disorder. This would explain the large range of its C—C bond lengths and C—C—C angles. This feature has already been observed for some cyclopentadienyl complexes (Rogers *et al.*, 1981).

Refinement of a disordered model including two different orientations for ring 3 gave less acceptable agreement factors. Another method of refinement treating ring 3 as a rigid group did not succeed either.

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Dichloro(thiosemicarbazide)cadmium(II) Monohydrate

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Abstract. $[CdCl_2(CH_5N_3S)].H_2O$, $M_r = 292{\cdot}46$, monoclinic, Cc, $a = 10{\cdot}135\,(4)$, $b = 13{\cdot}961\,(7)$, $c = 6{\cdot}887\,(3)$ Å, $\beta = 124{\cdot}05\,(6)°$, $V = 807{\cdot}4$ Å^3, $Z = 4$, $D_x = 2{\cdot}406$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 35$ cm^{-1}, $T = 293$ K, $R = 0{\cdot}027$ for 692 independent significant reflections. The structure is polymeric, the first such known with the ligand *cis* and bidentate. Each Cd is octahedrally coordinated. The central plane contains the thiosemicarbazide ligand, bonded to Cd through S and N(3) to give a five-membered ring, and two Cl atoms, Cd—Cl, 2·489 (4) and 2·633 (4) Å; Cd—S, 2·583 (3) Å; Cd—N 2·42 (1) Å. The coordination sphere is completed by a Cl from the plane above and an S from the plane below, Cd—Cl, 2·663 (5) Å; Cd—S, 2·919 (5) Å. The water molecule is not part of the coordination sphere, but is involved with it in five separate hydrogen bonds, acting as an acceptor from N(2) and N(3) in two adjacent thiosemicarbazides, as a single donor to one Cl atom, and as a shared donor to two other Cl.

Introduction. Thiosemicarbazide, a well known chelating agent, is used to characterize aldehydes, ketones, and polysaccharides. Some thiosemicarbazide derivatives are potential anti-tumor and anti-hypertensive agents, and others are active against influenza, protozoa, and smallpox (Gowda & Mahadevappa, 1977; Pillai, Nandi & Levinson, 1977). These authors attribute this biological activity to the ability of thiosemicarbazide to chelate trace metals. Thus, thiosemicarbazide is also used as a masking agent to minimize interferences from metals such as copper, nickel, and platinum in the determination of arsenic by atomic absorption methods (Kirkbright & Taddia, 1978). The conformational preferences of thiosemicarbazide in metal-complex formation are therefore of some interest. The majority of its metal complexes are discrete monomeric units in which the ligand has a *cis* conformation and is bidentate, bonding through S and the hydrazinic N atoms (Cavalca, Nardelli & Branchi, 1960; Cavalca, Nardelli & Fava, 1962;

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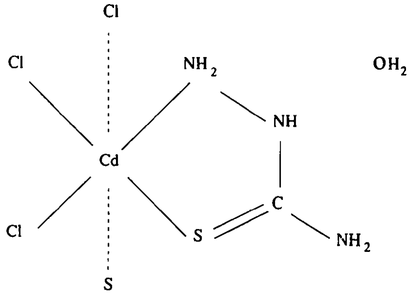
Grønbaek & Rasmussen, 1962; Grønbaek, 1963; Grønbaek Hazell, 1966; Villa, Manfredotti & Guastini, 1972). A polymeric silver complex is known in which the ligand has the *trans* conformation and is monodentate, bonding only through S (Fava Gasparri, Mangia, Musatti & Nardelli, 1968). We report the structure of the first known polymeric structure with the ligand *cis* and bidentate.



Experimental. Colorless needles of the complex separated after several days from an aqueous solution containing equimolar amounts of cadmium(II) chloride and thiosemicarbazide.

The crystal system and space group were determined from 25° precession photographs of the equatorial and first levels of the reciprocal lattice taken with Mo $K\alpha$ radiation. The observed systematic absences hkl with $h+k$ odd, $h0l$ with l odd, indicate space group Cc or $C2/c$. With $Z=4$ and with two Cl atoms in the formula unit, the former is more probable on chemical grounds, and was confirmed by the statistical distribution of intensities (Rogers, 1965).

