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Supplementary Material Available: Listing of physical properties of compounds 4-9 (3 pages). Ordering information is given on any current masthead page.

Preparation and Characterization of a Compound Containing the Octachloroditungstate (W^4-W) Ion, $[W_2Cl_8]^{4-}$

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Rapid development of the chemistry of the quadruply bonded Mo_2^{4+} unit¹ has not been followed by comparable progress in the chemistry of the isoelectronic W_2^{4+} unit. The reasons for this lack of close homology have only recently begun to emerge² and have interesting implications in the broader understanding of transition-metal chemistry. While the chemistry of W_2^{4+} has not been totally lacking and there are even a few classes of compounds, such as the $W_2(2\text{-oxypyridine})_4$ ³ and $W_2Cl_4(PR_3)_4$ ⁴ types, with stability comparable to that of their molybdenum analogues, the truly prototypal species $W_2(O_2CR)_4$ and $[W_2Cl_8]^{4-}$ have been extraordinarily elusive. Methods for preparing compounds of the former type have recently been found,⁵ but until now, no compound containing the simple $[W_2Cl_8]^{4-}$ ion has been proven to exist.^{6,7} That lacuna has now been filled.

During the preparation^{8a} of the $W_2Cl_4(PR_3)_4$ compounds by the Na/Hg reduction of $(WCl_4)_x$ in THF in the presence of PR_3 , it was noticed that in the absence of PR_3 a one-electron reduction of $(WCl_4)_x$ yielded $W_2Cl_6(THF)_4$, and a subsequent one-electron reduction (per W) of isolated $W_2Cl_6(THF)_4$ yielded an intense blue solution. We have now been able to isolate a blue powder from this solution that has the composition $Na_4(THF)_xW_2Cl_8$ (x is variable, usually 2-4).^{8,9} A THF solution of $Na_4W_2Cl_8$ begins

(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; Chapter 3.

(2) Cotton, F. A.; Hubbard, J. L.; Lichtenberger, D. L.; Shim, I. *J. Am. Chem. Soc.* **1982**, *104*, 679.

(3) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

(4) (a) Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430.

(b) Cotton, F. A.; Felthouse, T. R.; Lay, D. G. *Ibid.* **1980**, *102*, 1431.

(5) Sattelberger, A. P.; McLaughlin, K. W.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2880.

(6) An SCF-X α -SW calculation⁷ in 1977 on the $[W_2Cl_8]^{4-}$ ion (with an estimated W-W distance of 2.20 Å) led to the following conclusions: (1) There is "no indication that this ion should be incapable of existence or even particularly unstable". (2) Relative to $[Mo_2Cl_8]^{4-}$ and $[Re_2Cl_8]^{2-}$, "the destabilization of the δ orbital in $[W_2Cl_8]^{4-}$ should lead to oxidation or oxidative addition reactions involving the quadruple bond. This would account for ... the ... small number of W-W quadruply bonded systems" isolated up to that time. This was the first statement of the now accepted view as to why quadruply bonded W_2^{4+} compounds are frequently less stable² than their molybdenum analogues, and it provides the basis for designing synthetic procedures such as the present one that allow the isolation of such compounds.

(7) Cotton, F. A.; Kalbacher, B. *J. Inorg. Chem.* **1977**, *16*, 2386.

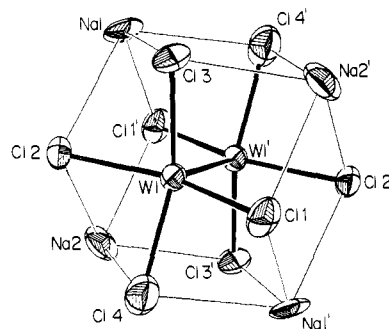


Figure 1. One of the two $[W_2Cl_8]^{4-}(Na^+)_4$ groups in the crystal of $Na_4(TMEDA)_4W_2Cl_8$. This one resides at the unit cell origin while the other, which is substantially identical, resides at the unit cell center. An inversion center lies at the midpoint of the W^4-W bond. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 30% of the electron density.

