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Self-Assembled 1D Water Cluster in a Supramolecular Architecture of Co^{II}(Tartrate)(Phenanthroline/Bipyridine): An Assessment of Magnetic Property

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The coordination polymer, $\{[Co(tart)(phen)]\cdot 6H_2O\}_n$ (**1**) (tart, tartrate dianion; phen, 1,10-phenanthroline) has been synthesized and characterized by single-crystal X-ray structure determination, magnetic measurement and thermal analysis. The structural analyses reveal two adjacent parallel 1D –[Co(phen)-tart-Co(phen)]– coordination polymers zipped through π-π interactions. The lattice water molecules, forming a 1D water cluster, function as glue to form a 3D supramolecular network through an extended hydrogen bonding. A comparison highlighting the structural differences with the corresponding 2,2′-bipyridine (bpy) derivative, $\{[Co(tart)(bpy)]\cdot 5H_2O\}_n$ (**2**) containing a less amount of lattice water molecules is discussed. The variable-temperature magnetic study of **1** has been carried out and interpretation of the already reported complex **2** has been re-visited: both polymers **1** and **2** show weak antiferromagnetic interaction.

Introduction

For the unusual properties and fundamental importance manifested in many biological and physico-chemical processes, water and hydrogen bonds have received considerable attention in current research.[1] The environment designed by the crystal host stabilizes various topologies of water clusters and plays an important role in the formation of different water morphology.[2] The structural study sometimes supported by theoretical and experimental research on such "discrete" water clusters is of great importance for the understanding of the behavior of bulk water or ice.[3] Recently, a number of papers describing the cooperative association of water molecules to form a variety of oligomers and clusters,[4,5] sometimes connected to form one dimensional,[6] layered aggregates,[7] and 3D "ice-like" open frameworks,[8] have been published. However, the study of larger water aggregates, which represent the bridge between cluster and bulk water, is still a challenging scientific endeavor.[9]

Here we report on the synthesis, X-ray crystal structure, and thermal study of a 3D supramolecular architecture, $\{[Co(tart)(phen)]\cdot 6H_2O\}_n$ (**1**) (tart, tartrate dianion; phen, 1,10-phenanthroline). The structural data are compared with analogous 2,2′-bipyridine (bpy) derivative, $\{[Co(tart)(bpy)]\cdot 5H_2O\}_n$ (**2**).[10] The magnetic behavior of **1** is also reported which questions the reliability of the corresponding data of **2**, demanding the re-magnetic measurement of **2**.

Results and Discussion

X-ray crystal structure analysis reveals that complex **1** consists of 1D polymeric chains, elongated along axis *a*, having Co(phen) units doubly chelated by tartrate dianion. The dianion acts as $\eta^4\mu$-tetradentate ligand through hydroxyl and carboxyl oxygen atoms and assumes a conformation as indicated by the torsion angle in the carbon atom skeleton of –151.13(18)°. The octahedral cobalt ligand arrangement is severely distorted with bond angles considerably deviating from ideal values (Table 1). The Co–N bond lengths average to 2.124(2) Å, and the Co–O(carboxylate) bond lengths, located in *trans* position to nitrogen atoms [2.058(2) and 2.047(2) Å], are slightly shorter than the others involving hydroxyl groups, of 2.163(2) and 2.172(2) Å. The polymers are arranged in pairs zipped by π-π interactions between phen aromatic rings with distances between ring centroids of 3.623(2) and 3.547(2) Å (Figure 1). The complex **1** is isomorphous and isostructural with the Mn^{II} and Cu^{II} derivatives.[11,12]

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Table 1. Selected bond length [Å] and angles [°] of **1**.

Co–N(1)	2.1232(19)	Co–O(3)	2.0472(18)
Co–N(2)	2.1258(17)	Co–O(5)	2.1630(17)
Co–O(1)	2.0579(17)	Co–O(6)	2.1722(17)
N(1)–Co–N(2)	77.84(7)	N(2)–Co–O(6)	89.70(7)
N(1)–Co–O(1)	159.51(8)	O(1)–Co–O(3)	101.26(8)
N(1)–Co–O(3)	92.18(8)	O(1)–Co–O(5)	75.81(6)
N(1)–Co–O(5)	88.63(7)	O(1)–Co–O(6)	92.59(7)
N(1)–Co–O(6)	105.61(7)	O(3)–Co–O(5)	91.27(7)
N(2)–Co–O(1)	93.22(7)	O(3)–Co–O(6)	76.71(6)
N(2)–Co–O(3)	160.46(7)	O(5)–Co–O(6)	161.50(6)
N(2)–Co–O(5)	105.07(7)		

