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Malte Sellin, Valerie Marvaud, Moritz Malischewski. Isolation and Structural Characterization of Eightfold Protonated Octacyanometalates $[M(CNH)_8]^{4+}$ ($M = Mo^{IV}, W^{IV}$) from Superacids. *Angewandte Chemie International Edition*, 2020, 10.1002/anie.202002366 . hal-02565286

HAL Id: hal-02565286

<https://hal.sorbonne-universite.fr/hal-02565286v1>

Submitted on 6 May 2020

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Cyanometalates

How to cite:

International Edition: doi.org/10.1002/anie.202002366

German Edition: doi.org/10.1002/ange.202002366

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

Malte Sellin, Valérie Marvaud, and Moritz Malischewski*

Dedicated to Professor Konrad Seppelt on the occasion of his 75th birthday

Abstract: Octacyanometalates $K_4[Mo(CN)_8]$ and $K_4[W(CN)_8]$ are completely protonated in superacidic mixtures of anhydrous hydrogen fluoride and antimony pentafluoride. The resulting hydrogen isocyanide complexes $[Mo(CNH)_8]^{4+}[SbF_6]^{-4}$ and $[W(CNH)_8]^{4+}[SbF_6]^{-4}$ 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 $N\cdots H\cdots F$ contacts. Low-temperature NMR measurements in HF confirmed rapid proton exchange even at $-40^\circ C$. Upon protonation, $\nu(C\equiv N)$ increases of about 50 cm^{-1} which is in agreement with DFT calculations.

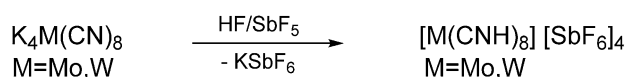
The lability of metal cyanides towards acids is well known and often a subject of safety warnings since highly toxic hydrogen cyanide might be released. In general, protonation of metal-bound cyano ligands ($M-C\equiv N$) at the terminal nitrogen atom leads to the corresponding metal complex with hydrogen 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 displaced 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 polycyanometalates, 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 that are formed upon protonation.

Although the first reports on octacyanometalates $[M(CN)_8]^{4-}$ ($M = Mo^{IV}, W^{IV}$) 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 octacyanometalate-based supramolecular coordination networks as well as polynuclear complexes and cluster compounds^[20-24] 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 octacyanometalates suitable building blocks for photomagnetic materials,^[25-28] while paramagnetic $[M(CN)_8]^{3-}$ ($M = Mo, W$) are promising building blocks for single-molecule magnets.^[29]

While treatment of octacyanometalates with hydrogen chloride gives adducts of the neutral acids $H_4[M(CN)_8]\cdot 6H_2O$ ($M = Mo, W$),^[30] $H_4[W(CN)_8]\cdot 4HCl\cdot 12H_2O$,^[31] and $H_4[Mo(CN)_8]\cdot 2O(C_2H_5)_2\cdot CH_3OH\cdot 2H_2O$,^[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 (Scheme 1). Although the fully protonated species $[M(CNH)_8][SbF_6]_4$ ($M = Mo, W$) are only



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

slightly soluble in anhydrous hydrogen fluoride at room temperature, their solubility can be slightly increased by adding small amounts of sulfur dioxide SO₂ as cosolvent. Highly moisture-sensitive yellow crystals form upon slow cooling to $-75^\circ C$ besides colorless crystals of KSBF₆.

$[Mo(CNH)_8]^{4+}[SbF_6]^{-4}\cdot 2HF$ and $[W(CNH)_8]^{4+}[SbF_6]^{-4}\cdot 2HF$ both crystallize in the monoclinic space group $P2_1/n$ and are isomorphous. The central metal is coordinated by eight (crystallographically different) protonated cyanide/hydrogen isocyanide ligands ($M-CNH$), resulting in a slightly distorted square-antiprismatic coordination geometry. The question whether the ligands are coordinated to the metal via carbon ($M-C\equiv NH$) or nitrogen ($M-N\equiv CH$) could be clearly answered by comparing the R factors and atomic displacement parameters of both structure solutions (see the Supporting Information). Due to the high overall data quality the

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<https://doi.org/10.1002/anie.202002366>.

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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 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).^[11–13]

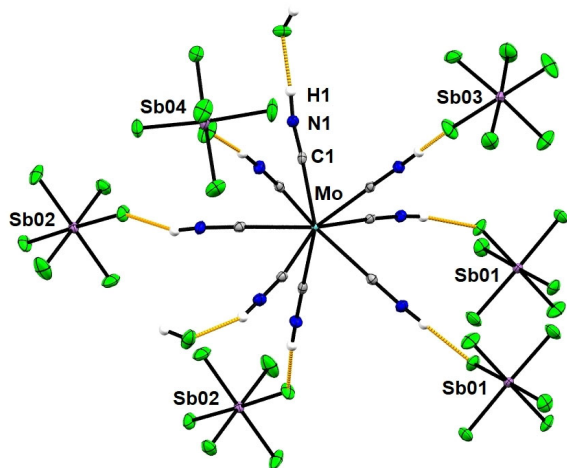


Figure 1. Selected short H...F contacts < 2 Å (in orange) in the crystal structure of $[\text{Mo}(\text{CNH})_8]^{4+} [\text{SbF}_6]_4^- \cdot 2\text{HF}$. Ellipsoids shown at 50% probability; C gray, N blue, H white, Mo turquoise, F green, Sb lavender.

