

Synthesis and Structure of Hexatungstochromate(III), $[\text{H}_3\text{Cr}^{\text{III}}\text{W}_6\text{O}_{24}]^{6-}$

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Dedicated to Prof. Hans J. Breunig on the occasion of his 70th birthday

Abstract: The hexatungstochromate(III) $[\text{H}_3\text{Cr}^{\text{III}}\text{W}_6\text{O}_{24}]^{6-}$ (**1**) was synthesized in aqueous, basic medium by simple reaction of chromium(III) nitrate nonahydrate and sodium tungstate dihydrate in a 1:6 ratio. Polyanion **1** represents the first Anderson-Evans type heteropolytungstate with a trivalent hetero element. The sodium salt of **1** with the formula $\text{Na}_6[\text{H}_3\text{Cr}^{\text{III}}\text{W}_6\text{O}_{24}]\cdot 22\text{H}_2\text{O}$ (**1a**) was fully characterized in the solid state by single crystal XRD, FT-IR spectroscopy, and thermogravimetric analysis.

Keywords: Anderson-Evans structure · Chromium · Polyoxometalates · XRD

Introduction

Polyoxometalates (POMs) are discrete, anionic metal-oxygen clusters of early *d* block metal ions in high oxidation states (e.g. W^{VI} , Mo^{VI} , V^{IV})^[1] with a very large structural and compositional variety, leading to interest in many different areas including materials science, catalysis, analytical chemistry, magnetism, and biomedical science.^[2] The number of *3d* metal-containing POMs is very large, but only a few structurally characterized chromium-containing POMs are known.^[3] The main obstacle for the development of Cr-POM chemistry is probably the kinetic inertness of $[\text{Cr}(\text{OH})_2]^{3+}$ towards ligand exchange in aqueous solution.^[4]

Chromium-containing POMs possess interesting physicochemical properties, and the paramagnetic Cr^{III} is EPR active, which can find applications in integrated information storage, quantum computing, molecule-based magnets and spintronics.^[5] In 1970, Perloff determined the crystal structure of hexamolybdochromate(III) $[\text{CrMo}_6\text{O}_{24}\text{H}_6]^{3-}$,^[3a] which was later described by Tsigidinos as $[\text{CrO}_6\text{Mo}_6\text{O}_{15+n}\text{H}_{2n}]^{3-}$.^[6] Lunk's^[3c-e] and

Mialane's^[3j] groups reported the first structural examples of Cr-containing heteropolytungstates. In 2008, Xue's group reported two Cr^{III}-substituted, sandwich-type heteropolymolybdates, $[\text{Cr}_2(\text{AsMo}_7\text{O}_{27})_2]^{12-}$ and $[\text{CrFe}(\text{AsMo}_7\text{O}_{27})_2]^{12-}$.^[3h,i] Recently, our group prepared two mono-Cr^{III}-substituted heteropolytungstates $[\text{Cr}^{\text{III}}(\text{HX}^{\text{V}}\text{W}_7\text{O}_{28})_2]^{13-}$ (X = P, As) by simple, one pot reactions, and these polyanions exhibit exceptionally large magnetic anisotropy.^[3l]

An important subclass of POMs is the $\{\text{XM}_6\text{O}_{24}\}$ structure type (also known as the Anderson-Evans structure), in which an octahedral XO_6 hetero group is surrounded by six edge-shared MO_6 octahedra. In 1948, Evans^[7] reported the first example by determining the structure of $[\text{TeMo}_6\text{O}_{24}]^{6-}$, which had originally been proposed by Anderson in 1937.^[8] To date, a large number of Anderson-Evans type polyanion derivatives $[\text{H}_n\text{XM}_6\text{O}_{24}]^{m-}$ (M = W, Mo) is known, with many different *p*- and *d*-block elements acting as octahedrally coordinated hetero groups XO_6 , with the oxidation states for X ranging from +2 to +6. The structural characterized tungsten-based derivatives $[\text{H}_n\text{XW}_6\text{O}_{24}]^{m-}$ include the following hetero elements: Te^{VI} ,^[9] Sb^{V} ,^[10] V^{V} ,^[11] Pt^{IV} ,^[12] Mn^{IV} ,^[13] Ni^{IV} ,^[14] Ni^{II} ,^[15a,b] and Mn^{II} .^[15c] On the other hand, the molybdate family $[\text{H}_n\text{XM}_6\text{O}_{24}]^{m-}$ is known for the following hetero elements: I^{VII} ,^[16] Te^{VI} ,^[7,8] Sb^{V} ,^[17] V^{V} ,^[18] Pt^{IV} ,^[19] Pd^{IV} ,^[20] Al^{III} ,^[21] Cr^{III} ,^[3a,g,6,22] Fe^{III} ,^[21b] Co^{III} ,^[21b,23] Ga^{III} ,^[24] Rh^{III} ,^[25] Mn^{II} ,^[21b] Co^{II} ,^[21a,26] Ni^{II} ,^[21b,27] Cu^{II} ,^[28] and Zn^{II} .^[21b,29] There are some reports on mixed addenda Anderson-Evans ions, such as $[\text{Ni}^{\text{II}}(\text{OH})_6\text{Mo}_x\text{W}_{6-x}\text{O}_{18}]^{4-}$,^[30] which was reinvestigated by Miwa's group.^[21b]

