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Two Novel 5f–3d Bimetallic Cyano-Bridged Complexes

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Bimetallic cyano-bridged uranyl Co and uranyl Fe compounds crystallize in the same space group but are not isomorphous and each comprises two different types of uranyl ion. The spectroscopic consequences with regard to band intensities and positions for the transitions at these different uranyl ion sites are novel and are rationalized.

Introduction

There has been considerable interest in 3d–4f bimetallic cyano-bridged complexes due to their catalytic, semiconductive and magnetic properties.[1] Du et al.[2] have listed another 15 applications. Although there have been several reports of 3d–5f complexes,[3] attention has not been directed towards cyano-bridged 3d–5f complexes, so that we decided to synthesize such complexes comprising the uranyl ion, because the electronic structure and spectroscopy of this actinide ion are well-documented.[4] Two novel complexes involving also the coordination of dimethylformamide (dmf) and aqua ligands to U^{VI} are reported herein: $[UO_2(H_2O)_4(dmf)_2]_{0.5}$·$\{UO_2[M(CN)_6](dmf)_2\}$, M = Co (**1**), Fe (**2**) and their spectroscopic properties have been investigated.

Results and Discussion

Crystal Structures

Compound **1** comprises two ionic components (Figure 1, a). The anionic component is a cyano-bridged infinite layer in which the U^{VI} cation is seven-coordinate in a pentagonal-bipyramidal geometry, bonding to two oxygen atoms [U1–O1, 1.727(7) Å, U1–O2, 1.761(7) Å], two dmf molecules [U1–O3, 2.325(6) Å, U1–O4, 2.359(5) Å], and three cyanide groups from different $[Co(CN)_6]^{3-}$ ions [U1–N1, 2.494(6) Å, U1–N2a, 2.499(6) Å, U1–N5b, 2.492(6) Å]. The Co^{III} cation is octahedrally coordinated by six cyanide groups (Co–C, 1.884–1.904 Å), with three of them connecting three different U^{VI} cations. The U^{VI} ions bridge other $[Co(CN)_6]^{3-}$ ions through cyanide groups, forming an infinite two-dimensional anionic layer parallel to the *bc* plane (Figure 2, a). The cationic component comprises discrete centrosymmetric $[UO_2(H_2O)_4(dmf)_2]^{2+}$ cations, situated above and below the anionic layer, each forming O–H···N interactions with it. This U^{VI} cation is eight-coordinate in a hexagonal bipyramidal geometry, being coordinated by

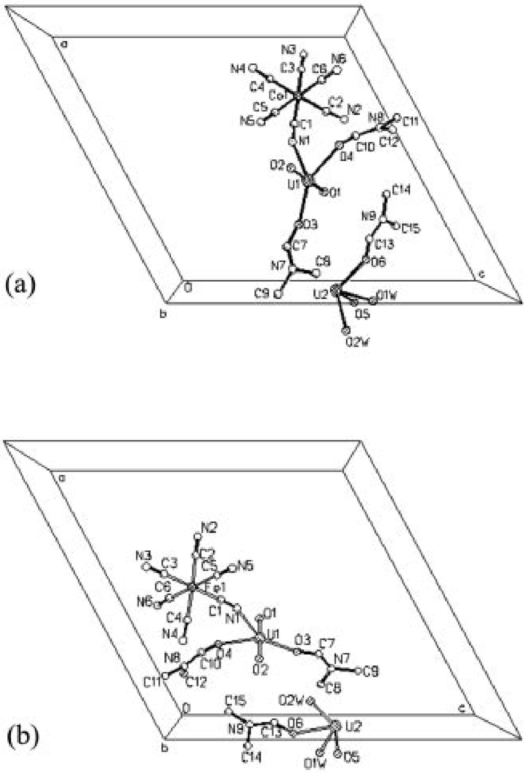

Figure 1. Atom labeling in the asymmetric unit: (a) $[UO_2(H_2O)_4(dmf)_2]_{0.5}$·$\{UO_2[Co(CN)_6](dmf)_2\}$ (**1**); (b) $[UO_2(H_2O)_4(dmf)_2]_{0.5}$·$\{UO_2[Fe(CN)_6](dmf)_2\}$(**2**) .

