**Tungsten Cyanide Complexes**

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# The Heptacyanotungstate(IV) Anion: A New 5d Transition-Metal Member of the Rare Heptacyanometallate Family of Anions

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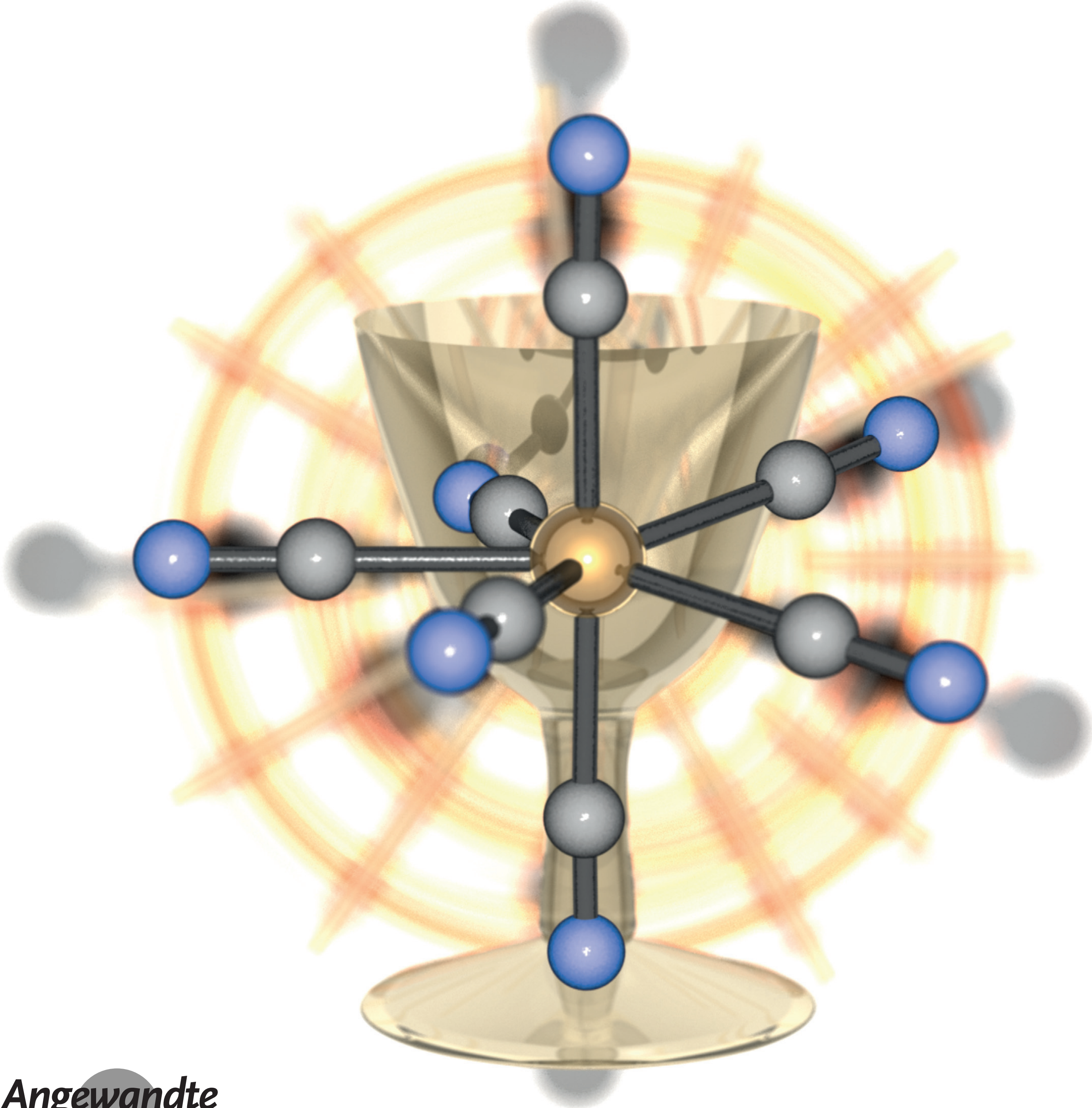

