Pergamon

Polyhedron Vol. 16, No. 14, pp. 2527–2530, 1997

0277–5387/97 $17.00+0.00

PII: S0277–5387(96)00443–3

Synthesis and X-ray crystal structure of a barium complex with 2-methoxy-2,6,6-trimethylheptane-3,5-dionate

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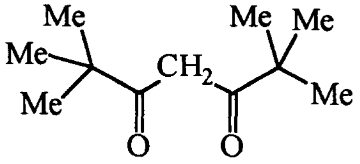
(Received 6 June 1996; accepted 29 August 1996)

Abstract—The preparation and crystallographic characterization of a barium complex with 2-methoxy-2,6,6-trimethylheptane-3,5-dionate (L) are described. The structure consists of dimeric complexes of $Ba_2L_4(H_2O)_{1.81}$. The coordination numbers of both barium atoms are nine owing to eight oxygen atoms from the four ligands L and a water molecule. © 1997 Elsevier Science Ltd

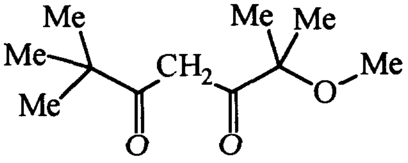
Keywords: β-diketonate metal complexes; 2-methoxy-2,6,6-trimethylheptane-3,5-dione; barium complexes; X-ray structure.

Barium dipivaloylmethanate, $Ba_4(thd)_8$ (Hthd = 2,2,6,6-tetramethylheptane-3,5-dione), and its hydrates are often used as precursors for the preparation of $YBa_2Cu_3O_{7-x}$ superconducting films. More volatile barium compounds are of current interest.

In this respect, a new barium complex with 2-methoxy-2,6,6-trimethylheptane-3,5-dionate (L) was synthesized and investigated. The HL molecule differs from Hthd in having a substituent in the 2 position.



Hthd



HL

Compound $[Ba_2L_4(H_2O)_{1.81}]$ (1) was prepared by dissolving barium metal in a slight excess of a boiling heptane solution of HL. Colourless transparent crystals of **1** were obtained by slow evaporation of the solvent. A single crystal of **1** sealed in a glass capillary.

The crystal data for **1** $[Ba_2(C_{44}H_{76}O_{12})(H_2O)_{1.81}]$ are: $M = 1104$, triclinic system, space group $P\bar{1}$, $a = 10.245(4)$, $b = 11.630(4)$, $c = 22.953(7)$ Å; $\alpha = 98.08(2)$, $\beta = 95.48(2)$, $\gamma = 94.68(2)°$; $V = 2683(1)$ Å^3; $Z = 2$, $D_c = 1.367$ g cm^{-3}. Intensities of 7861 independent reflections were measured ($2\Theta_{max} = 52°$) on an Enraf–Nonius CAD-4 diffractometer (monochromated Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 15.1$ cm^{-1}, $T = 293$ K). The structure was solved by direct methods (SHELXS86 [1]) and refined by the least-squares technique in a full-matrix anisotropic approximation for all non-hydrogen atoms (without disordered methyl carbons of all Bu^t groups and water molecules) to $R(F) = 0.071$ and $wR(F^2) = 0.176$ (refinement of F^2 using SHELXL93 [2]).

The structure of **1** consists of dimeric complexes of $Ba_2L_4(H_2O)_{1.81}$ (Fig. 1). Both barium atoms [Ba(1) and Ba(2)] are bound to four L$^-$ ligands which act as tridentate bridging ligands towards each barium atom. Each of the ligands coordinates one Ba atom by two β-diketonate oxygen atoms [O(2), O(3), O(5) and O(6) to Ba(1); O(8), O(9); O(11), and O(12) to

