

O1A—Sb1—C12A <sup>i</sup>	80.48 (7)	O1B—Sb2—C12B <sup>ii</sup>	82.15 (7)
O2A—Sb1—C12A <sup>i</sup>	73.30 (8)	O2B—Sb2—C12B <sup>ii</sup>	91.34 (8)
C13A—Sb1—C12A <sup>i</sup>	157.79 (3)	C13B—Sb2—C12B <sup>ii</sup>	167.73 (3)
C11A—Sb1—C12A <sup>i</sup>	102.62 (4)	C12B—Sb2—C12B <sup>ii</sup>	93.26 (4)
C12A—Sb1—C12A <sup>i</sup>	108.34 (3)	C11B—Sb2—C12B <sup>ii</sup>	101.07 (3)
P1A—O1A—Sb1	134.07 (16)	P1B—O1B—Sb2	137.54 (16)
P2A—O2A—Sb1	133.82 (17)	P2B—O2B—Sb2	133.86 (18)

Symmetry codes: (i) 2 - x, -y, 2 - z; (ii) 2 - x, 1 - y, 1 - z.

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

D—H...A	D—H	H...A	D...A	D—H...A
C25A—H25B...C11B	0.97	2.66	3.608 (3)	163
C25B—H25D...C11A <sup>i</sup>	0.97	2.60	3.559 (3)	168

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

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different  $\varphi$  angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in  $\omega$ . The crystal-to-detector distance was 4 cm and the detector swing angle was -35°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections; it was found to be negligible. Although data were collected to a  $2\theta_{\max}$  of 66.3°, only reflections having  $2\theta$  less than 55° were used for structure solution and refinement. The structure was solved by direct methods and refined by full-matrix least squares. Although all H atoms were located from a difference Fourier map, they were geometrically fixed and allowed to ride on their parent C atoms since free refinement led to unrealistically short C—H distances.

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

The authors would like to thank the Malaysian Government and both Universiti Sains Malaysia and Universiti Kebangsaan Malaysia (for research grants R&D Nos. 190-9609-2801 and 03-02-02-005, respectively). KC thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1263). Services for accessing these data are described at the back of the journal.

## References

- Carmalt, C. J., Cowley, A. H., Decken, A., Lawson, Y. G. & Norman N. C. (1996). *Acta Cryst.* **C52**, 931–933.  
 Golic, L. & Milicev, S. (1978). *Acta Cryst.* **B34**, 3379–3381.  
 Milicev, S. & Hadzi, D. (1977). *Inorg. Chim. Acta*, **21**, 201–207.  
 Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.  
 Porter, S. K. & Jacobson, R. A. (1970). *J. Chem. Soc. A*, pp. 1356–1359.  
 Sheldrick, G. M. (1995). *SHELXTL. Structure Determination Programs*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction of Area Detector Data*. University of Göttingen, Germany.

Siemens (1996a). *SAINT Software Reference Manual*. Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1996b). *SMART Software Reference Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Yamin, B. M., Fun, H.-K., Sivakumar, K., Yip, B. C. & Shawkataly, O. B. (1996). *Acta Cryst.* **C52**, 600–602.

*Acta Cryst.* (1999). **C55**, 174–176

## A binuclear cadmium(II) complex: bis[bis(N,N-diisopropylthiocarbamato)-cadmium(II)]

FANG-FANG JIAN,<sup>a</sup> ZUO-XIANG WANG,<sup>a</sup> HOONG-KUN FUN,<sup>b†</sup> ZHI-PING BAI<sup>a</sup> AND XIAO-ZENG YOU<sup>a</sup>

<sup>a</sup>Coordination Chemistry Institute & State Key Laboratory of Coordination Chemistry, Nanjing University, Center for Advanced Studies in Science and Technology of Microstructures, Nanjing 210093, People's Republic of China, and <sup>b</sup>X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: hkfun@usm.my

(Received 16 April 1998; accepted 21 September 1998)