It has also been demonstrated that organic functionalities can be attached to one or both sides of the Anderson-Evans

framework, in particular by the groups of Hasenknopf,^[31] Cronin,^[32] Wang,^[33] Wei,^[34] Wu,^[35] and Song.^[36]

Here, we report on the synthesis and structure of the chromium-centered Anderson-Evans type polytungstate derivative.

Experimental Section

Synthesis

All chemicals were commercially available and used without further purification.

Synthesis of $\text{Na}_6[\text{H}_3\text{Cr}^{\text{III}}\text{W}_6\text{O}_{24}]\cdot 22\text{H}_2\text{O}$

Method 1

A sample of $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (0.20 g, 0.50 mmol) was dissolved in 20 mL of 1 M sodium acetate solution at pH 6.9, followed by addition of $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ (0.99 g, 3.00 mmol). The mixture was stirred for 1 h at 80 °C, allowed to cool to room temperature, and then filtered (final pH 8). Slow evaporation at room temperature led to the formation of green crystals of **1a** within three days (yield 0.15 g, 14%). IR (cm^{-1}): 947 (m), 880 (s), 656 (s), 559 (w), 511 (m), 440 (m). Anal. calcd (found): Na 6.71 (7.15), W 53.65 (53.76), Cr 2.53 (2.69). Mw 2076.4 g/mol.

Method 2

A sample of $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (0.40 g, 1.00 mmol) was dissolved in 20 mL of 0.5 M sodium acetate solution at pH 6, followed by addition of $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ (2.64 g, 8.00 mmol). The mixture was stirred for 1 h at 80 °C, allowed to cool to room temperature, and then filtered (final

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pH 8). Slow evaporation at room temperature led to the formation of green crystals of **1a** within two days (yield 0.4 g, 19% based on Cr). The identity of **1a** was established by single crystal XRD and IR.

Instrumentation

Infrared spectra were recorded on a Nicolet Avatar 370 FT-IR spectrophotometer using KBr pellets. The following abbreviations were used to assign the peak intensities: w = weak; m = medium; s = strong; br = broad. Thermogravimetric analysis was carried out on a TA Instruments SDT Q600 thermobalance with a 100 mL/min flow of nitrogen; the temperature was ramped from 20 to 800 °C at a rate of 5 °C/min. Elemental analysis was performed by CNRS, Service Central d'Analyse, Solaize, France.

X-ray Crystallography

A single crystal of **1a** was mounted on a Hampton cryoloop in light oil for data collection at 100 K. Data collection and indexing were performed on a Bruker D8 SMART APEX II CCD diffractometer with kappa geometry (graphite monochromator, λ (Mo K α) = 0.71073 Å). Data integration was performed using *SAINTE*.^[37] Routine Lorentz and polarization corrections were applied. Multiscan absorption corrections were performed using *SADABS*.^[38] Direct methods (*SHELXS*) successfully located the tungsten atoms, and successive Fourier syntheses (*SHELXL*) revealed the remaining atoms.^[38] Refinements were full-matrix least squares against $|F|^2$ using all data. In the final refinement, the heavy atoms (Cr, W, Na) of the polyanion were refined anisotropically; the O atoms were refined isotropically. Crystallographic data are summarized in Table 1. The complete X-ray crystallographic data (CIF format) is available free of charge via the internet at the Fachinformationszentrum (FIZ) Karlsruhe (<http://www.fiz-karlsruhe.de/icsd.html>) under the CSD number 429800.

