DOI: 10.1002/ejic.201001040

Facile Preparation of Paramagnetic Ru^{III} and Os^{III} Hexacyanides

Kira E. Vostrikova*[a] **and Eugenia V. Peresypkina**[a]

Keywords: Ruthenium / Osmium / Hexacyanometallates / Oxidation / 18-crown-6

Diamagnetic $K_4[M(CN)_6]$, M = Ru^{II}, Os^{II} are easily and quantitatively transformed into paramagnetic $[M(CN)_6]^{3-}$ in methanol with the help of crown ethers. Hexacyanoosmate(II) is oxidized by air, whereas for hexacyanoruthenate(II), H_2O_2 is needed. These two cyanometallates, (K@18-crown-6)$_3$[M(CN)$_6$]·*n*Solv, were characterized both in solution and in the solid state. The compounds were obtained as single crystals, and their crystal and molecular structures were determined by X-ray diffraction analysis. In the proposed synthetic method, the use of methanol minimizes hydrolysis and considerably increases the yield and purity.

Introduction

Coordination chemistry involving cyanometallates is in fast expansion. Their use as building blocks for designing molecular magnetic materials has illustrated the effectiveness of the cyanide bridge as an exchange coupling mediator.[1] Various transition metal analogues of Prussian blue (PB) were found to behave as high-temperature molecular magnets, photoswitchable magnetic solids, antidotes for radioactive poisoning, molecular sieves, and hydrogen storage materials.[2] But of special interest is the application of cyanometallates in the field of single molecule magnets (SMMs). Recent theoretical approaches have emphasized the use of highly anisotropic orbitally degenerated cyano complexes such as $[Re(CN)_7]^{3-}$, $[Mo(CN)_6]^{3-}$, $[Ru(CN)_6]^{3-}$, and $[Os(CN)_6]^{3-}$ for engineering SMMs with high blocking temperatures.[3] Communications confirming the potential of such synthons have appeared very recently.[4] Taking into consideration the price of rare noble metal compounds, a development of reliable methods for their preparation is very important.

While for $[Re(CN)_7]^{3-}$ a reproducible and efficient preparation involving a simple ligand exchange was reported,[5] the already described syntheses of Ru^{III} or Os^{III} hexacyanometallates are based on the oxidation of $[M^{II}(CN)_6]^{4-}$ potassium salts by Ce^{4+} in aqueous media followed by precipitation as tetraphenylarsonium or phosphonium salts, respectively.[6a,6b] When using these procedures for preparative purposes, a row of insuperable difficulties arise. In our hands, for both compounds, and especially for the Ru derivative, these synthetic procedures were poorly reproducible; the yields were much lower than reported, and in both cases the purity of the compounds obtained were unpredictable. Most samples were contaminated by important amounts of greenish impurities. A record on the use of $[PPN]_3[Os(CN)_6]$ [PPN = bis(triphenylphosphane)iminium][7] as starting material was found in the literature. However, neither was its synthesis reported nor was any reference for results published earlier given by the authors. The only paper mentioned was allegedly devoted to the synthesis of $[Ph_4As]_3[Os(CN)_6]$,[6b] describing, in fact, $[Ph_4P]_3[Os(CN)_6]$. Therefore, it seemed important to develop a more reliable protocol to prepare paramagnetic hexacyanoruthenate and hexacyanoosmate salts.

We report such a procedure affording in a straightforward and clean manner new derivatives of trivalent Ru and Os hexacyanometallates that are soluble in organic media.

Results and Discussion

As was previously reported,[6c] $[Ru(CN)_6]^{3-}$ is very unstable in aqueous solution. Hydrolysis and over-oxidation, especially in presence of an oxidant such as Ce^{4+}, are responsible for its spontaneous decomposition. Therefore, the best way to increase the stability of the compound is to perform the synthesis in organic media. Both $K_4M^{II}(CN)_6$ compounds are only sparingly soluble in methanol. However, when three equivalents of 18-crown-6 were added, both derivatives of Ru and Os gradually dissolved. After stirring overnight, only a small amount of white precipitate was still present (less than 2% of the starting weight) in both the Ru and Os solutions. After additional stirring, a color change from light blue to lemon yellow was observed for $K_4[Os(CN)_6]$.

The oxidation process, involving oxygen from air (or H_2O_2, vide infra) can be followed by UV/Vis spectroscopy. The absorption spectra of the reaction mixture and of the tetraphenylphosphonium salt prepared according to the published procedure[6b] are displayed in Figure 1, where the

---

[a] Nikolaev Institute of Inorganic Chemistry SB RAS,
3 Lavrentiev avenue, Novosibirsk 630090, Russian Federation
Fax: +7-383-3309489
E-mail: vosk@niic.nsc.ru

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201001040.

