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Isolation and structural characterization of eight-fold protonated octacyanometallates [M(CNH)₈]⁴⁺ (M=Mo^{IV},W^{IV}) from Superacids

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Dedicated to the 75th anniversary of Professor Konrad Seppelt

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Abstract: Octacyanometallates K₄[Mo(CN)₈] and K₄[W(CN)₈] are completely protonated in superacidic mixtures of anhydrous hydrogen fluoride and antimony pentafluoride. The resulting hydrogen isocyanide complexes [Mo(CNH)₈]⁴⁺ [SbF₈]⁻₄ and [W(CNH)₈]⁴⁺ [SbF₈]⁻₄ are the first examples of eight-coordinate homoleptic metal complexes containing hydrogen isocyanide (CNH) ligands. The complexes were crystallographically characterized, revealing hydrogen-bonded networks with short N⁻⁻H⁻⁻F contacts. Low-temperature NMR measurements in HF confirmed rapid proton exchange even at -40 °C. Upon protonation, \tilde{v} (C=N) increases of about 50 cm⁻¹ which is in agreement with DFT-calculations.

The lability of metal cyanides towards acids is well-known and often a subject of safety warnings since highly toxic hydrogen cyanide might be released. In general, protonation of metal bound cyano ligands $(M-C\equiv N)$ at the terminal nitrogen atom leads to the corresponding metal complex with hydrogen isocyanide as a ligand $(M-C\equiv N-H)^{+,[1-2]}$ In contrast, only a small number of metal complexes with hydrogen cyanide as a ligand are known $(M-N\equiv C-H)^{.[3-9]}$ Although hydrogen isocyanide CNH is a good ligand for transition metals, it can be substituted by donor solvents (e.g. water) or nucleophilic counteranions.^[10] Subsequently the liberated hydrogen isocyanide CNH can isomerize to its thermodynamically more stable tautomer hydrogen cyanide HCN.

The superacidic mixtures HF/AsF₅ or HF/SbF₅ have recently been used for the protonation of organic nitriles^[11-12] and even HCN^[13] as well as for the preparation of highly electrophilic organic cations.^[14-15] Even though one could expect that the use of superacids should immediately lead to the destruction of polycyanometallates, these systems have the advantage that even the formed AsF₆⁻ or SbF₆⁻ anions are very weak nucleophiles and therefore much weaker ligands than the CNH ligands which are formed upon protonation.

Although the first reports on octacyanometallates $[M(CN)_8]^4$ - $(M=Mo^{IV},W^{IV})$ date to the beginning of the 20th century,^[16-19] they got a lot of attention from coordination and magnetochemists in the past decades. Since the early 2000s, a plethora of octacyanometallate-based supramolecular coordination

networks as well as polynuclear complexes and cluster compounds $^{[20\mathcal{2}0\mathcal{2}24]}$ have been reported. The ease of oxidation of $[M(CN)_8]^4$ (M=Mo,W) to $[M(CN)_8]^3$ and the accessibility of an excited triplet state for $[M(CN)_8]^4$ (M=Mo,W) by light irradiation make octacyanometallates suitable building blocks for photomagnetic materials, $^{[25\mathcal{2}2\mathcal{2}2\mathcal{2}3\mathcal{2}}$ while paramagnetic $[M(CN)_8]^3$ (M=Mo,W) are promising building blocks for single-molecule magnets. $^{[29]}$

While treatment of octacyanometallates with hydrogen chloride gives adducts of the neutral acids $H_4[M(CN)_8] \cdot 6 H_2O$ (M=Mo,W),^[30] $H_4[W(CN)_8] \cdot 4 HCl \cdot 12 H_2O^{[31]}$ and $H_4[Mo(CN)_8] \cdot 2 O(C_2H_5)_2 \cdot CH_3OH \cdot 2 H_2O$,^[32] complete (octa-) protonation is achieved by reacting $K_4[M(CN)_8] \cdot 2H_2O$ (M=Mo,W) with anhydrous hydrogen fluoride and a large excess of antimony pentafluoride SbF₅. Although the fully protonated species $[M(CNH)_8]$ [SbF₆]₄ (M=Mo,W) are only slightly soluble in anhydrous hydrogen fluoride at room temperature, their solubility can be slightly increased by adding small amounts of sulfur dioxide SO₂ as co-solvent. Highly-moisture sensitive yellow crystals form upon slow cooling to -75°C besides colourless crystals of KSbF₆.

K₄M(CN)₀	HF/SbF ₅	[M(CNH) ₀] [SbF ₆] ₄	
M=Mo.W	- KSbF ₆	M=Mo.W	

Scheme 1. Preparation of $[M(CNH)_8]^{4+}$ $[SbF_6]^{-4}$ (M=Mo,W)

 $[Mo(CNH)_8]^{4+} [SbF_6]_4 \bullet 2HF and [W(CNH)_8]^{4+} [SbF_6]_4 \bullet 2HF both crystallize in the monoclinic space group P2_1/n and are isomorphous. The central metal is coordinated by 8 (crystallographically different) protonated cyanide / hydrogen isocyanide ligands (M-CNH), resulting in a slightly distorted square-antiprismatic coordinated to the metal via carbon (M-C=NH) or nitrogen (M-N=CH) could be clearly answered by comparing the R factors and atomic displacement parameters of both structure solutions (see supporting information). Due to the high overall data quality the positions of all hydrogen atoms could be located via difference-electron-density map.$

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The M-C-N-H bonds are close to linear (varying from 172-179°), while all terminal hydrogen atoms of the hydrogen isocyanide ligands form strong hydrogen bonds to the fluorine atoms of the SbF₆⁻ ions and co-crystallized HF molecules. In the molybdenum compound the MCNH^{...}**F** distances are in the range of 1.718(3)-1.994(4) Å. Thus, the **N**-(H)-**F** distances are relatively short (2.584(2)-2.709(2) Å) and in a similar range as in protonated nitriles with hexafluorometallate counteranions (2.5-2.8 Å).^[11-13]



Figure 1. Selected short $H \oplus F$ contacts < 2 Å (in orange) in the crystal structure of $[Mo(CNH)_8]^{4+}$ $[SbF_6]^{-4}$ • 2HF. Ellipsoids shown at 50% probability; C grey, N blue, H white, Mo turquoise, F green, Sb lavender

The Mo-C bond lengths in [Mo(CNH)₈]⁴⁺ [SbF₆]⁻₄ • 2HF (2.140(2)-2.168(2) Å) are very similar to the Mo-C bond lengths in K₄[Mo(CN)₈] • 2H₂O (Mo-C 2.163(5) Å).^[33] 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,^[11] the latter is more similar to free HCN (1.157(1) Å).^[34] Bond lengths in $[W(CNH)_8]^{4+}$ $[SbF_6]^{-4}_{-4}$ • 2HF are very similar to the analogous Mo compound (see Table 1). This finding is also supported by DFT calculations (M06L/Def2TZVP) on both [M(CNH)8]4+ and [M(CNH)8]4+ 8 HF (M=Mo,W). The latter was chosen as a model to simulate the influence of hydrogen bonding in the crystal. Interestingly, the comparison 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 $[M(CNH)_8]^{4+}$, $[M(NCH)_8]^{4+}$, $[M(CNH)_8]^{4+} \cdot 8$ HF and $[M(NCH)_8]^{4+} \cdot 8$ 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 modelled in the calculations.

The IR spectra of $[M(CNH)_8]^{4+}$ $[SbF_6]_4^{-} \cdot 2HF$ (M=Mo,W) both display a very broad band above 3000 cm⁻¹ which can be attributed to N-H stretching. Additionally, a weak band at 1615 cm⁻¹ can be assigned to N-H bending, since both bands were shifted during deuteration experiments with DF/SbF₅. While an isotopic ratio of 1.37 is observed for the δ (NH)/ δ (ND) deformation vibrations (close to the theoretical value of 1.41) the corresponding value for the v(NH)/v(ND) stretching vibrations is only ≈1.2. Similar effects have been observed before^[35] and are caused by strong hydrogen-bonding which has a larger influence on stretching vibrations than on deformation vibrations.



Figure 2. IR-Spectra showing the shifted CN stretching frequency upon protonation

IR and Raman spectra of $[M(CNH)_8]^{4+}$ $[SbF_6]^-_4 \cdot 2HF$ (M=Mo,W) both reveal an increase of the CN stretching vibration of about 50 cm⁻¹ compared to K₄[M(CN)₈] \cdot 2H₂O. A similar blue-shift has already been observed in IR spectra of neutral polycyanometallate acids.^[36-40] This bond-strengthening effect upon protonation is caused by the increased polarisation of the carbon nitrogen bond. This observation goes in line with the shortening of the carbon-nitrogen distance in the solid state structure.

