

Fig. 2. The crystal structure projected along *a*. Broken lines indicate the Ni coordination bonds.

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## Structure of Bis[salicylaldehyde thiosemicarbazonato(1-)]chromium(III) Perchlorate Trihydrate, [Cr(C<sub>8</sub>H<sub>8</sub>N<sub>3</sub>OS)<sub>2</sub>]ClO<sub>4</sub>·3H<sub>2</sub>O\*

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**Abstract.**  $M_r = 593.9$ , monoclinic,  $P2_1/c$ ,  $a = 12.868$  (4),  $b = 14.630$  (6),  $c = 13.363$  (4) Å,  $\beta = 107.58$  (2)°,  $V = 2398.2$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.64$  Mg m<sup>-3</sup>,  $Mo K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 0.801$  mm<sup>-1</sup>,  $F(000) = 1220$ ,  $T = 293$  K, final  $R = 0.048$  for 2568 reflections. The Cr<sup>III</sup> ion is octahedrally coordinated by the two tridentate ligands, in the meridional configuration. The O and S atoms of the salicylidene-iminato groups are each arranged *cis* in the Cr octahedron while the imine N atoms are *trans*. Hydrogen-bond formation occurs between the amine groups and water molecules. The perchlorate ions are linked to the complex cation by a hydrogen bond involving a molecule of water. Water molecules lie in

well defined positions in the lattice and play an important role in the crystal packing.

**Introduction.** Semicarbazides, thiosemicarbazides and their derivatives have been the subject of many studies owing to their potential use as drugs whose action is related to chelation of trace metals (Petering & Van Giessen, 1965).

Derivatives of semicarbazide and thiosemicarbazide with trivalent metallic ions have been studied and postulated as octahedral with two ligand molecules acting in a tridentate manner (Ablov & Gerbeleu, 1965). Owing to thione-thiol equilibrium the thiosemicarbazides (Walter & Schlichting, 1973) neutralize either one or two charges of the metallic ion. Several of these possibilities have been proposed and confirmed by crystallographic techniques (Ryabova, Ponomarev,

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Zelentsov & Atovmyan, 1981; Biyushkin, Gerasimov & Belov, 1981).

Here we report the molecular and crystal structure of the title compound. Synthesis of the ligand and its metallic derivative was carried out following the procedure described by Ablov & Gerbeleu (1965).

**Experimental.** Prismatic crystal  $0.22 \times 0.22 \times 0.52$  mm, Nicolet R3 four-circle diffractometer, graphite-monochromated Mo  $K\alpha$  radiation, lattice parameters from 25 machine-centred reflections with  $4.2 < 2\theta < 16.9^\circ$ , 3455 reflections with  $3 < 2\theta < 45^\circ$ , 2568 independent with  $I > 2.5\sigma(I)$ ,  $R_{\text{int}} = 0.0160$ , index range  $h -13 \rightarrow 12$ ,  $k 0 \rightarrow 15$ ,  $l 0 \rightarrow 14$ ,  $\omega$ -scan mode, variable scan speed, scan width  $1.0$  ( $^\circ\theta$ ), two standard reflections ( $502$ ,  $102$ ) monitored every 50 measurements, Lp correction, numerical absorption correction applied (Sheldrick, 1981); structure solved by combination of direct methods and partial structure expansion by iterative  $E$ -Fourier procedure using *SHELXTL* (Sheldrick, 1981); least-squares anisotropic refinement of all non-H atoms; H atoms riding on bonded C with fixed isotropic  $U = 0.06 \text{ \AA}^2$ , coordinates of H bonded to N and O( $w$ ) refined, function minimized  $\sum w(\Delta F)^2$ ,  $w = \{\sigma^2(F_o) + G(F_o)^2\}^{-1}$ ,  $\sigma(F_o)$  based on counting statistics, final  $G = 0.00114$ ; isotropic extinction parameter  $X = 0.00016$ ;  $(\Delta/\sigma)_{\text{max}} < 0.07$ ;  $\Delta\rho -0.35$  to  $0.73 \text{ e \AA}^{-3}$ ; final  $R = 0.048$ ,  $wR = 0.062$ ; scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The final atomic coordinates are listed in Table 1.\* Fig. 1 shows the molecular conformation for one of the molecules of the racemate of the title compound [ $\text{Cr}(\text{SNO})_2$ ]; bond distances and angles for the non-H atoms are given in Table 2.

