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X-ray crystallographic studies of a Mn(II)-bridged biscalix[4]arene with a large inner cavity

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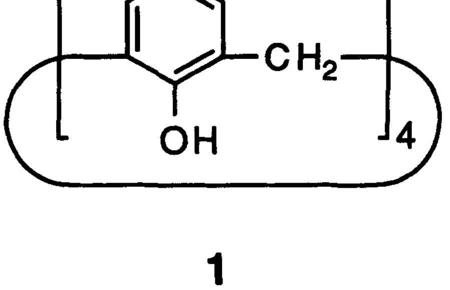
A complex isolated from a mixture of tetrasodium 5,11,17,23-tetrasulfonatocalix[4]arene-25,26,27,28-tetrol and Mn(II) has been analyzed by X-ray crystallography. The crystal packing diagram featured a clay-like bilayer structure as reported previously for the analogous crystals. Interestingly, Mn(II) ions present in the hydrophilic layer cross-link two hydrophobic layers through coordination to the sulfonato groups. Because of this complex formation the repeat unit of the layer (12.1 Å) is shorter than those for analogous systems (13.7–15.0 Å). The structure features a Mn(II)-bridged biscalix[4]arene with a large inner cavity. X-Ray crystallographic and ESR spectral data show that Mn(II) ions adopt a distorted octahedral coordination geometry with two sulfonato groups occupying the *cis* coordination. This is a novel coordination mode for a metal-bridged biscalix[4]arene in the solid state.

INTRODUCTION

It is known that manganese plays important catalytic roles in the active sites of certain metalloenzymes. It acts as a Lewis acid to polarize substrates or as an electron-source to mediate redox reactions.[1–4] The mechanistic aspects have been studied in a nonenzymatic model system as well as in an enzymatic system.[5] For example, Nair and Dismukes[6] reported that a binuclear Mn(III)-β-cyclodextrin complex mimics the catalytic activity of the photosynthetic water oxidizing enzyme. We considered that a similar multinuclear manganese complex may be formed in the presence of water-soluble calix[n]arenes because they also possess OH groups to bind to such multinuclear manganese complexes. As a prelude to this research project we recrystallized Mn(II) with tetrasodium 5,11,17,23-tetrasulfonatocalix[4]arene-25,26,27,28-tetrol (**1**). The X-ray crystallographic study of the complex disclosed that the Mn(II) ions do not interact with the OH groups but act as a "bridge" to cross-link the sulfonato groups, resulting in a biscalix[4]arene with a large inner cavity. Although a single *trans* linkage across the layer was reported by Atwood et al.[7] for the **1**•Cu(II) complex, this is the first example for the double *trans* linkages. This is a novel and expeditious method to prepare a calixarene-based large cavity as well as a rare example on a sulfonato-coordinated manganese complex.

RESULTS AND DISCUSSION

The crystal was obtained by crystallization of a mixture of **1** and $Mn(ClO_4)_2 \cdot 6H_2O$ in aqueous NaOH solution. The crystal data are summarized in Table 1. The positional parameters, bond lengths, and bond angles are summarized in Tables 2, 3, and 4, respectively. The crystal structure of **1** was resolved by Atwood's group.[8–11] We also determined the crystal structure of **1** on a trimethylanilinium ion.[12] These crystal systems all feature a clay-like bilayer structure with the lower OH-side



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turned to the hydrophobic inside and the upper sulfonato-side turned to the hydrophilic outside.[8-12] As shown in Figure 1, the **1**•Mn(II) complex also features the bilayer structure. Mn(II) ions reside in the hydrophilic layers sandwiched by the sulfonato groups. Strangely, we noticed that the repeat units (7.0 Å for the hydrophilic layer and 12.1 Å for the repeat distance)* are a little shorter than those reported previously (8.3–8.7 Å for the hydrophilic layer and 13.7–15.0 Å for the repeat distance).[9,12]** As mentioned later, this change is closely related to the bridge effect of the Mn(II) ions.

