Table 2. *Principal bond distances* (Å) *and angles* (°)

Anion			
Tc–Cl(1)	2·385 (7)	Tc–O(1)	2·06 (1)
Tc–Cl(2)	2·372 (8)	Tc–O(2)	2·08 (1)
Tc–Cl(3)	2·36 (2)	O(1)–C(2)	1·27 (2)
Tc–Cl(4)	2·29 (1)	O(2)–C(4)	1·28 (2)
Tc–N(3)	1·74 (3)	C(1)–C(2)	1·53 (3)
Tc–N(4)	1·71 (3)	C(2)–C(3)	1·38 (3)
N(3)–O(3)	1·20 (4)	C(3)–C(4)	1·42 (3)
N(4)–O(4)	1·16 (5)	C(4)–C(5)	1·47 (3)
Cation			
As–C(6)	1·91 (2)	As–C(24)	1·90 (4)
As–C(12)	1·93 (2)	average C–C	1·39 (3)
As–C(18)	1·92 (2)		
Anion			
Tc–N(3)–O(3)	158·6 (33)	Cl(3)–Tc–O(2)	175·3 (6)
Tc–N(4)–O(4)	152·1 (47)	Cl(3)–Tc–N(4)	93·8 (17)
Cl(1)–Tc–Cl(2)	172·6 (2)	Cl(4)–Tc–O(1)	178·7 (6)
Cl(1)–Tc–Cl(3)	97·5 (5)	Cl(4)–Tc–O(2)	89·7 (5)
Cl(1)–Tc–Cl(4)	93·0 (5)	Cl(4)–Tc–N(3)	91·2 (12)
Cl(1)–Tc–O(1)	86·8 (5)	O(1)–Tc–O(2)	89·0 (5)
Cl(1)–Tc–O(2)	86·9 (4)	O(1)–Tc–N(3)	90·1 (13)
Cl(1)–Tc–N(3)	92·1 (12)	O(1)–Tc–N(4)	175·8 (19)
Cl(1)–Tc–N(4)	90·6 (20)	O(2)–Tc–N(3)	178·6 (14)
Cl(2)–Tc–Cl(3)	87·8 (5)	O(2)–Tc–N(4)	87·6 (17)
Cl(2)–Tc–Cl(4)	92·0 (5)	Tc–O(1)–C(2)	126·3 (14)
Cl(2)–Tc–O(1)	88·1 (5)	Tc–O(2)–C(4)	126·9 (14)
Cl(2)–Tc–O(2)	87·7 (4)	C(1)–C(2)–C(3)	120·3 (18)
Cl(2)–Tc–N(3)	93·3 (12)	C(2)–C(3)–C(4)	128·4 (19)
Cl(2)–Tc–N(4)	94·2 (20)	C(3)–C(4)–C(5)	120·8 (19)
Cl(3)–Tc–O(1)	89·8 (6)		
Cation			
C(12)–As–C(18)	113·1 (8)	C(18)–As–C(24)	108·4 (9)
C(12)–As–C(6)	108·9 (9)	C(6)–As–C(24)	109·9 (9)
C(12)–As–C(24)	108·7 (11)	average C–C–C	120·0 (22)
C(18)–As–C(6)	107·8 (8)		

two ligands result in some loss of accuracy in the bond lengths and angles and detailed discussion of these is therefore not possible.

The pentane-2,4-dionato ligand bond distances and angles are comparable with those reported for other Tc complexes containing this ligand (Bandoli, Clemente, Mazzi & Roncari, 1978) and the non-disordered chlorines have bond distances to the Tc which are unremarkable. There are no significant intermolecular contacts.

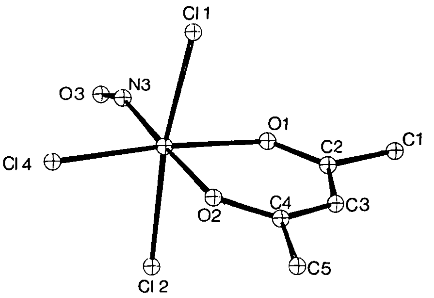

Fig. 1. Molecular structure and atom numbering for the anion showing one of the disordered arrangements where N(3), O(3) and Cl(4) are the disordered atoms.

