bonds which links shikimate ions and water molecules. All O—H act as H-bond donors except for H(3O) and H(90A) to yield 12 interactions with O···O in the range 2·674 (6)–2·928 (6) Å (Table 2). The O—H···O angles range from 146 (3) to 174 (3)° with the exception of two angles of 133 (5) and 139 (5)° involving water O(93)—H donors. The water molecules play a key role in the network, being involved in nine of the interactions.

The Na^+ ions have different oxygen environments. Na(1) has seven Na···O contacts (two from each shikimate, three from waters) in the range 2·402 (4)–2·687 (4) Å, forming a distorted pentagonal bipyramid. Na(2) has six Na···O (three from shikimates, three from waters) in the range 2·332 (3)–2·669 (4) Å forming an approximate octahedron.

References

ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, A. G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.
BUCOURT, R. & HAINAUT, D. (1965). *Bull. Soc. Chim. Fr.* pp. 1366–1378.
CONN, E. E. (1986). *Recent Advances in Phytochemistry*, Vol. 20: *The Shikimic Acid Pathway*. New York: Plenum Press.
EIJCKMANN, F. (1885). *Recl Trav. Chim. Pays-Bas*, **4**, 32–54.
FISCHER, H. O. L. & DANGSCHAT, G. (1934). *Helv. Chim. Acta*, **17**, 1200–1207.
FISCHER, H. O. L. & DANGSCHAT, G. (1935). *Helv. Chim. Acta*, **18**, 1204–1206, 1206–1213.
FISCHER, H. O. L. & DANGSCHAT, G. (1937). *Helv. Chim. Acta*, **20**, 705–716.
HALL, L. D. (1964). *J. Org. Chem.* **29**, 297–299.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
IUPAC–IUB (1968). *Eur. J. Biochem.* **5**, 1–8.
ROGERS, D. (1981). *Acta Cryst.* A**37**, 734–741.
SHELDRICK, G. M. (1983). *SHELXTL Users Manual*, revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.
WEISS, U. & EDWARDS, J. M. (1980). In *The Biosynthesis of Aromatic Compounds*. New York: John Wiley.

catena-(*N,N,N',N'*-Tetramethylethylenediamine)-di-μ-thiocyanato-*N,S*-cadmium(II)

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Abstract. $[Cd(C_6H_{16}N_2)(NCS)_2]$, $M_r = 344·68$, monoclinic, $C2/c$, $a = 14·672$ (3), $b = 8·520$ (2), $c = 11·164$ (3) Å, $\beta = 100·69$ (2)°, $V = 1371·3$ (6) Å^3, $Z = 4$, $D_x = 1·67$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1·72$ mm^{-1}, $F(000) = 688$, $T = 296$ K, $R = 0·043$ for 722 observed reflections. The Cd^{II} ion, mounted on a twofold axis, is octahedrally coordinated by two S and two N atoms of four symmetry-related thiocyanate groups [Cd–N = 2·340 (8), Cd–S = 2·704 (3) Å] and two N atoms of the tetramethylethylenediamine ligand, which is also sited on the twofold axis [Cd–N = 2·415 (8) Å]. The thiocyanate ions constitute double bridges, thereby building infinite chains of thiocyanate-linked Cd^{II} ions along the c axis.

Introduction. The complexes formed by the II*b* metal salts and nitrogen-containing ligands are found in a variety of coordination numbers and geometries (Dean, 1978). In particular, the thiocyanate ion is known to form metal–nitrogen and metal–sulfur bonds and also bridges through atoms —N—, —S— or through —N,S (*e.g.* Cingi, Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1985). As part of a systematic investigation of a series of MX_2(tmen) complexes, $M = Zn^{II}$, Cd^{II}, Hg^{II}; X

= CN, SCN, NO$_3$; tmen = N,N,N',N'-tetramethyl-ethylenediamine, we report here the X-ray crystal structure determination of the title complex. This investigation was undertaken to study the effect of the methyl groups linked to the N atoms on the structure of the complex, because infrared and Raman spectra (Iwamoto & Schriver, 1971) showed that the corresponding complex with ethylenediamine has a polymeric chain structure with the amine N bridging the Cd atoms, and in bis(ethylenethiourea)cadmium thiocyanate the Cd atoms are linked by NCS groups (Cavalca, Nardelli & Fava, 1960).