Results and Discussion

Synthesis and Structure

The novel polyanion $[\text{H}_3\text{Cr}^{\text{III}}\text{W}_6\text{O}_{24}]^{6-}$ (**1**) was synthesized in a one-pot procedure under conventional 'open beaker' conditions, by reaction of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in aqueous NaOAc solution at 80 °C. The results show that the optimal ratio of $\text{Cr}^{3+}/\text{WO}_4^{2-}$ is 1:6 for method 1 and 1:8 for method 2 (see Exp. Section). The ratio of $\text{Cr}^{3+}/\text{WO}_4^{2-}$ represents the stoichiometric ratio in method 1, but not in 2. The reason is that the final pH is crucial for the successful isolation of **1a**, which should be carefully adjusted to 7.5–8.5. The starting pH in method 1 is 6.9, but 6 in method 2,

Table 1. Crystal data for **1a**.

Compound	$\text{Na}_6[\text{H}_3\text{Cr}^{\text{III}}\text{W}_6\text{O}_{24}] \cdot 22\text{H}_2\text{O}$
Formula weight [g/mol]	2076.4
Crystal system	Triclinic
Space group	$P\bar{1}$
a [Å]	11.6313(10)
b [Å]	12.3305(11)
c [Å]	16.5066(13)
α [°]	68.336(2)
β [°]	85.209(2)
γ [°]	71.109(3)
Volume [Å ³]	2079.9(3)
Z	2
D_{calc} [g/cm ³]	3.316
Absorption coefficient	16.962
F(000)	1898
Crystal size [mm]	0.24 × 0.19 × 0.18
Theta range for data collection [°]	3.491 – 27.877
Reflections collected	64511
Independent reflections	9767
R(int)	0.0435
Goodness-of-fit on F ²	1.064
R_1 [I > 2 σ (I)] ^a	0.0387
wR_2 (all data) ^b	0.1041

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b Rw = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

and therefore, an excess of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ is needed in method 2 to keep the final pH in the range 7.5–8.5.

Single crystal X-ray analysis revealed that $[\text{H}_3\text{Cr}^{\text{III}}\text{W}_6\text{O}_{24}]^{6-}$ has the so-called Anderson-Evans structure, consisting of a ring of six edge-shared WO_6 octahedra surrounding the central CrO_6 unit (Fig. 1). Hence, polyanion **1** represents the first Anderson-Evans type heteropolytungstate with a trivalent hetero element. The title

polyanion is isostructural with the molybdenum derivative $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$, first reported in 1970.^[3a] The central Cr^{III} ion in **1** has an almost ideal octahedral coordination environment, with Cr–O distances in the range of 1.962(5)–2.006(5) Å. These distances are very similar to those observed in the molybdenum derivative $[\text{Cr}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$ (Cr–O 1.968(3)–1.986(3) Å). The W–O distances in **1** can be grouped in three sets, terminal (W=O_t

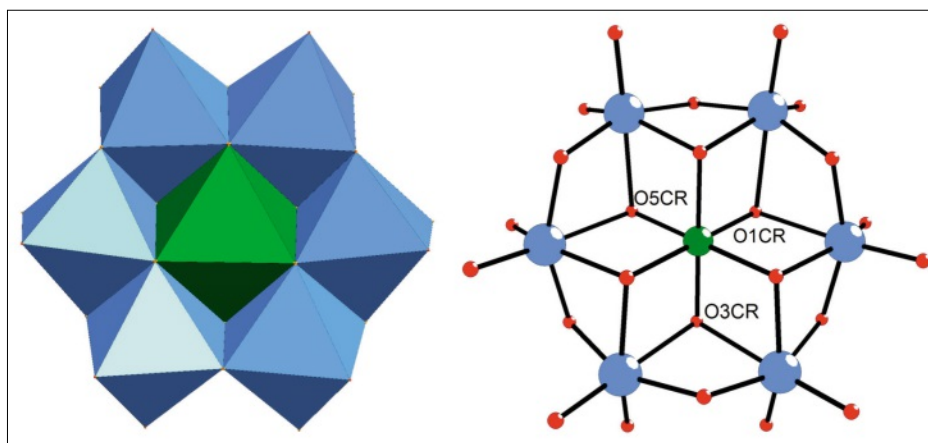


Fig. 1. Polyhedral (left) and ball-and-stick (right) representations of polyanion **1**. The positions of the three oxygens carrying non-disordered protons are indicated. Color code: W atoms and WO_6 octahedra (blue), Cr atom and CrO_6 octahedron (green), O atoms (red).