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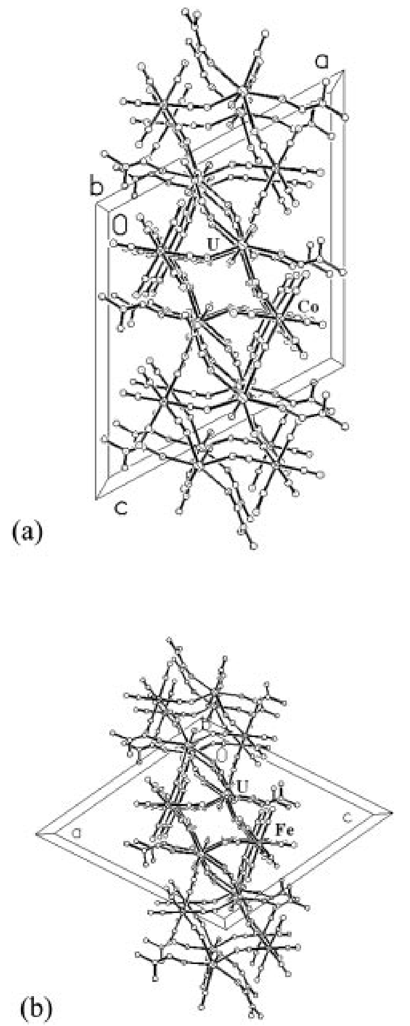
two oxo groups [U2–O5 = U2–O5c, 1.750(7) Å], two dmf molecules [U2–O6 = U2–O6c, 2.27(2) Å], and four aqua ligands [U2–O1W = U2–O1Wc, 2.58(2) Å;U2–O2W = U2–O2Wc, 2.39(2) Å]. The latter form O–H···N hydrogen bonds with the non-bridging cyanide group of the anionic layers, linking them into a three-dimensional network.



(a)

(b)

Figure 2. (a) Anionic layer viewed along the [010] direction in **1**; (b) **2**.

Although **1** and **2** both crystallize in the same space group $P2_1/c$ with very similar unit-cell dimensions, they are not isomorphous as the atoms take different positions in the unit cell (see parts a and b in Figure 1). However, compound **2** is isostructural to compound **1** in all respects, and the only difference is that the anionic layer in **2** runs parallel to the plane (1,–1,0), rather than parallel to the *bc* plane as in the case of **1** (see Figure 2, a and b).

Spectroscopic Properties of 1 and 2

The IR and Raman spectra of **1** and **2** exhibit at least four bands between 2120 and 2180 cm^{-1}, corresponding to terminal and bridging CN vibrations, with the energies for **1** being slightly higher than those for **2**, just as in $Cs_2LiM(CN)_6$ (M = Co, Fe).[5] The spectroscopic properties of **1** and **2** are interesting because they each contain uranium atoms in two types of coordination geometry: seven-coordinate U1 situated at a C_1 site and eight-coordinate U2 at a C_i site. Besides this, there are two U1 atoms for every U2 atom in the unit cell. Sixfold equatorial coordination of the uranyl ion exhibits rather different spectral characteristics as compared to fivefold, and drastic differences also occur for noncentrosymmetric vs. centrosymmetric uranyl ions.[4] Thus, as well as vibrations due to dmf and aqua ligands in the IR spectrum of **2**, two strong bands due to antisymmetric stretch of the uranyl ion are observed, at 933 and 949 cm^{-1}. The higher energy band is associated with sixfold equatorial coordination [c.f. $MUO_2(NO_3)_3$ M = Rb 962 cm^{-1}, M = Cs 956 cm^{-1}], whereas that at lower energy is due to fivefold coordinated UO_2^{2+} [c.f. $UO_2(H_2PO_2)_2{\cdot}H_2O$ 909 cm^{-1}].[4] Also, the relative intensities of the 933, 949 cm^{-1} bands are in the ratio 2:1, being consistent with the atom ratio U1:U2.

The 10-K absorption spectrum of **1** is shown in Figure 3. The lowest energy absorption bands of the uranyl ion correspond to the $\Sigma_g^+ \rightarrow \Pi_g$ ($D_{\infty h}$) electronic transition, and because this involves a large increase in bond length, a strong progression in the totally symmetric uranyl stretching mode, ν_s(OUO) is based upon the electronic origin. Now, for lower than fourfold symmetry of the uranyl ion the final state is not degenerate, and whereas the transition is magnetic dipole-allowed for centrosymmetric uranyl ions, additional electric dipole intensity is present when this is not the case. Finally, it has been found that a blue-shift occurs when the equatorial coordination number increases from 5 to 6.[4] With these facts in mind, the intense bands at lowest energy are marked and assigned to the electronic origins of uranyl ions U1 and U2, with that of the noncentrosymmetric U1 being more intense and at lower energy. The ν_s(OUO) progression frequency based upon the U1 origin (724 cm^{-1}) is about 10 cm^{-1} lower than the corresponding one for U2. The resolution of the absorption spectrum does not permit a clear, detailed interpretation but the intense

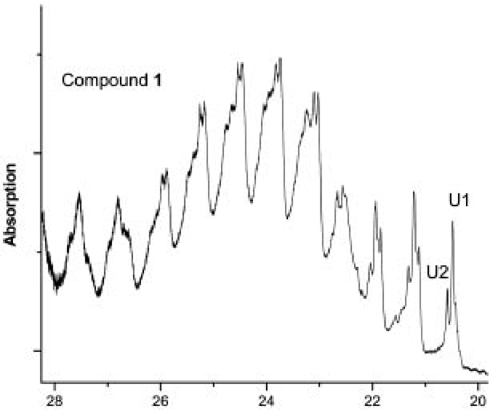


Figure 3. 10-K absorption spectrum of a crystal of **1** between 20000–28000 cm^{-1}.

bands commencing at 23021, 23102 cm^{-1} mark the beginning of a new progression, presumably of U1.

