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Crystal Structure of the Pentanuclear Complex Containing $Ru_2(chp)_4^+$ Units Linked by $Co(CN)_6^{3-}$

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Organic cyanides and metal cyanides have connected metal complexes to form one-, two-, or three-dimensional polymeric compounds.[1] Recently, the synthesis of polymeric compounds has expanded to metal-metal multiply-bonded compounds.[2] Organic cyanides, TCNE, bridge four $Rh_2(O_2CCF_3)_4$ units to form an extended two-dimensional layer[3] or bridge two $Rh_2(O_2CCH_3)_4$ units to form either 1,1- or *trans*-1,2 type one-dimensional polymers.[4] Metal cyanides, $Co(CN)_6^{3-}$ also bridge four $Rh_2(O_2CCH_3)_4$ units to form a two-dimensional sheet.[5] Jacobson mensioned that the Co $(CN)_6^{3-}$ group acts like TCNE eventhough $Co(CN)_6^{3-}$ can form three-dimensional polymer. We have interested in the diruthenium unit to study magnetic interactions through Co $(CN)_6^{3-}$ bridging groups. The pentanuclear complex, $K[\{Ru_2(chp)_4\}_2\{Co(CN)_6\}]$ (chp=6-chloro-2-hydroxypyridinato) has been synthesized and studied its structure and magnetic properties.

Reaction of a methanol solution of $[Ru_2(chp)_4](PF_6)$ with an aqueous solution of $K_3Co(CN)_6$ gave purple precipitate with yield of 75.5%. $[Ru_2(chp)_4](PF_6)$ was prepared by elimination of the axial chlorine atom from $Ru_2(chp)_4Cl_6$ with $AgPF_6$ in CH_2Cl_2 solution. The precipitate[7] was not soluble in any solvent. Dark purple crystals were obtained from the direct diffusion technique. An aqueous solution of $K_3Co(CN)_6$ was carefully layered by a methanol solution of $[Ru_2(chp)_4](PF_6)$. The CN stretching modes were observed in the IR sepctrum at 2133 cm^{-1} which is shifted from 2129 cm^{-1} of $K_3Co(CN)_6$. This blue shift indicates that the cobalt cynaide acts like a σ donor to diruthenium unit.

The $Ru_2(chp)_4^+$ units are bridged by $Co(CN)_6^{3-}$ to form a pentanuclear compound, $K[\{Ru_2(chp)_4\}_2\{Co(CN)_6\}]$[8] (Figure 1). There are two formula units in the tetragonal cell. The ruthenium atoms and cobalt atom reside on a 4 axis at 0, 1/2, z, and do the C and N atoms of *trans*-CN groups of the bridging ligand. In contrast to the dirhodium-cobaltcyanide polymer, the diruthenium units are coordinated by only two CN groups of $Co(CN)_6^{3-}$ that is *trans* each other. Chlorine atoms of the chp ligands block the one axial position of diruthenium unit and the bridging ligand, $Co(CN)_6^{3-}$, connect only two diruthenium units to form a pentanuclear compound. The distances of Ru(1)-Ru(2) and Ru(3)-Ru(4) are 2.254 (4) and 2.241(4) Å, respectively. The distances between Co and C atoms of the bridging CN groups are different (2.09 (6) and 1.85 (5) Å, repectively) from Co-C(3) (other CN groups) distance (1.80 (3) Å).

Magnetic moments[9] of the pentanuclear complex are shown in Figure 2. Also, the temperature dependence of the magnetic moments of $Ru_2(O_2CC_3H_7)_4Cl$[10] is shown for

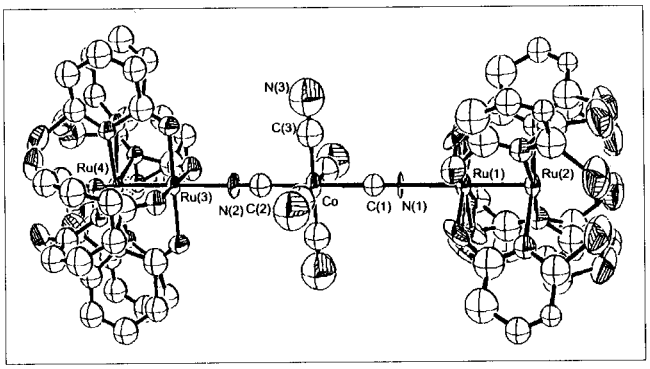

Figure 1. ORTEP drawing of $[\{Ru_2(chp)_4\}_2\{Co(CN)_6\}]^-$. Selected bond distances (A): Ru(1)-Ru(2) 2.258(4), Ru(3)-Ru(4) 2.236(4), Ru(1)-N(1) 2.12(3), Ru(3)-N(2) 2.29(3), Co-C(1) 2.12(3), Co-C(2) 1.92(5), Co-C(3) 1.71(3), C(1)-N(1) 0.92(4), C (2)-N(2) 1.00(5).