Table I. Dimensions of the $[W_2Cl_8]^{4-}$ Ions

Distances (Å)			
W(1)-W(1)'	2.259 (1) ^a	W(2)-Cl(5)	2.417 (3)
W(2)-W(2)'	2.254 (1)	-Cl(6)	2.437 (3)
mean W-W	2.257 [3] ^a	-Cl(7)	2.426 (3)
		-Cl(8)	2.446 (3)
W(1)-Cl(1)	2.426 (3)	mean W-Cl	2.429 [5]
-Cl(2)	2.421 (3)		
-Cl(3)	2.450 (4)		
-Cl(4)	2.412 (4)		
Angles (deg)			
W(1)'-W(1)-Cl(1)	103.58 (9)	W(2)'-W(2)-Cl(5)	104.27 (9)
-Cl(2)	103.12 (9)	-Cl(6)	103.6 (1)
-Cl(3)	103.6 (1)	-Cl(7)	103.70 (9)
-Cl(4)	103.9 (1)	-Cl(8)	103.13 (9)
		mean W-W-Cl	103.5 [1]

^a A number in parentheses is the estimated standard deviation of that individual value. A number in brackets is equal to $[\sum n_i \Delta_i^2 / n(n-1)]^{1/2}$, where Δ_i is the deviation of the i th value in a set of n such values from the arithmetic mean.

to deposit a black precipitate after a few minutes at 25 °C, and the solution eventually becomes colorless. At -20 °C the visible spectrum of a THF solution of $Na_4W_2Cl_8$ shows a peak at 600 nm with an ϵ of ~ 1600 , consistent with this compound being a sodium salt of $[W_2Cl_8]^{4-}$.^{10,11}

Initial attempts to isolate crystalline compounds containing the $[W_2Cl_8]^{4-}$ ion revealed that both thermal instability and sensitivity to oxidants (including coordinated solvents) posed problems. However, crystals of a tetramethylethylenediamine (TMEDA) derivative can be prepared $\sim 50\%$ of the time in the following manner. After the mixture of $Na_4W_2Cl_8$ and black decomposition product⁸ is extracted with a minimal amount of cold THF, approximately 5 equiv of TMEDA are added, and the solution is cooled to ~ -30 °C. After 1 day blue crystals have formed, usually mixed with some green microcrystalline decomposition product.

(8) Filtration of the intense blue solution through Celite followed by removal of the THF in vacuo leaves a blue powder mixed with an insoluble, finely divided black material. Extraction with minimal THF followed by filtration and removal of the THF in vacuo yields a blue powder that is virtually free of the black material. After the sample was pumped on at ~ 0.1 mmHg for 1 h, it had the approximate composition $Na_4(THF)_2W_2Cl_8$.^{9a} Another sample exposed to a high vacuum (< 1 μ mHg) at 25 °C overnight had the approximate composition $Na_4(THF)W_2Cl_8$.^{9b} We believe that the maximum possible equivalents of THF is 8 (i.e., $Na_4(THF)_8W_2Cl_8$; cf. $Na_4(TMEDA)_4W_2Cl_8$). The yield of $Na_4(THF)_xW_2Cl_8$ is limited because of the deficiency of chloride, but if one assumes that $2W_2Cl_6 + 2Na \rightarrow 0.5Na_4W_2Cl_8 + 2^+WCl_2$, then the yields are close to the theoretical 50%.

(9) (a) Anal. Calcd for $WC_4H_8Cl_4Na_2O$: C, 10.83; H, 1.82; Cl, 31.96. Found: C, 9.03; H, 1.57; Cl, 31.06. (b) Anal. Calcd for $WC_2H_4Cl_4Na_2O_{0.5}$: C, 5.89; H, 0.98; Cl, 34.78; Na, 11.28. Found: C, 4.96; H, 0.84; Cl, 33.83; Na, 11.80.

(10) The peak position is consistent with that for $[Mo_2Cl_8]^{4-}$ of ca. 480 nm in view of the correlation of Sattelberger and Fackler¹¹ for the series of $[M_2(CH_3)_2]^{4-}$ ions.

(11) Sattelberger, A. P.; Fackler, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 1258.

