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The Layered Planar Structure of Barium 1,3-Dithiepan-2-ylidenemalonate

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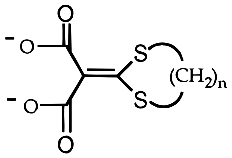
A unique two-dimensional infinite structure of barium 1,3-dithiepan-2-ylidenemalonate has been obtained via intermetallic coordination of the dicarboxylate groups. Nanotechnology has surged into mesoscopic physics and materials science during the last decade.[1−4] Recently, a major research effort focused on using the molecular building block approach to generate useful materials with three-dimensional organic,[5] metal−organic,[6] and inorganic frameworks.[7] Strategies for the construction of these materials have utilized hydrogen-bonding, metal−ligand bonds, and metal−cluster copolymerizations to link their molecular components. In particular, Krogmann's columnar structure is an example of a "nanowire" where electronic delocalization occurs through a linear platinum atom chain.[8] Simon *et al.* visualized the structural characteristics of a one-dimensional void metal with a periodic array of atomic scale bores.[9]

On the other hand, carboxylate ligands still continue to provide new exciting species because of their ubiquity as well as their interesting coordination behavior. The coordination properties of dicarboxylate ligands are extraordinarily versatile, including the ability to form polymeric species via bridging modes.[10] Among the dicarboxylate derivatives, the following ylidenemalonate ligands containing a dithioether ring are noninnocent systems: they can coordinate to a platinum atom via one of three distinct modes (O,O′-, O,S-, and S,S′-chelation) depending on the dithioether ring size.[11,12]



For this system, in addition, the close proximity of two carboxylate groups linked to an sp^2 carbon can facilely enable them to act as an intermetallic chelating ligand. In an effort to expand this coordination chemistry to alkaline earth metals, we report herein the synthesis and structural properties of barium 1,3-dithiepan-2-ylidenemalonate ($n = 4$).

Diethyl 1,3-dithiepan-2-ylidenemalonate (Et_2[DTEYM]) was prepared by the literature method.[13,14] The compound was hydrolyzed in the presence of KOH in 95% ethanol. The resultant potassium salt, K_2[DTEYM] (6.0 mmol), was stirred with $BaCl_2{\cdot}2H_2O$ (6.0 mmol) in 250 mL of water for 1 h. The reaction solution was condensed to 10 mL to precipitate the barium salt in 70% yield. The filtered product was washed with a mixture of water and methanol (1/1). The white product was recrystallized in water to obtain colorless crystals suitable for X-ray crystallography.[15] Anal. Calcd for $C_8H_8O_4S_2Ba{\cdot}2H_2O$: C, 23.69; H, 2.98. Found: C, 23.54; H, 2.91. IR (KBr, cm^{-1}): $\nu(COO)_{asym}$ 1574, 1543. Λ_M (H_2O, Ω^{-1} cm^2 mol^{-1}): 180.

Figure 1 shows a perspective view of the title compound as a PLUTON drawing. The barium and oxygen atoms are arranged in an infinite plate. Figure 2 depicts that a barium atom has a nine-coordinate geometry consisting of three different carboxylate bonding modes (chelated monodentate; bidentate;

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(1) Simon, J.; Engel, M. K.; Soulie, C. *New J. Chem.* **1992**, *16*, 287.
(2) Underhill, A. E. *Chem. Br.* **1991**, 708.
(3) Bradley, D. D. C. *Chem. Br.* **1991**, 719.
(4) Petty, M. C., Bryce, M. R., Bloor, D., Eds. *Introduction to Molecular Electronics*; Edward Arnold: London, 1995.
(5) Venkataraman, D.; Lee, S.; Zhang, J.; Moore, J. S. *Nature* **1994**, *371*, 591.
(6) Hoskins, B.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546.
(7) Kim, J.; Whang, D.; Lee, J. I.; Kim, K. *J. Chem. Soc., Chem. Commun.* **1993**, 1400.
(8) Krogmann, K. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 35.
(9) Snyder, C. J.; Simon, A. *J. Am. Chem. Soc.* **1995**, *117*, 1996.
(10) Oldham, C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: London, 1987; Vol. 2, p 435.
(11) Lee, S. S.; Jun, M.-J.; Kim, K. M., Jung, O.-S.; Sohn, Y. S. *Polyhedron* **1995**, *13*, 1397.
(12) Sohn, Y. S.; Kim, K. M.; Kang, S.-J.; Jung, O.-S. Submitted to *Inorg. Chem.*
(13) Katagiri, N.; Ise, S.; Watanabe, N.; Kaneko, C. *Chem. Pharm. Bull.* **1990**, *38*, 3242.
(14) Kosakada, T.; Taninaka, K.; Kuruno, H. Jpn. Kokai 78 03,519, 1978.
(15) Single-crystal X-ray diffraction data for $C_8H_8O_4S_2Ba{\cdot}2H_2O$ (a colorless parallelepiped crystal, 0.30 × 0.30 × 0.15 mm) were collected at 23(2) °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated molybdenum radiation ($\lambda = 0.710\,73$ Å). Data are as follows: monoclinic $P2_1/a$ (No. 14); $a = 12.299(5)$ Å, $b = 7.684(2)$ Å, $c = 14.839(5)$ Å, $\beta = 112.17(2)°$, $Z = 4$, $V = 1298.8(8)$ Å^3, $d_{cal} = 2.074$ g/cm^3; $\mu = 33.90$ cm^{-1}, $2\theta_{max} = 49.92°$, $\omega/2\theta$, $+h,+k,\pm l$; total data collected; unique data 1956; data with $I > 2\sigma(I)$ 1875; final $R = 0.0478$, $R_w = 0.1286$. The structure was solved using a method described elsewhere.[12]

