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LETTER

Formation and properties of $[Cd(S_2CNEt_2)I]_\infty$, an alternating copolymer of cadmium *N,N*-diethyldithiocarbamate and cadmium iodide

Anne-Kathrin Duhme, Siegfried Pohl and Henry Strasdeit*
Fachbereich Chemie der Universität Oldenburg,
Carl-von-Ossietzky-Strasse 9–11, D-2900 Oldenburg
(F.R.G.)

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Cadmium(II) and *N,N*-diethyldithiocarbamate, $Et_2NCS_2^-$, form two types of homoleptic complexes, namely $[Cd(S_2CNEt_2)_2]_2$ and $[Cd(S_2CNEt_2)_3]^-$ [1–3]. The dimeric nature of the former complex has been confirmed by X-ray structure determination [4]. The reaction of $[Cd(S_2CNR_2)_2]_2$ complexes with two equivalents of I_2 results in the oxidation of the dithiocarbamato ligands to the corresponding thiuram disulfides R_4tds (= $(R_2NCS_2)_2$) [5–7]. The compounds $[Cd(R_4tds)I_2]$ have been isolated as reaction products.

From a preparative point of view, $[Cd(S_2CNEt_2)_2]_2$ has the advantage of being soluble in some 'non-coordinating' solvents like chloroform and dichloromethane. Its dissociation product $[Cd(S_2CNEt_2)_2]$ detectable in chloroform solutions [4] is coordinatively unsaturated. Thus the ligand supply can easily be controlled, and the Lewis acidity is relatively high – a situation rather uncommon in cadmium coordination chemistry. We have tried to enhance the Lewis acidity by reacting $[Cd(S_2CNEt_2)_2]_2$ with *one* equivalent of I_2, i.e. by substituting two monodentate I^- for two bidentate $Et_2NCS_2^-$ ligands. In these experiments, the formation of the novel compound $[Cd(S_2CNEt_2)I]_\infty$ was observed.

Experimental

Synthesis of $[Cd(S_2CNEt_2)_2]_2$

A solution of 3.08 g (10.0 mmol) of $Cd(NO_3)_2 \cdot 4H_2O$ in 50 ml of methanol was added dropwise to a stirred solution of 4.51 g (20.0 mmol) of $NaS_2CNEt_2 \cdot 3H_2O$ in 50 ml of methanol. The precipitate was isolated, washed with methanol and dried *in vacuo*. For recrystallization, the product was dissolved in 125 ml of chloroform at *c*. 40 °C. The clear solution was allowed to cool down to room temperature. Subsequently, it was stored at 0 °C for 24 h. The crystals which had formed were isolated and dried *in vacuo*. Further crops were obtained by stepwise evaporation of the mother liquor. Yield 3.4 g (83%). *Anal.* Calc. for $C_{20}H_{40}Cd_2N_4S_8$: C, 29.37; H, 4.93; Cd, 27.49; N, 6.85; S, 31.36. Found: C, 29.45; H, 4.98; Cd, 27.54; N, 6.80; S, 31.47%. Infrared band positions and crystallographic unit-cell dimensions were identical to literature data [1, 4].

Synthesis of $[Cd(S_2CNEt_2)I]_\infty$

A solution of 254 mg (1.00 mmol) of I_2 in 50 ml of chloroform was added to a stirred solution of 818 mg (1.00 mmol) of $[Cd(S_2CNEt_2)_2]_2$ in 50 ml of chloroform. The resulting clear and faintly yellow solution was allowed to stand undisturbed at room temperature. After a few hours, the first small needle-shaped crystals appeared. After 3 days, the product was isolated, washed with chloroform and dried *in vacuo*. Yield 0.53 g (68%). *Anal.* Calc. for $C_5H_{10}CdINS_2$: C, 15.49; H, 2.60; Cd, 29.00; I, 32.74; N, 3.61; S, 16.55. Found: C, 15.58; H, 2.68; Cd, 29.06; I, 32.88; N, 3.62; S, 16.51%.

X-ray structure determination of $[Cd(S_2CNEt_2)I]_\infty$

Suitable single crystals of $[Cd(S_2CNEt_2)I]_\infty$ were obtained according to the procedure described above, but with use of a six times higher dilution of the reactants. A crystal of dimensions 0.78×0.08×0.06 mm was fixed to the top of a glass capillary by a drop of cyanacrylate adhesive. Intensity data were collected on a Siemens/STOE AED2 automated four-circle diffractometer at 24±1 °C (ω–2θ scan, $3° \leq 2\theta \leq 52°$, 2482 measured reflections, 2072 unique reflections, 1825 'observed' reflections with $I > 2\sigma(I)$, empirical absorption correction (ψ scan)). Details of the routine procedures of data collection and reduction used in our laboratory are given elsewhere [8].