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

full coincidence of the two spectra in the visible region and their good agreement with data for $(n\mathrm{Bu}_4\mathrm{N})_3[\mathrm{Os(CN)}_6]$ can be seen.[6b,8a] The difference in the 200–289 nm range is due to the cationic part of the compounds. The average time for completion of air oxidation was found to be 48–56 h, depending on the concentration. Air oxidation of Os cyanide in nonaqueous solvents has already been mentioned,[8a,9] and its easy oxidation in methanol corresponds well to the value of the redox potential reported by Slep.[6b] The oxidation by-products, KOH and $\mathrm{KHCO_3}$, make the solution basic, and could promote oxidation of the CN ligand.[6c] To prevent this process, a stoichiometric amount of anhydrous HCl was added. The latter should be prepared by saturation of $\mathrm{CH_3OH}$ by dry gaseous hydrochloride. Note that such in situ prepared $[\mathrm{K@18\text{-}crown\text{-}6}]_3[\mathrm{Os(CN)}_6]$ can be used as a precursor without isolation. However, it is not recommended to store such a methanol solution for a long time, because some degradation occurred after a few weeks. Alternatively, it is possible to extract the target compound with $\mathrm{CH_2Cl_2}$ or $\mathrm{CHCl_3}$ after evaporation of methanol. This allows the separation of $[\mathrm{K@18\text{-}crown\text{-}6}]_3[\mathrm{Os(CN)}_6]$ from potassium chloride. Accordingly, single crystals were readily obtained by slow diffusion of $\mathrm{Et_2O}$ into a $\mathrm{CH_2Cl_2}$ solution.

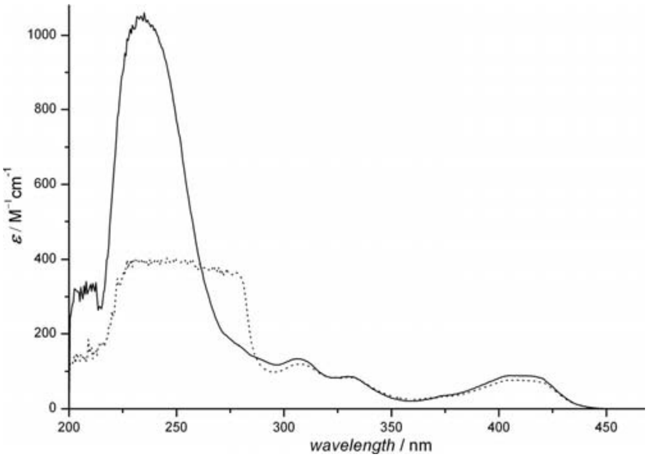

Figure 1. UV/Vis spectra in $\mathrm{CH_3OH}$ solution. Solid line: reaction mixture {18-crown-6, $\mathrm{K_4[Os(CN)_6]}$ (2 mmol L^{-1}), $\mathrm{H_2O_2}$}; dashed line: $(\mathrm{Ph_4P})_3[\mathrm{Os(CN)}_6]$ (7.5 mmol L^{-1}) synthesized according to ref.[6b]

In contrast to $\mathrm{K_4[Os(CN)_6]}$, its Ru analogue is not oxidized by air in methanol containing 18-crown-6. However, oxidation to the $\mathrm{Ru^{III}}$ species is achieved with a stoichiometric amount of concentrated $\mathrm{H_2O_2}$ at room temperature. The UV/Vis spectra for the compound generated by hydrogen peroxide and for $[\mathrm{Ru(CN)_6}]^{3-}$ (as reference) are presented in Figure 2. As observed for the Os analogue, there is a good correspondence with the literature data in the visible wavelength range.[8] Note that oxidation by hydrogen peroxide is also an alternative and more rapid route for the preparation of the $\mathrm{Os^{III}}$ species. Therefore, for an express preparation of $[\mathrm{M^{III}(CN)_6}]^{3-}$ derivatives, one equivalent of $\mathrm{H_2O_2}$ was gradually added to a suspension of $\mathrm{K_4[M(CN)_6]}$ and three equivalents of crown ether in methanol. After stirring for one hour, the solution was neutralized by an equimolar amount of HCl in methanol solution and filtered. Such a procedure resulted in a solution ready for subsequent use as a precursor for preparing $\mathrm{Ru^{III}}$- or $\mathrm{Os^{III}}$-containing heterometallic clusters or extended species.

