Inorg. Chem. **2001,** *40,* 6870−6878

Articles

Reactions of 2-Mercaptobenzoic Acid with Divalent Alkaline Earth Metal Ions: Synthesis, Spectral Studies, and Single-Crystal X-ray Structures of Calcium, Strontium, and Barium Complexes of 2,2′-Dithiobis(benzoic acid)[†,‡]

Ramaswamy Murugavel,* Kanhayalal Baheti, and Ganapathi Anantharaman

Department of Chemistry, Indian Institute of Technology—Bombay, Powai, Mumbai 400 076, India

Received May 16, 2001

The treatment of $MCl_2{\cdot}nH_2O$ (M = Ca, Sr, or Ba) with 2-mercaptobenzoic acid (H-2-MBA) in a 1:2 ratio in an $EtOH/H_2O/NH_3$ mixture leads to the formation of extended polymeric solids $[\{Ca(OOCC_6H_4SSC_6H_4COO)(H_2O)_2\}{\cdot}0.5(C_2H_5OH)]_n$ (**1**), $[\{Sr(OOCC_6H_4SSC_6H_4COO)(H_2O)_2\}{\cdot}0.5(C_2H_5OH)]_n$ (**2**), and $[\{Ba_2(OOCC_6H_4SSC_6H_4COO)_2(H_2O)_2\}{\cdot}0.5H_2O]_n$ (**3**), respectively. In all of the cases, under the reaction conditions employed, the H-2-MBA ligand undergoes thiol oxidation to form 2,2′-dithiobis(benzoic acid) (H_2-DTBB). While the DTBB forms a 1:1 complex with heavier alkaline earth metals (**1**−**3**), only an ammonium salt, $[(HOOCC_6H_4SSC_6H_4COOH)(HOOCC_6H_4SSC_6H_4COONH_4)]$ (**4**), was obtained as the final product in the reaction of H-2-MBA with $MgCl_2{\cdot}6H_2O$. Compounds **1**−**4** have been characterized with the aid of elemental analysis, thermal analysis, and infrared spectroscopic studies. All of the products are found to be thermally stable and do not melt on heating to 250 °C. Thermogravimetry on complexes **1**−**3** indicates the loss of coordinated and lattice water/solvent molecules below 200 °C (for complex **2**) or 350 °C (for complexes **1** and **3**). The solid-state structures of all of the derivatives **1**−**4** have been established by single-crystal X-ray diffraction studies. The calcium and strontium coordination polymers **1** and **2** are isomorphous. The DTBB ligands in **1** and **2** are hexadentate, and the compounds have a channel structure in which solvent ethanol molecules are included. In compound **3**, barium ion forms a complex 3-dimensional coordination polymer where both the carboxylate and the sulfur centers of the DTBB ligands (which are hepta- and octadentate) coordinate to the metal.

Introduction

Until recently, the chemistry of alkaline earth metals has been a largely underdeveloped area of coordination chemistry. There have been a few studies on the coordination behavior of these metals in both aqueous and nonaqueous media.[1−5] The alkaline earth metals play an important role in the biochemistry of virtually all living organisms. They are distributed in most cells and tissues, often in considerable concentrations, and a constant supply is indispensable for unrestricted performance of biological functions. Magnesium and calcium are the most prominent alkaline earth metals in biological systems. Magnesium is present solely as the solvated or complexed dication Mg^{2+}, basically as a part of the osmotic equilibria in and outside of the cells and in all tissues.[6,7] Magnesium cations induce or stabilize tertiary structures[8] or enhance certain functionalities of enzymes. Calcium is the most prominent metal involved in structural biology. It is the main constituent of bones and teeth. These two metal ions play an essential role in the activation of enzymes, complexation with nucleic acids, nerve impulse transmission, muscle contraction, and carbohydrate metabolism.[9−12] A range of model complexes containing these two metals have been prepared as probes to elucidate the mode of binding of these metals.[13,14] The studies have focused on the use of aspartate, glutamate, orontate, or pyroglutamate ligands[13] as careful investigation of the calcium or magnesium binding sites on proteins has shown that the acidic groups of L-aspartic acid

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[‡] Dedicated to Professor K. Venkatesan on the occasion of his 70th birthday.

* Author to whom correspondence should be addressed. Tel.: +(22) 576 7163 or 576 8163. Fax: +(22) 572 3480. E-mail: rmv@iitb.ac.in.

[†] Coordination Chemistry of Alkaline Earth Metal Ions. 3. Part 2: Murugavel, R.; Karambelkar, V. V.; Anantharaman, G.; Walawalkar, M. G. *Inorg. Chem.* **2000**, *39*, 1381−1390.

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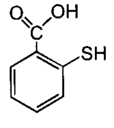
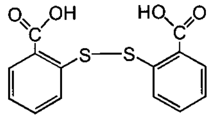
10.1021/ic010519b CCC: $20.00

and L-gluatmic acid are the key anchoring positions for these ions.[15−17] On the other hand, barium and strontium are considered as *trace elements* in the body. Strontium is rated nontoxic, and traces of it appear to be essential, though the reason for this is not yet known. Barium causes typical heavy metal poisoning even at low concentrations if soluble compounds are applied.[18] Barium and strontium metals have been known as antagonists for potassium and calcium, respectively.[19] In the process of binding to various sites, the ions compete with other common metal ions, some of which are antagonists through a different specificity. This specificity is predominantly governed by the charge and size of the cation, as well as by the resulting *effective coordination number and geometry.* An improved understanding of the function of biological cations is thus to be expected from a detailed study of the coordinating properties of the metals competing with various ligating groups.

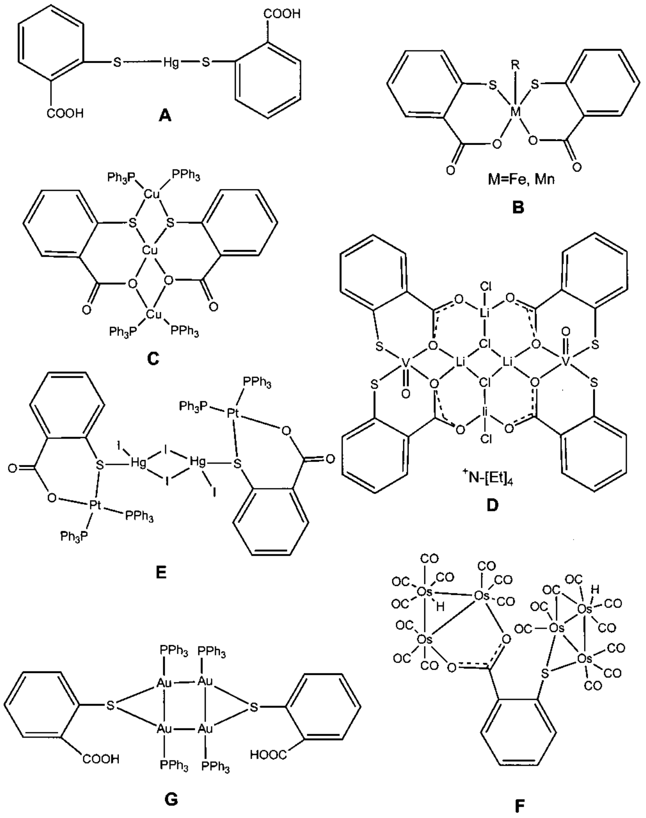
Schmidbaur,[20] Drake,[3] and others[21,22] have unraveled the coordination behavior of salicylic acid (H-SA) toward group 2 metal cations in the solid state.[23] We have recently reported an exhaustive study on the coordination behavior of 2-aminobenzoic acid (H-2-ABA) toward these metal ions.[24] This has been of importance as H-2-ABA is an important precursor to tryptophan, one of the 20 biologically important α-amino acids. A number of studies on the coordination chemistry of these metals with various *β*-diketones have also appeared in the recent literature.[5]


