

Preliminary communication

**The crystal and molecular structure
of bis[2-((dimethylamino)methyl)phenyl]cadmium(II)**

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Abstract

The crystal and molecular structure of bis[2-((dimethylamino)methyl)phenyl]cadmium(II) compound is reported. The structure consists of trigonally bipyramidal molecules with a vacant axial site. The vacant site is blocked by an adjacent cadmium atom with a relatively short metal–metal separation of 3.176 Å.

There has been considerable interest in, and debate about, the significance of the interaction of nitrogen donors with diorgano derivatives of the group 12 metals [1]. Cyclometallated complexes of these metals with (dimethylaminomethyl)benzene (dmab) were first reported by Atwood et al. [1], but only the mercury complex proved amenable to a single-crystal X-ray study [1]. We now report the unusual crystal and molecular structure of the cadmium complex.

The title complex was obtained, by use of standard Schlenk techniques, from the reaction of monolithiated (dimethylaminomethyl)benzene [2] with anhydrous cadmium chloride in dry tetrahydrofuran. When the solution was kept in a deep freeze (ca. -25°C) for one week, small rhombic crystals separated. These were mounted under an inert atmosphere in thin walled capillary tubes, and X-ray data collected immediately*.

The structure of $\text{Cd}(\text{dmab})_2$ is shown in Fig. 1 and the fractional atomic coordinates are listed in Table 1. The arrangement around each cadmium can be

* The ^1H NMR spectrum was in agreement with that already published [1]. *Crystal data:* $\text{C}_{18}\text{H}_{24}\text{N}_2\text{Cd}$, $M = 380$, orthorhombic, space group $P4n2$, a 12.480(5), b 12.480(8), c 13.003(5) Å, V 2025 Å³, $D_c = 1.248$ gm cm⁻³, $Z = 4$, $\mu(\text{Mo-K}\alpha) 10.7$ cm⁻¹, $R = 0.0512$ ($w = 1/(\sigma^2(F) + 0.0001(F)^2)$, $R_w = 0.0698$) for 2314/2960 reflections ($F > 3\sigma(F_0)$) measured on a diffractometer (Nonius CAD4). Atomic thermal parameters, full lists of bond lengths and angles and F_o/F_c values are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

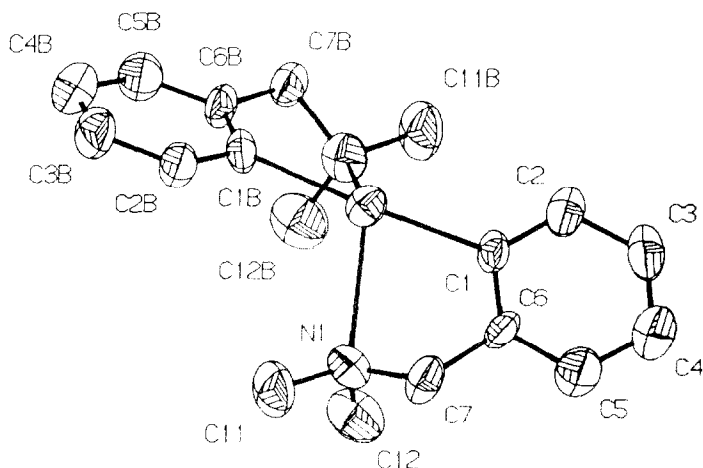


Fig. 1. The structure of the bis[2-(dimethylamino)methyl]phenylcadmium(II), a single atropisomer is shown. Selected bond lengths (Å) and angles ($^{\circ}$) are as follows: C(1)–Cd(1) 2.154(8), Cd(1)–Cd(1a) 3.176(4), N(1)–Cd(1) 2.598(9), C(1)–Cd(1)–C(1b) 174.31(11), N(1)–Cd(1)–C(1) 75.9(3), Cd(1a)–Cd(1)–C(1) 87.16(15), C(2)–C(1)–Cd(1) 127.6(6), C(7)–N(1)–Cd(1) 97.9(7), C(12)–N(1)–Cd(1) 112.1(7), N(1)–Cd(1)–C(1b) 107.22(13), N(1)–Cd(1)–N(1b) 116.12(14), Cd(1a)–Cd(1)–N(1) 121.94(16), C(6)–C(1)–Cd(1) 115.0(7), C(11)–N(1)–Cd(1) 115.9(7).

