

The Structures of $[\text{Ni}(\text{C}_{14}\text{H}_{32}\text{N}_6)(\text{NCS})_2] \cdot \text{H}_2\text{O}$ and $[\text{Ni}(\text{C}_{14}\text{H}_{32}\text{N}_6)(\text{NO}_2)]\text{ClO}_4$. Conformation and Configuration in a Tetradentate Bis-hydrazone Ligand

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Abstract

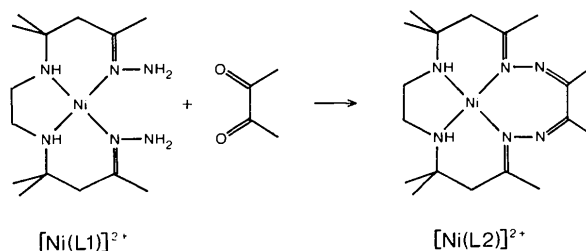
(3,5,5,10,10,12-Hexamethyl-1,2,6,9,13,14-hexaaza-tetradeca-2,12-diene)bis(thiocyanato-*N*)nickel(II) monohydrate, $[\text{Ni}(\text{L1})(\text{NCS})_2] \cdot \text{H}_2\text{O}$, $M_r = 477.3$, crystallizes in the monoclinic space group $P2_1/n$, with [at 294 (± 1) K] $a = 11.227$ (6), $b = 12.088$ (6), $c = 16.890$ (6) Å, $\beta = 99.39$ (3)°, $V = 2261.5$ Å³, $Z = 4$; D_m (by flotation) = 1.36, $D_c = 1.401$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 1.059$ mm⁻¹. The final $R = 6.0\%$ for 2257 counter reflexions. The tetradentate ligand L1 adopts a near-planar configuration in the irregular octahedral Ni-atom environment, with *trans* N-bonded thiocyanate ligands [Ni–N = 2.116 (8) and 2.077 (8) Å]. The Ni–N lengths to L1 are equal within error, and average 2.134 (5) Å. $[\text{Ni}(\text{L1})(\text{NO}_2)]\text{ClO}_4$, $M_r = 488.6$, crystallizes in the monoclinic space group $C2/c$, with [at 294 (± 1) K] $a = 31.144$ (9), $b = 11.278$ (3), $c = 14.920$ (4) Å, $\beta = 123.37$ (1)° (reduced cell: $a' = 26.103$ Å, $b' = b$, $c' = c$, $\beta' = 94.85^\circ$), $V = 4376.6$ Å³, $Z = 8$; D_m (by flotation) = 1.49, $D_c = 1.483$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 1.054$ mm⁻¹. The final $R = 4.1\%$ for 2539 reflexions. L1 is in a folded configuration, with the remaining positions in the irregular octahedral coordination geometry occupied by the asymmetrically bonded, bidentate nitrite ligand [Ni–O = 2.132 (4) and 2.171 (4) Å]. The Ni–N bond lengths to L1 range from 2.071 (4) to 2.097 (3) Å.

Introduction

The use of dihydrazine and dihydrazone ligands in Schiff-base-type condensation reactions has been extensively studied (Kerwin & Melson, 1972; Peng & Goedken, 1973). Such syntheses utilize the steric benefits of template condensations to give products containing macrocyclic ligands, while overcoming the masking of nucleophilic character which occurs when an amine is coordinated to a metal (Lindoy, 1971).

The condensation reaction of 2,3-butanedione with the Ni^{II} complex of the tetradentate ligand

3,5,5,10,10,12-hexamethyl-1,2,6,9,13,14-hexaazatetradeca-2,12-diene, L1, proceeds *via* several isolable intermediates to yield a complex of the diazine [16] macrocycle 3,4,7,9,9,14,14,16-octamethyl-1,2,5,6,10,13-hexaazacyclohexadeca-2,4,6,16-tetraene, L2 (Curtis, 1980).



Several derivatives of $[\text{Ni}(\text{L1})]^{2+}$ have been prepared (Curtis, 1980). The crystal structures of two are reported here: $[\text{Ni}(\text{L1})(\text{NCS})_2] \cdot \text{H}_2\text{O}$ (I), in which L1 is planar, and $[\text{Ni}(\text{L1})(\text{NO}_2)] \cdot \text{ClO}_4$ (II), in which L1 is folded. These structures provide an opportunity to observe the flexibility of the ligand and provide a comparison with the structural work on the condensation product, which is presented in the following paper (Davis, Einstein & Willis, 1982).