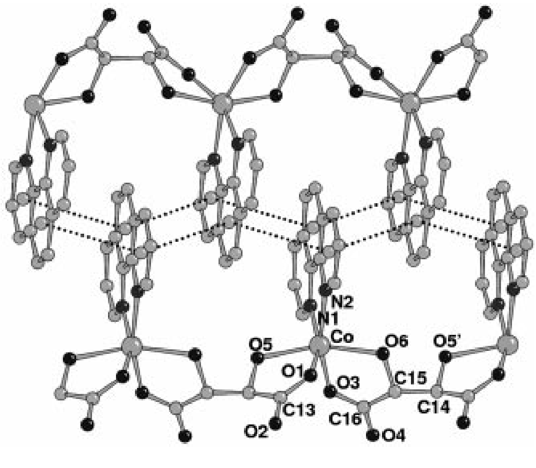

Figure 1. Coordination polymeric chains zipped by π-π interactions in **1**.

The complex $\{[Co(tart)(bpy)]\cdot 5H_2O\}_n$ (**2**), containing a smaller amount of guest water molecules, is isostructural to **1** and has been reported recently.[10] However, subtle differences are apparent between the two structures. The intrachain Co–Co distances in **1** and **2** are comparable within 2–3σ [6.617(3) vs. 6.629(1) Å, respectively], but the shortest metal–metal separation between coupled chains in **1** is 8.870 Å, significantly larger than the value of 7.507 Å measured in the bpy analogue (**2**).[10] This feature is ascribed due to the less bulky bpy which lacks the ethylene bridge and allows a better interdigitation between adjacent 1D chains.

The six crystallographically independent lattice water molecules, held together by hydrogen bonds with an ordered proton arrangement form a cluster sitting between the pairs of 1D coordination chains (Figure 2).

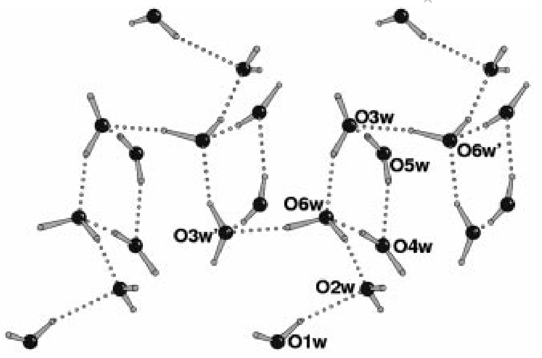

Figure 2. View of the hydrogen-bonding motif of the water molecules in **1**.

The water network consists of tetramers [O(3w–6w)] connected through the O(6w)–H···O(3w) hydrogen bond. In addition, two water molecules [O(2w) and O(1w)] are appended in sequence to the rhomboid structural motif at O(6w). The ΔFourier map allows to detect all the water hydrogen atoms and O(2w), O(3w), and O(6w) show a tetrahedral environment, as these behave as double donors and acceptors. This feature is evident for O(6w) from Figure 2, while the tetrahedral geometry about molecules O(2w) and O(3w) is completed, respectively, through the donor properties towards O(1), O(3), and O(2) of the tartrate dianion (Table 1S). The dicarboxylate provides potential hydrogen bonding intermolecular interactions, beside its coordination ability towards metal ions.

The H-bonds between the water cluster and the tartrate oxygen atoms build up a supramolecular 3D network. The O···O distances of hydrogen bonds engaging water molecules as H donor average to 2.79 Å, while those involving the hydroxyl tartrate oxygen (mean 2.62 Å) indicate slightly stronger interactions.

On the other hand, it is worth to note that the water molecules in $\{[Co(tart)(bpy)]\cdot 5H_2O\}_n$ (**2**) form a totally different 1D sequence containing cyclic pentamers sharing a side with an appended dimer.[10] Thus, in complex **1** the water molecules are structured by the cobalt polymers and the crystal structure may simulate the interactions occurring between the polymer and the water in a ca. 9 M frozen concentrated solution. Interestingly, among the numerous water networks reported in the literature,[4–8] complex **1** as well as **2**,[10] Mn^{II} and Cu^{II} derivatives[11–12] represent examples where the structured water molecules are not involved in any weak or strong direct interaction with the metal ion.

Thermal analysis reveals that complexes start dehydration at about 35 °C and lose all the lattice water molecules in a number of steps overlapping to each other. The deaquated species collapses immediately upon deaquation at about 150 °C.