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Structure of Dibromo(thiosemicarbazide)cadmium(II) Monohydrate

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Abstract. $[CdBr_2(SCN_3H_5)].H_2O$, $M_r = 381{\cdot}354$, monoclinic, Ia (No. 9), $a = 7{\cdot}063$ (1), $b = 14{\cdot}234$ (4), $c = 8{\cdot}751$ (5) Å, $\beta = 100{\cdot}28$ (2)°, $V = 865{\cdot}7$ (3) Å^3, $Z = 4$, $F(000) = 704$, $D_x = 2{\cdot}926$, Nb-filtered Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å), μ(Mo $K\alpha$) = 118·3 cm^{-1}, $T = 298$ (3) K, $R(F) = 0{\cdot}031$ for 1125 observed reflections. The coordination geometry about Cd is an octahedron formed by three Br, two S and one N atoms. The crystal structure consists of infinite parallel chains of coordinated cadmium atoms linked to each other by a double bridge of Br and S. The water molecule is located between the chains and is connected by hydrogen bonds with the N atoms of the organic ligands.

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Introduction. $CdCl_2(SCN_3H_5)(H_2O)$ has been found to exhibit interesting electro-optic properties (Xutang, Minsua, Dong & Zongsau, 1986). In order to find out whether a further improvement is possible by means of crystal engineering, the corresponding bromide was synthesized. Crystals were obtained by means of solution growth and physical investigations were started. The results will be reported elsewhere (Wenshan *et al.*, in preparation). For an evaluation and deeper understanding of the observed properties a structure determination had to be made and is reported in the present paper.

Experimental. A crystal with approximate dimensions 0·40 × 0·35 × 0·15 mm was measured on a Syntex $P2_1$ four-circle diffractometer. Lattice constants were obtained from Weissenberg photographs and refined with 18 accurately centred reflections with $30 < 2\theta < 35°$ on the diffractometer. The reflections were recorded at room temperature by the θ–2θ scan method up to $2\theta = 55°$. A quarter of the Ewald sphere was measured; intensities were evaluated from the Lehmann–Larsen algorithm. Three reference reflections, monitored periodically after 97 measurements, showed no significant variation. The systematic extinctions (*hkl* with $h+k+l$ odd and *h*0*l* with *h* and *l* odd) indicated the (non-standard) space groups *Ia* or *I*2/*a*. The particular physical properties of the crystals and the statistical analysis on the X-ray data were indicative of polar symmetry. The reflections were corrected for absorption by the Gaussian integration method, for Lorentz–polarization and secondary-extinction effects. The structure was solved by the heavy-atom method using 1247 unique reflections, 1125 of which were considered as observed with $I > 3\sigma(I)$. Equivalent reflections were averaged in the non-centrosymmetric crystal class *m*. The refinement was carried out by a least-squares full-matrix technique based on *F*, fixing the origin on the structure centroid by a dedicated algorithm (Flack & Schwarzenbach, 1987). Atomic scattering factors and dispersion corrections were taken from Cromer & Waber (1974).

The final agreement was $R = 0{\cdot}031$ and $wR = 0{\cdot}041$, with anisotropic atoms, unit weights and no H atoms. The enantiomorph-polarity parameter (Bernardinelli & Flack, 1985, 1987; Flack, 1983) converged to 0·006 (27) indicative of the correct polarity of the structure. On the last difference Fourier synthesis, the highest residuals were smaller than 0·9 e Å^{-3} and located at distances of 1·3 Å from the Cd and Br atoms. No hydrogen atoms could be located probably due to the high absorption effect (agreement without absorption correction was 0·125). The X-ray analysis and geometrical calculation were carried out respectively by *XRAY* (Stewart, Kundell & Baldwin, 1972) and *PARST* (Nardelli, 1983). Diagrams were prepared with *ORTEP*II (Johnson, 1976). Further information on data collection and structure refinement is given in Table 1. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 2.*