X-ray data collection

Samples of (I) and (II) were supplied by Professor Neil F. Curtis, Victoria University of Wellington, Wellington, New Zealand. Crystals of (I) are royal blue while (II) are violet. Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) was used to obtain Weissenberg and precession photographs which established space group $P2_1/n$ (systematic absences $h0l: h + l = 2n + 1$ and $0k0: k = 2n + 1$) for (I) and Cc or $C2/c$ (systematic absences $hkl: h + k = 2n + 1$ and $h0l: l = 2n + 1$) for (II). The choice of centrosymmetric space group $C2/c$ was confirmed in the subsequent refinement.

The crystals were mounted on a Picker FACS-I computer-controlled four-circle diffractometer fitted with a scintillation detector and a pulse-height analyser. Centring of 12 of the strongest reflexions with $2\theta > 25^\circ$

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Table 1. *Experimental conditions for data collection*

	(I)	(II)
Crystal size (mm)	0.7 × 0.7 × 0.7	0.3 × 0.4 × 0.6
Inner data: 2θ range (°)	0 → 30	0 → 20
scan width (°)	1.6	1.8
Outer data: 2θ range (°)	30 → 45	20 → 45
scan width (°)	1.6	1.2
Variation of standards	±3%	±3%
Number of measured data	2927	2859
Number of observed data	2257	2539

(graphite-monochromated Mo Kα radiation, λ = 0.70926 Å) for each crystal gave setting angles which were used in a least-squares refinement of cell and orientation parameters.

A unique set of intensities was collected for each compound. A symmetrical θ–2θ scanning mode was employed with a scan speed of 2° min⁻¹. The selected scan widths (chosen in each instance to take account of the size and shape of the diffracted rays) were increased to allow for dispersion, and background counts of 10 s were measured at both scan limits. Details of the data collection for each crystal are included in Table 1.

The intensities were measured in two sets based on 2θ values (Table 1). After every 100 reflexions two standard reflexions were monitored to check instrumental stability and the crystal orientation. No sample decomposition was observed. Absorption was neglected in each case since the estimated maximum error in *F* was negligible for [Ni(L1)(NCS)₂].H₂O and 1.1% for [Ni(L1)(NO₂)ClO₄].

Measured intensities were corrected for Lorentz and polarization effects, and were classed as observed if $I > 2.3\sigma_1$, where $\sigma_1 = [T + (t_s/t_b)^2(B_1 + B_2) + (kI)^2]^{1/2}$; *T* is the total count, *B*₁ and *B*₂ are the background counts, *t*_s is the scan time, *t*_b is the total background time, *k* is a constant set at 0.03, and *I* is the net count.

Solution and refinement

In each structure the heavy-atom positions were determined from the Patterson synthesis. Subsequent electron-density maps and least-squares refinement led to the location of the remaining non-hydrogen atoms. At this stage anisotropic temperature factors were assigned, first to the heavy atoms, and then to the lighter atoms. H atoms were located from difference maps or were calculated [*r*_{C–H} = 0.95, *r*_{N–H} = 0.87 Å (Churchill, 1973)]. They were included in the structure factor calculations (with isotropic *B* = 5.0 Å²) but their parameters were not refined. In (II) it was noticed that the thermal parameters in one chelate ring [C(13) through C(18)] were extremely anisotropic, suggesting that there might be disorder due to two alternative conformations of the ring. Each of these C atoms was

split over two half-occupied positions. Refinement of this model, initially with isotropic temperature factors and then anisotropically, gave a chemically reasonable model.

Refinement was continued until all shift-to-error ratios were <0.2. The final agreement factors ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) were 0.060 (249 variables) for (I) and 0.041 (317 variables) for (II). The major features in final difference maps were ±0.6 (1) e Å⁻³ near the Ni atom in (I) and ±0.4 (1) e Å⁻³ near the Ni atom and perchlorate group in (II). Examination of the average values of $w(|F_o| - |F_c|)^2$ showed no systematic trends as a function of (sin θ)/λ or |*F*_o|.