The blue crystals dissolve in THF to give a blue solution which turns green in ~ 10 min. No homogeneous green product has yet been isolated. The blue crystals were shown by X-ray crystallography to be $\text{Na}_4(\text{TMEDA})_4\text{W}_2\text{Cl}_8$; in THF solution at 0°C the 600-nm band with ϵ 1600 was observed, and a satisfactory elemental analysis was obtained.¹²

Of 20 well-formed, single, blue-green, dichroic crystals, mounted and sealed in capillaries under nitrogen, only two were sufficiently stable (ca. 50% loss of intensity during ca. 48 h of exposure to X-rays) to provide sets of diffraction data. With these data the structure was solved and refined.¹³⁻¹⁵ The two independent, centrosymmetric $[\text{W}_2\text{Cl}_8]^{4-}$ ions are essentially equivalent. The one residing at the origin is depicted, along with its neighboring Na^+ ions, in Figure 1. The key dimensions are listed in Table I. These may be compared with corresponding dimensions of the $[\text{Mo}_2\text{Cl}_8]^{4-}$ ion,¹⁶ in which have been found the following: Mo-Mo, 2.134-2.150 Å; Mo-Cl, 2.45-2.47 Å (mean values); Mo'-Mo-Cl, $105.0 \pm 0.2^\circ$. The W-W distance is thus about 0.11-0.13 Å longer than the Mo-Mo bond and the mean W-Cl bond is slightly (ca. 0.02 Å) shorter than the Mo-Cl bond, both of which were anticipated in an earlier discussion.¹⁷

As indicated in Figure 1 the sodium ions are closely associated with the $[\text{W}_2\text{Cl}_8]^{4-}$ ions so that one Na^+ ion caps each vertical face of the rectangular prism having on its 4-fold axis the W_2^{4+} unit.¹⁸ The $\text{Na}^+\cdots\text{Cl}$ distances range from 2.815 to 2.902 Å, with a mean value of 2.85 [1] Å. One TMEDA molecule is coordinated through both N atoms to each sodium ion, with Na-N distances ranging from 2.47 to 2.59 Å and having a mean value of 2.52 [2] Å.

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Registry No. WCl_4 , 13470-13-8; $\text{W}_2\text{Cl}_6(\text{THF})_4$, 77479-88-0; $\text{Na}_4\text{W}_2\text{Cl}_8$, 83232-08-0; $\text{Na}_4(\text{TMEDA})_4\text{W}_2\text{Cl}_8$, 83232-09-1.

Supplementary Material Available: Table S1, crystallographic data and data collection parameters; Table S2, positional parameters and their estimated standard deviations for $\text{Na}_4(\text{TME-}$

$\text{DA})_4\text{W}_2\text{Cl}_8$; Table S3, thermal parameters (B 's) and their estimated standard deviations for $\text{Na}_4(\text{TMEDA})_4\text{W}_2\text{Cl}_8$; Table S4, observed and calculated structure factors for $\text{Na}_4(\text{TME-DA})_4\text{W}_2\text{Cl}_8$; Table S5, bond distances and bond angles in $\text{Na}_4(\text{TMEDA})_4\text{W}_2\text{Cl}_8$ (37 pages). Ordering information is given on any current masthead page.

Novel Catalytic Oxidations of Terminal Olefins by Cobalt(II)-Schiff Base Complexes

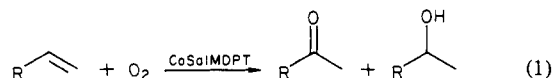
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We report the selective catalytic oxidation of terminal olefins by molecular oxygen to the corresponding 2-ketone and 2-alcohol by using CoSalMDPT^1 complexes (reaction 1). Experiments were



conducted to rule out the possibility of a free radical initiated autoxidation mechanism. The results of these experiments and further details concerning this novel reaction are reported here.

The oxidation of linear olefins by O_2 to produce ketones has been reported for a number of homogeneous transition-metal catalysts.² The $\text{RhCl}_3/\text{Cu}(\text{II})$ catalyst³ is particularly efficient and selective. Palladium(II)-copper(II) catalyst mixtures readily oxidize linear olefins via the well-known Wacker mechanism.⁴ Attempts at oxidizing linear olefins with first-row transition-metal catalysts usually have resulted in reaction products typical of autoxidations,⁵ which include a high degree of oxidized polymer as well as cleavage products.

CoSalMDPT catalyzes the oxidation of terminal olefins (for example, 1-hexene, 3-methyl-1-hexene, styrene, and 3-buten-1-ol) to the methyl ketone and 2-alcohol. The olefin substrate chosen to determine additional reaction parameters⁶ was 1-hexene. A plot of the production of 2-hexanone at various temperatures is shown in Figure 1. The O_2 uptake correlates with the amount of 2-hexanone and 2-hexanol produced, indicating a nearly stoichiometric oxidation of 1-hexene. Polymer formation is not observed. When ethanol is used as solvent, acetaldehyde is observed in the final reaction mixture. A study of the reaction rates shows an approximate first-order dependence on cobalt concentration and 1-hexene concentration (experiments 1-4 in Table I). A zero-order dependence on O_2 pressure is observed in the 30-90-psi range studied.

