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Notes

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Aspects of Organocadmium Chemistry. 3.[1] Chelate-Supported Alkyls and Aryls of Zinc, Cadmium, and Mercury: Crystal and Molecular Structure of Bis[2-((dimethylamino)methyl)phenyl]mercury(II)

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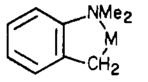
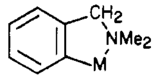
In exploring further the relative propensity toward complex formation with nitrogen donors of diorganozinc, -cadmium, and -mercury derivatives,[1,4] we have synthesized a series of such compounds in which cyclization may occur by coordination through N to the metal center. This was achieved by introducing functionalized organo substituents through reactions of the lithio reagents derived from *N*,*N*-dimethyl-*o*-toluidine or *N*,*N*-dimethylbenzylamine, which have previously been used by Manzer and Guggenberger to obtain cyclometalated transition-metal complexes of types A and B, respectively.[5,6] In this way we were able to isolate the new compounds MR_2: R = *o*-(dimethylamino)benzyl, type A for M = Zn (**1**) or Cd (**2**) and R = *o*-((dimethylamino)methyl)phenyl, type B for M = Zn (**3**), Cd (**4**), or Hg (**5**). However, yields and crystal quality were consistently poor except for the mercury diaryl (**5**), and although compounds **1**–**4** showed enhanced thermal stability over simple two-coordinated diorgano species, they were still found to be rather air and light sensitive. Such considerations combined to frustrate the principal objective of this study, which was a structural comparison by X-ray crystallography of an appropriate trio of homoleptic Zn, Cd, and Hg derivatives. The structure of bis[2-((dimethylamino)methyl)phenyl]mercury(II) has been determined, however, revealing an intramolecular Hg–N distance of 2.89 (1) Å, a result which bears significantly on arguments advanced in the recent literature[7,8] relating to mercury–nitrogen bonding.



A



B

Experimental Section

(a) Syntheses. Compounds **1**–**5** were synthesized with use of standard inert-atmosphere techniques by treatment of dry MCl_2 in THF solution with Li reagents prepared from *N*,*N*-dimethyl-*o*-toluidine or *N*,*N*-dimethylbenzylamine, as described by Manzer and Guggenberger.[5,6] The following procedure is representative:

To a stirring solution of $HgCl_2$ (8.8 g, 32 mmol) in THF (40 mL) was added over 0.5 h a THF solution of $LiC_6H_4CH_2NMe_2$ (9.1 g, 65 mmol). After 18 h at ambient temperature the mixture was evacuated to dryness and extracted with Et_2O to give a pale yellow solution. On reduction of the volume and cooling, large colorless plates of the *product* (**5**) were formed (37%); mp 68 °C. Anal. Calcd for $C_{18}H_{24}HgN_2$: C, 46.11; H, 5.16; N, 5.97. Found: C, 46.10; H, 5.22; N, 5.92.

The diorganozinc and -cadmium derivatives **1**–**4** were isolated in low yields (<20%) from reactions which parallelled that described above. The white *products*, mp 97, 66, 87, and 110 °C, respectively, which were identified initially by IR spectroscopy and by the ^1H and ^{13}C NMR measurements (Table I), precipitated as powders that could not be induced to crystallize. The solid materials darkened on exposure to air and/or daylight, and combustion analysis was not attempted; however, each compound proved to be sufficiently volatile for further characterization by mass spectrometry, and using CH_4 chemical ionization (Finnegan 3300: GC–MS unit) showed polyisotopic fragment ions as follows (*m*/*e*: *M* = calculated molecular weight in amu): **1**, 361 (*M* + 29), 333 (*M* + 1); **2**, 383 (*M* + 1); **3**, 361 (*M* + 29), 333 (*M* + 1); **4**, 383 (*M* + 1); **5**, 511 (*M* + 41), 499 (*M* + 29), 471 (*M* + 1). Fragmentation under electron impact was not investigated.

Reaction of an analytically pure sample of the mercury compound (**5**) with Zn powder (7 days, 25 °C, THF) afforded in quantitative yield a product shown by IR and NMR spectroscopy to be identical with the zinc derivative (**3**) obtained as indicated above. Under conditions that led to formation of compounds **1** and **2**, reaction with $HgCl_2$ failed to generate a mercury analogue.

(b) X-ray Data Collection and Refinement. The unit cell was uniquely determined to be $P2_1/n$ by observation of the systematic absences $0k0$, $k = 2n$, and $h0l$, $h + l = 2n$. Data collection was carried out by utilizing the parameters outlined in Table II, and 968 reflections were considered observed ($I > 3\sigma(I)$). The intensities were corrected for Lorentz, polarization, and absorption (μ = 83.2 cm^{-1}) effects.

