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Isolation and Molecular Structure of Hexacyanoruthenate(III)

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The $[Ru(CN)_6]^{3-}$ ion is synthesized in aqueous solution and isolated as $[Ph_4As]_3[Ru(CN)_6]\cdot 2H_2O$ (**1**). Compound **1** crystallizes as orange needles in the monoclinic space group $P2_1/n$ with cell parameters $a = 11.346(2)$ Å, $b = 23.107(5)$ Å, $c = 25.015(5)$ Å, $\beta = 99.55(3)°$, $V = 6467.1(22)$ Å^3, $Z = 4$. The octahedral anion has Ru–C bond lengths in the range 2.023(6)–2.066(6) Å. DFT calculations reproduce experimental geometries for $[M(CN)_6]^{3-}$ (M = Fe, Ru) equally well and yield significantly higher spin densities on the cyanide ligands in $[M(CN)_6]^{3-}$ (M = Ru, Os) than in $[Fe(CN)_6]^{3-}$.

Magnetic materials based on molecular cyano complexes have received much interest recently,[1] and this class of materials encompasses today magnets with ordering temperatures at or above room temperature.[2] There has been a concomitant growth of interest in simple molecular cyano complexes as possible building blocks for such materials. Thus, the last years have seen, for example, the synthesis and characterization of the paramagnetic cyano complexes $[Mn(CN)_6]^{2-}$, $[Mn(CN)_4]^{2-}$, and $[Ti(CN)_6]^{3-}$.[3]

Another possibly interesting paramagnetic building block is the hexacyanoruthenate(III) ion. Although the existence of $[Ru(CN)_6]^{3-}$ has been known for more than half a century,[4] its chemistry is still only partly characterized. For many years, the complex was only known as yellow aqueous solutions obtained by oxidizing $[Ru(CN)_6]^{4-}$ with PbO_2, Ce(IV), or H_2O_2.[5] Attempts at isolating simple salts from these solutions were always in vain, and the instability of aqueous solutions of $[Ru(CN)_6]^{3-}$ was even made the subject of a detailed study.[6] However, a decade ago Eller and Fischer demonstrated that $[Ru(CN)_6]^{3-}$ could be obtained analytically pure as its bu_4N^+ salt, by employing DMF as the reaction solvent.[7] Their procedure required the preliminary conversion of $K_4[Ru(CN)_6]$ to $(bu_4N)_4[Ru(CN)_6]$ via $H_4[Ru(CN)_6]$ before oxidation. We have found that these steps can be circumvented. By judicious choice of conditions, direct isolation of $[Ru(CN)_6]^{3-}$ from aqueous solution is indeed possible and convenient.[8]

A search among counterions satisfying the criteria of fast precipitation of $[Ru(CN)_6]^{3-}$ and good solubility of the Ru(II) salt proved $[Ph_4As]^+$ to be the best suited. Adding $[Ph_4As]Cl$ to a $[Ru(CN)_6]^{3-}$ solution obtained by oxidation with an equivalent amount of Ce(IV) precipitates yellow-orange needle-shaped crystals. In general, the most pure product is obtained by using less than the equivalent amount of precipitant. Crystals of X-ray quality can be obtained by slow addition (dropwise over 15 min) in combination with using a deficit of $[Ph_4As]^+$. An X-ray structure determination[9] of $[Ph_4As]_3[Ru(CN)_6]\cdot 2H_2O$ (**1**) confirms that it contains discrete $[Ru(CN)_6]^{3-}$ ions with an almost perfect octahedral coordination (Figure 1). The $[Ru(CN)_6]^{3-}$ ions lie on general positions in channels defined by the cations. There are no close contacts between anions and cations. The arrangement

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(8) $K_4[Ru(CN)_6]\cdot 3H_2O$ was prepared by a slight modification of the literature method[13] employing $K_4[Ru_2OCl_{10}]$ as the starting material.[14] $Ce(SO_4)_2\cdot 4H_2O$ was obtained from Fluka and used as received. $K_4[Ru(CN)_6]\cdot 3H_2O$ (100 mg, 0.214 mmol) was dissolved in distilled water (7 mL), and $Ce(SO_4)_2\cdot 4H_2O$ (86.6 mg, 0.214 mmmol) was added. The yellow suspension was stirred vigorously for 2 min at RT and filtered (longer reaction times leads to contamination with a green byproduct). Solid $[Ph_4As]Cl$ (162 mg 0.387 mmol) was added, and the solution was stirred and then left in the cold for 15 min for precipitation. The product was isolated by filtration and washed with ice cold water. Yield 97 mg (54%) of yellow needles. Anal. Calcd for $C_{78}H_{64}As_3N_6O_2Ru$: C, 64.9; H, 4.47; N, 5.82. Found: C, 63.9; H, 4.23; N, 5.75. IR (KBr pellet): 545 cm^{-1} (m) (ν_{Ru-C}), 2130 (w), 2087(vs), and 2038 cm^{-1} (vs) (ν_{C-N}). The dry solid is stable for months at RT, but it is photosensitive. Solutions decompose over a period of hours, with the rate depending on concentration and pH. Decomposition is fast in acidic solutions.

