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Preliminary Communication

$HB(3,5\text{-}Me_2pyrazolyl)_3^-$ as an encapsulating ligand for Ba^{II} *

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Abstract

Reaction of BaI_2 with $K[HB(3,5\text{-}Me_2pz)_3]$ in THF gives $Ba[HB(3,5\text{-}Me_2pz)_3]_2$, which retains its solid-state S_6 symmetry in THF solution. The large metal ion is effectively shielded from intermolecular interactions. There are no short intramolecular methyl/Ba contacts. The metal thus has coordination number six, with a Ba–N bond length of 2.760(1) Å and an intraligand angle ∡N–Ba–N of 71.48(5)°.

The design of volatile metal complexes consists of minimizing intermolecular interactions while minimizing molecular weight. The challenge is particularly acute for neutral compounds of bivalent metals, for which the two required anionic ligands must be supplemented by adequate steric effects and/or additional donor functionality [1]. The response to this problem for Ba^{II} (needed for chemical vapor deposition (CVD) applications) began with use of β-diketonate derivatives, which exhibit an unfortunate tendency for aggregation via a bridging ligand oxygen [2]. The demand of a large metal such as Ba^{II} for high (up to 10 in molecules) coordination number [3] has led to incorporation of NH_3, H_2O and MeOH ligands, but these cause aggregation by intermolecular hydrogen bonding [4]. The next development in the use of β-diketonates was the employment of both acyclic [5] and cyclic [6] polyethers as co-ligands. Although some of these species are liquids at room temperature, their CVD performance is marred by the loss of neutral ligands on attempted volatilization. One proposed remedy is to have a donor center covalently linked to the anionic ligand [7,8]. We report here a further step in attacking this problem, which involves use of a combination of steric hindrance and "pendant donor" functionality in a readily-available ligand.

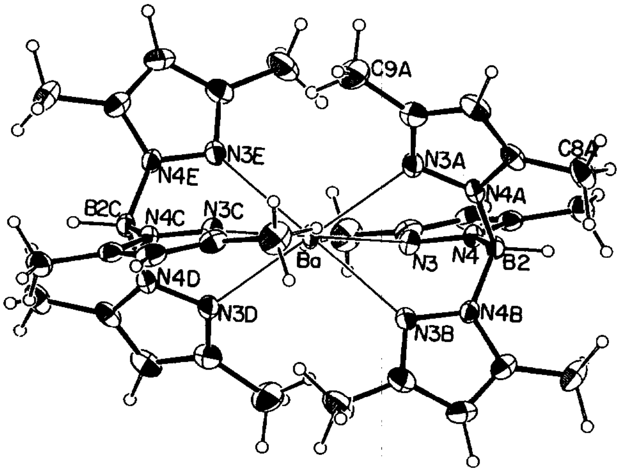

Fig. 1. ORTEP drawing of $Ba[HB(3,5\text{-}Me_2pz)_3]_2$ showing selective atom labelling. Open circles are hydrogen, unlabelled ellipses are carbon, and the crystallographic S_6 axis lies horizontally in this view.

Reaction of BaI_2 with $KHB(3,5\text{-}Me_2pz)_3$ in THF, followed by filtration to remove KI and slow evaporation of solvent in a stream of dinitrogen, gave large crystals of $Ba[HB(3,5\text{-}Me_2pz)_3]_2$ [9]. Proton and $^{13}C\{^1H\}$ NMR spectra in THF-d_8 reveal S_6 symmetry (*i.e.*, there are six equivalent $3,5\text{-}Me_2pz$ rings, with chemical shifts distinct from those of $KHB(3,5\text{-}Me_2pz)_3$ [10*]). A single-crystal X-ray diffraction study [11*] (Fig. 1) shows the molecule to have crystallographic S_6 symmetry, with six-coordinate barium, a Ba–N distance of 2.760(1) Å and an intra-ligand N–Ba–N angle of 71.48(5)°. As is evident from Fig. 1, barium is not coplanar with the otherwise planar $3,5\text{-}Me_2pz$ ring, but the N–B–N angle (111.2°) is unexceptional. The $HB(3,5\text{-}Me_2pz)_3^-$ ligand is thus exceptionally adaptable to metals of very different size (compare $Mg[HB(3,5\text{-}Me_2pz)_3]_2$ with Mg–N = 2.169(2)–2.197(3) Å and ∡N–Mg–N = 85.6–87.0°) [12].