The fact that only two molecules could be accommodated in the unit cell led us to believe that the mercury was positioned at an inversion center. The fairly rigid adherence to the condition hkl, $h + k + l = 2n$, that would be so imposed backed up this assumption. Placement of the mercury at an inversion center gave an *R* value of 0.18, and the subsequent difference Fourier revealed the coordinates of the remaining non-hydrogen atoms. After full-matrix least-squares refinement of the non-hydrogen atoms, it was possible to locate the methylene hydrogen atoms. The phenyl hydrogens were placed at calculated positions (C–H = 0.98 Å), and then four more cycles of least-squares refinement were conducted with all hydrogens riding on the appropriate carbon. This led to final values of $R\ [=\sum||F_o| - |F_c||/\sum|F_o|] = 0.047$ and $R_w\{=[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}\} = 0.058$. All refinements were carried out by using the Busing and Levy full-matrix least-squares program ORFLS. (Other crystallographic programs used on a UNIVAC 1110 computer include ORTEP (thermal ellipsoid drawings, by C. K. Johnson) and BPL (least-squares planes, by W. E. Hunter.) No corrections were made for extinction. Neutral-atom scattering factors were taken from the compilations of Cromer and Waber[9] for Hg, N, and C, whereas those for H were taken from ref 10.

Results and Discussion

Atomic parameters and bond distances and angles are collected in Tables III and IV. Thermal parameters, hydrogen atom coordinates, and the best least-squares plane for the molecule are available in supplementary Tables S1–S3. Two views of the molecule are shown in Figure 1, emphasizing the centrosymmetric arrangement in which geometry about the Hg atom is planar and also lies close to coplanarity with both the coordinating phenyl ring systems. The C–Hg–C axis is

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Table I. ^{1}H and ^{13}C NMR Spectral Data[a]

	^{1}H			^{13}C		
compd	CH_3	CH_2	C_6H_5	CH_3	CH_2	C_6H_5
1	2.32 (6)	1.43 (2)	6.90 br 7.24 br } (4)	45.4	13.1	117.8, 122.9, 124.7, 131.0, 145.9,[b] 150.6[b]
2	2.38 (6)	1.67 (2)	6.90 br 7.20 br } (4)	44.8	19.7	117.9, 122.5, 123.9, 130.0, 140.0,[b] 150.0[b]
o-$CH_3C_6H_4NMe_2$	2.62 (6)	2.29 (2)	7.00 br (4)	44.0	18.2	118.3, 122.6, 126.4, 131.0, 131.9,[b] 152.7[b]
3	2.33 (6)	3.63 (2)	7.70 br (3) 7.15 br (1)	46.0	67.8	124.8, 125.9, 139.3, 146.9,[b] 156.7[b]
4	2.28 (6)	3.45 (2)	7.11 br (3) 7.70 br (1)	45.8	68.1	126.0, 126.2, 126.6, 140.2, 147.3[c]
5	2.24 (6)	3.42 (2)	7.23 br (3) 7.47 br (1)	45.2	67.2	126.3, 126.7, 128.5, 138.1, 147.3,[b] 170.3[b]
$C_6H_5CH_2NMe_2$	2.20 (6)	3.36 (2)	7.27 (5)	44.7[d]	63.7[d]	126.3, 127.5, 128.2, 138.6[b]

[a] All spectra recorded in $CDCl_3$; chemical shifts (ppm positive) downfield from Me_4Si. Relative intensity in ^{1}H spectra given in parentheses; br = broad. The ^{1}H data were recorded on a Perkin-Elmer R32 spectrometer (90 MHz); ^{13}C data were obtained with a Nicolet TT-14 Fourier transform NMR spectrometer (15.1 MHz). [b] Reduced peak intensity due to diminished nuclear Overhauser enhancement. [c] Sixth resonance not observed. [d] Assignment confirmed by ^{1}H–^{13}C coupling pattern in gated ^{13}C spectrum.

Table II. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $Hg(NC_9H_{12})_2$

formula	$C_{18}H_{24}HgN_2$
diffractometer	Enraf-Nonius CAD-4
mol wt	469.0
cryst system	monoclinic
space group	$P2_1/n$
cell constants	
a, Å	6.186 (3)
b, Å	12.146 (5)
c, Å	12.095 (5)
β, deg	101.46 (4)
cell vol, Å	890.6
molecules/unit cell	4
ρ(calcd), g cm^{-3}	1.75
μ(calcd), cm^{-1}	83.2
radiation	Mo Kα
max cryst dimens, mm	0.31 × 0.32 × 0.39
scan width, deg	0.85 + 0.20 tan θ
std reflcns	400, 040, 004
decay of stds	±2%
reflcns measd	1927
2θ range, deg	1-50
reflcns, $I \geqslant 3\sigma(I)$	968
no. of parameters varied	97
largest parameter shift/esd	0.01
GOF	3.39
R	0.047
R_w	0.058