The unit-cell dimensions were derived from a least-squares fit to the setting angles for 12 general reflections in the range $3{\cdot}5 \le \theta \le 13{\cdot}3°$. Intensity measurements were made on a crystal needle of size $0{\cdot}10 \times 0{\cdot}10 \times 0{\cdot}42$ mm, using a Nicolet $P3m$ diffractometer operated in the $\theta/2\theta$ mode with Mo $K\alpha$ radiation. Reflections were measured in the range $0 \le h \le 12$, $0 \le k \le 16$, $-6 \le l \le 6$, to a maximum value of $(\sin\theta)/\lambda$ of 0·596 Å^{-1}. The 715 independent reflections thus measured yielded 692 intensities significantly above background [$I > 2{\cdot}5\sigma(I)$, 96·6%]. The symmetrically equivalent reflections $\bar{1}12$ and $\bar{1}\bar{1}2$ were used as standards and measured after every 50 reflection cycles. Over the course of the experiment, fluctuations about the individual mean intensities of the two standards were <2·4%, and the two means differed by 2·3%.

The Patterson method was used to locate the four heavy atoms, and Fourier and difference Fourier methods were used to locate the remaining atoms in the complex. Refinement was by block-diagonal least-squares methods minimizing the function $\sum w(|F_o| - |F_c|)^2$. All appropriate positional parameters were varied, anisotropic thermal parameters were adopted for the non-H atoms and isotropic B values refined for each H atom. At convergence, R was 0·0266 for the significant reflections,* 0·0271 for the complete data set, wR was 0·0272, and the standard deviation of an observation of unit weight was 2·26. The maximum shift-to-e.s.d. ratio in the final cycle of refinement was 0·29, the average 0·05. Weights were assigned as $1/[\sigma^2(F_o) + gF_o^2]$, with $g = 0{\cdot}00001$. Inclusion of anomalous-dispersion terms for Cd in a separate refinement gave poorer agreement ($R = 0{\cdot}0284$ for the significant reflections) and did not significantly affect the positions of the heavy atoms, so no account has been taken of that effect. The distribution of signs for $|F_o| - |F_c|$ was sufficiently random that no absorption corrections seemed necessary. Atomic scattering factors were taken from Cromer & Waber (1974) except that for H, which was taken from Stewart, Davidson & Simpson (1965). A final difference electron-density map showed maximum and minimum peaks of 1·22 and 0·75 e Å^{-3} grouped around the site of the Cd atom.

All computations were carried out using programs written in this laboratory for the Tandy TRS-80 model 2000 personal computer.

Discussion. The analysis shows the thiosemicarbazide acts as a *cis* bidentate ligand, bonding to Cd through S and N(3). Cd is octahedrally coordinated with the thiosemicarbazide and the two Cl atoms forming the central plane. The complex is polymeric, with the apical positions on Cd occupied by a Cl atom from the layer below and the S atom from the layer above. The water molecule is not part of the Cd coordination sphere, but is involved in hydrogen bonding with it. A stereoscopic view of the structure is shown in Fig. 1 [*ORTEP*, Johnson (1976)] and atomic coordinates are given, with their e.s.d.'s, in Table 1. Bond lengths and angles (not involving H) are given in Fig. 2.

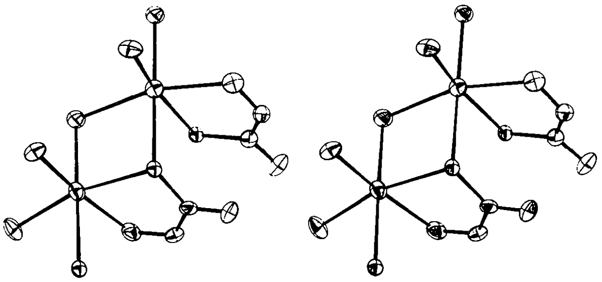


Fig. 1. Stereoscopic view of two monomeric units of the polymeric complex (excluding water of hydration and H atoms). Thermal ellipsoids are drawn to enclose the 50% probability level.

