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COMMUNICATION

A NEW BARIUM COMPLEX BASED ON "$Ba(dpm)_2$": $Ba_6(dpm)_{10}(H_2O)_6(O_2)$. AN UNEXPECTED BARIUM PEROXO-β-DIKETONATE STRUCTURALLY CHARACTERIZED

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Abstract—The title compound consists of an octahedron of barium atoms connected together by dpm and aqua ligands in which the O_2^{2-} group, bridging the six metal atoms, has a long O—O bond.

Substituted metal β-diketonates are the most studied volatile barium containing precursors. The main ligand used is dpm (dpmH = 2,2,6,6-tetramethyl-3,5-heptanedione) yielding a series of "$Ba(dpm)_2$" complexes: $Ba_5(dpm)_9(H_2O)_3(OH)$,[1] $[Ba(dpm)_2]_4$,[2] $Ba(dpm)_2(CH_3OH)_3 \cdot (CH_3OH)$,[3] $Ba(dpm)_2(H_2O)_2(CH_3OH)_2$,[4] $[Ba(dpm)_2(Et_2O)]_2$,[5] and $[Ba(dpm)_2(NH_3)_2]_2$.[6] Recently we have reported the crystal structure of a volatile barium complex $[Ba(dpm)_2(ArOH)_2(THF)]_2$ (**1**) which dissociated upon heating (200°C/10^{-1} mmHg) into a barium-containing compound for which the spectroscopic and elemental analyses are in accordance with the formula $[Ba(dpm)_2(ArOH)]_n$, $n > 2$ (**2**).[7] Many attempts to obtain single crystals of this sublimate have finally yielded to give an unexpected complex $Ba_6(dpm)_{10}(H_2O)_6(O_2)$ (**3**) whose structural characterization is reported here.

The title compound **3** was obtained by slow recrystallization from the toluene solution of **2** at 5°C, after many weeks. The structure of **3** is illustrated in Fig. 1.† The structure consists of an octa-

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† Crystal data for $C_{110}H_{202}O_{28}Ba_6$: $M = 2796.8$, orthorhombic, crystal size (mm) 0.4 × 0.4 × 0.3, space group *Pbca*, $a = 18.546(3)$, $b = 27.275(6)$, $c = 29.872(7)$ Å, $V = 15{,}110(5)$ Å^3, $Z = 4$, $F(000) = 5688^{e-}$, $D = 1.23$ Mg m^{-3}, μ(Mo-K_α = 1.48 mm^{-1}, scan type = $\omega - 2\theta$, h, k, l, limits = $+h$, $+k$, $+l$. $R^* = 0.079$ for 7484 observed reflections. 13,394 reflections measured, $2\theta_{max} = 50°$, three check reflections with 15% intensity decay at 293 K; of these 12,604 were unique and 7484 which had $F_o^2 > 2.5\sigma(F_o)^2$ where used for all calculations. The data were collected on a Siemens P3 diffractometer using Mo-K_α ($\lambda = 0.71073$ Å) radiation. The positions of the barium atoms were found automatically from a three-dimensional Patterson map using SHELXS 86.[8] All remaining non-hydrogen atoms were located in successive difference electron density map calculations using SHELX 76.[9] An absorption correction was applied by the program DIFABS[10] at the end of the isotropic refinement. Refinement on F to $R = 0.079$, $R_\omega^* = 0.139$. Only the barium and oxygen atoms were refined anisotropically. The coordinates of the carbon atoms were kept fixed at the values found in the difference Fourier syntheses. 154 parameters, weighting scheme $\omega = 1/[\sigma^2(F) + 0.0004F^2]$. $\Delta/\sigma = 0.016$, max and min height in final $\Delta\rho$ map 1.8 to −1.1 e$^-$ Å^{-3} respectively. All calculations were performed on a VAX 3100 computer. Atomic coordinates, bond lengths, angles and thermal parameters are given as supplementary material.

The quantity minimized in the least-squares procedure is: $\omega(|F_o| - |F_c|)^2$. $R = \Sigma||F_o| - |F_c||/|F_o|$; $R_\omega = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega(F_o)^2]^{1/2}$.