Refinement was by full-matrix least-squares minimizing the function $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma_F^2$ [$\sigma_F = \sigma_I / (Lp)(2F_o)$]. Neutral scattering factors for all atoms and anomalous dispersion corrections for Ni and Cl were taken from *International Tables for X-ray Crystallography* (1974).

Computer programs have been referenced previously (Einstein & Jones, 1972). Fractional coordinates for the two structures are given in Tables 2 and 3. Table 4 gives the bond lengths and angles. Fig. 1 shows the

Table 2. *Fractional atomic coordinates* (×10⁴, ×10⁵ for Ni) *and temperature factors* (Å² ×10³) for [Ni(L1)(NCS)₂].H₂O

In this and all other tables, least-squares e.s.d.'s are given in parentheses. $U_{eq.} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq.}
Ni	-1299 (6)	-528 (6)	25541 (4)	38.3 (1)
S(1)	3588 (2)	746 (2)	4344 (1)	59 (1)
S(2)	-3535 (2)	-746 (2)	470 (1)	89 (2)
N(71)	1307 (5)	305 (4)	3495 (3)	49 (4)
N(72)	-1481 (5)	-525 (5)	1624 (3)	51 (4)
N(1)	-544 (4)	-1379 (4)	3309 (3)	43 (3)
N(2)	-1503 (4)	951 (4)	2923 (3)	42 (3)
N(3)	373 (4)	1492 (4)	2096 (3)	41 (3)
N(4)	1071 (4)	-869 (4)	1897 (3)	46 (3)
N(5)	341 (5)	-2207 (4)	3518 (4)	58 (4)
N(6)	921 (5)	-2014 (5)	1867 (3)	57 (4)
C(5)	-1416 (5)	-1395 (5)	3714 (4)	44 (4)
C(6)	-1480 (6)	-2218 (6)	4379 (4)	59 (5)
C(7)	-2422 (6)	-573 (5)	3518 (4)	54 (4)
C(8)	-2086 (5)	669 (5)	3637 (4)	43 (4)
C(9)	-1224 (6)	879 (5)	4396 (4)	56 (4)
C(10)	-3257 (6)	1333 (6)	3614 (5)	70 (5)
C(11)	-1115 (6)	2128 (5)	2886 (4)	52 (4)
C(12)	-628 (6)	2283 (6)	2120 (4)	61 (5)
C(13)	1046 (5)	1548 (5)	1398 (4)	43 (4)
C(14)	213 (6)	1197 (6)	638 (4)	57 (5)
C(15)	1499 (6)	2736 (6)	1295 (4)	62 (5)
C(16)	2149 (6)	784 (5)	1598 (4)	51 (5)
C(17)	1928 (5)	-451 (5)	1601 (4)	45 (4)
C(18)	2771 (7)	-1164 (6)	1213 (5)	70 (5)
C(71)	2257 (6)	482 (5)	3847 (4)	40 (4)
C(72)	-2325 (6)	-610 (5)	1151 (4)	48 (4)
O(1)	-4391 (11)	534 (10)	1828 (8)	121 (6)†

† Isotropic *U*.

Table 3. Fractional atomic coordinates ($\times 10^4$, $\times 10^5$ for Ni and Cl) and temperature factors ($\text{\AA}^2 \times 10^3$) for $[\text{Ni}(\text{L}1)\text{NO}_2](\text{ClO}_4)$