The crystal structure of  $\text{Cr}(\text{SNO})_2$  consists of an approximately octahedrally complexed metal cation, a perchlorate anion and three water molecules, which are held together by an extensive network of hydrogen bonds.

The cation has a bis-tridentate ligand arrangement, in the meridional configuration. Similar configurations occur in bis[*N*-(2-aminoethyl)salicylideneaminato]chromium(III) iodide (Gardner, Gatehouse & White, 1971) and in bis[*N*-(2-aminoethyl)salicylideneaminato]iron(III) chloride monohydrate (Summerton, Diamantis & Snow, 1978).

The geometry of the two unique ligands is essentially the same. No significant differences occur between the C—O and C—S distances.

\* List of structure amplitudes, anisotropic thermal parameters, H atom coordinates and the results of mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39907 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The C=S bonds [ $1.702$  (5) and  $1.707$  (5)  $\text{\AA}$ , for ligands *A* and *B* respectively] are almost of the same magnitude as the C=S double bond in ammine-(salicylaldehyde 4-phenylthiosemicarbazonato)nickel(II),  $1.717$  (9)  $\text{\AA}$  (Soriano-García, Toscano, Valdés-Martínez & Fernández, 1985), in thiosemicarbazide,  $1.713$  (5)  $\text{\AA}$  (Hansen & Hazell, 1969) and in thiosemicarbazide hydrochloride,  $1.692$  (3)  $\text{\AA}$  (Coghi, Manotti Lanfredi & Tiripicchio, 1976).

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

	$x$	$y$	$z$	$U_{\text{eq}}$
Cr	2517 (1)	6087 (1)	4002 (1)	31 (1)
Cl	2858 (1)	703 (1)	4105 (1)	52 (1)
S(1A)	2555 (1)	7721 (1)	4220 (1)	41 (1)
S(1B)	2409 (1)	6190 (1)	2162 (1)	41 (1)
N(1A)	897 (3)	6284 (2)	3777 (3)	32 (1)
N(2A)	503 (3)	7175 (3)	3722 (3)	39 (1)
N(3A)	767 (4)	8699 (3)	3953 (4)	50 (2)
N(1B)	4146 (3)	6083 (3)	4167 (3)	33 (1)
N(2B)	4485 (3)	5968 (3)	3282 (3)	40 (1)
N(3B)	4131 (3)	5933 (3)	1514 (3)	56 (2)
O(1A)	2254 (2)	4778 (2)	3825 (3)	46 (1)
O(1B)	2866 (2)	5911 (2)	5496 (2)	41 (1)
O(11)	3853 (4)	248 (4)	4204 (5)	127 (3)
O(12)	3050 (6)	1594 (4)	4363 (7)	172 (4)
O(13)	2400 (5)	279 (4)	4822 (4)	122 (3)
O(14)	2125 (5)	523 (6)	3126 (4)	165 (4)
O(15)	3300 (3)	927 (3)	1281 (3)	60 (2)
O(16)	1604 (3)	4047 (3)	1495 (3)	75 (2)
O(17)	1811 (3)	2202 (3)	1779 (3)	76 (2)
C(1A)	370 (3)	4695 (3)	3776 (3)	35 (2)
C(2A)	1397 (4)	4294 (3)	3864 (3)	36 (2)
C(3A)	1480 (4)	3339 (3)	3954 (4)	46 (2)
C(4A)	587 (4)	2806 (4)	3932 (4)	54 (2)
C(5A)	-409 (4)	3189 (4)	3845 (4)	52 (2)
C(6A)	-517 (4)	4111 (4)	3766 (4)	46 (2)
C(7A)	162 (3)	5651 (3)	3714 (3)	36 (2)
C(8A)	1189 (4)	7883 (3)	3953 (3)	36 (2)
C(1B)	4758 (4)	6369 (3)	6043 (4)	39 (2)
C(2B)	3747 (3)	6206 (3)	6237 (3)	35 (2)
C(3B)	3719 (4)	6315 (3)	7268 (4)	44 (2)
C(4B)	4626 (4)	6572 (4)	8068 (4)	49 (2)
C(5B)	5614 (4)	6729 (4)	7878 (4)	59 (2)
C(6B)	5669 (4)	6625 (4)	6882 (4)	57 (2)
C(7B)	4904 (4)	6245 (3)	5031 (4)	43 (2)
C(8B)	3760 (4)	6017 (3)	2319 (4)	39 (2)

