Inorganica Chimica Acta, 76 (1983) L33–L34

A New Type of Di-μ-Sulphido Bridge with Tungsten(V): Preparation and Structure of the Di-μ-Sulphido-bis-(dichloro-oxo-tungsten(V)) Anion

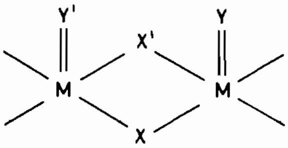
MICHAEL G. B. DREW, ELIZABETH M. PAGE and DAVID A. RICE

Department of Chemistry, The University, Whiteknights, Reading, RG6 2AD, U.K.

Received July 22, 1982

There is considerable current interest in the synthesis and structural characterisation of binuclear species containing close metal–metal contacts.

Surprisingly, in spite of extensive work in this field few compounds have been characterised in which there is (at least in a formal sense) a single W–W bond. This paucity of information is in marked contrast to the situation with molybdenum(V) where many examples of species based upon the fragment (1) are known [1–4].



Only two tungsten compounds having the moiety (1) have been fully characterised. in $[W_2O_4(EDTA)]^{2-}$ [5, 6] (EDTA = ethylenediaminetetraacetate) both tungsten atoms are bonded to the EDTA ligand and are bridged by oxygen atoms, while in $[(W_2S_4)(WS_4)_2]^{2-}$ [7], two WS_4^{2-} ions are coordinated to either end of a W(S)–(μ-S)$_2$–W(S) core. In $[(W_2S_4)(WS_4)_2]^{2-}$ the W(V)···W(V) distance between the core atoms is 2.950 Å while the W(V)···W(VI) distances are 3.100 and 3.161 Å (no standard deviations are given). It is suggested that the former distance (2.950 Å) represents a single W–W bond. An alternative explanation is that there is an interaction involving all four tungsten atoms brought about by the six bridging sulphur atoms.

Against this background, we report the synthesis of a binuclear species containing fragment (1) in which Y=Y′=O and X=S′=S.

Treatment of the tungsten(VI) compound WCl_2OS [8] with $(Ph_4As)Cl$ (1:2 molar ratio in CH_2Cl_2 under air and moisture free conditions) gave two products, one soluble the other insoluble, in the reaction medium. Recrystallization of the soluble compound gave crystals suitable for single crystal X-ray studies which revealed the product to be $(Ph_4As)_2[Cl_2W(O)–(\mu\text{-}S)_2–W(O)Cl_2]$ (Fig. 1).

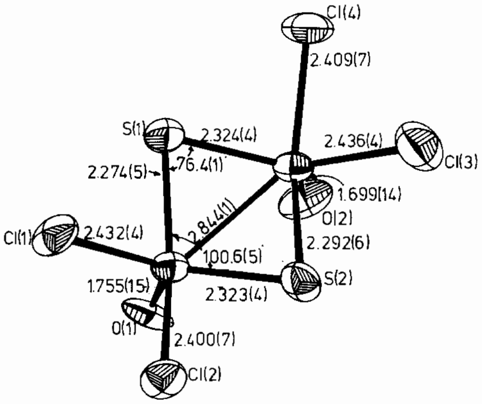


Fig. 1. Structure of $[Cl_2W(O)–(\mu\text{-}S)–W(O)Cl_2]^{2-}$.

Crystal Data

$C_{48}H_{40}W_2As_2Cl_4O_2S_2$, M = 1371.3, space group $P2_1/c$, monoclinic, $Z = 4, a = 15.97(1), b = 15.10(1), c = 21.10(1)$ Å, $\beta = 109.7(1)°$, $U = 4791.7$ Å^3. 4614 independent reflections above background were measured on a diffractometer and refined to R 0.071.

The dimer exists in the syn (or non-centrosymmetric) form with a dihedral angle of 149° between the two WS_2 planes. This angle is similar to that seen in $[(WS_4)(S)–(\mu\text{-}S)_2–W(S)(WS_4)]^{2-}$ (147.5°) and in a whole series of related molybdenum complexes [1–4].

