

- JEFFREY, J., LAPPERT, M. F., LUONG-THI, N. T., WEBB, M., ATWOOD, J. L. & HUNTER, W. E. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1593–1605.
- JONES, S. B. & PETERSON, J. L. (1981). *Inorg. Chem.* **20**, 2889–2894.
- LAUHER, J. W. & HOFFMANN, R. (1976). *J. Am. Chem. Soc.* **98**, 1729–1742.
- MOORE, E. J., STRAUS, D. A., ARMANTROUT, J., SANTARSIERO, B. D., GRUBBS, R. H. & BERCAW, J. E. (1983). *J. Am. Chem. Soc.* **105**, 2068–2070.
- MUIR, K. M. (1971). *J. Chem. Soc. A*, pp. 2663–2666.
- PROUT, K., CAMERON, T. S., FORDER, R. A., CRITCHLEY, S. R., DENTON, B. & REES, G. V. (1974). *Acta Cryst.* **B30**, 2290–2304.
- RODDICK, D. M., SANTARSIERO, B. D. & BERCAW, J. E. (1982). Unpublished results.
- SANNER, R. D., MANRIQUEZ, J. M., MARSH, R. E. & BERCAW, J. E. (1976). *J. Am. Chem. Soc.* **98**, 8351–8357.
- SANTARSIERO, B. D., MOORE, E. J. & BERCAW, J. E. (1982). Unpublished results.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- TELLER, R. G. & BAU, R. (1981). *Struct. Bonding (Berlin)*, **44**, 1–82.
- TOOGOOD, G. E. & WALLBRIDGE, M. G. H. (1982). *Adv. Inorg. Chem. Radiochem.* **25**, 267–340.
- WILSON, A. J. C. (1942). *Nature (London)*, **150**, 151–152.
- WOLCZANSKI, P. T. (1981). PhD Thesis, California Institute of Technology.
- WOLCZANSKI, P. T., THRELKEL, R. S. & BERCAW, J. E. (1979). *J. Am. Chem. Soc.* **101**, 218–220.

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The Structure of *catena*-Di- μ -chloro-iodo($1H^+$ -*S*-methylisothiocarbonohydrazidium-*N*)cadmium(II), $C_2H_9CdCl_2IN_4S$

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Abstract. $M_r = 431.391$, orthorhombic, $Pnma$, $a = 17.702$ (3), $b = 7.462$ (2), $c = 8.060$ (2) Å, $V = 1064.7$ (4) Å³, $Z = 4$, $T = 295$ K, $D_m = 2.68$, $D_x = 2.69$ Mg m⁻³, $\lambda(\text{Mo } K\alpha_1) = 0.70926$ Å, $\mu(\text{Mo } K\alpha_1) = 55.652$ cm⁻¹, $F(000) = 800$, $R = 0.0496$ for 556 reflections. The structure consists of polymeric chains of edge-shared octahedra running parallel to **b** held together by weak N—H...Cl and N—H...I hydrogen bonds and van der Waals contacts.

Introduction. This study is part of a systematic investigation on the behaviour of a thiocarbonohydrazide derivative (*S*-methylisothiocarbonohydrazide, *S*-tcaz) as ligand in metal complexes. To the authors' knowledge this structure has turned out to be the only example of a six-coordinate polymeric mixed-halogen cadmium(II) complex with a protonated ligand so far studied by X-ray analysis. The known $CdCl_3^-$ complexes form polymeric chains of face-shared octahedra and the only studied complex of the $[CdCl_3LH]$ type is monomeric and tetrahedral.