$$U_{\text{eq.}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq.}}$
Ni	10777 (2)	13158 (5)	18973 (4)	40.5 (4)
Cl	34977 (6)	11180 (14)	23651 (13)	61 (1)
O(11)	3308 (3)	1594 (5)	1351 (5)	110 (5)
O(12)	3697 (3)	1993 (6)	3155 (6)	127 (7)
O(13)	3163 (4)	662 (6)	2588 (5)	128 (8)
O(14)	3762 (3)	70 (6)	2567 (5)	196 (9)
O(71)	865 (2)	-279 (3)	983 (3)	59 (2)
O(72)	437 (1)	238 (3)	1616 (3)	60 (2)
N(7)	487 (2)	-511 (4)	1066 (4)	65 (3)
N(1)	1684 (1)	1975 (3)	1832 (3)	37 (2)
N(2)	532 (1)	2299 (3)	552 (3)	38 (2)
N(3)	1028 (1)	2724 (3)	2728 (3)	37 (2)
N(4)	1542 (2)	328 (4)	3277 (4)	49 (3)
N(5)	2179 (1)	1571 (4)	2651 (3)	51 (3)
N(6)	1744 (2)	-700 (4)	3166 (4)	72 (3)
C(5)	1670 (2)	2840 (4)	1252 (4)	39 (3)
C(6)	2157 (2)	3365 (3)	1468 (5)	69 (4)
C(7)	1177 (2)	3404 (4)	385 (4)	46 (3)
C(8)	681 (2)	2690 (4)	-205 (3)	41 (3)
C(9)	731 (2)	1583 (5)	-730 (4)	58 (3)
C(10)	262 (2)	3487 (5)	-1085 (4)	64 (3)
C(11)	358 (2)	3286 (4)	937 (4)	47 (3)
C(12)	476 (2)	3034 (5)	2048 (4)	48 (3)
C(13)	1185 (10)	2644 (24)	3934 (18)	37 (9)
C(13') [†]	1301 (11)	2487 (24)	3891 (24)	40 (11)
C(14)	1200 (12)	3730 (21)	4460 (17)	88 (10)
C(14')	1036 (16)	3436 (32)	4232 (31)	126 (15)
C(15)	832 (5)	1651 (11)	3968 (10)	90 (9)
C(15')	1848 (7)	2872 (18)	4443 (9)	80 (10)
C(16)	1727 (5)	2002 (10)	4426 (8)	32 (7)
C(16')	1219 (6)	1361 (13)	4156 (10)	98 (11)
C(17)	1820 (5)	781 (12)	4264 (10)	30 (7)
C(17')	1575 (6)	470 (14)	4134 (14)	65 (10)
C(18)	2154 (15)	49 (30)	5228 (25)	111 (17)
C(18')	1966 (14)	-55 (33)	5172 (28)	108 (15)

[†] Atoms corresponding to the alternative positions of the disordered chelate ring C(13) through C(18) are denoted by primes, i.e. C(13') through C(18').

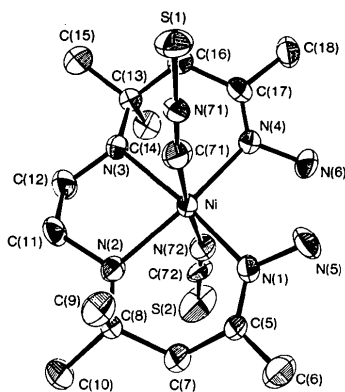


Fig. 1. A perspective view of the $[\text{Ni}(\text{L}1)(\text{NCS})_2]$ molecule, showing the thermal motion (50%) and labelling.

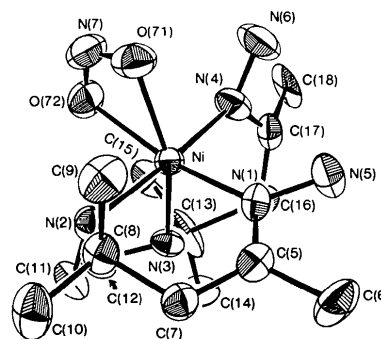


Fig. 2. A perspective view of the $[\text{Ni}(\text{L}1)(\text{NO}_2)]^+$ cation showing the thermal motion (50%) and labelling. Only one of the two positions of the disordered chelate [C(13) to C(18)] is shown.

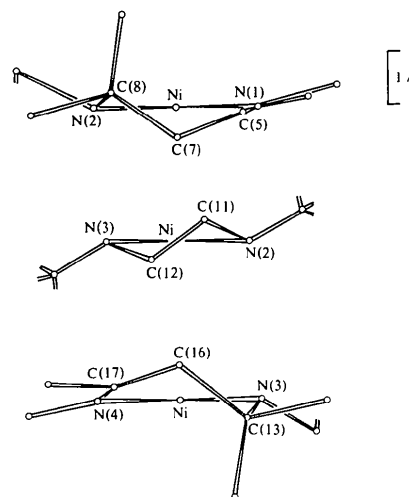


Fig. 3. The conformations of the chelate rings in $[\text{Ni}(\text{L}1)(\text{NCS})_2]$ as generated in each case by the displacements of atoms from the plane containing the Ni and two donor atoms. The planes used to generate these diagrams are given in the deposited data.

