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Structure of *catena*-Poly[(1,3-thiazolidine-2-thionecadmium)-μ-chloro-μ_3-chloro]

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(*Received* 11 *February* 1985; *accepted* 4 *July* 1985)

Abstract. [CdCl$_2$(C$_3$H$_5$NS$_2$)]$_n$, M_r = 302·5, monoclinic, $P2_1/c$, a = 3·933 (1), b = 22·418 (5), c = 9·934 (2) Å, β = 112·81 (4)°, V = 807·4 Å^3, Z = 4, D_m = 2·47 (2), D_x = 2·49 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 3·74 mm^{-1}, F(000) = 576, room temperature, final R = 0·049 for 1214 observed reflections. The structure is polymeric, with octahedrally coordinated Cd linked into infinite chains by double Cl bridges, which are further condensed in pairs by Cl bridges. The S-bonded 1,3-thiazolidine-2-thione ligand completes the coordination sphere about Cd with a Cd–S distance of 2·605 (2) Å. There is an intramolecular hydrogen bond between the N atom and equatorial Cl [N···Cl 3·343 (8) Å and N–H···Cl 158°].

Introduction. The thiazolidine-2-thione (ttz) ligand is a potentially ambidentate ligand with either the exocyclic S or heterocyclic N atom available for coordination (Raper, Oughtred & Nowell, 1983). As part of our programme of structure determinations of metal complexes of ttz, the results for tetrakis(1,3-thiazolidine-2-thione)palladium(II) dichloride–1,3-thiazolidine-2-thione (1:2) have been published (Kubiak & Głowiak, 1982).

Spectroscopic and magnetic-susceptibility studies of the interaction of Cd^{II} with ttz (Preti & Tosi, 1976) have suggested that the Cd(ttz)$_2$ complex is tetrahedral and has a polymeric structure with the ligands linked to the metal ion through the S and N atoms.

In an attempt to obtain crystallographic evidence of the coordination sites, we have prepared the CdCl$_2$(ttz) complex in the low pH region and undertaken its X-ray analysis.

Experimental. Clear, colourless crystals from cadmium(II) chloride and ttz at room temperature (293 K), dimensions 0·15 × 0·09 × 0·10 mm; D_m by flotation in bromoform–benzene; monoclinic from Weissenberg photographs, $P2_1/c$; Syntex $P2_1$ computer-controlled four-circle diffractometer, scintillation counter, Mo $K\alpha$ radiation, graphite monochromator; cell parameters by least squares from setting angles of 15 reflections; 1432 independent reflections; variable $\theta/2\theta$ scan, scan rate 2·0–29·3° min^{-1} (depending on intensity), $2\theta_{\max}$ = 60°; two standards measured every 30 reflections, no significant change; corrections for Lorentz and polarization, not for absorption; 1214 with $F > 8\sigma(F)$ used for structure determination, index range h 0→4, k 0→26, l −11→10; calculations performed on a Nova 1200 computer with programs supplied by Syntex (1976); neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); heavy-atom method, full-matrix least squares (on F); non-H atoms refined with anisotropic and H atoms with fixed positional and isotropic thermal parameters, 82 variables; $(\Delta/\sigma)_{\max}$ = 0·10; $\Delta\rho_{\max}$ = ±0·40 e Å^{-3}; R = 0·049, wR = 0·051, S = 5·72, $w = 1/\sigma^2(F)$.

Discussion. Final atomic parameters are given in Table 1* and interatomic distances and angles in Table 2. A view of the coordination polyhedron about the Cd^{II} ion, ligand stereochemistry and the atom-numbering scheme are presented in Fig. 1. Fig. 2 shows the polymeric structure viewed along **b**.

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* Lists of structure amplitudes, anisotropic thermal parameters, calculated H-atom parameters, torsion angles and least-squares-planes' calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42325 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The asymmetric unit consists of $CdCl_2(C_3H_5NS_2)$. The 1,3-thiazolidine-2-thione ligand is monodentate and S-bonded to the metal. The crystal structure may be described as a polymer made up of octahedrally coordinated Cd^{II}. These are separated by one unit-cell translation along **a** [3·933 (1) Å] and are linked to their neighbours by double Cl bridges, forming infinite $-Cd-Cl_2-Cd-$ ribbons. A second such chain, running parallel to the first, is linked to it by Cd–Cl bonds similar to those in polymeric di-μ-chloro-imidazole-cadmium(II) (Nassimbeni & Rodgers, 1976) and 2-amino-4,5-dihydro-3H^+-1,3-thiazolium trichloro-cadmate(II) (Kubiak, Głowiak & Kozłowski, 1983). The octahedral coordination sphere of Cd^{II} is completed by the exocyclic S atom from the 1,3-thiazolidine-2-thione ligand.