Experimental. Colourless prismatic crystals grown by very slow evaporation from aqueous solution of cadmium dichloride and *S*-methylisothiocarbonohydrazide hydroiodide, D_m by flotation, crystal $0.30 \times 0.19 \times 0.13$ mm, Siemens AED diffractometer, Nb-

filtered $Mo K\alpha_1$, lattice parameters refined by least squares on 18 reflections ($8 < \theta < 15^\circ$), 1125 hkl (including 111 systematic absences), $0 \leq h \leq 21$, $0 \leq k \leq 8$, $0 \leq l \leq 9$, $3 < \theta < 25^\circ$ ($\theta/2\theta$ scan), 1014 independent, 556 observed with $I \geq 2\sigma(I)$ (1 standard reflection, checked after every 50, no decomposition of specimen), Lp correction, absorption ignored, atomic scattering factors and anomalous-scattering corrections from *International Tables for X-ray Crystallography* (1974), heavy-atom technique, anisotropic full-matrix least squares (*SHELX76*, Sheldrick, 1976), ΔF synthesis not valuable in locating all H atoms, $\sum w| \Delta F |^2$ minimized, unit weights in the first cycles of refinement then $w = k[\sigma^2(F_o) + g F_o^2]^{-1}$ ($k = 0.0421$, $g = 0.119638$) in the last cycles, final $R = 0.0496$, $R_w = 0.056$,* $(\Delta/\sigma)_{\max} = 0.48$, max. height in final difference Fourier = $1.3 e \text{ \AA}^{-3}$, Cyber 76 computer of the Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna, with the financial support of the University of Parma.

* Lists of calculated and observed structure factors and of anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38596 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Table 1 gives coordinates for non-hydrogen atoms. Bond lengths and angles are given in Table 2.

Fig. 1 shows the molecular structure of (CdCl₂LH)_n (where LH = S-tcazH⁺) and the slightly distorted octahedral coordination of the cadmium atom. The metal atoms, correlated by a centre of symmetry, are linked to their neighbours in the *y* direction by double chloride

Table 1. Final atomic coordinates ($\times 10^4$) and B_{eq} (\AA^2) values with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}^*
Cd	5080 (1)	2500	5362 (2)	2.17 (5)
I	5670 (1)	2500	8608 (2)	3.22 (5)
Cl	5947 (3)	4985 (6)	4054 (5)	2.47 (10)
S	3463 (4)	2500	-455 (9)	4.07 (22)
N(1)	3639 (10)	2500	2810 (30)	2.37 (54)
N(2)	4444 (9)	2500	2535 (25)	2.26 (52)
N(3)	2415 (10)	2500	1889 (29)	3.29 (63)
N(4)	2201 (13)	2500	3570 (30)	4.97 (84)
C(1)	3144 (14)	2500	1532 (32)	3.42 (82)
C(2)	2563 (15)	2500	-1637 (34)	3.88 (93)

$$* B_{eq} = \frac{2}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Table 2. Bond distances (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

Cd-Cl ⁱ	2.628 (5)	S-C(1)	1.70 (3)
Cd-Cl ⁱⁱⁱ		S-C(2)	1.86 (3)
Cd-Cl ⁱ	2.655 (5)	N(1)-N(2)	1.44 (2)
Cd-Cl ⁱⁱ		N(1)-C(1)	1.35 (3)
Cd-I	2.817 (2)	N(3)-N(4)	1.41 (3)
Cd-N(2)	2.54 (2)	N(3)-C(1)	1.32 (3)
I-Cd-N(2)	175.5 (4)	Cd-Cl-Cd ⁱ	91.6 (2)
Cl-Cd-Cl ⁱⁱ	165.9 (1)	C(1)-S-C(2)	101.5 (1.2)
Cl-Cd-Cl ⁱ	88.4 (1)	N(2)-N(1)-C(1)	121.6 (2.0)
Cl-Cd-Cl ⁱⁱⁱ	89.8 (2)	Cd-N(2)-N(1)	107.5 (1.4)
Cl ⁱ -Cd-Cl ⁱⁱ	90.0 (2)	N(4)-N(3)-C(1)	118.2 (2.2)
Cl-Cd-N(2)	84.2 (1)	N(1)-C(1)-N(3)	117.8 (2.3)
Cl ⁱ -Cd-N(2)	81.7 (1)	S-C(1)-N(3)	122.0 (2.0)
I-Cd-Cl	99.0 (1)	S-C(1)-N(1)	120.2 (1.9)
I-Cd-Cl ⁱ	95.1 (1)		

Symmetry code

(i) $1-x, 1-y, 1-z$; (ii) $1-x, -\frac{1}{2}+y, 1-z$; (iii) $x, \frac{1}{2}-y, z$.

