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Synthesis and Characterization of High-Spin Cobalt(II)-Based "Inorgainc Tennis Ball"

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The cavities in coordination boxes, cages, and capsules are attracting much attention because of their encapsulation, catalytic reaction, and stereoselective transformation properties.[1,2] "Inorganic Tennis Ball" ("ITB") was named to the supramolecule obtained from the self-assembly of $Cu(BF_4)_2$ and $(dach)Pt^{II}(BETMP)$ ($dach$ = $trans$-1,2-diaminocyclohexane and BETMP = bisethylthiomethylidenepropanedioate).[3] The cavity and hydrophobic pocket in the ITB have shown recognition properties for anions and pyridine molecules.[4] It is essential to modify the metal sites in order to induce novel magnetism, encapsulation or reaction properties from ITB. We have devoted efforts to find out other transition metals that can replace copper(II) in the ITB. We now report the synthesis and characterization of a new cobalt(II)-based ITB and its magnetic properties.

BETMP is a multidentate ligand with two sulfur atoms and two carboxylate groups. A diamineplatinum(II) moiety, $(dach)Pt(II)$, was reported to be coordinated to the ligand exclusively by two sulfur atoms[5] while copper(II) ion, on the other hand, by carboxylate oxygens.[6] To reveal the coordination property of cobalt(II) ion to the ligand, cobalt(II) sulfate and potassium sulfate was reacted with two equivalents of Ba[BETMP] in water. After stirring for 2 h, the precipitate ($BaSO_4$) was removed by filtration, and recrystallization in methanol/ether of the crude product obtained by evaporation of the filtrate afforded the crystalline compound $K_2Co(BETMP)_2(HOCH_3)_2$ (**1**) (Figure 1).[7] Two carboxylates and two methanols coordinate cobalt(II), where the distance from cobalt(II) to methanol oxygen is 2.165(4) Å. Compound **1** was reacted with two equivalent $(dach)Pt(NO_3)_2$ in methanol. After removal of KNO_3 by filtration, crystalline compound $[[\{(dach)Pt(BETMP)\}_2-Co(OHCH_3)]_2(NO_3)][NO_3]_3$ (**2·[NO_3]_3**) was obtained by slow evaporation of the filtrate (Scheme 1).

ESI-MS spectrum[8] of the methanol solution of **2·[NO_3]_3** detected the ions of m/z = 784.7 and 1207.4 which corresponds to $[2-(OHCH_3)_2]^{3+}$ and $[(2-(OHCH_3)_2)\cdot NO_3]^{2+}$, respectively, unique ions proving the existence of the tennis ball structure in the solution.

Figure 2 shows the crystal structure of of **2**.[9] Compound **2** is a dimer composed of two homo copies. Hydrogen bonding interactions between NH of one copy and carboxylate oxygens of the other (the distances of N⋯O range from 2.97
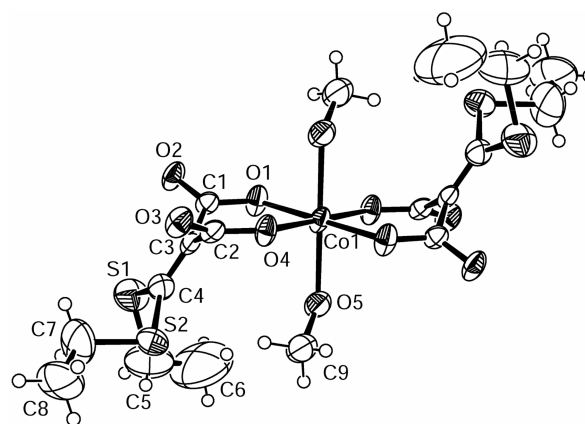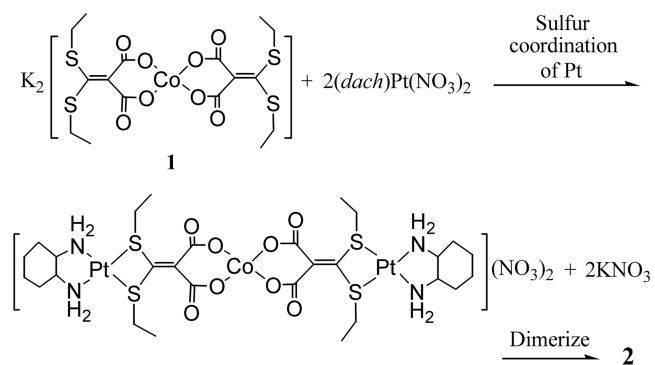

Figure 1. ORTEP drawing of the anionic part of **1**. The molecule has inversion symmetry. Bond distances (Å): Co(1)-O(1), 2.042(3); Co(1)-O(4), 2.076(3); Co(1)-O(5), 2.165(4).