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* Lists of structure factors, bond distances and angles involving H, and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44322 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and isotropic thermal parameters*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}/B(Å^2)
Cd	0·00000	0·06414 (5)	0·00000	2·19
Cl(1)	−0·1205 (4)	0·2122 (2)	0·0384 (5)	2·87
Cl(2)	−0·1709 (3)	−0·0686 (2)	0·0336 (4)	2·57
S	0·1870 (3)	−0·0648 (2)	0·0114 (4)	1·55
O	0·578 (1)	0·2168 (6)	0·104 (2)	3·23
N(1)	0·487 (1)	−0·0404 (7)	0·164 (2)	3·12
N(2)	0·356 (1)	0·0997 (6)	0·111 (2)	2·16
N(3)	0·220 (1)	0·1526 (7)	0·042 (2)	2·47
C	0·355 (1)	0·0013 (8)	0·102 (7)	1·97
H(N1)	0·62 (1)	−0·031 (8)	0·28 (2)	4 (3)
H′N(1)	0·52 (2)	−0·06 (1)	0·21 (3)	7 (4)
H(N2)	0·47 (1)	0·113 (8)	0·19 (2)	3 (2)
H(N3)	0·26 (2)	0·18 (1)	0·18 (2)	6 (4)
H′(N3)	0·18 (2)	0·18 (1)	−0·11 (3)	7 (5)
H(O)	0·69 (1)	0·203 (7)	0·17 (2)	1 (1)
H′(O)	0·54 (2)	0·229 (7)	−0·03 (2)	4 (3)

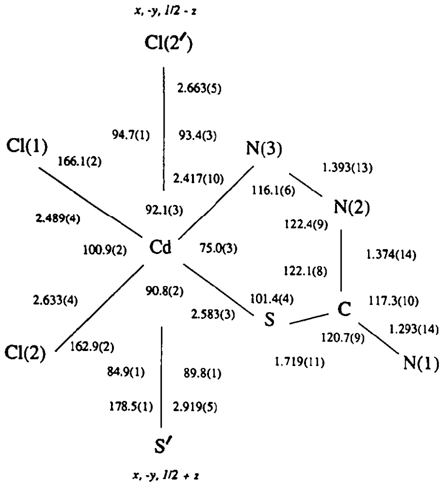

Fig. 2. Bond lengths (Å) and angles (°) not involving H. Bond angles not given in the figure are: Cl(2)—Cd—Cl(2′), 96·1 (1); Cl(1)—Cd—S′, 84·0 (1); S′—Cd—N(3), 85·6 (2); S—Cd—Cl(2′), 91·3 (1)°. Symmetry transformations from the parent molecule are indicated in italics.

The geometry of thiosemicarbazide bonding to Cd may be compared to that found in the *cis* and *trans* isomers of bis(thiosemicarbazide)cadmium(II) sulfate (Larsen & Trinderup, 1975). The Cd—S bond length of 2·583 (3) Å is longer than that found for that *cis* isomer, 2·545 (2) Å, or for its *trans* analog, 2·514 (2) Å. At the same time, the Cd—S—C bond angle is larger than in that structure, 101·4 (4) *vs* 97·9 (2)° for the *cis* sulfate and 98·2 (1)° for the *trans* sulfate. The Cd—N(3) bond length in our complex is also longer than that found for both isomers of the sulfate, 2·417 (10) *vs* 2·367 (5) Å, and for all but one other Cd—N bond length for octahedral Cd, which range from 2·279 to 2·43 (2) Å (Rodesiler, Charles, Griffith, Lewinski & Amma, 1986; Turner, Rodesiler & Amma, 1982). In the same way the bond angle Cd—N(3)—N(2) is also larger than in the sulfate, 116·1 (6) *vs* 112·1 (3) and 112·7 (2)°. By contrast, the S—Cd—N(3) bond angle in our complex is smaller than in the sulfate, 75·0 (3) *vs* 77·9 (1)° in the *cis* isomer and 79·2 (1)° in the *trans* isomer of the sulfate. These data indicate that the thiosemicarbazide is not as tightly bound to Cd in our complex as in the sulfate.

The Cd—Cl bond to the singly coordinated Cl atom, 2·489 (4) Å, is the shortest known for this type and, coupled to the weaker bonding of the thiosemicarbazide ligand, attests to a significant transfer of electron density from Cd to the bond. The bonds from Cd to the doubly coordinated Cl atoms, 2·633 (4) and 2·663 (5) Å, are significantly longer but comparable to other Cd—Cl bonds to singly and doubly coordinated Cl in other octahedral Cd complexes. Values ranging from 2·589 (1) to 2·629 (1) Å are found for doubly coordinated Cl in $Cd_2MgCl_6.12H_2O$ (Ledésert & Monier, 1982) and from 2·601 (1) to 2·647 (1) Å in $CdNi_2Cl_6.12H_2O$ (Leclaire & Borel, 1982) for bonds to singly coordinated Cl.