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).^[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 $[\text{W}(\text{CNH})_8]^{4+} [\text{SbF}_6]_4^- \cdot 2\text{HF}$ 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 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,

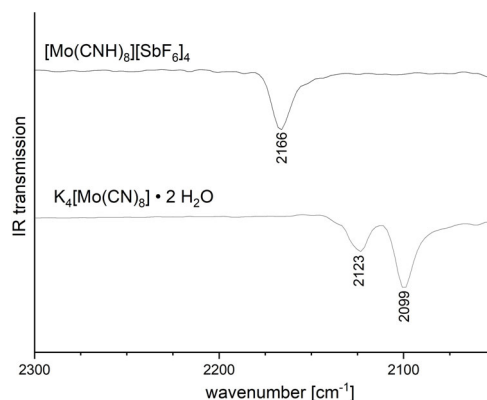


Figure 2. IR spectra showing the shifted CN stretching frequency upon protonation.

since both bands were shifted during deuteration experiments with 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 ≈ 1.2 (Table 2). Similar effects have been observed before^[35] 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 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.^[36–40] 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 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 $[M(\text{CNH})_8]^{4+}$ $[\text{SbF}_6]^-_4$ ($M = \text{Mo}, \text{W}$) 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°C (Table 3). The ^{14}N NMR spectrum of a solution of $[\text{Mo}(\text{CNH})_8]^{4+} [\text{SbF}_6]^-_4$ shows a broad, unresolved peak at ($\delta = -182$ ppm) which is significantly shifted compared to $\text{K}_4\text{Mo}(\text{CN})_8$ in water ($\delta = -95$ ppm). A similar shift was observed for the protonation of acetonitrile ($\delta(\text{CH}_3\text{CN}) = -134$ ppm; $\delta(\text{CH}_3\text{CNH}^+) = -241$ ppm).^[11] 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 $\text{K}_4(\text{Mo}(\text{CN})_8)$ ($\delta = 149$ ppm).

Table 3: NMR data, recorded in a mixture of HF and SO_2 at -40°C ; chemical shifts δ in ppm.

	^{13}C	^{14}N
$\text{K}_4\text{Mo}(\text{CN})_8$ in D_2O	+149	-95
$\text{K}_4\text{W}(\text{CN})_8$ in D_2O	+143	-98
$[\text{Mo}(\text{CNH})_8]^{4+} [\text{SbF}_6]^-_4$ in HF	+121	-182
$[\text{W}(\text{CNH})_8]^{4+} [\text{SbF}_6]^-_4$ 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 $\text{H}_4\text{Fe}(\text{CN})_6$ by HF/ BF_3 where it was not possible to freeze-out proton exchange even at the melting point of the solvent (-84°C).^[41] Although the product $[\text{Fe}(\text{CNH})_6][\text{BF}_4]_2$ was reported to be stable for months in anhydrous HF, it decomposed in vacuum by losing HF and BF_3 to give $\text{H}_4\text{Fe}(\text{CN})_6$. 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 $[\text{Fe}\{\text{CNH}-\text{O}(\text{H})\text{Et}\}_6]\text{Cl}_2$ 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 $\text{K}_4\text{M}(\text{CN})_8$ by the superacid HF/ SbF_5 . Since isocyanides CNR are good σ -donor but weak π -acceptor ligands,^[43] they provide an effective stabilization of the Mo^{4+} and W^{4+} ions. The resulting square-antiprismatic complexes $[\text{M}(\text{CNH})_8]^{4+}$ ($M = \text{Mo}^{\text{IV}}, \text{W}^{\text{IV}}$) are diamagnetic and fulfill the 18-electron rule. While M–C bond lengths remain almost unchanged, protonation slightly shortens the $\text{C}\equiv\text{N}$ bond, which is supported by an increase of $\nu(\text{CN})$ by 50 cm^{-1} . Additionally, the crystal structures display networks of strong $\text{H}\cdots\text{F}$ 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.^[44]

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) – Projektnummer 387284271 – SFB 1349. Gefördert durch die Deutsche Forschungsgemeinschaft (DFG) – Projektnummer 387284271 – SFB 1349. Computing time was made available by HPC Service of ZEDAT, FU Berlin.

Conflict of interest

The authors declare no conflict of interest.

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

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Manuscript received: February 14, 2020

Revised manuscript received: March 23, 2020

Accepted manuscript online: March 24, 2020

Version of record online: ■■■■■, ■■■■■

Communications

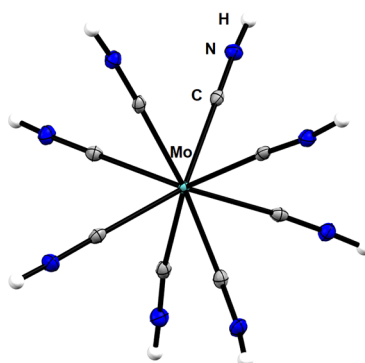


Cyanometalates

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Isolation and Structural Characterization of Eightfold Protonated Octacyanometalates $[M(\text{CNH})_8]^{4+}$ (M = Mo^{IV} , W^{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 Mo^{4+} and W^{4+} with eight hydrogen isocyanide ligands are formed and could be fully characterized.