The unit structure for (**1**•Mn(II))$_2$ is shown in Figure 2. Two **1**'s adopt a cone conformation slightly distorted from C_{4v} symmetry. The dihedral angles between the phenyl rings and the mean plane of the four ArCH$_2$Ar methylene groups are 119.1° (phenyl ring bearing S1-O4

Table 1 Crystallographic Data

Compound	**1**•Mn
Formula	$C_{28}H_{20}O_{16}S_4Na_4Mn{\bullet}9.5H_2O$
Fw	1058.7
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	14.912(1)
b, Å	24.354(2)
c, Å	11.858(1)
β, deg	97.285(7)
V, +^{3}	4271.6(6)
*D*calc, g cm^{-3}	1.570
μ, cm^{-1}	54.6
Z	4
Crystal size, mm	0.3×0.25×0.25
R	0.113
Rw	0.161

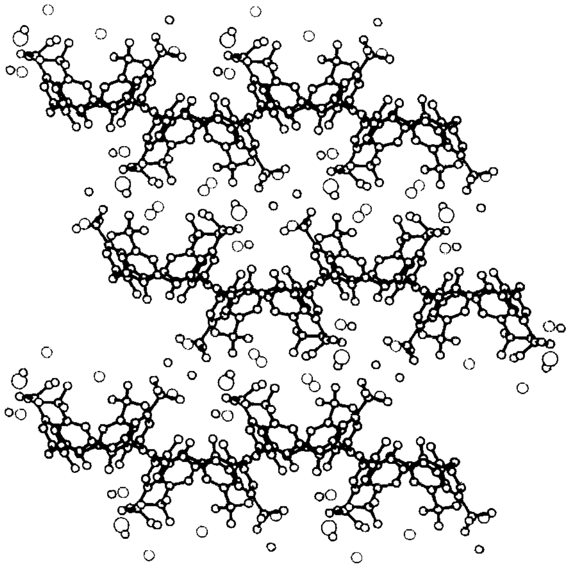

Figure 1 Crystal packing diagram: carbon and sulfur(black), oxygen(red), sodium(green), and manganese(blue). (See color plate I at end of journal.)

