

## Bis( $\mu$ -3,5-di-*tert*-butylcatecholato-O<sup>1</sup>:O<sup>1</sup>,O<sup>2</sup>)bis[tris(pyridine-*N*)-cadmium(II)] dipyridine solvate

Georgy K. Fukin,<sup>a</sup> Lev N. Zakharov,<sup>a\*</sup> Stanislav V. Maslennikov,<sup>b</sup> Alexander V. Piskunov<sup>b</sup> and Vladimir K. Cherkasov<sup>a</sup>

<sup>a</sup>G. A. Razuvaev Institute of Organometallic Chemistry, Tropinina 49, Nizhny Novgorod, Russia, and <sup>b</sup>Department of Chemistry, Nizhny Novgorod State University, Gagarin 23, Nizhny Novgorod, Russia  
Correspondence e-mail: lz@imoc.sinn.ru

Received 26 February 2001

Accepted 23 May 2001

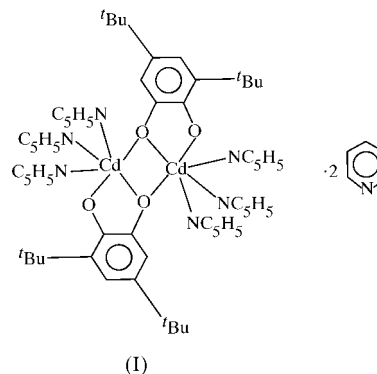
X-ray diffraction shows that the title cadmium(II) complex, [Cd<sub>2</sub>(C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>6</sub>]·2C<sub>5</sub>H<sub>5</sub>N, has a dimeric structure in which two (py)<sub>3</sub>Cd(3,5-di-*tert*-butylcatecholate) units (py is pyridine) are connected by two bridging O atoms, the coordination of the Cd atoms being distorted octahedral. There are two symmetrically independent dimers in the crystal structure; one is in a general position and the other lies about an inversion centre. In both cases, the bridging Cd—O distances between the Cd—catecholate units [2.224 (2)–2.237 (2) Å] are shorter than the bridging Cd—O distances within the catecholate cycle [2.273 (2)–2.281 (2) Å]. The Cd—N<sub>py</sub> distances are 2.354 (2)–2.471 (2) Å. Besides the main molecules, the crystal also contains pyridine solvate molecules.

### Comment

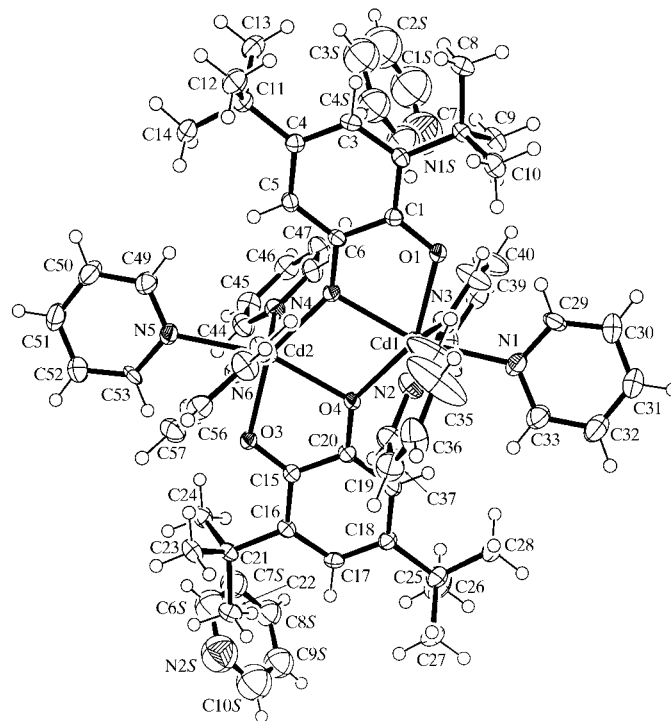
The title complex, (I), was synthesized by the reaction of 3,5-di-*tert*-butyl-1,2-benzoquinone with cadmium in pyridine solution. The X-ray diffraction study shows that (I) is a dimeric complex of cadmium in which the two (py)<sub>3</sub>Cd(3,5-di-*tert*-butylcatecholate) units are connected by two bridging O atoms, the environment of the Cd atoms being a distorted octahedron (Fig. 1). There are two symmetrically independent molecules of (I) in the crystal structure; one is in a general position, (Ia), and the other on an inversion centre, (Ib). Molecule (Ia) has an approximately centrosymmetric structure.