$[\text{Ni}(\text{L}1)(\text{NCS})_2]$ molecule, and Fig. 2 the $[\text{Ni}(\text{L}1)(\text{NO}_2)]^+$ cation. Figs. 3 and 4 illustrate the conformations adopted by the chelate rings of the tetradentate ligand. Figs. 5 and 6 compare the torsion angles within this ligand in the two configurations.*

Description and discussion

The geometry of the coordination sphere of the Ni atom of (I) is close to octahedral. The Ni—N lengths to the tetradentate ligand are equal within error [mean

* For both compounds, lists of structure factors, anisotropic thermal parameters, H-atom coordinates, angles for the perchlorate group and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36326 (46 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

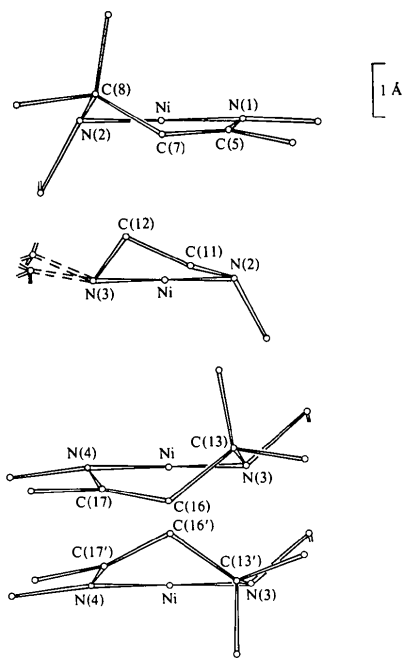


Fig. 4. The conformations of the chelate rings adopted by the tetradentate ligand *L1* in [Ni(*L1*)(NO₂)]⁺. Both positions of the disordered chelate [*i.e.* C(13) to C(18) and C(13') to C(18')] are shown.

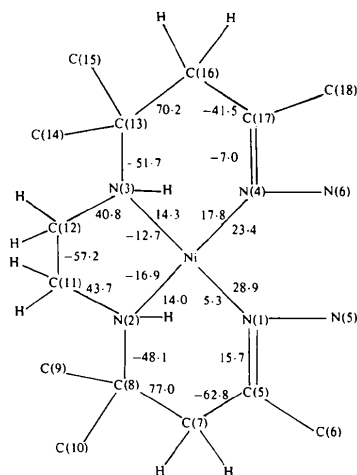


Fig. 5. Torsion angles about the tetradentate ligand *L1* in [Ni(*L1*)(NCS)₂]. E.s.d.'s are $\sim 0.4^\circ$ for Ni–N, $\sim 0.7^\circ$ others.

$2.134(5) \text{ \AA}^*$ and within the range of bond lengths suggested for such ligands (Curtis, 1968). There is no suggestion of the Ni–N(imine) bonds being shorter than the Ni–N(amine) bonds, though differences of as much as 0.04 \AA have been observed for some [14] dieneN₄ macrocycles (Curtis, 1979). Two of the N–Ni–N angles depart significantly from right angles:

* E.s.d. in the mean is given by $\sigma = \left[\frac{\sum_m (l_m - \bar{l})^2}{m(m-1)} \right]^{1/2}$ where l_m is the length of the m th bond, \bar{l} is the mean length and m is the number of bonds.

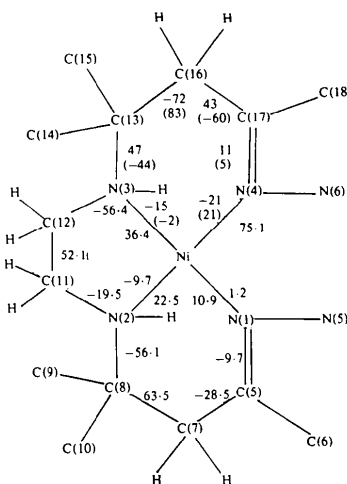


Fig. 6. Torsion angles about the tetradentate ligand *L1* in [Ni(*L1*)(NO₂)]⁺. In the disordered chelate values for both orientations are given (primed values in parentheses). E.s.d.'s are, in the ordered region, $\sim 0.3^\circ$ for Ni–N, $\sim 0.7^\circ$ others; in the disordered region, $\sim 1.3^\circ$ for Ni–N, $\sim 2.3^\circ$ others.