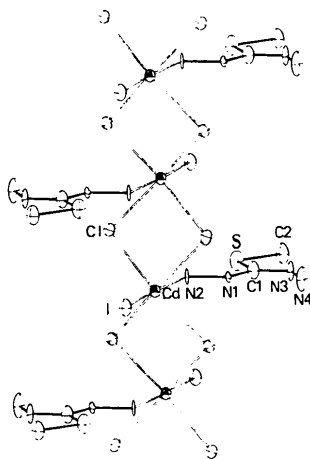


Fig. 1. Perspective view of the polymeric chain. Thermal ellipsoids are drawn at the 30% probability level (Johnson, 1965).

bridges forming polymeric chains of edge-shared octahedra. The coordination is completed by the Cd-I and Cd-N bonds which are almost perpendicular [$87.3(1)$ and $88.2(3)^\circ$, respectively] to the plane of the coordinated Cl atoms. The Cd and I atoms and the organic ligand molecule lie on a crystallographic mirror. The displacement of the metal atom from the equatorial plane, formed by the Cl atoms which are coplanar by symmetry, is $0.324(2) \text{\AA}$ towards the iodine atom. The Cd-Cl distances agree with those found in other octahedral chloride-cadmium complexes (Cannas, Marongiu & Saba, 1980) while a similar comparison is not possible for the Cd-I distance. In fact, this kind of cadmium complex is the first to be reported. The Cd-N distance [$2.54(2) \text{\AA}$] is one of the longest found in octahedral Cd complexes, probably because of the protonation of the coordinated molecule. In Cd(thiamine)Cl₃·0.6H₂O (Cramer, Maynard & Ibers, 1981) the complex is tetrahedral and monomeric with Cd-N = $2.239(2) \text{\AA}$, but in this case the coordinated N is far from the protonated fragment *i.e.* the thiazolium ring. If the protonated N(4) is a hydrazinic nitrogen, as one would expect, then the N(2) coordinated hydrazonic nitrogen must be *cis* with respect to the sulphur atom. Nevertheless, because of the large delocalization around C(1) and the impossibility of identifying unambiguously the H atoms on the difference electron-density map, it was not possible to assign the formal double bond to C(1)-N(1) or C(1)-N(3). Further, the possible hydrogen bonds involving N(1) and N(3) are practically equivalent and bifurcated [$N(1)\cdots Cl^i$, $N(1)\cdots Cl^{iii} = 3.23(2)$, $N(3)\cdots Cl^{iv}$, $N(3)\cdots Cl^v = 3.28(2) \text{\AA}$; symmetry codes not given in Table 2: (iv) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; (v) $-\frac{1}{2}+x, y, \frac{1}{2}-z$]. The conformation of the S-tcazH⁺ is also related to the presence of the methyl group and therefore is similar to that found in *S*-methylisothiocarbonohydrazide hydroiodide (Bigoli, Leporati & Pellinghelli, 1978). The bond distances and angles in the organic molecule are not significantly different from those observed in the above mentioned work.

Packing (Fig. 2) is determined by van der Waals contacts or possible hydrogen bonds involving the N

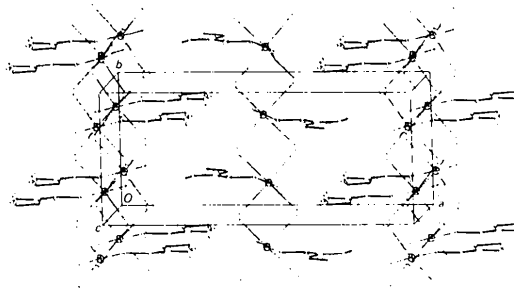


Fig. 2. Perspective view along *c* of the packing. The thermal ellipsoids enclose 30% probability (Johnson, 1965).

atoms of the organic molecule and iodine or chlorine atoms of the same or adjacent chains.