1.722(6)–1.763(6) Å), doubly-bridging ($W-O_b$: 1.916(6)–1.965(5) Å), and triply-bridging ($W-O_c$: 2.094(5)–2.413(5) Å). The same trend can be observed for the molybdenum analogue $[Cr(OH)_6Mo_6O_{18}]^{3-}$ (see Table 2). Bond valence sum (BVS) calculations for **1** suggest that the triply bridging μ_3 -oxo groups $O1CR$, $O3CR$, and $O5CR$ are monoprotonated (1.09, 1.18, and 1.22 respectively). Hence, polyanion **1** is tri-protonated, whereas Perloff's $[Cr(OH)_6Mo_6O_{18}]^{3-}$ is hexa-protonated, which is probably due to the pH differences during synthesis (8 versus 4.5).

In the solid-state lattice of **1a**, each polyanion is surrounded by five Na^+ counter cations, which are bound to a total of six terminal $W=O$ oxygens of each polyanion (see Fig. 2). Two nearest neighbor polyanions are linked by the two $Na(1)$ ions, and the distance between the central Cr atoms is about 6.771(4) Å. Moreover, the two neighboring polyanions are further linked with other Na^+ ions to give an extended 3D network.

Fourier-transform Infrared Spectrum (FTIR)

The Fourier transform infrared (FTIR) spectrum of **1a** shows a fingerprint region characteristic for the tungsten-oxo framework (Fig. 3). The bands at about 947 cm^{-1} and 880 cm^{-1} arise from antisymmetric stretching vibrations of the terminal $W=O$ bonds and $Cr-O-W$ bridges, respectively. The strong band at approximately 656 cm^{-1} is associated with the antisymmetric stretching of $W-O-W$ bridges, whereas the medium band at 511 cm^{-1} and a weak band at 559 cm^{-1} correspond to bending vibrations of $W-O-W$ bridges. The medium to strong bands at around 440 cm^{-1} originate from the bending vibrations of the $Cr-O-W$ bridges.

Thermogravimetric Analysis

The thermogram of **1a** (Fig. 4) shows a weight loss which starts at room temperature with a dehydration step ending at *ca.* $400\text{ }^\circ\text{C}$, corresponding to the loss of ~ 23 crystal water molecules and further loss of 1.5 compositional waters, involving the protons attached covalently to the polyanion [% calc. (found): 21.7 (20.5)].

Conclusions

The Cr^{III} -containing hexatungstate $[H_3Cr^{III}W_6O_{24}]^{6-}$ (**1**) was prepared by a simple, one-pot reaction of $Cr(NO_3)_3 \cdot 9H_2O$ and $Na_2WO_4 \cdot 2H_2O$ in sodium acetate medium. Polyanion **1** represents the first chromium-derivative of the Anderson-Evans type heteropolytungstate family. The title compound was characterized in the solid state by IR spectroscopy, single-crystal

Table 2. Comparison of bond lengths between $[H_3Cr^{III}W_6O_{24}]^{6-}$ (**1**) and $[Cr(OH)_6Mo_6O_{18}]^{3-}$.

	1		$[Cr(OH)_6Mo_6O_{18}]^{3-}$	
	Bond length [Å]	Average bond length [Å]	Bond length [Å]	Average bond length [Å]
Cr–O	1.962(5)–2.006(5)	1.982	1.968(3)–1.986(3)	1.647
M···M M = W, Mo	~ 3.150–3.192	3.175	~ 3.309–3.351	3.329
M=O _t	1.722(6)–1.763(6)	1.746	1.695(3)–1.720(4)	1.701
M–O _b	1.916(6)–1.965(5)	1.943	1.907(3)–1.985(5)	1.941
M–O _c	2.094(5)–2.413(5)	2.209	2.270(3)–2.347(3)	2.291