the angle subtended by the five-membered chelate ring is $81.6(3)^\circ$ and non-chelated N(1)–Ni–N(4) = $100.5(3)^\circ$. A further distortion from regular octahedral geometry is a small puckering of the ligand donor atoms: the coordinating N atoms deviate -0.20 , 0.22 , -0.23 and 0.19 \AA from the least-squares plane of these atoms plus Ni. This distortion is reflected in the angles, subtended at Ni, between the equatorial donors and the thiocyanate N atoms. Torsion angles about the bonds of the chelate rings are shown in Fig. 5. The five-membered ring approximates a cyclopentane half chair while the six-membered rings approximate the half-chair conformation of cyclohexene (Eliel, Allinger, Angyal & Morrison, 1965). Curtis (1979) has classified the conformations of such cyclohexene-type chelate rings according to the displacements, from the *MN*₂ plane, of the C atoms α and β to the double bond. If C_β [*i.e.* C(7) or C(16)] is displaced further on the same side of this plane than C_α [*i.e.* C(8) or C(13)], then it is an *A* conformation, but if the C_β displacement is less than, or on the opposite side from, C_α then it is a *B* conformation. As can be seen in Fig. 4, both rings are of type *B*. The bond angles at the central methylene groups of both rings suggest some angular strain at these C atoms. Similar effects have been seen in related complexes, with these angles being as much as 120 – 121° (Kilbourn, Ryan & Dunitz, 1969). The asymmetric amine N atoms, N(2) and N(3), have the same chirality, and thus, by virtue of the centrosymmetric space group, the crystal contains a racemic mixture of *RR* and *SS* enantiomers. This is in keeping with the apparent tendency of *cis*-bonded chiral N centres to be *rac* rather than *meso* (*i.e.* with *RS* enantiomers).

Table 4. Selected bond lengths (Å) and angles (°) in [Ni(L1)(NCS)₂].H₂O (I) and [Ni(L1)(NO₂)](ClO₄) (II)

In (I) X = N; in (II) X = O. In the disordered region of (II), the values for both orientations are given.