## Abstract

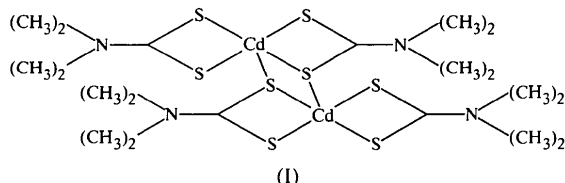
The title compound, bis[ $\mu$ -(N,N-diisopropylthiocarbamato)-S,S':S][bis(N,N-diisopropylthiocarbamato-S,S')-cadmium(II)], [Cd<sub>2</sub>(C<sub>7</sub>H<sub>14</sub>NS<sub>2</sub>)<sub>4</sub>], a binuclear complex, consists of two bis(N,N-diisopropylthiocarbamato)-cadmium complex units bridged by Cd—S bonds. Each Cd<sup>II</sup> atom has a distorted tetragonal pyramidal environment and the inversion-related complex forms an edge-shared tetragonal pyramidal geometry with a Cd...Cd distance of 3.6049 (6) Å.

## Comment

The development of effective antidotes for cadmium intoxication has proven to be a task of considerable difficulty. The reasons for this difficulty are quite numerous. The normal physiological processes by which cadmium is immobilized involve its bonding to an intracellular protein in the liver and the kidney (Cherian & Goyet, 1978). This metal–intracellular protein complex, Cd metallothionein, can destroy the kidney. The general goal of chelate therapy is usually the development of chelating agents which will reduce the body burden of a toxic metal by transforming it into a form in which it can be excreted in the urine. In recent years, it has become apparent that dithiocarbamates can mobilize cadmium

† On sabbatical leave at the Coordination Chemistry Institute, Nanjing University, People's Republic of China.

from its intracellular deposits (Gale *et al.*, 1984; Shinobu *et al.*, 1984). The present study was undertaken to obtain structure information on the coordination chemistry of cadmium with some dithiocarbamates and we present here the title compound, (I).



The coordination sphere of the Cd<sup>II</sup> ion is best described as having distorted tetragonal pyramidal geometry. The Cd atom is coordinated to four S atoms at distances ranging from 2.546(1) to 2.599(1) Å and to a fifth S atom at a much longer distance of 2.820(1) Å; these distances are similar to those found in bis(dibutylthiocarbamate)cadmium(II) [Cd{S<sub>2</sub>CN(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>}<sub>2</sub>] (Casas *et al.*, 1989). The fifth S atom, S2<sup>i</sup>, is from a third ligand which is in the coordination polyhedron of a centrosymmetrically related Cd<sup>II</sup> ion [symmetry code: (i) 1 - *x*, 1 - *y*, -*z*]. Thus, each bridging sulfur simultaneously occupies an equatorial coordination site on one Cd<sup>II</sup> ion and an apical site on the other Cd<sup>II</sup> ion to form an edge-shared tetragonal pyramidal geometry. The Cd<sup>II</sup> ion deviates from the S1/S2/S3/S4 mean plane by 0.6809(4) Å towards S2<sup>i</sup>. Since the bridging network Cd1—S2—Cd1<sup>i</sup>—S2<sup>i</sup> is around the inversion centre, it is strictly planar, with a Cd1...Cd1<sup>i</sup> separation of 3.6049(6) Å and S2—Cd1—S2<sup>i</sup> and Cd1—S2—Cd1<sup>i</sup> angles of 96.67(3) and 83.33(3)°, respectively. The Cd1—S2—Cd1<sup>i</sup>—S2<sup>i</sup> and S1/S2/S3/S4 mean planes form a dihedral angle of 85.55(2)°.

The S2—C7 distance [1.765(4) Å] is longer than the other S—C bond lengths; the N1—C7 and N2—

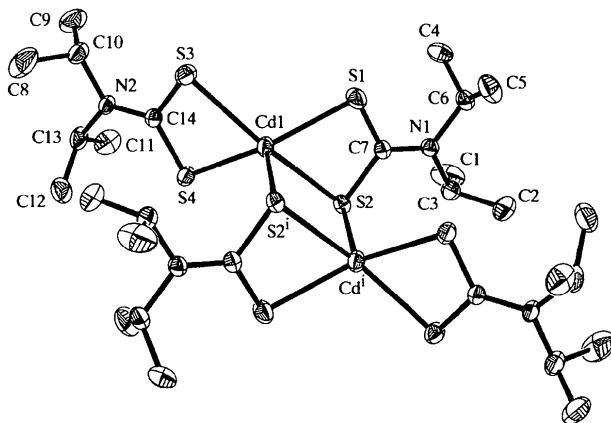


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme [symmetry code: (i) 1 - *x*, 1 - *y*, -*z*].