***Abstract:*** *The heptacyanotungstate(IV) anion was isolated in the salt* $(n\text{-}Bu_4N)_3[W^{IV}(CN)_7]$ *(**1**) from the reduction of* $(n\text{-}Bu_4N)_3[W^{V}(CN)_8]$ *with concomitant loss of one cyanide ligand. The anion in **1** adopts a slightly distorted pentagonal bipyramidal geometry with an average W−C distance of 2.169 Å. The spectroscopic and magnetic properties are described.*

The field of transition-metal cyanide chemistry, and, indeed, coordination chemistry, dates back to the discovery of Prussian Blue, $Fe_4[Fe(CN)_6]_3{\cdot}14\text{–}16\,H_2O$, by Diesbach and Dippel over three centuries ago. The field has enjoyed a remarkable rebirth in the past two decades owing, in large measure, to the prominent role of cyanide complexes as building blocks for molecular materials including single molecule magnets (SMMs).[1] Of particular interest in the vein of new directions in the field is the synthesis of new paramagnetic 4d and 5d homoleptic cyanometallates.[2] These compounds engage in stronger magnetic interactions with other spin centers as a result of diffuse valence orbitals and exhibit much higher magnetic anisotropy owing to increased spin-orbit coupling and mixing of the ground state with low-lying excited states. The heavier elements also tolerate a wider range of oxidation states than their 3d congeners, a situation that allows for more facile tuning of the electronic configuration. Our interest in this topic was piqued by theoretical calculations that predict 4d and 5d cyanometallates with orbital degeneracy in the ground state are promising candidates for the design of high blocking-temperature SMMs owing to highly anisotropic exchange coupling.[3] In particular the isoelectronic anions $[Mo^{III}(CN)_7]^{4-}$ and $[Re^{IV}(CN)_7]^{4-}$ were identified as important examples owing to the orbital degeneracy resulting from a $d^3$ electronic configuration in a pentagonal bipyramidal geometry.[4] The only known 3d heptacyanometallate is $[V^{III}(CN)_7]^{4-}$ which was structurally characterized in 1972.[5]

Our recent results have verified the advantages of incorporating the Group VI 4d homoleptic anions $[Mo^{III}(CN)_6]^{3-}$[6] and $[Mo^{III}(CN)_7]^{4-}$[7] into polynuclear complexes. Predictions by Ruiz and co-workers that certain combinations of 3d/4d metal ion pairs with a cyanide bridge, for example, the $Mo^{III}\text{–}CN\text{–}V^{II}$ linkage, would lead to extremely strong superexchange interactions[8] were validated in the case of the pentanuclear trigonal bipyramidal complex $[V^{II}(tmphen)_2]_3[Mo^{III}(CN)_6]_2$ (tmphen = 3,4,7,8-tetramethylphenanthroline) prepared by us. This compound exhibits the strongest antiferromagnetic coupling observed through a cyanide bridge with $J_{V\text{-}Mo} = -114\ cm^{-1}$.[6] These predictions were also supported by the successful synthesis of high-$T_c$ bulk magnets incorporating $[Mo^{III}(CN)_7]^{4-}$.[9] Another excellent example of this concept is our finding that a linear trinuclear compound with $[Mo^{III}(CN)_7]^{4-}$, that is, $[Mn^{II}(L_{N5Me})]_2[Mo^{III}(CN)_7]$ ($L_{N5Me}$ = 2,6-bis[1-(2-(*N*-methylamino)ethyl]pyridine), exhibits the highest energy barrier ($U_{eff} = 40.5\ cm^{-1}$) for a cyanide-containing SMM.[2] Earlier Long and co-workers had reported interesting results with the isoelectronic $[Re^{IV}(CN)_7]^{3-}$ cyanometallate in combination with the precursors $[(PY5Me_2)M(CH_3CN)](PF_6)_2$ ($PY5Me_2$ = 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine; M = $Mn^{II}$, $Ni^{II}$) which yielded pentanuclear starlike $Mn_4Re$ and $Ni_4Re$ complexes. Both products exhibit SMM behavior in addition to redox-switchable and charge transfer phenomena for Mn and Ni analogues, respectively.[10]

