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ARTICLE TYPE

Encapsulation of Manganese and Cobalt Complexes within Resorcin[4]arene Dimers

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The syntheses and single-crystal X-ray structures of Mn-and Co-DMSO inclusion complexes with *C*-propylresorcin[4]arene dimers are reported. The Mn complex exists in one form (1), whereas the Co complex exists in two forms (2a and 2b). The hydrogen-bonded, head-to-head dimers of 1 and 2a are isostructural, with the macrocycles connected by tri-solvent bridges.The di-solvent bridged hydrogen bonds of 2b connect diagonal macrocycles.

The endeavours to create robust metal-coordinated nanocages with calixarene-based macrocycles have driven the efforts of several supramolecular chemists.[1-8] Structurally similar to the 'calyx/vase-shaped' calixarenes, pyrogallol[4]arenes and resorcin[4]arenes are cyclic oligomers of 1,2,3-trihydroxybenzene and 1,3-dihydroxybenzene, respectively. Partial deprotonation of two out of three hydroxyls on each pyrogallol, followed by direct metal coordination results in the formation of eight-metallated dimeric and twenty four-metallated hexameric nanocapsules.[9-13] In contrast, direct metal coordination to the resorcin[4]arene macrocycle has only been achieved twice, with zirconium and silver, and did not result in the formation of discrete nanocapsules.[14, 15]The zirconium(IV) resorcin[4]arene complex by Solariet al.[14] has a 4:1::metal:macrocycle ratio, wherein each metal centre coordinates with a hydroxyl group from adjacent resorcins of the cone conformer of a given bowl. The silver(I) resorcin[4]arene complex by Munakata et al.,[15] on the other hand, has a 2:1::metal:macrocycle ratio, wherein each metal centre coordinates with hydroxyl groupsfrom oppositely facing resorcins of a given macrocycle, facilitated by the pinched arrangement of the boat stereoisomer.Formation of other reported examples of resorcin[4]arene-metal complexes wasassisted by introducing modifications or ligands, such as bromide, cyanide, pyridine, sulphonato and carboxylic acid, at the central carbon position located between the two hydroxyl groups.[16, 17] The additional central group not only provides a metal-coordination site but also extends the cavity size in some cases.

In the current study, we report the synthesis and single-crystal X-ray structure of *C*-propylresorcin[4]arene⊂manganese/cobalt complexes, where *C*-propylresorcin[4]arene is abbreviated asRsC_3, with C_3 referring to the length of the alkyl chain off the bridging carbon.**1**($[(RsC_3)\subset(Mn(DMSO)_3)](DMSO)_2NO_3]$),**2a** ($[(RsC_3)_2\subset(Co(DMSO)_3)(DMSO)_2NO_3]$), and **2b** ($[(RsC_3)\subset(Co(DMSO)_3)](DMSO)_3NO_3(C_6H_5NO_2)]$)were synthesized frommetal nitrate salts, RsC_3 and a DMSO/nitrobenzene mixture. The macrocycle, RsC_3,was synthesized and cyclized through acid catalysis of resorcin with butanal.[18]Inclusion complexes **1, 2a** and **2b** were formed from the addition of a dimethylsulfoxide(DMSO) solution of metal(II) nitrate to a heated nitrobenzenic solution of RsC_3, at 2:1(Mn:RsC_3) and 1:1 (Co:RsC_3) metal-to-resorcin[4]arene ratios. The resultant mixture wasthen heated upto 150°C for aboutten minutes, followed by slow evaporation under airflow at RT.Subjecting these solvent mixtures to air flow over a period of several days yielded inclusion complexes **1** (Mn) and **2b** (Co), suitable for single-crystal X-ray diffraction studies. Interestingly, the resulting supernatant of inclusion complex **2b** when exposed to RT for over a week yielded a new crystal form: **2a**.