Experimental. Crystals of the title compound were grown from a solution of stoichiometric amounts of cadmium thiocyanate and tmen in methanol by slow evaporation at room temperature. Prismatic colourless crystals 0·10 × 0·10 × 0·03 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$; cell parameters by least squares on setting angles for 24 reflections, $8 < \theta < 17°$; ω–2θ scans, scan width $(0·60 + 0·35\tan\theta)°$, max. scan speed 6·7° min^{-1}; max range of hkl: $-17 < h < 17$, $k < 10$, $l < 13$; $\theta_{max} = 25°$; standard $6\bar{2}\bar{1}$ varied $\pm3·1\%$ of mean intensities over data collection; 1267 reflections measured, 1198 unique, $R_{int} = 0·02$, 722 observed above $3\sigma(I)$; Lp and absorption corrections (transmission factors 0·88–0·95); structure solved by Patterson and difference Fourier techniques. In final cycles of full-matrix least-squares refinement all non-H atoms anisotropic. H atoms included at positions found in difference synthesis, all with common isotropic temperature factor that refined to $U = 0·11$ Å^2. Inspection of F_c and F_o values indicated a correction for secondary extinction required ($F_{corr} = F_c$ | $1·0 - \chi F_c^2/\sin\theta$ | where χ refined to 6×10^{-8} in the final run). Function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1/|\sigma^2(F) + 0·0007F^2|$, 71 parameters refined, excluding unobserved reflections; $R = 0·043$, $wR = 0·045$. Max. $(\Delta/\sigma) = 0·002$, $S = 1·06$; $\Delta\rho$ excursions within 0·53 and $-0·52$ e Å^{-3}; scattering factors for non-H atoms from Cromer & Mann (1968) with corrections for anomalous dispersion from Cromer & Liberman (1970), for H from Stewart, Davidson & Simpson (1965); programs used $SHELX76$ (Sheldrick, 1976), $ORTEP$ (Johnson, 1965). Most of the calculations were performed on a VAX 11/780 computer of the Instituto de Física e Química de São Carlos.

Discussion. Final atomic positions and equivalent isotropic temperature factors are given in Table 1.* Interatomic distances and angles are given in Table 2.

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* Lists of H-atom positions, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44865 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq}
Cd	0·5	0·6196 (1)	0·25	3·20 (3)
S	0·3703 (2)	0·4139 (3)	0·1411 (2)	4·7 (1)
N(1)	0·5903 (6)	0·842 (1)	0·3383 (8)	4·6 (3)
N(2)	0·4203 (6)	0·384 (1)	$-0·0869$ (7)	4·7 (3)
C(1)	0·6752 (8)	0·860 (2)	0·287 (1)	6·4 (5)
C(2)	0·6176 (9)	0·826 (2)	0·472 (1)	7·0 (5)
C(3)	0·4006 (6)	0·397 (1)	0·0071 (9)	3·9 (3)
C(4)	0·528 (1)	0·973 (1)	0·319 (1)	8·0 (6)

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

Cd–S	2·704 (3)	N(1)–C(2)	1·48 (1)
Cd–N(1)	2·415 (8)	N(1)–C(4)	1·43 (2)
Cd–N(2^i)	2·340 (8)	N(2)–C(3)	1·14 (1)
S–C(3)	1·64 (1)	C(4)–C(4^{ii})	1·61 (2)
N(1)–C(1)	1·47 (1)		
S–Cd–N(1)	168·2 (2)	N(1)–Cd–N(2^i)	90·7 (3)
S–Cd–N(2^i)	93·1 (2)	N(1)–Cd–N(1^{ii})	76·6 (3)
S–Cd–S^{ii}	99·20 (8)	N(1^{ii})–Cd–N(2^i)	90·5 (3)
S–Cd–N(1^{ii})	92·2 (2)	N(2^i)–Cd–N(2^{iii})	178·5 (3)
S^{ii}–Cd–N(2^i)	86·0 (2)	S–C(3)–N(2)	178·8 (9)

Symmetry codes: (i) $1-x$, $1-y$, $-z$; (ii) $1-x$, y, $\tfrac{1}{2}-z$; (iii) x, $1-y$, $\tfrac{1}{2}+z$.
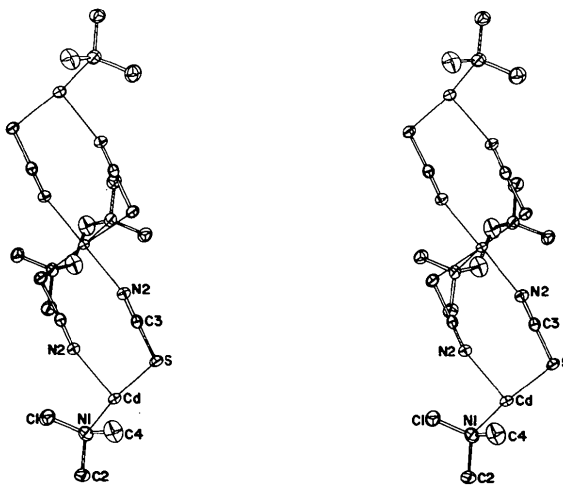

Fig. 1. Stereoscopic projection of the structure down the b axis.