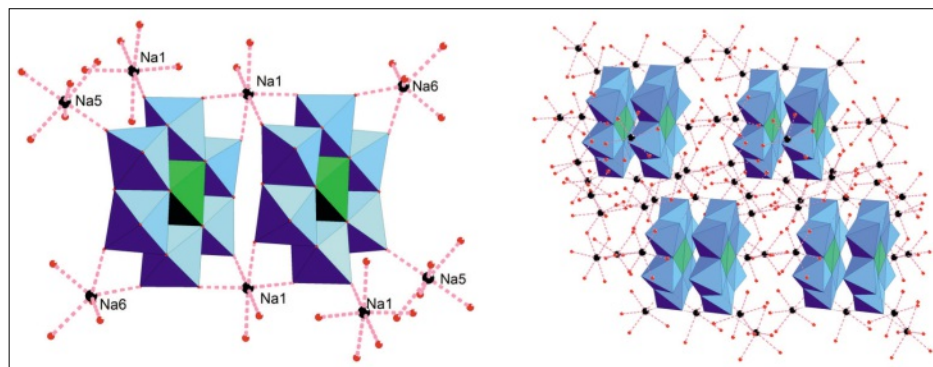


Fig. 2. Solid-state lattice of **1a** showing the polyanions being surrounded by Na^+ counter cations (large pink balls). Water molecules are shown as small red balls, and the $Na^+ \cdots OH_2$ interactions as dashed lines. Notice that not all Na^+ ions could be found by single crystal XRD (see text for details).

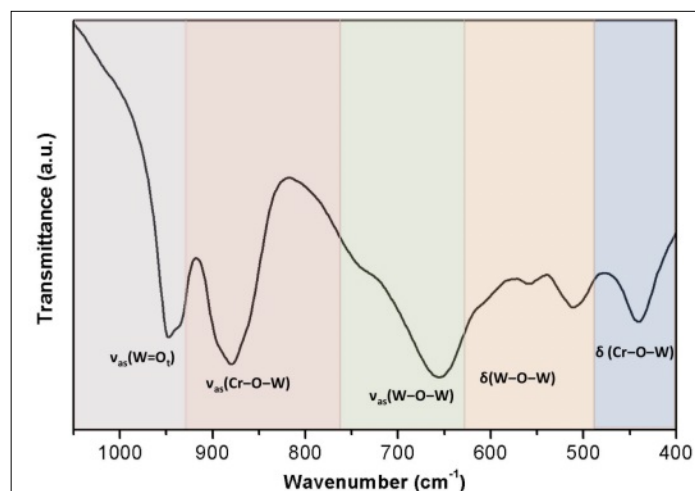


Fig. 3. FTIR spectrum of **1a**.

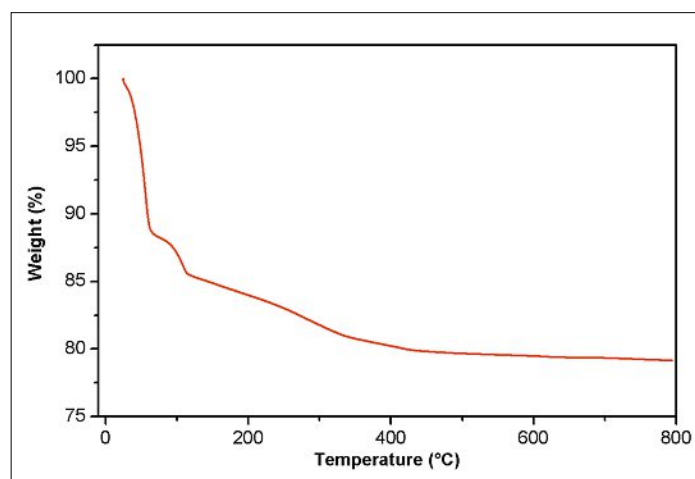


Fig. 4. Thermogram of **1a** from room temperature to $800\text{ }^\circ\text{C}$.

XRD, elemental and thermal analysis. We have already isolated several other, novel chromium-containing POMs, which will be reported elsewhere.