Crystal data for $C_5H_{10}CdINS_2$ are: $M = 387.59$, monoclinic, space group $P2_1/c$; $a = 7.466(1)$, $b = 9.433(1)$, $c = 15.659(1)$ Å; $\beta = 94.69(1)°$, $V = 1099.1$ Å^3, $Z = 4$, $D_{calc} = 2.342$ g cm^{-3}, μ(Mo Kα) = 50.5 cm^{-1}. The structure was solved by direct methods. In the final structural model, the positions of all non-hydrogen atoms were refined. Hydrogen atoms were included on idealized positions and were given fixed U values of 0.08 (CH_2) and 0.10 (CH_3) Å^2, respectively. All non-hydrogen atoms were refined anisotropically. At convergence, $R = 0.023$ was obtained

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*Author to whom correspondence should be addressed.

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TABLE 1. Atomic coordinates and equivalent isotropic displacement factors (×100)[a]

Atom	x	y	z	U_{eq} (Å^2)
Cd	0.24872(4)	0.96789(4)	0.02269(2)	4.51(1)
I	0.42826(3)	0.86653(3)	−0.11042(2)	4.61(1)
S(1)	−0.06868(13)	0.80287(12)	0.00915(6)	4.15(2)
S(2)	0.17960(15)	0.86271(13)	0.16357(7)	5.01(2)
N	−0.1498(4)	0.7607(4)	0.1706(2)	4.4(1)
C(1)	−0.0289(5)	0.8051(4)	0.1206(2)	3.7(1)
C(2)	−0.1181(7)	0.7626(5)	0.2652(3)	5.6(1)
C(3)	−0.1781(8)	0.9001(6)	0.3024(3)	7.1(1)
C(4)	−0.3295(6)	0.7103(6)	0.1366(3)	6.2(1)
C(5)	−0.3312(9)	0.5536(6)	0.1178(4)	8.5(2)

[a] For the definition of U_{eq} see ref. 12. The standard deviation of U_{eq} was estimated by the method given in ref. 13 (eqn. (2) therein).

TABLE 2. Distances (Å) and bond angles (°)

Cd–I	2.741(1)	S(1)–C(1)	1.746(4)
Cd–I′[a]	3.099(1)	S(2)–C(1)	1.732(4)
Cd–S(1)	2.829(1)	N–C(1)	1.311(5)
Cd–S(1″)[b]	2.573(1)	N–C(2)	1.481(5)
Cd–S(2)	2.511(1)	N–C(4)	1.481(5)
Cd···Cd′[a]	3.923(1)	C(2)–C(3)	1.506(7)
Cd···Cd″[b]	3.773(1)	C(4)–C(5)	1.507(8)
I–Cd–I′	95.8(1)	Cd–I–Cd′	84.2(1)
I–Cd–S(1)	102.1(1)	Cd–S(1)–Cd″	88.5(1)
I–Cd–S(1″)	115.2(1)	Cd–S(1)–C(1)	81.1(1)
I–Cd–S(2)	132.7(1)	Cd″–S(1)–C(1)	103.1(1)
I′–Cd–S(1)	158.1(1)	Cd–S(2)–C(1)	91.5(1)
I′–Cd–S(1″)	92.2(1)	C(1)–N–C(2)	122.1(3)
I′–Cd–S(2)	91.0(1)	C(1)–N–C(4)	122.4(4)
S(1)–Cd–S(1″)	91.5(1)	C(2)–N–C(4)	115.4(4)
S(1)–Cd–S(2)	67.5(1)	S(1)–C(1)–S(2)	117.8(2)
S(1″)–Cd–S(2)	111.1(1)	S(1)–C(1)–N	121.6(3)
		S(2)–C(1)–N	120.6(3)
		N–C(2)–C(3)	111.7(4)
		N–C(4)–C(5)	112.2(4)

[a] Symmetry transformation 1−x, 2−y, $\bar{z}$. [b] Symmetry transformation $\bar{x}$, 2−y, $\bar{z}$.