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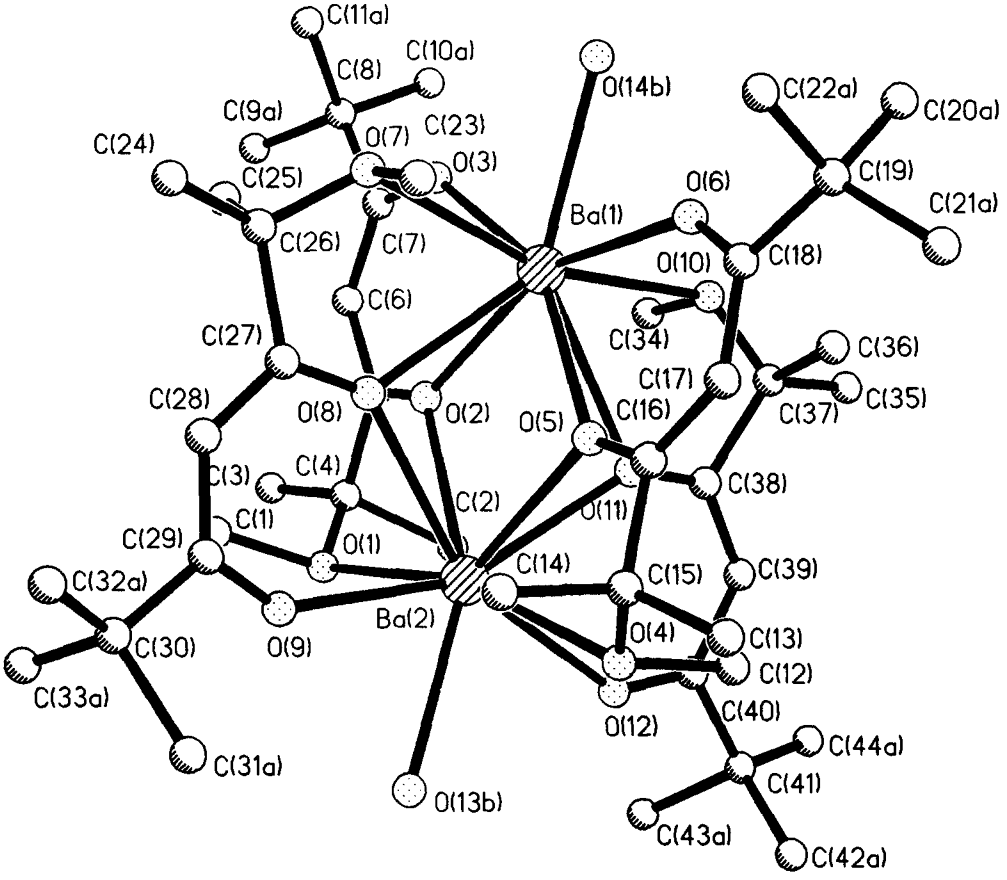

Fig. 1. Molecular structure and atom-numbering scheme for the molecule of $[Ba_2L_4(H_2O)_{1.81}]$.

Table 1. Selected bond lengths (Å) and bond angles (°) for complex **1**

Ba(1)—O(2)	2.70(1)	Ba(1)—O(3)	2.71(1)
Ba(1)—O(5)	2.69(1)	Ba(1)—O(6)	2.70(1)
Ba(1)—O(7)	2.99(1)	Ba(1)—O(8)	2.77(1)
Ba(1)—O(10)	2.94(2)	Ba(1)—O(11)	2.895(9)
Ba(1)—O(14A)*	2.90(2)	Ba(1)—O(14B)*	2.66(4)
Ba(2)—O(1)	2.98(1)	Ba(2)—O(2)	2.83(1)
Ba(2)—O(4)	2.97(1)	Ba(2)—O(5)	2.83(1)
Ba(2)—O(8)	2.72(1)	Ba(2)—O(9)	2.68(1)
Ba(2)—O(11)	2.68(1)	Ba(2)—O(12)	2.80(1)
Ba(2)—O(13A)*	2.83(3)	Ba(2)—O(13B)*	2.7(1)