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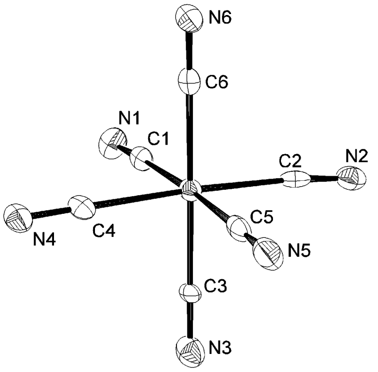

Figure 1. Molecular structure of $[Ru(CN)_6]^{3-}$ in **1**. Bond lengths (Å): Ru−C1, 2.066; Ru−C2, 2.064; Ru−C3, 2.023; Ru−C4, 2.025; Ru−C5, 2.054; Ru−C6, 2.064; C1−N1, 1.161; C2−N2, 1.143; C3−N3, 1.145; C4−N4, 1.165; C5−N5, 1.141; C6−N6, 1.147. Displacement ellipsoids are drawn at the 50% probability level.

of the water molecules is complex: half of the water molecules are not hydrogen bonded, one-quarter are hydrogen bonded to one cyanide ligand (2.664 Å), and one-quarter bridge two cyanide ligands of the same anion (2.995 and 3.175 Å). The Ru−CN bond lengths range from 2.023 to 2.066 Å with an average of 2.050(8) Å. This is significantly longer than those found in $K_4[Ru^{II}(CN)_6]\cdot 3H_2O$ (1.912 Å) with nonbridging $[Ru^{II}(CN)_6]^{4-}$ ions, but close to the distance found in $KLa[Ru^{II}(CN)_6]\cdot 4H_2O$ where the $[Ru^{II}(CN)_6]^{4-}$ ions bridge La^{3+} centers. The average Ru−C bond length in **1** is on the other hand slightly shorter than the value (2.066 Å) found for the *cis* situated cyanide ligands in the nitrido-bridged Ru(IV) dimer: $K_5[Ru_2N(CN)_{10}]\cdot 3H_2O$. This trend is in accordance with a low, but not vanishing, degree of back-bonding in the Ru(III) complex. The C−N bond lengths lie in the range 1.142(6)−1.165(7) Å and are unexceptional. The C−N stretching frequencies in **1** determined by infrared spectroscopy show a larger splitting than observed for the $[Ru(CN)_6]^{4-}$ but carry little information concerning the relative importance of back-bonding in the two systems.

The temperature variations of the magnetic susceptibility and moment of **1** are shown in Figure 2 and corroborate that **1** consists of magnetically isolated low-spin d^5 ions. The data have been fitted with $g_{iso} = 1.952(7)$ and a TIP of $7.94(7) \times 10^{-4}$ cm^{-3} mol^{-1}. A complete d^5 calculation yields $\langle\psi_E|\hat{L} + 2\hat{S}|\psi_U\rangle^2 = 2.0$. When the splitting of the $^2T_2$ term is approximated as $^3/_2\zeta_{4d}$ this requires that $\zeta_{4d} = 880$ cm^{-1} to be compared with $\zeta_{4d} = 932$ cm^{-1} for atomic Ru^0.[10]

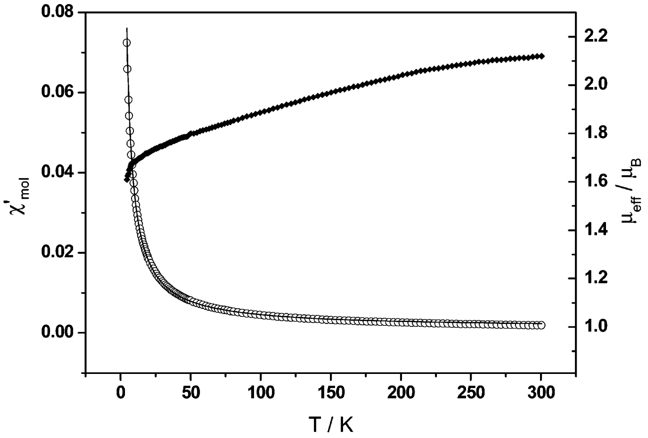

Figure 2. Temperature variation of the magnetic susceptibility (○) and moment (◆) of **1**. The full line depicts the fit of the susceptibility data.

