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$[Tc^{I}(CN)_3(CO)_3]^{2-}$ and $[Re^{I}(CN)_3(CO)_3]^{2-}$: Case Studies for the Binding Properties of CN^{-} and CO

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The cyano carbonyl complexes $[^{99}Tc(CN)_3(CO)_3]^{2-}$ and $[Re(CN)_3(CO)_3]^{2-}$ were synthesized and fully characterized. These complexes are additional members of the well-known d^6 transition metal complex series $[M(CN)_3(CO)_3]^{n-}$. The analytical data obtained in this study thus offer a unique opportunity to study similarities and differences of cyanide and carbonyl binding in transition metal complexes.

Metal complexes containing the two isoelectronic ligands cyanide and carbon monoxide belong to the most fundamental compounds of inorganic chemistry. The first complex containing a combination of both ligands, $[Fe^{II}(CN)_5(CO)]^{3-}$, was reported more than 100 years ago.[1] The recent discovery of $[Fe(CN)_x(CO)_y]$ units as catalytic centers of NiFe and Fe-only hydrogenases[2−6] has sparked a revival in studies of metal cyano carbonyl compounds extending also to complexes of metals other than iron.[7−11] The synthesis and characterization of these compounds has provided fundamental knowledge about complexes of the type $[M(CO)_x(CN)_y]$, necessary for a deeper understanding of the hydrogenase enzymes in particular as well as cyano and carbonyl complexes in general.[12]

Prominent among cyano carbonyl complexes is the $[M(CN)_3(CO)_3]^{n-}$ series, where complexes with M = Mo,[13] Mn,[9] Fe,[10] and Ru[9] (all in their d^6 electronic configuration) have been synthesized and structurally characterized. The corresponding rhenium species has been reported, but only very limited analytical data is available.[14] Here we report synthesis, structures, and properties of the Tc^{I} complex of this series together with a more detailed study of the Re^{I} compound. The data obtained in this investigation allows fundamental comparisons between the binding properties of the two isoelectronic ligands CO and CN^{-} as well as the properties of the different d^6 metal centers within this series.

As the short-lived complexes *fac*-$[M(H_2O)_3(CO)_3]^{+}$ (M = ^{99m}Tc, ^{188}Re) have been proved to be powerful radiopharmaceutical precursors for the labeling of biomolecules,[15] properties and substitution behavior of their long-lived counterparts **1a** (M = ^{99}Tc) and **1b** (M = Re) in aqueous solution have been extensively studied.[16−18]

Treatment of **1a** or **1b** with the strongly π-accepting ligand NO^{+} (isoelectronic with CO) is known to result in the substitution of one CO ligand and the formation of *fac*-$[M(H_2O)_3(NO)(CO)_2]^{2+}$ (M = ^{99}Tc, Re).[19] Under high pressure of ^{13}CO, the exchange of ^{12}CO for ^{13}CO was detected by NMR for **1a** in water within days.[17] In this experiment, a fraction of the molecules even undergo complete carbonylation resulting in the formation of $[^{99}Tc(CO)_6]^{+}$. On the other hand, no more than two CO ligands are substituted when $[Re(CO)_5Cl]$ is reacted with CN^{-} under harsh conditions[14] thus leaving the “*fac*-

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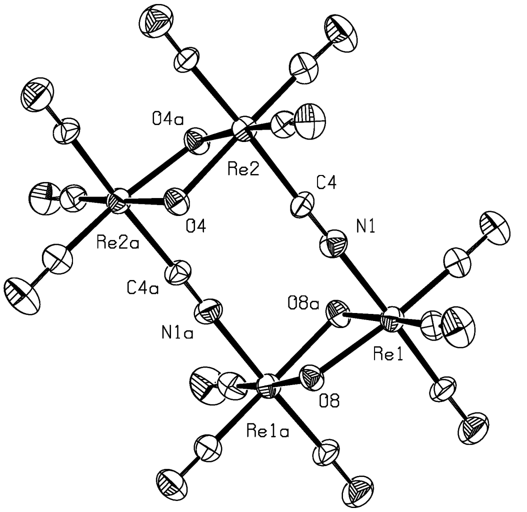

Figure 1. ORTEP drawing of the anion $[(CO)_3(\mu\text{-}OH)Re(\mu\text{-}CN)Re(\mu\text{-}OH)(CO)_3]_2{}^{2-}$ (**2b**) showing thermal ellipsoids at 50% probability.