H-2-MBA

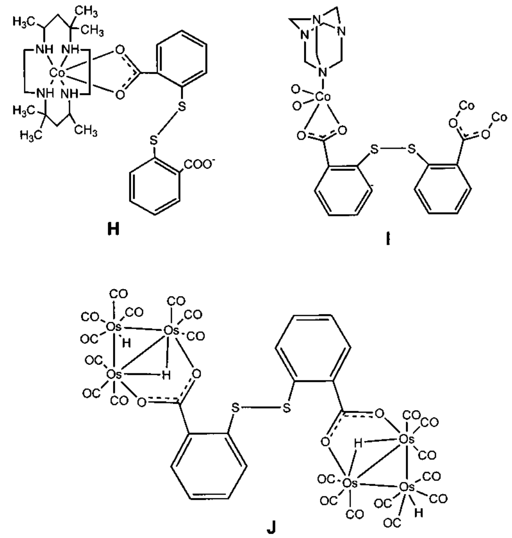

H$_2$-DTBB

Another important ligand in the series of 2-substituted benzoic acids is the 2-mercaptobenzoic acid (H-2-MBA), which, unlike the previously investigated H-SA[20−22] and H-2-ABA,[24] provides both hard and soft donor centers, which makes its chemistry interesting. It can bind to hard metal ions through the carboxylate group and to soft metal ions through the sulfide function (Scheme 1).[25] 2,2′-Dithiobis(benzoic acid) (H$_2$-DTBB), which is the oxidation product of H-2-MBA, can also function as a useful ligand in transition metal coordination chemistry (Scheme 2).[26]

Scheme 1



Scheme 2



However, to our knowledge, the use of either H-2-MBA or H$_2$-DTBB as a ligand toward s-block elements has not been investigated at all. This observation is somewhat surprising although the group 2 metal ions, carboxylate functionality, and the sulfide group are biologically important entities.[27] Further, the recently unraveled rich coordination chemistry of H-2-ABA toward these ions[24] prompted us to investigate the use of H-2-

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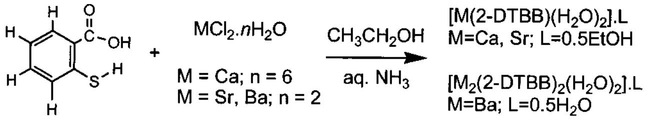
Table 1. Analytical, Physical, and Spectroscopic Data for **1**−**4**

			elemental anal.[a] (%)				
compd	yield (%)	mp (°C)	C	H	N	S	IR spectra[b] (cm^{-1})
1	70	>300	44.36 (44.65)	3.67 (3.74)		15.93 (15.89)	3434(br), 1626(s), 1582(vs), 1545(vs), 1470(m), 1041(m), 855(m), 755(s), 666(m)
2	65	>300	39.96 (39.94)	3.18 (3.35)		15.06 (14.22)	3553(br), 1604(vs), 1598(s), 1539(vs), 1406(vs), 1289(m), 1045(m), 860(m), 755(s), 663(s)
3	65	>300	39.31 (36.22)	2.33 (2.28)		13.32 (13.82)	3460(br), 1604(s), 1585(vs), 1545(vs), 1387(vs), 1289(m), 1045(m), 854(m), 749(s), 645(s)
4	30	285−287	52.19 (53.4)	3.74 (3.68)	2.07 (2.22)	*c*	3177(m), 1690(w), 1591(s), 1545(s), 393(s), 282(m), 821(m), 735(s), 703(m), 644(m).

[a] Calculated values in parentheses. [b] Recorded as KBr plates. [c] Not determined.

Scheme 3



MBA in group 2 metal chemistry. The results of these investigations reporting the (a) synthesis and isolation of the DTBB−group 2 metal ion complexes in the solid state, (b) spectroscopic characterization, (c) thermal behavior, and (d) single-crystal X-ray molecular structure determinations of the calcium, strontium, and barium complexes are presented in this paper. An attempt to prepare the analogous magnesium complex, resulting in the isolation of the ammonium salt of DTBB, is also described herein.

Results and Discussion

Synthesis. The synthesis of compounds **1**−**3** were accomplished by the reaction of $MCl_2 \cdot nH_2O$ (M= Ca, Sr, or Ba) with H-2-MBA under basic conditions from a solution of ethanol and water (Scheme 3). Addition of aqueous ammonia was necessary to neutralize the HCl generated during the reaction. The reduction of the volume of the reaction mixture to half of its original volume and leaving it for a few days produced analytically pure crystalline products in each case. Examination of these crystalline products by analytical and spectroscopic methods revealed them to be $[\{Ca(OOCC_6H_4SSC_6H_4COO)(H_2O)_2\} \cdot 0.5(CH_3CH_2OH)]_n$ (**1**), $[\{Sr(OOCC_6H_4SSC_6H_4COO)(H_2O)_2\} \cdot 0.5(CH_3CH_2OH)]_n$ (**2**), and $[\{Ba_2(OOCC_6H_4SSC_6H_4COO)_2(H_2O)_2\} \cdot 0.5H_2O]_n$ (**3**), respectively (vide infra). Surprisingly, when the reaction was carried out with $MgCl_2 \cdot 6H_2O$, the final product obtained did not contain any magnesium. Examination of the product rather revealed it to be $[(HOOCC_6H_4SSC_6H_4COOH)(HOOCC_6H_4SSC_6H_4COONH_4)]$ (**4**) (hereafter, disulfide adduct), which is an adduct of DTBB and its monoammonium salt.

Thus, in each case, the aromatic −SH group has undergone oxidation to form the disulfide-linked 2,2′-dithiobis(benzoic acid). Oxidation of thiols into disulfides is a well-known reaction.[26a,28,29] There are several reports in the literature describing the oxidation of thiols into disulfides even in air, on TLC plates, or in the presence of iodine.[28]

Further, in order to assess how essential ammonia is to this reaction and whether it has any role to play in the facile oxidation of H-2-MBA, we carried out the above reaction without adding ammonia. The analytical data and the melting point of the products obtained in each case confirm that only the free H_2-DTBB ligand is formed (without it coordinating to the metal). To support this supposition, we also carried out the reactions from independently synthesized H_2-DTBB with the metal chlorides. Expectedly, no metal complex formation was observed. Thus, the addition of ammonia is essential for the formation of the carboxylate anion.

Repeated attempts to prepare the magnesium DTBB complex, using any of the above three methods, did not yield the expected product. While the reaction did not proceed in the absence of ammonia, its addition to the reaction medium leads to the facile formation of the ammonium salt **4**. However, this observation is not surprising due to the well-known ability of the Mg^{2+} ion to form $Mg[(OH_2)_6]^{2+}$, even in the presence of several strong ligands.[30]

While the complexes **1**−**3** have been obtained in good yield (~70%) in analytically pure form, the yield for **4** was only about 30%. All the four compounds are very stable and do not melt or decompose below 250 °C.

Analytical Data and Spectral Characterization. As mentioned above, the empirical formula and the composition of the products **1**−**3** could be established from the analytical data (Table 1). For example, in the case of compounds **1** and **2** it accounts for the presence of two additional water molecules coordinated to the metal and half an ethanol molecule per 1:1 formula unit of M:DTBB. On the other hand, the observed values for **3** suggest a 1:1 complex with 1.25 water molecules per metal ion. The X-ray studies on these complexes, however, clearly establish the exact nature of the water and ethanol molecules (coordinated or uncoordinated) (vide infra). The analytical data for **4** suggests that it is a 1:1 complex of NH_4-H-DTBB and H_2-DTBB without any water molecule.

