(2)	8489 (3)	5842 (6)	4135 (5)	6·3
C(3)	6923 (6)	2732 (5)	3338 (4)	6·2
C(4)	5258 (7)	1233 (5)	2657 (5)	7·4
C(5)	3825 (6)	1226 (4)	4064 (5)	6·6
C(6)	3549 (3)	5670 (3)	1910 (3)	2·8
O(1)	578 (14)	−316 (13)	−1842 (10)	12·0
O(2)	−1821 (9)	−891 (14)	0 (15)	12·8
O(3)	631 (13)	−922 (14)	770 (14)	12·6
O(4)	511 (12)	1616 (10)	1153 (15)	13·6

Table 2. *Bond distances* (Å) *and angles* (°) *within the complex cation, with e.s.d.'s in parentheses*

Ni–N(1)	1·979 (2)	N(1)–Ni–N(2)	86·3 (1)
Ni–N(2)	1·965 (2)	N(1)–Ni–N(3)	91·1 (1)
Ni–N(3)	2·081 (3)	N(2)–Ni–N(3)	88·4 (1)
N(1)–C(1)	1·486 (4)	Ni–N(1)–C(1)	106·4 (2)
N(1)–C(5$^{\rm i}$)	1·485 (6)	Ni–N(1)–C(5$^{\rm i}$)	118·1 (2)
N(2)–C(2)	1·473 (4)	Ni–N(2)–C(2)	107·5 (2)
N(2)–C(3)	1·480 (6)	Ni–N(2)–C(3)	120·0 (2)
N(3)–C(6)	1·154 (4)	N(1)–C(1)–C(2)	107·3 (3)
C(1)–C(2)	1·480 (8)	N(2)–C(2)–C(1)	106·9 (3)
C(3)–C(4)	1·496 (6)	N(2)–C(3)–C(4)	112·1 (4)
C(4)–C(5)	1·495 (7)	C(3)–C(4)–C(5)	113·3 (3)
C(6)–S	1·629 (3)	C(4)–C(5)–N(1$^{\rm i}$)	111·8 (3)
		N(3)–C(6)–S	176·7 (2)
		Ni–N(3)–C(6)	149·6 (2)

Symmetry code: (i) $1-x, 1-y, 1-z$.

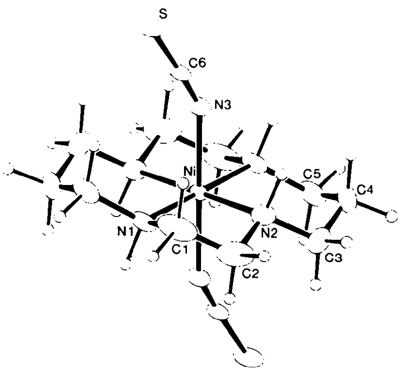

Fig. 1. A perspective drawing of $[Ni(NCS)_2([14]aneN_4)]^+$.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42390 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

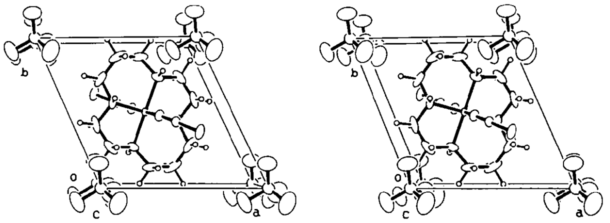

Fig. 2. A stereoscopic drawing of the crystal structure along the *c* axis.

The average in-plane Ni—N and Ni—NCS bond distances are 1·972 (7) and 2·081 (3) Å, respectively, which are significantly shorter than those in the corresponding Ni^{II} complex [2·074 (6) and 2·121 (10) Å, respectively]. The distortion from a regular to an elongated octahedron in the Ni^{III} complex is larger than that in the Ni^{II} complex. The in-plane Ni—N bond distances are almost the same as those in [Ni^{III}Cl$_2$([14]aneN$_4$)]ClO$_4$ reported previously (Ito, Sugimoto, Toriumi & Ito, 1981).

The Ni—N(NCS) bond is tilted by 2·1° from the normal to a best plane formed with the four in-plane N atoms and Ni. The Ni—N—C and N—C—S angles within the NCS$^-$ group are 149·6 (2) and 176·7 (2)°, respectively, while those in the corresponding Ni^{II} complex range from 156·2 (2) to 168·2 (2)° and from 177·8 (5) to 179·2 (2)°. The orientation of the NCS$^-$ group is mainly determined by an intermolecular hydrogen bond described below.

Fig. 2 shows a stereoview of the crystal structure. The NCS$^-$ group is involved in an intermolecular hydrogen bond between the S atom and the secondary amine group of the neighboring complexes with a distance of 3·271 (2) Å, forming a linear chain along the *c* axis.

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Structure du Phosphono-3 Propionate(3—) de Cuivre(II) Octahydraté

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Abstract. Diaquabis[3-phosphonopropionato(3—)]-tricopper(II)–water(1/6), [Cu$_3$(C$_3$H$_4$O$_5$P)$_2$(H$_2$O)$_2$].-6H$_2$O, $M_r = 636{\cdot}6$, monoclinic, $P2_1/c$, $a = 5{\cdot}022$ (5), $b = 12{\cdot}340$ (5), $c = 16{\cdot}390$ (8) Å, $\beta = 109{\cdot}7$ (1)°, $V = 956$ (1) Å^3, $Z = 2$, $D_m = 2{\cdot}17$, $D_x = 2{\cdot}21$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 34$ cm^{-1}, $F(000) = 642$, $T = 298$ K, $R = 0{\cdot}028$, $wR = 0{\cdot}031$ for 1565 independent reflexions. The copper ions exhibit octahedral or square-pyramidal coordination. One octahedron is connected with two pyramids leading to the formation

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