Table 2 Positional Parameters for the **1**•Mn(II) Complex

Atom	*x*	*y*	*z*
Mn(1)	-0.2786(4)	0.5395(2)	0.7179(4)
S(1)	-0.2042(2)	0.5901(1)	0.4690(2)
S(2)	-0.0863(2)	0.6025(1)	1.0776(2)
S(3)	0.4075(2)	0.5771(1)	0.9147(2)
S(4)	0.2454(2)	0.5969(1)	0.2961(2)
Na(1)	-0.1460(4)	0.4536(2)	0.4908(5)
Na(2)	-0.2717(3)	0.6365(2)	1.1812(3)
Na(3)	0.1096(3)	0.5240(2)	0.0724(5)
Na(4)	0.4636(3)	0.5749(2)	0.2178(4)
O(1)	-0.0056(5)	0.7934(3)	0.6088(6)
O(2)	-0.1349(6)	0.5495(4)	0.4944(8)
O(3)	-0.2367(6)	0.5906(4)	0.3493(6)
O(4)	-0.2774(5)	0.5836(4)	0.5381(7)
O(5)	0.0506(5)	0.7846(3)	0.8199(6)
O(6)	-0.0447(5)	0.5520(3)	1.0440(7)
O(7)	-0.1844(5)	0.6011(4)	1.0499(7)
O(8)	-0.0605(6)	0.6157(4)	1.1970(6)
O(9)	0.2105(5)	0.7809(3)	0.7805(6)
O(10)	0.3938(5)	0.5642(4)	1.0311(6)
O(11)	0.3746(7)	0.5330(4)	0.8373(7)
O(12)	0.5017(5)	0.5896(4)	0.9040(7)
O(13)	0.1591(5)	0.7956(3)	0.5461(6)
O(14)	0.2489(6)	0.5495(4)	0.3710(7)
O(15)	0.3339(5)	0.6090(4)	0.2649(7)
O(16)	0.1741(6)	0.5919(4)	0.2014(7)
O(17)	0.4429(6)	0.4817(4)	0.2803(7)
O(18)	-0.2603(6)	0.5139(4)	0.9150(7)
O(19)	-0.1053(7)	0.5422(5)	0.7692(9)
O(20)	-0.3274(7)	0.6314(5)	0.7863(9)
O(21)	-0.0188(7)	0.4560(5)	0.6325(9)
O(22)	-0.3974(5)	0.5798(4)	1.1222(7)
O(23)	0.5661(9)	0.4399(7)	0.457(1)
O(24)	0.5472(6)	0.6088(4)	0.3897(7)
O(25)	0.434(1)	0.107(1)	0.885(2)
O(26)	0.285(1)	0.0236(8)	0.803(1)
O(27)	0.385(1)	0.0621(9)	0.616(1)
C(1)	-0.0577(7)	0.7477(5)	0.5732(9)
C(2)	-0.1167(6)	0.7255(5)	0.6438(8)
C(3)	-0.1624(6)	0.6781(5)	0.6108(9)
C(4)	-0.1516(6)	0.6531(5)	0.5050(8)
C(5)	-0.0962(7)	0.6773(5)	0.4342(9)
C(6)	-0.0484(6)	0.7247(5)	0.4665(8)
C(7)	-0.1322(7)	0.7521(5)	0.7548(8)
C(8)	0.0193(7)	0.7432(5)	0.8775(8)
C(9)	0.0770(6)	0.7153(5)	0.9638(8)
C(10)	0.0446(7)	0.6732(5)	1.0251(9)
C(11)	-0.0459(7)	0.6567(5)	0.9999(8)
C(12)	-0.1046(7)	0.6831(5)	0.9114(9)
C(13)	-0.0714(6)	0.7256(5)	0.8519(8)
C(14)	0.1754(6)	0.7332(5)	0.9919(9)
C(15)	0.2515(7)	0.7323(5)	0.8111(8)
C(16)	0.3101(6)	0.7102(5)	0.7374(8)
C(17)	0.3552(6)	0.6617(5)	0.7697(8)
C(18)	0.3447(7)	0.6368(5)	0.8731(8)
C(19)	0.2857(6)	0.6599(5)	0.9448(9)
C(20)	0.2380(6)	0.7067(5)	0.9116(8)
C(21)	0.3252(6)	0.7376(5)	0.6260(8)
C(22)	0.1743(6)	0.7462(4)	0.4947(8)
C(23)	0.1099(6)	0.7244(5)	0.4130(8)
C(24)	0.1301(6)	0.6781(5)	0.3538(8)
C(25)	0.2154(7)	0.6534(4)	0.3785(8)
C(26)	0.2787(7)	0.6739(5)	0.4662(8)
C(27)	0.2586(6)	0.7191(5)	0.5271(8)
C(28)	0.0165(6)	0.7505(5)	0.3907(8)

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*The thickness of the hydrophilic layer is defined as the perpendicular distance between the planes comprising the sulfur-bonded aromatic carbon atoms.[7] The repeat distance is defined as the sum of the hydrophilic layer and the hydrophobic layer.[9]

However, the thickness of the hydrophilic layer for the **1•Yb(III) complexs was estimated to be 7.51 Å.[7]