The aforementioned success with 4d and 5d heptacyanide compounds prompted us to explore the possibility of synthesizing heretofore unknown heptacyanometallate analogues of tungsten. To date, the only homoleptic cyanotungstate species is the well-established $[W(CN)_8]^{3-/4-}$.[11] Previous reports of subcoordinate tungsten cyanide species include $K_3[W^{III}(CN)_6]$ reported by Yoo and co-workers in 1965,[12] which was later shown to actually be $K_2[W^{III}(CN)_5{\cdot}H_2O]$ with an unknown impurity,[13] and $K_5[W^{II}(CN)_7]$ reported by Griffith.[14] Spectroscopic and elemental data were provided in support of these species, but no crystal structures have been reported. Our attempts to reproduce the synthesis of the $[W^{II}(CN)_7]^{2-}$ anion led only to $K_4[W^{IV}(CN)_8]$, which has also been confirmed by other groups.[15] Herein we report the first genuine heptacyanotungstate salt which was characterized by crystallography, spectroscopy, and SQUID magnetometry.

Isolation of $(n\text{-}Bu_4N)_3[W^{IV}(CN)_7]$ was achieved by reduction of $(n\text{-}Bu_4N)_3[W^{V}(CN)_8]$ with $CoCp_2$ (cobaltocene) in $CH_3CN$ under an inert atmosphere. The reaction produces a yellowish green solution which was collected by filtration after stirring for 12 h. Addition of $Et_2O$ produced a greenish-white precipitate, $(n\text{-}Bu_4N)_3[W^{IV}(CN)_7]$ (**1**) and $[Co^{III}(Cp)_2]_4[W^{IV}(CN)_8]{\cdot}x\,MeCN$ (by-product), which was recrystallized from $CH_3CN/Et_2O$ to give colorless crystals of **1**. Compound **1** is stable under an inert atmosphere but quickly decomposes in air in solution and in the solid state.

X-ray crystallographic analysis of a single crystal of **1** reveals that the anion in $(n\text{-}Bu_4N)[W^{IV}(CN)_7]$ adopts a slightly distorted pentagonal bipyramidal (PBP) geometry, as depicted in Figure 1 and Figure S1 in the Supporting Information, similar to both the $[Mo^{III}(CN)_7]^{4-}$ and $[Re^{IV}(CN)_7]^{3-}$ analogues.[10a,16] The W−C bond lengths vary between 2.148(4) and 2.172(4) Å, longer than the W−C distances of 2.118–2.154 Å in $Na_3[W^{V}(CN)_8]$.[17]

The bond lengths are also slightly longer than those reported for $Mo^{IV}\text{−}CN$ in $K_4[Mo^{IV}(CN)_8]$ whose average is 2.163 Å.[18] The C−N bond lengths in **1** range from 1.142(5) to 1.155(5) Å which is typical for C−N bonds in cyanometallates. The W−C bonds are also longer than those of the $(n\text{-}Bu_4N)_3[Re^{IV}(CN)_7]$ and $K_4[Re^{III}(CN)_7]{\cdot}2\,H_2O$ analogues; these vary between 2.064–2.123 Å and 2.077–2.099 Å, respectively.[10a] The axial C−W−C bond angles are 178.54(13)° and

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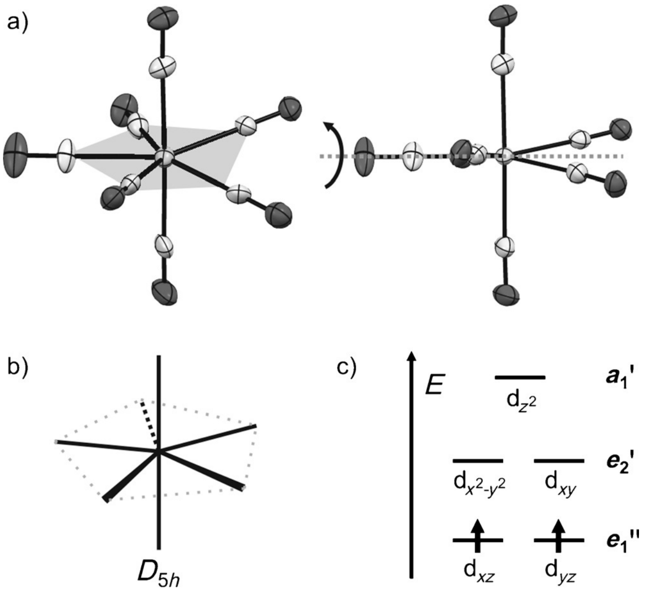

