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)

A. R. AL-ARFAJ,[a] J. H. REIBENSPIES,[b] A. A. ISAB[a] AND M. SAKHAWAT HUSSAIN[a]†

[a]*Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia, and* [b]*Department of Chemistry, Texas A&M University, College Station, TX 77843 USA. E-mail: reibenspies@chemvx.tamu.edu*

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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, $[CdCl_2(C_3H_6N_2S)_2]$, 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^{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^{I} and Cu^{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^{I} and Cu^{II} complexes. This work represents a significant increase in the quality

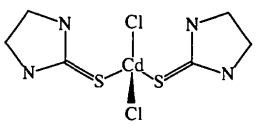
† On leave at the Department of Chemistry, Texas A&M University, College Station, TX 77840, USA.

of the structure of the title compound over the earlier work.

Comment

We have previously reported the synthesis, NMR measurements and X-ray structures of a series of gold complexes of 1,3-imidazolidine-2-thione (Imt) and its *N*-substituted derivatives as a part of our ongoing research into model compounds of anti-arthritic gold drugs (Hussain & Isab, 1984, 1985*a*,*b*; Isab & Hussain, 1986*a*). The copper(II) complexes of Imt and its analogs have also been reported, and the ^{13}C NMR shift for the thione C atom was related to the complexation of these thiones (Isab & Hussain, 1986*b*). The spectroscopic and structural studies have been further extended to other metals such as Ag^{I}, Hg^{II} and Cd^{II}.

In the present communication, we report an accurate redetermination of the X-ray structure of dichlorobis(1,3-imidazolidine-2-thione)cadmium(II), (I), in order to compare the bond distances and angles as a function of the metal atom in coordinated Imt. The present complex was reported in 1968 (Cavalca *et al.*, 1968) but no fractional coordinates were given and the *R* factor was reported as 0.138. The desired structural comparisons were not appropriate at this stage of refinement.



(I)

The Cd atom in the complex has a tetrahedral geometry with all angles close to the tetrahedral angles except for the S1—Cd1—S2 angle of 117.74 (6)°, which is significantly different from other similar angles. The Cl1 atom is involved in N—H···Cl intramolecular hydrogen contacts with two Imt moieties, N2···Cl1 and N3···Cl1 being 3.27 (1) and 3.22 (1) Å, respectively. The coplanarity of the Cl1, Cd1, S1 and S2 atoms, and the atoms of the heterocyclic ring contributes to the observed hydrogen bonding. No intramolecular hydrogen bonding was observed between Cl2 and any of the atoms in the two Imt moieties. The Cd1—Cl1 distance of 2.507 (2) Å is significantly longer than the Cd1—Cl2 distance of 2.487 (2) Å because of the involvement of Cl1 in intramolecular hydrogen bonding. A non-crystallographic mirror plane exists along Cl1—Cd1—Cl2 with two Imt rings symmetrically disposed across the plane (pseudo-mirror at approximately *x*, 0.156, *z*). The two non-equivalent Imt molecules are symmetrically tilted with respect to the Cd—S bonds placing N2—H···Cl1 and N3—H···Cl1 atoms in linear positions suitable for intramolecular hydrogen bonding.

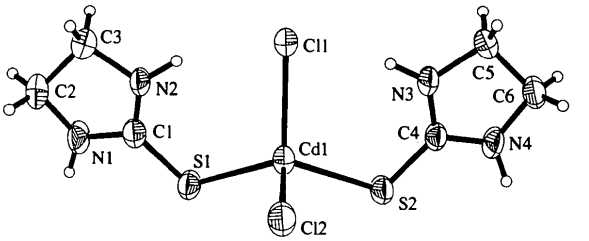


Fig. 1. View of dicholorobis(1,3-imidazolidine-2-thione)cadmium(II) showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

The Cd—S distances of 2.525 (2) and 2.535 (2) Å in the present tetrahedral complex are significantly longer than the corresponding distances in Au^{I} and Cu^{II} complexes. However, there is no significant difference in the C—S distances of 1.72 (6) and 1.710 (6) Å from that in Au^{I} and Cu^{II} complexes. The Imt moiety forms a trigonal complex $[(Imt)_2AuCl]$ with gold showing Au—S distances of 2.279 (8) Å (Jones, Guy & Sheldrick, 1976), whereas the substituted analog of Imt, namely PrImt, forms an ionic complex $[(PrImt)_2Au]Cl$ with Au—S distances of 2.283 (3) to 2.291 (3) Å, and C—S distances of 1.70 (1) and 1.73 (1) Å (Hussain & Isab, 1985*b*). Another substituted Imt, namely EtImt, forms a linear complex [(EtImt)AuCl] with an Au—S distance of 2.25 (1) Å and a C—S distance of 1.74 (2) Å (Hussain & Isab, 1984). The Cu^{II} atom forms a trigonal complex $[(PrImt)_2CuCl]$ with PrImt having Cu—S distances of 2.209 (2) and 2.223 (3) Å, and C—S distances of 1.672 (9) and 1.707 (8) Å (Hussain, Al-Arfaj & Hussain, 1990).