The geometry of the thiosemicarbazide itself is comparable to that reported for the sulfate. The non-H atoms of the ligand are planar to within 0·013 (8) Å, but are not coplanar with the central coordination plane, which is inclined to the other at an angle of 20·3 (9)°. The Cd atom is displaced by 0·18 (4) Å from the best plane through the four central chelating atoms in a direction toward the apical Cl of an adjacent layer. These four atoms are themselves subject to average displacements from the plane of ±0·035–0·045 Å.

The complex is a monohydrate but the water molecule does not take part in the coordination sphere of Cd which is completed by a weak bond to the S atom

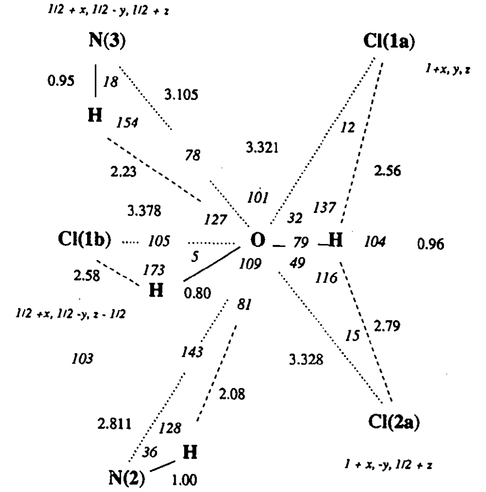

Fig. 3. Hydrogen bonding involving the water molecule. Distances (Å) and angles (italics) (°). Symmetry transformations from the parent molecule are indicated in italics. Other angles of interest are: Cl(1*a*)—O—Cl(1*b*), 81·7 (2); Cl(1*b*)—O—Cl(2*a*), 151·0 (3)°.

of an adjacent layer, producing a polymeric structure. The water molecule stabilizes the crystal structure, however, by participation in five separate hydrogen bonds. It acts as an acceptor in a hydrogen bond from N(2) in the parent ligand, and from N(3) of an adjacent thiosemicarbazide. One of the water H atoms participates in a single donor bond to Cl(1) of a symmetry-related neighbor, and the other takes part in a bifurcated donation to Cl(1) and Cl(2) of two other neighbors. Details are shown in Fig. 3.

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A Tetrahedrally Surrounded Nickel(II) Complex: The Structure of Dichloro[2-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine-*N*,*P*]nickel(II)

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Abstract. $[\mathrm{NiCl_2(C_{21}H_{22}NP)}]$, $M_r = 449{\cdot}01$, triclinic, $P\bar{1}$, $a = 10{\cdot}220$ (8), $b = 13{\cdot}820$ (20), $c = 16{\cdot}550$ (2) Å, $\alpha = 76{\cdot}48$ (7), $\beta = 73{\cdot}49$ (4), $\gamma = 76{\cdot}84$ (8)°, $V = 2146$ (4) Å^3, $Z = 4$, $D_x = 1{\cdot}390$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54184$ Å, $\mu = 41{\cdot}34$ cm^{-1}, $F(000) = 928$, $T = 298$ K, $R = 0{\cdot}0485$ for 5090 observed reflections. The asymmetric unit consists of two independent molecules which show only minor differences in the corresponding bond distances and angles, but significant differences in some of the torsion angles of the six-membered metalla ring which has a boat conformation. The Ni$^{\mathrm{II}}$ atoms are tetrahedrally surrounded by two Cl atoms, one P and one N atom.

Introduction. The catalytic activity of nickel–phosphine complexes in the cross-coupling of Grignard reagents with aryl and alkenyl halides was reported by Corriu & Masse (1972) and Tamao, Sumitani & Kumada (1972). Since then a wide variety of nickel and palladium catalysts have been developed and some of them have been found to be very successful in cross-coupling reactions (Jolly, 1982). In recent years, asymmetrical cross-coupling with a chiral transition-metal catalyst has become very popular. Recently we reported the crystal structure of a chiral Pd catalyst: dichloro({(1*R*)-[(2*S*)-2-(diphenylphosphino)-1-ferrocenyl]-ethyl}-dimethylamine-*N*,*P*)palladium(II), $\mathrm{PdCl_2(ppfa)}$

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