Efforts to encapsulate Ba^{II} with two $C_5(alkyl)_5$ anions are promising, but the two rings are bent "back"

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* In honor of the 65th birthday of Michael Lappert, a leader in the study of bulky ligands.

* Reference number with asterisk indicates a note in the list of references.

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(*i.e.*, towards one another), leaving an open side of the metal coordination sphere which can interact intermolecularly (in the case of $(C_5Me_5)_2Ba$ [13]) or intramolecularly (in the case of $(C_5{}^iPr_4H)_2Ba$ [14]). The latter compound is the most volatile organobarium compound yet reported (subliming at 90°C and 0.01 torr). In the pyrazolate derivative, the pyrazole methyl groups show no tendency to interact intermolecularly. The shortest intermolecular distance (C8′/Ba) is 5.23 Å. The *intra*molecular C9A/Ba distance is 4.01 Å, which is nonbonding. In spite of the absence of intermolecular interactions in $Ba[HB(3,5\text{-}Me_2pz)_3]_2$, the melting point is high (308–314°C) and the volatility low (a temperature of 143°C at 3×10^{-5} torr is needed) compared with that of $(C_5{}^iPr_4H)_2Ba$.

It is of interest that the $HB(3,5\text{-}Me_2pz)_3^-$ ligand has recently been shown [15] to be able to suppress the stereochemical activity of the lone pair of Pb^{II} in $Pb[HB(3,5\text{-}Me_2pz)_3]_2$. This was attributed to the fact that end-to-end (interligand) repulsions would be excessive if the molecule were distorted away from S_6 symmetry (by lone pair "expression"). We find the Ba^{II} compound to be isomorphous with that of Pb^{II}, and so intramolecular interligand repulsions are accommodated identically in both compounds. As a consequence, the metal in $Ba[HB(3,5\text{-}Me_2pz)_3]_2$ is completely shielded from possible intermolecular interactions (as well as from coordination of THF) even though barium is the largest metal so far coordinated by $HB(3,5\text{-}Me_2pz)_3^-$ [16*].

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10 ^1H NMR (300 MHz, 25°C): δ 2.04 (s, 18H, CH_3), 2.11 (s, 18H, CH_3), 5.51 (s, 6H, CH) for $KHB(3,5\text{-}Me_2pz)_3$. δ 1.93 (s, 18H, CH_3), 2.28 (s, 18H, CH_3), 5.61 (s, 6H, CH) for $Ba[HB(3,5\text{-}Me_2pz)_3]_2$. $^{13}C\{^1H\}$ NMR (75.4 MHz, 25°C): δ 12.90 (s, CH_3), 14.06 (s, CH_3), 103.74 (s, CH), 143.74 (s, ring carbon), 145.91 (s, ring carbon) for $KHB(3,5\text{-}Me_2pz)_3$. δ 13.29 (s, CH_3), 13.47 (s, CH_3), 105.22 (s, CH), 145.05 (s, ring carbon), 148.06 (s, ring carbon) for $Ba[HB(3,5\text{-}Me_2pz)_3]_2$.

11 Crystallographic data (−165°C): $a = 11.123(2)$, $c = 25.495(5)$ Å with $Z = 3$ in space group $R\bar{3}$. $R(F) = 0.0189$ and $R_W(F) = 0.0196$ with 1404 reflections with $F > 3\sigma(F)$ and anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were refined. Tables of atom coordinates and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

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