The W–W distance (2.844(1) Å) is comparable to the distances observed in other dimeric tungsten(V) compounds in which the metal atoms are bridged by sulphur or selenium atoms (2.791 Å in $(Et_2NCS_2)_2(MeO)_2W–(\mu\text{-}S)_2–W(MeO)_2(S_2CNEt_2)_2$ [9], and 2.862 Å $[Cl_4W–(\mu\text{-}Se)–(\mu\text{-}Se_2)–WCl_4]^{2-}$ [10]). The distance is shorter than that seen in $[(W_2S_4)(WS_4)_2]^{2-}$ [7], but some 0.3 Å longer than the W–W distance in $[W_2O_4(EDTA)]^{2-}$ [5, 6] (2.542 Å). The change of some 0.3 Å on going from bridging oxygen to bridging sulphur atoms is also seen in related molybdenum complexes [1–4]. The W–S distances (range from 2.274(5) to 2.324(4) Å) are close to those in $(Et_2NCS_2)_2(MeO)_2W–(\mu\text{-}S)_2–W(OMe)_2(S_2CNEt_2)_2$ (range from 2.362(5) to 2.375(4) Å) and within the wide range of values seen in $[(S_4W)W(S)–(\mu\text{-}S)_2–W(S)(WS_4)]^{2-}$ (2.228 to 2.441 Å [7]) but longer than the W(V)–S terminal bond in $WCl_3S(MeSCH_2)_2$ (2.146(11) Å [11]). The diamagnetism of $[Cl_2W(O)–(\mu\text{-}S)_2–W(O)Cl_2]^{2-}$ and the short metal–metal distance indicates the

0020-1693/83/0000-0000/$03.00

presence of a metal–metal interaction. It is worthy of note that in this W(V) compound the bridging atoms are sulphur whereas in the tungsten(VI) compound WCl_2OS the evidence from infra red measurements suggests the presence of terminal W–S and bridging W–O–W. Similarly in the tungsten(VI) complex $WCl_4S \cdot WCl_2OS \cdot (MeOCH_2)_2$ [12] the two metal atoms are linked by a bridging oxygen atom coordinating *trans* to the W–S multiple bond.

The two W–O terminal bonds are in the expected range and are probably not significantly different and two ν(W–O) stretches are observed at 974 and 939 cm^{-1}. The isolation of a tungsten(V) compound from the reaction of WCl_2OS is interesting. It is known that under similar condition WCl_6 yields WCl_6^- [13] but that WCl_4O and WCl_4S both give simple tungsten(VI) anions of the type $[WCl_5Y]^-$ [14]. It has yet to be determined whether reduction of the metal proceeds with a simultaneous formation of the $(S_2)^{2-}$ group, a process which recent evidence has shown to occur readily amongst transition metals or whether interaction with the solvent takes place giving HCl and $CHCl_3$. This latter route must be the one followed during the reduction of WCl_6 [13].

Attempts have been made to determine the nature of the other product from the reaction and undoubtedly a monomeric tungsten(V) compound is formed but attempts to determine crystal structures have been beset by disorder problems as commonly observed with $(XPh_4)^+$ (X = As or P) cations [14].

Acknowledgements

We thank Dr. M. B. Hursthouse of Q.M.C. London for collecting the data and the University of Reading for support of E.M.P.

References

1 B. Spivack, *Coord. Chem. Rev., 17,* 99 (1975).
2 J. T. Huneke and J. H. Enemark, *Inorg. Chem., 17,* 3698 (1978).
3 W. E. Newton, J. W. McDonald, dK. Yamouchi and J. H. Enemark, *Inorg. Chem., 18,* 1621 (1979).
4 G. Bunzey, J. H. Enemark, J. K. Howie and D. T. Sawyer, *J. Am. Chem. Soc., 99,* 4168 (1977).
5 S. Khalil, B. Sheldrick, A. B. Soares and A. G. Sykes, *Inorg. Chim. Acta, 25,* L83 (1977).
6 S. Khalil and B. Sheldrick, *Acta Cryst., B34,* 3751 (1978).
7 F. Secheresse, J. Lefebvre, J. C. Daran and Y. Jeanin, *Inorg. Chim. Acta, 45,* L45 (1980).
8 G. W. A. Fowles, R. J. Hobson, D. A. Rice and K. J. Shanton, *J. Chem. Soc. Chem. Comm.,* 552 (1976).
9 A. Bino, F. A. Cotton, Z. Dori, S. Koch, H. Kuppers, M. Miller and J. C. Sekutowski, *Inorg. Chem., 17,* 3245 (1978).
10 M. G. B. Drew, G. W. A. Fowles, E. M. Page and D. A. Rice, *J. Am. Chem. Soc., 101,* 5827 (1979).
11 M. G. B; Drew, G. F. Griffin and D. A. Rice, *Inorg. Chim. Acta, 34,* L192 (1979).
12 D. Britnell, M. G. B. Drew, F. W. A. Fowles and D. A. Rice, *Chem. Comm.,* 462 (1972).
13 H. J. Seifert and W. Eichler, *Inorg. Nucl. Chem. Letters, 11,* 11 (1975).
14 M. G. B. Drew, G. W. A. Fowles, E. M. Page and D. A. Rice, *J. Chem. Soc. Dalton,* 2409 (1981).