The products **1**−**3** were insoluble in all common organic solvents and also hot water. Hence no studies could be conducted in solution, and these products were only characterized using solid-state studies. For example, the recorded IR spectra as KBr plates showed a broad band at 3400−3550 cm^{-1} corresponding to the presence of water molecules in the complex. Compound **4** does not show any absorption at 3400, indicating the absence of water molecules. The rest of the spectral region for all four of the compounds is almost similar.

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Thermal Analysis. Thermal analysis for all of the products was carried out in an atmosphere of dinitrogen to establish the content of coordinated and uncoordinated water molecules in the complexes. The weight loss for the calcium complex **1** between 100 and 350 °C corresponds to the loss of the half ethanol molecule and the two coordinated water molecules, consistent with our formulation for this compound (vide supra). There is a continuous weight loss from 370 to 600 °C, whose origin is unclear, though it is probably due to the breaking of the aryl ring and the release of CO_2 and SO_2. The material left at 600 °C corresponds to 30% of the weight of the original material and can be easily attributed to $CaCO_3$. In the case of complex **2,** the first weight loss occurs between 52 and 172 °C, which corresponds to the loss of half ethanol and two water molecules. This compound loses all of its coordinated and lattice water/solvent molecules below 200 °C. Expectedly, there was no weight loss between 172 and 350 °C. The material left after the last weight loss corresponding to 35% of the weight of the starting material is $SrCO_3$.

In the case of the barium complex **3** also the first weight loss of about 4% occurs up to 330 °C, which can be attributed to loss of the water molecules. There were two more weight losses in the temperature regions 330−410 and 410−513 °C, which probably accounts for the aryl ring breaking and giving away CO_2 and SO_2. The material left at the end of the TGA run is 50% of the starting material, corresponding to 2 equiva of $BaCO_3$ along with some other impurities. Thus in all cases (**1**−**3**), after heating the sample up to 600 °C, only metal carbonates were obtained.

X-ray Crystallography. Although it has been possible to derive the exact composition and to some extent the structural formula of all of the compounds from the analytical, spectroscopic, and thermal analysis data, the information is insufficient to establish the actual modes of binding of the ligands to the metal ions.[31] Moreover, the presence of both hard and soft coordinating centers on the ligand makes it very difficult to assign the actual structure of the molecules. Hence, to have a clear understanding of the structures of these compounds, detailed X-ray structural investigations have been carried out for compounds **1**−**4**, and the results are described below.

Structures of $[\{Ca(OOCC_6H_4SSC_6H_4COO)(H_2O)_2\}\cdot0.5(C_2H_5OH)]_n$ (1) and $[\{Sr(OOCC_6H_4SSC_6H_4COO)(H_2O)_2\}\cdot0.5(C_2H_5OH)]_n$ (2). The polymeric DTBB complexes of both calcium and strontium are isomorphous and crystallize in the monoclinic centrosymmetric space group *C*2/*c* with the above molecular formula unit in the asymmetric part. A perspective view of a section of the polymeric network in **1**, also revealing the geometry around the calcium ions, is shown in Figure 1. Selected bond distances and angles in complexes **1** and **2** are listed in Tables 2 and 3, respectively.

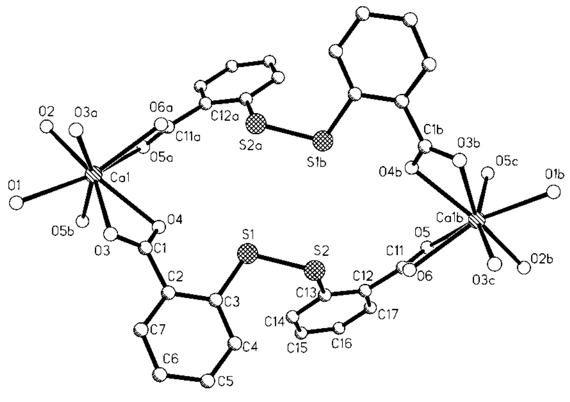

Figure 1. A perspective view of a section of the coordination polymer **1** with atom-labeling scheme. The structure of **2** is isomorphous.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Ca(1)−O(2)	2.374(2)	Ca(1)−O(5a)	2.3790(2)
Ca(1)−O(3b)	2.3971(2)	Ca(1)−O(1)	2.475(2)
Ca(1)−O(6c)	2.489(2)	Ca(1)−O(4)	2.498(2)
Ca(1)−O(3)	2.522(2)	Ca(1)−O(5c)	2.5376(2)
Ca(1)−Ca(1b)	3.8133(2)	Ca(1)−Ca(1d)	3.8951(2)
S(1)−C(3)	1.794(2)	S(1)−S(2)	2.0439(1)
S(2)−C(13)	1.785(3)	O(3)−C(1)	1.260(3)
O(3)−Ca(1b)	2.3971(2)	O(4)−C(1)	1.244(3)
O(5)−C(11)	1.264(3)	O(5)−Ca(1e)	2.3790(2)
O(5)−Ca(1c)	2.5376(2)	O(6)−C(11)	1.248(3)
O(6)−Ca(1c)	2.489(2)		

O(2)−Ca(1)−O(5a)	84.59(7)	O(2)−Ca(1)−O(3b)	88.87(7)
O(5a)−Ca(1)−O(3b)	158.93(6)	O(2)−Ca(1)−O(1)	80.75(8)
O(5a)−Ca(1)−O(1)	85.36(7)	O(3b)−Ca(1)−O(1)	73.81(7)
O(2)−Ca(1)−O(6c)	98.99(8)	O(5a)−Ca(1)−O(6c)	124.17(6)
O(3b)−Ca(1)−O(6c)	76.62(6)	O(1)−Ca(1)−O(6c)	150.43(7)
O(2)−Ca(1)−O(4)	152.33(7)	O(5a)−Ca(1)−O(4)	76.34(7)
O(3b)−Ca(1)−O(4)	115.73(6)	O(1)−Ca(1)−O(4)	116.86(8)
O(6c)−Ca(1)−O(4)	76.26(7)	O(2)−Ca(1)−O(3)	153.44(7)
O(5a)−Ca(1)−O(3)	98.99(7)	O(3b)−Ca(1)−O(3)	78.37(7)
O(1)−Ca(1)−O(3)	73.38(7)	O(6c)−Ca(1)−O(3)	100.53(7)
O(4)−Ca(1)−O(3)	51.63(6)	O(2)−Ca(1)−O(5c)	77.81(7)
O(5a)−Ca(1)−O(5c)	75.26(7)	O(3b)−Ca(1)−O(5c)	122.85(7)
O(1)−Ca(1)−O(5c)	152.21(6)	O(6c)−Ca(1)−O(5c)	51.96(5)
O(4)−Ca(1)−O(5c)	78.05(6)	O(3)−Ca(1)−O(5c)	128.65(6)
C(3)−S(1)−S(2)	105.59(9)	C(13)−S(2)−S(1)	103.94(8)

[a] Symmetry transformations used to generate equivalent atoms: (a) $x, -y, z + {}^1/_2$; (b) $-x, -y + 1, -z + 1$; (c) $-x, y, -z + {}^1/_2$; (d) $-x, -y, -z + 1$; (e) $x, -y, z - {}^1/_2$.

The eight-coordinate calcium ions shown in Figure 1 are bridged by the two DTBB ligands, where two carboxylate groups chelate each calcium ion. Each of the carboxylate groups shown in Figure 1, apart from chelating a calcium ion, is also involved in bridging a neighboring calcium ion (through O(3) or O(5)). Because of this simultaneous chelating and bridging ability of the carboxylate groups, a polymeric network results in the solid state, as shown in Figure 2. For the sake of clarity, this polymeric network is also schematized and shown along with the ball-and-stick plot. Another interesting feature of this polymeric network is the role of coordinated water molecules. Two water molecules (O(1) and O(2)) coordinate to each calcium ion in a terminal fashion (no bridging mode of coordination is observed). In contrast, in the 2-ABA complexes of group 2 metals,[24] the coordinated water molecules often bridge the adjacent metal ions/chains and aid the formation of the three-dimensional structure.

