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# Isolation and Structural Characterization of Eightfold Protonated Octacyanometalates $[M(CNH)_8]^{4+}$ ( $M = Mo^{IV}, W^{IV}$ ) from Superacids

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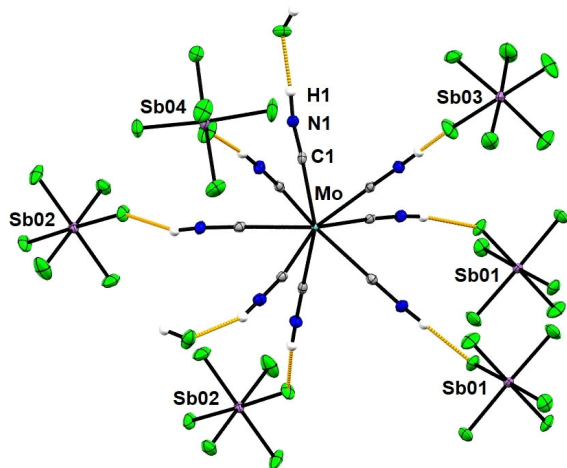
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positions of all hydrogen atoms could be located via difference electron density map.

The M–C–N–H bonds are close to linear (varying from 172–179°; Figure 1), while all terminal hydrogen atoms of the hydrogen isocyanide ligands form strong hydrogen bonds to the fluorine atoms of the  $\text{SbF}_6^-$  ions and cocrystallized HF molecules. In the molybdenum compound the  $\text{MCNH}\cdots\text{F}$  distances are in the range of 1.718(3)–1.994(4) Å. Thus, the  $\text{N}(\text{H})\cdots\text{F}$  distances are relatively short (2.584(2)–2.709(2) Å) and in a similar range to those in protonated nitriles with hexafluorometalate counteranions (2.5–2.8 Å).<sup>[11–13]</sup>



**Figure 1.** Selected short H...F contacts < 2 Å (in orange) in the crystal structure of  $[\text{Mo}(\text{CNH})_8]^{4+} [\text{SbF}_6]_4^- \cdot 2\text{HF}$ . Ellipsoids shown at 50% probability; C gray, N blue, H white, Mo turquoise, F green, Sb lavender.

The Mo–C bond lengths in  $[\text{Mo}(\text{CNH})_8]^{4+} [\text{SbF}_6]_4^- \cdot 2\text{HF}$  (2.140(2)–2.168(2) Å) are very similar to the Mo–C bond lengths in  $\text{K}_4[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$  (Mo–C 2.163(5) Å).<sup>[33]</sup> However, changes in C–N bond lengths are more significant. In the fully protonated species, the C–N bond lengths are in the range of 1.128(3)–1.136(3) Å and therefore shorter than in the potassium salt (1.152(6) Å). While the former value resembles more the C–N bond length in protonated nitriles,<sup>[11]</sup> the latter is more similar to free HCN (1.157(1) Å).<sup>[34]</sup> Bond lengths in  $[\text{W}(\text{CNH})_8]^{4+} [\text{SbF}_6]_4^- \cdot 2\text{HF}$  are very similar to the analogous Mo compound (see Table 1). This finding is also supported by DFT calculations (M06L/Def2TZVP) on both  $[\text{M}(\text{CNH})_8]^{4+}$  and  $[\text{M}(\text{CNH})_8]^{4+} \cdot 8\text{HF}$  (M = Mo, W). The latter was chosen as a model to simulate the influence of hydrogen bonding in the crystal. Interestingly, the comparison

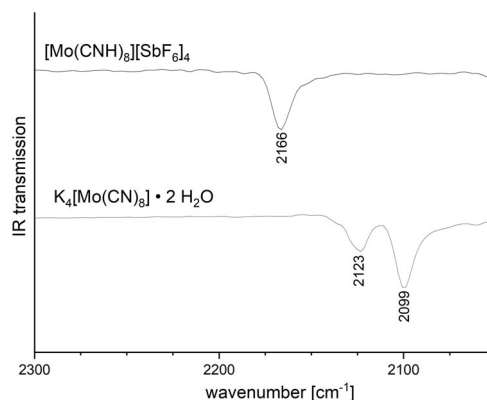
**Table 1:** Experimental and calculated bond lengths in Å.

