

RefinementRefinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.037$ $wR(F^2) = 0.090$ $S = 1.149$

5978 reflections

280 parameters

H-atom parameters

constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 4.3508P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 1.037 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -1.568 \text{ e } \text{\AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)Table 1. Selected geometric parameters (\AA , $^\circ$)

Cd1—S1	2.5875 (10)	O2—C18	1.403 (6)
Cd1—S2	2.5795 (10)	N1—N2	1.384 (4)
Cd1—I1	2.7470 (4)	N1—C7	1.271 (5)
Cd1—I2	2.7020 (4)	N2—C8	1.319 (5)
S1—C8	1.725 (4)	N3—C8	1.327 (5)
S2—C17	1.724 (4)	N4—N5	1.389 (4)
O1—C4	1.372 (5)	N4—C16	1.280 (5)
O1—C9	1.429 (6)	N5—C17	1.326 (5)
O2—C13	1.368 (5)	N6—C17	1.318 (5)
S1—Cd1—I2	110.14 (2)	S2—Cd1—I2	111.93 (2)
S1—Cd1—I1	109.09 (3)	I2—Cd1—I1	115.73 (1)
S2—Cd1—S1	100.02 (3)	C8—S1—Cd1	96.6 (1)
S2—Cd1—I1	108.76 (2)	C17—S2—Cd1	102.6 (1)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N6—H6C...S1	0.86	2.70	3.522 (4)	160
N2—H2B...S2 ⁱ	0.86	2.60	3.431 (3)	162
N3—H3C...I1 ⁱⁱ	0.86	3.00	3.735 (4)	144
N5—H5B...I1 ⁱⁱⁱ	0.86	3.06	3.901 (4)	167
N6—H6B...O1 ^{iv}	0.86	2.15	2.895 (5)	144

Symmetry codes: (i) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (ii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iii) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (iv) $x-1, y, z$.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1305). Services for accessing these data are described at the back of the journal.

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Dichlorobis(dimethylformamide-*O*)bis-(4-nitrobenzaldehyde thiosemicarbazone-*S*)-cadmium(II)

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Abstract

The title complex, $[\text{CdCl}_2(\text{C}_3\text{H}_7\text{NO})_2(\text{C}_8\text{H}_8\text{N}_4\text{O}_2\text{S})_2]$, crystallizes in space group $P\bar{1}$ with half a molecule in the asymmetric unit. The Cd atom lies on an inversion centre and is octahedrally coordinated to two O atoms from the dimethylformamide ligands, two S atoms from the thiosemicarbazone ligands and two Cl atoms.

Comment

Metal-thiosemicarbazone complexes are emerging as a new class of experimental anticancer compounds which can provide non-platinum therapeutic agents with

