Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.147$
$S = 1.153$
5477 reflections
317 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 5.8729P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.002$
$\Delta\rho_{\max} = 0.290$ e Å^{-3}
$\Delta\rho_{\min} = -0.256$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0002 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cr1—C4	2.234 (4)	Cr1—Cl1	2.3308 (14)
Cr1—C1	2.250 (4)	Cr2—C25	2.177 (5)
Cr1—C2	2.253 (4)	Cr2—C24	2.182 (5)
Cr1—C5	2.262 (4)	Cr2—C21	2.185 (5)
Cr1—C3	2.265 (5)	Cr2—C23	2.193 (4)
Cr1—Cl3	2.3195 (14)	Cr2—C22	2.208 (4)
Cr1—Cl2	2.3208 (14)		
Cl3—Cr1—Cl2	95.02 (6)	Cl2—Cr1—Cl1	97.92 (6)
Cl3—Cr1—Cl1	98.34 (6)		

Most of the non-H atoms were located by direct methods and the remainder were found in difference Fourier syntheses. Anisotropic displacement parameters were refined for all non-H atoms. All H atoms were located from difference syntheses. In the final refinement, the positions of the H atoms were idealized with a riding model which imposed geometric constraints on the positional parameters of the H atoms used in the refinement [C—H = 0.96 Å and $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$].

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *SDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Siemens, 1994). Software used to prepare material for publication: *SHELXTL*.

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First Hg$^{\rm II}$–ω-Thiocaprolactam Complex

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Abstract

The X-ray crystal structure of bis(1-azacycloheptane-2-thione-*S*)dichloromercury(II), $[{\rm HgCl_2(C_6H_{11}NS)_2}]$, is reported, which is the first structurally characterized complex of ω-thiocaprolactam with a heavy metal. The molecule exhibits disymmetric Hg—Cl distances of 2.480 (2) and 2.613 (2) Å, while the two organic fragments are coordinated with identical Hg—S bond lengths of 2.496 (2) Å.

Comment

Solvent extraction of heavy metals such as Hg$^{\rm II}$ is important from the point of view of environmental protection problems. Extracting reagents containing sulfur as a donor atom are particularly effective and selective for Hg$^{\rm II}$ (Bromberg, Lewin & Warshawsky, 1993; Inoue, Yasukawa & Miura, 1994; Zuo & Muhammed, 1995). On the other hand, 2-thioxohexamethyleneimine (ω-thiocaprolactam) has been tested as an analytical reagent (Sikorska-Tomicka, 1984, 1985). The syntheses, crystal structure determinations and reactivities of several of its complexes have been reported with Cu$^{\rm I}$

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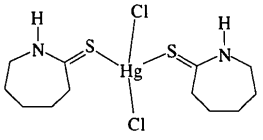
(Akrivos *et al.*, 1992; Karagiannidis, Akrivos, Aubry & Skoulila, 1991; Karagiannidis, Akrivos, Kojic-Prodic & Luic, 1992; Karagiannidis, Akrivos, Mentzafos & Hountas, 1991; Karagiannidis, Akrivos, Mentzafos & Terzis, 1991; Kojic-Prodic *et al.*, 1992) and Rh^{II} (Lifsey *et al.*, 1987). Recently, ω-thiocaprolactam was found to be a very selective ligand for binding Hg^{II} and Cu^{II} (Nuñez, 1996). In the present communication, we report the crystal structure of dichlorobis(2-thioxohexamethyleneimine-*S*)mercury(II), (I), with the aim of contributing to the proposal of a solvent-extraction mechanism.



(I)

The compound crystallizes in the triclinic system. It should be mentioned that this cell can be transformed to a pseudo-C-centered monoclinic cell (matrix transformation: $0\bar{1}0$, $01\bar{2}$, 100). Nevertheless, in a sample of five single crystals, none actually presented $2/m$ symmetry.

The molecule is built up of a monomeric $HgCl_2$ unit with two organic ligands coordinated to the Hg atom *via* the S atom, yielding a distorted tetrahedral geometry for the metal center (Fig. 1). In contrast to the three other $HgCl_2L_2$ complexes reported, where *L* is a fragment coordinated *via* the S atom of a thiocarbonyl group (Bandoli *et al.*, 1975; Cannas *et al.*, 1981; Chieh, 1977), the Hg—Cl bond lengths of the title compound are significantly disymmetric, with a difference of 0.13 Å. This is a consequence of the relative conformation of both ω-thiocaprolactam ligands, which produces close intramolecular H-atom contacts from both amine groups to the same Cl atom: Cl2···H1*A* 2.344 (7) and Cl2···H2*A* 2.365 (7) Å. On the other hand, the Cl1 atom is implicated in the formation of a three-dimensional network of weak intermolecular hydrogen bonds involving H atoms of two methylene fragments of one organic ligand, C13 and C16; Cl···H distances for C—H···Cl contacts are 2.878 (9) and 2.746 (8) Å for C13 and C16, respectively.

