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## Tris(methyl 2-methyldithiocarbazate)nickel(II) Chloride $\frac{1}{2}$ Ethanol Trihydrate

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**Abstract.**  $[\text{Ni}\{\text{NH}_2\text{N}(\text{CH}_3)\text{C}(\text{S})\text{SCH}_3\}_3]\text{Cl}_2 \cdot 3\text{H}_2\text{O} \cdot 0.5\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_9\text{H}_{24}\text{N}_6\text{NiS}_6^{2+} \cdot 2\text{Cl}^- \cdot 3\text{H}_2\text{O} \cdot 0.5\text{C}_2\text{H}_5\text{OH}$ , trigonal,  $R\bar{3}c$ ,  $a = b = 14.354$  (2),  $c = 45.738$  (5) Å,  $U = 8181$  Å<sup>3</sup>,  $D_m = 1.50$  (by flotation),  $Z = 12$ ,  $D_c = 1.499$  Mg m<sup>-3</sup>,  $F(000) = 3835$ ,  $\mu(\text{Mo } K\alpha) = 1.369$  mm<sup>-1</sup>. The structure was solved by Patterson and Fourier techniques and refined to  $R = 0.0306$  by least-squares calculations. The geometry of the coordination around the Ni atom is a distorted octahedron with the ternary symmetry retained, the chromophore being  $\text{NiS}_3\text{N}_3$  in three five-membered chelate rings. One of the two Cl atoms is surrounded octahedrally by six equivalent water molecules. The ethanol molecule, which lies on the threefold axis, shows three different degrees of disorder.

**Introduction.** Dithiocarbazic acid derivatives have been studied in recent years because of their biological

activity (Terada, Uda, Okitsu, Kametani & Kubota, 1977; Kubota, Uda, Mori, Kametani & Terada, 1978) and because of their coordinating properties as potential polydentate ligands (Monaci, Tarli, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1980).

The present study is part of an investigation in progress in our laboratory on the complexes of the methyl ester of N-substituted dithiocarbazic acid,  $R'R''\text{NNR}'''\text{C}(\text{S})\text{SCH}_3$ . Whilst only one Ni complex is formed with  $\text{NH}_2\text{NHC}(\text{S})\text{SCH}_3$  ( $= L'$ ),  $[\text{Ni}L'_3]\text{Cl}_2$ , two different Ni complexes of  $\text{NH}_2\text{N}(\text{CH}_3)\text{C}(\text{S})\text{SCH}_3$  ( $= L$ ) can be prepared with two different metal/ligand ratios,  $[\text{Ni}L_2\text{Cl}_2]$  and  $[\text{Ni}L_3]\text{Cl}_2$ . Crystals of the last complex, with three ligand molecules coordinated to the metal, can be obtained only in the presence of water molecules, which are essential for the stabilization of the complex.

In order to study the coordinating properties of this

ligand and to clarify the influence of water on these properties, we have undertaken the X-ray analysis of the title compound.

A crystal of 0.30 × 0.25 × 0.18 mm was used for crystal-data and intensity measurements on a  $P2_1$  Syntex automated diffractometer by the  $\theta$ - $2\theta$  scan technique with graphite-monochromated Mo  $K\alpha$  radiation. Only the intensities of 906 independent reflections having  $I \geq 3\sigma(I)$  were used throughout the refinement, corrected for background and for Lorentz and polarization effects. No absorption correction was applied. Unit-cell dimensions were determined by

Table 1. Final atomic coordinates with standard deviations in parentheses

	x	y	z
Ni	0	0	0.13211 (2)
S(1)	0.11862 (9)	-0.03676 (9)	0.15983 (2)
S(2)	0.35458 (10)	0.04926 (12)	0.14939 (3)
N(1)	0.1388 (3)	0.0890 (3)	0.10638 (7)
N(2)	0.2350 (3)	0.0957 (3)	0.11729 (8)
C(1)	0.2311 (4)	0.0389 (4)	0.1402 (1)
C(2)	0.3316 (4)	0.1605 (5)	0.0992 (1)
C(3)	0.3229 (5)	-0.0430 (6)	0.1782 (1)
C(4)	0	0	0.2344 (10)
OC	0.0405 (28)	0.0900 (28)	0.2340 (7)
O <sub>w</sub>	0.1427 (4)	-0.0021 (4)	0.0525 (1)
Cl(1)	0	0	0
Cl(2)	0.4666 (2)	0	0.2500
H(N1)	0.1475 (34)	0.1474 (34)	0.1056 (9)
H'(N1)	0.1295 (34)	0.0593 (38)	0.0879 (9)
H(O <sub>w</sub> )	0.1094 (49)	-0.0046 (48)	0.0360 (13)
H'(O <sub>w</sub> )	0.1476 (44)	-0.0512 (44)	0.0533 (12)
H(C2)	0.3220 (49)	0.2087 (50)	0.0873 (13)
H'(C2)	0.3398 (63)	0.1161 (63)	0.0847 (16)
H''(C2)	0.3885 (49)	0.1902 (56)	0.1132 (13)
H(C3)	0.3820 (52)	-0.0235 (51)	0.1870 (13)
H'(C3)	0.2800 (47)	-0.0418 (46)	0.1939 (12)
H''(C3)	0.2754 (53)	-0.1120 (56)	0.1712 (15)

Table 2. Main bond distances (Å) and angles (°), with standard deviations in parentheses

Ni-S(1)	2.384 (2)	C(2)-H(C2)	0.94 (6)
Ni-N(1)	2.108 (5)	C(2)-H'(C2)	0.97 (8)
S(1)-C(1)	1.684 (5)	C(2)-H''(C2)	0.95 (8)
S(2)-C(1)	1.754 (5)	C(3)-H(C3)	0.85 (8)
S(2)-C(3)	1.761 (8)	C(3)-H'(C3)	0.95 (6)
N(1)-N(2)	1.425 (5)	C(3)-H''(C3)	0.94 (9)
N(1)-H(N1)	0.79 (5)	C(4)-OC	1.12 (5)
N(1)-H'(N1)	0.93 (4)	O <sub>w</sub> -H(O <sub>w</sub> )	0.88 (6)
N(2)-C(1)	1.313 (6)	O <sub>w</sub> -H'(O <sub>w</sub> )	0.74 (6)
N(2)-C(2)	1.477 (9)		
S(1)-Ni-N(1)	82.4 (1)	N(1)-N(2)-C(1)	119.9 (5)
S(1 <sup>a</sup> )-Ni-N(1)	173.3 (1)	N(1)-N(2)-C(2)	114.6 (4)
S(1 <sup>b</sup> )-Ni-S(1 <sup>b</sup> )	94.3 (1)	C(1)-N(2)-C(2)	125.2 (4)
S(1 <sup>b</sup> )-Ni-N(1)	91.7 (1)	S(1)-C(1)-S(2)	121.9 (5)
Ni-S(1)-C(1)	97.7 (2)	S(1)-C(1)-N(2)	123.9 (4)
C(1)-S(2)-C(3)	104.3 (4)	S(2)-C(1)-N(2)	114.2 (5)
Ni-N(1)-N(2)	115.9 (3)		

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

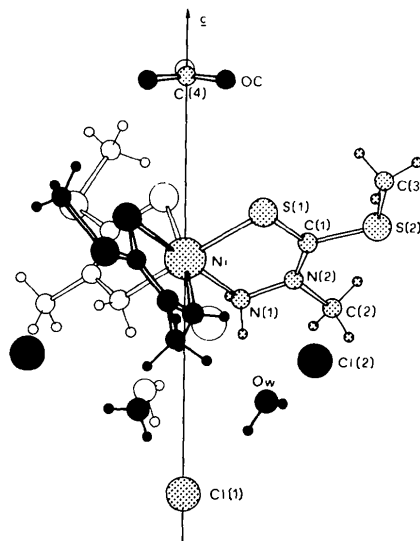


Fig. 1. A view of the structure showing the ternary symmetry around the  $c$  axis. For a description of the ethanol molecule lying on the threefold axis and the atom labelled OC, see text.

least-squares analysis of diffractometer measurements using 15 reflections with  $2\theta > 25^\circ$ .

The positions of the Ni, Cl and S atoms were found from a Patterson map. The lighter atoms, including the H atoms, were found from the subsequent Fourier syntheses. A full-matrix least-squares refinement converged to  $R = 0.0306$ . Final atomic coordinates are listed in Table 1.\* Geometrical details are described in Fig. 1 and in Table 2.