***Figure 1.*** a) Molecular structure of the $[W^{IV}(CN)_7]^{3-}$ anion with thermal ellipsoids set at 50% probability, W gray (central atom), C light gray, N dark gray, emphasizing its pentagonal bipyramidal geometry (b). c) The qualitative d-orbital energy-splitting diagram for pentagonal bipyramidal geometry and the ground-state electronic configuration of **1**.

177.06(15)° and the cyanide ligands in the equatorial plane are distorted from planarity (between +10° and −8°). Similar distortions were noted for $K_4[Mo^{III}(CN)_7]\cdot H_2O$ and $(n\text{-}Bu_4N)_3[Re^{IV}(CN)_7]$.[10a,19]

In the solid, state compound **1** exhibits two sharp and strong ν(CN) stretches at 2110 and 2079 cm$^{-1}$ (Figure S2 a) confirming that the geometry of the $[W^{IV}(CN)_7]^{3-}$ anion is close to the ideal pentagonal bipyramid (IR selection rules for $D_{5h}$ allow only two vibrations: $A_2''$ and $E_1'$). The two main features are accompanied by weak shoulder/peaks at 2121-(sh), 2091 and 2068 cm$^{-1}$ which is in accord with the slight structural distortion from the ideal $D_{5h}$ symmetry observed in the single-crystal X-ray structural model. It is also not unusual for solid-state splitting effects to be observed. The IR spectrum recorded in dichloromethane solution is similar to that of the solid with two main ν(CN) bands at 2112 and 2082 cm$^{-1}$ and slightly shifted weak features. These results indicate that the complex maintains a distorted pentagonal bipyramidal geometry in solution (Figure S2 a). The ν(CN) stretches are lower in frequency than the corresponding stretches of $(n\text{-}Bu_4N)_3[W(CN)_8]$ which appear at 2139 cm$^{-1}$ and 2129 cm$^{-1}$. This shift is consistent with the decrease in oxidation state resulting in weaker σ-bonding. The ν(CN) frequencies are also close to the values reported by Griffith at al. for $K_5[W^{II}(CN)_7]$[14] (a compound whose composition remains to be verified) and to the $A_2$“ and $E_1'$ stretches reported for pentagonal bipyramidal $K_4[Mo^{III}(CN)_7]$.[16] It is noteworthy that exposing **1** to air results in the appearance of a new band located at 2144 cm$^{-1}$ (Figure S2 b).

The electronic absorption spectrum in MeCN solution (Figure S3) exhibits a weak feature at 391 nm ($\varepsilon = 9.9\,\text{M}^{-1}\text{cm}^{-1}$) which corresponds to the lowest spin-allowed $e_2' \leftarrow e_1''$ d–d transition and is similar to the corresponding absorption features reported for other heptacyanometallates: $(n\text{-}Bu_4N)_3[Re(CN)_7]$[10a] in MeCN and $K_4[Mo^{III}(CN)_7]\cdot 2\,H_2O$ in water.[16] There are also several features below 350 nm attributed to metal-to-ligand charge transfer (MLCT) and higher d–d transitions. It is noted that exposing the solution of **1** to air leads to an irreversible color change to orange and the appearance of a new absorption at 447 nm with concomitant decrease in intensity of absorption bands below 350 nm (Figure S3).

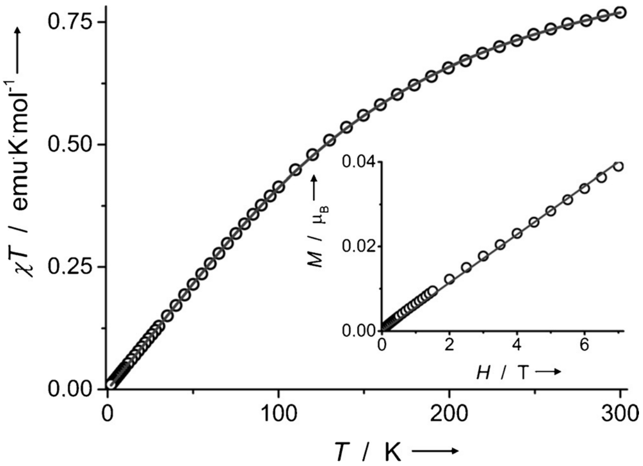

***Figure 2.*** $\chi_M T$ versus $T$ ($H_{DC}$ = 0.1 T) and $M$ versus $H$ (inset; $T$ = 1.8 K)) for **1**. Gray lines are the best fits to the experimental data (for details, see text).