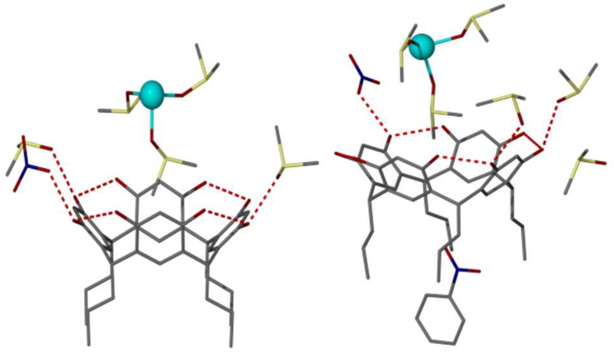

Fig. 1. Ball and stick representation of the asymmetric units of two forms of *C*-propylresorcin[4]arene-metal complexes.Left:**1, 2a** $[(RsC_3)\subset(Mn/Co\text{-}(DMSO)_3)](DMSO)_2NO_3]$; Right: **2b** $[(RsC_3)\subset(Co(DMSO)_3)](DMSO)_3NO_3(C_6H_5NO_2)]$. The red lines designate intra- and intermolecular hydrogen bonds. H atoms have been removed for clarity. Colour codes: C:grey; O:red; Co:teal; S:yellow; N:blue.

Inclusion complexes **1**and **2a** crystallize in the triclinic space group *P-1*, where each of the metals lies on an inversion centre. Each asymmetric unit (ASU) consists of a bowl of RsC_3, a metal(II) centre, a nitrate anion, and a total of five DMSO solventmolecules (Fig. 1). We note that the formulas given above for these complexes represent the chemical composition of the ASU. Of the five DMSO molecules, three bind directly to the metal centre. Each DMSO is disordered over two positions with a partial occupancy of 50%. The remaining two DMSO moleculesare located exteriorly with respect to the macrocycle andhave full occupancies. The exterior DMSO molecules are positioned along opposite faces of the resorcin[4]arenes and the nitrate anion is positioned next to an exterior DMSO molecule. The DSMO and nitrate residing along the same side of the macrocycle interact with the hydroxyls with O···O distances of 2.632(5) and 2.661(4) for the Mn (**1**) and 2.622(3) and 2.636(5) Å forthe Co (**2a**) complex (Fig. 1). The oppositely positioned

DMSO also interacts with a RsC_3 hydroxyl, with an O···O distance of 2.588(4) Å for the Mn (**1**) and 2.582(3) Å for the Co (**2a**) complex. The cone conformers of both **1** and **2a** are slightly pinched, with the centroid-to-centroid distances of 6.50 by 7.18Å for **1** and 6.37 by 7.25 Å for **2a**. The pinched distance is measured between the centroids of oppositely positioned resorcins, where the centroid of each aromatic ring is calculated from the carbon atoms. In addition, intramolecular hydrogen bonds existbetween the upper rim hydroxyls of the macrocycles for both **1** and **2a**, with O···O distances ranging from 2.735(3) to 2.791(4) Å. These results clearly indicate that the two metal inclusion complexes **1** (Mn) and **2a** (Co) are isostructural in nature.Despite the structural similarity in **1** and **2a,** it may initially appear that a higher metal-to-macrocycle ratio was required to synthesize complex **1**. However, the precrystallization of **2b,** which has a Co:RsC_3 ratioof 1:2 (from the crystal lattice) shifts the equilibrium towards a higher metal:macrocycle ratio (similar to **1**) in the resulting supernatant, which allows subsequent crystallization of **2a**.

The Co-$(DMSO)_3$ guest complex of crystal **2b** is organized in the cavity in a similar manner to that of crystal **2a.**However, the exterior solvent molecules are assembled differently and the ASU of **2b** contains two additional solvent molecules, DMSO and nitrobenzene. Fig. 1 shows that the nitrate is positioned along one face of the macrocycle and three DMSO molecules are positioned along the opposite face of the macrocycle. The O···O distance between the resorcin hydroxyl and nitrate is 2.637(10) Å and those between the resorcin hydroxyls and two exteriorly positioned DMSO molecules are 2.644(15) and 2.644(16) Å. The third DMSO molecule only interacts with an adjacently positioned macrocycle, with an O···O distance of 2.644(16) Å. Nitrobenzene, on the other hand, is situated between the alkyl tails with the nitro group facing the lower rim of the macrocycle. The centroid-to-centroid distances between the oppositely positionedaromatic rings or the pinching in the macrocycle for **2b** (6.59 by 7.09 Å) is similar to that of **1** (6.50 by 7.18 Å). For all three complexes, the DMSO molecules on the metal centre do not interact with the free solvent or the upper rim hydroxyls.