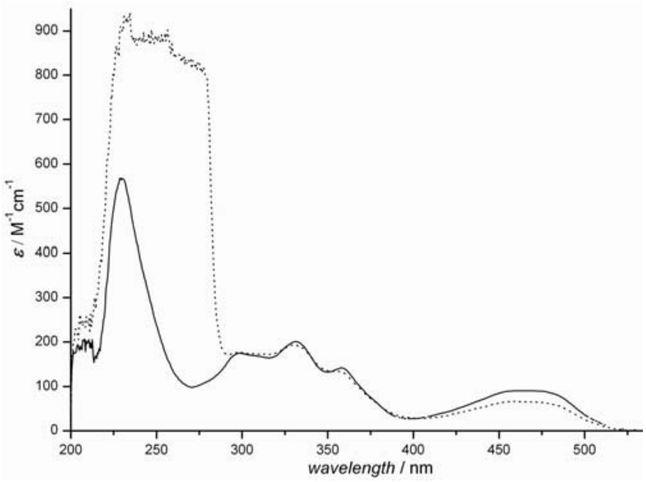

Figure 2. UV/Vis spectra in $\mathrm{CH_3OH}$ solution. Solid line: reaction mixture {18-crown-6, $\mathrm{K_4[Ru(CN)_6]}$ (3.33 mmol L^{-1}), $\mathrm{H_2O_2}$}; dashed line: $(\mathrm{Ph_4P})_3$ $[\mathrm{Ru(CN)_6}]$, (7.5 mol L^{-1}) synthesized according to ref.[6a]

Such an easy preparation of the $[\mathrm{Ru(CN)_6}]^{3-}$ and $[\mathrm{Os(CN)_6}]^{3-}$ species takes advantage of the lowering of the oxidation potential of the $\mathrm{Ru^{II}}$ and $\mathrm{Os^{II}}$ precursors in methanol as already reported for the Os compound and $[\mathrm{Fe(CN)_6}]^{4-}$.[6b] Accordingly, a less aggressive oxidant than $\mathrm{Ce^{IV}}$, such as $\mathrm{H_2O_2}$, may be used. Thus, overoxidation and hydrolysis are minimized.

Both $[\mathrm{K@18\text{-}crown\text{-}6}]_3[\mathrm{M(CN)_6}]$ compounds were crystallized from organic media. Because they have high solubility in methanol, the single crystals were obtained either by slow concentration of MeOH-*i*PrOH solutions or by diffusion of $\mathrm{Et_2O}$ into $\mathrm{CH_2Cl_2}$ solutions. Although these two complexes are both triclinic, their structures are not isomorphic. The transition-metal coordination spheres are slightly distorted octahedra, in which the M–C and C–N bond lengths ($\mathrm{Os–C_{av}} = 2.063$, $\mathrm{Ru–C_{av}} = 2.053$, $\mathrm{C–N_{av}} = 1.14$ Å) agree well with those already reported.[6] In contrast to the Ru complex, in the Os species there are two crystallographically independent $[(\mathrm{K@18\text{-}crown\text{-}6})_2\mathrm{M(CN)_6}]$ fragments.

However, in both structures, all $\mathrm{M^{III}}$ ions are located at a center of symmetry and are connected to two $[\mathrm{K@18\text{-}crown\text{-}6}]^+$ fragments through *trans* cyanide ligands (Figure 3); the third cation is isolated and is linked to oxygen atoms of water or *i*PrOH (Figure 4); in addition, some of the CN groups are linked by hydrogen bonds to $\mathrm{H_2O}$ (2.76 Å) or *i*PrOH molecules (2.80–2.87 Å). Relevant parameters are $\mathrm{K–NC_{(Os)}}$ 2.752 and 2.787 Å, $\mathrm{K–N–C_{(Os)}}$ 129.27 and 134.84°; $\mathrm{K–NC_{(Ru)}}$ 2.776 Å and $\mathrm{K–N–C_{(Ru)}}$ 135.34°. While the bond length values are within the range observed for complexes of other transition metals involved in CN coordination to $[\mathrm{K@18\text{-}crown\text{-}6}]^+$ (N–K 2.741–

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

2.860 Å),[10] the value of the K–N–$C_{(M)}$ angle (about 135°) is considerably smaller than those observed in the literature (178.81–174.33°)[10a,10b] and closer to the values 155.77 and 148.30° determined in a Co–porphyrinato complex.[10c] This low value is probably the consequence of steric hindrance. While all macrocyclic molecules in $[(K@18\text{-crown-}6)_2\text{-}Ru(CN)_6]$ are disordered by rotation over two close positions with ratios of 0.8/0.2 and 0.7/0.3, only one of the three crystallographically different 18-crown-6 molecules in $[(K@18\text{-crown-}6)_2Os(CN)_6]$ is partially conformationally disordered. This explains the significant difference in R_1 values of the structures.