Delocalization of spin density onto the cyanide ligands promotes intermolecular exchange coupling and is thus an important factor in achieving high magnetic ordering temperatures in materials based on cyanometalate building blocks.[1] The superiority of cyano complexes of low-valent metal centers from the left-hand side of the transition series in this respect has thus been rationalized by invoking a higher degree of covalency due to better energy matching between metal d-orbitals and cyanide π*-orbitals. However, another possible promotor for spin delocalization is low-lying LMCT-states, which indirectly infer radical character on the ligands. This possibility would be favored by very oxidizing systems such as the $[Ru(CN)_6]^{3-}$ ion. It has been shown that the lowest excited states of $[Ru(CN)_6]^{3-}$ are of LMCT character and that the system is a rare example of a LMCT-emitter. The energies of the lowest LMCT states determined from emission spectroscopy were found to be ca. 19000 cm^{-1}.[11] The best experimental handle on the spin density on the cyanide ligands would be well resolved EPR spectra. We, therefore, attempted solid dilutions of $[Ru(CN)_6]^{3-}$ in various salts of $[Co(CN)_6]^{3-}$ but never observed any superhyperfine splittings. As an alternative, we chose to examine the spin density distributions in $[M(CN)_6]^{3-}$ (M = Fe, Ru, and Os) by DFT calculations.[12] Since the structure of $[Os(CN)_6]^{3-}$ is not known experimentally, we chose to calculate the optimized geometries of all three species in order to treat the systems on as equal a footing as possible. Calculated bond length data and spin densities are presented in Table 1. It is seen that the spin densities on the terminal nitrogen

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(9) Crystal data for $[Ph_4As]_3[Ru(CN)_6]\cdot 2H_2O$ (**1**) at 120(2) K: $C_{78}H_{64}As_3N_6O_2Ru$, MW = 1439.15, orange needle, 0.50 × 0.08 × 0.06 mm^3, $P2_1/n$, a = 11.346(2) Å, b = 23.107(5) Å, c = 25.015(5) Å, β = 99.55(3)°, V = 6467.1(22) Å^3, Z = 4, ρ_{calcd} = 1.478 mg/mm^3, Mo Kα radiation (λ = 0.71073 Å), μ = 1.819 mm^{-1}. A crystal of **1** was cooled using a Cryostream nitrogen gas cooler system. The data were collected on a Siemens SMART Platform diffractometer with a CCD area sensitive detector. There were 7415 unique observed ($I > 2.0\sigma(I)$) reflections used for the structure solution. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 of all data. Programs used for data collection, data reduction, and absorption were SMART, SAINT, and SADABS.[15,16] The program SHELXTL 95[17] was used to solve the structures, and for molecular graphics. PLATON[18] was used for molecular geometry calculations. Final R/R_w = 0.0645/0.0799, GOF = 1.094 for 811 parameters. The final Fourier difference synthesis showed minimum and maximum peaks of −0.966 and 0.778 e Å^{-3}.

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(12) DFT calculations were performed with the Amsterdam Density Functional (ADF) program suite version 2000.[19−21] Slater-type orbital basis sets of triple-ζ quality for the valence orbitals were employed with polarization functions on the ligand atoms (3d for C and N) and additional valence p orbitals on the metal atoms (ADF basis set IV). Frozen core approximations were used on the metals up to 2p, 3d, and 4d on Fe, Ru, and Os, respectively. The Vosko−Wilk−Nusair correlation functional was employed in the LDA calculations. In the GC calculations, the exchange functional proposed by Becke (B88)[22] and the correlation functional due to Perdew (P86)[23] were used. To facilitate the calculations, the symmetries were restrained to O_h. All charge and spin densities were based on Mulliken analyses.[24]

Table 1. Calculated Geometries and Spin Densities for $[M(CN)_6]^{3-}$ (M = Fe, Ru, Os)

	Fe			Ru			Os		
	LDA	GGA	ZORA	LDA	GGA	ZORA	LDA	GGA	ZORA
M−C (Å)	1.908	1.969		2.057	2.106		2.099	2.145	
C−N (Å)	1.175	1.181		1.174	1.181		1.175	1.182	
spin (M)	1.034	1.034	1.038	0.755	0.840	0.834	0.727	0.815	0.845
spin (C)	−0.033	−0.042	−0.043	−0.022	−0.034	−0.032	−0.022	−0.036	−0.038
spin (N)	0.041	0.036	0.036	0.063	0.061	0.060	0.068	0.067	0.064

atoms are approximately twice as large in the ruthenium and osmium complexes as in the hexacyanoferrate(III) ion. The geometries calculated by the local density approximation (LDA) are closer to the experimental X-ray structure data than those calculated using a gradient corrected functional (GGA) for both hexacyanoferrate(III) and hexacyanoruthenate(III): $Fe^{exp} = 1.931$ Å,[25] $Fe^{LDA} = 1.908$ Å, $Fe^{GGA} = 1.969$ Å, $Ru^{exp} = 2.050$ Å, $Ru^{LDA} = 2.057$ Å, and $Ru^{GGA} = 2.106$ Å. The reason is probably a compensation of the overbinding normally observed for LDA by the treatment of the high-charged, gaseous ions. No significant change of the calculated properties or trends results from invoking relativistic corrections on the scalar level by use of the ZORA formalism. The latter calculations were single point calculations employing the geometrical data from the nonrelativistic GGA calculations.

In conclusion, the $[Ru(CN)_6]^{3-}$ ion has significantly higher spin density on the cyanide ligands than its iron congener and may thus be an interesting building block for magnetic materials. Investigations along these lines are currently being undertaken.

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Supporting Information Available: Crystallographic data in CIF format and the IR spectrum of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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