Tl_2Br_4. It is quite different from the dioxane complexes formed by the analogous gallium (Beamish, Small & Worrall, 1979) and indium dihalides (Sinclair & Worrall, 1982). Bond distances and angles are given in Table 2; tetrahedral distances [Tl(1)—Br] are similar to those observed in the parent halide [mean distance 2·51 (3) Å, Hazell, 1963]. The Tl^+ ion [Tl(2)] is at the centre of a distorted dodecahedron (Fig. 1) and is surrounded by six Br atoms (from four different tetrahedra) and two O atoms; the Tl(2)—Br distances are similar to other ionic eight-coordinate Tl^+—Br distances, *e.g.* 3·46 Å in Tl_2Br_4 where Tl^+ is at the centre of a distorted dodecahedron (Hazell, 1963), and 3·44 Å in TlBr which has a CsCl structure (Lee, 1971). The Tl^+ ions are bridged by weakly attached dioxane molecules in the chair conformation to form chains parallel to the *c* axis (Fig. 2). The Tl(2)—O distances, which have high e.s.d.'s, are similar to those observed in other ionic Tl^I complexes, *e.g.* Tl_3FCO_3, Tl—O 2·89 (6) Å (Alcock, 1973); $Tl.C_6H_2N_3O_7$, Tl—O 2·83–3·22 (2) Å (Herbstein, Kapon & Wielinski, 1977). We attribute these high e.s.d.'s to the mobility of the ligand due to its weak attachment; it is well known that Tl^+ is a very weak acceptor for 'hard' ligands such as oxygen (Lee, 1971); complexes of Tl^I which have been reported and which give more precise Tl—O distances are in the main those which contain negatively charged ions, *e.g.* acetate (Brown & Faggiani, 1980), salicylate (Hughes & Truter, 1972) and picrate (Herbstein, Kapon & Wielinski, 1977). The interaction between the charged ions will be stronger than the ion-dipole of a neutral ligand such as dioxane.

The fairly regular coordination around Tl^I suggests that the $6s^2$ lone pair of electrons is stereochemically inactive. This effect has been recently discussed (Brown & Faggiani, 1980).

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catena-Di-*μ*-thiocyanato-*N*,*S*-bis(1*H*-1,2,4-triazole-*N*⁴)cadmium, $[Cd(C_2H_3N_3)_2(NCS)_2]$; a Third Structure Type of Composition $M(NCS)_2(1,2,4\text{-triazole})_2$

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Abstract. M_r = 366·70, triclinic, $P\bar{1}$, a = 5·717 (2), b = 7·573 (2), c = 7·683 (2) Å, α = 79·54 (2), β = 68·70 (2), γ = 89·36 (2)°, V = 304·2 Å^3, Z = 1, D_m = 1·99 (1), D_x = 2·00 Mg m^{-3}, Mo $K\alpha$, λ = 0·71073 Å, μ = 2·11 mm^{-1}, $F(000)$ = 174·94, room temperature, R = 0·019 for 1722 independent reflections. The compound was crystallized from an aqueous solution of cadmium thiocyanate and 1,2,4-triazole. Cd^{2+} is octahedrally coordinated by two monodentate N(4)-bonded 1,2,4-triazole ligands (*trans* oriented) with Cd—N = 2·317 (1) Å, two (*trans*) thiocyanate N atoms, Cd—N = 2·330 (2) Å, and two thiocyanate S atoms, Cd—S = 2·754 (1) Å. The thiocyanate ions constitute double bridges, thereby building infinite linear chains of thiocyanate-linked Cd^{2+} ions running parallel in one direction in the crystal. The structure differs from previous compounds of composition $M(NCS)_2$(1,2,4-triazole)$_2$ that contain bidentate 1,2,4-triazole ligands and N-bonded thiocyanate anions.