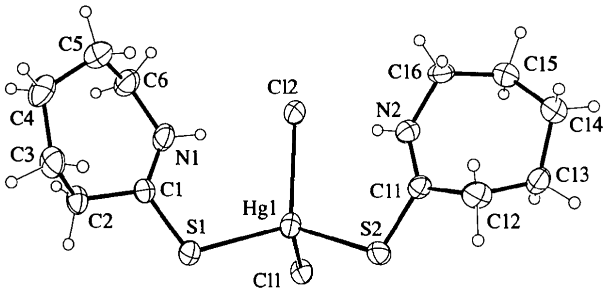


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids.

Coordinated thiocaprolactam molecules retain the chair conformation of the free molecule (Mozzhukhin *et al.*, 1993), with C—S—Hg angles close to 109°, as expected for essentially sp^3-hybridized S atoms. Hg—S bond lengths are within the range of those observed for the above-mentioned $HgCl_2L_2$ complexes. C—S bond lengths are found to be very similar to that observed for the free molecule [1.677 (4) Å at room temperature (Nũnez, Bernès & De Gyves, 1997) or 1.681 Å for the structure at 173 K (Mozzhukhin *et al.*, 1993)] and those observed for Cu^I complexes, which are in the range 1.67–1.71 Å. This observation confirms the character of the double bond for the thiocarbonyl group of the ω-thiocaprolactam, coordinated or free, and is indicative of the poor ability of the ω-thiocaprolactam to coordinate transition metals. This is also reflected in the Hg—S bond lengths of 2.496 (2) Å, significantly longer than, for example, the Hg—S distance of 2.382 (2) Å observed in a complex with a thione as ligand (Norris *et al.*, 1983). Studies on the coordination properties of thiocaprolactam with heavy metals are underway.

Experimental

The title compound was obtained by reaction of mercury(II) chloride with ω-thiocaprolactam (1:1 ratio) in chloroform, stirred at room temperature for 4 d and recrystallized from acetone.

Crystal data

[$HgCl_2(C_6H_{11}NS)_2$]
M_r = 529.93
Triclinic
$P\bar{1}$
a = 7.126 (1) Å
b = 8.795 (1) Å
c = 15.082 (1) Å
α = 73.41 (1)°
β = 85.82 (1)°
γ = 76.78 (1)°
V = 881.9 (2) Å^3
Z = 2
D_x = 1.996 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 36 reflections
θ = 2.5–12.0°
μ = 9.256 mm^{-1}
T = 293 (2) K
Plate
0.25 × 0.20 × 0.10 mm
Colorless

Data collection

Siemens *P*4/*PC* diffractometer
θ–2θ scans
Absorption correction:
27 ψ scans (Fait, 1991)
T_{min} = 0.156, T_{max} = 0.396
3872 measured reflections
3072 independent reflections
2492 reflections with $I > 2\sigma(I)$

R_{int} = 0.033
θ_{max} = 25°
$h = -1 \rightarrow 8$
$k = -9 \rightarrow 10$
$l = -17 \rightarrow 17$
3 standard reflections every 97 reflections intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.087$
$S = 1.030$
3072 reflections
173 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.73$ e Å^{-3}
$\Delta\rho_{\min} = -0.73$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0064 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Hg1—Cl1	2.480 (2)	S1—C1	1.688 (8)
Hg1—S2	2.496 (2)	S2—C11	1.702 (8)
Hg1—S1	2.496 (2)	N1—C1	1.300 (11)
Hg1—Cl2	2.613 (2)	N2—C11	1.301 (10)
Cl1—Hg1—S2	109.36 (7)	S1—Hg1—Cl2	109.50 (7)
Cl1—Hg1—S1	109.09 (7)	C1—S1—Hg1	110.3 (3)
S2—Hg1—S1	115.31 (7)	C11—S2—Hg1	111.1 (3)
Cl1—Hg1—Cl2	104.46 (7)	C1—N1—C6	125.5 (7)
S2—Hg1—Cl2	108.57 (7)	C11—N2—C16	126.5 (7)

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995). Software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1061). Services for accessing these data are described at the back of the journal.

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Dichlorobis(1,3-imidazolidine-2-thione-*S*)-cadmium(II)

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Abstract

The redetermination of the crystal structure of a cadmium(II) complex of 1,3-imidazolidine-2-thione (Imt) coordinated with two molecules of Imt and two Cl$^-$ ions, [CdCl$_2$(C$_3$H$_6$N$_2$S)$_2$], has been performed in order to obtain accurate parameters and to study the effects of the metal coordination on the metal–S and C—S bonds in Imt complexes. The Cd$^{\rm I}$—S distances of 2.525 (2) and 2.535 (2) Å in the present tetrahedral complex are significantly longer than the corresponding distances in the Au$^{\rm I}$ and Cu$^{\rm II}$ complexes of Imt, but there is no significant difference in the C—S distances of 1.721 (6) and 1.710 (6) Å from that in Au$^{\rm I}$ and Cu$^{\rm II}$ complexes. This work represents a significant increase in the quality

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