Alkaline Earth Diazapentadienyl Compounds: Structure of $[Ba_2\{(C_6H_{11})NC(Me)CHC(Me)\text{-}N(C_6H_{11})\}_3\{(SiMe_3)_2N\}]$**

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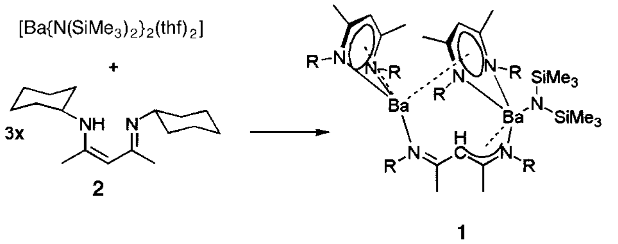
Dedicated to Dr. Ronald Snaith
on the occasion of his 50th birthday

Interest in encapsulation of barium ions in covalent sheaths for chemical vapor deposition (CVD) of superconducting oxides has stimulated investigation of the coordination chemistry of barium. Of all ligand platforms, β-diketonates have been much the most studied,[1] followed by substituted cyclopentadienyl ligands.[2] Indeed, barium cyclopentadienyl complexes (and indenyl and fluorenyl complexes) comprise virtually the entire state of current structural knowledge of barium organometallic compounds.[2, 3] We chose to apply the diazapentadienyl (DAP) ligand system[4] to the problem of enforcing molecularity upon barium compounds for CVD. The DAP ligand has much in common with the β-diketonate family, but we reasoned on the basis of our earlier work on lithium complexes of this ligand class[4j] that it would be less likely to bridge two metals. Moreover, we considered that the DAP ligands may show some of the character of their pentadienyl parents,[5] thus adding to the recent extension of organometallic chemistry of barium beyond that of five-membered π-bonded rings (a solvate of the barium salt of 2-pyridylphenylmethane has been recently characterized).[6]

The reaction shown in Scheme 1 yielded small crystals of **1**. Solution and refinement of the structure of **1** from data collected by using synchrotron X-radiation[7] provided the first structural information on alkaline earth DAP complexes,[8] in which this versatile ligand type[4] is found in *three* different bonding modes, *two* of which are novel, all within the same dinuclear molecule.



Scheme 1. Synthesis of **1**. R = cyclohexyl.

The complex retains a single terminal bis(trimethylsilyl)amido ligand from the starting material.[9] It is somewhat surprising that this amido unit, so often found in a bridging role, is terminal. Instead, the bridging function is undertaken by two DAP ligands in an unprecedented fashion (Figure 1):[10] One DAP ligand chelates Ba1 through N4 and N5 with bond lengths similar to those determined in β-ketoiminatobarium complexes.[11] The NCCCN core of this ligand is nearly planar (root mean square (RMS) deviation: 0.017 Å), with a moderately obtuse envelope angle (defined as the angle between the NCCCN mean plane and the NBaN plane) of 139.9°. This unremarkable envelope angle[12] indicates that N4 and N5 are σ-bonded to Ba1. However, on the other side of this ring Ba2 lies at a much sharper envelope angle of 99.3°, which would seem to indicate that this ligand is π-bonding to Ba2. The Ba2–C30, Ba2–C32, and Ba2–C33 lengths are somewhat longer than the π bonds in $[(i\text{Pr}_4C_5H)_2Ba]$[2b] (mean Ba–C: 2.94(2) Å). Rather, the situation is more akin to that in $[Ba\{(Pz^*)_3Ge\}_2](Pz^* = 3,5\text{-dimethylpyrazol-1-yl})$,[13] where two Pz* rings bind to Ba side-on, principally through Ba–N contacts (mean Ba–N: 2.947 Å; cf. mean Ba2–N4/N5: 2.984(5) Å). In the Pz* ring (a cyclic analogue of DAP), the Ba–C distances are also rather long (mean 3.409 Å).[13] However, the role of the bridging ligand in **1** as a π donor to Ba2 is not in doubt; its presence in that region forces the other bridging ligand into a most unusual conformation (vide infra). Another DAP ligand binds in a more conventional terminal mode, principally through N6 and N7, with rather shorter σ bonds to Ba2. The envelope angle of 107.9° and the shorter Ba–C bonds indicate considerable η^5 character.