O(2)—Ba(1)—O(3)	63.3(3)	O(2)—Ba(1)—O(5)	92.9(3)
O(2)—Ba(1)—O(6)	155.9(3)	O(2)—Ba(1)—O(7)	102.6(3)
O(2)—Ba(1)—O(8)	59.8(3)	O(2)—Ba(1)—O(10)	86.6(4)
O(2)—Ba(1)—O(11)	60.1(3)	O(2)—Ba(1)—O(14A)	120.9(5)
O(2)—Ba(1)—O(14B)	140.7(9)	O(3)—Ba(1)—O(5)	155.1(3)
O(3)—Ba(1)—O(6)	140.7(3)	O(3)—Ba(1)—O(7)	87.4(3)
O(3)—Ba(1)—O(8)	98.4(3)	O(3)—Ba(1)—O(10)	85.1(4)
O(3)—Ba(1)—O(11)	109.0(3)	O(3)—Ba(1)—O(14A)	57.6(5)
O(3)—Ba(1)—O(14B)	77.4(9)	O(5)—Ba(1)—O(6)	63.4(3)
O(5)—Ba(1)—O(7)	91.0(3)	O(5)—Ba(1)—O(8)	60.8(3)
O(5)—Ba(1)—O(10)	101.7(4)	O(5)—Ba(1)—O(11)	60.1(3)
O(5)—Ba(1)—O(14A)	145.8(5)	O(5)—Ba(1)—O(14B)	126.0(9)
O(6)—Ba(1)—O(7)	83.5(3)	O(6)—Ba(1)—O(8)	107.7(3)
O(6)—Ba(1)—O(10)	93.4(4)	O(6)—Ba(1)—O(11)	101.1(3)
O(6)—Ba(1)—O(14A)	83.2(5)	O(6)—Ba(1)—O(14B)	63.4(9)
O(7)—Ba(1)—O(8)	56.4(3)	O(7)—Ba(1)—O(10)	164.0(4)
O(7)—Ba(1)—O(11)	142.8(3)	O(7)—Ba(1)—O(14A)	77.5(5)
O(7)—Ba(1)—O(14B)	74.5(9)	O(8)—Ba(1)—O(10)	138.8(4)
O(8)—Ba(1)—O(11)	87.6(3)	O(8)—Ba(1)—O(14A)	129.8(5)
O(8)—Ba(1)—O(14B)	130.9(9)	O(10)—Ba(1)—O(11)	53.2(4)
O(10)—Ba(1)—O(14A)	86.6(6)	O(10)—Ba(1)—O(14B)	90.1(9)
O(11)—Ba(1)—O(14A)	139.6(5)	O(11)—Ba(1)—O(14B)	140.6(9)
O(1)—Ba(2)—O(2)	54.3(3)	O(1)—Ba(2)—O(4)	164.8(4)
O(1)—Ba(2)—O(5)	140.9(3)	O(1)—Ba(2)—O(8)	90.5(4)
O(1)—Ba(2)—O(9)	87.4(4)	O(1)—Ba(2)—O(11)	100.0(3)
O(1)—Ba(2)—O(12)	91.3(3)	O(1)—Ba(2)—O(13A)	71.0(7)
O(1)—Ba(2)—O(13B)	100(2)	O(2)—Ba(2)—O(4)	140.0(3)
O(2)—Ba(2)—O(5)	87.3(3)	O(2)—Ba(2)—O(8)	58.8(3)
O(2)—Ba(2)—O(9)	106.0(3)	O(2)—Ba(2)—O(11)	61.2(3)
O(2)—Ba(2)—O(12)	103.1(3)	O(2)—Ba(2)—O(13A)	123.9(7)
O(2)—Ba(2)—O(13B)	153(2)	O(4)—Ba(2)—O(5)	54.2(3)
O(4)—Ba(2)—O(8)	102.3(3)	O(4)—Ba(2)—O(9)	91.4(4)
O(4)—Ba(2)—O(11)	87.6(3)	O(4)—Ba(2)—O(12)	80.6(3)
O(4)—Ba(2)—O(13A)	95.8(7)	O(4)—Ba(2)—O(13B)	66(2)
O(5)—Ba(2)—O(8)	59.6(3)	O(5)—Ba(2)—O(9)	98.0(3)
O(5)—Ba(2)—O(11)	61.0(3)	O(5)—Ba(2)—O(12)	106.0(3)
O(5)—Ba(2)—O(13A)	142.2(7)	O(5)—Ba(2)—O(13B)	116(2)
O(8)—Ba(2)—O(9)	62.0(4)	O(8)—Ba(2)—O(11)	93.2(3)
O(8)—Ba(2)—O(12)	155.2(3)	O(8)—Ba(2)—O(13A)	115.4(7)
O(8)—Ba(2)—O(13B)	119(2)	O(9)—Ba(2)—O(11)	154.3(3)
O(9)—Ba(2)—O(12)	142.8(3)	O(9)—Ba(2)—O(13A)	56.1(7)
O(9)—Ba(2)—O(13B)	59(2)	O(11)—Ba(2)—O(12)	62.2(3)
O(11)—Ba(2)—O(13A)	149.5(7)	O(11)—Ba(2)—O(13B)	141(2)
O(12)—Ba(2)—O(13A)	88.5(7)	O(12)—Ba(2)—O(13B)	85(2)

* Site occupied O(13A), 0.67(2); O(13B), 0.14(4); O(14A), 0.58(2); O(14B), 0.42(2).

Ba(2)] and the other Ba atom by the β-diketonate and the methoxy group oxygens [O(7), O(8), O(10) and O(11) to Ba(1); O(1), O(2), O(4) and O(5) to Ba(2)].

Each barium atom is included in two six-membered and two five-membered chelate rings. In the six-membered rings, the Ba—O distances range from 2.68 to 2.80 Å (Table 1, Fig. 1), whereas in the five-membered rings, the Ba—O distances lie between 2.77 and 2.99 Å. Note that the former distances are shorter than the latter distances. In the related compounds, $Ba_4(thd)_8$ [3], $Ba_5(thd)_9Cl(H_2O)_7$ [4], and $Ba_6(thd)_{12}(H_2O)_{13}$ [5], the Ba—O distances are 2.47–3.04, 2.57–3.11 and 2.54–2.95 Å, respectively. Additionally, the Ba atoms are coordinated to disordered water molecules. One of the water molecules [O(13)] has a total occupancy factor of 0.81(3). Thus, the coordination numbers of the atoms Ba(1) and Ba(2) are nine, owing to eight oxygen atoms of four L^- ligands and a water molecule. The local symmetry of the complex is close to $\bar{4}$.

The Ba $\cdots$ Ba distance in the dimer **1** [3.901(1) Å] is shorter than those reported in references [3–5] (4.186–4.194, 4.382–5.457, 4.195–5.170 Å, respectively).

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