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X-ray Crystal Structures and Two-dimensional $\pi \cdots \pi$ Stacking Interaction of $Cr^{III}(X_4SQ)_3 \cdot 4C_6H_6$ (X=Cl and Br)

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Tris(tetrahalogeno-*o*-semiquinonate) chromium (III) complexes, $Cr^{III}(Cl_4SQ)_3 \cdot 4C_6H_6$ (**1**) and $Cr^{III}(Br_4SQ)_3 \cdot 4C_6H_6$ (**2**), crystallize in an isostructural form; tetragonal, $P4_12_12$ with a = 13.452(2) Å, c = 24.78(2) Å, V = 4484(3) Å^3 and a = 13.7465(7) Å, c = 25.680(1) Å, V = 4852.6(4) Å^3 for **1** and **2**, respectively. The inner coordination environments of the complex molecules are similar to that of previously reported crystal, $Cr^{III}(Cl_4SQ)_3 \cdot CS_2 \cdot 1/2C_6H_6$, while both complexes show strong $\pi \cdots \pi$ interaction between the three SQ ligands and the four solvate benzene molecules, resulting the formation of two-dimensional $\pi \cdots \pi$ stacking array. The effect of $\pi \cdots \pi$ interactions was evaluated by thermogravimetric and differential scanning calorimetric analysis where the weigh loss corresponding to the four benzene molecules was observed up to 500 K indicative of the interactions between the ligands and solvated benzene molecules.

Keywords: semiquinonate; chromium (III); $\pi \cdots \pi$ interaction; benzene

INTRODUCTION

Chromium complexes with paramagnetic semiquinonate (SQ) ligands have attracted much attention because these show unusual and unique redox, magnetic, and optical properties that appear to be governed by strong interactions between the unpaired electrons and the corresponding

spins localized on the metal center and the ligands.[1] We have presented molecular charge-transfer (CT) compounds of a series of ligand-based mixed-valence redox isomers, $[Cr^{III}(X_4SQ)(X_4Cat)_n]^{n-}$ (n = 0–2, Cat = catecholate, X = Cl and Br).[2] The compounds have been synthesized by the reaction between tris(tetrahalogeno-*o*-semiquinonate) chromium (III), $Cr^{III}(X_4SQ)_3 \cdot 4C_6H_6$, and electron donors. The reaction affords 1-D chain, 2-D honeycomb and brick-wall type molecular assemblies with intra- and intermolecular mixed-valence states.

The complex, $Cr^{III}(Cl_4SQ)_3$, has been thermally synthesized by the reaction of $Cr(CO)_6$ with tetrachloro-*o*-benzoquinone (Cl_4BQ) by Pierpont et al. in 1974.[3] They have also reported the electro- and magnetochemical properties of the complex together with the crystal structure of $Cr^{III}(Cl_4SQ)_3 \cdot CS_2 \cdot 1/2C_6H_6$.[1(b),(c)],[4] In fact, the complex was obtained as $Cr^{III}(Cl_4SQ)_3 \cdot 4C_6H_6$ with four solvated benzene molecules under the synthetic condition they used, however, only the cell dimension and space group are known to date.[5] There are some of *o*-quinone complexes cocrystallized with aromatic solvates exhibiting $\pi \cdots \pi$ stacking interactions with the ligand moieties of the complexes.[6] The interaction could involve net CT between the donor and acceptor molecules, which often plays an important role in molecular-based conducting materials. In this paper the crystal structures of $Cr^{III}(Cl_4SQ)_3 \cdot 4C_6H_6$ will be presented for the first time together with isostructural bromine analog, $Cr^{III}(Br_4SQ)_3 \cdot 4C_6H_6$.

EXPERIMENTAL

Materials

Syntheses of the complexes were carried out under the procedure reported previously.[2(a)] Single crystals of the complexes were obtained by recrystallization from hot benzene/dichloromethane. Violet prismatic crystals were obtained and used for X-ray diffraction experiments.

Physical Measurements

Thermogravimetric analyses were made on Rigaku Thermo Plus 2 TG8120 over the temperature range of 295–773 K.