Scheme 1. Synthesis of ITB, **2**.

to 3.03 Å) are important driving forces for the formation of the dimer. The close contacts between two sulfurs in different copies (these distances range from 3.62 to 3.75 Å) seem to also contribute to the gathering of the two copies. A NO_3^- anion is centered at the cavity inside the dimer. The distance between Co(II) and methanol oxygen is 2.129(18) Å. This distance, along with that of **1**, is similar to those often observed in other cobalt complexes.[10]

Figure 3 shows the electron paramagnetic resonance (EPR) spectrum of the compound **2·[NO_3]_3** in frozen solution state.[11] The broad EPR feature from 75 to 360 mT
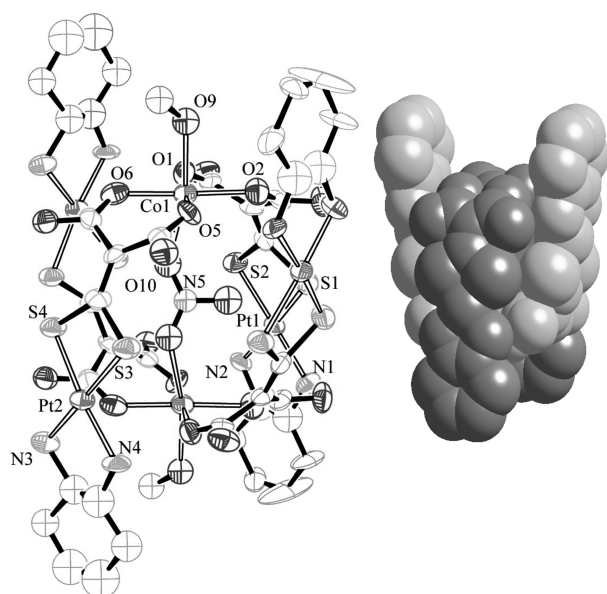
Figure 2. ORTEP drawing (left) and space-filling diagram (right) of **2**. Hydrogens, and ethyl groups attached to sulfur atoms are omitted for clarity. Methanols are omitted in the space-filling diagram. The molecule has S_4 symmetry. Bond distances (Å): Co(1)-O(9), 2.129(18); Pt(1)-S(1), 2.266(6); Pt(1)-S(2), 2.267(6).
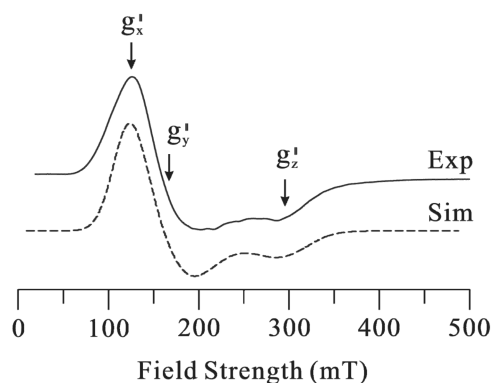

Figure 3. EPR spectrum (solid line) obtained from the frozen solution state of **2**·[NO₃]₃ in methanol at 4 K and the corresponding simulation (dotted line). Experimental conditions: microwave frequency, 9.109 GHz; microwave power, 1 mW; modulation frequency, 100 kHz. Simulation Parameters: **g'** = [g'ₓ g'ᵧ g'_z] = [5.2 3.9 2.2], **dg** (g-strain) = [1.7 1.5 0.5].

unambiguously indicates the presence of the high spin Co(II) ($S=3/2$, d^7) in which the EPR transition occurs within the lower Kramers doublet ($m_s = \pm 1/2$) at 4 K. Unresolved hyperfine structure at $g'_y \sim g'_z$ may be attributed to the ⁵⁹Co nuclei ($I = 7/2$). High spin Co(II) complexes have in general broad EPR spectra, caused by g-strain as wells as the ⁵⁹Co hyperfine coupling.[12] The EPR spectrum can be described by a fictitious $S = 1/2$ spin system, H' = μ_B**S'·g'·H₀**, where μ_B is the Bohr magneton and the **g'**-tensor directions are parallel to zero-field splitting tensor, **D**.[13] Considering g-strain as a only factor of the line-broadening, fitting of the experimental spectrum gave **g'** = [g'ₓ g'ᵧ g'_z] = [5.2 3.9 2.2] with g-

strain values of **dg** = [1.7 1.5 0.5].

In conclusion, we have shown the first preparation of "ITB" having a high-spin Co(II) ion. Since high-spin Co(II) complexes provide various magnetic properties depending on the structures and energy schemes,[14] this will contribute to extension of the chemistry with respect to the fascinating supramolecule, ITB.

Supporting Information Available: X-ray crystallographic data for **1** and **2**·[NO₃]₃ in CIF format, and ESI-MS spectrum of **2**·[NO₃]₃.

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7. All the X-ray data were collected on an Enraf-Nonius CAD4 automated diffractometer equipped with a Mo X-ray tube at room temperature. Crystal data of **1**: triclinic, $P\bar{1}$ (No.2), $Z = 1$, $a = 7.2415(19)$ Å, $b = 8.8575(16)$ Å, and $c = 13.519(2)$ Å, $\alpha = 104.580(14)°$, $\beta = 90.401(17)°$, $\gamma = 95.754(18)°$, $V = 834.5(3)$ Å³, $\mu = 1.064$ mm⁻¹, $d_{calc} = 1.460$ g/cm³, R1 = 5.19, wR2 = 11.31% for 2961 unique reflections ($I \geq 2\sigma(I)$) and 178 variables. The structure solution and refinement of the data were handled with the SHELXS-86 and SHELXL-97 programs.
8. See Supporting Information.
9. Crystal data of **2**·[NO₃]₃·2(CH₃OH): *monoclinic, C2/c* (No.15), Z = 4, $a = 27.364(8)$ Å, $b = 26.262(8)$ Å and $c = 19.215(6)$ Å, $\beta = 122.63(2)°$, $V = 11629(21)$ Å³, $\mu = 5.280$ mm⁻¹, $d_{calc} = 1.524$ g/cm³, R1 = 6.87, wR2 = 17.61% for 4268 unique reflections ($I \geq 2\sigma(I)$ and 457 variables.
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