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- [1] a) M. T. Pope, 'Heteropoly and Isopoly Oxometalates', Springer, Berlin, **1983**; b) M. T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34; c) M. T. Pope, U. Kortz, 'Polyoxometalates', in 'Encyclopedia of Inorganic and Bioinorganic Chemistry', John Wiley & Sons, Ltd.: Hoboken, NJ, **2012**.
- [2] a) J. T. Rhule, C. L. Hill, D. A. Judd, R. F. Schinazi, *Chem. Rev.* **1998**, *98*, 327; b) M. V. Vasylyev, R. Neumann, *J. Am. Chem. Soc.* **2003**, *126*, 884; c) I. M. Mbomekalle, B. Keita, L. Nadjjo, P. Berthet, K. I. Hardcastle, C. L. Hill, T. M. Anderson, *Inorg. Chem.* **2003**, *42*, 1163; d) J. J. Barras-Almenar, E. Coronado, A. Müller, M. T. Pope, 'Polyoxometalate Molecular Science', Kluwer: Dordrecht, The Netherlands **2004**; e) S. Berardi, G. La Ganga, M. Natali, I. Bazzan, F. Puntoriero, A. Sartorel, F. Scandola, S. Campagna, M. Bonchio, *J. Am. Chem. Soc.* **2012**, *134*, 11104; f) A. Sartorel, M. Bonchio, S. Campagna, F. Scandola, *Chem. Soc. Rev.* **2013**, *42*, 2262;
- [3] a) A. Perloff, *Inorg. Chem.* **1970**, *9*, 2228; b) J. Peng, L.-Y. Qu, Y.-G. Chen, *Inorg. Chim. Acta* **1991**, *183*, 157; c) K. Wassermann, H.-J. Lunk, R. Palm, J. Fuchs, *Acta Cryst., Sect. C* **1994**, *50*, 348; d) K. Wassermann, R. Palm, H.-J. Lunk, J. Fuchs, N. Steinfeldt, R. Stoesser, *Inorg. Chem.* **1995**, *34*, 5029; e) K. Wassermann, H.-J. Lunk, R. Palm, J. Fuchs, N. Steinfeldt, R. Stösser, M. T. Pope, *Inorg. Chem.* **1996**, *35*, 3273; f) A. S. J. Wery, J. M. Gutierrez-Zorrilla, A. Luque, M. Ugalde, P. Roman, L. Lezamma, T. Rojo, *Acta Chem. Scand.* **1998**, *52*, 1194; g) L. Ouahab, S. Golhen, Y. Yoshida, G. Saito, *J. Cluster Sci.* **2003**, *14*, 193; h) L. Li, Q. Shen, G. Xue, H. Xu, H. Hu, F. Feng, J. Wang, *Dalton Trans.* **2008**, 5698; i) H. Xu, L. Li, B. Liu, G. Xue, H. Hu, F. Fu, J. Wang, *Inorg. Chem.* **2009**, *48*, 10275; j) J. D. Compain, P. Mialane, A. Dolbecq, I. M. Mbomekallé, J. Marrot, F. Sécheresse, C. Duboc, E. Rivière, *Inorg. Chem.* **2010**, *49*, 2851; k) L. J. Batchelor, R. Shaw, S. J. Markey, M. Helliwell, E. J. L. McInnes, *Chem. Eur. J.* **2010**, *16*, 5554; l) W. Liu, J. H. Christian, R. Al-Oweini, B. S. Bassil, J. van Tol, M. Atanasov, F. Neese, N. S. Dalal, U. Kortz, *Inorg. Chem.* **2014**, *53*, 9274.
- [4] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, 'Advanced Inorganic Chemistry', 3. ed.; John Wiley & Sons, Inc.: New York, **1999**; p. 830.