Thus, six carboxylate oxygen atoms and two water molecules surround each calcium ion. In other words, the DTBB ligand is hexadentate in both **1** and **2**, with no sulfur−metal interaction. In the polymeric network, when viewed at an angle perpendicular to that shown in Figure 2, the presence of microporous channels (Figure 3; view normal to 010 plane) is revealed. Interestingly, these micropores incorporate solvent ethanol molecules (see Experimental Section). The TGA studies described (vide supra) indicate that these ethanol molecules can be easily removed from these channels at temperatures below 200 °C. The M···M nonbonded distance, which defines the width of the channel (Figure 3), is 11.451 Å in the calcium complex **1** and 11.694 Å in the strontium complex **2**. The nonbonded S···S distances in **1** are 3.883, 4.036, and 4.704 Å,

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[31] The paucity of structural data on DTBB complexes necessitated a structural study. In fact all of the reported crystal structures involve a transition metal ion as the central atom.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**[a]

Sr(1)−O(5a)	2.515(2)	Sr(1)−O(3b)	2.528(2)
Sr(1)−O(2)	2.531(2)	Sr(1)−O(6c)	2.639(2)
Sr(1)−O(3)	2.646(2)	Sr(1)−O(5c)	2.650(2)
Sr(1)−O(1)	2.651(3)	Sr(1)−O(4)	2.655(2)
Sr(1)−C(11c)	3.005(3)	Sr(1)−Sr(1b)	3.9669(6)
Sr(1)−Sr(1d)	4.0466(6)	S(1)−S(2)	2.0483(1)
S(2)−C(13)	1.787(3)	O(3)−C(1)	1.270(4)
O(3)−Sr(1b)	2.528(2)	O(4)−C(1)	1.239(4)
O(5)−C(11)	1.270(4)	O(5)−Sr(1e)	2.515(2)
O(5)−Sr(1c)	2.650(2)	O(6)−C(11)	1.249(3)
O(6)−Sr(1c)	2.639(2)		
O(5a)−Sr(1)−O(3b)	161.47(8)	O(5a)−Sr(1)−O(2)	81.81(8)
O(3b)−Sr(1)−O(2)	95.11(8)	O(5a)−Sr(1)−O(6c)	121.91(7)
O(3b)−Sr(1)−O(6c)	76.56(7)	O(2)−Sr(1)−O(6c)	105.80(9)
O(5a)−Sr(1)−O(3)	93.77(7)	O(3b)−Sr(1)−O(3)	79.90(8)
O(2)−Sr(1)−O(3)	150.53(8)	O(6c)−Sr(1)−O(3)	101.26(8)
O(5a)−Sr(1)−O(5c)	76.86(8)	O(3b)−Sr(1)−O(5c)	120.86(7)
O(2)−Sr(1)−O(5c)	80.83(8)	O(6c)−Sr(1)−O(5c)	49.38(7)
O(3)−Sr(1)−O(5c)	126.74(7)	O(5a)−Sr(1)−O(1)	88.88(8)
O(3b)−Sr(1)−O(1)	72.63(8)	O(2)−Sr(1)−O(1)	77.58(9)
O(6c)−Sr(1)−O(1)	149.19(8)	O(3)−Sr(1)−O(1)	73.20(8)
O(5c)−Sr(1)−O(1)	155.60(8)	O(5a)−Sr(1)−O(4)	74.68(8)
O(3b)−Sr(1)−O(4)	112.25(7)	O(2)−Sr(1)−O(4)	151.47(8)
O(6c)−Sr(1)−O(4)	74.45(9)	O(3)−Sr(1)−O(4)	49.02(7)
O(5c)−Sr(1)−O(4)	78.31(7)	O(1)−Sr(1)−O(4)	117.25(9)
C(3)−S(1)−S(2)	105.39(2)	C(13)−S(2)−S(1)	103.82(1)

[a] Symmetry transformations used to generate equivalent atoms: (a) $x, -y, z + 1/2$; (b) $-x, -y + 1, -z + 1$; (c) $-x, y, -z + 1/2$; (d) $-x, -y, -z + 1$; (e) $x, -y, z - 1/2$.

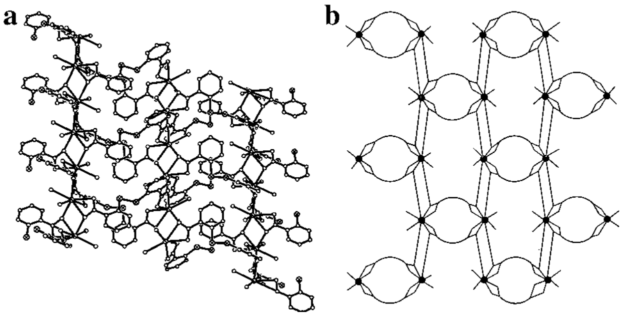

Figure 2. (a) Packing diagram of **1** viewed normal to the 100 plane; this plot also clearly shows the propagation of Ca polymer through the bridging mode of coordination. (b) The schematized diagram of the plot on the left, clearly showing the hexadenticity of DTBB ligand and also eight-coordinate Ca^{2+} ions.

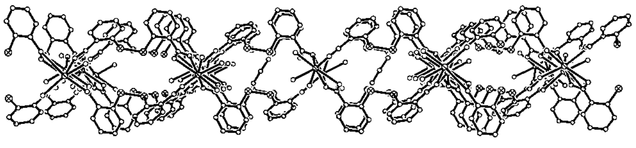

Figure 3. Packing diagram of **1** viewed normal to the 010 plane, clearly showing the presence of a channel structure. The solvent ethanol molecules trapped in these channels are also shown.

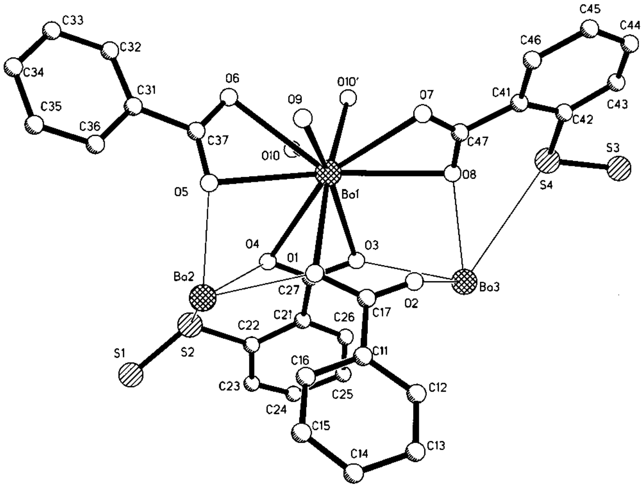

Figure 4. A perspective view of the contents of the asymmetric part of the unit cell of **3**. The coordination geometry around Ba(1) is fully shown, while only the unique binding atoms around Ba(2) and Ba(3) are included. Their centrosymmetric counterparts are not shown.

while the corresponding values in **2** are 3.969, 4.077, and 4.821 Å. It is also worthwhile to note that the M···M distances along the metal polymer axis in these molecules are only marginally longer than the sum of the van der Waals radii (Figure 2).[32] While the Ca···Ca separations in **1** along the polymer axis are 3.813(1) and 3.895(1) Å, the Sr···Sr separations in **2** are 3.967(1) and 4.044(1) Å.