Crystallographic Data Collection and Refinement of Structures

Diffraction measurements were performed on a Rigaku mercury diffractometer with CCD two-dimensional detector with Mo Kα radiation employing a graphite monochromator. Intensity data were collected in 480 frames with an ω scan width of 0.5° and exposure times 40 and 100 s for **1** and **2**, respectively. Empirical absorption correction using the program REQABA[7] was performed for all the data. The structures were solved by direct methods[8] and expanded using Fourier techniques.[9] The final cycles of the full-matrix least-squares refinements were based on the observed reflections ($I > 3\sigma(I)$ (**1**) and $4\sigma(I)$ (**2**)). All the calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[10] In complex **2** the disorder of the benzene molecules was found at the final stage, thus, its atom positions were refined under a rigid condition: tetragonal, $P4_12_12$, **1**: $a = 13.452(2)$ Å, $c = 24.78(2)$ Å, V

= 4484(3) Å^3, ρ_{calcd} = 1.632 g·cm^3, 1914 reflections, R (R_w) = 0.052 (0.059), **2**: a = 13.7465 (7) Å, c = 25.680 (1) Å, V = 4852.6(4) Å^3, ρ_{calcd} = 2.238 g·cm^3, 1229 reflections, R (R_w) = 0.059 (0.063).

RESULTS AND DISCUSSION

Crystal Structures

Complexes **1** and **2** crystallize by recrystallization from dichloromethane/benzene solution in an isostructural form. Figure 1 shows ORTEP drawing of **1** with the atom numbering scheme. As shown in Figure 1 only one-half of ligands are crystallographically independent. The geometry of the chromium ion is distorted octahedron with six oxygen atoms from the three bidentate ligands **I**, **II**, and **I'**. The

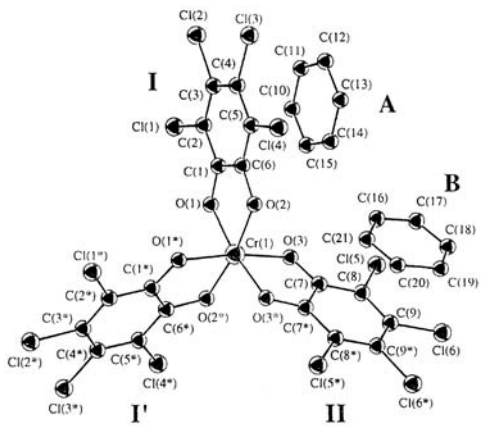

FIGURE 1. ORTEP drawing of **1** (**2**) with hydrogen atoms omitted. Crystallographically independent ligands and benzenes are designated **I**–**II** and **A**–**B**, respectively.

average Cr–O distances are 1.956(5) and 1.95(1) Å for **1** and **2**, respectively. These distances are similar to that of $Cr^{III}(Cl_4SQ)_3 \cdot CS_2 \cdot 1/2C_6H_6$ and compare well with distances for typical Cr(III) complexes with O_6 coordination environments. It has been found that typical C–O bond distances for benzoquinone, semiquinonate, and catecholate are 1.23, 1.29, and 1.35 Å, respectively.[1(a)] The C–O bond distances in general increase with the reduction of the ligand because of antibonding nature of C–O bond in π^* orbital of the ligand.[11] The C–O bond distances of ligands **I** and **II** of **1** are found to be 1.297(9) and 1.280(8) Å, respectively, while those of **2** are 1.31(3) and 1.32(3) Å, respectively. These values indicate the SQ form of each ligand similar to $Cr^{III}(Cl_4SQ)_3 \cdot CS_2 \cdot 1/2C_6H_6$.[1(c)] The observed O–Cr–O angles also similar to those of complexes with the SQ ligands reported so far.[1(c)],[12]

Crystal Packing Structures

As shown in Figure 2(a), ligand **I** (**I'**) forms infinite mixed-stack chains with benzene **A** molecules along the *a*(*b*)-axis. The mean interplanar separation is 3.36(1) Å with the dihedral angle of 3.5(3)°. Figure 2(b) illustrates the overlap mode of these stacks along the normal direction of the mean plane of the ligand **I**. Six-memberedrings of the ligand and the benzene molecule show well-overlap region with slight slipping. Thus, each complex molecule is linked to two adjacent molecules through benzene solvate bridges, resulting in the formation of a two-dimensional polymeric array in the *ab*-plane (Figure 3). Additionally, ligand **II** is sandwiched by two benzene molecules **B** along the *c*-axis making discrete-type benzene **B**···ligand **II**···benzene **B** trimer unit (Figures 2(c)