- [5] a) G. Christou, *Acc. Chem. Res.* **1989**, *22*, 328; b) K. L. Taft, G. C. Papaefthymiou, S. J. Lippard, *Inorg. Chem.* **1994**, *33*, 1510; c) D. A. Garanin, E. M. Chudnovsky, *Phys. Rev. B* **1997**, *56*, 11102; d) J. M. Clemente-Juan, E. Coronado, *Coord. Chem. Rev.* **1999**, *193-195*, 361; e) M. N. Leuenberger, D. Loss, *Nature* **2001**, *410*, 789; f) J. M. Poblet, X. Lopez, C. Bo, *Chem. Soc. Rev.* **2003**, *32*, 297; g) M. A. Aldamen, J. M. Clemente-Juan, E. Coronado, C. Martí-Gastaldo, A. Gaita-Ariño, *J. Am. Chem. Soc.* **2008**, *130*, 8874; h) P. C. E. Stamp, A. Gaita-Ariño, *J. Mater. Chem.* **2009**, *19*, 1718; i) Y. F. Song, R. Tsunashima, *Chem. Soc. Rev.* **2012**, *41*, 7384; j) H.-J. Lunk, *Chem. Texts* **2015**, DOI 10.1007/s40828-015-0007-z.
- [6] G. A. Tsigdinos, Doctoral Dissertation, Boston University, **1961**.
- [7] H. T. Evans, *J. Am. Chem. Soc.* **1948**, *70*, 1291.
- [8] J. S. Anderson, *Nature* **1937**, *140*, 850.
- [9] K. J. Schmidt, G. J. Schrobilgen, J. F. Sawyer, *Acta Cryst., Sect. C* **1986**, *42*, 1115.
- [10] a) H. Naruke, T. Yamase, *Acta Cryst., Sect. C* **1992**, *48*, 597; b) H. Naruke, N. Kajitani, T. Konya, *J. Solid State Chem.* **2011**, *184*, 770.
- [11] S. O. Kin'ones, A. Ita, G. Z. Kaziev, V. A. Volodina, V. K. Bel'skij, V. E. Zavodnik, *Zhurnal Neorganicheskoy Khimii* **2001**, *46*, 1076.
- [12] a) U. Lee, A. Kobayashi, Y. Sasaki, *Acta Cryst., Sect. C* **1983**, *39*, 817; b) U. Lee, H. Ichida, A. Kobayashi, Y. Sasaki, *Acta Cryst., Sect. C* **1984**, *40*, 5; c) U. Lee, *Acta Cryst., Sect. E* **2002**, *58*, i130.
- [13] A. L. Nolan, R. C. Burns, G. A. Lawrance, D. C. Craig, *Acta Cryst., Sect. C* **2000**, *56*, 729.
- [14] H. H. K. Hau, Ph.D. Thesis, Boston University, **1970**, Diss. Abs., **1970**, 31B, 2600.
- [15] a) U. C. Agarwala, Ph.D. Thesis, Boston University, **1960**; Diss. Abs., **1960**, 31B, 2600; b) C.-Y. Sun, S.-X. Liu, L.-H. Xie, C.-L. Wang, B. Gao, C.-D. Zhang, Z.-M. Su, *J. Solid State Chem.* **2006**, *179*, 2093; c) A. V. Oreshkina, G. Z. Kaziev, S. Holguin Quinones, A. I. Stash, P. A. Shipilova, *Russ. J. Coord. Chem.* **2011**, *37*, 845.
- [16] a) H. Kondo, A. Kobayashi, Y. Sasaki, *Acta Cryst., Sect. B* **1980**, *36*, 661; b) C. Rosu, T. J. R. Weakley, *Acta Cryst., Sect. C* **2000**, *56*, e170; c) H. An, E. Wang, D. Xiao, Y. Li, L. Xu, *Inorg. Chem. Commun.* **2005**, *8*, 267.
- [17] A. Ogawa, H. Yamato, U. Lee, H. Ichida, A. Kobayashi, Y. Sasaki, *Acta Cryst., Sect. C* **1988**, *44*, 1879.
- [18] M. Cindrić, N. Strukan, V. Vrdoljak, M. Devčić, B. Kamenar, *J. Coord. Chem.* **2002**, *55*, 705.
- [19] a) U. Lee, *Acta Cryst., Sect. C* **1994**, *50*, 1657; b) H. C. Joo, K. M. Park, U. Lee, *Acta Cryst., Sect. C* **1994**, *50*, 1659; c) U. Lee, H. C. Joo, *Acta Cryst., Sect. C* **2000**, *56*, e311; d) U. Lee, H.-C. Joo, *Acta Cryst., Sect. E* **2006**, *62*, i241; e) U. Lee, H.-C. Joo, *Acta Cryst., Sect. E* **2007**, *63*, i11; f) U. Lee, H.-C. Joo, K.-M. Park, *Acta Cryst., Sect. E* **2010**, *66*, i25.
- [20] S. Angus-Dunne, R. C. Burns, D. C. Craig, G. A. Lawrance, *Z. Anorg. Allg. Chem.* **2010**, *636*, 727.