The magnetic properties of **1** were measured in the solid state using a MPMS-XL SQUID magnetometer. The $\chi T$ value at room temperature is 0.77 emu K mol$^{-1}$ (Figure 2), which is less than the spin-only value of 1.00 emu K mol$^{-1}$ expected for an $S = 1$ system assuming the d-orbital splitting presented in Figure 1 c and $g$-factor of 2.0. The $\chi T$ value steadily decreases to zero as the temperature is lowered (Figure 2) which is ascribed to a significant zero field splitting (zfs) with large positive $D$ value. The best fit using the Hamiltonian in Equation (1):

$$\hat{H} = DS_z^{2+}E(S_x^2 - S_y^2) + \mu_B\mu_0 H_z g S \tag{1}$$

(where $D$ and $E$ are the axial and rhombic crystal field parameters, $S = 1$ is the spin of the system, $g$ is the $g$-factor and $Hz$ is the applied magnetic field) leads to the following parameters: $g = 1.9(1)$, $D = 330(10)$ cm$^{-1}$, $E = 110(5)$ cm$^{-1}$. The magnetization at 1.8 K (Figure 2, inset) has a maximum value of 0.04 $\mu_B$ at 7 T without saturation, indicating that the ground state is non-magnetic. The best fit parameters from the $M(H)$ dependence: $g = 2.0(1)$, $D = 430(10)$ cm$^{-1}$, and $E = 41(5)$ cm$^{-1}$ are consistent with those obtained from the $\chi T(T)$ fitting. Simultaneous fitting of both $\chi T(T)$ and $M(H)$ does not lead to satisfactory results (Figure S4). The $M$ versus $HT^{-1}$ plot is shown in Figure S5. The best fit parameters are similar to those obtained from $M(H)$ dependence: $g = 2.0(1)$, $D = 430(10)$ cm$^{-1}$, and $E = 38(5)$ cm$^{-1}$. The obtained $D$ value is very large, but not entirely unreasonable for a pentagonal bipyramidal 5d metal ion complex.[20] It is unlikely that the magnetic properties of **1** arise from spin-orbit coupling since the orbital angular momentum for a $d^2$ pentagonal bipyramidal complex should be quenched. Nevertheless, we concede that the large inherent spin-orbit coupling of 5d elements may still play a role owing to the slight distortion from the ideal pentagonal bipyramidal geometry. Our attempts to include the orbital contribution in the fits led to severe overparametrization and were unsuccessful, leading to poor results and/or non-physical, negative $g$ values. A deeper understanding of the magnetic properties of the heptacyanotungstate(IV) anion is being pursued by employing advanced measurements including XMCD, HF-EPR, and ab initio calculations. These results will be reported in due course.

In summary, the seven coordinate cyanotungstate(IV) anion $[\mathrm{W}^{\mathrm{IV}}(\mathrm{CN})_7]^{3-}$ is reported as a new member of the homoleptic transition-metal cyanide family. Given the maturity of the topic of cyanide chemistry, new examples of such species after all of these years are rare and exciting findings. The $(n\text{-Bu}_4\mathrm{N})_3[\mathrm{W}^{\mathrm{IV}}(\mathrm{CN})_7]$ salt is paramagnetic at room temperature with two unpaired electrons and exhibits a non-magnetic ground state at low temperature due to a large positive $D$ parameter. Work on related $\mathrm{W}^{\mathrm{III}}$ compounds is underway as well as efforts to incorporate this new cyanometallate into multinuclear assemblies.