In order to understand metal-catalyzed oxidations, it is always necessary to consider the possibility of the very common free radical initiated autoxidation⁷ mechanism. Thus, upon discovery

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(1) CoSalMDPT = cobalt(II) bis(salicylidene- γ -iminopropyl)methylamine.

(2) Sheldon, R. A.; Kochi, J. K. *Adv. Catal.* **1976**, *25*, 272.

(3) Mimoun, H.; Perez Machirant, M. M.; Sfeé de Roch, I. *J. Am. Chem. Soc.* **1978**, *100*, 5437.

(4) Tsuji, J.; Shimizu, I.; Yamamoto, K. *Tetrahedron Lett.* **1976**, *34*, 2975.

(5) Lyons, J. E. *ACS Adv. Chem. Ser.* **1974**, *132*, 64.

(6) All catalytic reactions were conducted in Parr pressure bottles submerged in a temperature-controlled oil bath. Besides monitoring oxygen consumption, 0.2 mL aliquots of the reaction mixture were withdrawn at various time intervals and analyzed by GC. 2-Octanone was added as an internal standard. The concentration of 2-hexanone plus 2-hexanol was calculated from a calibration curve.

(12) Anal. Calcd for $\text{WC}_{12}\text{H}_{32}\text{Cl}_4\text{Na}_2\text{N}_4$: C, 23.86; H, 5.34; N, 9.28; Cl, 23.48. Found: C, 23.77; H, 5.30; N, 8.96; Cl, 23.09.

(13) Data were collected on an Enraf-Nonius CAD-4 diffractometer at 22°C following conventional procedures.¹⁴ The space group is $P\bar{1}$ with unit cell dimensions $a = 11.907$ (3) Å, $b = 15.462$ (2) Å, $c = 13.640$ (1) Å, $\alpha = 89.50$ (1)°, $\beta = 98.80$ (1)°, $\gamma = 90.30$ (2)°, $V = 2482$ (1) Å³, $Z = 2$. Full details of the data collection and refinement are available in Table S1 (supplementary material). Data were corrected for Lorentz and polarization effects and for absorption by the empirical ψ -scan method. Data for the two crystals were merged by using approximately 500 equivalent reflections by the method of Rae and Blake.¹⁵ All calculations were performed on a PDP 11/60 computer at B. A. Frenz and Associates, College Station, TX. The positions of the two independent tungsten atoms were obtained from a Patterson function and indicate that $[\text{W}_2\text{Cl}_8]^{4-}$ units are located on inversion centers at $0,0,0$ and $1/2, 1/2, 1/2$. All other non-hydrogen atoms were found in a series of alternating difference maps and least-squares refinements. In the final refinement cycles hydrogen atoms were omitted, carbon atoms were refined isotropically, and all other atoms were refined anisotropically, giving final residuals of $R_1 = 0.076$ and $R_2 = 0.095$, and the largest shift/error ratio in any parameter was 0.04. The only peaks above random noise in the final difference map were three within <1 Å of the tungsten atoms. Several attempts to refine the structure in monoclinic space groups gave inferior results. The final positional and thermal parameters and a list of structure factors are available as supplementary material, Tables S2, S3, and S4, respectively.

(14) See, for example: Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S.; Kudarski, R. *Inorg. Chem.* **1982**, *21*, 1656.

(15) Rae, A. D.; Blake, A. B. *Acta Crystallogr.* **1966**, *20*, 586.

(16) Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 7, 2698; **1970**, *9*, 346.

(17) Cotton, F. A.; Extime, M. W.; Felthouse, T. R.; Kolthammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040.

(18) In this structure no evidence was found for any significant ($>1\%$) secondary orientation of the W_2^{4+} unit in the Cl_8 quasi-cube, though this sort of disorder is rather common (cf. ref 1, pp 344-347) in such compounds. Perhaps the proximity of the Na^+ ions on all four vertical faces repels the positively charged tungsten atoms from the positions they would have in one of the secondary orientations.