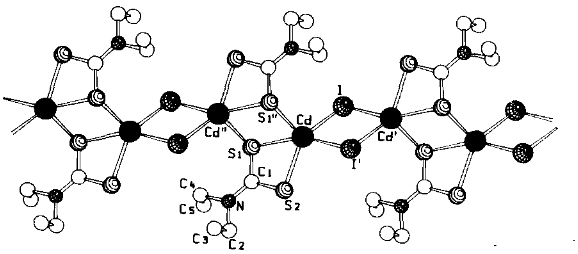

Fig. 1. Structure and atomic labelling scheme of $[Cd(S_2CNEt_2)I]_\infty$. Three repetitive units of the type $\{Cd(\mu\text{-}S_2CNEt_2)_2Cd(\mu\text{-}I)_2\}$ are shown. Hydrogen atoms are omitted for clarity.

($R_w = 0.024$, $g = 0.0002$ (see ref. 8 for definitions); 91 parameters, largest shift/e.s.d. for final cycle: 0.001, largest peak in final difference map: 0.56 e Å^{-3}).

Final atomic coordinates are listed in Table 1. Distances and bond angles are given in Table 2. Computer programs used were SHELXS-86 [9], SHELX [10] and SCHAKAL [11]. The structure and atomic labelling scheme are given in Fig. 1.

Results and discussion

Chloroform solutions of iodine are immediately decoloured by $[Cd(S_2CNEt_2)_2]_2$. Depending on the molar ratio, two different redox reactions proceed

$$[Cd(S_2CNEt_2)_2]_2 + I_2 \longrightarrow 2\{Cd(S_2CNEt_2)I\} + Et_4tds \qquad (1)$$

$$[Cd(S_2CNEt_2)_2]_2 + 2I_2 \longrightarrow 2[Cd(Et_4tds)I_2] \qquad (2)$$

In the solid state $\{Cd(S_2CNEt_2)I\}$ forms a linear polymer. The solution structure before crystallization is unclear. The presence of a mononuclear three-coordinate complex seems unlikely. For binuclear complexes, at least four alternatives exist: $[ICd(\mu\text{-}S_2CNEt_2)_2CdI]$, $[(Et_2NCS_2)Cd(\mu\text{-}I)_2Cd(S_2CNEt_2)]$, $[(Et_4tds)Cd(\mu\text{-}S_2CNEt_2)_2CdI_2]$ and $[\{Cd(S_2CNEt_2)I\}_2(\mu\text{-}Et_4tds)]$.

$[Cd(S_2CNEt_2)_2]_2/I_2$ reaction mixtures have been treated with several chelating ligands L to stabilize the low-molecular-weight precursor of $[Cd(S_2CNEt_2)I]_\infty$ by complexation. However, no mixed L/dithiocarbamato complexes could be obtained. With 1,4,7-triazacyclononane (tacn) and 1,4,7-trithiacyclononane (ttcn) crystalline compounds of the composition $CdLI_2$ were isolated. They probably consist of $[CdL_2]^{2+}$ and $[CdI_4]^{2-}$ ions. In contrast to reaction (1), 50% of the starting complexes remained unchanged

$$2[Cd(S_2CNEt_2)_2]_2 + 2I_2 + 2L \longrightarrow$$
$$[Cd(S_2CNEt_2)_2]_2 + [CdL_2][CdI_4] + 2Et_4tds \quad (3)$$

L = tacn, ttcn

$[Cd(S_2CNEt_2)_2]_2$ and $[Cd(S_2CNEt_2)I]_\infty$ have nearly identical infrared spectra in the range 250–4000 cm^{-1}. This is understandable from their close structural relation (see below). Both compounds show interesting chemical-ionization mass spectra (reagent gas iso-butane). The mass range up to *m/e* 1200 was investigated. For $[Cd(S_2CNEt_2)_2]_2$ prominent peaks from cadmium-containing species were observed at *m/e* 411, 670, 819 and 1078. The corresponding ions are $[Cd(S_2CNEt_2)_2]^+$, $[Cd_2(S_2CNEt_2)_3]^+$, $[Cd(S_2CNEt_2)_2]_2^+$ and $[Cd_3(S_2CNEt_2)_5]^+$, respectively. These formulas do not take into account a possible proton capture in some cases. The peaks exhibited characteristic patterns due to the relatively large number (eight) of naturally occurring cadmium isotopes. The identity of $[Cd_3(S_2CNEt_2)_5]^+$ was confirmed by comparison with a computer-simulated isotopic abundance pattern. The trinuclear complex is not preorganized in the solid-state structure of $[Cd(S_2CNEt_2)_2]_2$, i.e. there are no covalent interactions between the dimers. The largest ion reported for the electron-impact spectrum of $[Cd(S_2CNEt_2)_2]_2$ was $[Cd(S_2CNEt_2)_2]^+$ [14].