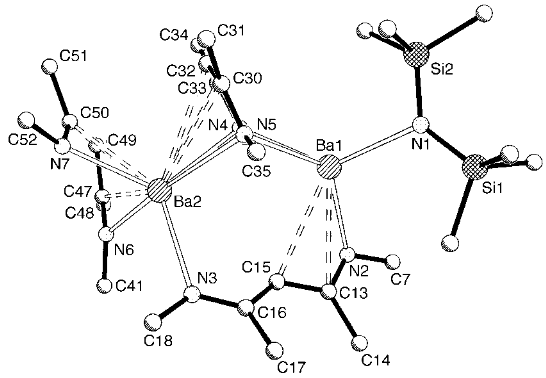


Figure 1. Crystal structure of **1**. Hydrogen atoms and methylene carbon atoms of the cyclohexyl groups are omitted for clarity. Selected bond lengths [Å]: Ba1–N1 2.613(4), Ba1–N2 2.703(4), Ba1–N4 2.829(4), Ba1–N5 2.841(4), Ba1–C15 3.125(5), Ba1–C13 3.192(5), Ba2–N 7 2.635(4), Ba2–N 6 2.689(4), Ba2–N4 2.860(4), Ba2–N3 2.873(4), Ba2–N5 3.108(4), Ba2–C50 3.161(5), Ba2–C49 3.202(5), Ba2–C30 3.210(5), Ba2–C47 3.244(5), Ba2–C32 3.345(5), Ba2–C33 3.408(5), N2–C13 1.327(7), N3–C16 1.317(6), N4–C30 1.335(7), N5–C33 1.317(6), N6–C47 1.313(7), N7–C50 1.321(6), C13–C15 1.425(7), C15–C16 1.424(7), C30–C32 1.429(7), C30–C33 1.423(7), C47–C49 1.426(8), C49–C50 1.416(7).

The coordination of Ba2 is completed by a σ bond to N3 of the third DAP ligand, which in fact appears to bond more in

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the manner of a 1-aza-allyl fragment to Ba1. This novel opening of the ligand into a W-conjugated conformation is notable because methyl groups reside in the 2- and 4-positions (C14 and C17; Figure 1). A loose analogy may be drawn with pentadienylmagnesium, which adopts a W-conjugated, σ-C-bonded structure in its complex with tetramethylethyenediamine, but which is converted to a U-shaped structure in the 2,4-dimethyl-substituted congener, even while remaining as a η^1 ligand.[5] In **1** the disfavored Me–Me interaction is moderated by a slight out-of-plane twisting of the two methyl groups, but overall, the W-conjugated DAP fragment is close to planar (RMS deviation from N2-C13-C15-C16-N3 plane: 0.070 Å). The ligand adopts this unusual mode to relieve steric interaction between its own cyclohexyl groups and those of the other bridging ligand, these now being orthogonally disposed. Though the bond lengths within the W-conjugated DAP are indicative of full delocalization, Ba1 binds to the ligand in a η^3-1-aza-allyl mode, and lies 1.922 Å above the N2-C13-C15 plane. The most comparable structure is a recent 1-azapentadienyl complex in which potassium ions lie above and below the first three atoms of the delocalized anion to form a polymeric structure.[14] However, in that case the 1-azapentadienyl unit adopts a "sickle", and not a W conformation. Within Group 2 chemistry, there are no structurally characterized aza-allyl complexes, and within heavy alkaline earth organometallic chemistry as a whole there are only two noncyclic ligands in structurally determined complexes, $[Ca(2,4\text{-}t\mathrm{Bu}_2C_5H_5)_2(thf)]$, which also adopts a U-shaped η^5 conformation,[15] and the aforementioned $[Ba\{PhCH(C_5H_4N\text{-}2)\}_2(thf)\{MeO(CH_2)_2\}_2O]$.[6]

While we failed in our original intention to produce monomeric barium complexes for CVD due to the determination of the barium ions to raise their coordination number and hence the nuclearity of the molecule, the unexpected contortions undergone by the ligands in fulfilling this task have contributed to a new chapter in heavy alkaline earth organometallic chemistry,[3] a chapter which should rapidly expand if the prevalence for π bonding revealed here approaches that recently established for the similarly sized potassium ion.[16] Indeed, this prevalence may explain the differing regiochemistry and superior selectivity of electrophilic attack upon allylbarium reagents over their lithium or magnesium counterparts.[17] Other workers employing N-centered ligands of higher denticity have obtained monomeric barium complexes,[13, 18] though compounds with sufficiently low lattice energies to qualify as attractive CVD agents have yet to appear from this approach. We are continuing the search for the optimum encapsulation topology by replacing the cyclohexyl arms of our ligand with ether-containing lariats.[11]

