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Mixed Carboxylate-Bridged Dimanganese(II/III) Compounds Prepared by an O_2-Dependent Oxidative Cleavage of Ketones

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The structure of an O_2-sensitive Mn(II)–Mn(II) complex with an unsymmetrical perchlorate bridge is reported. This complex promotes an O_2-dependent oxidative cleavage of ketones giving mixed carboxylate complexes.

Due to their low cost and toxicity, manganese coordination compounds are growing in their importance as homogeneous catalysts in oxidation reactions.[1] Mn(III)−salen[2] and dimanganese μ-oxo-di-μ-acetato complexes[3] catalyze asymmetric alkene epoxidation using oxygen atom sources, but not using dioxygen itself. The oxo-bridged dimanganese(IV) compound $[(tacn)Mn(\mu\text{-}O)_3Mn(tacn)]^{2+}$ has been shown to be useful in bleaching reagents.[4] We report here the noncatalytic oxidation of ketones which occurs under mild conditions in the presence of a dimanganese complex and air.

The white $[Mn_2(bpbp)(ClO_4)(THF)_2](ClO_4)_2{\cdot}H_2O$ (**1**) was obtained from the reaction of Hbpbp (Hbpbp = 2,6-bis((*N*,*N*′-bis-(2-picolyl)amino)-methyl)-4-tertbutylphenol) with 1 equiv of triethylamine and 2 equiv of manganese(II) perchlorate in THF under dinitrogen. Recrystallization of **1** in methylene dichloride (containing H_2O ~ 50 ppm) gave $[Mn_2(bpbp)(ClO_4)(H_2O)_2](ClO_4)_2{\cdot}H_2O$ (**2**). Elemental analyses are consistent with the formulations of **1** and **2**. Solid samples of the $Mn(II)_2$ complexes **1** and **2** turn dark brown/black within hours when exposed to air. The structure[5] of the cation of **2** is shown in Figure 1. The dimanganese(II) site is occupied by two waters and a perchlorate anion which spans the metal atoms unsymmetrically, with the two $Mn{-}OClO_3$ bonds differing by 0.318(1) Å. A smaller difference is seen in the two $Mn{-}OH_2$ bonds (0.024(1) Å) and in the remaining distances to the $bpbp^-$ donor atoms. Compound **2** is the first example of a perchlorate-bridged dimanganese compound. Indeed, only a few μ-1,2-perchlorate bridged bimetallic complexes, mainly of copper and silver, are known.[6] ESI mass spectra of **1** and **2** indicate analogous coordination modes of the inner sphere perchlorate anions in both products (*m/z* 390.1, $[Mn_2(bpbp)(ClO_4)]^{2+}$, 100%; *m/z* 879.2, $\{[Mn_2(bpbp)(ClO_4)](ClO_4)\}^+$, ~50%).

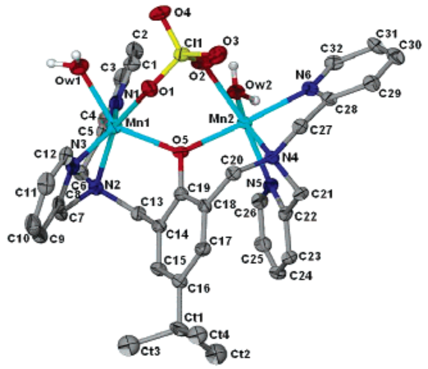

Figure 1. X-ray crystal structure of the cation in **2**. Important metric parameters in Å: Mn1···Mn2, 3.805(1); Mn1−O5, 2.105(1); Mn2−O5, 2.111(1); Mn1−Ow1, 2.157(1); Mn2−Ow2, 2.133(1); Mn1−O1, 2.652(1); Mn2−O2, 2.334(1).

Acetone solutions of **1** standing in air darken within 3 h. A uniform dark green crystalline product was recovered from the open flask after standing for several days. The crystals were very weakly diffracting, and X-ray diffraction analysis did not give a fully conclusive identification of the carboxylate-like auxiliary ligands in the $Mn_2(bpbp)$-based product.[7] Bands at 1604 and 1481 cm^{-1} in the infrared spectrum are typical of syn-bridging carboxylate ligands (ν_{as}(OCO) and ν_s(OCO), respectively). Using ESI mass spectrometry, the product was identified to be a mixture of bis-formate/acetate-bridged Mn(II)−Mn(III) compounds. Figure 2 shows an ESI

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(2) Zhang, W.; Loebach, J. L.; Wilson, S. B.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801−2803.

(3) Brinksma, J.; Hage, R.; Kerschner, J.; Feringa, B. L. *Chem. Commun.* **2000**, 537−538.