$[Re(CO)_3]^{+}$" core intact. A similar result in the reaction of **1a** or **1b** with CN^- would demonstrate once again the different reactivity of the ligand CN^- when compared to its isoelectronic counterparts NO^+ and CO.[20]

Treatment of **1b** with 10 equiv of KCN in water at pH $\approx$ 10 resulted in the formation a white precipitate. A single crystal analysis revealed the product to be the tetranuclear cluster $[(CO)_3(\mu\text{-}OH)Re(\mu\text{-}CN)Re(\mu\text{-}OH)(CO)_3]_2{}^{2-}$, **2b** (Figure 1). Complex **2b** is exceptionally stable: attempts to cleave **2b** with CN^- or strong chelates such as 2,2′-bipyridine were not successful. Treatment with acid resulted in the decomposition of the tetramer to regain complex **1b.**

To avoid the formation of the unreactive product **2b**, the same reaction was carried out in methanol. After 2 h at room temperature, **1b** was quantitatively converted to one single new species as detected by HPLC. No further change was observed after heating the reaction mixture for another 48 h. Addition of Ph_4AsCl to an aqueous solution of the reaction product precipitated the $AsPh_4{}^+$ salt of $[Re(CN)_3(CO)_3]^{2-}$ (**3b**). The technetium complex $[^{99}Tc(CN)_3(CO)_3]^{2-}$ (**3a**) was synthesized and isolated correspondingly.

Evidence for the facial coordination of three carbonyl and three cyanide ligands in **3a** and **3b** was provided by IR spectroscopy. Two strong CO and two weak CN^- bands could be observed, characteristic for C_{3v} symmetry. For products obtained from reactions with isotope enriched $K^{13}CN$ (90% ^{13}C), only the set of bands at higher wavenumbers shifted significantly. Thus, they belong unambiguously to the coordinated CN^- ligands (Figure 2). Since this observation indicates decoupling of CN^- and CO vibrations to a great extent, it seemed justified to perform a Cotton–Kraihanzel force field analysis[21] for each set of ligands separately. The calculated vibrational force constants indicate a much stronger bond within the CN^- ligand (17.5 and 17.2 mdyn/Å for **3a** and **3b**, respectively) compared to the values for the coordinated CO (16.2 mdyn/Å for both **3a** and **3b**).

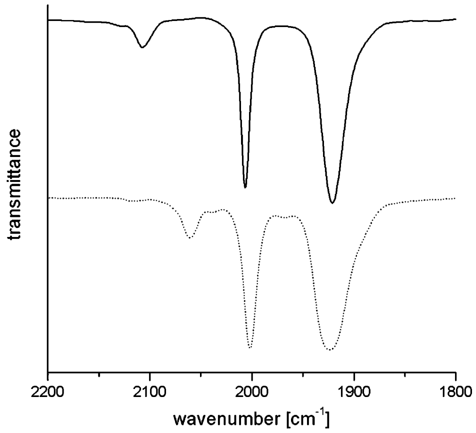

Figure 2. IR spectra of **3b** (—) and the 70% cyanide ^{13}C enriched species $[Re(^{13}CN)_3(CO)_3]^{2-}$ (···).

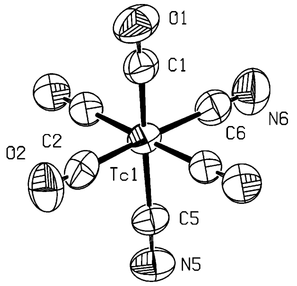

Figure 3. Molecular structure of the anion $[^{99}Tc(CN)_3(CO)_3]^{2-}$ (**3a**) with 50% probability shown.

Table 1. Selected Structural Data and Force Constants for Complexes $[M(CN)_3(CO)_3]^{n-}$

	VIa		VIIa		VIIIa
	Mo[a]	Mn[b]	Tc	Re	Ru[b]
$d_{av}(M-CO)$ [Å]	*c*	1.79	1.93	1.93	1.96
$d_{av}(M-CN)$ [Å]	*c*	2.01	2.14	2.14	2.07
$\angle_{av}(OC-M-CO)$ [deg]	*c*	92.7	91.1	91.6	93.7
$\angle_{av}(NC-M-CN)$ [deg]	*c*	87.7	88.5	87.5	87.8
$f_{CO}{}^{d}$ [mdyn/Å]	14.1	16.0	16.2	16.2	17.8
$f_{CN}{}^{d}$ [mdyn/Å]	16.4	17.0	17.5	17.2	18.1

[a] Data calculated from ref 13. [b] Data from ref 9. [c] No data shown as CN^- and CO were found to be completely disordered in the crystal. [d] Calculated from the IR stretching modes according to ref 21.

A crystallographic analysis of **3a** and **3b** confirmed the facial coordination of three cyanide and three carbonyl ligands around the metal center in a nearly perfect octahedron (Figure 3). For **3a**, one *trans* pair of CO and CN^- ligands was disordered. For the other ligand pairs, CO and CN^- ligands can be crystallographically distinguished. The average metal–carbon bond distance $M-C(O)_{av}$ is 1.93(1) Å for both **3a** and **3b** which is much shorter than the 2.14(1) Å found for $M-C(N)_{av}$. No significant difference was found for the bond length within the ligands, whereas both complexes show smaller bond angles for NC–M–CN compared to OC–M–CO (Table 1).