**Discussion.** The complex ion consists of a Ni atom coordinating to the non-substituted S and N atoms of three bidentate molecules with the formation of five-membered chelate rings. The geometry of the coordination product is distorted octahedral, but the ternary symmetry is retained. The Ni atom is on the threefold axis, and the S and N atoms are on opposite planes with respect to the metal atom. The Ni-S (2.384 Å) and Ni-N (2.108 Å) distances fall in the range typical of Ni octahedral S and N complexes. The interatomic distances, C-S (1.684 Å), C-N (1.313 Å) and N-N (1.425 Å), in the chelate ring are consistent with an extensive delocalization over the ring plane. The whole ligand molecule is planar, the mean deviation from planarity being 0.04 Å.

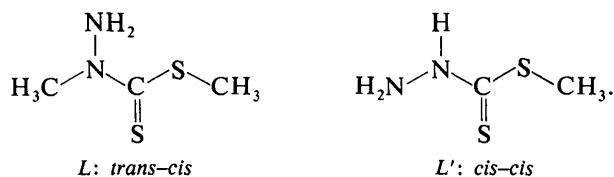
The ethanol molecule shows three degrees of disorder: (a) As the C atom of the  $-\text{CH}_2\text{OH}$  group, C(4), is on the threefold axis, the  $\text{CH}_3$  and OH groups

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34940 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

are statistically distributed among three equivalent positions and are therefore indistinguishable. As the C—O and C—C distances in ethanol are different (1.426 and 1.544 Å), this distribution causes an apparent vibrational effect. (b) As the CH<sub>3</sub>—CH<sub>2</sub>—OH angle is 109°, while those at the equivalent positions must be 120°, there is an apparent libration effect for the CH<sub>3</sub> and OH groups (atom labelled OC). Because of this effect, the bond between C(4) and the average position OC is greatly shortened: 1.12 (5) Å *vs* the expected mean value of 1.48 Å [see point (a)]. These apparent vibration and libration effects lead to values of  $b_{ij}$  for the ethanol atoms which are much larger than those of the other light atoms in the structure. (c) As the 32(a) point symmetry (00 $\frac{1}{2}$ ) is present at 0.72 Å from the molecular plane, the atoms of the alcohol are distributed between two close symmetry-related positions.

Cl(1), as mentioned above, is surrounded octahedrally by six equivalent water molecules at distances of 3.165 (5) Å, very close to those in HCl.6H<sub>2</sub>O (Taesler & Lundgren, 1978); Cl(2) is involved in a close net of interactions with H atoms belonging to O<sub>w</sub>, N(1) and C(2), Cl—H distances falling in the range 2.46–3.08 Å.

The coordination behaviour of dithiocarbazic acid derivatives can be correlated with their conformational properties (Manotti Lanfredi, Tiripicchio, Tiripicchio Camellini, Monaci & Tarli, 1977). These studies show that the most stable conformations for the free ligands *L* and *L'* are:



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## 1,11-Bis(2-nitrophenoxy)-3,6,9-trioxaundecane–Potassium Isothiocyanate\*

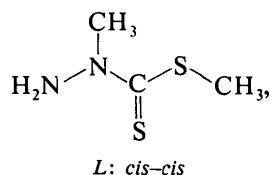
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**Abstract.** C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O<sub>9</sub>·KSCN,  $M_r = 533.6$ ,  $P2_1/c$ ,  $a = 8.156$  (3),  $b = 13.380$  (4),  $c = 23.425$  (5) Å,  $\beta =$

When it is coordinated, the ligand *L* must have the *cis-cis* conformation



the only one allowing it to chelate to the Ni atom. The energy required for this conformational change probably decreases the coordinating ability of the ligand *L* compared to that of *L'*. Hence, under the same crystallization conditions, both [NiL<sub>2</sub>Cl<sub>2</sub>] and [NiL<sub>3</sub>]Cl<sub>2</sub> are formed.

In the presence of H<sub>2</sub>O molecules, as we have observed from the structure determination, the [NiL<sub>3</sub>]<sup>2+</sup> and [(H<sub>2</sub>O)<sub>6</sub>Cl]<sup>−</sup> complex ions are energetically preferred to the coordination of the Cl to the metal. The energy gain so obtained can lead to the conformational change (and therefore to the coordination to the metal atom) of a third ligand molecule.

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\* Structures of Polyether Complexes. XII. Part XI: Weber & Saenger (1980b).

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97.84 (5)°,  $Z = 4$ ,  $d_c = 1.399$  Mg m<sup>−3</sup>, m.p. 368 K. The structure was solved from 2227 X-ray diffractometer data (graphite-monochromated Mo  $K\alpha$  radiation), and refined to  $R = 7.1\%$ . The ligand wraps around the cation which is eightfold coordinated to all the ether O atoms, to one O atom of each nitro group and to the N