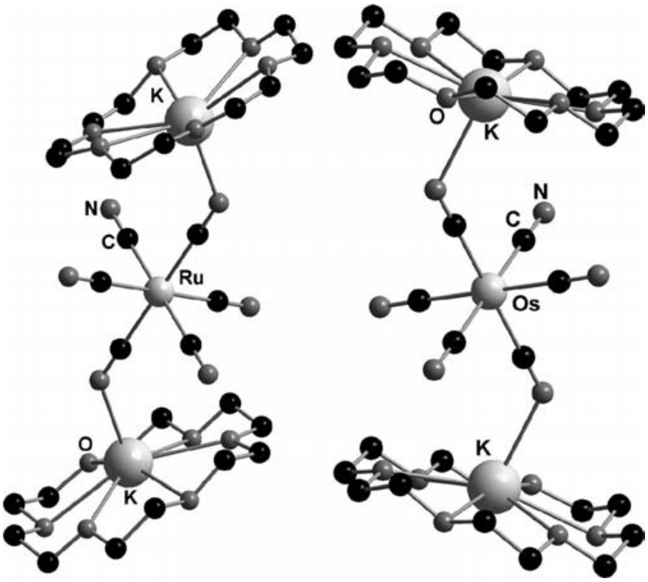

Figure 3. Molecular fragments of $[(K@18\text{-crown-}6)_2M(CN)_6]$ for the Ru (left) and Os (right) compounds. Hydrogen atoms and disorder are omitted for clarity.

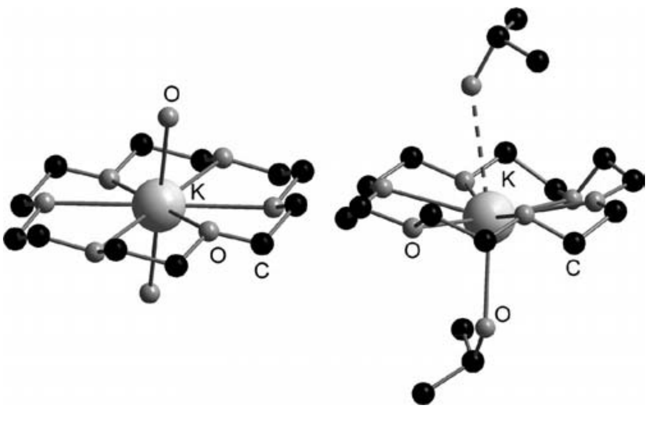

Figure 4. Left: $[(K@18\text{-crown-}6)(H_2O)_2]$ in $(K@18\text{-crown-}6)_3[Ru(CN)_6]$ (K–O_{aqua} 2.721 Å); right: $[(K@18\text{-crown-}6)(i\text{-}C_3H_8OH)_2]$ in $(K@18\text{-crown-}6)_3[Os(CN)_6]$ (distances K–O*i*Pr_{OH} are 2.742 and 3.341 Å). Hydrogen atoms and minor disordered parts of 18-crown-6 and isopropyl alcohol are omitted for clarity.

In the crystal, as a result of the steric demand of the isopropyl fragments, $[K@18\text{-crown-}6]_3[Os(CN)_6]\cdot 2.3iPrOH\cdot 2.85H_2O$ does not form any extended hydrogen-bond network (Figure 5, upper part). In contrast, in the case of ruthenocyanide (Figure 5, lower part), one can see chains of hydrogen-bonded $[Ru(CN)_6]$ and $[(K@18\text{-crown-}6)(H_2O)_2]$ coordination fragments. To the best of our knowledge, there is only one structural characterization of the compound involving the potassium@18-crown-6 cation and hexacyanometallate, a polymeric $[K@18\text{-crown-}6][Ag(CN)_2]$.[10a] One report mentions the determination of the molecular structure by single-crystal X-ray diffraction analysis of $(18\text{-Crown-}6\text{-}K)K_3[Mo(CN)_7](MeOH)$. As we understood, this compound was used as a precursor for the synthesis of pentanuclear bimetallic clusters. However, in the synthetic details, this precursor appeared to be $(18\text{-crown-}6\text{-}K)_4Mo(CN)_7$,[11] and no crystallographic data of the corresponding complex is available. Miyasaka[12] also used $(K@18\text{-crown-}6)_3$ $[M(CN)_6]$ ($M = Fe^{3+}$) as starting material, but no corresponding structural information was reported.