	(I)	(II)		(I)	(II)
Ni-N(1)	2.146 (7)	2.081 (3)	Ni-N(4)	2.124 (7)	2.072 (4)
Ni-N(2)	2.133 (7)	2.097 (4)	Ni-N(3)	2.134 (7)	2.072 (4)
Ni-X(71)	2.116 (8)	2.132 (4)	Ni-X(72)	2.077 (8)	2.171 (4)
N(5)-N(1)	1.41 (1)	1.418 (5)	N(6)-N(4)	1.39 (1)	1.372 (5)
N(1)-C(5)	1.28 (1)	1.289 (6)	N(4)-C(17)	1.26 (1)	1.33 (2), 1.24 (2)
C(5)-C(6)	1.51 (1)	1.489 (7)	C(17)-C(18)	1.51 (1)	1.48 (4), 1.47 (4)
C(5)-C(7)	1.50 (1)	1.501 (6)	C(17)-C(16)	1.51 (1)	1.46 (3), 1.51 (3)
C(7)-C(8)	1.55 (1)	1.519 (7)	C(16)-C(13)	1.54 (1)	1.60 (3), 1.40 (3)
C(8)-C(9)	1.50 (1)	1.527 (6)	C(13)-C(14)	1.52 (1)	1.44 (4), 1.60 (4)
C(8)-C(10)	1.54 (1)	1.532 (7)	C(13)-C(15)	1.54 (1)	1.59 (3), 1.49 (3)
C(8)-N(2)	1.50 (1)	1.504 (6)	C(13)-N(3)	1.50 (1)	1.58 (2), 1.48 (3)
N(2)-C(11)	1.50 (1)	1.484 (6)	N(3)-C(12)	1.48 (1)	1.479 (6)
C(11)-C(12)	1.50 (1)	1.515 (7)	O(71)···O(72)		2.096 (5)
N(71)-C(71)	1.15 (1)		N(72)-C(72)	1.14 (1)	
C(71)-S(1)	1.62 (1)		C(72)-S(2)	1.64 (1)	
O(71)-N(7)		1.276 (6)	O(72)-N(7)		1.246 (6)
Cl-O(1)		1.394 (7)	Cl-O(3)		1.358 (13)
Cl-O(2)		1.394 (7)	Cl-O(4)		1.376 (8)
N(1)-Ni-N(2)	90.7 (3)	92.5 (1)	N(3)-Ni-N(4)	89.3 (3)	93.4 (2)
N(1)-Ni-N(3)	164.7 (3)	97.0 (2)	N(2)-Ni-N(3)	81.6 (3)	83.1 (1)
N(1)-Ni-N(4)	100.5 (3)	94.8 (2)	N(2)-Ni-N(4)	165.2 (3)	172.2 (1)
N(1)-Ni-X(71)	85.4 (3)	104.0 (2)	N(2)-Ni-X(71)	99.4 (3)	91.8 (1)
N(1)-Ni-X(72)	92.6 (3)	162.2 (2)	N(2)-Ni-X(72)	84.5 (3)	86.3 (1)
N(3)-Ni-X(71)	83.0 (3)	158.6 (2)	N(4)-Ni-X(71)	91.0 (3)	89.0 (2)
N(3)-Ni-X(72)	99.9 (3)	100.4 (2)	N(4)-Ni-X(72)	85.6 (3)	87.5 (2)
X(71)-Ni-X(72)	175.4 (3)	58.4 (2)			
Ni-N(1)-N(5)	117.6 (5)	115.5 (3)	Ni-N(4)-N(6)	113.2 (5)	116.7 (3)
Ni-N(1)-C(5)	125.9 (6)	127.3 (3)	Ni-N(4)-C(17)	127.7 (6)	124.6 (6), 125.0 (7)
N(5)-N(1)-C(5)	115.0 (7)	116.2 (4)	N(6)-N(4)-C(17)	118.6 (8)	113.2 (7), 116.9 (8)
Ni-N(2)-C(8)	122.4 (5)	116.9 (3)	Ni-N(3)-C(13)	121.4 (5)	124 (1), 112 (1)
Ni-N(2)-C(11)	107.5 (5)	107.6 (3)	Ni-N(3)-C(12)	108.0 (5)	102.3 (3)
C(8)-N(2)-C(11)	114.7 (7)	113.6 (4)	C(13)-N(3)-C(12)	118.3 (7)	108 (1), 123 (1)
N(1)-C(5)-C(7)	118.9 (8)	122.6 (4)	N(4)-C(17)-C(16)	122.2 (8)	118 (1), 118 (1)
N(1)-C(5)-C(6)	122.6 (8)	120.2 (4)	N(4)-C(17)-C(18)	121.2 (9)	123 (1), 126 (2)
C(6)-C(5)-C(7)	118.3 (8)	117.1 (4)	C(18)-C(17)-C(16)	116.6 (8)	118 (2), 116 (2)
C(5)-C(7)-C(8)	117.0 (7)	120.5 (4)	C(13)-C(16)-C(17)	117.8 (7)	128 (2), 110 (2)
C(7)-C(8)-N(2)	103.9 (7)	110.8 (3)	C(16)-C(13)-N(3)	106.9 (7)	98 (1), 115 (2)
C(7)-C(8)-C(9)	112.7 (8)	111.9 (4)	C(16)-C(13)-C(14)	112.4 (8)	115 (2), 108 (2)
C(7)-C(8)-C(10)	108.3 (7)	107.5 (4)	C(16)-C(13)-C(15)	108.4 (7)	104 (2), 116 (3)
N(2)-C(8)-C(9)	110.1 (7)	107.8 (4)	N(3)-C(13)-C(14)	109.3 (7)	118 (2), 100 (2)
N(2)-C(8)-C(10)	110.2 (8)	110.2 (4)	N(3)-C(13)-C(15)	110.4 (7)	107 (2), 110 (2)
C(9)-C(8)-C(10)	111.3 (8)	108.6 (4)	C(14)-C(13)-C(15)	109.5 (8)	113 (2), 105 (2)
N(2)-C(11)-C(12)	107.8 (8)	111.2 (4)	N(3)-C(12)-C(11)	109.2 (7)	106.6 (4)
Ni-N(71)-C(71)	162.3 (7)		Ni-N(72)-C(72)	167.3 (8)	
N(71)-C(71)-S(1)	179 (1)		N(72)-C(72)-S(2)	179 (1)	
Ni-O(71)-N(7)		95.1 (3)	Ni-O(72)-N(7)		94.1 (3)
O(71)-N(7)-O(72)		112.5 (4)			

The Ni-N(thiocyanate) distances of 2.116 and 2.077 (9) Å are somewhat shorter than the Ni-N distances for the tetradentate ligand. The interatomic distances within these ligands are comparable with those found in other thiocyanate complexes (Brown & Lingafelter, 1963). Departures from linearity at the N atom are commonly found, varying from 111° in tetrahedral K₂Co(NCS)₄, through 160° in binuclear Cu(C₅H₅N)(NCS)₂, to 180° in Ni(NH₃)₄(NCS) (Brown & Lingafelter, 1963). We believe that the values found for (I) [162.3 and 167.3 (8)°] originate from packing forces alone.