The temperature-dependent magnetic susceptibility measurement[13] for **1** has been carried out on a polycrystalline sample in the temperature range 2–300 K. The $\chi_M T$ vs. T plot for **1** (χ_M is the molar magnetic susceptibility for one Co^{II} ion) is shown in Figure 3. $\chi_M T$ value at 300 K is $3.6\ cm^3 mol^{-1} K$ which progressively decreases up to $2.05\ cm^3 mol^{-1} K$ at 2 K.

Based on the reasoning already reported by us[14] relating to the calculation of an estimated J value, we have used the two-exponential Rueff expression,[15,16] $\chi_M T = A \exp(-E_1/kT) + B \exp(-E_2/kT)$ $\{A + B$ equals the Curie constant [about $2.8–3.4\ cm^3 mol^{-1} K$ for octahedral cobalt(II) ions], and E_1, E_2 represent the “activation energies” corresponding to the spin-orbit coupling and the antiferromagnetic exchange interaction$\}$, which is suitable for any temperature greater than the possible T_c. The best-fit values obtained

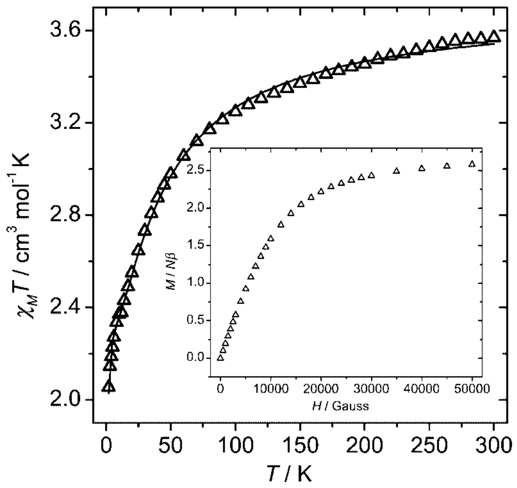

Figure 3. Top: $\chi_M T$ vs. T plot for complex **1** (solid line represents the best fit). Inset: plot of the reduced magnetization ($M/N\beta$) vs. H at 2 K for **1**.

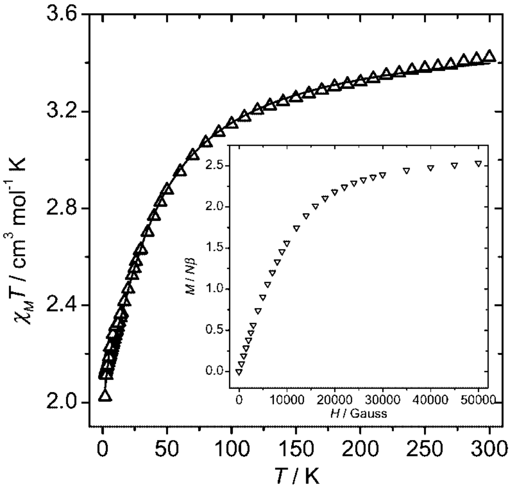

Figure 4. $\chi_M T$ vs. T plot for complex **2** (solid line represents the best fit). Inset: plot of the reduced magnetization ($M/N\beta$) vs. H at 2 K for **2**.

with this procedure are: $A + B = 3.41$ cm^3 mol^{-1} K, in perfect agreement with those given in the literature for the Curie constant ($C \approx 2.8$–3.4 cm^3 mol^{-1} K),[15,16] $E_1/k = 42.32$ K which is of the same magnitude to those reported by Rueff *et al* for several one- and two-dimensional cobalt(II) complexes.[16] As far as the antiferromagnetic exchange interaction, the value found is very weak ($E_2/k = 0.35$ K), corresponding to $J = -0.70$ K ($= -0.50$ cm^{-1}), according to the Ising chain approximation, $\chi_M T \propto \exp(J/2kT)$. The small J value is compatible with the two possible exchange pathways between Co atoms. One is across the saturated dicarboxylate {with the long bridging spacer [O(6)–O(5) distance of 2.76 Å, O(6)–C(15)–C(14)–O(5′) torsion angle of –38.8°]} which should be a very weak exchange interaction. The other exchange pathway is through the π-π stacking of the phenanthroline ring, which is very weak in this system. The small J value agrees with those reported by Coronado et al. for a series of Co^{II} (as well as Mn^{II}, Fe^{II}, and Ni^{II}) complexes with tartrate as ligand.[17] The reduced magnetization curve, $M/N\beta$, at 2 K tends to $2.5N\beta$ at 5 T (Figure 3, inset) in perfect agreement with the values reported for isolated or quasi-isolated cobalt(II) ions.[15] Interestingly, Lu et al. reported a ferromagnetic interaction for the bpy derivative **2**.[10]

After going through the magnetic result we have identified a wrong interpretation in fitting the magnetic data of **2** (assuming that there is no spin-orbit coupling). Thereby we have repeated the synthesis and structural characterization of complex **2**. The structural results match those already reported,[10] but the magnetic results (Figure 4) follow those of complex **1**. Corresponding fitting parameters are $A + B = 3.43$, $E_1/k = 36.97$ K, $E_2/k = 0.21$ K, $J = -0.42$ K ($= -0.30$ cm^{-1}). The J value for **1** and **2** are almost equal based on the accuracy of the fitting method. Thus the J value is weak and equally antiferromagnetic for the two complexes as expected.