Table 3 Bond Lengths (Å) for the **1**•Mn(II) Complex

Atom(1)-Atom(2)	*Length*	*Atom(1)-Atom(2)*	*Length*
Mn(1)-O(4)	2.39(1)	C(2)-C(7)	1.51(1)
Mn(1)-O(14)	2.47(1)	C(3)-C(4)	1.42(1)
Mn(1)-O(17)	2.51(1)	C(4)-C(5)	1.38(1)
Mn(1)-O(18)	2.40(1)	C(5)-C(6)	1.38(2)
Mn(1)-O(19)	2.58(1)	C(6)-C(28)	1.54(1)
Mn(1)-O(20)	2.52(1)	C(7)-C(13)	1.52(1)
S(1)-O(2)	1.435(9)	C(8)-C(9)	1.42(1)
S(1)-O(3)	1.441(8)	C(8)-C(13)	1.41(1)
S(1)-O(4)	1.453(9)	C(9)-C(10)	1.38(2)
S(1)-C(4)	1.75(1)	C(9)-C(14)	1.53(1)
S(2)-O(6)	1.456(9)	C(10)-C(11)	1.40(1)
S(2)-O(7)	1.458(7)	C(11)-C(12)	1.43(1)
S(2)-O(8)	1.455(8)	C(12)-C(13)	1.38(2)
S(2)-C(11)	1.76(1)	C(14)-C(20)	1.56(1)
S(3)-O(10)	1.455(8)	C(15)-C(16)	1.42(1)
S(3)-O(11)	1.456(9)	C(15)-C(20)	1.38(1)
S(3)-O(12)	1.459(8)	C(16)-C(17)	1.39(2)
S(3)-C(18)	1.76(1)	C(16)-C(21)	1.52(1)
S(4)-O(14)	1.455(9)	C(17)-C(18)	1.40(1)
S(4)-O(15)	1.445(9)	C(18)-C(19)	1.42(2)
S(4)-O(16)	1.451(9)	C(19)-C(20)	1.37(2)
S(4)-C(25)	1.78(1)	C(21)-C(27)	1.51(1)
O(1)-C(1)	1.39(1)	C(22)-C(23)	1.38(1)
O(5)-C(8)	1.33(1)	C(22)-C(27)	1.43(1)
O(9)-C(15)	1.36(1)	C(23)-C(24)	1.38(2)
O(13)-C(22)	1.38(1)	C(23)-C(28)	1.52(1)
C(1)-C(2)	1.40(1)	C(24)-C(25)	1.40(1)
C(1)-C(6)	1.41(1)	C(25)-C(26)	1.41(1)
C(2)-C(3)	1.37(2)	C(26)-C(27)	1.37(2)

coordinating to Mn(II)), 131.5°, 127.0°, and 124.8° (phenyl ring bearing S4-O14 coordinating to Mn(II)). Clearly, the two proximal phenyl rings used for the bridge formation stand up whereas the residual two phenyl rings are more or less flattened.

In Figure 3 the crystallographically important atoms present in the Mn(II) coordination sphere are illustrated. The (**1**•Mn(II))$_2$ has C_i symmetry and the complex structure of the two Mn(II)'s is the same. Each Mn(II) adopts an octahedral coordination including four water oxygens and two sulfonate oxygens. The two sulfonato groups occupy a *cis* position relative to an octahedron, one as an equatorial ligand and one as an apical ligand. The distances between Mn(II) and water oxygens (2.39–2.58 Å)

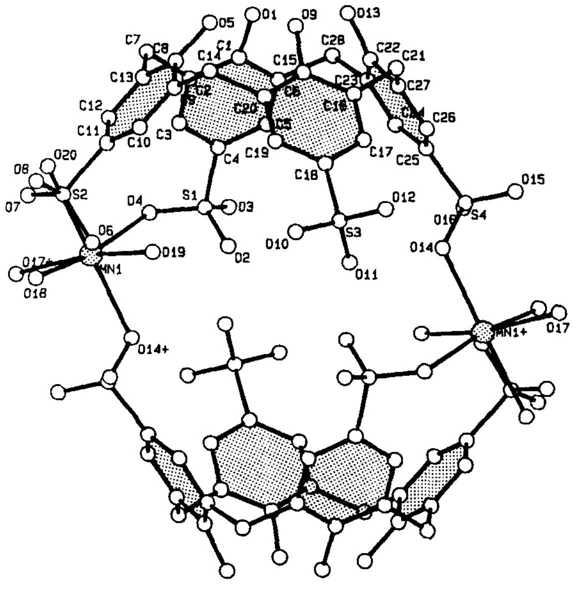


Figure 2 Mn(II)-Bridged dimeric structure of (**1**•**Mn(II)**)^2. Hydrogen atoms are omitted for clarify.