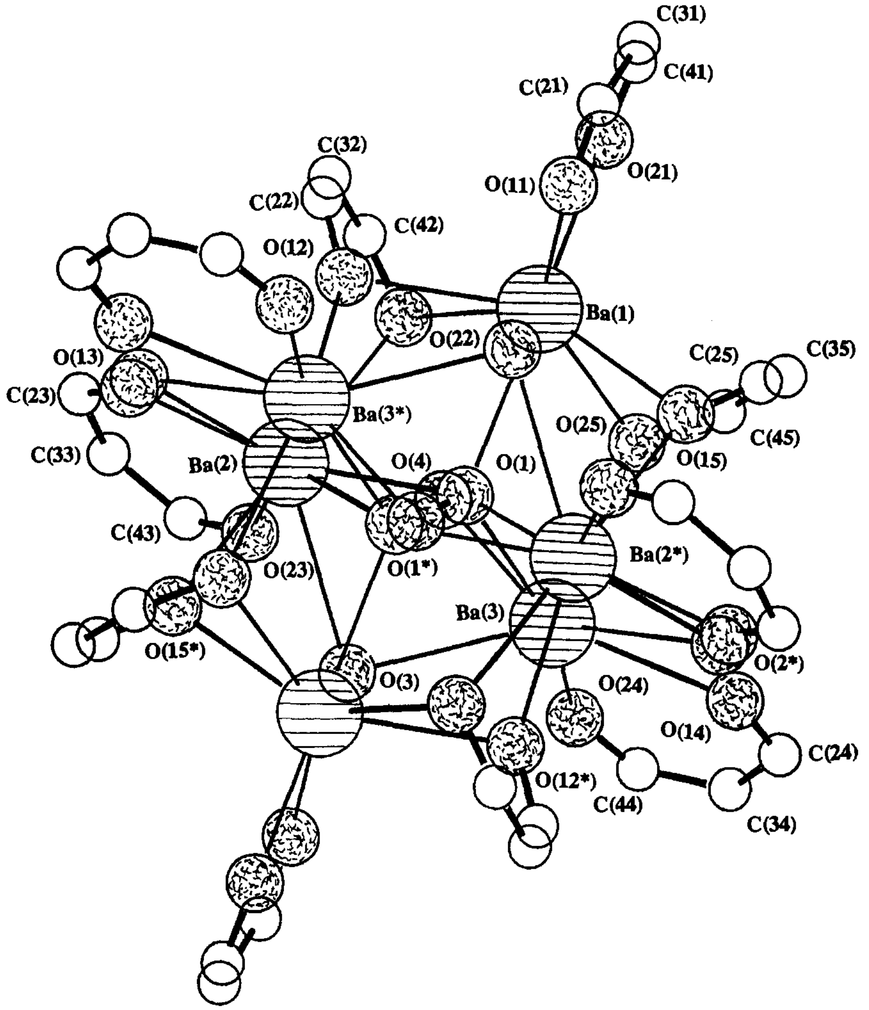


Fig. 1. Atomic numbering scheme of $Ba_6(dpm)_{10}(H_2O)_6(O_2)$ with the terminal methyl groups of the dpm ligand omitted for clarity. The metal–oxygen distances (Å) are: Ba(1)—Ba(2) 4.163(2), Ba(1)—Ba(3) 4.524(2), Ba(2)—Ba(3) 4.300(2), O(1)—O(1*) 1.51(2), O(12)—Ba(1) 2.81(1), O(1)—Ba(1) 2.75(1), O(12)—Ba(2) 3.04(1), O(1)—Ba(3) 2.76(1), O(12)—Ba(3*) 2.98(1), O(1)—Ba(2) 2.70(1), O(22)—Ba(1) 2.76(1), O(22)—Ba(2) 2.85(1), O(1)—Ba(2*) 2.69(1), O(15)—Ba(1) 2.73(1), O(11)—Ba(1) 2.70(1), O(15)—Ba(2*) 2.76(1), O(21)—Ba(1) 2.56(1), O(25)—Ba(1) 2.76(1), O(13)—Ba(2) 2.64(2), O(25)—Ba(3) 2.72(1), O(23)—Ba(2) 2.71(1), O(2)—Ba(2) 2.93(2), O(14)—Ba(3) 2.73(1), O(2)—Ba(3*) 3.13(2), O(24)—Ba(3) 2.58(2), O(3)—Ba(2) 3.07(1), O(3)—Ba(3) 2.92(1), O(4)—Ba(3) 2.75(2). Selected bond angles (°): O(1)—Ba(2)—O(1*) 32.5(5), Ba(2)—O(1)—Ba(2*) 148(2), Ba(1)—O(1)—Ba(2) 99.7(4), Ba(3)—O(1)—Ba(2) 104.0(4), Ba(1)—O(1)—Ba(3) 110.5(4), Ba(1)—O(1)—O(1*) 124.9, Ba(3)—O(1)—O(1*) 124.3, O(11)—Ba(1)—O(21) 65.6(4), O(13)—Ba(2)—O(23) 64.8(4), O(14)—Ba(3)—O(24) 65.2(4), Ba(2)—O(2)—Ba(3*) 82.6, Ba(2)—O(3)—Ba(3) 91.6(3), Ba(1)—O(12)—Ba(2) 90.7(4), Ba(1)—O(22)—Ba(2) 95.9(4), Ba(1)—O(15)—Ba(2*) 97.5, Ba(1)—O(25)—Ba(3) 111.5(5), O(12)—Ba(1)—O(22) 62.3(4), O(12)—Ba(2)—O(22) 58.5(4), O(15)—Ba(1)—O(25) 64.7(4).