- [21] a) L. C. W. Baker, G. Foster, W. Tan, F. Scholnick, T. P. McCutcheon, *J. Am. Chem. Soc.* **1955**, *77*, 2136; b) K. Nomiya, T. Takahashi, T. Shirai, M. Miwa, *Polyhedron* **1987**, *6*, 213; c) H. Y. Lee, K. M. Park, U. Lee, H. Ichida, *Acta Cryst., Sect. C* **1991**, *47*, 1959; d) V. Shivaiah, S. Das, *J. Chem. Sci.* **2005**, *117*, 227;
- [22] a) C. W. Wolfe, M. L. Block, L. C. W. Baker, *J. Am. Chem. Soc.* **1955**, *77*, 2200; b) U. Lee, *Acta Cryst., Sect. E* **2007**, *63*, i5.
- [23] U. Lee, H.-C. Joo, J.-S. Kwon, M.-A. Cho, *Acta Cryst., Sect. E* **2001**, *57*, i112.
- [24] O. W. Rollins, J. E. Earley, *J. Am. Chem. Soc.* **1959**, *81*, 5571.
- [25] Y. Ozawa, Y. Hayashi, K. Isobe, *Acta Cryst., Sect. C* **1991**, *47*, 637.
- [26] a) A. L. Nolan, R. C. Burns, G. A. Lawrance, *J. Chem. Soc., Dalton Trans.* **1996**, 2629; b) A. L. Nolan, C. C. Allen, R. C. Burns, D. C. Craig, G. A. Lawrance, *Aust. J. Chem.* **1998**, *51*, 825; c) U. Lee, H. C. Joo, *Acta Cryst., Sect. C* **2000**, *56*, e423.
- [27] U. Lee, H.-C. Joo, J.-S. Kwon, *Acta Cryst., Sect. E* **2002**, *58*, i6.
- [28] F. Ito, T. Ozeki, H. Ichida, H. Miyamae, Y. Sasaki, *Acta Cryst., Sect. C* **1989**, *45*, 946.
- [29] C. C. Allen, R. C. Burns, G. A. Lawrance, P. Turner, T. W. Hambley, *Acta Cryst., Sect. C* **1997**, *53*, 7.
- [30] E. Matijević, M. Kerker, H. Beyer, F. Theubert, *Inorg. Chem.* **1963**, *2*, 581.
- [31] a) B. Hasenknopf, R. Delmont, P. Herson, P. Gouzerh, *Eur. J. Inorg. Chem.* **2002**, 1081; b) S. Favette, B. Hasenknopf, J. Vaissermann, P. Gouzerh, C. Roux, *Chem. Commun.* **2003**, 2664; c) P. R. Marcoux, B. Hasenknopf, J. Vaissermann, P. Gouzerh, *Eur. J. Inorg. Chem.* **2003**, 2406; d) M.-P. Santoni, A. K. Pal, G. S. Hanan, A. Proust, B. Hasenknopf, *Inorg. Chem.* **2011**, *50*, 6737.
- [32] a) Y.-F. Song, D.-L. Long, L. Cronin, *Angew. Chem. Int. Ed.* **2007**, *46*, 3900; b) J. Zhang, Y.-F. Song, L. Cronin, T. Liu, *J. Am. Chem. Soc.* **2008**, *130*, 14408.
- [33] a) Q. Wu, Y.-G. Li, Y.-H. Wang, R. Clerac, Y. Lu, E.-B. Wang, *Chem. Commun.* **2009**, 5743; b) Q. Wu, W.-L. Chen, D. Liu, C. Liang, Y.-G. Li, S.-W. Lin, E. Wang, *Dalton Trans.* **2011**, *40*, 56.
- [34] a) J. Zhang, J. Hao, Y. Wei, F. Xiao, P. Yin, L. Wang, *J. Am. Chem. Soc.* **2010**, *132*, 14; b) J. Zhang, J. Luo, P. Wang, B. Ding, Y. Huang, Z. Zhao, J. Zhang, Y. Wei, *Inorg. Chem.* **2015**, *54*, 2551.
- [35] a) Y. Yan, H. Wang, B. Li, G. Hou, Z. Yin, L. Wu, V. W. W. Yam, *Angew. Chem. Int. Ed.* **2010**, *49*, 9233; b) L. Yue, H. Ai, Y. Yang, W. Lu, L. Wu, *Chem. Commun.* **2013**, *49*, 9770.
- [36] a) C.-G. Lin, W. Chen, Y.-F. Song, *Eur. J. Inorg. Chem.* **2014**, 3401; b) Y. Ji, J. Hu, L. Huang, W. Chen, C. Streb, Y.-F. Song, *Chem. Eur. J.* **2015**, *21*, 6469.
- [37] SAINT, Bruker AXS Inc.: Madison, Wisconsin, USA, **2007**.
- [38] G. M. Sheldrick, *Acta Cryst., Sect. A* **2008**, *64*, 112.