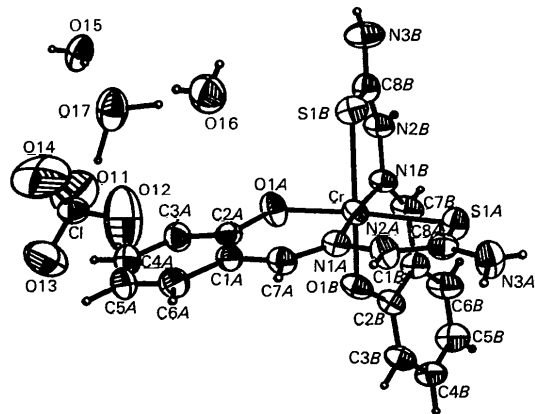


Fig. 1. The molecular conformation, showing atom numbering. The thermal ellipsoids are drawn at the 50% probability level.

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

Cr—S(1A)	2.407 (1)	Cr—S(1B)	2.425 (1)
Cr—N(1A)	2.034 (4)	Cr—N(1B)	2.041 (4)
Cr—O(1A)	1.947 (3)	Cr—O(1B)	1.927 (3)
Cl—O(11)	1.414 (6)	Cl—O(12)	1.352 (6)
Cl—O(13)	1.411 (7)	Cl—O(14)	1.387 (5)
S(1A)—C(8A)	1.702 (5)	S(1B)—C(8B)	1.707 (5)
N(1A)—N(2A)	1.393 (5)	N(1A)—C(7A)	1.307 (6)
N(2A)—C(8A)	1.336 (6)	N(3A)—C(8A)	1.311 (6)
N(1B)—N(2B)	1.388 (6)	N(1B)—C(7B)	1.288 (5)
N(2B)—C(8B)	1.344 (5)	N(3B)—C(8B)	1.307 (7)
O(1A)—C(2A)	1.324 (6)	O(1B)—C(2B)	1.332 (5)
C(1A)—C(2A)	1.419 (6)	C(1A)—C(6A)	1.423 (7)
C(1A)—C(7A)	1.422 (6)	C(2A)—C(3A)	1.404 (7)
C(3A)—C(4A)	1.382 (8)	C(4A)—C(5A)	1.371 (8)
C(5A)—C(6A)	1.358 (8)	C(1B)—C(2B)	1.421 (7)
C(1B)—C(6B)	1.406 (6)	C(1B)—C(7B)	1.433 (7)
C(2B)—C(3B)	1.398 (7)	C(3B)—C(4B)	1.376 (6)
C(4B)—C(5B)	1.389 (8)	C(5B)—C(6B)	1.363 (8)
S(1A)—Cr—S(1B)	93.1 (1)	S(1A)—Cr—N(1A)	82.0 (1)
S(1B)—Cr—N(1A)	95.7 (1)	S(1A)—Cr—N(1B)	90.4 (1)
S(1B)—Cr—N(1B)	81.5 (1)	N(1A)—Cr—N(1B)	171.8 (1)
S(1A)—Cr—O(1A)	171.2 (1)	S(1B)—Cr—O(1A)	89.0 (1)
N(1A)—Cr—O(1A)	89.3 (1)	N(1B)—Cr—O(1A)	98.3 (1)
S(1A)—Cr—O(1B)	91.1 (1)	S(1B)—Cr—O(1B)	169.4 (1)
N(1A)—Cr—O(1B)	94.6 (1)	N(1B)—Cr—O(1B)	88.7 (1)
O(1A)—Cr—O(1B)	88.4 (1)	O(11)—Cl—O(12)	109.9 (4)
O(11)—Cl—O(13)	106.4 (4)	O(12)—Cl—O(13)	109.4 (5)
O(11)—Cl—O(14)	109.8 (4)	O(12)—Cl—O(14)	116.3 (5)
O(13)—Cl—O(14)	104.6 (4)	Cr—S(1A)—C(8A)	97.5 (2)
Cr—S(1B)—C(8B)	97.0 (2)	Cr—N(1A)—N(2A)	118.7 (3)
Cr—N(1A)—C(7A)	126.8 (3)	N(2A)—N(1A)—C(7A)	114.4 (4)
N(1A)—N(2A)—C(8A)	120.6 (3)	Cr—N(1B)—N(2B)	119.0 (2)
Cr—N(1B)—C(7B)	124.8 (4)	N(2B)—N(1B)—C(7B)	116.0 (4)
N(1B)—N(2B)—C(8B)	120.2 (4)	Cr—O(1A)—C(2A)	129.6 (3)
Cr—O(1B)—C(2B)	127.3 (3)	C(2A)—C(1A)—C(6A)	118.5 (4)
C(2A)—C(1A)—C(7A)	124.5 (4)	C(6A)—C(1A)—C(7A)	117.0 (4)
O(1A)—C(2A)—C(1A)	122.8 (4)	O(1A)—C(2A)—C(3A)	119.6 (4)
C(1A)—C(2A)—C(3A)	117.6 (4)	C(2A)—C(3A)—C(4A)	121.3 (5)
C(3A)—C(4A)—C(5A)	121.4 (5)	C(4A)—C(5A)—C(6A)	119.0 (5)
C(1A)—C(6A)—C(5A)	122.2 (5)	N(1A)—C(7A)—C(1A)	124.9 (4)
S(1A)—C(8A)—N(2A)	120.6 (3)	S(1A)—C(8A)—N(3A)	121.9 (4)
N(2A)—C(8A)—N(3A)	117.5 (4)	C(2B)—C(1B)—C(6B)	119.2 (5)
C(2B)—C(1B)—C(7B)	122.6 (4)	C(6B)—C(1B)—C(7B)	118.1 (5)
O(1B)—C(2B)—C(1B)	122.7 (4)	O(1B)—C(2B)—C(3B)	120.0 (4)
C(1B)—C(2B)—C(3B)	117.2 (4)	C(2B)—C(3B)—C(4B)	122.0 (5)
C(3B)—C(4B)—C(5B)	120.8 (5)	C(4B)—C(5B)—C(6B)	118.7 (4)
C(1B)—C(6B)—C(5B)	122.2 (5)	N(1B)—C(7B)—C(1B)	126.1 (5)
S(1B)—C(8B)—N(2B)	120.8 (4)	S(1B)—C(8B)—N(3B)	121.6 (3)
N(2B)—C(8B)—N(3B)	117.6 (4)		