Compound	M–C (expt.)	C–N (expt.)	M–C (calc.)	C–N (calc.)
$[\text{Mo}(\text{CNH})_8]^{4+}$	2.140(2)– 2.168(2)	1.128(3)– 1.136(3)	2.203	1.146
$[\text{W}(\text{CNH})_8]^{4+}$	2.142(2)– 2.169(2)	1.127(3)– 1.137(3)	2.211	1.147

revealed that C–N bond lengths were totally unaffected, while M–C bond lengths decreased slightly in the calculated HF solvates. However, it has to be stated that the calculated M–C bond lengths were significantly longer than the experimentally found values.

Additionally, frequency calculations turned out to be even more problematic. The comparison between the calculations for  $[\text{M}(\text{CNH})_8]^{4+}$ ,  $[\text{M}(\text{NCH})_8]^{4+}$ ,  $[\text{M}(\text{CNH})_8]^{4+} \cdot 8\text{HF}$ , and  $[\text{M}(\text{NCH})_8]^{4+} \cdot 8\text{HF}$  (M = Mo, W) with the reaction products was inconclusive. Probably this is caused by the high ionic charges and strong hydrogen bonding which are insufficiently modeled in the calculations.

The IR spectra of  $[\text{M}(\text{CNH})_8]^{4+} [\text{SbF}_6]_4^- \cdot 2\text{HF}$  (M = Mo, W; Figure 2) both display a very broad band above 3000  $\text{cm}^{-1}$  which can be attributed to N–H stretching. Additionally, a weak band at 1615  $\text{cm}^{-1}$  can be assigned to N–H bending,



**Figure 2.** IR spectra showing the shifted CN stretching frequency upon protonation.

since both bands were shifted during deuteration experiments with  $\text{DF/SbF}_5$ . While an isotopic ratio of 1.37 is observed for the  $\delta(\text{NH})/\delta(\text{ND})$  deformation vibrations (close to the theoretical value of 1.41) the corresponding value for the  $\nu(\text{NH})/\nu(\text{ND})$  stretching vibrations is only  $\approx 1.2$  (Table 2). Similar effects have been observed before<sup>[35]</sup> and are caused by strong hydrogen bonding, which has a greater influence on stretching vibrations than on deformation vibrations.

IR and Raman spectra of  $[\text{M}(\text{CNH})_8]^{4+} [\text{SbF}_6]_4^- \cdot 2\text{HF}$  (M = Mo, W) both display an increase of the CN stretching vibration by about 50  $\text{cm}^{-1}$  compared to  $\text{K}_4[\text{M}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ . A similar blueshift has already been observed in IR spectra of neutral polycyanometalate acids.<sup>[36–40]</sup> This bond-strengthening effect upon protonation is caused by the increased polarization of the carbon–nitrogen bond. This observation

**Table 2:** Experimental IR data in  $\text{cm}^{-1}$ .

	$[\text{Mo}(\text{CNH})_8]^{4+}$	$[\text{Mo}(\text{CND})_8]^{4+}$	$[\text{W}(\text{CNH})_8]^{4+}$	$[\text{W}(\text{CND})_8]^{4+}$
$\nu(\text{NH})/\nu(\text{ND})$	3082 (b)	2529 (b)	3030 (b)	2525 (b)
$\nu(\text{CN})$	2166 (m)	1960 (b)	2145 (m)	1970 (b)
$\delta(\text{NH})/\delta(\text{ND})$	1615 (m)	1182 (m)	1620 (m)	1180 (m)

is in line with the shortening of the carbon–nitrogen distance in the solid state structure.

Despite the relatively low solubility of  $[M(CNH)_8]^{4+}$   $[SbF_6]^-_4$  ( $M = Mo, W$ ) in pure anhydrous HF even at room temperature, it was possible to record NMR spectra of the products by using a solvent mixture of HF and  $SO_2$  at  $-40^\circ C$  (Table 3). The  $^{14}N$  NMR spectrum of a solution of  $[Mo(CNH)_8]^{4+} [SbF_6]^-_4$  shows a broad, unresolved peak at ( $\delta = -182$  ppm) which is significantly shifted compared to  $K_4Mo(CN)_8$  in water ( $\delta = -95$  ppm). A similar shift was observed for the protonation of acetonitrile ( $\delta(CH_3CN) = -134$  ppm;  $\delta(CH_3CNH^+) = -241$  ppm).<sup>[11]</sup> Only one signal at  $\delta = 121$  ppm is displayed in the  $^{13}C$  NMR spectrum, which indicates an upfield shift upon protonation compared to aqueous  $K_4(Mo(CN)_8)$  ( $\delta = 149$  ppm).