Extensive use of the Cambridge Crystallographic Data Files has been made for the bibliographic search.

References

BIGOLI, F., LEPORATI, E. & PELLINGHELLI, M. A. (1978). *Cryst. Struct. Commun.* **7**, 527–530.

CANNAS, M., MARONGIU, G. & SABA, G. (1980). *J. Chem. Soc. Dalton Trans.* pp. 2090–2094.

CRAMER, R. E., MAYNARD, R. B. & IBERS, J. A. (1981). *J. Am. Chem. Soc.* **103**, 76–81.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99–100, 149–150. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

SHELDRIK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.

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Structure of Trimethyl(phenyl)ammonium Bis[dimercaptomaleodinitrilato(2-)-*S,S'*]nickelate(III), [N(CH₃)₃(C₆H₅)]Ni(C₄N₂S₂)₂

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Abstract. $M_r = 475.28$, monoclinic, $P2_1/n$, $a = 14.737$ (1), $b = 7.296$ (9), $c = 20.970$ (3) Å, $\beta = 108.931$ (8)°, $V = 2133$ Å³, $Z = 4$, $D_x = 1.48$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.237$ mm⁻¹, $F(000) = 960$, room temperature, final $R = 0.056$ for 1860 unique reflections. The stacking of the anion is diadic and one-dimensional along the b axis.

Introduction. The 1,2-dithiolato ligands $R_2C_2S_2^{2-}$ are known to form transition-metal complexes having remarkable oxidation–reduction behaviour, including the formation of abnormal valence states of the metal (McCleverty, 1968; Wing & Schlupp, 1970). These metal chelates often crystallize with columnar ionic packing arrangements in the solid state, which produces interesting magnetic, electrical and optical properties. Some of the d^7 chelates with Ni, Pd and Pt have been found to exhibit an antiferromagnetic exchange along the chain (Maki, Edelstein, Davison & Holm, 1964). Magnetic studies together with X-ray data suggest that the spin correlation occurs through S-atom d -orbital interaction with the metal ion of an adjacent chelate molecule (Weiher, Melby & Benson, 1964). Such pairwise spin correlation is very sensitive to the intrastack separation, which in turn depends on the nature and bulkiness of the cation used. For example, in the case of $R^+Ni(mnt)_2$ [mnt : dimercaptomaleodinitrilato(2-)] where R^+ is spherical quaternary ammonium (Kobayashi & Sasaki, 1977) or phosphonium

(Fritchie, 1966), or a planar cation like tropylium (Manoharan, Noordik, de Boer & Keijzers, 1981), N -methylphenazinium (Kuppusamy, Mahadevan, Seshasayee & Manoharan, 1983), or N,N,N',N' -tetramethyl- p -phenylenediamine (Ramakrishna & Manoharan, 1983 *a*) segregated stacking of cations and chelate anions has been observed. Of these, systems with an alternating chelate stack (dimeric) are found to have strong exchange demagnetization ($J \sim 400$ – 600 cm⁻¹) (Weiher, Melby & Benson, 1964). Recent EPR work on $[NEt_4][Ni(mnt)_2]$ showed the system to be distinctive in being by far the best example of a one-dimensional (1D) system (Ramakrishna & Manoharan, 1983 *b*).

We are studying the magnetic behaviour (by EPR and susceptibility measurements) to obtain a clear understanding of the cooperative phenomenon existing in such low-dimensional systems. In this paper we report the crystal and molecular structure of the title compound $\{[NMe_3Ph][Ni(mnt)_2]$ hereafter $\}$.

Experimental. Black, shiny needles of $[NMe_3Ph][Ni(mnt)_2]$ obtained by the procedure of Davison & Holm (1967) using trimethyl(phenyl)ammonium iodide as the quaternary ammonium salt.

Unit-cell parameters obtained by least-squares refinement of the θ values of 25 high-angle reflections. Crystal $0.35 \times 0.13 \times 0.65$ mm, three-dimensional intensity data collected on an Enraf–Nonius CAD-4