Experimental Section

2: After the procedure of Hansson et al.,[19] addition of $TiCl_4$ (6 mL, 54.7 mmol) in *n*-hexane (10 mL) to an ice-cooled solution of cyclohexylamine (35 mL, 150 mmol) in *n*-hexane (75 mL) with stirring (10 min) caused formation of an orange solid. At room temperature, 2,4-pentanedione (2.5 mL, 25 mmol) was added dropwise. The mixture was agitated by magnetic stirring and ultrasound (1 h). Diethyl ether (100 mL) was added, and the mixture was filtered. Slow removal of solvent from the filtrate produced crystals (1.5 g, 23%) of **2.** M.p. 58–60. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.5-1.85$ (m, 20H, $CH(CH_2)_5$), 1.89 (s, 6H, *Me*CCHCMe), 3.4(quintet,2H, $CH(CH_2)_5$),4.39 (s, 1H, MeCC*H*CMe), 11.4 (br s, 1H, N*H*). FAB-MS: *m*/*z*: 263 [*M*H$^+$]. Satisfactory C, H, and N analyses were obtained.

1: Under a dry argon blanket, 40–60 petroleum ether (10 mL) was added to $[Ba\{N(SiMe_3)_2\}_2(thf)_2]$ (0.49 g, 0.825 mmol)[9] and **2** (0.256 g, 0.95 mmol). The solution was evaporated to dryness and redissolved in toluene (5 mL). Very small crystals of **1** · toluene (0.193 g, 0.147 mmol, 35.67% based on barium) formed overnight at −25 °C. M.p. 126–130 °C. ^{1}H NMR (200 MHz, C_6D_6, 293 K): $\delta = 0.53$ (s, 18H, $Si(CH_3)_3$), 1.4–2.2 (m, 60H, $CH(CH_2)_5$), 2.22 (br s, 18H, $(CH_3C(NR)CHC(NRBa)CH_3)$, 3.58 (br septet, 6H, $N(CH(CH_3)_5)$, 4.3-5.3 (br s 3H, $CH_3C(NR)CHC(NRBa)$-CH_3). Satisfactory C, H and N analyses were obtained for **1** · toluene.

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[8] Crystal data: $C_{64}H_{113}Ba_2N_7Si_2$, $M_r = 1311.47$, triclinic, space group $P\bar{1}$, $a = 13.2834(2)$, $b = 14.2820(3)$, $c = 19.4521(4)$ Å, $\alpha = 80.399(1)$, $\beta = 88.190(1)$, $\gamma = 70.442(1)^\circ$, $V = 3427.5(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.271$ g cm^{-3}; synchrotron radiation (CCLRC Daresbury Laboratory Station 9.8,[6] silicon monochromator, 0.6879 Å), $\mu = 1.22$ mm^{-1}, $T = 160$ K. 17453 data (13177 unique, $R_{int} = 0.0363$, $\theta < 27^\circ$), were collected on a Siemens SMART CCD diffractometer using narrow frames (0.3° in ω), and were corrected semiempirically for absorption and incident beam decay (transmission 0.54–1.00). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G. M.Sheldrick, SHELXTL manual, Siemens Analytical X-ray Instruments, Madison WI, USA, 1994, version 5) to give $wR2 = \{\Sigma[w(F_o^2(F_c^2)_2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.1088$, conventional $R = 0.0452$ for F values of 8223 reflections with $F_o^2 > 2y\sigma(F_o^2)$, $S = 0.824$ for 690 parameters. Isotropic H atoms were constrained; other atoms were refined anisotropically. Residual electron density extremes were 1.33 and −1.50 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication

no. CCDC-100681. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Structural and Spectroscopic Characterization of a Mononuclear Hydroperoxo – Copper(II) Complex with Tripodal Pyridylamine Ligands[**]