Table 2. Experimental IR data in cm⁻¹

Table 1. Experimental and calculated bond distances in Å						
Compound	M-C (exp).	C-N (exp.)	M-C (calc.)	C-N (calc.)		
[Mo(CNH)8] ⁴⁺	2.140(2)- 2.168(2)	1.128(3)- 1.136(3)	2.203	1.146		
[W(CNH)8]4+	2.142(2)- 2.169(2)	1.127(3)- 1.137(3)	2.211	1.147		

		[Mo(CNH)8] ⁴⁺	[Mo(CND)8] ⁴⁺	[W(CNH)8] ⁴⁺	[W(CND)8] ⁴⁺
	v(NH)/v(ND)	3082 (b)	2529 (b)	3030 (b)	2525 (b)
•	v(CN)	2166 (m)	1960 (b)	2145 (m)	1970 (b)
-	$\delta(NH)/\delta(ND)$	1615 (m)	1182 (m)	1620 (m)	1180 (m)

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

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solvent mixture of HF and SO2 at -40 °C. The ¹⁴N-NMR of a solution of [Mo(CNH)₈]⁴⁺ [SbF₆]⁻₄ shows a broad, unresolved peak at (δ = -182 ppm) which is significantly shifted compared to $K_4Mo(CN)_8$ in water (δ = -95 ppm). A similar shift was observed for the protonation of acetonitrile (δ (CH₃CN= -134 ppm; $\delta(CH_3CNH^+) = -241 \text{ ppm}).^{[11]}$

Only one signal at δ = 121 ppm is displayed in the ¹³C NMR spectrum which indicates high-field-shift upon protonation compared to aqueous $K_4(Mo(CN)_8 (\delta = 149 \text{ ppm}))$.

Table 3. NMR Data; chemical shift δ in ppm

	¹³ C	¹⁴ N
K4Mo(CN)8 in D2O	+149	-95
K ₄ W(CN) ₈ in D ₂ O	+143	-98
$[Mo(CNH)_8]^{4+}[SbF_6]^{-}_4\text{in}HF$	+121	-182
$[W(CNH)_8]^{4+} [SbF_6]^{-}_4 \text{ in } HF$	+115	-179

It was not possible to detect a peak for the CNH ligand in the ¹H NMR, since rapid exchange between the CNH group and the highly acidic solvent mixture is expected. A similar problem was reported for the protonation of H₄Fe(CN)₆ by HF/BF₃ where it was not possible to freeze-out proton exchange even at the melting point of the solvent (-84°C).^[41] Although the product [Fe(CNH)₆][BF₄]₂ was reported to be stable for months in anhydrous HF, it decomposed in vacuum by losing HF and BF₃ to give H₄Fe(CN)₆. However, it has to be stated that under much more basic conditions, namely in presence of ethanol, a socalled supramolecular complex with the formula [Fe{CNH-O(H)Et₆Cl₂ was crystallographically characterized. ^[42]

In summary, we report the first successful isolation of homoleptic metal complexes with eight hydrogen isocyanide ligands by exhaustive protonation of K₄M(CN)₈ by the superacid HF/SbF₅. Since isocyanides CNR are good σ -donor but weak π -acceptor ligands ^[43] they provide an effective stabilization of the Mo⁴⁺ and W⁴⁺ ions. The resulting square-antiprismatic complexes [M(CNH)8]4+ (M=Mo^{IV},W^{IV}) are diamagnetic and fulfil the 18electron-rule.

While M-C bond lengths remain almost unchanged, protonation slightly shortens the C=N bond, which is supported by an increase of v(CN) by 50 cm⁻¹. Additionally, the crystal structures display networks of strong H...F hydrogen bonds. These results suggests that polycyanometallates 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.[44]

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Keywords: cyanides • hydrogen bonds • isocyanide ligands • protonation • superacidic systems

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All eight cyano groups in octacyanometallates $Mo(CN)_8^{4-}$ and $W(CN)_8^{4-}$ are protonated under superacidic conditions without formation of HCN. Instead homoleptic complexes of Mo^{4+} and W^{4+} with eight hydrogen isocyanide ligands are formed and fully characterized.