Inorganica Chimica Acta, 26 (1978) L27–L28
©Elsevier Sequoia S. A., Lausanne – Printed in Switzerland

A Dimeric Cyano-Rhenium Complex with Sulphur Bridges and a Direct Metal–Metal Bond: Preparation and X-Ray Crystal Structure of $(Ph_4P)_4[Re_2(\mu_2\text{-}S)_2(CN)_8]^{4-}\cdot 6H_2O$

MICHAEL LAING

Department of Chemistry, University of Natal, Durban, South Africa 4001

JEAN-MARIE BREGEAULT

Laboratoire de Cinétique Chimique, Université Pierre et Marie Curie, 75230 Paris Cédex 05, France

WILLIAM P. GRIFFITH

Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY, U.K.

Received November 26, 1977

We recently reported [1] that $[Re^{IV}Cl_6]^{2-}$ abstracts sulphur from a KSCN/KCN melt to give salts of $[Re_4(\mu_3\text{-}S)_4(CN)_{12}]^{4-}$. This anion contains a Re_4S_4 cubane-like core in which direct Re–Re bonds of 2.755(5) Å are spanned by triply bridging sulphur atoms; Re–S of 2.34(1) Å. We now find that salts of another cyanorhenium(IV) species, $[Re_2S_2(CN)_8]^{4-}$, can be obtained by reaction of an aqueous perrhenate solution in excess cyanide with H_2S at room temperature followed by precipitation with appropriate cations. These compounds have been characterised by full elemental analysis.

Deep blue crystals of the tetraphenylphosphonium salt were obtained by slow evaporation of a methanol–water solution under nitrogen. The crystals are orthorhombic, space group *Pnna*; $a = 30.07(9)$, $b = 23.95(3)$, $c = 13.37(1)$ Å, $U = 9628$ Å^3, $D_m = 1.45$ gcm^{-3}, $Z = 4$ (*i.e.* half of the formula/asymmetric unit; required symmetry of anion = 2, with two independent S atoms each on the 2-fold axis). Data were measured on a Philips four-circle diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.7107$ Å) for θ between 3 and 23°. Of 7414 reflexions measured, 5613 were classed as observed ($I > 1.65\sigma(I)$). The coordinates of the Re and S atoms were deduced from a Patterson map, and the remaining atoms were located from the subsequent Fourier map. The structure has been refined by block diagonal least squares (isotropic, heavy atoms only) to $R = 0.17$.

The anion contains a planar $[Re_2(\mu_2\text{-}S)_2]$ unit with four CN groups bonded to each Re atom. The anions are linked in a complicated network with the waters of crystallisation, one axial and one equatorial CN group on each Re being involved. The axial CN groups are bent away from each other; mean angles are: C(ax)–Re–C(eq) = 83°, C(eq)–Re–C(eq) = 82°. The Re–S lengths of 2.33 Å are similar to those found in $[Re_4S_4(CN)_{12}]^{4-}$; the S···S separation of 3.86 Å shows that there is negligible bonding between the two S atoms. The Re–Re bond length of 2.60 Å is very short and certainly accounts for the observed diamagnetism of the compound. This length should be compared with that of 3.02 Å in $Re_2(CO)_{10}$ [2] and the Re···Re separation of 3.886 Å in $[(C_2H_5)_2PSSRe(CO)_3]_2$ in which there is no formal metal–metal bond [3]. A similar shortening of a metal–metal bond from tetramer to dimer has been observed for $[Fe_4S_4Cl_4]^{2-}$ and $[Fe_2S_2Cl_4]^{2-}$, though in these cases the formal oxidation states of the iron are different. The relationship between the magnitude of the difference and electronic structure is not clear [4].

The overall geometry of the anion is similar to that of $[Mo_2S_2(CN)_8]^{6-}$ which is the only other reported μ-S thiocyano complex of this type [5]. This is not surprising as the formal electron count is the same, but the longer Mo–Mo bond of 2.644 Å suggests that the metal–metal interaction is far stronger in $[Re_2S_2(CN)_8]^{4-}$. There is a strong polarised band at 183 cm^{-1} in the Raman spectrum of a methanolic solution of the complex. This is assigned by comparison with spectra of other bridged rhenium complexes [6] to a stretching mode of the Re_2S_2 unit.

This PPh_4^+ salt is thus the first purely sulphur-bridged complex of rhenium to be structurally characterised and the first such species to be shown to contain a short Re–Re bond. This reaction is another example of the ability of cyanorhenate(IV) systems to abstract sulphur atoms, this time from H_2S, and to incorporate them into a tightly-bound Re_nS_n framework.

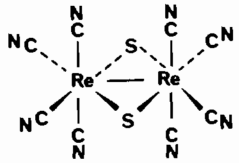

Figure 1. Schematic drawing of the anion $[Re_2(\mu_2\text{-}S)_2(CN)_8]^{4-}$.

Acknowledgements

We thank the South African Council for Scientific and Industrial Research for financial support, and Dr. G. Gafner, National Physical Research Laboratory, CSIR, for collecting the intensity data.

References

1 M. Laing, P. M. Kiernan and W. P. Griffith, *Chem. Commun.*, 221 (1977).

2 L. F. Dahl, E. Ishishi and R. E. Rundle, *J. Chem. Phys.*, *26*, 1750 (1957).

3 G. Thiele, G. Liehr and E. Lindner, *Berichte, 107*, 442 (1974).

4 M. A. Bobrik, K. O. Hodgson and R. H. Holm, *Inorg. Chem.*, *16*, 1851 (1977).

5 M. G. B. Drew, P. C. H. Mitchell and C. F. Pygall, *Angew. Chem.*, *15*, 784 (1976).

6 J. San Filippo and H. J. Sniadochi, *Inorg. Chem.*, *12*, 2326 (1973).