The structure consists of a network of Cd^{II} chains bridged together by pairs of thiocyanate groups along the c axis. The Cd atom, placed on a twofold axis, is coordinated to two amine nitrogens of the tmen ligand (which is also sited on the twofold axis) and to two S and two N atoms of four NCS$^-$ groups (symmetry related by pairs), as shown in Fig. 1, which is a stereoscopic projection of the structure down the b axis.

The bonds between Cd and bridging thiocyanato are essentially identical, to within experimental accuracy, to those found in the literature (Cavalca, Nardelli & Fava, 1960; Bigoli, Braibanti, Pellinghelli & Tiripicchio, 1972; Haasnoot, de Keyzer & Verschoor, 1983). A significant difference is found in the Cd—N(2) bond which is much longer (2·53 Å) in the ethylenethiourea complex (Cavalca, Nardelli & Fava, 1960). The Cd—N(2) distance is shorter than the Cd—N(1) distance [2·340 (8) vs 2·415 (8) Å], as found in other polymeric Cd compounds (Haasnoot, de Keyzer & Verschoor, 1983). The Cd—N(2)—C(3) angle is 164·3 (8)°.

References

BIGOLI, F., BRAIBANTI, A., PELLINGHELLI, M. A. & TIRIPICCHIO, A. (1972). *Acta Cryst.* B28, 962–966.
CAVALCA, L., NARDELLI, M. & FAVA, G. (1960). *Acta Cryst.* 13, 125–130.
CINGI, M. B., LANFREDI, A. M. M., TIRIPICCHIO, A., HAASNOOT, J. G. & REEDIJK, J. (1985). *Inorg. Chim. Acta,* 101, 49–61.
CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891–1898.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
DEAN, P. A. W. (1978). *Prog. Inorg. Chem.* 24, 109.
HAASNOOT, J. G., DE KEYZER, G. C. M. & VERSCHOOR, G. C. (1983). *Acta Cryst.* C39, 1207–1209.
IWAMOTO, T. & SCHRIVER, D. F. (1971). *Inorg. Chem.* 10, 2428–2432.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
SHELDRICK, G. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

Structures of *catena*-Di-μ-chloro- and *catena*-Di-μ-bromo-(2,2-bipyridine)copper(II)

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Abstract. (I) $[CuCl_2(C_{10}H_8N_2)]_\infty$, $M_r = 290\cdot63$, triclinic, $P\bar{1}$, $a = 7\cdot288$ (2), $b = 9\cdot640$ (2), $c = 9\cdot771$ (2) Å, $\alpha = 55\cdot36$ (3), $\beta = 69\cdot29$ (2), $\gamma = 70\cdot48$ (3)°, $V = 520$ (1) Å^3, $Z = 2$, $D_x = 1\cdot855$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0\cdot71073$ Å, $\mu = 2\cdot585$ mm^{-1}, $F(000) = 290$, $T = 291$ K, $R = 0\cdot0425$ for 1450 unique observed reflections. The crystal consists of alternating spaced chains, oriented along the x axis. The coordination polyhedron around the Cu atom can be described as a distorted octahedron. The basal plane is formed by the two N atoms of the 2,2'-bipyridine ligand and two Cl atoms. The axial sites are occupied by Cl atoms from the other monomeric units. Cu—N(1) = 2·029 (3), Cu—N(2) = 2·027 (3), Cu—Cl(1) = 2·267 (1), Cu—Cl(2) = 2·267 (1), Cu—Cl(1^i) = 3·035 (1), Cu—Cl(2^{ii}) = 3·106 (1), Cu—Cu^i = 3·876 (1) and Cu—Cu^{ii} = 3·802 (1) Å. (II) [CuBr$_2$-(C$_{10}$H$_8$N$_2$)]$_\infty$, $M_r = 379\cdot55$, monoclinic, $C2/c$, $a = 16\cdot966$ (4), $b = 9\cdot287$ (2), $c = 7\cdot490$ (2) Å, $\beta = 111\cdot60$ (2)°, $V = 1097$ (2) Å^3, $Z = 4$, $D_x = 2\cdot297$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0\cdot71073$ Å, $\mu = 9\cdot117$ mm^{-1}, $F(000) = 724$, $T = 291$ K, $R = 0\cdot0716$ for 708 unique observed reflections. The crystal consists of alternating spaced chains along the z axis. The coordination polyhedron around the Cu atom can be described as a distorted octahedron. The basal plane is formed by the two N atoms of the 2,2'-bipyridine ligand and two Br atoms. The axial sites are occupied by Br atoms from the other monomeric units. Cu—N(1) = 2·030 (6), Cu—Br(1) = 2·410 (1), Cu—Br(1'') = 3·175 (1), Cu—Cu'' = 3·974 (1) Å.

Introduction. As far as their structure is concerned, copper(II) compounds display a rich variety of