

The Structure of Tris(thiosemicarbazide)nickel(II) Dichloride Monohydrate

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The meridional isomer of tris(thiosemicarbazide)nickel(II) dichloride monohydrate crystallizes in space group *Pbca*, with $a=8.89$, $b=16.14$, $c=20.86$ Å, $Z=8$. Nickel-ligand bond lengths are found to be about 10% longer than in the corresponding bis compound and the five-membered rings formed by chelation, planar in the bis, are found to be non-planar in the tris compound, suggesting the absence of π bonding to the metal in the tris compound.

Bis(thiosemicarbazide)nickel(II) sulphate (Grønbaek & Rasmussen, 1962) contains planar five-membered rings with short nickel-ligand distances. With the corresponding tris(thiosemicarbazide) (Fig. 1) there is a rare opportunity to compare the structures of compounds of a ligand bound to the same metal in the same oxidation state but with different stoichiometry. Accordingly we have carried out a crystallographic investigation of tris(thiosemicarbazide)nickel(II) dichloride monohydrate.

Experimental

The compound was prepared by the method of Jensen (Jensen & Rancke-Madsen, 1934) and recrystallized from water in the form of blue prisms (Dana & Ford, 1966). Elementary analysis for C, H, N and Cl was in agreement with the formula, $\text{Ni}(\text{CN}_3\text{H}_5\text{S})_3\text{Cl}_2 \cdot \text{H}_2\text{O}$.

A crystal of maximum dimension 0.64 mm was mounted parallel to *a* along the longest edge and another of maximum dimension 0.3 mm parallel to *c* along the shortest edge. With Cu *K* α radiation ($\lambda =$

1.5418 Å) oscillation and Weissenberg photographs were obtained. The unit cell was found to be orthorhombic with the following dimensions at 22°C:

$$\begin{aligned} a &= 8.89 (2) \text{ \AA} \\ b &= 16.64 (6) \\ c &= 20.86 (2) . \end{aligned}$$

The density determined by flotation was 1.785 g cm^{-3} ; with eight $\text{Ni}(\text{CN}_3\text{H}_5\text{S})_3\text{Cl}_2 \cdot \text{H}_2\text{O}$ units the calculated density is 1.81 g cm^{-3} . From the systematic absences ($0kl$, $k=2n+1$; $h0l$, $l=2n+1$; $hk0$, $h=2n+1$) the space group is *Pbca*.

The multi-film technique was employed to obtain equi-inclination Weissenberg photographs for $0-7k1$ and $hk0-2$. Intensities were measured visually with a calibrated film strip. Scale factors were found from common reflexions. Lorentz and polarization corrections were applied in the usual way. No correction for absorption was made. The number of non-zero, independent reflexions was 2532. Atomic scattering factors given by Cromer & Waber (1965) were used.

Solution and refinement of structure

The programs used to solve the structure were compiled by G. M. Sheldrick of the University of Cambridge. Direct methods were used, phases being obtained for 409 reflexions with values of E lying between 5.135 and 1.567. From the E map the coordinates of some of the heavy atoms were obtained. After several cycles of full-matrix least-squares refinement R was 0.343. A difference map enabled the remaining atoms (except hydrogen) to be found. Eight cycles of refinement with anisotropic temperature factors for the heavy atoms gave $R=0.0809$.* Table 1 gives the final positional and thermal parameters, Table 2 the interatomic distances and Table 3 the bond angles.

* The list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30336 (10pp.). Copies may be obtained through: The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

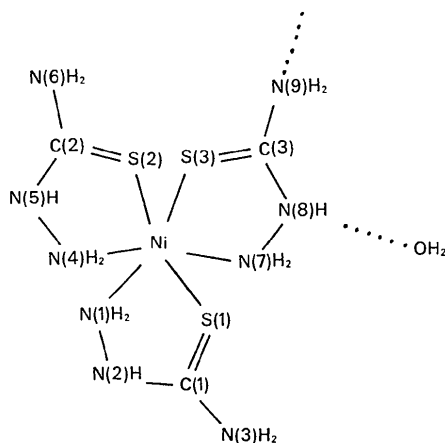


Fig. 1. Structure of the tris(thiosemicarbazide)nickel(II) cation showing the numbering of the heavy atoms. Dotted lines indicate H-bonding to water molecules.

Table 1. Fractional coordinates and temperature factors ($\times 10^4$)