Table 1. *Additional information on data collection and structure refinement*

Crystal	
Volume (mm^3)	0·0011
Transmission factors	[0·051,0·300]
Data collection	
Scan width	1° left and right of $K\alpha_1/\alpha_2$
Scan speed (° min^{-1})	[2·0,10·0]
Background	stationary, at each end of scan
Range counted	for 40% of the whole scan time
Range of *hkl*	−1,−18,−11 to 9,18,11 ($5 < 2\theta < 55°$)
Standard reflections	$01\bar{5}$, $\overline{21}3$, $13\bar{4}$
Variation standard intensities	12%
Collected reflections	2446
Reflections without Friedel separation	1009
Friedel pairs	238
Reflections collected with equivalents	96%
Internal agreement	0·067 (unique reflections) 0·054 (separated Friedel pairs) and 0·087 (with absorption correction and Friedel pairs)
Refinement	
Positional and thermal parameters	81
Observations per parameter	13
Maximum final shift/e.s.d.	0·011
Durbin–Watson *D* statistics	1·59

Table 2. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Cd	−0·0001 (2)	0·0636 (1)	0·0001 (1)	0·0317 (3)
Br(1)	0·2088 (2)	−0·0718 (1)	0·1794 (1)	0·0347 (5)
Br(2)	0·1636 (3)	0·2172 (1)	0·1197 (2)	0·0395 (5)
S	−0·1819 (6)	−0·0605 (2)	−0·1829 (4)	0·0264 (10)
C	−0·2666 (22)	0·0069 (10)	−0·3433 (15)	0·030 (4)
N(1)	−0·3422 (23)	−0·0349 (10)	−0·4730 (14)	0·046 (5)
N(2)	−0·2593 (19)	0·0996 (8)	−0·3451 (12)	0·031 (4)
N(3)	−0·1803 (20)	0·1524 (8)	−0·2100 (13)	0·033 (4)
O	−0·4683 (19)	0·2192 (8)	−0·5728 (13)	0·050 (4)

Discussion. The asymmetric unit contains one formula unit. The structure consists of infinite chains of $[CdBr_2SCN_3H_5]_n$ parallel to the *a* axis as shown in Fig. 1. Each Cd atom is at the centre of a slightly distorted octahedron (Fig. 2) formed by three Br, two S and one N atoms. Consecutive octahedra share a common edge with one Br and one N atom. The distances of the two bridge ligands to the Cd atoms indicate the existence of slightly asymmetric but strong

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* Lists of structure factors, anisotropic thermal parameters and weighted least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44777 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bonds. The Cd—Br(1) distances are 2·743 (2) and 2·802 (2) and Cd—S (thiosemicarbazide) 2·569 (3) and 2·983 (4) Å respectively. The distortion of the coordination octahedron is mainly caused by the relatively small bite of the bidentate thiosemicarbazide ligand (Table 3) and its rigid planar configuration which is almost perpendicular to the chain direction, as indicated by the data in Table 4 (supplementary material).* The water molecule acts as a transverse intermolecular weak bridge between adjacent polymeric chains on the corresponding thiosemicarbazide. The short contact distances N(2)···O and O···N(3)′ (in position $x;\frac{1}{2}-y;z-\frac{1}{2}$) respectively of 2·83 (2) and 3·13 (2) Å are characteristic for hydrogen bonds between two distinct symmetry-equivalent ligands.