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Hydroperoxo – copper species are key intermediates in biological oxidations catalyzed by copper enzymes, such as dopamine β-hydroxylase (DβH),[1] galactose oxidase (GO),[2] and superoxide dismutase (SOD).[3] Characterization of these hydroperoxo intermediates is very difficult due to their short lifetimes. Hydroperoxo– or alkylperoxo – copper(II) complexes could be used as model compounds of hypothetical reaction intermediates in these oxidations. Recently the spectroscopic characterization of binuclear hydroperoxo – copper(II) complexes and X-ray structural characterization of mononuclear acylperoxo – copper(II) complexes were reported by Karlin et al.[4] and Kitajima et al.[5] However, the thermal instability of these compounds prevented their complete characterization. To confirm the structural characterization of the $\text{Cu}^{\text{II}}-\text{OOH}^-$ species, we prepared a mononuclear copper complex with a newly designed tripodal pyridylamine ligand, bis(6-pivalamide-2-pyridylmethyl)-(2-pyridylmethyl)amine (bppa), and subjected it to reaction with hydrogen peroxide. Here we describe the structural and spectroscopic characterization of the resulting mononuclear hydroperoxo – copper complex cation $[\text{Cu}^{\text{II}}(\text{bppa})(\text{OOH}^-)]^+$, the first example of an isolated copper – hydroperoxo species.

The addition of a large excess of hydrogen peroxide to a MeCN solution of $[\text{Cu}^{\text{II}}(\text{bppa}^-)]\text{ClO}_4$ (**1**)[6] or $[\text{Cu}^{\text{II}}(\text{bppa})(\text{CH}_3\text{COO})]\text{ClO}_4$ (**2**)[6] at room temperature resulted in a slight color change from greenish blue to green. The absorption spectra of the reaction product **3,** which is stable for a month at room temperature, exhibited well-separated bands in the d–d region at 830 nm ($\varepsilon = 250\,\text{M}^{-1}\text{cm}^{-1}$) and 660 nm ($\varepsilon = 150\,\text{M}^{-1}\text{cm}^{-1}$) and an intense band near 380 nm ($\varepsilon = 890\,\text{M}^{-1}\text{cm}^{-1}$). The ESR spectrum of a solution of **3** is typical of a trigonal-bipyramidal mononuclear copper complex ($g_{\parallel} = 2.004$, $g_{\perp} = 2.207$, $A_{\perp} = 75$, and $A_{\parallel} = 109$ G at 77 K in MeOH), suggesting that one of the axial positions has been coordinated by an anionic donor ligand such as a deprotonated hydrogen peroxo ion. The resonance Raman spectra of a solution of **3** in MeCN measured at room temperature (laser excitation wavelength 441.6 nm) revealed a strong resonance-enhanced Raman band at 856 cm^{-1}, which shifted to 810 cm^{-1} ($\Delta\tilde{\nu} = 46$ cm^{-1}) when ^{18}O-labeled H_2O_2 was used. This range is characteristic for $\nu(\text{O}-\text{O})$ vibrations of peroxide species and is in close proximity to those found in free $\text{H}_2{}^{16}\text{O}_2$ and $\text{H}_2{}^{18}\text{O}_2$ (873 and 826 cm^{-1}).[7] Interpretation of the vibrational data indicates that the hydroperoxo moiety is bound to the copper(II) ion and the intense absorption band near 380 nm can be assigned to the charge-transfer transition of the hydroperoxo group to copper(II) ion. The ESI mass spectrum of a solution of **3** in MeCN showed positive and negative ions with prominent peak clusters at *m/z* 584 and 784, the observed masses and isotope patterns of which corresponded to the $[\text{Cu}^{\text{II}}(\text{bppa})(\text{OOH}^-)]^+$ and $\{[\text{Cu}^{\text{II}}(\text{bppa})(\text{OOH}^-)](\text{ClO}_4)_2\}^-$ ions. The use of ^{18}O-labeled H_2O_2 caused these features to shift, as expected, to *m/z* 588 and 788. The intense green color of **3** is maintained throughout the mass spectroscopic experiment, suggesting that the complex is very stable. It is thus clear from these findings that **3** can be best formulated as $[\text{Cu}^{\text{II}}(\text{bppa})(\text{OOH}^-)]^+$. The electronic absorption, ESR, resonance Raman, and ESI mass spectra, as described above, represent the first evidence for the successful synthesis of a mononuclear hydroperoxo – copper(II) complex in solution.

A solution of **3** in MeCN stored in a cold room produced a dark green crystal suitable for X-ray diffraction measurements. The crystal structure of the complex **3**[8] (Figure 1) revealed that the coordination geometry around the copper(II) ion is an axially compressed trigonal bipyramid. The three pyridine nitrogen atoms are in the equatorial plane (Cu–N(2A) 2.099(5), Cu–N(2B) 2.136(4), Cu–N(2C) 2.051(6) Å), and one of the axial positions is occupied by a nitrogen atom

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