Infrared spectroscopic data for CN^- stretching frequencies merit special consideration for both compounds. A full set of spectra for the M^{II} precursors and the prepared M^{III} compounds is presented in the Supporting Information. While for the Os species, the spectra registered in KBr pellets and in carbofluorinated oil (see Figure S1) are almost identical, for the Ru compound one can see a dramatic difference (Figure S2). In carbofluorinated oil, the most intense peak appears at 2100 cm^{-1} with a shoulder at about 2050 cm^{-1}, whereas in KBr pellets, the more intense peak is observed at 2054 cm^{-1}. This is caused by partial reduction of $[Ru(CN)_6]^{3-}$ to $[Ru(CN)_6]^{4-}$ in KBr, as already reported by Fischer.[8b]

X-band electron paramagnetic resonance (EPR) spectra of frozen solutions in methanol showed a single broad resonance for both cyanometallates at $g = 1.80$ for Os and $g = 1.85$ for Ru (see Supporting Information, Figures S8 and S9). The magnetic moments calculated from susceptibility data measured at room temperature were 1.5 and 2.1 μ_B for the osmium and ruthenium complexes, respectively. Such values are in agreement with those estimated from EPR g factors and are consistent with literature data.[6a,6b,8b,13]

Conclusions

Paramagnetic hexacyanoruthenate(III) and hexacyanoosmate(III), interesting building blocks for designing anisotropic high-spin clusters in relation with SMMs, are easily prepared in high yields when the Ru^{II} and Os^{II} precursors are oxidized in methanol with either air (for Os) or H_2O_2. This is enabled by the presence of 18-crown-6, which puts these insoluble precursors in solution. In contrast to earlier synthetic protocols using cerium(IV) salts as oxidant, oxidation by air or hydrogen peroxide creates the opportunity to use these valuable cyanometallates in situ as far as no additional transition metals are present in the reaction mixture. In addition to high yields and purity, this synthetic method permits to realize Os^{III} and Ru^{III} cyanide coordination chemistry in organic solution. Work in this direction is under way.