The Ca−O distances in **1** vary over the range 2.374(2)−2.538(2) Å and are comparable to the values found in the literature for Ca−O linkages.[33] In general the Ca−O(chelate) carboxylate distances (av 2.512 Å) are longer than the Ca−O(bridge) carboxylate distances (2.388 Å) (Table 2). One of the water molecules is more tightly bound to the Ca ion than the other (2.374(2) and 2.475(2) Å). The angles around the eight-coordinated calcium ions vary over a large range (51.63(6)−158.93(6)°). While the smaller values are associated with the O−Ca−O chelate angles, the larger values correspond to O−Ca−O angles which are roughly trans to each other. A similar behavior in the Sr−O distances and O−Sr−O angles is observed in **2**. A comparison of the structural parameters of **1** and **2** with those of previously reported DTBB complexes of transition metals is discussed (vide infra).

Crystal Structure of $[\{Ba_2(OOCC_6H_4SSC_6H_4COO)_2(H_2O)_2\}\cdot 0.5H_2O]_n$ (3). The DTBB complex of barium crystallizes in the orthorhombic centrosymmetric space group *Pccn*. The asymmetric part of the unit cell is composed of three[34] barium atoms, two DTBB ligands, and two coordinated water molecules, along with a one-half lattice water molecule. A perspective view of the contents of the asymmetric part of the unit cell, also showing the complete coordination environment around Ba(1), is shown in Figure 4. Table 4 lists key bond lengths and bond angles in **3**.

As it can been seen from Figure 4, there are three types of barium ions in **3**. While Ba(1) (with full occupancy) is nine coordinate, Ba(2) and Ba(3) (both with 0.5 occupancy) are eight coordinate. However, the coordination geometries around Ba(2) and Ba(3) are not identical. The coordination sphere around Ba(1) is composed of three carboxylate chelates (O(3)/O(4), O(5)/O(6), O(7)/O(8)), one monodentate carboxylate (O(1)), and two water molecules which are terminally coordinated (O(9) and O(10)).[35] All of the above-mentioned chelating carboxylates also bridge the neighboring barium ions; while O(5)/O(6) and O(7)/O(8) carboxylates bridge through one of their oxygen centers (O(5) and O(8)), the O(3)/O(4) carboxylate bridges on either side through both of the oxygen atoms. Thus, Ba(2) is surrounded by three bridging carboxylate oxygens (O(1), O(4), and O(5)), and additionally by a sulfur atom coming form the disulfide linkage (S(2)), and their centrosymmetric counterparts. Ba(3) also essentially has a similar coordination

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[32] The sum of Ca···Ca and Sr···Sr van der Waals radii are 3.58 and 3.84 Å, respectively.

[33] Poonia, N. S.; Bajaj, A. V. *Chem. Rev.* **1979**, *79*, 389.

[34] In fact three crystallographically independent Ba ions are observed, but the total occupancy adds up to 2.

[35] Of the two coordinated water molecules, O(10) has a positional disorder with the occupancies of 0.6 and 0.4 (O(10) and O(10′)).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **3**[a]

Ba(1)−O(10′)	2.69(2)	Ba(1)−O(7)	2.710(1)
Ba(1)−O(9)	2.73(3)	Ba(1)−O(1)	2.778(1)
Ba(1)−O(5)	2.826(1)	Ba(1)−O(3)	2.847(1)
Ba(1)−O(6)	2.877(1)	Ba(1)−O(4)	2.891(1)
Ba(1)−O(8)	2.931(1)	Ba(1)−O(10)	3.00(5)
Ba(1)−C(47)	3.14(2)	Ba(2)−O(5a)	2.627(1)
Ba(2)−O(5)	2.627(1)	Ba(2)−O(4a)	2.694(1)
Ba(2)−O(4)	2.694(1)	Ba(2)−O(1)	2.693(1)
Ba(2)−O(1a)	2.693(1)	Ba(2)−S(2a)	3.379(6)
Ba(2)−S(2)	3.379(6)	Ba(2)−Ba(1a)	4.071(1)
Ba(3)−O(2b)	2.688(1)	Ba(3)−O(2)	2.688(1)
Ba(3)−O(8)	2.689(1)	Ba(3)−O(8b)	2.689(1)
Ba(3)−O(3b)	2.696(1)	Ba(3)−O(3)	2.696(1)
Ba(3)−S(4)	3.610(6)	Ba(3)−S(4b)	3.610(6)
Ba(3)−Ba(1b)	4.2649(1)	S(1)−S(2)	2.045(7)
S(3)−S(4)	2.050(8)		
O(10′)−Ba(1)−O(7)	79.7(8)	O(10′)−Ba(1)−O(9)	112.5(1)
O(7)−Ba(1)−O(9)	66.1(7)	O(10′)−Ba(1)−O(1)	168.5(9)
O(7)−Ba(1)−O(1)	103.9(5)	O(9)−Ba(1)−O(1)	78.9(8)
O(10′)−Ba(1)−O(5)	117.1(7)	O(7)−Ba(1)−O(5)	129.4(5)
O(9)−Ba(1)−O(5)	63.3(6)	O(1)−Ba(1)−O(5)	69.2(4)
O(10′)−Ba(1)−O(3)	91.1(9)	O(7)−Ba(1)−O(3)	115.2(5)
O(9)−Ba(1)−O(3)	155.8(8)	O(1)−Ba(1)−O(3)	77.4(4)
O(5)−Ba(1)−O(3)	111.9(4)	O(10′)−Ba(1)−O(6)	72.6(7)
O(7)−Ba(1)−O(6)	109.5(6)	O(9)−Ba(1)−O(6)	67.4(8)
O(1)−Ba(1)−O(6)	115.5(4)	O(5)−Ba(1)−O(6)	46.8(4)
O(3)−Ba(1)−O(6)	128.5(5)	O(10′)−Ba(1)−O(4)	104.7(8)
O(7)−Ba(1)−O(4)	157.9(5)	O(9)−Ba(1)−O(4)	128.4(7)
O(1)−Ba(1)−O(4)	67.8(4)	O(5)−Ba(1)−O(4)	68.5(4)
O(3)−Ba(1)−O(4)	44.1(3)	O(6)−Ba(1)−O(4)	92.3(5)
O(10′)−Ba(1)−O(8)	73.5(7)	O(7)−Ba(1)−O(8)	45.3(4)
O(9)−Ba(1)−O(8)	109.7(6)	O(1)−Ba(1)−O(8)	101.0(4)
O(5)−Ba(1)−O(8)	168.5(4)	O(3)−Ba(1)−O(8)	70.4(4)
O(6)−Ba(1)−O(8)	141.1(4)	O(4)−Ba(1)−O(8)	114.4(4)
O(10′)−Ba(1)−O(10)	41.3(1)	O(7)−Ba(1)−O(10)	120.4(1)
O(9)−Ba(1)−O(10)	133.0(1)	O(1)−Ba(1)−O(10)	132.5(1)
O(5)−Ba(1)−O(10)	92.9(1)	O(3)−Ba(1)−O(10)	69.1(8)
O(6)−Ba(1)−O(10)	66.9(8)	O(4)−Ba(1)−O(10)	64.7(1)
O(8)−Ba(1)−O(10)	98.5(1)	O(10′)−Ba(1)−C(47)	72.6(7)
O(5a)−Ba(2)−O(5)	92.1(6)	O(5a)−Ba(2)−O(4a)	74.4(4)
O(5)−Ba(2)−O(4a)	163.2(4)	O(5a)−Ba(2)−O(4)	163.2(4)
O(5)−Ba(2)−O(4)	74.4(4)	O(4a)−Ba(2)−O(4)	120.6(5)
O(5a)−Ba(2)−O(1)	94.9(4)	O(5)−Ba(2)−O(1)	73.5(4)
O(4a)−Ba(2)−O(1)	116.8(4)	O(4)−Ba(2)−O(1)	72.0(4)
O(5a)−Ba(2)−O(1a)	73.5(4)	O(5)−Ba(2)−O(1a)	94.9(4)
O(4a)−Ba(2)−O(1a)	72.0(4)	O(4)−Ba(2)−O(1a)	116.8(4)
O(1)−Ba(2)−O(1a)	163.6(7)	O(5a)−Ba(2)−S(2a)	107.7(3)
O(5)−Ba(2)−S(2a)	144.5(3)	O(4a)−Ba(2)−S(2a)	51.7(3)
O(4)−Ba(2)−S(2a)	79.8(3)	O(1)−Ba(2)−S(2a)	75.6(3)
O(1a)−Ba(2)−S(2a)	118.6(3)	O(5a)−Ba(2)−S(2)	144.5(3)
O(5)−Ba(2)−S(2)	107.7(3)	O(4a)−Ba(2)−S(2)	79.8(3)
O(4)−Ba(2)−S(2)	51.7(3)	O(1)−Ba(2)−S(2)	118.6(3)
O(1a)−Ba(2)−S(2)	75.6(3)	S(2a)−Ba(2)−S(2)	72.8(2)
O(2b)−Ba(3)−O(2)	99.2(6)	O(2b)−Ba(3)−O(8)	171.3(4)
O(2)−Ba(3)−O(8)	72.3(4)	O(2b)−Ba(3)−O(8b)	72.3(4)
O(2)−Ba(3)−O(8b)	171.3(4)	O(8)−Ba(3)−O(8b)	116.3(6)
O(2b)−Ba(3)−O(3b)	76.3(4)	O(2)−Ba(3)−O(3b)	103.7(4)
O(8)−Ba(3)−O(3b)	103.5(4)	O(8b)−Ba(3)−O(3b)	76.4(4)
O(2b)−Ba(3)−O(3)	103.7(4)	O(2)−Ba(3)−O(3)	76.3(4)
O(8)−Ba(3)−O(3)	76.4(4)	O(8b)−Ba(3)−O(3)	103.5(4)
O(3b)−Ba(3)−O(3)	180.0(6)	O(2b)−Ba(3)−S(4)	137.6(3)
O(2)−Ba(3)−S(4)	112.9(3)	O(8)−Ba(3)−S(4)	48.1(3)
O(8b)−Ba(3)−S(4)	75.5(3)	O(3b)−Ba(3)−S(4)	70.0(3)
O(3)−Ba(3)−S(4)	110.0(3)	O(2b)−Ba(3)−S(4b)	112.9(3)
O(2)−Ba(3)−S(4b)	137.6(3)	O(8)−Ba(3)−S(4b)	75.5(3)
O(8b)−Ba(3)−S(4b)	48.1(3)	O(3b)−Ba(3)−S(4b)	110.0(3)
O(3)−Ba(3)−S(4b)	70.0(3)	S(4)−Ba(3)−S(4b)	59.0(2)