Anisotropic temperature factors are defined as $[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2]$. The significant figures of the standard deviations are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Ni	1348 (1)	2016 (1)	1273 (1)	
Cl(1)	4629 (2)	3734 (1)	570 (1)	
Cl(2)	2901 (2)	480 (1)	3147 (1)	
S(1)	3863 (2)	1500 (1)	1199 (1)	
S(2)	2172 (2)	3219 (1)	1794 (1)	
S(3)	8752 (2)	2433 (1)	1132 (1)	
N(1)	880 (7)	837 (3)	963 (3)	28 (1)
N(2)	1959 (8)	280 (4)	1165 (3)	33 (1)
N(3)	4380 (8)	-32 (4)	1433 (3)	39 (2)
N(4)	885 (6)	1660 (3)	2218 (2)	24 (1)
N(5)	716 (7)	2323 (4)	2640 (3)	34 (1)
N(6)	1046 (8)	3618 (4)	2917 (3)	41 (2)
N(7)	1535 (7)	2564 (3)	378 (3)	28 (1)
N(8)	524 (7)	3220 (3)	327 (3)	32 (1)
N(9)	3316 (8)	1176 (4)	-557 (3)	39 (2)
C(1)	3385 (8)	525 (4)	1269 (3)	23 (1)
C(2)	1254 (8)	3039 (4)	2495 (3)	25 (1)
C(3)	-753 (8)	3205 (4)	643 (3)	25 (1)
O	2072 (7)	4453 (3)	-323 (3)	43 (1)

	β_{11}	β_{22}	β_{33}
Ni	152 (7)	214 (5)	235 (6)
Cl(1)	224 (10)	392 (9)	315 (8)
Cl(2)	225 (10)	323 (8)	419 (9)
S(1)	145 (9)	199 (7)	332 (8)
S(2)	209 (10)	205 (7)	245 (7)
S(3)	162 (9)	303 (8)	355 (9)

Table 2. Interatomic distances (Å)

Ni—S(1)	2.405 (8)
Ni—S(2)	2.399 (8)
Ni—S(3)	2.432 (8)
Ni—N(1)	2.114 (11)
Ni—N(4)	2.103 (10)
Ni—N(7)	2.087 (11)
S(1)—C(1)	1.688 (11)
N(1)—N(2)	1.403 (13)
N(2)—C(1)	1.352 (13)
N(3)—C(1)	1.329 (12)
S(2)—C(2)	1.704 (11)
N(4)—N(5)	1.432 (12)
N(5)—C(2)	1.323 (12)
N(6)—C(2)	1.322 (12)
S(3)—C(3)	1.702 (11)
N(7)—N(8)	1.422 (12)
N(8)—C(3)	1.314 (13)
N(9)—C(3)	1.337 (11)
N(9)—O	2.939 (13)
N(8)—O	2.824 (13)
Cl(1)—O	3.178 (13)

Discussion of the structure

The molecular geometry is depicted in Fig. 2. The coordination about nickel places the atoms in a plane with the sulphur atoms (Table 4) and also in another plane with the three coordinated nitrogen atoms. The compound is therefore the meridional isomer.

Table 3. Bond angles ($^\circ$)

S(2)—Ni—S(1)	92.5 (3)
S(3)—Ni—S(1)	168.5 (1)
S(3)—Ni—S(2)	96.1 (3)
N(4)—Ni—N(1)	89.2 (4)
N(7)—Ni—N(1)	98.6 (4)
N(7)—Ni—N(4)	168.6 (2)
N(1)—Ni—S(1)	80.2 (4)
N(1)—Ni—S(2)	168.2 (2)
N(1)—Ni—S(3)	92.4 (4)
N(4)—Ni—S(1)	98.1 (4)
N(4)—Ni—S(2)	82.6 (3)
N(4)—Ni—S(3)	90.5 (4)
N(7)—Ni—S(1)	91.5 (4)
N(7)—Ni—S(2)	90.8 (4)
N(7)—Ni—S(3)	80.9 (4)
C(1)—S(1)—Ni	96.0 (5)
C(2)—S(2)—Ni	95.5 (4)
C(3)—S(3)—Ni	92.5 (5)
C(1)—N(2)—N(1)	119.4 (8)
C(2)—N(5)—N(4)	121.6 (7)
C(3)—N(8)—N(7)	119.7 (8)
N(2)—N(1)—Ni	113.0 (6)
N(5)—N(4)—Ni	112.4 (6)
N(8)—N(7)—Ni	110.7 (6)
N(2)—C(1)—S(1)	121.0 (6)
N(3)—C(1)—S(1)	121.9 (7)
N(3)—C(1)—N(2)	117.0 (8)
N(5)—C(2)—S(2)	122.0 (6)
N(6)—C(2)—S(2)	120.8 (6)
N(6)—C(2)—N(5)	117.3 (8)
N(8)—C(3)—S(3)	122.6 (6)

The N(8)—O and N(9)—O distances (Table 2) indicate H-bonding between these nitrogen atoms and the water molecules as shown in Fig. 2. This conclusion is reinforced by the observed coplanarity of C(3), N(7), N(8) and O (Table 4). The twelve-membered ring formed by H-bonding is centrosymmetric.