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

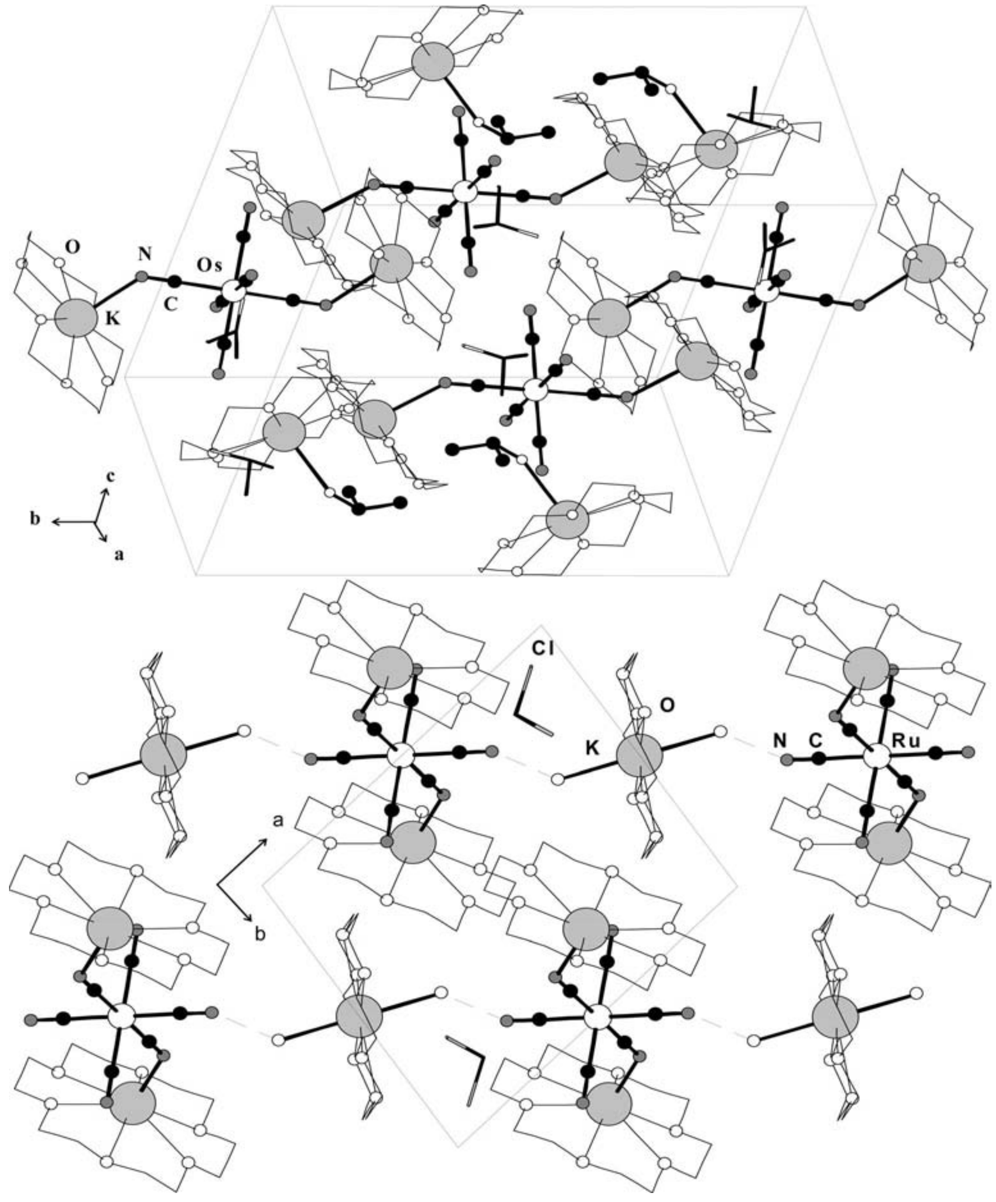

Figure 5. Crystal packing for $[K@18\text{-crown-}6]_3\ [Os(CN)_6](iPrOH)_{2.3}(H_2O)_{2.85}$ (upper part) and for $[K@18\text{-crown-}6]_3[Ru(CN)_6](H_2O)_2(CH_2Cl_2)_2$ (lower part). Hydrogen atoms and minor disordered components of 18-crown-6 molecules are omitted for clarity.

Experimental Section

Synthetic Details: All solvents and commercially available chemicals were used without additional purification. Dry gaseous HCl was used to prepare methanol solutions. The concentration of hydrochloride was determined by NaOH titration of aqueous diluted solutions. The final molarity of the MeOH/HCl mixture (0.1 M) was adjusted by addition of solvent. $K_4[Ru(CN)_6]$ and 18-crown-6 were purchased from Sigma–Aldrich. $K_4[Os(CN)_6]$ was prepared as described previously.[14] Attention: protection against light is needed during the synthesis and work with paramagnetic cyanometallates, especially for Ru compounds. A Scimitar FTS 2000 spectrometer was used to record the IR spectra. UV/Vis measurements were performed by using a UV-2201 Shimadzu spectrophotometer. EPR spectra were recorded in methanol at 78 K by means of a Varian E-109 spectrometer operating at X-band frequency with 2,2-diphenyl-1-picrylhydrazyl as a standard. The magnetic susceptibility was measured with an apparatus employing the Faraday method at 297 K. The samples were sealed in ampoules to protect them from the loss of solvate molecules. Corrections for diamagnetic atoms were applied in the calculations of μ_{eff}.

$(K@18\text{-crown-}6)_3[Os(CN)_6]$: To $K_4[Os(CN)_6]\cdot 2H_2O$ (54 mg, 0.1 mmol) and 18-crown-6 (80 mg, 0.3 mmol) was added methanol (10 mL), and the mixture was stirred overnight. A small amount of white insoluble solid was then filtered off. The lemon yellow solution was stirred for 2 d in air. CH_3OH was evaporated under reduced pressure, and the remaining solid was extracted a few times with CH_2Cl_2; the solvent was dried and evaporated to give a lemon yellow powder (116 mg, 90%). $(K@18\text{-crown-}6)_3[Os(CN)_6]\cdot 2H_2O$ (1293.36): calcd. C 39.03, N 6.50, H 5.93, K 9.07; found C 39.1, N 6.7, H 5.8, K 9.2. IR (carbofluorinated oil, ν_{CN}): $\tilde{\nu}$ = 2091 (s) and 2073(w, sh) cm^{-1}. $\mu_{\text{eff}} = 1.45\ \mu_B$.

$(K@18\text{-crown-}6)_3[Ru(CN)_6]$ (Hydrogen Peroxide Route): The following method was used for the synthesis of both Ru and Os compounds. To $K_4[Ru(CN)_6]\cdot xH_2O$ (42 mg, 0.1 mmol) and 18-crown-6

(80 mg, 0.3 mmol) was added methanol (5 mL). After stirring for 4 h, H_2O_2 (30%, 60 µL, 0.05 mmol) was added. The color of the solution immediately changed to bright yellow. Stirring was continued for one hour, then HCl was added (0.5 mL of 0.1 M methanol solution). CH_3OH was evaporated under reduced pressure, the remaining solid was extracted a few times with CH_2Cl_2 to give a yellow powder after removal of the solvent (112 mg, 93%). (K@18-crown-6)$_3$[Ru(CN)$_6$]·2H$_2$O (1203.31): calcd. C 41.92, N, 6.98, H 6.37, K 9.7; found C 42.0, N 6.8, H 6.2, K 9.9. IR (carbofluorinated oil, ν_{CN}): $\tilde{\nu}$ = 2100 cm^{-1}. μ_{eff} = 2.11 μ_B.