[a] Symmetry transformations used to generate equivalent atoms: (a) $x, -y, -z + {}^{1}/_{2}$; (b) $-x + {}^{5}/_{2}, -y + {}^{1}/_{2}, z$.

environment (O(2), O(3), O(8), and S(4), and their centrosymmetric counterparts) (Figure 4).

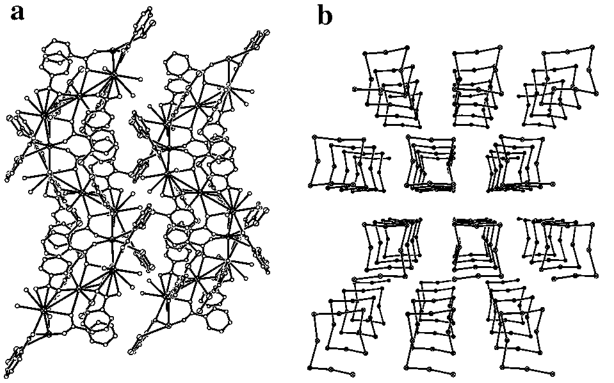

Figure 5. (a) Packing diagram of the coordination polymer **3** showing how the single polymeric chains of barium are connected to each other through the disulfide linkage of the DTBB ligand. (b) Packing diagram of the barium chains in the solid state, clearly depicting the formation of barium springs.

It is interesting to determine the exact mode of coordination (denticity) of the two DTBB ligands (DTBB-1 and DTBB-2) in the asymmetric part of **3**. The DTBB-1 ligand (having the S(1)−S(2) linkage) is octadentate; it is tridentate through one of its carboxylates, tetradentate through the other carboxylate, and monodentate through one of the sulfurs of the disulfide linkages. On the other hand, the DTBB-2 ligand is heptadentate; it is tridentate through each of its carboxylates and monodentate through its disulfide. Thus, the DTBB ligands in complex **3** show the maximum denticity among all of the structurally characterized compounds of this ligand.[26]

Owing to the large denticity of DTBB in **3**, the solid-state structure results in a densely packed three-dimensional polymeric structure. The structure is too complex to be described in detail, unlike **1** and **2**, and hence a perspective view of the packing of the coordination polymer is shown in Figure 5a. At a close approximation, the strands of the coordination polymers are linked together through disulfide bridges. Removal of atoms other than barium results in Figure 5b, which shows how the Ba ions are placed within these polymeric strands (see also Supporting Information). These strands, in fact, spiral around in the third dimension (the alternate strands spiral in clockwise and counterclockwise directions, respectively) to form barium springs. Although these springs appear to be independent of each other, in the crystal, they are all linked to each other through the DTBB ligands. It should be noted that, in these springs, every alternate ion is of Ba(1) type and every third ion is either Ba(2) or Ba(3). Quite surprisingly, the observed Ba⋯Ba distances (Ba(1)−Ba(2) 4.069(2) Å and Ba(1)−Ba(3) 4.264(2) Å) are well within the sum of van der Waals radii (4.28 Å). This observation contrasts with the M⋯M contacts, which are larger than the sum of van der Waals radii in the case of **1** and **2** and could be attributed to the presence of sulfur coordination to the metal in **3**. Further, the ability of a sulfur atom to participate in metal binding in **3** can be alluded to the increased soft character of the heavier group 2 metal ion.

The bond angles around the nine-coordinate Ba(1) vary over a wider range (41.2(1)−168.5(9)°) compared to the eight-coordinate Ba(2) and Ba(3) atoms (51.7(3)−163.6(7)° and 48.1(3)−171.3(4)°, respectively). The Ba(1)−O distances vary in the range 2.69(2)−3.00(2) Å, with the average value of 2.82 Å.[36] The shortest and the longest Ba(1)−O bonds are associated

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(36) In general, the coordination geometry and the metric parameters in **3** are comparable to those found in several carboxylate complexes of barium containing additional macrocyclic ligands. For example, see the following: (a) Voegele, J. C.; Thierry, J. C.; Weiss, R. *Acta Crystallogr., Sect. B* **1974**, *30*, 70. (b) Burns, J. H.; Musikns, C. *Inorg. Chem.* **1977**, *16*, 1619.

