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Crystal Structure of the Pentanuclear Complex Containing Ru₂(chp)₄⁺ Units Linked by Co(CN)₆³⁻

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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 Rh₂(O₂CCF₃)₄ units to form an extended two-dimensional layer³ or bridge two Rh₂(O₂CCH₃)₄ units to form either 1,1- or *trans*-1,2 type one-dimensional polymers.⁴ Metal cyanides, Co(CN)₆³⁻ also bridge four Rh₂(O₂CCH₃)₄ units to form a two-dimensional sheet.⁵ Jacobson mentioned that the Co(CN)₆³⁻ group acts like TCNE even though Co(CN)₆³⁻ can form three-dimensional polymer. We have interested in the diruthenium unit to study magnetic interactions through Co(CN)₆³⁻ bridging groups. The pentanuclear complex, K[{Ru₂(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 [Ru₂(chp)₄](PF₆) with an aqueous solution of K₃Co(CN)₆ gave purple precipitate with yield of 75.5%. [Ru₂(chp)₄](PF₆) was prepared by elimination of the axial chlorine atom from Ru₂(chp)₄Cl₆ with AgPF₆ in CH₂Cl₂ solution. The precipitate⁷ was not soluble in any solvent. Dark purple crystals were obtained from the direct diffusion technique. An aqueous solution of

K₃Co(CN)₆ was carefully layered by a methanol solution of [Ru₂(chp)₄](PF₆). The CN stretching modes were observed in the IR spectrum at 2133 cm⁻¹ which is shifted from 2129 cm⁻¹ of K₃Co(CN)₆. This blue shift indicates that the cobalt cyanide acts like a σ donor to diruthenium unit.

The Ru₂(chp)₄⁺ units are bridged by Co(CN)₆³⁻ to form a pentanuclear compound, K[{Ru₂(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 diruthenium-cobaltcyanide polymer, the diruthenium units are coordinated by only two CN groups of Co(CN)₆³⁻ 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)₆³⁻, 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, respectively) from Co-C(3) (other CN groups) distance (1.80 (3) Å).

Magnetic moments⁹ of the pentanuclear complex are shown in Figure 2. Also, the temperature dependence of the magnetic moments of Ru₂(O₂CC₃H₇)₄Cl¹⁰ is shown for

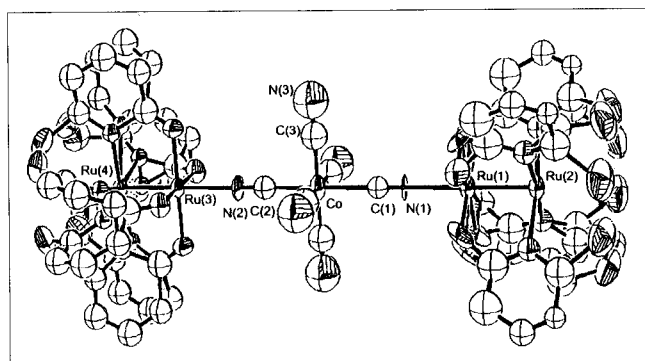


Figure 1. ORTEP drawing of $[\{\text{Ru}_2(\text{chp})_4\}_2\{\text{Co}(\text{CN})_6\}]^-$. Selected bond distances (Å): Ru(1)-Ru(2) 2.258(4), Ru(3)-Ru(4) 2.236(4), Ru(1)-N(1) 2.12(3), Ru(3)-N(2) 2.29(3), Co-C(1) 2.12(3), Co-C(2) 1.92(5), Co-C(3) 1.71(3), C(1)-N(1) 0.92(4), C(2)-N(2) 1.00(5).

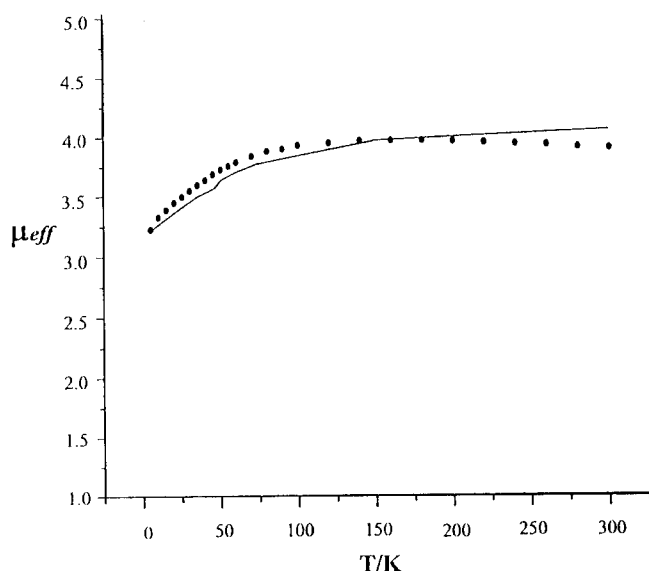


Figure 2. Magnetic moments per Ru₂ unit of the pentanuclear compound as a function of temperature. Solid line is the temperature dependence of the magnetic moments of Ru₂(O₂CC₃H₇)₄Cl from 300 to 5 K, reported by Telser and Drago¹⁰.

comparison. The latter compound has been reported as isolated S=3/2 systems, even though it is a 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)₆³⁻ 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 Ru₂(chp)₄⁺ units which have only one open axial position, allow to make a linear (one-dimensional) pentanuclear compound. Such Ru₂(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)₆³⁻. On the other hand, if we use Ru₂(O₂CCH₃)₄⁺ units which have two open axial positions, we can synthesize one-, or two-dimensional polymers. Detailed study utilizing Ru₂(chp)₄⁺ and Ru₂(O₂CCH₃)₄⁺ units to make one-dimensional or two-dimensional compound is in progress.

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- Charkravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1985**, *24*, 1263. Ru₂(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.
- Anal. Found: C: 32.64, H: 1.28, N: 11.41 Calcd.: C: 32.76, H: 1.44, N: 11.63.
- 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) Å³, Z=2, Dc=1.614 Mg/m³, μ(Mo-Kα, 0.71073 Å)=1.551 mm⁻¹. The X-ray data were collected on Siemens Smart CCD Area Detector System. 16171 intensity data were collected in the range 0.89 < θ < 25.26°. 1731 unique data were used for refinement with SHELX-97 program. The chp groups bridging diruthenium unit are disordered. One can see 8 chp ligands around diruthenium unit. Final R=0.1053 and Rw=0.2873 (> 2σ(I)) with 109 parameters (Goodf=0.981). Even though 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.
- Magnetic 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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