Introduction. Thiocyanates of divalent first-row transition metals are known to form either linear trinuclear, or two-dimensional layered compounds with 1,2,4-triazole (trz) as ligands. The overall composition is $M(NCS)_2(trz)_2$ (Haasnoot & Groeneveld, 1977). These types of compounds are easily distinguished by their

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infrared spectra, because the triazole ligands are present in different tautomers. The infrared spectrum of the Cd compound, however, showed the presence of a third coordination mode of the triazole ring, probably with monodentate triazole. The structure determination of this compound is reported here.

Experimental. Crystals of the title compound grown from a solution of stoichiometric amounts of cadmium thiocyanate and 1,2,4-triazole in water by slow evaporation at room temperature. Single crystal 0·3 × 0·3 × 0·2 mm selected and mounted in a glass capillary. D_m determined by flotation in a mixture of iodomethane and 1,3-dibromopropane. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation monochromated by graphite. Setting angles of 18 reflections with θ between 13° and 15° used to calculate the lattice parameters. 2062 reflections measured, $\theta < 30°$, $-8 \leq h \leq 8$, $-10 \leq k \leq 10$, $0 \leq l \leq 10$; intensities of standard reflections $\bar{2}42$, $3\bar{3}1$ and $\bar{1}\bar{4}2$ varied 8%, a polynomial correction according to this variation was applied to all reflections. Absorption correction applied using Monte Carlo methods (de Graaff, 1973), transmission coefficients 0·55 to 0·69. After merging equivalent reflections ($R_{\text{int}} = 0{\cdot}016$) 1762 independent reflections remained, 1722 considered observed [$I > 2\sigma(I)$]. In the final stages of the refinement data corrected for extinction according to the method of Zachariasen (1967). Scattering factors and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974). Structure solved by Patterson and difference Fourier techniques. Four cycles of isotropic refinement (using F values) yielded $R = 0{\cdot}15$. H located by a difference Fourier synthesis. 91 parameters refined; all atoms except H were refined anisotropically, the position of Cd was fixed at (0,0,0). The R value decreased from 0·032 to 0·019 by the extinction correction. The final value of wR was 0·026 with $w = (\sigma_F)^{-2}$; $S = 1{\cdot}58$. Ratio of the maximum least-squares shift to error 0·01. Maximum and minimum heights in the final difference Fourier map 0·59 and $-0{\cdot}91$ e Å^{-3}, respectively, with a statistical height of 0·14 e Å^{-3}. The maximum secondary-extinction correction was 47% in F. All computer programs used were written or modified by the crystallography section in our laboratory. Illustrations were prepared with the aid of a modified version of the computer program *ORTEP* (Johnson, 1965).

Discussion. Final atomic parameters are given in Table 1.* As Fig. 1 shows, the structure consists of linear arrays of Cd^{2+} ions running parallel to the a axis. The Cd atoms are linked together by double bridges of NCS^- ions. The triazole ligands coordinate *via* N(4) to Cd. The parallel chains are linked together by hydrogen bridges of the H(1)—N(1)—N(2) part of the triazole rings: N(1)···N(2′) = 2·932 (2) Å and N(1)···H(1)···N(2′) = 133 (1)°. Using these hydrogen bridges the Cd arrays are ranged into parallel layers. These layers are mutually connected by van der Waals forces and weak additional hydrogen bridges between the nitrogen H atoms and the thiocyanate S atoms [N(1)···S = 3·440 (2) Å], not shown in the figure. The rather strong N—H···N hydrogen bond is further illustrated by the infrared spectrum where the $\nu_{\text{N—H}}$ is found as a rather strong and relatively narrow band at 3265 cm^{-1}, whereas this band is found at about 2950 cm^{-1} (and very broad) for the layered $M(NCS)_2(trz)_2$ structures and for the trimeric α-$Ni(NCS)_2(trz)_2$ (Haasnoot & Groeneveld, 1977).

