

Research Note

SYNTHESIS AND CRYSTAL STRUCTURE OF [PPh₄]₂ [WS₄(CuNCS)₄]

A. Taeb,¹ A. Beheshti² and N.K. Javadi²

¹Department of Chemical Engineering, Iran University of Science & Technology
Tehran, Islamic Republic of Iran

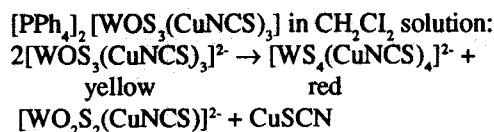
²Department of Chemistry, Shahid Chamran University,
Ahwaz, Islamic Republic of Iran

Abstract

The crystals of [WS₄(CuNCS)₄]²⁻ anion have been isolated from CH₂Cl₂ solution and examined by X-ray structural analysis as well as by IR spectroscopy. The unit cell is monoclinic with a= 14.3796(13), b= 18.039(11), c= 22.5956(23)Å, β= 96.053(8)°, space group P2₁/n (14), Z= 4. The crystal structure was refined by the least-squares calculations to a final R-value of 0.0398 (R_w = 0.0443) for 2777 unique observed reflections [F>3σ |F|].

The structure was investigated partly because of continuing research into the Cu-M-S (M= Mo, W) systems, which may be relevant to the biological antagonism between copper and the molybdenum or tungsten atom [1], and partly because of the desire to determine the bonding mode adopted by coordinated ambient pseudo-halide ion (CNS⁻) by X-ray diffraction and infrared spectroscopy.

The thiocyanate group is considered to be approximately in the same position as chloride in the spectrochemical series, whilst the isothiocyanate falls between water and ammonia i.e. $\text{Cl}^- \equiv -\text{SCN}^- < \text{F}^- < \text{H}_2\text{O} < -\text{NCS}^- < \text{NH}_3 < \text{CN}^-$. The thiocyanate ion as a ligand can also act as a bident bridging ligand (-SCN-) and form polymer complexes. Accordingly, the tris-[isothiocyanato-copper(1)] tungsten(VI) and molybdenum(VI) clusters [2,3] are unstable with respect to disproportionation into [MS₄(CuNCS)₄]²⁻ and [MS₄(CuNCS)₂]²⁻ anions (M= Mo, W) in CH₂Cl₂ solution. This is in sharp contrast to the reported stability of the [PPh₄]₂[MS₄(CuCl)₃]. CH₃CN (M= Mo, W) clusters [4] in the same solvent. In this paper, we report on some of the structural information of the [PPh₄]₂[WS₄(CuNCS)₄] crystal that was prepared by the disproportioning of



Experimental Section

The red compound was crystallized by vapour diffusion i.e. a tube containing the [PPh₄]₂[WOS₃(CuNCS)₃] in CH₂Cl₂ was kept for 3 days at ambient temperature in a closed desiccator with a tube of n-pentane. The red crystals were carefully isolated from CH₂Cl₂ solution and washed with dry diethyl ether (2×2 ml) and were finally dried under vacuum.

Crystal Structure Determination

The relevant experimental parameters and crystal data are collected in Table 1. A freshly prepared and carefully scattering factors were taken from International Tables [5]. The structure was solved with direct method [6]. All atoms were refined with anisotropic temperature coefficients.

All calculations were carried out on a Vax 3100 computer at the Department of Chemical Engineering, Iran University of Science and Technology. The computer programs MolEN [6] were used. A list of observed and

Keywords: Cluster; Copper; