A Unique Bridging Dichromate Ligand in [Mn₂(Cr₂O₇)₂(bpy)₄] (bpy = 2,2′-Bipyridine)

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Hexavalent chromium complexes, most notably dichromates, have long been recognized to cause genotoxic and mutagenetic effects in all kinds of living cells, leading to development of cancer in humans.[1] Between physiologically accessible pH values of 2–6 the $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions are in equilibrium.[2] Genotoxicity patterns in bacteria suggest distinctive mechanisms of interaction of Cr(VI) and Cr(III) with DNA; Cr(III) is found to induce DNA–protein and DNA–DNA cross-links and thus reduces the fidelity of DNA replication, whereas Cr(VI) unbalances nucleotide pools and, due to its strong oxidizing power, induces single strand breaks in DNA.[3] The observed carcinogenecity of Cr(VI) depends on its ability to form oxoanions which cross the cell membrane by the anion transport system.[4] Since the dichromates are considered to be noncoordinating, the observed cytotoxicity of Cr(VI) compounds has been interpreted in terms of an uptake–reduction model proposed by Wetterhahn and co-workers,[1d,e] which takes into account the kinetic stability of Cr(III) complexes with DNA and considers the *in vivo* reduction of Cr(VI) species brought about by complexation with glutathione, a biologically prevalent tripeptide reductant.

We have recently confirmed,[5] using Raman spectroscopy as a probe of structure, that the complexation between the reduced glutathione and $Cr_2O_7^-$ takes place in aqueous solution whereupon a glutathione–Cr(VI) thioester is formed as previously proposed.[1e] Herein, we report the synthesis and structural characterization of a neutral complex [Mn₂(Cr₂O₇)₂(bpy)₄] (bpy = 2,2′-bipyridine), 1, involving an unprecedented bridging coordination of the dichromate ion via the terminal oxo atoms. While the chromate anion has been shown to coordinate in a bridging fashion,[6] there are no, as far as we are aware, structurally characterized instances of the dichromate coordination.[7] The structural parameters of the coordinated $Cr_2O_7^{2-}$ in 1 and the dichromate anions in crystalline $K_2Cr_2O_7$[8] are similar,[9] implying that the electron
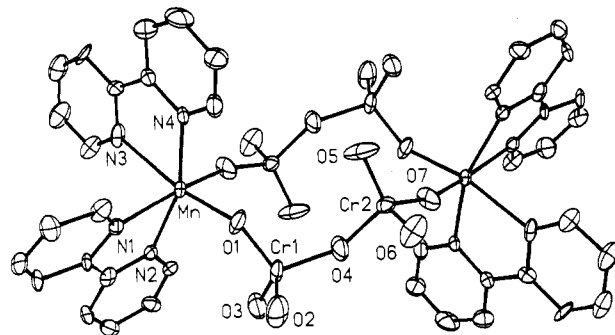

Figure 1. Structure and atom labeling scheme for **1**. Thermal ellipsoids are at 30% probability level. Selected bond distances (Å) and bond angles (deg) are as follows: Mn–O1 = 2.109(8), Mn–O7′ = 2.071(8), Mn–N1 = 2.237(9), Mn–N2 = 2.224(9), Mn–N3 = 2.322(10), Mn–N4 = 2.237-(9), Cr1–O1 = 1.612(7), Cr1–O2 = 1.562(9), Cr1–O3 = 1.615(9), Cr1–O4 = 1.752(8), Cr2–O5 = 1.558(9), Cr2–O6 = 1.584(9), Cr2–O7 = 1.651(8); O1–Mn–N1 = 90.3(3), O1–Mn–N2 = 104.3(3), N1–Mn–N2 = 72.8(3), O1–Mn–N3 = 160.4(4), N1–Mn–N3 = 86.1(3), N2–Mn–N3 = 93.04, O1–Mn–N4 = 89.3(3), N1–Mn–N4 = 94.4(3), N(2)–Mn–N4 = 161.1(3), N3–Mn–N4 = 71.8(4), O1–Mn–O7′ = 97.0(3), N1–Mn–O7′ = 165.1(3), N2–Mn–O7′ = 92.7(3), N3–Mn–O7′ = 91.2-(3), N4–Mn–O7′ = 98.7(3), O1–Cr1–O2 = 111.7(5), O1–Cr1–O3 = 110.1(4), O2–Cr1–O3 = 105.2(5), O1–Cr1–O4 = 110.4(4), O2–Cr1–O4 = 111.9(4), O3–Cr1–O4 = 107.5(4), O4–Cr2–O5 = 111.9(4), O4–Cr2–O6 = 107.3(5), O5–Cr2–O6 = 109.2(5), O4–Cr2–O7 = 107.1(4), O5–Cr2–O7 = 111.9(4), O6–Cr2–O7 = 109.3(4), Mn–O1–Cr1 = 135.5-(5), Cr1–O4–Cr2 = 136.1(5), Cr2–O7–Mn′ = 164.1(5).

donation from the oxo atom to Mn(II) is from an essentially nonbonding lone pair.

The structure of **1** (Figure 1) contains a center of inversion with two $\mu_{1,5}$-dichromato bridges between the two Mn(II) atoms, forming a 12-membered "polymetalloether" ring with a Mn⋯Mn separation of 7.880 Å and two terminal bpy ligands on each Mn completing the ligation.[10] The coordination about Mn is distorted octahedral, with bond angles ranging from 71.8 to 104.3°. The Mn–O bonds average 2.090 Å, which compares to those of the (μ-carboxylato)dimanganese(II) linkages.[11] The spatial arrangement of metals themselves (Figure 2) adopts an octahedral-like geometry, with nonbonded metal–metal distances ranging from 3.276 (across Cr–O–Cr) to 7.880 Å (Mn⋯Mn).

Surprisingly, there is a 29° difference in the two Mn–O–Cr angles (164.1(5)° at O1 vs 135.5(5)° at O7′), although the Mn–O bond lengths are not significantly different (Figure 1). As a result, there are two distinctive Mn⋯Cr distances, 3.686 and 3.449 Å, about each Mn. Exactly why this so is not clear. The Mn–N3 bond (2.322(10) Å) trans to Mn–O1 is longer than the other three Mn–N bonds (2.232(9) Å, average), which may indicate a trans effect that is not present with the Mn–O7 counterpart. The widening of angle at the oxo atom implies a

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(7) Complex 1 was synthesized by mixing 0.724 g (2 mmol) of Mn-(ClO₄)₂·6H₂O dissolved in 40 mL of water with 0.312 g (2 mmol) of bpy in 20 mL of acetone to give a yellow solution, followed by addition of 0.588 g (2 mmol) of K₂Cr₂O₇ in 40 mL of water to give an orange solution. After 10 min, blackish microcrystals of **1** precipitated, which were filtered and washed with copious amounts of cold water. Yield: 1.98 g (84 %). Compound 1 is insoluble in any of the common solvents, and hence, its X-ray quality crystals were obtained by treating a solution of 2 mmol of Mn(ClO₄)₂·6H₂O in 500 mL of water with 2 mmol of the ligand (in 20 mL of acetone), followed by adding 0.1 g of K₂Cr₂O₇ in 500 mL of water and allowing the reaction mixture to stand overnight at room temperature. Anal. Calcd for C₄₀H₃₂N₈O₁₄Mn₂Cr₄: C, 41.16; H, 2.74; N, 9.60. Found: C, 40.01; H, 2.50; N, 9.04.

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(9) The Cr–O–Cr angles are larger in **1** (136.1(5)°) than those in the Cr₂O₇²⁻ ions in triclinic K₂Cr₂O₇ (124.0(1) and 127.6(2)°).[8]

(10) X-ray data: An orange-brown crystal having the dimensions 0.12 × 0.20 × 0.22 mm was mounted on a Nicolet R3m/V diffractometer. The structure was determined at –50 °C using Mo Kα radiation. Crystal data: C₄₀H₃₂N₈O₁₄Cr₄Mn₂; space group *Pcba* (orthorhombic), with *a* = 16.376(4) Å, *b* = 16.488(4) Å, *c* = 16.659(5) Å, *V* = 4498 Å³, *Z* = 4, *R* = 0.056, and R_w = 0.041 for 1469 observed ($I > 3\sigma(I)$) reflections. Data collection was in the range $4 \le 2\theta \le 45°$. The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares refinement.