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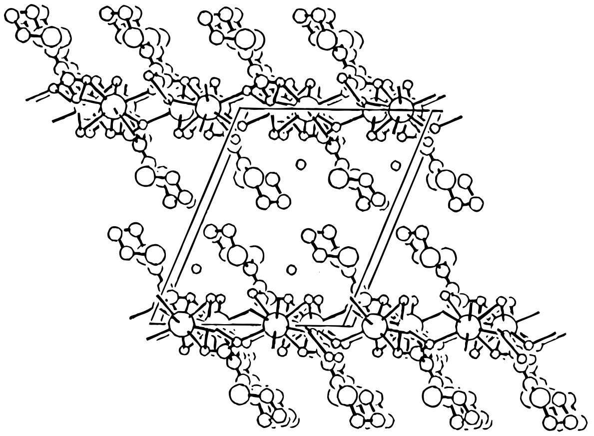
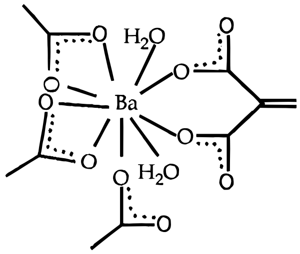
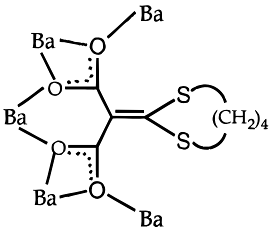


Figure 1. Perspective view of the compound as a PLUTON drawing including the unit cell, viewed along the *z* axis. The spheres in decreasing order of size represent barium, sulfur, carbon, and oxygen atoms, with the unit cell outlined in black. Hydrogen atoms are omitted for clarity.

monodentate) along with two bridged-oxygen bonds (of solvated waters).



The distortion is predominantly responsible for the typical bite angle of bidentate carboxylates. Oxygen atoms of the DTEYM ligand in the present compound are bonded to the barium atom in contrast to the case of the S,S′-chelated diammineplatinum(II) analog, which may be explicable on the basis of the concept of hard and soft acids and bases. The Ba−O bond distances are in the range 2.706(6)−2.970(6) Å, very close to the corresponding bond distances (2.64−3.09 Å) in barium acetate.[16] One of two solvated water molecules is bridged between barium atoms whereas another is positioned between two thioether rings. There are two intraplate Ba···Ba distances of 4.32 Å (between-layer) and 4.62 Å (in-plane). The distortion of the local geometry around the barium atom may in part be ascribed to between-layer interactions. The two carboxylate groups of the present DTEYM ligand characteristically bond with five barium atoms in the following fashion:



The dihedral angle between the two carboxylate planes in a DTEYM ligand is 74.6(6)°, presumably due to an electrostatic repulsion between the two adjacent anionic carboxylate groups. Such a conformation of the two carboxylate groups seems to exclude the resonance of an α,β-unsaturated system containing sulfur atoms: the C═C bond length (1.337(12) Å) is very similar to that of a normal double bond (1.33−1.34 Å),[17] but it is prominently shorter than the corresponding bond (1.374(9) Å) of (DACH)Pt(DTOYM), which exhibits a significant resonance in the system.[11] In particular, such unique chelating and bridging coordination modes for each carboxylate group in the title complex seem to hamper the intramolecular S···O interaction which is favored in (DACH)Pt(DTOYM): the shortest S···O distance of the present compound (2.86 Å) is explicitly longer than that of (DACH)Pt(DTOYM) (2.53 Å).[11] The most striking feature is that the title compound is a two-dimensional infinite structure formed via intermetallic coordination of the DTEYM ligand, where the organic group of the seven-membered dithioether ring is arranged on both faces of the barium−oxygen plate.

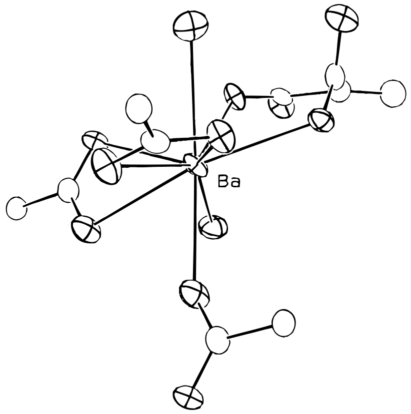


Figure 2. ORTEP drawing of the barium environment shown at the 50% probability level.

The solvated water molecules evaporate in the temperature range 81−117 °C. Thus the crystal structure begins to collapse in this range. The title compound is soluble in water, and its molar conductivity ($\Lambda_M = 180\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$) in aqueous solution reflects the fact that it is easily dissociated in solution. Nevertheless, its water solubility is very important in the synthesis of other metal analogs, which may be useful as conducting or magnetic materials. Further experiments to prepare similar complexes with heavy metal ions are in progress.

In conclusion, the present system is significant as a rare example of a metalloid plate covered by an organic group with a periodic array of atomic scale. Understanding the features of the DTEYM ligand may be a clue to the development of analogous materials that exhibit desirable nanoproperties.

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Supporting Information Available: Tables of crystallographic details, non-hydrogen positional parameters, bond distances and angles, anisotropic and isotropic thermal parameters of non-hydrogen atoms, and hydrogen coordinates and isotropic thermal parameters (6 pages). Ordering information is given on any current masthead page.

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(16) Groombridge, C. J.; Harris, R. K.; Hursthouse, M. B.; Walker, N. P. *J. Solid State Chem.* **1985**, *59*, 306.

(17) Allen, F. H.; Kennard, O.; Watson, D. G. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.