Table III. Final Fractional Coordinates for $Hg(NC_9H_{12})_2$

atom	x/a	y/b	z/c
Hg	0.000	0.000	0.000
N	0.295 (2)	0.030 (1)	0.215 (1)
C(1)	0.235 (3)	−0.127 (1)	0.023 (1)
C(2)	0.426 (3)	−0.118 (1)	0.100 (1)
C(3)	0.586 (3)	−0.199 (2)	0.108 (2)
C(4)	0.547 (4)	−0.291 (2)	0.044 (2)
C(5)	0.356 (4)	−0.302 (2)	−0.038 (2)
C(6)	0.197 (3)	−0.220 (2)	−0.048 (2)
C(7)	0.484 (3)	−0.015 (2)	0.171 (1)
C(8)	0.352 (4)	0.143 (2)	0.260 (2)
C(9)	0.236 (4)	−0.042 (2)	0.299 (2)

Table IV. Bond Distances and Angles

(a) Distances (Å)

Hg–C(1)	2.10 (2)	Hg–N	2.89 (1)
C(1)–C(2)	1.35 (2)	C(1)–C(6)	1.41 (2)
C(2)–C(3)	1.39 (2)	C(2)–C(7)	1.52 (3)
C(3)–C(4)	1.36 (3)	C(4)–C(5)	1.39 (3)
C(5)–C(6)	1.39 (3)	N–C(7)	1.48 (2)
N–C(8)	1.50 (2)	N–C(9)	1.44 (2)

(b) Angles (deg)

N–Hg–N′	180	C(1)–Hg–C(1)′	180
C(1)–Hg–N	71 (1)	C(7)–N–Hg	92 (1)
C(8)–N–Hg	120 (1)	C(9)–N–Hg	111 (1)
C(1)–Hg–N′	109 (1)	Hg–C(1)–C(6)	119 (1)
Hg–C(1)–C(2)	121 (1)	C(2)–C(3)–C(4)	120 (2)
C(1)–C(2)–C(3)	120 (2)	C(4)–C(5)–C(6)	119 (2)
C(3)–C(4)–C(5)	121 (2)	C(1)–C(2)–C(7)	122 (2)
C(5)–C(6)–C(1)	120 (2)	C(2)–C(7)–N	113 (1)
C(3)–C(2)–C(7)	117 (2)	C(7)–N–C(9)	111 (1)
C(7)–N–C(8)	109 (2)	C(8)–N–C(9)	112 (2)

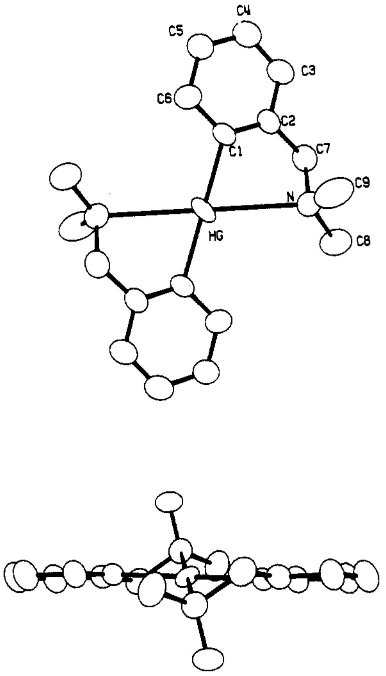

Figure 1. Molecular geometry of compound **5**: (a) perpendicular and (b) parallel to the mercury coordination plane.

constrained exactly to linearity by crystallographic symmetry with Hg–C = 2.10 (2) Å, in close agreement with values reported previously for the three diaryls HgR_2: R = Ph,[11] C_6F_5,[12] or 2,4,6-C_6H_2-t-Bu_3.[13] Other bond lengths in the structure are unremarkable, but the orientation of the dimethylamino groups is immediately striking in that it brings the N atom near its closest possible approach to Hg, at 2.89 (1) Å.