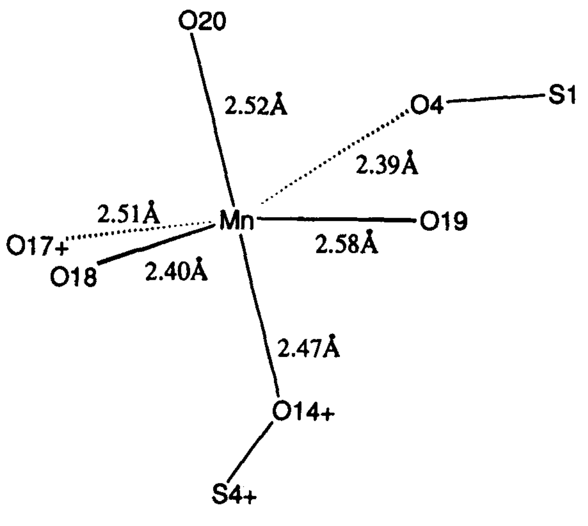


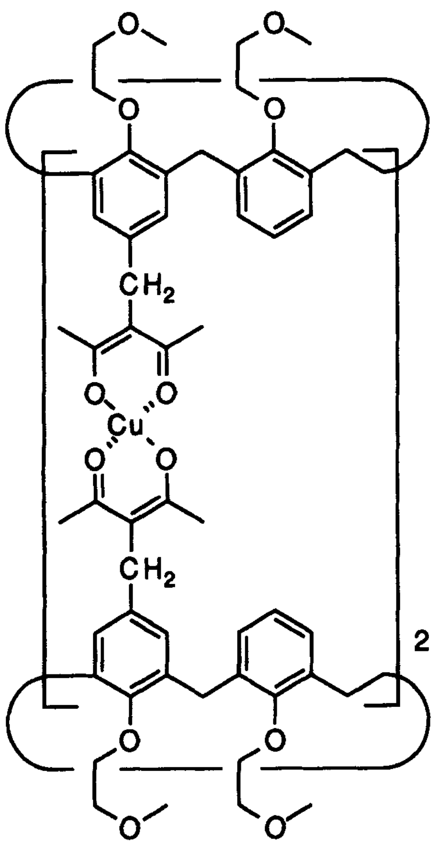
Figure 3 Octahedral coordination geometry of the Mn(II) complex.

Table 4 Bond Angles (°) for the **1**•Mn(II) Complex

Atom(1)-Atom(2)-Atom(3)	*Angle*
O(2)-S(1)-O(3)	110.9(5)
O(2)-S(1)-O(4)	112.3(5)
O(2)-S(1)-C(4)	105.4(5)
O(3)-S(1)-C(4)	108.4(5)
O(6)-S(2)-O(7)	111.6(5)
O(6)-S(2)-C(11)	107.7(5)
O(7)-S(2)-O(8)	111.0(5)
O(7)-S(2)-C(11)	107.5(5)
O(8)-S(2)-C(11)	106.2(5)
O(10)-S(3)-O(11)	111.3(5)
O(10)-S(3)-O(12)	112.3(4)
O(10)-S(3)-C(18)	108.0(5)
O(11)-S(3)-O(12)	110.5(5)
O(12)-S(3)-C(18)	106.7(5)
O(14)-S(4)-O(15)	110.7(5)
O(14)-S(4)-O(16)	111.8(5)
O(14)-S(4)-C(25)	105.8(5)
O(15)-S(4)-O(16)	115.0(5)
C(1)-C(6)-C(5)	118.4(9)
C(5)-C(6)-C(28)	121.3(9)
C(2)-C(7)-C(13)	109.7(9)
C(8)-C(13)-C(12)	120.9(9)
O(5)-C(8)-C(13)	120.4(9)
C(9)-C(8)-C(13)	119.(1)
C(8)-C(9)-C(10)	120.9(9)
C(8)-C(9)-C(14)	119.8(9)
C(10)-C(9)-C(14)	119.3(8)
C(9)-C(10)-C(11)	119.6(9)
C(17)-C(16)-C(21)	119.5(9)
S(2)-C(11)-C(10)	119.2(8)
C(10)-C(11)-C(12)	121.(1)
S(3)-C(18)-C(19)	120.5(8)
S(4)-C(25)-C(24)	120.1(7)
S(4)-C(25)-C(26)	119.3(8)
C(25)-C(26)-C(27)	120.2(9)
C(14)-C(20)-C(19)	119.8(9)
C(21)-C(27)-C(22)	122.8(9)
C(21)-C(27)-C(26)	118.9(9)
C(6)-C(28)-C(23)	111.0(8)
O(13)-C(22)-C(27)	118.2(8)
C(22)-C(23)-C(24)	119.6(8)
C(24)-C(23)-C(28)	120.4(8)
O(15)-S(4)-C(25)	106.6(5)
O(16)-S(4)-C(25)	106.2(5)
O(3)-S(1)-O(4)	111.9(5)
O(4)-S(1)-C(4)	107.6(5)
O(6)-S(2)-O(8)	112.6(5)
O(1)-C(1)-C(2)	119.7(9)
O(1)-C(1)-C(6)	118.5(9)
C(2)-C(1)-C(6)	122.(1)
C(1)-C(2)-C(3)	119.(1)
C(1)-C(2)-C(7)	122.(1)
C(3)-C(2)-C(7)	118.9(9)
C(2)-C(3)-C(4)	120.(1)
O(11)-S(3)-C(18)	107.9(5)
S(1)-C(4)-C(3)	119.5(8)
S(1)-C(4)-C(5)	120.6(8)
C(3)-C(4)-C(5)	120.(1)
C(4)-C(5)-C(6)	121.(1)
C(11)-C(12)-C(13)	119.1(9)
C(1)-C(6)-C(28)	120.3(9)
C(7)-C(13)-C(8)	119.8(9)
C(7)-C(13)-C(12)	119.3(9)
C(9)-C(14)-C(20)	112.5(8)
O(5)-C(8)-C(9)	120.6(9)
O(9)-C(15)-C(16)	117.1(9)
O(9)-C(15)-C(20)	120.9(9)
C(16)-C(15)-C(20)	122.(1)
C(15)-C(16)-C(17)	117.8(9)
C(15)-C(16)-C(21)	123.(1)
C(16)-C(17)-C(18)	121.(1)
S(2)-C(11)-C(12)	120.2(8)
S(3)-C(18)-C(17)	119.3(8)
C(17)-C(18)-C(19)	120.(1)
C(18)-C(19)-C(20)	120.(1)
C(24)-C(25)-C(26)	120.6(9)
C(14)-C(20)-C(15)	120.(1)
C(15)-C(20)-C(19)	120.(1)
C(16)-C(21)-C(27)	112.9(8)
C(22)-C(27)-C(26)	118.3(8)
O(13)-C(22)-C(23)	120.4(8)
C(23)-C(22)-C(27)	121.4(9)
C(22)-C(23)-C(28)	120.1(9)
C(23)-C(24)-C(25)	119.6(8)