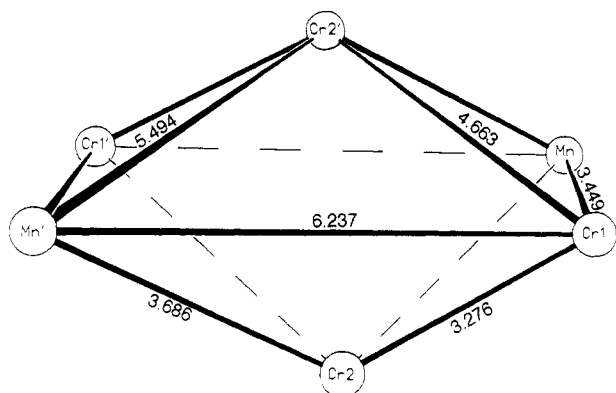(11) Bossek, U.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chim. Acta.* **1989**, *165*, 123.

Figure 2. Schematic diagram of the polymetal core in **1** showing nonbonded metal–metal distances (Å).

larger sp than sp^2 orbital character in the σ-bonding, which should result in stronger metal–oxygen bonds, but the bond length data do not show any appreciable variations. Also, there are no H atoms (from bpy) within the van der Waals radii of the oxo atoms which, by providing a preferential interaction via H-bonding, could potentially alter the Mn–O–Cr angles. Thus, we speculate that the differences might be simply due to the steric requirements of forming this unusual 12-membered ring.

An interesting feature of compound **1** is the formation of an oxo bridge between two different metals with highly disparate valences, Mn(II) and Cr(VI). Apparently, the resultant "mixed-valent" heterobimetallic Mn(II)–O–Cr(VI) system represents a substantial stabilization relative to an intermetal electron-transfer excited state, most probably due to a large amount of reorganizational energy required to break the d^5 and d^0 stable configurations on Mn^{2+} and Cr^{6+}, respectively. These energetic constrains should be responsible for the fact that Mn^{2+} is not oxidized under the conditions at which complex **1** is formed.[7] The strongly valence-trapped nature of this core, which is reflected structurally by the Cr–O bond (1.631(8) Å, average) being substantially shorter than the Mn–O bond (2.090(8) Å, average), also represents a highly unsymmetrical Mn–O–Cr triatomic oscillator to the extent that its individual bonds should vibrate as a pair of essentially independent local diatomic oscillators. Indeed, the Raman spectra of **1** show only vibrations associated with the dichromate and the bpy subunits of the complex.

Figure 3 compares the 568.2-nm excited Raman spectra of solid [Mn$_2$(Cr$_2$O$_7$)$_2$(bpy)$_4$] (**1**) and K$_2$Cr$_2$O$_7$, showing that both spectra are totally dominated by bands arising from the terminal CrO$_3$ group vibrations and the skeletal modes of the Cr–O–Cr bridges of the dichromate moieties.[5,12] The strongest is the totally symmetric CrO$_3$ stretching mode, ν_s(CrO$_3$), which in solid K$_2$Cr$_2$O$_7$ appears as a doublet centered at ~910 cm^{-1} due to nonequivalent geometry of the Cr$_2$O$_7{}^{2-}$ ions in crystals.[8] A single polarized peak (Figure 3, inset) is seen in this region at 887 cm^{-1} in the spectrum of **1** and is therefore assigned to ν_s(CrO$_3$), its shift to lower frequency indicating some weakening of the Cr–O bonds upon dichromate binding to Mn. Similarly, the ν_{as}(CrO$_3$) asymmetric stretches (~885 and 920–970 cm^{-1}) and the δ(CrO$_3$) bendings modes (360–390 cm^{-1}) of K$_2$Cr$_2$O$_7$ are perturbed and occur at lower frequencies in **1**. The two stretching and one bending vibrations of the Cr–O–Cr bridge have been previously assigned in K$_2$Cr$_2$O$_7$ to bands near 560 (ν_s(CrOCr)), 750 (ν_{as}(CrOCr)), and 220 cm^{-1} (δ(CrOCr)),[5,12] and ν_s(CrOCr) and δ-(CrOCr) are located near 527 and 230 cm^{-1}, respectively, in the spectrum of **1**.