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(5) White crystals of $[Mn_2(bpbp)(ClO_4)(H_2O)_2](ClO_4)_2{\cdot}H_2O$ (**2**) are orthorhombic $P2_12_12_1$ (No. 19), Z = 4, $a = 10.2237(2)$ Å, $b = 19.7900(4)$ Å, $c = 21.1923(4)$ Å. $T = 120$ K. λ(Mo Kα) = 0.710 73 nm. A total number of 54 873 reflections were collected, of which 6235 were unique (5994 with $I > 2\sigma(I)$). $R_1 = 0.0339$ ($I > 2\sigma(I)$) and $wR_2 = 0.0814$ (all data).

(6) See for example: O‘Connor, C. J.; Firmin, D.; Pant, A. K.; Babu, B. R.; Stevens, E. D. *Inorg. Chem.* **1986**, *25*, 2300−2307. Tani, K.; Yamagata, T.; Tatsuno, Y.; Saito, T.; Yamagata, Y.; Yasuoka, N. *Chem. Commun.* **1986**, 494−495. Rodesiler, P. F.; Amma, E. L. *Inorg. Chem.* **1972**, *11*, 388−395. Rao, C. P.; Rao, A. M.; Rao, C. N. R. *Inorg. Chem.* **1984**, *23*, 2080−2085.

10.1021/ic0498135 CCC: $27.50

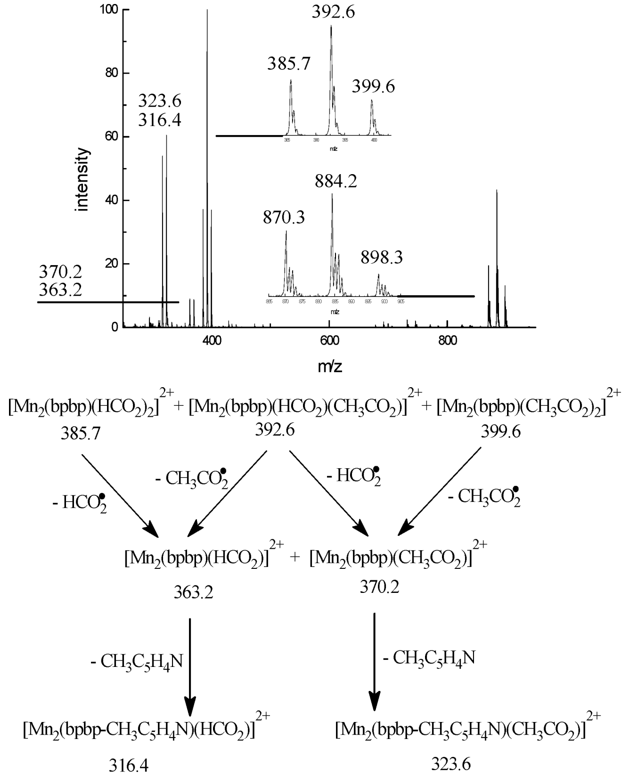

Figure 2. ESI mass spectrum of acetone-derived product, in nitromethane solution (tube lens 80 V), with assignments and fragmentation pathways. The singly charged perchlorate ions pairs *m*/*z* 870.3, 884.2, and 898.3 are not included in the chart.

mass spectrum of one single crystal. Two groups of three peaks are observed: doubly charged ions centered at *m*/*z* 392.6 and the corresponding singly charged perchlorate ion pairs centered at *m*/*z* 884.2. Furthermore, as the tube lens potential is increased, two sets of signal pairs, 14 mass units apart, grow in. The spectrum in Figure 2 was recorded at high tube lens potential and thus shows these daughter ions. Through the use of tandem MS/MS and selective collision induced dissociation (CID), we have identified these latter ions as daughter ions of the three ions centered at *m*/*z* 392.6. The doubly charged ions at *m*/*z* 385.7, 399.6, and 392.6 can be assigned to a bis-formate, bis-acetate, and a formate-acetate-bridged complex, respectively, i.e., $[Mn_2(bpbp)(HCO_2)_2]^{2+}$, $[Mn_2(bpbp)(CH_3CO_2)_2]^{2+}$, and $[Mn_2(bpbp)(HCO_2)(CH_3CO_2)]^{2+}$. Calculated isotopic patterns give accurate fits. The daughter ions at *m*/*z* 363.2 and 370.2 are due to acetate/formate radical loss to give $[Mn_2(bpbp)(HCO_2)]^{2+}$ and $[Mn_2(bpbp)(CH_3CO_2)]^{2+}$, respectively, and hence are consistent with the appearance of two daughter ions from the three parent ions. The more intense pair of peaks located 93 mass units below these latter two peaks corresponds to CID of a ligand methylpyridyl arm from the mono-formate and mono-acetate complex ions, respectively. Furthermore, the selection and CID of the formate-containing ions resulted in the loss of the mass equivalent of CO_2 (not shown); this does not occur for the acetate containing ions.

The only feasible source of the formate and acetate bridging groups in the mixture of products obtained from the reaction described above is from the solvent used, acetone. We suggest that O_2-dependent oxidative cleavage of acetone has generated the appropriate one carbon atom and two carbon atom precursors for the formate and acetate groups of the product.