Table 3. Hydrogen-bond distances (Å) and angles (°)

D—H...A	Position of acceptor atom	D...A	D—H	H...A	∠D—H...A
N(2A)—H(2A)...O(17)	-x, 0.5+y, 0.5-z	2.848 (6)	0.80	2.05	176.4
N(3A)—H(3A)...O(16)	-x, 0.5+y, 0.5-z	2.971 (6)	1.00	2.00	165.4
N(2B)—H(2B)...O(15)	1-x, 0.5+y, 0.5-z	2.732 (7)	0.95	1.79	170.7
O(15)—H(15A)...O(1B)	x, 0.5-y, -0.5+z	2.879 (7)	0.69	2.26	152.8
O(16)—H(16A)...O(13)	x, 0.5-y, -0.5+z	2.899 (7)	0.74	2.20	152.1

The salicylideneaminato group and thiosemi-carbazide fragments in both ligands are essentially planar, but the planes formed by the atoms of these two bridging fragments are twisted with respect to each other through angles of 12.3 (6) and 22.9 (7)° for ligands *A* and *B*, respectively.

The hydrogen-bonding interactions between the complex cation, perchlorate ion and water molecules are listed in Table 3. Three of the six amine H atoms are donated to three different water molecules, while only one of the coordinated O atoms acts as an acceptor, to the H atom of another water molecule. The perchlorate ion is linked to the cation through a water molecule.

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The metal environment in the complex cation is approximately octahedral, with the S and O atoms of the two different ligands *cis* to each other and the imine N atoms *trans*.

The deviation from octahedral symmetry of the Cr(SNO)<sub>2</sub> unit is indicated by the bond lengths, angles and interplanar angles. The metal–ligand bond lengths are not equal; the two Cr–O bonds average 1.937 Å, those to the S atoms average 2.416 Å and those to the imine N atoms average 2.038 Å. The angles O(1A)—Cr—S(1A), O(1B)—Cr—S(1B) and N(1A)—Cr—N(1B) all deviate somewhat from the ideal octahedral 180° [171.2 (1), 169.4 (1) and 171.8 (1)°, respectively]. The twelve angles subtended at the metal atom by adjacent donor atoms range from 81.5 (1) to 98.3 (1)°, compared to the 90° required for a perfect octahedron.