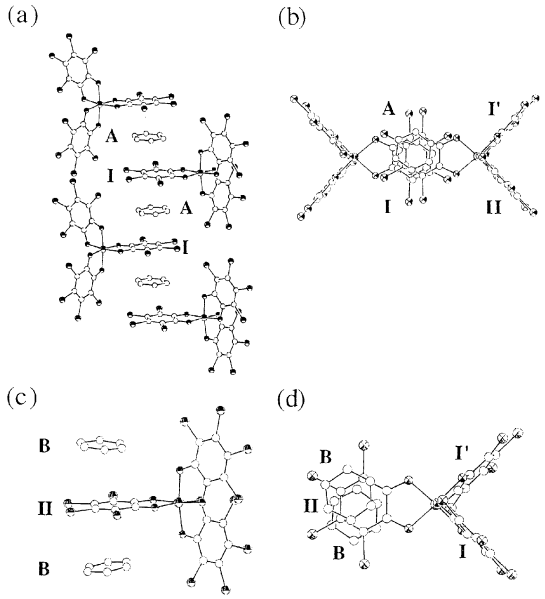

FIGURE 2. (a) Mixed-stacking chain of ligand **I**···benzene **A** along the *a*(*b*)-axis and (b) projection of the chain along the normal direction of the mean plane of the ligand **I**. (c) The π··· π interactions between ligand **II** and benzene **B** and (d) projection of the stacking interaction along the normal direction of the mean plane of the ligand **II**.

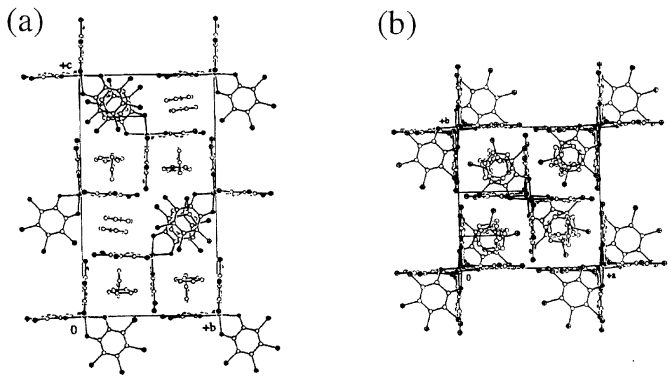

FIGURE 3. Crystal packings of **1** (**2**) along the (a) *a*- and (b) *c*-axes.

and (d)). The mean interplanar separation is 3.61(2) Å, which is longer than that for the ligand **I**···benzene **A**, and the dihedral angle between them is found to be 5.8(4)°. The two observed mean separations are comparable to that of $Cr^{III}(Cl_4SQ)_3 \cdot CS_2 \cdot 1/2C_6H_6$, where the ligand and benzene molecules form discrete stacking interaction with the separation of 3.45 Å and the dihedral angle of 5.4°.[1(c)]

Thermogravimetric Analyses

To evaluate π···π interactions between the complex and benzene molecules, the thermogravimetric and differential scanning calorimetry have been carried out for **1** and **2**. As shown in Figure 4, rapid weight loss take place up to 500 K. Weight loss at this temperature correspond to 28.3 and 18.8 % for **1** and **2**, respectively. The liberation of four solvate benzene molecules account for these weight loss for **1** ($4C_6H_6$,

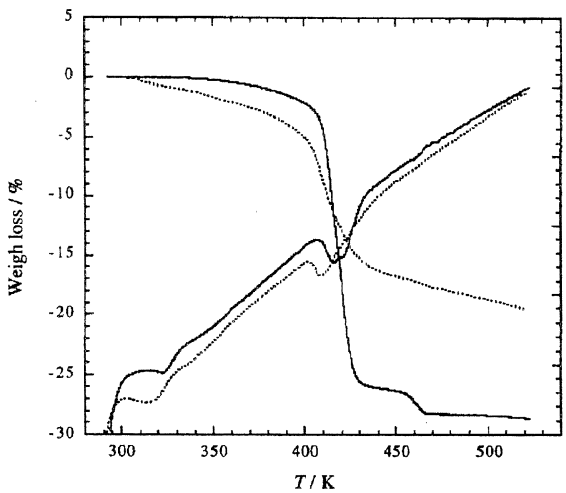

FIGURE 4. Thermogravimetric data for **1** (–) and **2** (···).

28.3 %) and **2** ($4C_6H_6$, 19.1 %). The temperature is higher than that of boiling point of the benzene molecule under the ambient pressure (353 K), reflecting the effect of the interactions in the crystal phases.

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