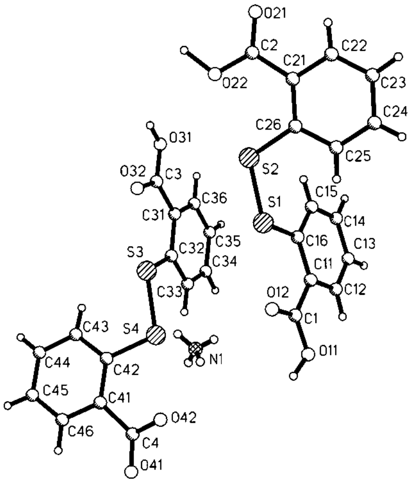

Figure 6. A perspective view of the disulfide adduct **4**.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **4**

	Bond Lengths		
S(1)−C(16)	1.796(3)	S(1)−S(2)	2.041(1)
O(11)−C(1)	1.311(4)	O(12)−C(1)	1.208(4)
S(2)−C(26)	1.792(4)	O(21)−C(2)	1.243(4)
O(22)−C(2)	1.287(4)	S(3)−C(32)	1.794(4)
S(3)−S(4)	2.043(1)	O(31)−C(3)	1.318(4)
O(32)−C(3)	1.219(4)	S(4)−C(42)	1.793(3)
O(41)−C(4)	1.237(4)	O(42)−C(4)	1.278(4)
	Hydrogen Bond Lengths		
N1···O12	2.751(6)	N1···S4	3.247(4)
N1···O42	3.125(5)	O11···O21	2.656(4)
N1···S2	3.337(5)	N1···O32	2.744(5)
N1···O22	3.091(5)	O31···O41	2.639(4)
O22···O42	2.460(3)		
	Bond Angles		
C(16)−S(1)−S(2)	105.53(1)	O(12)−C(1)−O(11)	122.2(3)
O(12)−C(1)−C(11)	122.7(3)	O(11)−C(1)−C(11)	115.1(3)
C(15)−C(16)−S(1)	122.0(3)	C(11)−C(16)−S(1)	119.7(3)
C(26)−S(2)−S(1)	105.98(1)	O(21)−C(2)−O(22)	122.4(3)
O(21)−C(2)−C(21)	120.2(3)	O(22)−C(2)−C(21)	117.4(3)
C(25)−C(26)−S(2)	120.7(3)	C(21)−C(26)−S(2)	120.5(3)
C(32)−S(3)−S(4)	105.05(1)	O(32)−C(3)−O(31)	122.0(3)
O(32)−C(3)−C(31)	122.4(3)	O(31)−C(3)−C(31)	115.6(3)
C(33)−C(32)−S(3)	122.7(3)	C(31)−C(32)−S(3)	119.3(3)
C(42)−S(4)−S(3)	106.26(1)	O(41)−C(4)−O(42)	123.5(3)
O(41)−C(4)−C(41)	119.6(3)	O(42)−C(4)−C(41)	116.9(3)

with the coordinated water molecules. The Ba(2)−O and Ba(3)−O distances are almost invariant, with the average values being 2.66 and 2.68 Å, respectively. While the Ba(2)−S(2) bond length is fairly short (3.379(6) Å), the Ba(3)−S(4) bond is considerably elongated (3.610(6) Å).

Crystal Structure of [(HOOCC$_6$H$_4$SSC$_6$H$_4$COOH)(HOOCC$_6$H$_4$SSC$_6$H$_4$COONH$_4$)] (4). Disulfide adduct **4** crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with four molecules of the 1:1 adduct in the unit cell. The molecular structure of the 1:1 adduct along with the NH_4^+ ion is shown in Figure 6. The selected bond angles and bond distances are given in the Table 5. The involvement of the NH_4^+ ion in hydrogen bonding to produce an extended solid is pictorially depicted in Figure 7. The packing diagram of **4** in the solid state, and viewed down *y*-axis, is shown in Figure 8. All of the S−S bond lengths in the asymmetric part are almost equal (2.040(1) and 2.042(1) Å). This value compares well with the literature values for other disulfides (appoximately 2.05 Å).[37]

Table 6. Comparison of Structural Data on the Complexes/Adducts of DTBB

compd	M	ligand denticity	S···S (Å)	C−S−S−C (deg)	ref
H[a]	Co	2	2.048(1)	−88.3(1)	26a
I[a]	Co	4	2.063(3)	83.2(4)	26b
J[a]	Os	4	2.039(10)	86(1)	26c
1	Ca	6	2.044(1)	94.7(1)	this work
2	Sr	6	2.048(1)	94.9(2)	this work
3	Ba	7, 8	2.045(7)	−84.5(9), −87.5(9)	this work
4	NH$_4$		2.041(1)	−84.6(2), −101.0(2)	this work

[a] For the structural formulas of **H**−**J**, see Scheme 2.

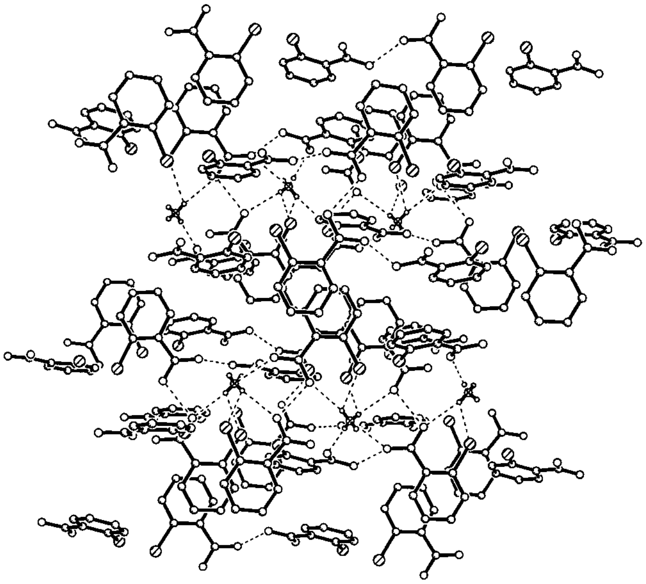

Figure 7. Packing diagram of **4**, showing the role of NH_4^+ ions in forming a hydrogen-bonded polymeric network.

The C−S−S−C dihedral angles in the two DTBB units of **4** are −84.6(2)° and −101.0(2)°, respectively. These values clearly indicate that the aryl substituents on the two sulfur atoms are neither cis (expected value 0°) nor trans (expected value 180°) with respect to each other. The observed values are close to 90°, indicating an approximate perpendicular disposition of the aryl rings with respect to each other (see Figure 8). Further there are two short nonbonded S···O contacts in each molecule originating from the sulfur atom and the oxygen atom of the carboxyl group which is attached to the aryl ring (see contact S(1)···O(12) 2.614(3) Å, S(2)···O(22) 2.738(2) Å, S(3)···O(32) 2.607(3) Å, S(4)···O(42) 2.755(2) Å; sum of van der Waals radii is 3.25 Å). The presence of the NH_4^+ ion is the source of extensive hydrogen bonds in the lattice. Apart from the O−H···O hydrogen bonding between the adjacent neighbors (Figure 7), additional N−H···O and N−H···S hydrogen bonds are formed to result in a supramolecular array of disulfide adducts (Figures 8).

Before concluding, it is of interest to compare a few key structural parameters, which are common in **1**−**4**, along with those of the previously reported metal complexes of DTBB ligands. The parameters of interest are the S···S bond distances and the C−S−S−C dihedral angles (Table 6). Very little change or no changes are observed in the S···S distances. In general, the C−S−S−C dihedral angles are close to 90° for all of the compounds described in Table 6. This observation is quite interesting, since the state of the ligand (coordinate or free) does not seem to have an effect in the observed angles. Another important factor that emerges from Table 6 is the increase in

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Table 7. Crystal Data and Experimental Details for the Structure Determination of **1**−**4**

	1	**2**	**3**	**4**
empirical formula	$C_{15}H_{15}CaO_{6.5}S_2$	$C_{15}H_{15}O_{6.5}S_2Sr$	$C_{28}H_{21}Ba_2O_{10.5}S_4$	$C_{28}H_{23}NO_8S_4$
fw	403.47	451.01	928.37	629.71
temp, K	293(2)	293(2)	293(2)	203(2)
wavelength, (Å)	0.70930	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)	*Pcnn* (No. 52)	$P2_1/n$ (No. 14)
a, Å	22.549(11)	22.396(3)	13.107(3)	11.3619(9)
b, Å	7.538(2)	7.765(1)	19.339(4)	12.0443(10)
c, Å	21.597(5)	21.767(1)	24.883(8)	21.126(3)
α, deg	90	90	90	90
β, deg	114.34(3)	114.25(1)	90	94.01(1)
γ, deg	90	90	90	90
vol, $Å^3$; *Z*	3345(2); 8	3451.3; 8	6307(3); 8	2883.9(5); 4
ρ(calcd), g cm^{-3}	1.602	1.736	1.955	1.450
μ, mm^{-1}	0.657	3.397	2.804	0.381
F(000)	1640	1784	3592	1304
θ, deg	1.98−24.95	1.99−24.96	1.64−22.50	3.52−22.53
total reflns	3115	3206	4410	5841
unique reflns	2927	3021	4128	3773
GOF on F^2	1.079	1.025	0.873	1.061
R1[a] [$I > 2\sigma(I)$]	0.0341	0.0342	0.0794	0.0421
WR2[a] [$I > 2\sigma(I)$]	0.0949	0.0859	0.1287	0.0859

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$.

