Tris(1,10-phenanthroline)copper(II) di-μ-iodo-bis(diiodomercurate) dimethyl sulfoxide monohydrate

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In the cationic complex present in the title compound, $[Cu(C_{12}H_8N_2)_3][Hg_2I_6] \cdot C_2H_6OS \cdot H_2O$, the copper(II) center adopts a highly distorted octahedral geometry, ligated by the six N atoms of three 1,10-phenanthroline ligands. The structure includes an iodide-bridged dimeric mercurate anion for neutrality and uncoordinated dimethyl sulfoxide and water molecules.

Comment

Examples of monomeric tris-chelated complexes of copper(II) involving neutral N,N'-donors are limited and uncommon because of pronounced Jahn–Teller distortions (Anderson, 1972, 1973; Bertini *et al.*, 1979; Cullen & Lingafelter, 1970; Folgado *et al.*, 1990; Majumdar *et al.*, 1998). The generalized synthetic method for this type of compound was developed by Goswani and co-workers (Choudhury *et al.*, 1992; Choudhury, Deb & Goswami, 1994; Choudhury, Deb, Kharmawaphlang & Goswami, 1994; Deb *et al.*, 1991; Kakoti *et al.*, 1992; Kharmawaphlang *et al.*, 1995), following the silver(I)-assisted metal exchange strategy. We have examined the exchange reaction between $Cu(phen)I_2$ and $Hg(phen)I_2$ (phen is 1,10-phenanthroline) with the hope of preparing tris-chelates of Cu^{II}. Since Hg^{II} is a much softer Lewis acid than Cu^{II}, it was expected that the Hg^{II} center in $Hg(phen)I_2$ would accept softer iodide ions from $Cu(phen)I_2$ and provide a harder phen molecule, a typical N,N'-donor ligand, to the Cu^{II} center (Pearson, 1963).

(I)
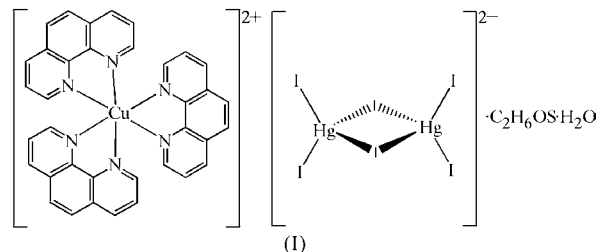
A black solid was produced from the reaction of $Cu(phen)I_2$ with $Hg(phen)I_2$. When this solid was recrystallized, two

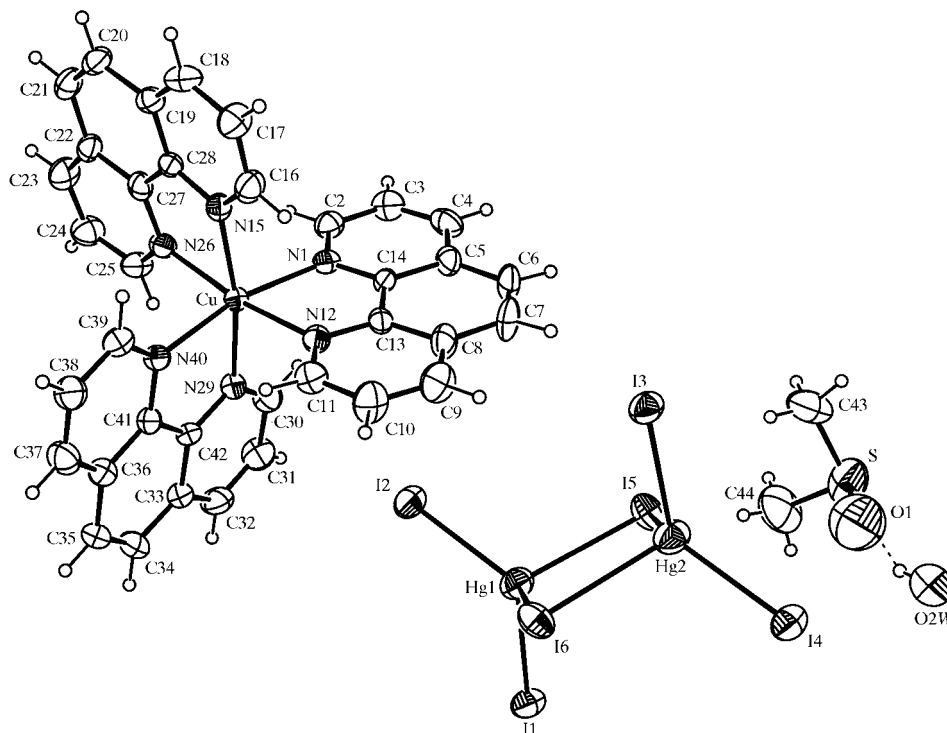**Figure 1**
ORTEP-3 (Farrugia, 1997) drawing of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids.