hedron of barium atoms that has undergone tetragonal compression along the Ba(2)—Ba(2*) axis. A peroxide anion sits on the origin in the plane defined by the Ba(1), Ba(3), Ba(1*) and Ba(3*) atoms (Fig. 2). The O—O moeity acts as an μ-$\eta^2:\eta^2$ peroxo with the apical Ba(2) and Ba(2*) atoms and as a μ^4-O_2^{2-} ion bridging the basal four barium atoms. The same core structure is also adopted in a similar ionic compound $[Ba_6(dpm)_{10}(H_2O)_4(OH)_2(O_2)][HNHEt_3]_2$ recently reported, obtained by slow evaporation of a solution of $Ba(dpm)_2$ in NEt_3 through a semipermeable butyl rubber membrane.[11] Each barium atom is coordinated to one terminal dpm group. The remaining

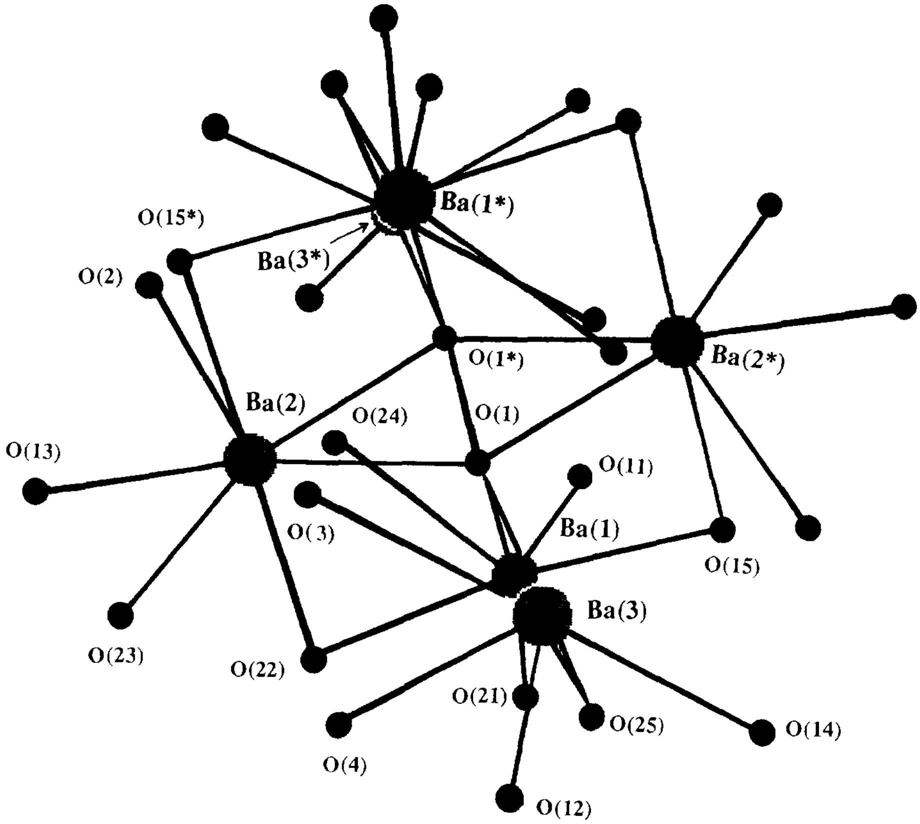
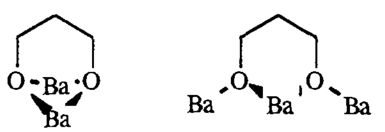


Fig. 2. O_2^{2-} group packing in the Ba_6O_{28} core.

four dpm ligands are bridging three barium atoms; two centrosymmetrically related dpm ligands have a coordination mode (a) and the other two are of type (b):



(a) (b)

Six aqua ligands (four doubly bridging and two terminal) are present and preserve the electroneutrality of the compound. They complete the degree of coordination of nine of the apical barium atoms and the octacoordination of two basal barium atoms whereas the other two barium atoms are heptacoordinated.[12] The O—O peroxo-bridge bond length of 1.51(2) Å marks it as a true peroxo compound, although this value is toward the upper end of the range observed in other peroxo transition metal complexes[13] and longer than in solid H_2O_2 (1.453 Å). Unfortunately, in the infrared, the expected O—O stretching vibration is hidden by the absorption bands of the dpm ligands.[14] The Ba—O$\{(O_2)^{2-}\}$ distances are within the range of normal values, ⟨2.755 Å⟩ for basal bonds and ⟨2.695 Å⟩ for apical bonds.

Bridged peroxo compounds of the first-row transition metals are well established;[13,15] for the main-group metals reports are scarce[16] and, to our knowledge, the only structurally characterized peroxo complexes for group IIA metals are the title compound and $[Ba_6(dpm)_{10}(H_2O)_4(OH)_2(O_2)][HNHEt_3]_2$. Although the mode of formation of the peroxo-bridged complexes is not at present understood, the ability of the very oxophilic barium element to easily react with dioxygen is demonstrated here. Work is in progress to explain the origin of the barium peroxo-β-diketonate.

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