The 10 K luminescence spectrum of **1** is also dominated by the transitions from the lowest energy site U1. The symmetric and antisymmetric OUO stretching frquencies are 857 ± 5 cm^{-1} and 943 cm^{-1}, respectively, and the progressions are observed up to 5 members.

Conclusions

In summary, two cyano-bridged 3d–5f complexes **1** and **2** have been synthesized with three-dimensional structures comprising uranyl groups arranged in cationic and anionic layers. Although both compounds crystallize in space group $P2_1/c$ with very similar unit-cell dimensions, they are not isomorphous. The electronic absorption and emission spectra of the uranyl ions in **1** are dominated by the uranyl ions of site symmetry C_1, which are subjected to less restrictive optical selection rules and more numerous than those of site symmetry C_i.

Experimental Section

Physical Methods: Electronic absorption spectra were obtained between 300 and 10 K at the resolution 2 cm^{-1} by a Biorad FTS-60A spectrometer equipped with a photomultiplier tube detector. The sample was placed in an Oxford Instruments closed-cycle cryostat. Emission spectra were recorded at temperatures down to 10 K using a tunable pulsed laser (Panther OPO system pumped by the third harmonic of a Surelite Nd:YAG). The signal was collected at 90° by an 0.5 m Acton monochromator, with gratings blazed at 250 nm (1800 grooves/mm), 500 nm (1200 groove/mm), and 750 nm (600 groove/mm), respectively, and a back-illuminated SpectruMM CCD detector. Infrared and Raman spectra were recorded with a Perkin–Elmer 2000 FTIR spectrometer equipped with a Raman unit.

Materials and Synthesis of Compounds 1 and 2: For compound **1**, $UO_2(NO_3)_2\cdot 6H_2O$ (0.151 g; 0.3 mmol; Strem 99.99%) was dissolved in 10 cm^3 water (solution A). Yellow $K_3Co(CN)_6$ (0.067 g; 0.2 mmol; Acros 95%) was dissolved in 10 cm^3 dmf, to which solution A was added dropwise with continuous stirring, and the resulting solution was stirred for another 30 min in the dark and filtered. The filtrate was allowed to stand for several weeks in the dark at room temperature for crystallization. Compound **2** was prepared analogously using a molar ratio $UO_2(NO_3)_2\cdot 6H_2O$: $K_3Fe(CN)_6$ of 3:2. **1:** $C_{15}H_{25}CoN_9O_8U_{1.5}$ (875.41): calcd. C 20.58, H 2.88, N 14.40; found C 20.36, H 1.93, N 14.17. **2:** $C_{15}H_{25}FeN_9O_8U_{1.5}$ (872.34): calcd. C 20.65, H 2.87, N 14.45; found C 20.24, H 1.61, N 14.38. IR of **2** (cm^{-1}): $\tilde{\nu}$ = 3339 w (H_2O), 2131 sh, 2137 s, 2147 sh, 2157 m CN, 1651 ms (C=O), 949 m, 933 s (UO_2 asymm.), 872 vw, 856 vw (UO_2 symm.). Raman of **1** (cm^{-1}): 2178 s, 2161 m, 2151 m, 2146 sh CN, 862 vs. (UO_2 symm.), 2951 m, 1657 vw, 1440 m, 1427 vs, 687 m dmf.

X-ray Crystallography: Intensity data of compounds **1** and **2** were collected with a Bruker SMART 1000 CCD diffractometer with graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å) at 293 K. The structures were solved by direct methods and refined by full-matrix least-squares based on F^2 using the SHELXTL program package. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated geometrically except for those of the water molecules, which were located from the ΔF maps. The crystallographic data of the complexes **1** and **2** are summarized in Table S1, and selected bond lengths and angles are given in Table S2 (see Supporting Information; for details see the footnote on the first page of this article). Complex **1**, $C_{15}H_{25}CoN_9O_8U_{1.5}$: $P2_1/c$, a = 16.066(2) Å, b = 11.365(1) Å, c = 16.884(2) Å, α = 90°, β = 118.323(2)°, γ = 90°, Z = 4, R_1 = 0.0456. Complex **2**, $C_{15}H_{25}FeN_9O_8U_{1.5}$: a = 16.154(2) Å, b = 11.373(1) Å, c = 16.975(2) Å, α = 90°, β = 118.651(2)°, γ = 90°, Z = 4, R_1 = 0.0441.

CCDC-281906 and -281907 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Crystal data and structure refinement parameters, bond lengths and angles, hydrogen bonds, descriptions of structure; Raman, infrared and emission spectra are available from the authors.

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