Repetition of the experiment using diethyl ketone and ^{13}C-labeled acetone ($(^{13}CH_3)_2CO$) as solvent/substrate furnishes further support for the dimanganese-complex-promoted ketone oxidation. Solid products were isolated from both reactions. The ESI mass spectra of the diethyl-ketone-derived product show a mixture of acetate and propionate-bridged complexes completely homologous to the acetone-derived product,[9] proving unequivocally that the source of the carboxylate bridging groups is the ketone solvent, and not, for example, CO_2. The ^{13}C-labeled acetone-derived product shows the appropriate isotopomers. A CID experiment of the doubly charged ion now at *m*/*z* 400.6 ($[Mn_2(bpbp)(CH_3CO_2)^*{}_2]^{2+}$)[10] results in a dissociation of labeled acetate showing that it is acetone-derived since this was the only source of ^{13}C.[9]

While the products and reproducibility of this unusual ketone oxidation reaction are beyond doubt, we are unable to unravel any mechanistic details. The significant asymmetric coordination of the bridging perchlorate anion shown by the X-ray structure of **2** leads to speculation that an interaction of the bimetallic site of a labile Mn(II)−Mn(II) complex of $bpbp^-$ with O_2 may also be asymmetric, i.e., centered at only one of the manganese ions, after partial or full decoordination of the bridging perchlorate ligand. A "-(bpbp)Mn_2O_2" species might bind and react with the ketone to form an alkylperoxide parallel to noncatalyzed autoxidations.[11] Alternatively, a "(bpbp)Mn_2O_2" species might be the precursor for a "manganyl" species produced by cleavage of the O−O bond. Oxidative acetone C−C cleavage would give the appropriate one and two carbon atom precursors

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(7) Green crystals of $[Mn_2(bpbp)(RCO_2)_2](ClO_4)_2$, R = H/$CH_3$, are monoclinic $P2_1/n$ (No. 14), $Z = 4$, $a = 12.271(2)$ Å, $b = 22.127(5)$ Å, $c = 16.473(3)$ Å, $\beta = 95.599(5)°$. $T = 120$ K. λ(Mo Kα) = 0.710 73 nm. A total number of 39 803 reflections were collected, of which 12 906 were unique (2076 with $I > 2\sigma(I)$). $R_1 = 0.097$ ($I > 2\sigma(I)$) and $wR_2 = 0.088$ ($I > 2\sigma(I)$).The structure was modelled as mixed-valent $[Mn_2(bpbp)(CH_3CO_2)_2](ClO_4)_2{\cdot}CH_3CN$, and all atoms were refined isotropically. Only reflections with $I > 2\sigma(I)$ were used in the refinement which gave a data-to-parameter ratio of 7.8. The electron density of the methyl moiety of the acetate group(s) is without doubt; however, the quality of the data is not sufficient for determining the occupation of a methyl carbon atom/hydrogen atom of an acetate vs formate group. Thus, as indicated by the mass spectrum run after dissolution of a *single* crystal, a cocrystallized mixture of all the three compounds is implied. In our experience, Mn(II)−Mn(III) compounds of phenolato-hinged dinucleating ligands containing two identical carboxylate bridges, prepared from reactions containing carboxylate ions,[8] form well-diffracting crystals, in contrast to the acetone-derived products we have prepared.

(8) For example: Diril, H.; Chang, H.-R.; Nilges, M. J.; Zhang, X.; Larsen, S. K.; Potenza, J. A.; Schugar, H. J.; Isied, S. S.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1989**, *111*, 5102−5214. M. Ghiladi, M.; McKenzie, C. J.; Meier, A.; Powell, A. K.; Wocadlo, S. *J. Chem. Soc., Dalton Trans.* **1997**, 4010−4018.

(9) See Supporting Information.

(10) The *m*/*z* value indicates the ion contains two ^{13}C atoms; however, we cannot assign these to the methyl or carboxylate carbon atoms of the acetate moiety from this information.

(11) Sharp, D. B.; Patton, L. W.; Whitcomb, S. E. *J. Am. Chem. Soc.* **1951**, *73*, 5600−5603. Sharp, D. B.; Whitcomb, S. E.; Patton, L. W.; Moorhead, A. D. *J. Am. Chem. Soc.* **1952**, *74*, 1802−1803.

for the formate and acetate groups found in the products. The amount of water in reactions appears to be crucial: No solid product was obtained if water was deliberately added. Water is expected to compete strongly with acetone and dioxygen for coordination to manganese, and significant water concentrations may inhibit the reaction. In addition to the novelty of this reaction, and the starting perchlorate-bridged Mn(II)$_2$ complex, we are unaware of other methods for generating mixed-carboxylate bridged binuclear compounds, like the acetate−formate Mn(II)−Mn(III) complex generated using the acetone oxidation pathway.

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Supporting Information Available: ESI mass spectra of ^{13}C-labeled product and diethyl-ketone-derived product. Crystallographic data in CIF format for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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