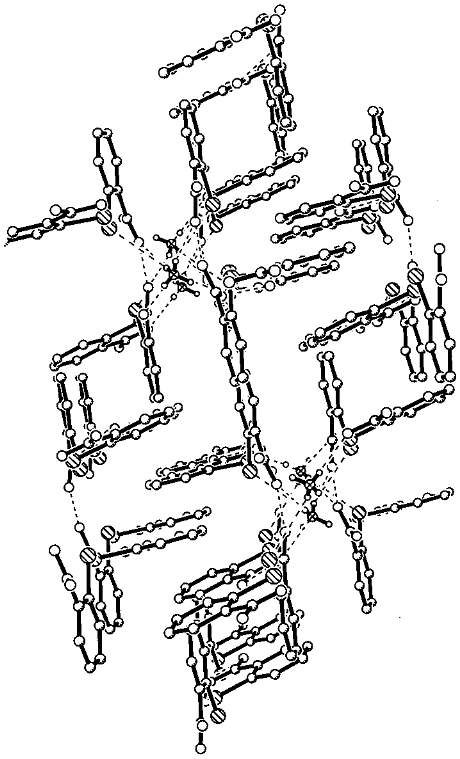

Figure 8. Packing diagram of **4** (viewed down the "*Y*" axis) showing the disposition of the aryl rings with respect to the disulfide linkage.

the denticity of the DTBB ligand on moving from transition metals (**H**−**J**) to group 2 metal ions (**1**−**3**).

Conclusion

In this contribution, we have thus presented a systematic and detailed study of the reactions of group 2 metal chlorides with 2-mercaptobenzoic acid. Under the experimental conditions employed, in each case, the thiol group undergoes facile oxidation to form the H_2-DTBB ligand, which in turn coordinates to the metal ions. While the coordination is exclusively through the carboxylate groups of the DTBB ligands in the case of hard metal ions such as calcium and strontium, the disulfide linkage also participates in the metal binding in the case of the softer barium ion. The binding of disulfide linkage to barium ion may have some role to play in heavy metal poisoning by barium in physiological systems. This observation probably needs to be further investigated in future studies. Thus our current research efforts in group 2 metal chemistry are concentrated on the systematic investigation of other bifunctional ligands particularly possessing different degrees of hard−soft basic centers.

Experimental Section

General Procedures. Commercial grade solvents were purified by employing conventional procedures and were freshly distilled prior to their use.[38] Deionized water used in all the reactions and was doubly distilled prior to its use. Starting materials $MgCl_2{\cdot}6H_2O$, $CaCl_2{\cdot}6H_2O$, $SrCl_2{\cdot}2H_2O$, $BaCl_2{\cdot}2H_2O$, and H-2-MBA were procured from commercial sources and used as received. The starting materials and the reaction products described are all air-stable and hence were routinely handled under normal laboratory conditions without any precautions to exclude oxygen and moisture.

Instruments. The melting points were measured in glass capillaries and are reported uncorrected. Elemental analyses were performed on a Carlo Eraba (Italy) model 1106 elemental analyzer and Thermoquest Flash EA 1112 series CHNS analyzer. Infrared spectra were recorded on a Nicolet Impact 400 spectrometer as KBr diluted thin plates in the solid state. Thermogravimetric analysis and differential thermal analysis were carried out at the RSIC, IIT−Bombay on a DuPont thermal analyzer, model 2100, under a stream of nitrogen gas. Other methods and instruments employed in this study have been described earlier.[39,40]

Preparation of Complexes 1−3. H-2-MBA (1.34 g, 9.0 mmol) was dissolved in ethanol (30 mL) and diluted with water (15 mL). Metal chloride $MCl_2{\cdot}nH_2O$ (M = Ca, Sr, Ba; n = 6, 2, 2; 4.5 mmol) dissolved in water (25 mL) was added to the above solution. To this mixture was added aqueous NH_3 (25%) (15 mL) dropwise till the reaction mixture became slightly basic. The resulting solution was concentrated to half of its original volume on a water bath, filtered, and kept for crystallization. Colorless crystals suitable for diffraction studies were obtained after 2 days in each case. The isolated yields, melting point, analytical data, and IR spectral data are given in Table 1.

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(40) Murugavel, R.; Sathiyendiran, M.; Walawalkar, M. G. *Inorg. Chem.* **2001**, *40*, 427.

Reaction of H-2-MBA with $MgCl_2 \cdot 6H_2O$. H-2-MBA (1.34 g, 9 mmol) was dissolved in ethanol (30 mL) and mixed with $MgCl_2 \cdot 6H_2O$ (0.91 g, 4.5 mmol) dissolved in water (20 mL). The resultant solution was warmed at 50 °C for 30 min. To this solution was added aqueous NH_3 (25%) (15 mL) dropwise, and the resulting solution was heated on a water bath for 1 h, during which a dark brown precipitate was formed. This precipitate was separated from the solution by filtration, and the solution was concentrated and kept for crystallization. Brown colored crystals of $[(HOOCC_6H_4SSC_6H_4COOH)(HOOCC_6H_4SSC_6H_4COONH_4)]$ (**4**) were obtained after 3 days. Yield: 30% (see Table 1).

X-ray Diffraction Studies of 1−4. A suitable crystal was chosen from the crop of crystals as obtained for **1**−**4**. While the data collection for compounds **1**−**3** was carried out on a Nonius MACH-3 diffractometer, the intensity data for **4** was obtained on a Siemens-Stoe AED 2 diffractometer. Intensity data collection and cell determination were carried out using a monochromatized Mo Kα radiation in both of the diffractometers. The data were suitably processed, and the space group determination was carried out by examining the systematic absences. Structure solution was achieved by direct methods by using SHELXS-96[41] software. Further structural refinement and identification of lighter atoms were carried out by the refinement program SHELXL-97.[42] The hydrogen atoms in all four compounds have been geometrically fixed and were refined using a riding model. All of the non-hydrogen atoms were refined with anisotropic thermal motions while only isotropic thermal motion was taken into account for the hydrogen atoms during the refinement. The final *R* factors and other details pertaining to data collection, structure solution, and final refinement for all of the compounds are given in Table 7.

Acknowledgment. Generous financial support by DST, New Delhi (SP/S1/F19/98) (for the purchase of a MBraun Glovebox), and CSIR (01(1546)/98/EMR-II) for carrying out this work is gratefully acknowledged. This work was also supported by a DAE Young Scientist Research Award to R.M. The authors thank the DST funded Single Crystal X-ray Diffractometer Facility at IIT—Bombay for the X-ray diffraction data and the RSIC, IIT—Bombay, for the TGA and DTA measurements. The authors thank Dr. M. G. Walawalkar for her useful input at various stages of this work. Thanks are due to Garuda Chemicals, Mumbai, for a gift of mercaptobenzoic acids.

Supporting Information Available: Crystallographic data in CIF format. X-ray data (including experimental details, atomic coordinates, complete bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for compounds **1**−**4**) (Tables S1−S20 and Figures S1−S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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