The central Cd<sub>2</sub>O<sub>2</sub> and the two chelate CdO<sub>2</sub>C<sub>2</sub> fragments are planar within 0.004, 0.012 and 0.020 Å, respectively, for (Ia), and within 0.007 and 0.007 Å, respectively, for (Ib). The dihedral angles between the Cd<sub>2</sub>O<sub>2</sub> and the CdO<sub>2</sub>C<sub>2</sub> fragments are 4.43 (14) and 6.15 (13)° for (Ia), and 6.93 (16)° for (Ib). The O—C and C—C distances in the chelate metalocycles in (I) [1.316 (3)–1.343 (3) and 1.440 (4)–1.442 (4) Å, respectively,

are typical for the catecholate ligand (Pierpont & Lange, 1994). The Cd—N<sub>py</sub> distances in (I) are 2.354 (2)–2.471 (3) Å (Table 1).



In both (Ia) and (Ib), the bridging Cd—O distances between the Cd—catecholate units [2.224 (2)–2.237 (2) Å] are shorter than the bridging Cd—O distances within the catecholate cycles [2.278 (2)–2.281 (2) Å]. Similar features have been found in other dimeric and tetrameric catecholate complexes of different metals, *e.g.* Zn (Reynolds & Coucovanis, 1998), Fe (Shoner & Power, 1992) and Co (Olmstead *et al.*, 1988), as well as in the sulfur analogue on Zn, bis( $\mu$ -1,2-benzenedithiolato-*S,S'*; *S,S'*)bis[(2,2'-bipyrimidine-*N,N'*)-zinc(II)] (Gronlund *et al.*, 1995). The non-bridging bonds Cd1—O1, Cd2—O3 and Cd3—O6 [2.206 (2), 2.209 (2) and 2.219 (2) Å, respectively] are shorter than the bridging Cd—O bonds.



**Figure 1**  
The molecular structure of molecule (Ia) and the pyridine solvate molecules, shown with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

Besides the main (*Ia*) and (*Ib*) molecules, the crystal of (*I*) also contains pyridine solvate molecules. No shortened intermolecular contacts were found in the crystal structure of (*I*).

## Experimental

3,5-Di-*tert*-butyl-1,2-benzoquinone was prepared according to the usual method of Muller *et al.* (1957). Pyridine was freshly distilled after drying by standard techniques (Gordon & Ford, 1972). The synthesis of cadmium catecholate was performed under an atmosphere of dry oxygen-free argon. To cadmium turnings (135 mg, 1.2 mmol) was added 3,5-di-*tert*-butyl-1,2-benzoquinone (66 mg, 0.3 mmol) in pyridine (5 ml). The mixture was stirred at 343 K for 48 h. Pyridine (20 ml) was then added under warming to dissolve the yellow precipitate. The resulting hot solution was filtered from the unreacted metal. Slow cooling of the solution gave 150 mg of crystals of (*I*) suitable for X-ray analysis. A second crop of the product (34 mg) was obtained after partial removal of the solvent (yield 92%). The product was air sensitive and decomposes without melting at 532 K.

### Crystal data

$[\text{Cd}_2(\text{C}_{14}\text{H}_{20}\text{O}_2)_2(\text{C}_5\text{H}_5\text{N})_6] \cdot 2\text{C}_5\text{H}_5\text{N}$	$Z = 3$
$M_r = 1298.22$	$D_x = 1.346 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 15.743 (5) \text{ \AA}$	Cell parameters from 95 reflections
$b = 17.549 (6) \text{ \AA}$	$\theta = 5\text{--}27^\circ$
$c = 19.945 (7) \text{ \AA}$	$\mu = 0.72 \text{ mm}^{-1}$
$\alpha = 91.051 (7)^\circ$	$T = 110 (1) \text{ K}$
$\beta = 108.916 (6)^\circ$	Plate, yellow
$\gamma = 111.094 (6)^\circ$	$0.5 \times 0.4 \times 0.1 \text{ mm}$
$V = 4806 (3) \text{ \AA}^3$	