X-ray Crystallography: Diffraction data for both compounds were collected with a Bruker X8Apex CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å) using ϕ and ω scans of narrow (0.5°) frames. Both structures were solved by direct methods and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with the *SHELXTL* set of programs.[15a] Absorption corrections were applied empirically with the *SADABS* program.[15b] Hydrogen atoms were refined in geometrically calculated positions.

[K@18-crown-6]$_3$[Os(CN)$_6$](*i*PrOH)$_{2.3}$(H$_2$O)$_{2.85}$: Single crystals were obtained by slow evaporation of isopropyl alcohol/methanol solution. $C_{51.45}H_{96.10}K_3N_6O_{23.15}Os$, crystal size 0.27 × 0.09 × 0.02 mm (yellow plate), triclinic, space group $P\bar{1}$, a = 13.9844(5) Å, b = 15.0974(5) Å, c = 18.2461(6) Å, α = 106.3220(10)°, β = 90.2940(10)°, γ = 104.7010(10)°, V = 3563.8(2) Å^3, T = 150.0(2) K, Z = 2, $\rho_{calcd.}$ = 1.376 g cm^{-3}, $2\theta_{max}$ = 63.1°, μ = 2.036 mm^{-1}, 41558 reflections collected within $-20 \le h \le 19$, $-20 \le k \le 19$, $-25 \le l \le 22$, 19220 unique (R_{int} = 0.0326), 12997 $F_o \ge 4\sigma(F)$, 786 parameters, 3 restraints, R_1 = 0.0346, wR_2 = 0.0846, GooF = 1.035, residual electron density peaks of 1.137 and –0.955 e Å^{-3}. One of three crystallographically different 18-crown-6 molecules is partly disordered. Both coordinated to the potassium atom, solvate isopropyl alcohol and water molecules statistically occupy the same positions. A number of restraints were used during the refinement of the isopropyl alcohol molecules.

[K@18-crown-6]$_3$[Ru(CN)$_6$](H$_2$O)$_2$(CH$_2$Cl$_2$)$_2$: Single crystals were obtained by diffusion of Et$_2$O in CH$_2$Cl$_2$ solution. $C_{44}H_{80}Cl_4K_3N_6O_{20}Ru$, crystal size 0.73 × 0.12 × 0.03 mm (goldish-colored plates), triclinic, space group $P\bar{1}$, a = 11.5483(7) Å, b = 12.3695(8) Å, c = 12.5045(8) Å, α = 93.331(2)°, β = 112.096(2)°, γ = 98.560(2)°, V = 1623.86(18) Å^3, T = 150.0(2) K, Z = 1, $\rho_{calcd.}$ = 1.404 g cm^{-3}, $2\theta_{max}$ = 62.62°, μ = 0.667 mm^{-1}, 18297 reflections collected within $-15 \le h \le 14$, $-17 \le k \le 16$, $-16 \le l \le 16$, 8507 unique (R_{int} = 0.0497), 5823 $F_o \ge 4\sigma(F)$, 447 parameters, 3 restraints, R_1 = 0.0658, wR_2 = 0.1764, GooF = 1.030, residual electron density peaks of 2.141and –1.112 e Å^{-3}. Macrocycle molecules are disordered over two close positions with ratios 0.8/0.2 and 0.7/0.3 for two crystallographically independent molecules, respectively. They were refined and then fixed in the resulting values. A number of restraints were used during the refinement to fix C–C and O–C distances of the minor part of the 18-crown-6 molecule.

CCDC-789363 ([K@18-crown-6]$_3$[Os(CN)$_6$](*i*PrOH)$_{2.3}$(H$_2$O)$_{2.85}$) and CCDC-789362 ([K@18-crown-6]-$_3$[Ru(CN)$_6$](H$_2$O)$_2$(CH$_2$Cl$_2$)$_2$) 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 footnote on the first page of this article): The IR spectra of final products and starting materials, EPR spectra for (K@18-crown-6)$_3$[Os(CN)$_6$] and (K@18-crown-6)$_3$-[Ru(CN)$_6$], atom numbering and selected geometric parameters for [K@18-crown-6]$_3$[Os(CN)$_6$](*i*PrOH)$_{2.3}$(H$_2$O)$_{2.85}$, atom numbering and selected geometric parameters for [K@18-crown-6]$_3$[Ru(CN)$_6$](H$_2$O)$_2$(CH$_2$Cl$_2$)$_2$.