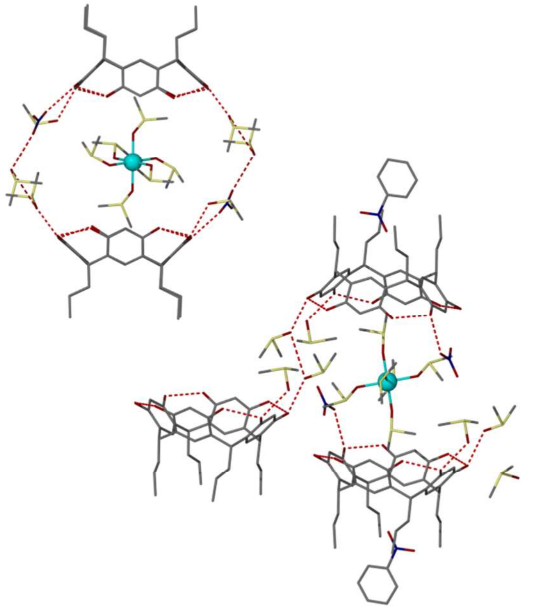

Fig.2. Ball and stick representations of the *C*-propylresorcin[4]arene-cobalt complexes **2a** (left) and **2b** (right). The red lines represent intra- and intermolecular hydrogen bond. H atoms have been removed for clarity. Colour codes: C:grey; O:red; Co:teal; S:yellow; N:blue.

Symmetry expansion of the ASU of **1** and **2a** yields an encapsulated octahedral metal centre within a macrocyclic dimeric framework connected via three solvent molecules (Fig. 2).The octahedral arrangement of metal centres is enabled through the displacement of nitrate ligands by DMSO.The macrocycles are bridgedvia a hydroxyl a hydroxyl-to-nitrate-to-DMSO-to-DMSO-to-hydroxyl hydrogen-bonded network, with O···O distances of 2.661(4), 3.333, 3.677, 2.588(4) Å, respectively, for **1** and 2.636(3), 3.405, 3.764, 2.582(3) Å, respectively, for **2a**. In contrast, complex **2b** is not a head-to-head bridged dimer. In fact, the bridging in **2b** is between diagonally positioned macrocycles, facilitated via two DMSO molecules. The hydroxyl-to-DMSO-to-DMSO-to-hydroxyl O···O distances are 2.664(16), 3.640 and 2.66(16) Å, respectively. The distance between the macrocycles in the two sets of dimers, as measured by the distance between the centroids of opposing bowls, differs by 2 Å. Specifically, these distances in the head-to-head tri-solvent bridged arrangements in **1** and **2a** are 10.53 and 10.21 Å respectively; the corresponding distance in the diagonal di-solvent bridged arrangement in **2b** is 12.26 Å.

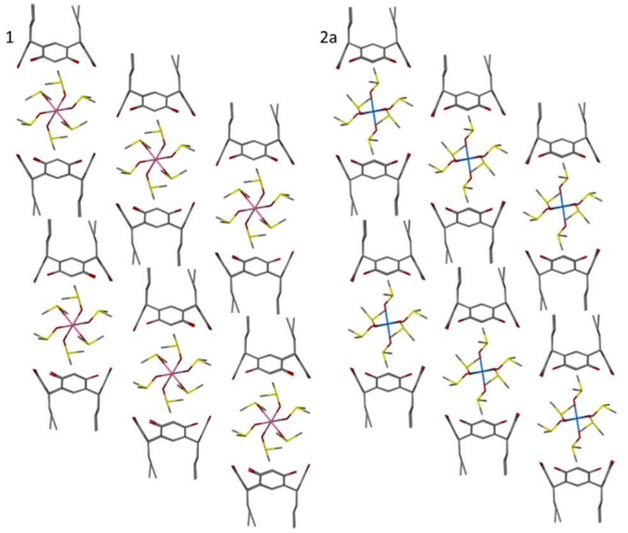

Fig. 3. Packing arrangement of complexes **1**and **2a**. H atoms and solvent molecules have been removed for clarity. Colour codes: C:grey; O:red; Mn:pink; Co:teal; S:yellow; N:blue.

Upon packing, analysis of the extended structure reveals additional intermolecular interactions between the layers of RsC_3 (Figs. 3 and 4).Adjacent dimeric units in a given layer of each crystal are offset and arranged along a diagonal. The interdigitation between the alkyl tails of **1** and **2a**is more pronounced than that of **2b**, due to the presence of the spacer nitrobenzene molecule in the later. The nitrobenzene molecule in **2b** separates the bowls of adjacent macrocycles, which inhibits any hydrogen bonding between the bowls. On the other hand, the hydroxyl groups of adjacent bowls in **1** and **2a** are within hydrogen-bonding distance of eachother. In addition, the nitrate anions connect the dimers via hydrogen bonds in **1** and **2a**.