C14 [1.326(4) Å] distances are shorter compared with other N—C distances indicating considerable double-bond character. This situation is similar to that found in bis(*N,N*-diisopropylthiocarbamate)copper (Iwasaki & Kobayashi, 1980), despite the different metal atom.

## Experimental

For the preparation of crystals of (I), bis(*N,N*-diisopropylthiocarbamate)cadmium(II) was dissolved in CH<sub>3</sub>CN. Crystals suitable for X-ray analysis were obtained by evaporation at room temperature over a period of two months.

### Crystal data

[Cd<sub>2</sub>(C<sub>7</sub>H<sub>14</sub>NS<sub>2</sub>)<sub>4</sub>]

*M<sub>r</sub>* = 930.04

Monoclinic

*P*2<sub>1</sub>/*n*

*a* = 11.6017(10) Å

*b* = 11.2268(11) Å

*c* = 16.7520(15) Å

β = 108.936(8)°

*V* = 2063.9(3) Å<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 1.497 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 39

reflections

θ = 5.549–12.622°

μ = 1.459 mm<sup>-1</sup>

*T* = 293(2) K

Parallelepiped

0.40 × 0.30 × 0.30 mm

Light yellow

### Data collection

Siemens P4 diffractometer

θ/2θ scans

Absorption correction:

empirical ψ scan

(XSCANS; Siemens, 1994)

*T<sub>min</sub>* = 0.599, *T<sub>max</sub>* = 0.646

5989 measured reflections

4742 independent reflections

3510 reflections with

*I* > 2σ(*I*)

*R<sub>int</sub>* = 0.036

θ<sub>max</sub> = 27.5°

*h* = -1 → 15

*k* = -1 → 14

*l* = -21 → 21

3 standard reflections

every 97 reflections

intensity decay: <3%

### Refinement

Refinement on *F*<sup>2</sup>

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.041

*wR*(*F*<sup>2</sup>) = 0.106

*S* = 0.950

4742 reflections

302 parameters

All H atoms refined

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0546*P*)<sup>2</sup>]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = -0.001

Δρ<sub>max</sub> = 0.421 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.467 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cd1—S1	2.5455 (11)	S3—C14	1.733 (3)
Cd1—S4	2.5541 (10)	S4—C14	1.733 (4)
Cd1—S2 <sup>i</sup>	2.5966 (10)	N1—C7	1.326 (4)
Cd1—S3	2.5994 (11)	N1—C3	1.494 (5)
Cd1—S2	2.8201 (10)	N1—C6	1.502 (5)
S1—C7	1.700 (4)	N2—C14	1.326 (4)
S2—C7	1.765 (4)	N2—C10	1.493 (5)
S2—Cd1 <sup>i</sup>	2.5966 (10)	N2—C13	1.495 (5)
S1—Cd1—S4	143.46 (4)	S1—Cd1—S2	66.71 (3)
S1—Cd1—S2 <sup>i</sup>	101.58 (4)	S4—Cd1—S2	97.05 (3)
S4—Cd1—S2 <sup>i</sup>	113.07 (3)	S2 <sup>i</sup> —Cd1—S2	96.67 (3)

S1—Cd1—S3	109.98 (4)	S3—Cd1—S2	153.93 (3)
S4—Cd1—S3	69.97 (3)	Cd1 <sup>1</sup> —S2—Cd1	83.33 (3)
S2 <sup>1</sup> —Cd1—S3	109.16 (4)		

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

All H atoms were located from a difference Fourier map and were refined isotropically.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXL93 and PARST (Nardelli, 1983).

This work is supported by NSFC project 29501001, NSF of Jiangsu Province project BK95024401 and the Malaysian Government research grant No. 190-9609-2801.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1201). Services for accessing these data are described at the back of the journal.

