Inorganica Chimica Acta, 37 (1979) L493
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

The Formation of Trinuclear $W_3S_9^{2-}$-Type Species from WS_4^{2-} by Condensation Redox Processes

A. MÜLLER, R. G. BHATTACHARYYA, E. KÖNIGER-AHLBORN, R. C. SHARMA

Faculty of Chemistry, University, D-4800 Bielefeld, F.R.G.

W. RITTNER†, A. NEUMANN

Institute of Inorganic Chemistry, University, D-3400 Göttingen, F.R.G.

G. HENKEL and B. KREBS

Institute of Inorganic Chemistry, University, D-4400 Münster, F.R.G.

Received July 2, 1979

Mo^{VI} containing species are easily reduced in aqueous solution by S_n^{2-} [1] and S^{2-} [2] with formation of sulfur-rich polynuclear complexes as $[Mo_2^V(S_2)_6]^{2-}$ or $[Mo_3^{IV}S(S_2)_6]^{2-}$ [1] and of the type $[Mo_2O_2S_2L_2]$ (in presence of ligands L like dtc^- [2]). A reduction even takes place by an intramolecular redox process: $[Mo^{IV}O_2S_2]^{2-}$ 'condenses' to $[Mo_2^VO_2S_2(S_2)_2]^{2-}$ in aqueous solution [3].

It will now be shown that in the case of W similar redox processes lead to trinuclear species of the W_3S_9-type like $[W_3OS_8]^{2-}$, the first polyoxothiometalate.

The formation of $[W_3S_9]^{2-}$ was not understood until now [4]. Deep red trinuclear species of the W_3S_9-type are formed by intramolecular redox reactions from yellow WS_4^{2-} under very different conditions (by solid state reactions, in aqueous or organic solutions): $[W_3S_9]^{2-}$ is formed by heating a mixture of $[(C_6H_5)_4P]Cl$ and $(NH_4)_2WS_4$ followed by recrystallisation of the reaction product in CH_3NO_2, $[W_3S_8(S_2CH_2)]^{2-}$ by heating $[(C_6H_5)_4P)_2$-WS_4 in a CH_2Cl_2/CH_3COCH_3 solution and $[W_3OS_8]^{2-}$ is formed when a dilute aqueous solution containing WS_4^{2-} is acidified with 0.1 *N* HCl. From the aqueous solution $Cs_2[W_3OS_8(H_2O)]\cdot 2H_2O$ can be isolated in high yield.

Crystals of $Cs_2[W_3OS_8(H_2O)]\cdot 2H_2O$ were examined by X-ray diffraction methods (space group $P2_1/n$; $a = 6.716(2)$, $b = 20.185(4)$, $c = 7.144(2)$ Å, $\beta = 101.42(2)°$, $\lambda = 0.7107$ Å for Mo-Kα, $U = 949.3$ Å^3, $Z = 2$, $D_c = 4.000$ g cm^{-3}, $\mu = 238.3$ cm^{-1}). The structure was solved by the heavy atom method and all non-hydrogen atoms were located by subsequent structure factor calculations and difference electron density maps. Least squares refinements (anisotropic thermal parameters for all atoms except O) converged at $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.078$ for 1499 independent reflexions [$0° \leq 2\theta \leq 48°$, $I > 1.96\,\sigma(I)$] measured on a Syntex $P2_1$ four circle diffractometer and corrected for absorption by an empirical method.

The structure with bond distances, which corresponds to that of $[W_3S_9]^{2-}$ and $[W_3S_8(S_2CH_2)]^{2-}$ is given in Fig. 1. The W–OH_2 interaction is very weak according to the *trans*-effect of the W=O bond. There is a statistical disorder of the central W atom on two positions.

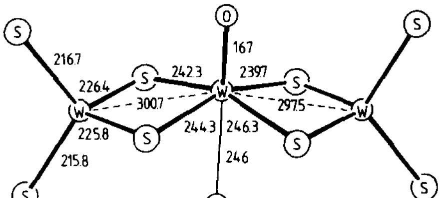

Fig. 1. Molecular structure of $[W_3OS_8(H_2O)]^{2-}$ with interatomic distances (pm); σ(W–W) 0.4, σ(W–S) 1.0, σ(W–O) 2 pm.

All above mentioned trinuclear anions are diamagnetic and are stabilized by W–W interactions (formally two W^V and one W^{IV}). Though the mechanism of the reactions is not known there is no doubt that S^{2-} is the reducing agent. According to electrochemical studies [5] in aqueous solution the initial step seems to be the protonation at the oxygen after formation of WOS_3^{2-} by hydrolysis. This favours both the condensation as well as the intramolecular redox reaction (this corresponds to the formation of $[Mo_2^VO_2S_2(S_2)_2]^{2-}$ from $[Mo^{VI}O_2S_2]^{2-}$).

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen.

References

1 A. Müller, R. G. Bhattacharyya and B. Pfefferkorn, *Chem. Ber., 112,* 778 (1979), and ref. cited.
2 V. R. Ott, D. S. Swieter and F. A. Schultz, *Inorg. Chem., 16,* 2538 (1977).
3 W. Rittner, A. Müller, A. Neumann, W. Bäther and R. C. Sharma, *Angew. Chem.* (in press).
4 E. Königer-Ahlborn and A. Müller, *Angew. Chem., 87,* 598 (1975).
5 A. Müller and R. C. Sharma, to be published.

---

† His co-authors regret to announce the untimely death of W. Rittner prior to submission of this paper.