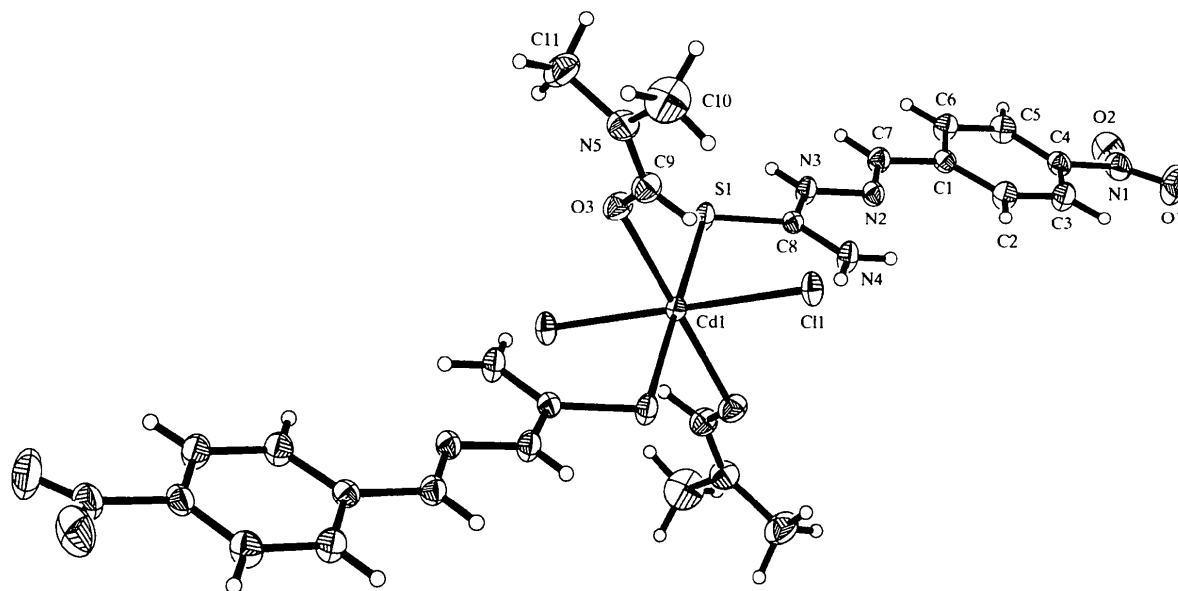


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as spheres of arbitrary radii.

remarkable antineoplastic activities against a number of transplantable spontaneous murine and human tumours (Subczynski *et al.*, 1987). In spite of the therapeutic value of thiosemicarbazides and their metal complexes, this has not resulted in many structure reports for these species (Padhye & Kauffman, 1985; Haiduc & Silvestru, 1990; West *et al.*, 1993), nor any systematic evaluation of the structure–activity relationships. In the present paper, the synthesis and X-ray structure of one such Cd complex, the title compound, (I), are reported. The structural features are compared with the parent compound and its related analogues.

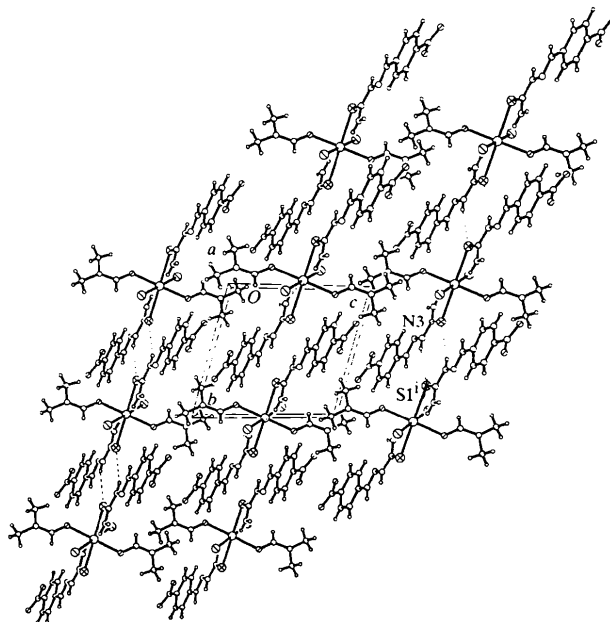
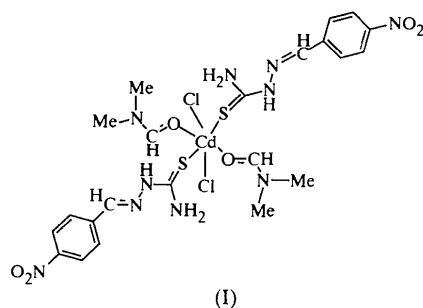


Fig. 2. The packing of the molecules in (I), viewed down the *a* axis. Hydrogen bonds are indicated by dashed lines.

The crystal of (I) contains individual neutral molecules. Generally, thiosemicarbazone derivatives may act as *N,S*-chelates or as monodentate *S* or *N* ligands, depending upon the preparative conditions. The present study used an acidic CdCl₂ solution during the reaction, which makes it difficult to coordinate the metal ions with monodentate ligands (Padhye & Kauffman, 1985).