The water molecule of crystallization connects [Ni(L1)(NCS)₂] molecules *via* weak hydrogen bonds. Specifically there are close contacts between H(O11) and S(2) of one molecule (2.03 Å) and H(O12) and N(5) of a symmetry-related molecule (1.95 Å). H(N2) and H(102) of the latter molecule also provide short contacts with O(1) (2.49 and 2.30 Å, respectively) with the four interactions forming a roughly tetrahedral array about O(1).

In (II) the Ni ion is coordinated with roughly octahedral geometry to the two O atoms of the nitrite ligand, and to the N atoms of the tetradentate ligand.

The major distortion from regular octahedral coordination arises from the extremely short bite of the bidentate nitrite ion [2.096 (5) Å]. L1 folds across the N(2)—N(4) diagonal so that N(1), N(2), N(4) and O(72) lie in one equatorial plane of the approximate octahedron, with N(3) axial to this plane. The Ni—N bond lengths, which range from 2.072 (4) to 2.097 (4) Å, are shorter than the corresponding lengths in (I). The N—Ni—N angles correspond reasonably closely to those in (I) despite the different ligand configuration. N(2)—Ni—N(3) formed by the five-membered chelate ring is 83.1 (1), and N(1)—Ni—N(4) is 94.8 (2)°; the latter shows the largest difference from its corresponding value in (I) [100.5 (3)°].

The configurations of the chelate rings are shown in Figs. 4 and 5. The five-membered ring adopts a conformation most closely related to the envelope conformer of cyclopentane. The folding of the tetradentate ligand is therefore creating some torsional bond strain along N(2)—C(11). The six-membered ring NiN(1)C(5)C(7)C(8)N(2) is a half chair with some bond-angle strain evident at C(7) [angle C(5)—C(7)—C(8) = 120.5 (4)°]. The disordered ring shows two possible half-chair conformers of cyclohexene which are interconvertible *via* chair inversion (Bucourt, 1974), but the rather large e.s.d.'s in the bond distances and angles do not permit a detailed analysis. Both configurations of this ring belong to Curtis's *B* classification, as does the other six-membered ring.

The nitrite ligand is coordinated to the Ni atom as an asymmetrically bound *O,O'*-bidentate chelate [Ni—O = 2.171 (3) and 2.132 (4) Å]. The structures of three other six-coordinate Ni^{II} complexes with bidentate nitrito groups have been reported: [Ni(tmen)₂(NO₂)₂] (tmen = tetramethylethylenediamine) where Ni—O = 2.066 and 2.150 (9) Å for one NO₂ group and 2.059 and 2.117 (9) Å for the other (Drew & Rogers, 1965); [Ni(*s*-deen)₂(NO₂)](BF₄) (deen = diethylethylenediamine) where Ni—O = 2.099 and 2.123 (3) Å (Birdy, Goodgame, McConway & Rogers, 1977); and [Ni(*s*-deen)₂(NO₂)](NO₂) where Ni—O = 2.151 and 2.155 (7) Å in one molecule and 2.148 and 2.153 (7) Å in the other (Goldberg & Marsh, 1979). In the first two of these complexes the Ni—O bonds are significantly asymmetric. In (II) there is also a significant difference in the N—O bond lengths [1.246 *cf.* 1.276 (6) Å], the shorter N—O bond being associated with the longer Ni—O distance. This is not observed for the other nitrito complexes mentioned

above, but another complex presently being studied in this laboratory, [Ni(C₁₈H₃₆N₆O)(NO₂)]ClO₄·0.5 H₂O, does show this correlation, with respective Ni—O and N—O distances of 2.144 (6), 1.31 (1) and 2.183 (6), 1.25 (1) Å. An equivalent relationship has also been observed in some bidentate nitrates (Addison, Logan, Wallwork & Garner, 1971).

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