are comparable with those between Mn(II) and sulfonato oxygens (2.39–2.47 Å). A survey of past literature reveals that there are a limited number of sulfonato-metal complexes in calixarene•metal complexes. In lanthanide complexes (Yb(III) and La(III)) the distances between Ln(III) and sulfonato groups are 2.33–2.49 Å.[7,13] In transition metal complexes, for example, the distance between Cu(II) and sulfonato group is 2.55 Å.[7,14] These values are all comparable with the distances between Mn(II) and sulfonato groups in (**1**•Mn(II))$_2$. The shrinkage of the hydrophilic layer is thus ascribable to the inter-layer cross-link by Mn(II), particularly, to the cross-link with the *cis*-configurational Mn(II) complex. It can also be seen from Figure 1 that in the hydrophobic bilayer, a sulfonato group in one layer and a hydroxyl group in another layer interact with each other via a Na$^+$ ion. This interaction may stabilize the bilayer and make the repeat unit of the hydrophobic layer shorter.

We also surveyed the literature of Mn(II) complexes with an octahedral coordination geometry. In $MnSO_4$ the Mn(II)-O bond lengths are 2.11 and 2.25 Å and the O-Mn(II)-O bond angles are 78.4–92.0°.[15] Similar values are seen for α-$MnSO_3$•$3H_2O$[16] and $Mg_7Zn_4Mn_2(SO_4)(OH)_{26}$•$8H_2O$.[17] These values are both comparable with the bond lengths (as in Figure 3) and the bond angles (77.9–102.9°; Table 4) in the **1**•Mn(II) complex. One can thus conclude that two Mn(II) ions in (**1**•Mn(II))$_2$ adopt an octahedral coordination geometry. To obtain further insights into the complex structure we measured the ESR spectra at room temperature and -173°C. It is known that theoretically, ^{55}Mn(I = 5/2) gives 6 lines and Mn(II) in a high-spin state features isotropic g- and A-values whereas Mn(II) in a low-spin state gives a perceptible ESR spectrum only at low temperature region and features large anisotropy in the g- and A-values.[18] As shown in Figure 4, powder sample of the **1**•Mn(II) complex gave 6 lines with g = 2.01 and A =