metal-organic compounds

differently colored types of crystals were formed in a dimethyl sulfoxide (DMSO)–water mixture; most of the sample crystallized as black crystallites, later identified by the elemental analysis as the bis-complex Cu(phen)$_2$HgI$_4$. The crystal structure of the minor product, *viz.* pale-green crystals, (I), is presented here.

Selected bond distances and bond angles for (I) are summarized in Table 1. The crystal structure consists of discrete [Cu(phen)$_3$]$^{2+}$ cations and [Hg$_2$I$_6$]$^{2-}$ anions in a 1:1 ratio (Fig. 1). The Cu^{II} center in the [Cu(phen)$_3$]$^{2+}$ cation is six-coordinated by the six N atoms of three phen ligands, forming a distorted octahedral Cu^{II}N$_6$ chromophore. The [Cu(phen)$_3$]$^{2+}$ ion exhibits a static Jahn–Teller effect, with two long Cu—N bonds of similar lengths at the axial site (Cu—N12 and Cu—N26). However, the remaining four shorter Cu—N bond distances in the equatorial plane are not equivalent, with a range of 2.082 (6)–2.128 (6) Å. In this respect, the distortion in the cation of (I) differs from what was observed previously for other tris-chelated Cu^{II} complexes involving N,N′-donors, such as [Cu(byp)$_3$](ClO$_4$)$_2$ (byp is 2,2′-bipyridine; Majumdar *et al.*, 1998), [Cu(en)$_3$](ClO$_4$)$_2$ (en is ethylenediamine; Bertini *et al.*, 1979; Cullen & Lingafelter, 1970) and [Cu(phen)$_3$](ClO$_4$)$_2$ (Anderson, 1973). The three larger N—Cu—N bond angles, where the two N atoms are in *trans* positions, differ by 8.5–13.2° from the ideal value of 180° for a perfect octahedron. The dihedral angles between the N/Cu/N planes of the coordinated phen ligands are 85.1 (2), 87.0 (2) and 87.2 (2)°, respectively.

The bridging Hg—I bond distances in (I) range from 2.9020 (8) to 2.9499 (8) Å, and those in the terminal positions range from 2.6903 (8) to 2.7301 (7) Å. These values are well within the reported bond distances (2.864–3.005 Å for bridging iodide and 2.574–2.756 Å for terminal iodide) in [Hg$_2$I$_6$]$^{2-}$ anions (Bell *et al.*, 2002; Fábry & Maximov, 1991; Pickardt & Wischlinski, 1999).

Packing stability of the structure of (I) is provided by hydrogen-bonding interactions between the DMSO molecule and the water molecule, and by C4—H4···Cg^i interactions (where Cg is the centroid of the C19–C22/C27/C28 ring; see Table 2). There is also a probable hydrogen bond between the H atom (not located) of the water molecule and the mercurate I atom [O2W···I4 = 3.830 (10) Å]. The intermolecular distance between the two parallel aromatic rings of the coordinated phen ligands in the packing structure is longer than 4.11 Å, indicating the absence of significant π–π interactions between them.