Acknowledgments

We gratefully acknowledge the support of the Russian Foundation for Basic Research (grant 08-03-00459-a) for this work.

---

[1] a) S. Ferlay, T. Mallah, R. Ouahès, P. Veillet, M. Verdaguer, *Nature* **1995**, *378*, 701–703; b) K. R. Dunbar, R. A. Heintz, *Prog. Inorg. Chem.* **1997**, *45*, 283–391 and references therein; c) K. E. Funck, M. G. Hilfiger, C. P. Berlinguette, M. Shatruk, W. Wernsdorfer, K. R. Dunbar, *Inorg. Chem.* **2009**, *48*, 3438–3452.

[2] a) M. Verdaguer, G. S. Girolami in *Magnetism: Molecules to Materials V* (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2005**, pp. 283–346; b) M. Shatruk, C. Avendano, K. R. Dunbar, *Prog. Inorg. Chem.* **2009**, *56*, 155–334 and references theirein.

[3] a) V. S. Mironov, *Dokl. Akad. Nauk* **2006**, *408*, 130–136; b) V. S. Mironov, L. F. Chibotaru, A. Ceulemans, *J. Am. Chem. Soc.* **2003**, *125*, 9750–9760.

[4] a) A. V. Palii, O. S. Reu, S. M. Ostrovsky, S. I. Klokishner, B. S. Tsukerblat, M. Hilfiger, M. Shatruk, A. Prosvirin, K. R. Dunbar, *J. Phys. Chem. A* **2009**, *113*, 6886–6889; b) D. E. Freedman, D. M. Jenkins, J. R. Long, *Chem. Commun.* **2009**, 4829–4831; c) D. E. Freedman, D. M. Jenkins, A. T. Iavarone, J. R. Long, *J. Am. Chem. Soc.* **2008**, *130*, 2884–2885.

[5] M. V. Bennett, J. R. Long, *J. Am. Chem. Soc.* **2003**, *125*, 2394–2395.

[6] a) J. Bendix, P. Steenberg, I. Søtofte, *Inorg. Chem.* **2003**, *42*, 4510–4512; b) P. Albores, L. D. Slep, L. M. Baraldo, R. Baggio, M. T. Garland, E. Rentschler, *Inorg. Chem.* **2006**, *45*, 2361–2363; c) F. M. Crean, K. Schug, *Inorg. Chem.* **1984**, *23*, 853–857.

[7] M. Hilfiger, M. Shatruk, A. Prosvirin, K. R. Dunbar, *Chem. Commun.* **2008**, 5752–5754.

[8] a) J. J. Alexander, H. B. Gray, *J. Am. Chem. Soc.* **1968**, *90*, 4260–4271; b) S. Eller, R. D. Fischer, *Inorg. Chem.* **1990**, *29*, 1289–1290.

[9] H. W. Kang, G. Moran, E. Krausz, *Inorg. Chim. Acta* **1996**, *249*, 231–235.

[10] a) J. A. Schlueter, U. Geiser, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2003**, *59*, m325; b) C. M. Whaley, T. B. Rauchfuss, S. R. Wilson, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2005**, *61*, m1918; c) M. Hoshino, H. Sonoki, Y. Miyazaki, Y. Iimura, K. Yamamoto, *Inorg. Chem.* **2000**, *39*, 4850.

[11] X.-Y. Wang, M. G. Hilfiger, A. Prosvirin, K. R. Dunbar, *Chem. Commun.* **2010**, *46*, 4484–4486.

[12] H. Miyasaka, H. Okawa, A. Miyazaki, T. Enoki, *Inorg. Chem.* **1998**, *37*, 4878–4883.

[13] M. Wanner, T. Scheiring, W. Kaim, L. D. Slep, L. M. Baraldo, J. A. Olabe, S. Záliš, E. J. Baerends, *Inorg. Chem.* **2001**, *40*, 5704–5707.

[14] L. M. Baraldo, M. S. Bessega, G. E. Rigotti, J. A. Olabe, *Inorg. Chem.* **1994**, *33*, 5890.

[15] a) *SHELXTL*, version 6.22, Bruker AXS Inc., Madison, WI, USA, **2003**; b) G. M. Sheldrick, *SADABS. Program for Absorption Correction with the SMART System.* University of Göttingen, Germany, **1996**.

Received: September 30, 2010
Published Online: January 11, 2011