Table 1. *Positional parameters and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i B_{ii}.$$

	x	y	z	B_{eq}(Å^2)
Cd	−0·09703 (18)	0·04432 (3)	0·15706 (6)	1·72 (4)
Cl(1)	−0·2063 (6)	−0·0648 (1)	0·0433 (2)	1·4 (1)
Cl(2)	−0·4290 (6)	0·0160 (1)	0·3323 (2)	1·6 (1)
S(1)	−0·0520 (8)	0·1574 (1)	0·2217 (2)	2·0 (2)
S(2)	0·0482 (9)	0·2279 (1)	0·4876 (3)	2·9 (2)
N	0·2824 (25)	0·1213 (3)	0·5018 (8)	2·3 (6)
C(1)	0·1081 (27)	0·1625 (4)	0·4043 (9)	1·8 (6)
C(2)	0·3606 (30)	0·2017 (4)	0·6664 (9)	2·4 (7)
C(3)	0·3460 (30)	0·1345 (4)	0·6528 (10)	2·4 (7)

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

Cd–Cl(1)	2·659 (2)	Cd···Cd^{i}	4·014 (1)
Cd–Cl(2)	2·627 (2)	Cd···Cd^{ii}	4·008 (1)
Cd–S(1)	2·605 (2)	Cd^{i}–Cd–Cd^{ii}	58·72 (2)
Cd–Cl(1^{i})	2·728 (2)		
Cd–Cl(1^{ii})	2·730 (2)		
Cd–Cl(2^{iii})	2·606 (2)		
Cl(1)–Cd–Cl(1^{i})	83·64 (7)	S(1)–Cd–Cl(1^{i})	90·51 (7)
Cl(1)–Cd–Cl(1^{ii})	83·89 (7)	S(1)–Cd–Cl(1^{ii})	88·24 (7)
Cl(1)–Cd–Cl(2)	91·10 (7)	S(1)–Cd–Cl(2^{iii})	96·76 (8)
Cl(1)–Cd–Cl(2^{iii})	90·85 (7)	Cl(1^{i})–Cd–Cl(1^{ii})	92·22 (7)
C(1)–Cd–S(1)	169·99 (8)	Cl(1^{i})–Cd–Cl(2^{iii})	85·16 (7)
Cl(2)–Cd–Cl(2^{iii})	97·45 (7)	Cl(1^{ii})–Cd–Cl(2^{iii})	174·37 (7)
Cl(2)–Cd–S(1)	94·33 (8)	Cd–Cl(1)–Cd^{i}	96·36 (7)
Cl(2)–Cd–Cl(1^{i})	174·17 (7)	Cd–Cl(1)–Cd^{ii}	96·11 (7)
Cl(2)–Cd–Cl(1^{ii})	84·71 (7)	Cd^{i}–Cl(1)–Cd^{ii}	92·22 (7)
		Cd–Cl(2)–Cd^{iv}	97·45 (8)
S(1)–C(1)	1·677 (9)	Cd–S(1)–C(1)	107·1 (3)
S(2)–C(1)	1·744 (9)	S(1)–C(1)–S(2)	120·5 (6)
S(2)–C(2)	1·822 (10)	S(1)–C(1)–N	128·0 (8)
N–C(1)	1·322 (11)	N–C(1)–S(2)	111·5 (7)
N–C(3)	1·452 (12)	C(1)–S(2)–C(2)	91·5 (5)
C(2)–C(3)	1·511 (14)	C(1)–N–C(3)	116·5 (8)
		S(2)–C(2)–C(3)	104·3 (7)
		N–C(3)–C(2)	106·3 (8)

Symmetry code: (i) $-x, -y, -z$; (ii) $-1-x, -y, -z$; (iii) $1+x, y, z$; (iv) $-1+x, y, z$.

The Cd···Cd separations 4·014 (1) Å $(-x,-y,-z)$ and 4·008 (1) Å $(-1-x,-y,-z)$ are in good agreement with values obtained in ammonium cadmium chloride (Rolies & De Ranter, 1978*a*) and related complexes.

Bonding differences between the triply bridging Cl(1) and doubly bridging Cl(2) atoms are reflected in the observed Cd–Cl lengths. The distance between Cd and Cl(1) of the same asymmetric unit is 2·659 (2) Å, but linkage between adjacent chains occurs by the bonds Cl(1)–Cd$(-x,-y,-z)$ and Cl(1)–Cd$(-1-x,-y,-z)$ with distances 2·728 (2) and 2·730 (2) Å respectively. Cl(2) lies at 2·627 (2) and 2·606 (2) Å from Cd and Cd$(x-1,y,z)$ respectively.

The Cd–S distance, 2·605 (2) Å, is normal and in agreement with the value in the related di-μ-chloro-bis[thioacetamide(chloro)cadmium(II)] (Rolies & De Ranter, 1978*b*).

The octahedron about Cd is somewhat distorted as the relevant angles indicate (Table 2). Cd is located 0·118 (1) Å out of the equatorial Cl(1^{i}),Cl(1^{ii}),Cl(2),-Cl(2^{iii}) plane in the direction of the S atom.