Experimental

Diiodo(1,10-phenanthroline)copper(II), Cu(phen)I$_2$, and diiodo-(1,10-phenanthroline)mercury(II), Hg(phen)I$_2$, were prepared according to the methods described by Li *et al.* (2000). A black precipitate was produced from the reaction of Cu(phen)I$_2$ (1.00 mmol) with Hg(phen)I$_2$ (1.10 mmol) in acetonitrile. This solid was dissolved in a DMSO–water mixture and allowed to crystallize slowly. Two differently colored types of crystals were formed; most of the crystals were black, but a small number of pale-green crystals of (I) were collected for X-ray study. Analysis calculated for

C$_{38}$H$_{32}$CuHg$_2$I$_6$N$_6$O$_2$S: C 24.50, H 1.73, N 4.51%; found C 25.53, H 1.44, N 4.59%

Crystal data

[Cu(C$_{12}$H$_8$N$_2$)$_3$][Hg$_2$I$_6$]·· C$_2$H$_6$OS·H$_2$O	D_x = 2.589 Mg m^{-3}
M_r = 1862.88	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4449
a = 12.6628 (10) Å	reflections
b = 18.8367 (15) Å	θ = 2.3–22.3°
c = 20.1380 (16) Å	μ = 10.81 mm^{-1}
β = 95.7890 (10)°	T = 295 (2) K
V = 4778.9 (7) Å^3	Block, pale green
Z = 4	0.25 × 0.17 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer	9373 independent reflections
φ and ω scans	5667 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	R_{int} = 0.046
T_{min} = 0.123, T_{max} = 0.339	θ_{max} = 26.0°
29955 measured reflections	h = −15 → 15
	k = −20 → 23
	l = −24 → 24

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2 + 0.3539P]$
$R[F^2 > 2\sigma(F^2)]$ = 0.041	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.094	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.00	$\Delta\rho_{max}$ = 0.97 e Å^{-3}
9373 reflections	$\Delta\rho_{min}$ = −0.80 e Å^{-3}
503 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Cu—N1	2.120 (6)	Hg1—I2	2.6903 (8)
Cu—N12	2.179 (6)	Hg1—I5	2.9020 (8)
Cu—N15	2.082 (6)	Hg1—I6	2.9151 (7)
Cu—N26	2.189 (6)	Hg2—I3	2.6967 (7)
Cu—N29	2.098 (6)	Hg2—I4	2.6914 (8)
Cu—N40	2.128 (6)	Hg2—I5	2.9248 (7)
Hg1—I1	2.7301 (7)	Hg2—I6	2.9499 (8)
N1—Cu—N12	77.9 (2)	I1—Hg1—I2	118.02 (2)
N1—Cu—N40	166.8 (2)	I5—Hg1—I6	93.86 (2)
N12—Cu—N26	171.5 (2)	I3—Hg2—I4	122.37 (2)
N15—Cu—N26	78.0 (2)	I5—Hg2—I6	92.661 (19)
N15—Cu—N29	169.1 (2)	Hg1—I5—Hg2	87.016 (19)
N29—Cu—N40	79.2 (2)	Hg1—I6—Hg2	86.309 (19)

Table 2
Hydrogen-bond geometry (Å, °).

Cg is the centroid of the C19–C22/C27/C28 ring.

D—H···A	D—H	H···A	D···A	D—H···A
O2W—H2W···O1	0.89 (8)	1.89 (10)	2.664 (14)	144 (15)
C4—H4···Cg^i	0.93	2.74	3.619 (10)	160

Symmetry code: (i) $-x, -y + 1, -z + 1$.

One H atom on water atom OW2 was located in a difference Fourier map and refined with a U_{iso}(H) value of 1.5U_{eq}(O); the other water H atom was not located. All other H atoms were refined using a riding model, with idealized geometry (C—H = 0.93–0.96 Å) and U_{iso}(H) values of 1.2U_{eq}(C) or 1.5U_{eq}(methyl C). Reflection (032) was omitted from the final cycles as an outlier reflection.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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