**Table 3:** NMR data, recorded in a mixture of HF and  $SO_2$  at  $-40^\circ C$ ; chemical shifts  $\delta$  in ppm.

	$^{13}C$	$^{14}N$
$K_4Mo(CN)_8$ in $D_2O$	+149	-95
$K_4W(CN)_8$ in $D_2O$	+143	-98
$[Mo(CNH)_8]^{4+} [SbF_6]^-_4$ in HF	+121	-182
$[W(CNH)_8]^{4+} [SbF_6]^-_4$ in HF	+115	-179

It was not possible to detect a peak for the CNH ligand in the  $^1H$  NMR spectrum, since rapid exchange between the CNH group and the highly acidic solvent mixture is expected. A similar problem was reported for the protonation of  $H_4Fe(CN)_6$  by HF/ $BF_3$ , where it was not possible to freeze-out proton exchange even at the melting point of the solvent ( $-84^\circ C$ ).<sup>[41]</sup> Although the product  $[Fe(CNH)_6][BF_4]_2$  was reported to be stable for months in anhydrous HF, it decomposed in vacuum by losing HF and  $BF_3$  to give  $H_4Fe(CN)_6$ . However, it has to be stated that under much more basic conditions, namely in presence of ethanol, a so-called supramolecular complex with the formula  $[Fe\{CNH-O(H)Et\}_6]Cl_2$  was crystallographically characterized.<sup>[42]</sup>

In summary, we report the first successful isolation of homoleptic metal complexes with eight hydrogen isocyanide ligands by exhaustive protonation of  $K_4M(CN)_8$  by the superacid HF/ $SbF_5$ . Since isocyanides CNR are good  $\sigma$ -donor but weak  $\pi$ -acceptor ligands,<sup>[43]</sup> they provide an effective stabilization of the  $Mo^{4+}$  and  $W^{4+}$  ions. The resulting square-antiprismatic complexes  $[M(CNH)_8]^{4+}$  ( $M = Mo^{IV}, W^{IV}$ ) are diamagnetic and fulfill the 18-electron rule. While M–C bond lengths remain almost unchanged, protonation slightly shortens the C≡N bond, which is supported by an increase of  $\nu(CN)$  by  $50\text{ cm}^{-1}$ . Additionally, the crystal structures display networks of strong  $H\cdots F$  hydrogen bonds. These results suggest that polycyanometalates are much more stable against protolysis than generally thought (at least in the absence of potent nucleophiles) which opens up new pathways to hydrogen-bonded networks for various applications.<sup>[44]</sup>

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** cyanides · hydrogen bonds · isocyanide ligands · protonation · superacidic systems

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- [45] CCDC 1983867 and 1983868 ( $[\text{C}_8\text{H}_{10}\text{F}_{26}\text{MoN}_8\text{Sb}_4]$  and  $[\text{C}_8\text{H}_{10}\text{F}_{26}\text{N}_8\text{Sb}_4\text{W}]$ ) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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## Communications

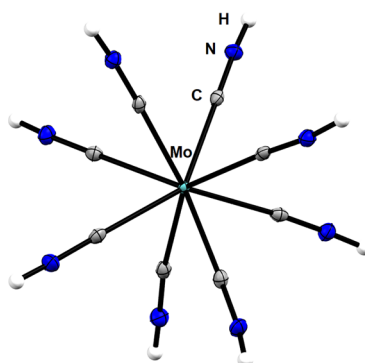


## Cyanometalates

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Isolation and Structural Characterization of Eightfold Protonated Octacyanometalates  $[M(\text{CNH})_8]^{4+}$  ( $M = \text{Mo}^{\text{IV}}, \text{W}^{\text{IV}}$ ) from Superacids



**Give me eight!** All eight cyano groups in the octacyanometalates  $\text{Mo}(\text{CN})_8^{4-}$  and  $\text{W}(\text{CN})_8^{4-}$  are protonated under superacidic conditions without formation of HCN. Instead homoleptic complexes of  $\text{Mo}^{4+}$  and  $\text{W}^{4+}$  with eight hydrogen isocyanide ligands are formed and could be fully characterized.