The environment around the Cd atom is distorted from ideal octahedral geometry. Each Cd atom is

coordinated octahedrally by two O atoms from the dmf ligand (dmf is dimethylformamide), two terminal Cl atoms and two S atoms from the thiosemicarbazone ligand. The chloride, dmf and thiosemicarbazone ligands are in *trans* positions. It can be seen from Fig. 1 that the thiosemicarbazone ligand remains planar, as in its free state. The bond distances for C=S [1.703 (2) Å], C—NH₂ [1.311 (2) Å] and C—NH [1.342 (2) Å] are

comparable with the corresponding average values of 1.702 (2), 1.310 (3) and 1.340 (3) Å, respectively, for the free thiosemicarbazone ligand (Tian *et al.*, 1996). The Cd—O and Cd—Cl bond lengths are 2.358 (1) and 2.5784 (4) Å, respectively, which correspond to those in other cadmium complexes (West *et al.*, 1993), whilst the Cd—S bond length [2.6995 (4) Å] is much longer than in the cadmium complexes discussed in our previous report (Tian *et al.*, 1997). The nitro group is twisted by 14.5 (1)° out of the plane of the phenyl group.

The N—H...S intermolecular interaction between the inversion-related molecules forms chains that run infinitely along the *b* axis (Fig. 2). The planar parts of the organic ligands and the orientation of the nitro group are influenced by the N—H...N and C—H...O intra-ligand interactions.

Experimental

The synthesis and structure of the parent compound were reported in our previous paper (Tian *et al.*, 1996). For the preparation of the title complex, the thiosemicarbazone (2.24 g, 10 mmol) dissolved in ethanol (50 ml) was added to cadmium chloride (1.83 g, 10 mmol) in ethanol (50 ml). The colourless crystalline solid formed after refluxing for 4 h, [CdCl₂(C₈H₈N₄O₂S)₂], was isolated and dried *in vacuo* with P₂O₅ (yield 2.1 g, 67%). Single crystals of (I) suitable for X-ray structure analysis were obtained by diffusing ether into a solution of [CdCl₂(C₈H₈N₄O₂S)₂] in dimethylformamide. Analysis indicated that the complex contains no solvent molecules.

Crystal data

[CdCl ₂ (C ₈ H ₈ NO) ₂ (C ₈ H ₈ -N ₄ O ₂ S) ₂]	Mo K α radiation
$M_r = 777.98$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 6425 reflections
$P\bar{1}$	$\theta = 2.63\text{--}33.21^\circ$
$a = 8.8298$ (3) Å	$\mu = 1.050$ mm ⁻¹
$b = 9.6918$ (3) Å	$T = 293$ (2) K
$c = 10.5786$ (3) Å	Block
$\alpha = 97.810$ (1)°	0.44 × 0.28 × 0.20 mm
$\beta = 111.192$ (1)°	Yellow
$\gamma = 105.250$ (1)°	
$V = 787.04$ (4) Å ³	
$Z = 1$	
$D_x = 1.641$ Mg m ⁻³	
D_m not measured	

Data collection

Siemens SMART CCD area-detector diffractometer	3352 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.015$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.655$, $T_{\text{max}} = 0.818$	$h = -11 \rightarrow 10$
5228 measured reflections	$k = -12 \rightarrow 12$
3530 independent reflections	$l = 0 \rightarrow 13$
	Intensity decay: negligible

Refinement

Refinement on F^2	$\Delta\rho_{\text{max}} = 0.409$ e Å ⁻³
$R[F^2 > 2\sigma(F^2)] = 0.024$	$\Delta\rho_{\text{min}} = -0.572$ e Å ⁻³
$wR(F^2) = 0.064$	Extinction correction: SHELXTL (Sheldrick, 1997)
$S = 1.037$	Extinction coefficient: 0.014 (2)
3530 reflections	Scattering factors from International Tables for Crystallography (Vol. C)
197 parameters	
H atoms constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2 + 0.1231P]$	
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\text{max}} = 0.001$	

Table 1. Selected geometric parameters (Å, °)

Cd1—O3	2.358 (1)	O3—C9	1.234 (2)
Cd1—Cl1	2.5784 (4)	N1—C4	1.469 (2)
Cd1—S1	2.6995 (4)	N2—C7	1.275 (2)
S1—C8	1.703 (2)	N2—N3	1.372 (2)
O1—N1	1.218 (3)	N3—C8	1.342 (2)
O2—N1	1.224 (3)	N4—C8	1.311 (2)
O3—Cd1—Cl1	92.88 (4)	Cl1—Cd1—S1	94.85 (2)
O3—Cd1—S1	92.10 (4)		

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

D—H...A	D—H	H...A	D...A	D—H...A
N3—H3B...S1 ⁱ	0.86	2.60	3.405 (2)	157
N4—H4A...Cl1 ⁱⁱ	0.86	2.58	3.346 (2)	149
N4—H4B...Cl1	0.86	2.45	3.253 (2)	156

Symmetry codes: (i) $-x, -1 - y, 1 - z$; (ii) $1 - x, -y, 1 - z$.