## References

- Casas, J. S., Sanchez, A., Bravo, J., Garcia-Fontan, S., Castellano, E. E. & Jones, M. M. (1989). *Inorg. Chim. Acta*, **158**, 119–126.
- Cherian, M. G. & Goyet, R. A. (1978). *Life Sci.* **23**, 1–9.
- Gale, G. R., Atkins, L. M., Walker, E. M., Smith, A. B. & Jones, M. M. (1984). *Ann. Clin. Lab. Sci.* **14**, 137–145.
- Iwasaki, H. & Kobayashi, K. (1980). *Acta Cryst.* **B36**, 1655–1657.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
- Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Shinobu, L. A., Jones, S. G. & Jones, M. M. (1984). *Acta Pharmacol. Toxicol.* **54**, 189–194.
- Siemens (1994). *XSCANS User's Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

*Acta Cryst.* (1999). **C55**, 176–178

## *trans*-Diaquabis(nicotinamide-*N*)bis(salicylate-*O*)copper(II)

NINA PETROVČIČ, BOJAN KOZLEVČAR, LJUBO GOLIČ, IVAN LEBAN AND PRIMOŽ ŠEGEDIN

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, PO Box 537, SI-1001 Ljubljana, Slovenia. E-mail: nina.petrovcic@uni-lj.si

(Received 23 April 1998; accepted 10 September 1998)

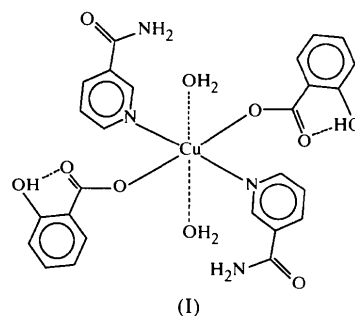
## Abstract

The Cu<sup>II</sup> atom in [Cu(C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] is octahedrally coordinated by N atoms from two nicotinamide ligands [at 2.018(2) and 2.019(2) Å], by O

atoms of two salicylate ligands [at 1.9656(19) and 1.9762(19) Å], and by *trans* water molecules at considerably different distances [2.373(3) and 2.894(4) Å]. Neutral monomeric units are held together by hydrogen bonds through water molecules and N and O atoms of the CONH<sub>2</sub> group of nicotinamide and carboxylate groups.

## Comment

Crystals of the title compound, [Cu(sal)<sub>2</sub>(nia)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], (I), where sal is salicylate (2-hydroxybenzoate, C<sub>7</sub>H<sub>5</sub>O<sub>3</sub><sup>-</sup>) and nia is nicotinamide (C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O), were isolated during systematic work on copper salicylates in our laboratory. The anhydrous form of [Cu(sal)<sub>2</sub>(nia)<sub>2</sub>] exists in both an orthorhombic (Hoang *et al.*, 1993) and a monoclinic form (Leban *et al.*, 1997). Recently, the crystal structure of *trans*-diaquabis(4-hydroxybenzoato-*O*)bis(nicotinamide-*N*)copper(II), with a short account of the structural chemistry and biological activity of these compounds, was also reported (Hökelek *et al.*, 1998). This compound is a crystallographically centrosymmetric complex in which two *trans* water molecules are located at 2.575(2) Å from the Cu<sup>II</sup> atom.



In the majority of monomeric *trans*-diaquacopper(II) complexes, the Cu atom is located either at a centre of symmetry or on a twofold axis, so that the Cu—O distances are the same [a survey of the Cambridge Structural Database (Allen & Kennard, 1993) gave 29 hits]. There are only a few examples where the copper octahedral complex is not centrosymmetric and the water molecules are coordinated either at different distances [e.g. IMDZNB (Kozhemyak *et al.*, 1980) and VANCAO (Biagini Cingi *et al.*, 1989)] or the Cu—O distances are essentially the same [e.g. HEWVAG (Castro *et al.*, 1994) and YUDNAM (Schindler & Szalda, 1995)].

Whereas the complex *trans*-diaquabis(4-hydroxybenzoato-*O*)bis(nicotinamide-*N*)copper(II) is centrosymmetric, the title complex (Fig. 1) crystallizes in the non-centrosymmetric space group *P*2<sub>1</sub> and the distances Cu—OW1 [2.373(3) Å] and Cu—OW2 [2.894(4) Å] are significantly different. This is in accord with previous thermogravimetric data (Kozlevčar *et al.*, 1996),