In the CI spectrum of $[Cd(S_2CNEt_2)I]_\infty$ peaks were found at *m/e* 389, 411, 672, 798 and 1078. They are tentatively assigned to $[Cd(S_2CNEt_2)I]^+$, $[Cd(SC)I_2]^+$, $[Cd_2(S_2CNEt_2)(SC)I_2]^+$, $[Cd_2(S_2CNEt_2)(SC)I_3]^+$ and $[Cd(S_2CNHEt)I]_3^+$ (or $[Cd_3(S_2CNEt_2)_5]^+$), respectively. Some of these ions may additionally contain an H atom from proton capture. The peak at *m/e* 1078 is certainly caused by a trinuclear ion. However, its exact composition is unclear. Polynuclear fragments are, of course, not unexpected for a polymeric compound.

Crystals of $[Cd(S_2CNEt_2)I]_\infty$ consist of linear $\cdots Cd(\mu\text{-}S_2CNEt_2)_2Cd(\mu\text{-}I)_2Cd(\mu\text{-}S_2CNEt_2)_2Cd(\mu\text{-}I)_2\cdots$ polymer chains (see Fig. 1). The polymer is built up from $\{Cd(S_2CNEt_2)_2CdI_2\}$ repetitive units. Hence, it can be regarded as an alternating copolymer of cadmium *N,N*-diethyldithiocarbamate and cadmium iodide. Neither of these individual compounds is known to exist in a one-dimensional $\cdots Cd(\mu\text{-}X)_2Cd(\mu\text{-}X)_2\cdots$ form ($X = S_2CNEt_2$ or I) structurally analogous to the copolymer. There are some other ways to look at the structure of $[Cd(S_2CNEt_2)I]_\infty$.

(i) The smallest building block is the $\{Cd(S_2CNEt_2)I\}$ monomer which is the contents of the asymmetric unit. The action of inversion centers generates the polymer strand.

(ii) Alternatively, sterically unsaturated dimers, namely $[ICd(\mu\text{-}S_2CNEt_2)_2CdI]$ or $[(Et_2NCS_2)Cd(\mu\text{-}I)_2Cd(S_2CNEt_2)]$, can be regarded as the basic units. These dimers form the polymer by sharing terminal ligands.

(iii) The $\{Cd(\mu\text{-}S_2CNEt_2)_2Cd\}^{2+}$ group is found in $[Cd(S_2CNEt_2)I]_\infty$ as well as in the starting material $[Cd(S_2CNEt_2)_2]_2$. Thus, it has survived the redox reaction – at least formally. In the polymer, the $\{Cd(\mu\text{-}S_2CNEt_2)_2Cd\}^{2+}$ groups are connected by μ-I double bridges.

The metric data of the $\mu\text{-}S_2CNEt_2$ ligands in $[Cd(S_2CNEt_2)I]_\infty$ and $[Cd(S_2CNEt_2)_2]_2$ show no significant differences. However, the $Cd(\mu\text{-}S)_2Cd$ rhombs, situated on inversion centers in both compounds, have somewhat different geometries. In the polymer, the Cd···Cd″ distance is 3.773(1) Å, and the S(1)–Cd–S(1″) angle is 91.5(1)°. The corresponding values of the dimer are 3.612 Å and 96.9(1)°. Thus, the $Cd(\mu\text{-}S)_2Cd$ rhomb in $[Cd(S_2CNEt_2)I]_\infty$ is elongated along the Cd···Cd and compressed along the S···S line. Both the $Cd(\mu\text{-}S)_2Cd$ and $Cd(\mu\text{-}I)_2Cd$ rhomb contain 'normal' (Cd–S(1″), Cd–I) and long, 'secondary' bonds (Cd–S(1), Cd–I′). The cadmium atom is five-coordinated. The geometry of the I_2S_3 coordination polyhedron is intermediate between tetragonal-pyramidal (tp) and trigonal-bipyramidal (tbp). The τ value [15] is $(158.1 - 132.7)/60 = 0.42$; the limiting values for ideal geometries are $\tau = 0$ (tp) and $\tau = 1$ (tbp).

Supplementary material

Lists of observed and calculated structure factors and anisotropic temperature factors have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische information mbH, D-7514 Eggenstein-Leopoldshafen 2, F.R.G., and may be obtained by quoting the deposition number CSD 54707, the authors and the literature citation.

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