Data collection: SMART (Siemens, 1996). Cell refinement: SAINT (Siemens, 1996). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL (Sheldrick, 1997). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL and PARST (Nardelli, 1995).

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Bis[2-(phenylazo)imidazole-*N*]silver(I) nitrate methanol solvate

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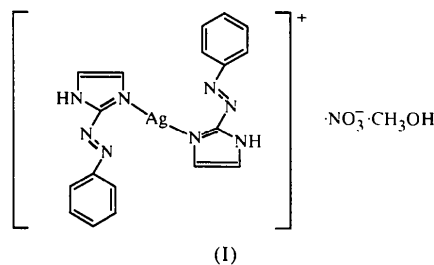
Abstract

The title compound, bis(2-phenyldiazenyl-1*H*-imidazole-*N*)silver(I) nitrate methanol solvate, [Ag(C₉H₈N₄)₂]NO₃·CH₃OH, is a monomeric complex linearly coordinated by two N atoms from two different imidazole rings, with Ag—N bond distances of 2.138 (3) and 2.147 (3) Å, and

an N—Ag—N bond angle of 174.9 (1)°. The crystal packing is stabilized by weak intramolecular N—H···O and O—H···O hydrogen bonds and an intermolecular N—H···O hydrogen bond involving the nitrate anion and the methanol solvent.

Comment

Recently, the design of molecular architectures with imidazole has aroused interest because of their role in understanding biomolecular interactions with metal ions and in providing models for the active sites of metallo-proteins. Ligands consisting of one imidazole ring as a pendant nitrogen donor from an azo function have been employed in the development of ruthenium(II) coordination chemistry, due to the unsymmetric *N*-donor sites in the azo-imine —N=N—C=N— function (Misra *et al.*, 1998). In this paper, we report the crystal structure of a silver complex of (2-phenylazo)imidazole, (I).



The molecular structure and atom-numbering scheme of (I) are shown in Fig. 1. The phenylazo group

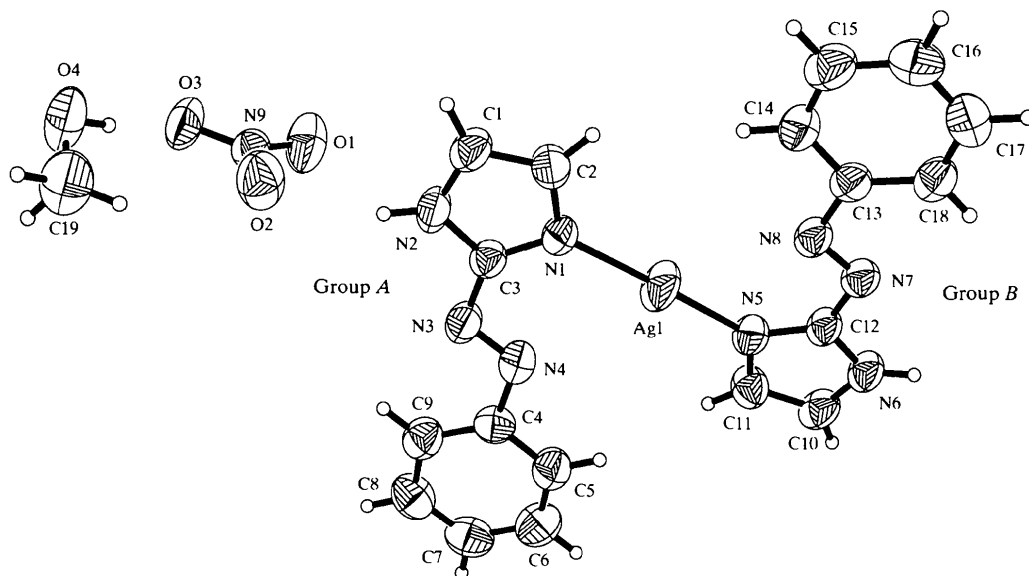


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as spheres of arbitrary radii.