described as being based on a trigonal bipyramid with a vacant equatorial site; the nitrogen atoms are equatorial, the aryl groups are axial, and each molecule is an atropisomer. The C–Cd–C axis is close to linear, 174° , with a Cd–C bond distance of 2.154(8) Å. This can be compared with other published values [3] for Cd–C distances of between 2.17 and 2.20 Å in some compounds with tris(trimethylsilyl)methyl and related ligands. However, this is the first diaryl cadmium complex to be investigated crystallographically.

In contrast to the structure of the analogous mercury complex [1], the N–M–N linkage here is not linear, the N–Cd–N angle being 116° ; the separation of these atoms in space is thus not maximised. The Cd–N distance 2.598(9) Å is smaller than

Table 1

Fractional atomic coordinates ($\times 10^4$) (with estimated standard deviations in parentheses) for bis[2-(dimethylamino)methyl]phenylcadmium(II)

	<i>x</i>	<i>y</i>	<i>z</i>
Cd(1)	900(5)	5900(5)	2500
C(1)	1780(5)	–5104(5)	3550(5)
C(2)	1578(6)	–5270(5)	4582(6)
C(3)	2276(8)	–5842(7)	5213(7)
C(4)	3212(8)	–6264(7)	4810(8)
C(5)	3416(7)	–6120(7)	3755(7)
C(6)	2737(7)	–5565(8)	3138(7)
C(7)	2966(10)	–5408(10)	1994(10)
N(1)	2737(5)	–4381(5)	1601(5)
C(11)	2717(10)	–4393(12)	476(8)
C(12)	3535(11)	–3637(12)	1962(9)

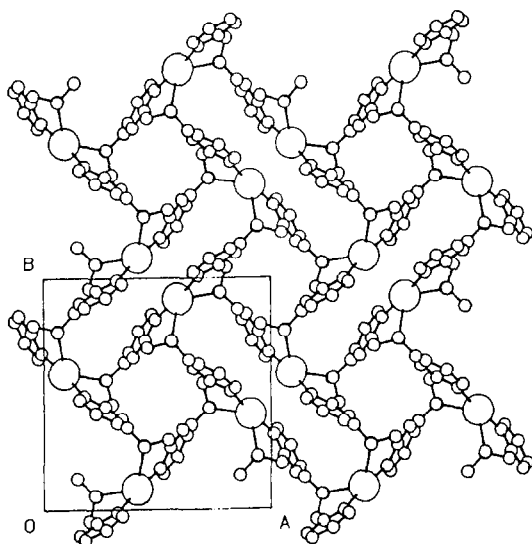


Fig. 2. Packing diagram for the title compound. Note that the paired molecules are of the same configuration; the 'dimeric units' lie on a site of 222 symmetry.

the sum of the Van der Waals radii [4] 3.15 Å, but longer than typical Cd–N distances, which may be exemplified by 2.27 Å in an ammine complex [5] and 2.36 Å in a 2,2'-bipyridyl complex [6].

The crystal packing is shown in Fig. 2. Pairs of molecules of the same absolute configuration face each other so that the unoccupied equatorial coordination site on each is blocked by the cadmium atom of the adjacent complex. The Cd–Cd contact distance is 3.176 Å, which is close to twice the Van der Waals radius of cadmium 3.20 Å [4].

In contrast to the structure of the mercury complex [1], which is fairly unremarkable, the title complex shows an unusual, if not unique, coordination geometry at cadmium. The structure probably reflects the domination of weak crystal packing forces over any electronic factors associated with the interaction between the lone pair on nitrogen and cadmium. The orientation of the nitrogens bears no obvious relationship to a simple hybridization scheme at cadmium. The unusual coordination mode for cadmium emphasises that, for a labile complex with weak bonds, the solid state structure may not be useful as a guide to electronic effects.

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