Metal-metal distances are of particular interest due to the potential magnetic properties of the material. The distances between metal centresof neighbouring dimers are 12.36, 12.35, and 12.95 Å, of diagonal dimers are 15.86, 15.83, and 12.98 Å, and of inter-layer dimers are 22.93, 22.52, and 20.79 Å for **1**,**2a** and **2b**, respectively. Thus, shortest metal-to-metal distance for all three complexes is between the neighbouring positioned dimers. Interestingly, the closest distance between adjacent metal centres of the dimers is similar to that of a ferrocene-enclosed pyrogallol[4]arene-based dimer (12.0 and 15.0 Å), but different from that of a ferrocene-enclosed pyrogallol[4]arene-based tubes (6.5 and 21.0 Å).[19] Previous magnetic studies suggest that the distances between the metal centres of **1**, **2a** and **2b** are not small enough to observe direct exchangeas is found for the tubes; however, we expect to see dipolar interactions forcing an antiferromagnetic alignmentwhere possible.[19]

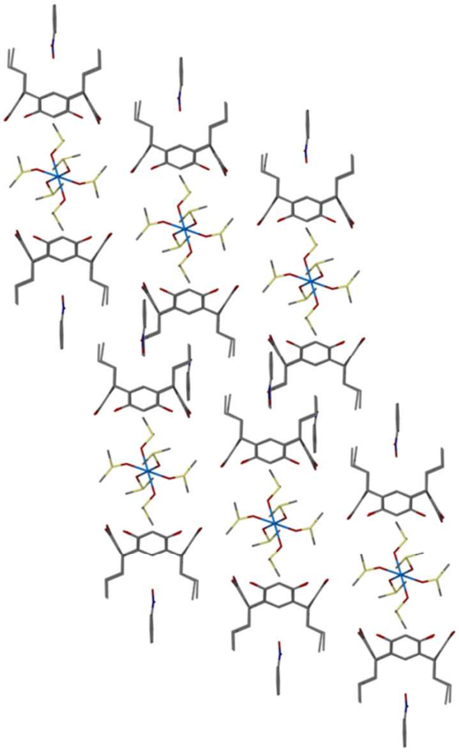

Fig.4. Packing arrangement of complex **2b**. H atoms and solvent molecules have been removed for clarity. Colour codes: C:grey; O:red; Co:teal; S:yellow; N:blue.

Conclusions

In summary, we discuss the synthesis and single-crystal X-ray diffraction structures of *C*-propylresorcin[4]arene-Mn and -Co inclusion complexes. The manganese-enclosed inclusion complex of RsC_3 exists in one form, whereas the cobalt-enclosed inclusion complexes of RsC_3 exist in two forms. The Mn (**1**) and one of the Co (**2a**) complexes are isostructural and are favoured at higher metal-to-macrocycle ratios. The isostructural complexes form tri-solvent bridged dimers with metal-to-metal distances suitable for antiferro-/ferromagnetic alignment: a property yet to be explored. The second Co complex (**2b**) has two additional solvent molecules (nitrobenzene and DMSO) in the ASU and exists as a di-solvent diagonally bridged dimer. To our knowledge, **1**,**2a** and **2b** are the first reported examples of metal inclusion complexes of resorcin[4]arene based hydrogen-bonded dimers.

Acknowledgements

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Notes and references

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Complex **1**: $C_{100}H_{156}N_2O_{32}S_{10}Mn_1$, M_r = 2273.92, triclinic, space group *P-1*,*a* = 12.3466(17), *b* = 12.604(17), *c* = 18.9081(3) Å,α= 89.008(2), β= 81.577(2), γ= 78.725(2)°,V = 2854.30(7) Å^3, *Z* = 1, ρ_{calc} = 1.323, λ(Mo-K$_\alpha$) = 0.7107 Å, *T* = 100(2) K, $2\theta_{max}$ = 25.95º, 30470 reflections collected, 11124 unique (R_{int} = 0.0985). Final *GooF* = 0.980, *R1* = 0.0674, *wR2* = 0.1929, *R* indices based on 5932 reflections with I >2sigma(I) (refinement on F^2).CCDC No:991672