### Data collection

Bruker SMART-1000 CCD area-detector diffractometer	27 455 independent reflections
$\theta/2\theta$ scans	16 608 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.034$
$T_{\text{min}} = 0.456$ , $T_{\text{max}} = 0.931$	$\theta_{\text{max}} = 30.1^\circ$
55 993 measured reflections	$h = -22 \rightarrow 22$
	$k = -24 \rightarrow 24$
	$l = -27 \rightarrow 28$

### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.050$	$w = 1/[\sigma^2(F_o^2) + (0.0665P)^2]$
$wR(F^2) = 0.133$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.96$	$(\Delta/\sigma)_{\text{max}} = 0.045$
27 455 reflections	$\Delta\rho_{\text{max}} = 4.89 \text{ e \AA}^{-3}$
1108 parameters	$\Delta\rho_{\text{min}} = -1.19 \text{ e \AA}^{-3}$

The positions of the H atoms were calculated using  $\text{Csp}^2\text{--H}$  and  $\text{Csp}^3\text{--H}$  distances of 0.93 and 0.96 Å, respectively, and the H atoms were treated as riding in the refinement. In the final difference map,

**Table 1**  
Selected bond lengths (Å).

Cd1—O1	2.206 (2)	O2—C6	1.341 (3)
Cd1—O4	2.224 (2)	O3—C15	1.316 (3)
Cd1—O2	2.278 (2)	O4—C20	1.343 (3)
Cd1—N3	2.381 (3)	C15—C20	1.440 (4)
Cd1—N2	2.404 (3)	Cd3—O6	2.219 (2)
Cd1—N1	2.440 (3)	Cd3—O5 <sup>i</sup>	2.231 (2)
O1—C1	1.323 (3)	Cd3—O5	2.273 (2)
C1—C6	1.441 (4)	Cd3—N8	2.354 (2)
Cd2—O3	2.209 (2)	Cd3—N9	2.376 (3)
Cd2—O2	2.237 (2)	Cd3—N7	2.453 (2)
Cd2—O4	2.281 (2)	O5—C59	1.338 (3)
Cd2—N6	2.373 (2)	O6—C64	1.319 (3)
Cd2—N4	2.384 (3)	C59—C64	1.442 (4)
Cd2—N5	2.471 (2)		

Symmetry code: (i)  $2 - x, 1 - y, -z$ .

there are two relatively high peaks ( $4.88$  and  $4.87 \text{ e \AA}^{-3}$ ) at the Cd atoms ( $Q1\text{--Cd}2$  and  $Q2\text{--Cd}1 = 0.71$  and  $0.72 \text{ \AA}$ , respectively) which cannot be interpreted as real atoms.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SMART*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We are grateful to both the X-ray Structural Centre of the General and Technical Chemistry Division of the Russian Academy of Sciences for kind permission to use the single-crystal diffractometer, and the Russian Foundation of Basic Research (grant Nos. 00-15-97439, 00-03-32807 and 00-03-42004) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1076). Services for accessing these data are described at the back of the journal.

## References

- Bruker (2000). *SMART*. Version 5.06. Bruker AXS Inc., Madison, Wisconsin, USA.
- Gordon, A. & Ford, R. (1972). *The Chemist's Companion. A Handbook of Practical Data, Techniques and References*. New York: Wiley.
- Gronlund, P. J., Wacholtz, W. F. & Mague, J. T. (1995). *Acta Cryst.* **C51**, 1540–1543.
- Muller, E., Ley, K. & Scherker, G. (1957). *Chem. Ber.* **B90**, 1530–1536.
- Olmstead, M. M., Power, P. P. & Sigel, G. A. (1988). *Inorg. Chem.* **27**, 580–583.
- Pierpont, C. G. & Lange, C. W. (1994). *Prog. Inorg. Chem.* **41**, 381–492.
- Reynolds, R. A. III & Coucouvanis, D. (1998). *Inorg. Chem.* **37**, 170–171.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Shoner, S. C. & Power, P. P. (1992). *Inorg. Chem.* **31**, 1001–1010.