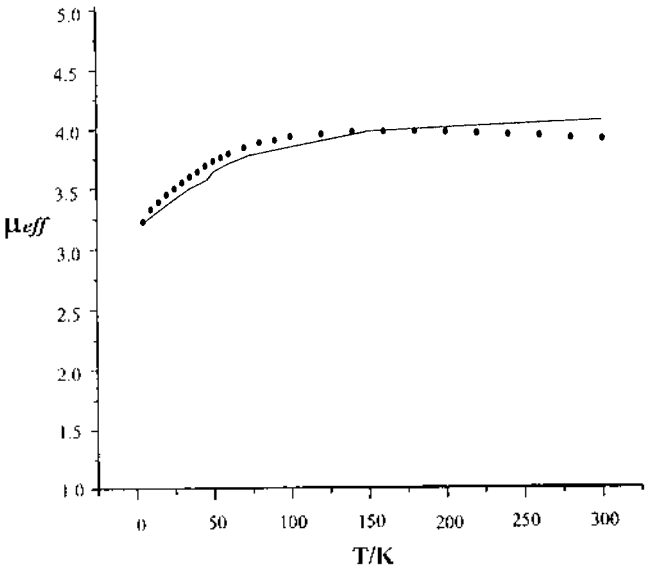

Figure 2. Magnetic moments per Ru2 unit of the pentanuclear compound as a function of temperature. Solid line is the temperture dependence of the magnetic moments of $Ru_2(O_2CC_3H_7)_4Cl$ from 300 to 5 K, reported by Telser and Drago[10].

comparison. The latter compound has been reported as isolated S=3/2 systems, eventhough it is an one-dimensional polymer. The pentanuclear complex contains the diruthenium units that show S=3/2 spin system. One can study how S=3/2 spin communicates through the $Co(CN)_6^{3-}$ bridging group. The behavior of the two complexes is similar. The decrease in magnetic moments at low temperature results from zero field splitting effects. The similarity of two plots indicates there is no significant magnetic interactions between two diruthenium units through the cobalt cyanide bridging ligand. The magnetic moment per diruthenium is 3.7 μ_B at room temperature.

The pentanuclear compound prepared in this work is the first example that involves the use of Ru2 units in such linkages. The $Ru_2(chp)_4^+$ units which have only one open axial position, allow to make a linear (one-dimensional) pentanuclear compound. Such $Ru_2(chp)_4^+$ units should be able to form a planar-type (two-dimensional) or an octahedral-type (three-dimensional) compound when connected to a suitable mononuclear bridging complex such as $Co(NCS)_6^{3-}$. On the other hand, if we use $Ru_2(O_2CCH_3)_4^+$ units which have two open axial positions, we can synthesize one-, or two-dimensional polymers. Detailed study utilizing $Ru_2(chp)_4^+$ and $Ru_2(O_2CCH_3)_4^+$ units to make one-dimensional or two-dimensional compound is in progress.

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6. Charkravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1985**, *24*, 1263. $Ru_2(chp)_4Cl$ consists of a ruthenium unit with four bridging chp ligands and an axial chlorine ligand. The four chp ligands all point the same way. So, one ruthenium atom is coordinated only by nitrogen atoms and the other only by oxygen atoms.
7. Anal. Found: C: 32.64, H: 1.28, N: 11.41 Calcd.: C: 32.76, H: 1.44, N: 11.63.
8. *Crystal Data*: Empirical formula Ru4 Co Cl8 N14 O14 C46 H32 K, Fw 1790.776, purple, size 0.15×0.15× 0.007 mm, space group P4/n (No. 129), a=11.0042 (4), b=11.9942 (4), c=22.926 (1) Å, V=3298.1 (2) Å^3, Z=2, Dc=1.614 Mg/m^3, μ(Mo-Kα, 0.71073 Å)=1.551 mm^{-1}. The X-ray data were collected on Simens Smart CCD Area Detector System. 16171 intensity data were collected in the range $0.89 < \theta < 25.26°$. 1731 unique data were used for refinement with SHELX-97 program. The chp groups briging diruthenium unit are disordered. One can see 8 chp ligands around diruthenium unit. Final R=0.1053 and Rw=0.2873 ($>2\sigma$(I)) with 109 parameters (Goodf=0.981). Eventhough the R value is a little high, the structure of the pentanuclear complex is quite valuable since this is the first example that a high spin system (S=3/2) is connected by the metal cyanide. Tables of atomic coordinates, bond lengths and angles and thermal parameters are available from Dr. Jun.
9. Megnetic susceptibility measurements were carried out on the solid sample in the temperature range, 5.0-300°K with a Quantum/MPMS SQUID (superconducting quantum interference device). The sample was quenched in a field of 10000 G.
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