Complex **2a**: $C_{100}H_{156}N_2O_{32}S_{10}Co_1$, M_r = 2277.91,0.10 x 0.10 x 0.25 mm, triclinic,space group *P-1*, *a* = 12.3562 (3), *b* = 12.5049(3), *c* = 19.3386(4) Å,α = 89.472(10), β = 80.700(10), γ = 79.300(10)°,V = 2896.85(12) Å^3,*Z* = 1, ρ_{calc} = 1.3056, λ(Cu-K$_\alpha$) = 1.54178 Å, *T* = 100(2)K, $2\theta_{max}$ = 72.18º, 28152 reflections collected, 10707 unique (R_{int} = 0.0244). Final *GooF* = 1.078, *R1* = 0.0584, *wR2* = 0.1659, *R* indices based on 9639 reflections with I >2sigma(I) (refinement on F^2).CCDC No:991671

Complex **2b:**$C_{116}H_{178}N_4O_{38}S_{12}Co_1$,$M_r$ = 2680.26, 0.15 x 0.20 x 0.30 mm, triclinic, space group *P-1*, *a* = 12.9496(16), *b* = 12.9821(16), *c* = 20.789(3) Å,α= 84.935(2), β= 82.643(2), γ= 77.463(10)°, V = 3376.9(7) Å^3, *Z* = 1, ρ_{calc} = 1.318, λ(Mo-K$_\alpha$) = 0.7107 Å, *T* = 100(2) K,$2\theta_{max}$= 22.0º, 24970 reflections collected, 8246 unique (R_{int} = 0.0389). Final *GooF* = 1.043, *R1* = 0.0982, *wR2* = 0.2741, *R* indices based on 5875 reflections with I >2sigma(I) (refinement on F^2).CCDC No:991670

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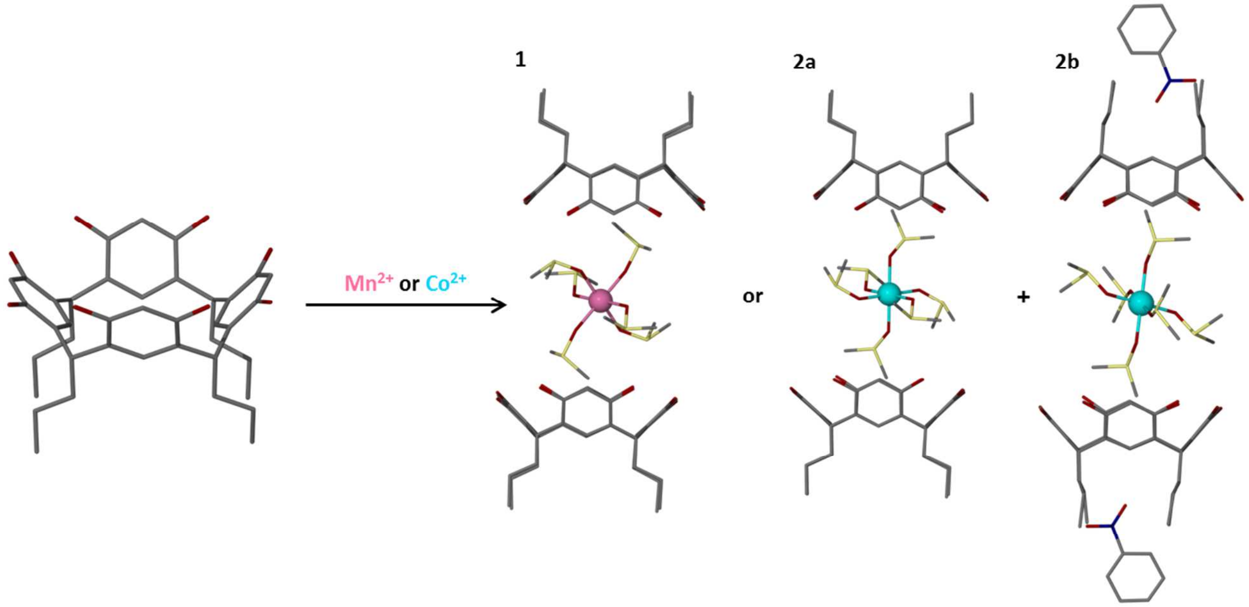
Table of Contents: Graphic and Graphical Abstract



Resorcin[4]arene capture of Mn^{2+} or Co^{2+} metals yieldsinclusion complexes **1**, **2a** and **2b**.