2

97.4 G. At -173°C the peaks became sharper but the *g*- and *A*-values were unchanged. The result clearly supports the view that Mn(II) in the complex adopts a high-spin state. In general, Mn(II) with a high-spin state (d_5) favourably adopts an octahedral coordination geometry.[19,20] As the ligand field stabilization energy for the regular octahedral coordination is "zero" and the ion radius (0.82 Å) is larger than those for first row (+2) transition metals,[21] large distribution from the regular coordination structure may be observed. In fact, the bond lengths and the bond angles in octahedral Mn(II) complexes are widely spread and Mn(II) can accept a fairly distorted octahedral coordination geometry.[15-17,19,20] In the present system, the Mn(II)-O bond lengths range from 2.39 Å to 2.58 Å and the O-Mn(II)-O bond angles range from 77.9° to 102.9°, resulting in a distorted octahedral complex structure.

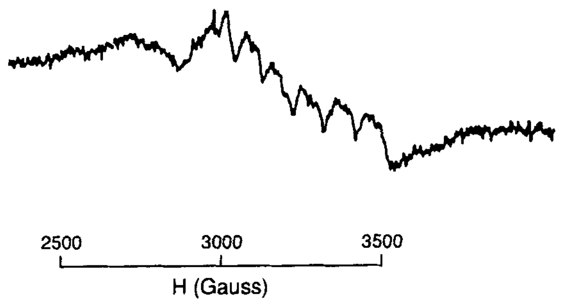


Figure 4 ESR spectrum of the powder of the **1**•Mn(II) complex at room temperature.

Very recently, we succeeded in the synthesis of a Cu(II)-bridged biscalix[4]arene (**2**) from calix[4]arene-25,26,27,28-tetrol via 6 steps.[22] This compound can recognize diamine substrates using a cavity composed of two Cu(II)-chelate complexes. The crystal structure of the **1**•Mn(II) complex which is prepared by crystallization of a mixture of **1** and Mn(II) is very similar to **2**. We believe that the biscalix[4]arene-based cavity in (**1**•Mn(II))$_2$ would be also useful for molecular recognition and that similar metal-bridged biscalix[4]arenes may also be formed in the solid state from other metal ions.

EXPERIMENTAL

Material

The synthesis of **1** was reported previously.[23] Compound **1** (150 mg, 0.18 mmol) and $Mn(ClO_4)_2$•$6H_2O$ (65 mg, 0.18 mmol) were dissolved in distilled water (5.0 mL). After stirring for 10 min aqueous 0.35 M NaOH solution (2.0 mL, 0.72 mmol) was added dropwise. After fitration the solution was saturated with NaCl and left at room temperature for four weeks. The single crystals were grown in this aqueous solution. Anal. Calcd for $C_{28}H_{20}O_{16}MnNa_4S_4$•$9.5H_2O$: C, 31.77; H, 3.72. Found: 32.97; H, 4.08.

ESR measurements

ESR spectra were measured with a JEOL JES-FEIXG spectrometer. The powdered sample of the **1**•Mn(II) crystal was subjected to the measurement at room temperature and -173°C.

X-ray crystallographic analysis

The crystals taken out of the aqueous solution became cloudy in the air. Therefore, we put the sample into a glass capillary (1 mm diameter) and sealed it with an adhesive agent. Integral intensities were collected by using graphite-monochromatized Cu-K_α radiation (λ=1.54184 Å) by the ω-2θ scan technique up to 2θ=130°. Of the 6796 reflections measured, the number of reflections observed was 5009 (I>3σ (I), where σ is the standard deviation observed from the counting statistics). The structure was solved by direct methods (MULTAN 11/82) and refined by full-matrix least-squares with anisotropic thermal parameters. For this purpose Mo1EN (an interactive structure solution procedure, Enraf-Norius, Delft, The Netherland (1990)) was used on a Micro VAX 3100 computer. An absorption correction was applied (see Table 1), but hydrogen atoms were not taken into account in the resolution process. The final R and R_w values were 0.113 and 0.161, respectively. A drop of the R-values is mainly due to the difficulty in setting water molecules in the crystal lattice. However, they are sufficient to discuss the bilayer structure and the unit structure.

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