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What does and what does not constitute a mercury–nitrogen bonding interaction has been exhaustively reviewed in a succession of papers by Canty et al.,[7,8,14] but the kind of orbital overlap that might lead to an increase in coordination number at Hg in HgA_2 derivatives while maintaining linearity of the A–Hg–A configuration has not been satisfactorily addressed in circumstances where A is not electron withdrawing. The structure of **5** reasserts this problem. On the basis of an interpretation[8] in which an Hg–N contact of 2.96 (2) Å is *definitely bonding* and Hg–As = 3.40 (5) Å in $[(C_6F_5)_2HgAsPh_2]_2CH_2$ should be viewed as *a significant interaction*, the ((dimethylamino)methyl)phenyl groups in **5** are clearly functioning as unsymmetrical chelating ligands (type B), i.e., with coordinate bonding from N to Hg. However, like the CHgC vector, the NHgN linkage is strictly linear, these two intersecting one another at 71° (Figure 1). Thus, any interpretation based[7] on electron donation of LP (lone pair) density on N into empty mercury $6p_{x,y}$ orbitals must necessarily involve only one of the latter. A similar conclusion can also be applied to several of the structures described by Canty and co-workers,[7,14] in which rather distant donor atoms face each other at or very close to 180° across a linear HgA_2 or HgAB unit in which bonds to A and B are short. Where A and/or B are strongly electron-withdrawing substituents 4- or 6-coordinate structures may result from addition of neutral ligands, attached by bonding that is largely ionic, in arrangements explicable in terms of simple electrostatics.[15] In these circumstances d–s mixing has also been invoked to account for distorted digonal coordination; such a situation, however, is held to be unlikely in diorganomercurials, for which feeble acceptor properties have been related to low charge on the metal and predominance of sp hybridization.[16] It should also be noted in this context that recently a more complex view of valence–orbital energy relationships for heavy atoms (e.g., 5d elements) has begun to emerge on the basis of relativistic effects.[17] In this note we simply wish to point out that interpretation of the structure adopted by compound **5** (and others like it[7,14]) seems to require either (a) d–s mixing in circumstances where this has hitherto been regarded as unlikely or (b) donation into a single acceptor orbital ($6p_x$ or $6p_y$) of electron density simultaneously from two donor LP hybrids, necessitating an orbital description based on three-center delocalized bonding and coincidentally predicating a long Hg–N distance, as is observed.

The long mercury–nitrogen bond in **5** may be placed in context by reference to structural data for other metal derivatives incorporating the chelate arrangement (B). The description of transition-metal 2-((dimethylamino)methyl)phenyl derivatives[5,6] has recently been extended to include crystallographic characterization for two chromium species;[18] while the structure of one of these is particularly interesting, it has no direct bearing on the present discussion. However, diphenyl(2-((dimethylamino)methyl)phenyl)tin(IV) bromide has also been investigated[19] by X-ray methods, revealing a pentacoordinate geometry that arises through intramolecular chelation. The resulting Sn–N bond (trans to Br) is unusually long, a result which indicates that chelating interaction involving the dimethylamino residue in $2\text{-}Me_2NCH_2C_6H_4$ metal compounds can in certain circumstances be weak. This conclusion is substantiated by a temperature dependence observed in the NMR spectra of a range of (2-((dimethylamino)methyl)phenyl)silanes, interpreted[20] in terms of dissociation of a pentacoordinate structure via reversible detachment of N from Si.

The spectroscopic data for **1**–**5**, particularly the NMR results given in Table I, provide disappointingly little further insight in terms of structure. The lack of any conspicuous changes over the series **3**–**5** suggests that a common geometry exists in solution for the three molecules, and this may correspond to the chelated arrangement characterized by the X-ray study of the mercury compound (**5**). One unusual feature encountered for the latter is the resolution of spin coupling to ^{199}Hg of both methylene C and H nuclei in appropriate spectra, both rather large at ^3J = 63 and ^4J = 18 Hz, respectively.

Acknowledgment. We thank the NSF (U.S.) and the NSERC (Canada) for financial support.

Registry No. **1**, 87101-91-5; **2**, 87101-92-6; **3**, 85380-67-2; **4**, 87101-93-7; **5**, 81352-61-6; $o\text{-}CH_3C_6H_4NMe_2$, 609-72-3; $C_6H_5CH_2NMe_2$, 103-83-3.

Supplementary Material Available: Listings of thermal parameters, least-squares planes, and observed and calculated structure factors for compound **5** (9 pages). Ordering information is given on any current masthead page.

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A Pulse Radiolysis Study of (Imidazole)pentaamminecobalt(III) Perchlorate in Water: Ligand to Metal Electron Transfer

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The inner-sphere electron-transfer mechanism involves the prior formation of a binuclear complex in which the metal centers of the oxidant and reductant are bridged by a ligand through which electron transfer occurs.[1] Ligand radicals have been suggested as intermediates in the metal ion reduction of many cobalt(III) ammine complexes.[2] Generally, detection of these putative intermediates has been frustrated by their short lifetimes, although limited evidence has been obtained by stopped-flow spectroscopy.[3] Recently, however, the radical binuclear intermediate, generated by the reaction of (pyrazine-2-carboxylato)pentaamminecobalt(III) with chromous ion, has been observed by ESR spectroscopy.[4] The prospect

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