The thiazolidine-2-thione ligand, which is described as N,S-bonded in $Cd(ttz)_2$ (Preti & Tosi, 1976), does not, however, act as a chelating agent in the present complex, but coordination takes place only through the

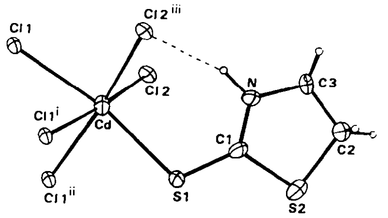

Fig. 1. View of the coordination polyhedron about the Cd^{II} ion, ligand stereochemistry and the atom-numbering scheme.

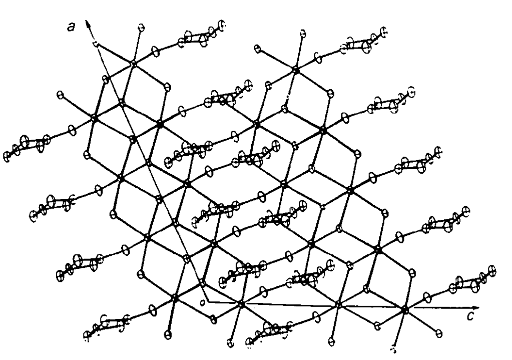

Fig. 2. Polymeric structure viewed along **b**.

thione S atom. The same behaviour is found in the Pd^{II} complex (Kubiak & Głowiak, 1982).

The geometry of ttz appears to be essentially unchanged on coordination. The bond lengths and angles do not differ significantly from those of uncoordinated 1,3-thiazolidine-2-thione (Raper *et al.*, 1983), but the 4,5-dihydrothiazole ring is less planar with deviations from the least-squares plane through S(1)S(2)C(1)N being −0·340 (12) and 0·182 (12) Å for C(2) and C(3) respectively $\{\Delta C_2^{[C(2),C(3)]} = 3{\cdot}2^\circ$ (Duax, Weeks & Rohrer, 1976)}.

One of the interesting features of this crystal structure is the intramolecular hydrogen bond between the heterocyclic N atom and equatorial $Cl(2^{iii})$ $[N\cdots Cl(2^{iii})$ 3·343 (8) Å and $N{-}H(1)\cdots Cl(2^{iii})$ 158°].

This work was supported by the Polish Academy of Sciences.

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Acta Cryst. (1985). C**41**, 1582–1585

Structure of *mer*-Dicarbonyl(selenocarbonyl)tris(trimethyl phosphite)chromium(0)

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(*Received* 3 *September* 1984; *accepted* 9 *July* 1985)

Abstract. $[Cr(CO)_2(CSe)\{P(CH_3O)_3\}_3]$, $M_r = 403{\cdot}157$, orthorhombic, $Pbca$, $a = 15{\cdot}483$ (3), $b = 15{\cdot}213$ (5), $c = 18{\cdot}997$ (3) Å, $V = 4474{\cdot}6$ Å^3, $Z = 8$, $D_x = 2{\cdot}396$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 46{\cdot}515$ cm^{-1}, $F(000) = 272$, $T = 118$ K, $R = 0{\cdot}042$ for 3091 observed reflections. The complex has meridional octahedral stereochemistry with the two CO groups *trans* to each other. Important structural features are Cr—C—Se = 176·9 (2)°, Cr—C(Se) = 1·785 (3), C—Se = 1·750 (3), mean Cr—C(O) = 1·893 (3), Cr—P (*trans* to CSe) = 2·373 (1), mean Cr—P = 2·282 (1) Å. The variations in bond lengths observed compared with those found in similar carbonyl and/or thiocarbonyl complexes illustrate the much better electron-withdrawing capacity of CSe compared to CO and CS.

Introduction. Transition-metal carbonyls have been known since the late 19th century (Mond, Langer & Quinke, 1890), but the first examples of analogous metal thio- and selenocarbonyls were only reported quite recently (Butler, 1977). While the structural behaviour of the CS ligand is quite well understood, there have been only two X-ray studies reported for selenocarbonyls: $(\eta\text{-}C_6H_5CO_2CH_3)Cr(CO)_2(CSe)$ (Saillard & Grandjean, 1978) and $RuCl_2(CO)(CSe)[(C_6H_5)_3P]_2$ (Clark, Grundy, Harris, James & Roper, 1975). Structural information, particularly from X-ray data, is important for the CSe ligand because, unlike CO and CS, the diatomic CSe molecule has eluded isolation even at very low temperatures (Steudel, 1967).

During the course of a kinetic investigation of arene substitution by tertiary phosphines and phosphites in arene chromium chalcocarbonyl complexes (equation 1), it became important for us to know the stereochemistry (*fac* or *mer*) of the final products in these reactions in order to rationalize the mechanism.

$$(\eta\text{-Arene})Cr(CO)_2(CX) + 3L \rightarrow L_3Cr(CO)_2(CX) + \text{arene} \quad (1)$$

[arene = C_6H_6, $C_6H_5CO_2CH_3$, *etc.*; X = S, Se; L = $(C_6H_5)_3P$, $(CH_3O)_3P$, *etc.*].

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