Table 3. *Bond distances, relevant contacts* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cd—Br(2)	2·603 (2)	Cd—Br′	2·802 (2)
Cd—Br(1)	2·743 (2)	Cd—S′	2·983 (4)
Cd—S	2·569 (3)	Cd—N(3)	2·400 (11)
S—C	1·717 (14)	C—N(2)	1·319 (18)
C—N(1)	1·309 (18)	N(2)—N(3)	1·428 (15)
N(2)···O	2·83 (2)	N′···O	3·13 (2)
S′—Cd—N(3)	86·8 (3)	Br(1)—Cd—Br′	94·7 (1)
Br′—Cd—N(3)	93·7 (3)	Br(1)—Cd—S	91·8 (1)
Br′—Cd—S′	177·8 (1)	Br(2)—Cd—N(3)	90·2 (3)
S—Cd—N(3)	75·3 (2)	Br(2)—Cd—S′	84·6 (1)
S—Cd—S′	89·8 (1)	Br(2)—Cd—Br′	93·3 (1)
S—Cd—Br′	92·4 (1)	Br(2)—Cd—S	164·7 (1)
Br(1)—Cd—N(3)	164·9 (3)	Br(2)—Cd—Br(1)	101·8 (1)
Br(1)—Cd—S′	85·2 (1)	Cd—S—C	100·8 (5)
Cd—N(3)—N(2)	115·6 (8)	N(1)—C—N(2)	117 (1)
S—C—N(2)	124 (1)	C—N(2)—N(3)	122 (1)
S—C—N(1)	119 (1)		

Equivalent atom	Independent atom	Symmetry transformation
Br′	Br(1)	$x-\frac{1}{2}; -y; z$
S′	S	$x+\frac{1}{2}; -y; z$
N′	N(3)	$x; -y+\frac{1}{2}; z-\frac{1}{2}$

This compound is similar to the dichloro analogue recently reported (Woode, Bryan & Bekoe, 1987). Transforming the space group *Ia* into the standard *Cc* ($|\mathbf{a}| = |-(\mathbf{a}' + \mathbf{c}')| = 10{\cdot}218$, $|\mathbf{b}| = |\mathbf{b}'| = 14{\cdot}234$, $|\mathbf{c}| = |\mathbf{a}'| = 7{\cdot}063$ Å and $\beta = 122{\cdot}57°$), the present crystal shows cell dimensions slightly larger than for the Cl derivative. This is to be expected for the larger bromine atom. By a small origin translation in the (**a**,**c**) plane, the two asymmetric units are practically in the same position each with comparable corresponding coordinates. Consequently the two crystals may be considered as isostructural. The two molecules show almost equal bond lengths and angles and the few relevant differences are mainly due to the halogen exchange. The Cd—Br distances are significantly longer than Cd—Cl, in agreement with the smaller radius of the chlorine atom. In addition, the Cd—S and Cd—N(3) bonds on the equatorial coordination plane are significantly shorter in the Br derivative. This is probably due to the *trans* effect of the opposite bromines performing a stronger electron π donation than Cl atoms.

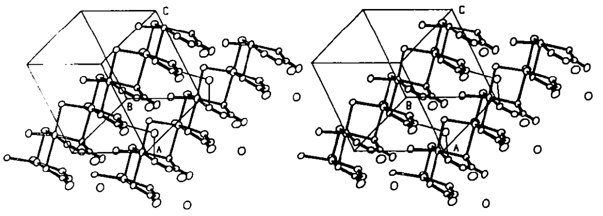

Fig. 1. Stereoscopic view of the crystal packing showing the polymeric chains and the water bridges. Thermal ellipsoids are represented with 50% probability.

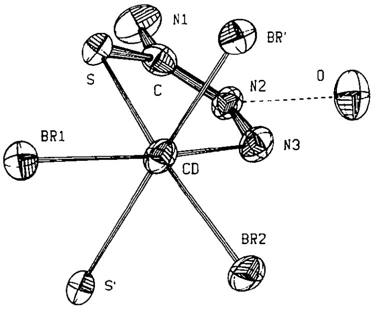

Fig. 2. View of the octahedral coordination of the Cd atom with numbering scheme; equivalent atom positions are indicated in Table 3. Thermal ellipsoids with 50% probability.

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* See deposition footnote.