In conclusion, the Cd—S distance in the present complex is longer than that in the complexes of Imt with other metals, whereas the C—S distances are not affected by the change in the metal atom. The observed difference in the *M*—S distances is partly the result of the difference in the coordination sphere of the various metals.

Experimental

The complex $[(Imt)_2CdCl_2]$ was prepared by adding two equimolar amounts of Imt suspended in methanol to an aqueous solution of $CdCl_2$. The mixed solutions were refluxed for 2–3 h. The solvents were evaporated at room temperature to low volume and the resulting crystals were collected. The compound was characterized by ^{1}H and ^{13}C NMR. The ^{13}C NMR spectra of the cadmium complex $[(Imt)_2CdCl_2]$ showed C-2 and C-4,5 resonances at 181.94 and 45.17 p.p.m., respectively. These signals were shifted by −3.10 for C-2 and −0.72 p.p.m. for C-4,5 with respect to the free Imt ligand which exhibits C-2 and C-4,5 shifts at 185.04 and 45.89 p.p.m., respectively.

Crystal data

$[CdCl_2(C_3H_6N_2S)_2]$
$M_r = 387.62$
Monoclinic
$P2_1/n$
$a = 6.2591\ (13)$ Å
$b = 14.616\ (3)$ Å
$c = 14.054\ (3)$ Å
$\beta = 96.71\ (3)°$
$V = 1276.9\ (4)$ Å^3
$Z = 4$
$D_x = 2.016$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5–15.0°$
$\mu = 2.429$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.40 × 0.20 × 0.12 mm
Colorless

Data collection

Siemens *R3M* diffractometer
ω scans
Absorption correction: empirical *via* ψ scans (*XEMP*; Siemens, 1990*c*)
$T_{min} = 0.616$, $T_{max} = 0.747$
2476 measured reflections
2257 independent reflections
1773 reflections with $I > 2\sigma(I)$

$R_{int} = 0.025$
$\theta_{max} = 25°$
$h = -7 \rightarrow 0$
$k = 0 \rightarrow 17$
$l = -16 \rightarrow 16$
3 standard reflections
every 97 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.107$
$S = 1.051$
2256 reflections
137 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 5.1265P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.608$ e Å^{-3}
$\Delta\rho_{min} = -0.931$ e Å^{-3}
Extinction correction: *SHELXL93*
Extinction coefficient: 0.0028 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cd1—Cl2	2.487 (2)	N2—C1	1.333 (8)
Cd1 Cl1	2.507 (2)	N2—C3	1.459 (7)
Cd1—S1	2.525 (2)	N3—C4	1.329 (7)
Cd1—S2	2.535 (2)	N3—C5	1.458 (7)
S1—C1	1.721 (6)	N4—C4	1.309 (7)
S2—C4	1.710 (6)	N4—C6	1.461 (8)
N1—C1	1.324 (7)	C2—C3	1.533 (9)
N1—C2	1.452 (8)	C5—C6	1.540 (9)
Cl2—Cd1—Cl1	106.27 (6)	C4—N4—C6	113.5 (5)
Cl2—Cd1—S1	108.81 (6)	N1—C1—N2	109.2 (5)
Cl1—Cd1—S1	108.75 (5)	N1—C1—S1	123.3 (5)
Cl2—Cd1—S2	105.55 (6)	N2—C1—S1	127.4 (4)
Cl1—Cd1—S2	109.11 (5)	N1—C2—C3	101.5 (5)
S1—Cd1—S2	117.74 (6)	N2—C3—C2	101.3 (5)
C1—S1—Cd1	106.2 (2)	N4—C4—N3	109.4 (5)
C4—S2—Cd1	106.8 (2)	N4—C4—S2	123.8 (5)
C1—N1—C2	111.9 (5)	N3—C4—S2	126.8 (4)
C1—N2—C3	111.5 (5)	N3—C5—C6	102.5 (5)
C4—N3—C5	112.0 (5)	N4—C6—C5	100.8 (5)

A suitable crystal was chosen and mounted on a glass fiber at room temperature with epoxy cement. ω scans of several intense reflections indicated acceptable crystal quality. The 2θ scan width was 2.0° + $K\alpha$ separation with a θ variable scan rate between 1.5 and 14.6° min^{-1}. Background measurement by stationary crystal and stationary counter technique at the beginning and end of each reflection for half the total scan time. The data was corrected for absorption. Intensities were corrected by a peak profiling method (Diamond, 1969) and for absorption (Siemens, 1990*c*). Carbon-bound H atoms were placed in idealized positions [C—H = 0.96 Å and U(H) = 1.2U(adjacent riding atom)]. Nitrogen-bound H atoms were located in a difference Fourier map. The H-atom parameters were not refined.

Data collection: *P3VAX* (Siemens, 1990*a*). Cell refinement: *P3VAX*. Data reduction: *XDISK* (Siemens, 1990*b*). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993*b*). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *CIFTAB* (Sheldrick, 1993*a*).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1043). Services for accessing these data are described at the back of the journal.

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