Table 1. *Positional parameters and isotropic B values* ($B_{\text{iso}} = \frac{8}{3}\pi^2\,\text{tr}\mathbf{U}$) *for* $Cd(NCS)_2(trz)_2$

	x	y	z	B_{iso} (Å^2)
Cd	0	0	0	2·56 (1)
N(1)	−0·0672 (3)	0·4234 (2)	0·3367 (2)	3·28 (5)
N(2)	0·1089 (3)	0·3377 (3)	0·3943 (3)	3·98 (6)
C(3)	0·1479 (4)	0·2011 (2)	0·3075 (3)	3·74 (7)
N(4)	0·0109 (3)	0·1949 (2)	0·1976 (2)	2·84 (5)
C(5)	−0·1226 (3)	0·3384 (2)	0·2205 (3)	3·07 (6)
H(1)	−0·138 (5)	0·516 (4)	0·380 (4)	3·8 (5)
H(3)	0·231 (6)	0·138 (4)	0·350 (5)	5·4 (7)
H(5)	−0·213 (6)	0·335 (5)	0·133 (5)	5·7 (7)
N	0·2764 (3)	−0·1847 (2)	0·0965 (2)	3·28 (5)
C	0·4132 (2)	−0·1920 (2)	0·1765 (2)	2·41 (5)
S	0·6048 (1)	−0·1979 (1)	0·2935 (1)	3·05 (2)

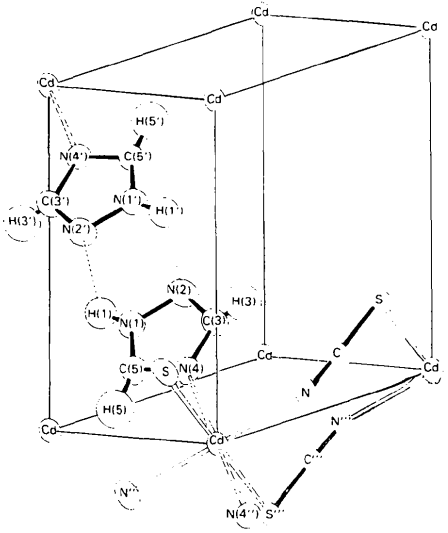

Fig. 1. Part of the structure of $Cd(NCS)_2(trz)_2$, showing numbering, the surroundings of Cd, the bridging between the Cd atoms and the H-bridging system (dotted lines), relative to the unit cell. Primed atoms are generated by $-x$, $1-y$, $1-z$, double primed by $-x$, $-y$, $-z$, triple primed by $1-x$, $-y$, $-z$.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38612 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Cd–N(4)	2·317 (1)	N(1)–H(1)	0·86 (3)
Cd–N	2·330 (2)	C(3)–H(3)	0·78 (3)
Cd–S	2·754 (1)	C(5)–H(5)	0·99 (4)
N(1)–N(2)	1·355 (2)	N–C	1·153 (2)
N(2)–C(3)	1·304 (2)	C–S	1·646 (2)
C(3)–N(4)	1·351 (2)	H(1)···N(2′)	2·27 (3)
N(4)–C(5)	1·322 (2)	N(1)···N(2′)	2·932 (2)
C(5)–N(1)	1·315 (2)		
N(4)–Cd–N	91·21 (6)	N(4)–C(5)–N(1)	109·6 (2)
N(4)–Cd–S	90·25 (4)	H(1)–N(1)–C(5)	127 (2)
N–Cd–S	91·08 (4)	H(1)–N(1)–N(2)	122 (2)
Cd–N–C	143·4 (1)	C(5)–N(1)–N(2)	110·5 (1)
N–C–S	178·4 (2)	H(1′)···N(2)–N(1)	104·4 (7)
C–S–Cd	96·3 (1)	H(1′)···N(2)–C(3)	152·3 (7)
Cd–N(4)–C(3)	132·2 (1)	N(1)–N(2)–C(3)	102·2 (1)
Cd–N(4)–C(5)	124·7 (1)	H(3)–C(3)–N(2)	107 (2)
C(3)–N(4)–C(5)	103·1 (2)	H(3)–C(3)–N(4)	138 (3)
H(5)–C(5)–N(4)	102 (2)	N(2)–C(3)–N(4)	114·6 (2)
H(5)–C(5)–N(1)	149 (2)	N(1)–H(1)···N(2′)	133 (1)