In conclusion, the first complex containing a structurally characterized $\mu_{1,5}$-coordination of dichromate has been synthe-
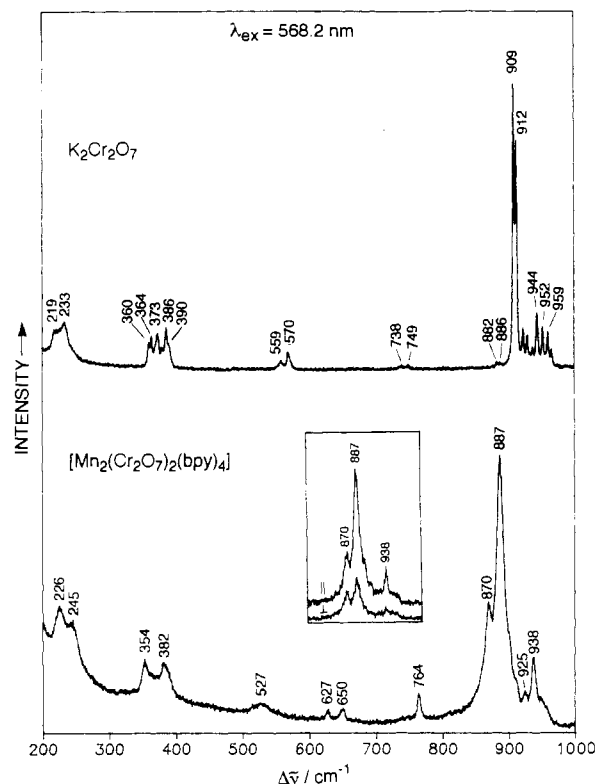

Figure 3. Solid state (KCl pellet) RR spectra of **1** (bottom) and K$_2$Cr$_2$O$_7$ (top) at room temperature. Conditions: frontscattering directly off the surface of spinning KCl pellets; 568.2-nm excitation wavelength from Coherent K-2 Kr$^+$ ion laser; laser power, 200 mW for **1** and 100 mW for K$_2$Cr$_2$O$_7$; 4 cm^{-1} slit widths; 4 scans, 1-s integration time each at 0.5-cm^{-1} increments. Inset shows parallel (∥) and perpendicular (⊥) components of the Raman spectrum of **1**.

sized. The *in vivo* reduction of dichromate with glutathione is slow,[13] and in view of the trace concentrations of divalent transition metals present *in vivo*, the formation of species similar to complex **1** may be envisioned with N-donor residues from nucleotide fragments. A $\mu_{1,5}$-coordination has been proposed to be involved in the dephosphorylation process with the structurally analogous diphosphate (pyrophosphate) and divalent transition metals with the N-6,N-7 site of adenine residue coordinated to divalent metals.[14] The complexing ability of Cr$_2$O$_7{}^{2-}$ also provides an insight into the mechanistic pathway of dichromate oxidations of various substrates, which might consist of an initial step involving its coordination of the electrophillic sites on the substrate via the terminal oxo atoms, followed by an oxo atom transfer step. For example, the oxidation of aldehydes to corresponding carboxylic acids with MnO$_4{}^-$ or Cr$_2$O$_7{}^{2-}$ as oxidant have been proposed to proceed via an oxo atom transfer.[15] Thus, Cr(VI) physiology and its toxicity may involve inter alia such processes as an oxidative damage to biomolecules caused by the strong oxidizing power of dichromate (Cr(VI)/Cr(III), E^0 = 1.33 V) and a possible coordination of Cr(VI) via Cr–oxy ether formation with subsequent reduction to the kinetically inert Cr(III).

Supplementary Material Available: Text describing the X-ray crystal structure determination, tables of X-ray crystallographic data atomic coordinates, thermal parameters, bond distances and angles, and least-squares planes, and figures showing the atom numbering scheme and unit cell packing for compound **1** (15 pages).

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