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[1] O. Kahn, *Philos. Trans. R. Soc. London Ser. A* **1999**, *357*, 3005–3023.
[2] X.-Y. Wang, C. Avendano, K. R. Dunbar, *Chem. Soc. Rev.* **2011**, *40*, 3213–3238.
[3] a) V. S. Mironov, *Dokl. Phys. Chem.* **2004**, *397*, 154–157; b) V. S. Mironov, L. F. Chibotaru, A. Ceulemans, *J. Am. Chem. Soc.* **2003**, *125*, 9750–9760.
[4] V. S. Mironov, *Dokl. Phys. Chem.* **2006**, *408*, 130–136.
[5] R. L. R. Towns, R. A. Levenson, *J. Am. Chem. Soc.* **1972**, *94*, 4345–4346.
[6] D. Pinkowicz, H. Southerland, X.-Y. Wang, K. R. Dunbar, *J. Am. Chem. Soc.* **2014**, *136*, 9922–9924.
[7] K. Qian, X.-C. Huang, C. Zhou, X.-Z. You, X.-Y. Wang, K. R. Dunbar, *J. Am. Chem. Soc.* **2013**, *135*, 13302–13305.
[8] E. Ruiz, A. Rodríguez-Fortea, S. Alvarez, M. Verdaguer, *Chem. Eur. J.* **2005**, *11*, 2135–2144.
[9] a) J. Milon, M.-C. Daniel, A. Kaiba, P. Guionneau, S. Brandès, J.-P. Sutter, *J. Am. Chem. Soc.* **2007**, *129*, 13872–13878; b) K. Tomono, Y. Tsunobuchi, K. Nakabayashi, S.-i. Ohkoshi, *Inorg. Chem.* **2010**, *49*, 1298–1300.
[10] a) M. V. Bennett, J. R. Long, *J. Am. Chem. Soc.* **2003**, *125*, 2394–2395; b) D. E. Freedman, D. M. Jenkins, A. T. Iavarone, J. R. Long, *J. Am. Chem. Soc.* **2008**, *130*, 2884–2885; c) J. M. Zadrozny, D. E. Freedman, D. M. Jenkins, T. D. Harris, A. T. Iavarone, C. Mathonière, R. Clérac, J. R. Long, *Inorg. Chem.* **2010**, *49*, 8886–8896.
[11] a) D. Pinkowicz, R. Podgajny, B. Nowicka, S. Chorazy, M. Reczynski, B. Sieklucka, *Inorg. Chem. Front.* **2015**, *2*, 10–27; b) B. Sieklucka, R. Podgajny, T. Korzeniak, B. Nowicka, D. Pinkowicz, M. Kozieł, *Eur. J. Inorg. Chem.* **2011**, 305–326; c) P. M. Kiernan, W. P. Griffith, *J. Chem. Soc. Dalton Trans.* **1975**, 2489–2494.
[12] J. S. Yoo, E. Griswold, J. Kleinberg, *Inorg. Chem.* **1965**, *4*, 365–368.
[13] J. R. Fowler, J. Kleinberg, *Inorg. Chem.* **1970**, *9*, 1005–1009.
[14] A. M. Soares, P. M. Kiernan, D. J. Cole-Hamilton, W. P. Griffith, *J. Chem. Soc. Chem. Commun.* **1981**, 84–85.
[15] H. I. Karunadasa, J. R. Long, *Angew. Chem. Int. Ed.* **2009**, *48*, 738–741; *Angew. Chem.* **2009**, *121*, 752–755.
[16] G. R. Rossman, F. D. Tsay, H. B. Gray, *Inorg. Chem.* **1973**, *12*, 824–829.
[17] L. D. C. Bok, J. G. Leipoldt, S. S. Basson, *Acta Crystallogr. Sect. B* **1970**, *26*, 684–692.
[18] J. L. Hoard, T. A. Hamor, M. D. Glick, *J. Am. Chem. Soc.* **1968**, *90*, 3177–3184.
[19] M. B. Hursthouse, K. M. A. Malik, A. M. Soares, J. F. Gibson, W. P. Griffith, *Inorg. Chim. Acta* **1980**, *45*, L81–L82.
[20] A. F. Williams, *A theoretical Approach to Inorganic Chemistry*, Springer, Berlin, Heidelberg, **1979**.

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