Conclusions

We have presented here the synthesis, crystal structure, magnetic behavior and thermal study of Co^{II}(tart)(phen/bpy) complexes having a well resolved water chain, which acts as glue in stabilizing the host chains and gives origin to a 3D supramolecular architecture. In phen derivative the water chain consists of cyclic tetramers with appended water dimers whereas in bpy derivative there is totally different 1D sequence containing cyclic pentamer sharing a side with an appended dimer. Thus, the study provides an example of a differently structured water cluster realized by modulating the size of the metal-organic framework. Both complexes show similar weak antiferromagnetic interaction, in agreement with structures.

Experimental Section

Complex 1: Single crystals of **1** were obtained by diffusing an aqueous solution (5 mL) of cobalt nitrate hexahydrate (0.291 g, 1 mmol) on a water/methanol (1:2) layer (15 mL) of disodium tartrate (0.150 g, 1 mmol) and phen (0.198 g, 1 mmol) mixture in a corked tube. The red colored single crystals were deposited at the junction of the two solutions after a few weeks, yield 74%, 0.366 g. $C_{16}H_{24}CoN_2O_{12}$ (495.30): calcd. C 38.76, H 4.84, N 5.65; found C 39.23, H 4.51, N 5.92. IR: $\tilde{\nu}$ = 3480–3030 (vs), 2868 (s), 2720 (s), 1618 (vs), 1518 (s), 1426 (s), 1361 (vs), 1294 (s), 1224 (w), 1126 (s), 1069 (w), 997 (vw), 924 (vw), 850 (s), 820 (s), 726 (vs), 642 (vw), 526 (vw) cm^{-1}.

Complex 2: Preparation by adopting the same procedure as described for **1**; bpy (0.156 g, 1 mmol) instead of phen, yield 70%, 0.317 g. $C_{14}H_{22}CoN_2O_{11}$ (453.27): calcd. C 37.06, H 4.85, N 6.18; found C 37.62, H 4.66, N 6.34. IR: $\tilde{\nu}$ = 3470–3050 (vs), 1640 (vs), 1605 (vs), 1474 (s), 1447 (s), 1363 (vs), 1313 (s), 1232 (w), 1176 (w), 1129 (s), 1057 (s), 1025 (w), 885 (w), 825 (w), 775 (w), 729 (w), 648 (vw) 532 (vs) cm^{-1}.

X-ray Diffraction Studies: Diffraction data of **1** were collected at room temperature on a Nonius DIP-1030H system, equipped with

Mo-K_α radiation (λ = 0.71073 Å) graphite-monochromatized. Cell refinement, indexing and scaling of the data set were carried out using programs Denzo[18] and Scalepack[18] The structure was solved by Patterson and Fourier analyses[19] and refined by the full-matrix least-squares method based on F_2 with all observed reflections.[19] The H atoms of water molecules were located on the ΔFourier map, others at geometrically calculated positions. All the calculations were carried out using program WinGX system, Ver 1.70.01.[20]

CCDC-632709 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for 1: $C_{16}H_{24}CoN_2O_{12}$, M = 495.30, orthorhombic, space group $P2_12_12_1$, a = 6.617(3), b = 15.313(3), c = 20.110(4) Å, V = 2037.7(11) Å^3, Z = 4, D_c = 1.615 g/cm^3, μ(Mo-K_α) = 0.910 mm^{-1}, F(000) = 1028, θ range = 2.66–29.65°. Final $R1$ = 0.0344, $wR2$ = 0.0871, S = 0.970 for 323 parameters and 22937 collected reflections, 5526 unique [R(int.) = 0.0400], of which 4614 with $I > 2\sigma(I)$, absolute structure parameter = 0.002(14), max. positive and negative peaks in the ΔF map: 0.299 and –0.326 eÅ^{-3}.

Supporting Information (see also the footnote on the first page of this article): ORTEP drawing and a Table containing H-bonding parameters of **1**.

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