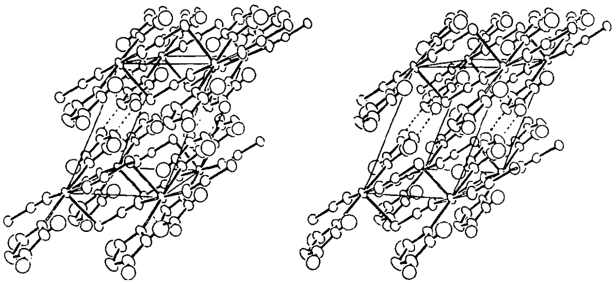

Fig. 2. Stereoscopic projection of the structure of $\mathrm{Cd(NCS)_2(trz)_2}$ showing the H-bridging system (dotted lines).

The bond distances and angles of the triazole ring (Table 2) are consistent with the values reported earlier for coordinating 1*H*-1,2,4-triazole. Compared to the only other known compound containing monodentate triazole, the ring distances are equal within standard deviations (Gorter & Engelfriet, 1981). Differences with free 1,2,4-triazole (Goldstein, Ladell & Abowitz, 1969; Deuschl, 1965) are also minor. Compared to 2,4-coordinating 1*H*-1,2,4-triazole (Engelfriet, den Brinker, Verschoor & Gorter, 1979; Engelfriet & Verschoor, 1981) small variations in the ring bond lengths are again observed, *i.e.* a slight shortening of the N(1)—C(5) and N(2)—C(3) bonds: 1·315 *vs* 1·325 Å for N(1)—C(5) and 1·304 *vs* 1·312 Å for N(2)—C(3). Moreover, the difference between the N(4)—C(3) and N(4)—C(5) bonds is reduced slightly. This may be an indication of a somewhat lower electron delocalization in the ring for the monodentate mode, as compared to the bidentate mode. The Cd—N distance is slightly shorter than the Cd—N(4) distance (2·317 *vs* 2·330 Å). In fact, the Cd—N distance falls in the higher part of the range for Cd—NCS distances, starting with 1·99 Å for Cd—NCS in the polymer of $\mathrm{Cd(NCS)_2(urea)_2}$, the structure of which can be compared with that described here (Tsintsadze, Tsivtsivadze & Orbeladze, 1975). This effect should be attributed to the coordination mode of the thiocyanate ion (bridging through N and S) and to the Cd—N—C angle (143°) which is just closer to an sp^2 configuration than the sp configuration angle. In fact, the present Cd—N distance is close to that in the N-bridging thiocyanate compound $\mathrm{Cd_2(NCS)_4}$(4-*tert*-butyltriazole)$_3$ (Groeneveld, Vos, Verschoor & Reedijk, 1982) in which the $\mathrm{SCN}{<}\begin{matrix}\mathrm{Cd}\\ \mathrm{Cd}\end{matrix}$ group has Cd—N distances of 2·352 and 2·437 Å. The origin of the present small Cd—N—C angle may be the packing of the Cd arrays and the formation of hydrogen bridges between them.

A value of 2·754 (1) Å was found for the Cd—S distance and 96·3 (1)° for the Cd—S—C angle. Most Cd—SCN distances reported in the literature lie between 2·60 and 2·85 Å, while most Cd—S—C angles are above 100° (Cavalca, Nardelli & Fava, 1960). The overall effect of short Cd—NCS distances and small Cd—N—C and Cd—S—C angles is closer packing of the Cd atoms in arrays (see Fig. 2).

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