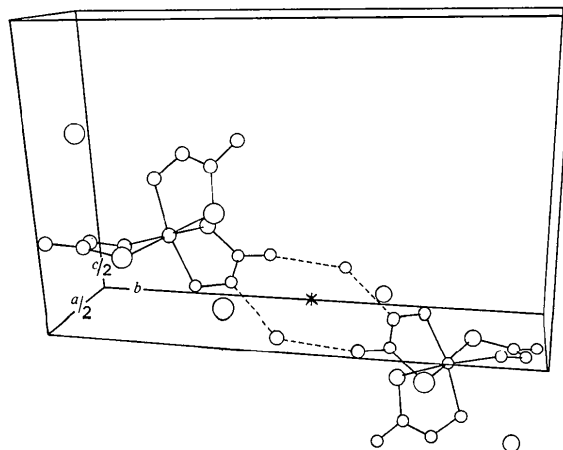


Fig. 2. Perspective view of a quarter of a unit cell showing the configuration of an H-bonded pair of tris(thiosemicarbazide)nickel(II) dichloride monohydrate species. The centre of symmetry is denoted by a star. The non-bonded atoms are chlorine and the atoms bound by dashed lines (denoting H-bonding) are oxygen. In the rings the sulphur atoms are drawn with the larger radius. (Drawn by the program HX88 compiled by Dr J. D. Lee, Loughborough University.)

Table 4. *Planarity analyses*The equation of the plane is $m(1)x + m(2)y + m(3)z = d$

I. Plane through		Deviations from plane (Å)	
C(3)N(7)N(8)O			
<i>m</i> (1)	0.4018	C(3)	0.0313
<i>m</i> (2)	0.3323	N(7)	0.0221
<i>m</i> (3)	0.8533	N(8)	-0.0666
<i>d</i>	2.6231	O	0.0131
II. Plane through			
S(1)C(1)N(1)N(2)N(3)			
<i>m</i> (1)	-0.2316	S(1)	0.0050
<i>m</i> (2)	0.1491	C(1)	0.0013
<i>m</i> (3)	0.9613	N(1)	-0.0187
<i>d</i>	1.9788	N(2)	0.0256
		N(3)	-0.0132
III. Plane through			
S(2)C(2)N(4)N(5)N(6)			
<i>m</i> (1)	0.8680	S(2)	-0.0007
<i>m</i> (2)	-0.2339	C(2)	0.0013
<i>m</i> (3)	0.4381	N(1)	0.0013
<i>d</i>	2.0634	N(2)	-0.0023
		N(3)	0.0004
IV. Plane through			
S(3)C(3)N(7)N(8)N(9)			
<i>m</i> (1)	0.4408	S(3)	0.0011
<i>m</i> (2)	0.4646	C(3)	0.0100
<i>m</i> (3)	0.7680	N(7)	-0.0140
<i>d</i>	3.2116	N(8)	0.0162
		N(9)	-0.0132
V. Plane through			
NiN(1)N(4)N(7)			
<i>m</i> (1)	0.9807	Ni	0.0990
<i>m</i> (2)	-0.1795	N(1)	-0.0066
<i>m</i> (3)	0.0775	N(4)	-0.0458
<i>d</i>	0.6801	N(7)	-0.0467
VI. Plane through			
NiS(1)S(2)S(3)			
<i>m</i> (1)	-0.1838	Ni	0.1029
<i>m</i> (2)	-0.4587	S(1)	-0.0479
<i>m</i> (3)	0.8694	S(2)	-0.0075
<i>d</i>	0.4434	S(3)	-0.0475

The Ni-N and Ni-S bond lengths are about 10% longer than the values reported for the bis cation (Grønbaek & Rasmussen, 1962) suggesting that the metal-ligand bonds are predominantly of σ character in the tris but possess significant π character in the

bis cation. This conclusion is supported by the non-planarity of the ligand rings in the tris cation. A measure of this distortion is the angle between the normals to the planes defined in each ring by the atoms of the ligand (planes II, III and IV in Table 4) and the bonds to the metal atom. These angles are 28.2, 22.6 and 33.1° respectively. Other examples (Grønbaek Hazell, 1972; Mathew, Palenik & Clark, 1973) lead to the conclusion that planar thiosemicarbazide rings generally have shortened metal-ligand distances. The biggest deviation from planarity occurs in the H-bonded ring. It is noteworthy that the C-S distance is shorter by 0.05 Å in the tris than in the bis compound, as a result of the loss of the large degree of delocalization of the type $\text{Ni-S=C} \leftrightarrow \text{Ni=S-C}$.

An examination of the infrared spectrum in the metal-ligand stretching region showed that both the Ni-S and the Ni-N frequencies are considerably lower in the tris than in the bis compound. In bis(thiosemicarbazide)nickel(II) dichloride the IR active Ni-S frequency was 377 cm^{-1} but in the tris compound the IR active Ni-S vibrations appeared at 274 and 248 cm^{-1} . Values observed for the Ni-N stretching vibrations were 522 cm^{-1} for the bis and 400 and 376 cm^{-1} for the tris compound.

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References

- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104-109.
- DANA, E. S. & FORD, W. E. (1966). *A Textbook of Mineralogy*. New York: John Wiley.
- GRØNBÆK, R. & RASMUSSEN, S. E. (1962). *Acta Chem. Scand.* **16**, 2325-2336.
- GRØNBÆK HAZELL, R. (1972). *Acta Chem. Scand.* **26**, 1365-1374.
- JENSEN, K. A. & RANCKE-MADSEN, E. (1934). *Z. anorg. allgem. Chem.* **219**, 243-255.
- MATHEW, M., PALENIK, G. J. & CLARK, G. R. (1973). *Inorg. Chem.* **12**, 446-451.