As expected for a complex with C_{3v} symmetry, the ^{99}Tc NMR spectrum of **3a** consists of a sharp singlet signal at -2198 ppm ($\Delta_{1/2} = 6.3$ Hz), shifted more than 1000 ppm upfield compared to **1a**[17] and therefore indicating a more electron-rich Tc^{I} complex.[22] Due to the coupling of three equivalent cyanide ligands to ^{99}Tc ($I = {}^{9}/_{2}$), the ^{99}Tc NMR spectrum of **2b** prepared with ^{13}C enriched $K^{13}CN$ showed

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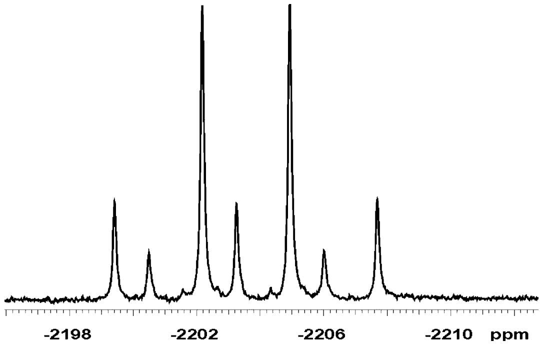

Figure 4. ^{99}Tc NMR spectrum of ca. 70% cyanide ^{13}C enriched **3a**.

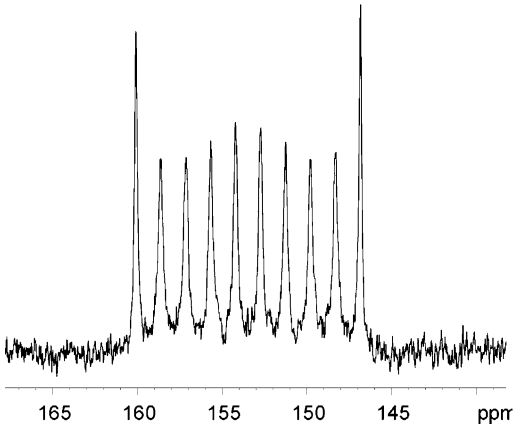

Figure 5. ^{13}C NMR spectrum of ca. 70% cyanide ^{13}C enriched **3a**.

a strong quadruplet as well as a weaker triplet and a very weak doublet for the doubly and singly ^{13}C labeled complexes (Figure 4). In the ^{13}C NMR spectrum, a decet was observed (Figure 5). Due to different relaxation times for the various spin states of ^{99}Tc, the outer lines of the ^{13}C spectrum are sharper than the inner. The $^{1}J_{^{99}\mathrm{Tc},^{13}\mathrm{C}}$ coupling constant is 186 Hz, much smaller than the only other $^{1}J_{^{99}\mathrm{Tc},^{13}\mathrm{C}}$ coupling constant known to date with 354 Hz for **1a**.[17] The main reason for the smaller coupling constant of **2b** might be the longer Tc−C distances for CN$^-$ when compared to CO bound to Tc. Addition of 10 equiv of NaCN to the sample at room temperature did not result in any exchange of ^{13}CN$^-$ for ^{12}CN$^-$ as evident from the unchanged coupling pattern of the ^{99}Tc NMR spectrum even after several days.

The analytical data of **3a** and **3b** allow comparisons with the data obtained for other compounds in the series $[M(CN)_3(CO)_3]^{n-}$. The direct neighbors of Tc in the periodic table are of course of special interest. Important data are given in Table 1. Clear trends in the bonding properties are obvious when comparing the two ligands and the various metals: (i) due to stronger π-back-bonding in the case of CO, metal−carbonyl bonds are significantly shorter than metal−cyanide bonds; (ii) stronger repulsions between the more tightly bound carbonyl ligands result in larger cone-angles for the tricarbonyl moieties when compared to the tricyano parts; (iii) comparing metal−ligand distances, the first-row transition metal Mn is significantly smaller than second-row Tc, Ru, and the lanthanide-contracted Re (the latter three having very similar sizes); (iv) as the negative charge of the complexes decreases from group VIa to VIIIa, π-back-bonding gets weaker, thereby increasing the ligand stretching force constants and decreasing the differences between f_{CN} and f_{CO}.

In conclusion, reactions of **1a** or **1b** with cyanide resulted in the formation of the complexes $[M(CN)_3(CO)_3]^{2-}$ (M = ^{99}Tc, Re). No substitution of CO ligands by CN$^-$ was observed, unlike in the cases of the isoelectronic but stronger π-accepting ligands NO$^+$ and CO for which substitution or at least self-exchange of coordinated carbonyls occurred. Instead, the findings of (i) large force constants for the stretching mode of coordinated CN$^-$, (ii) a rather electron-rich Tc^{I} metal center as indicated by ^{99}Tc NMR, and (iii) the very stable trans arrangement of CN$^-$ to the π-accepting CO all demonstrate that π-back-bonding plays only a minor role in the metal−cyanide bond. Instead, σ-donation strongly dominates cyanide binding.

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Supporting Information Available: X-ray crystallographic files (CIF), crystallographic tables, and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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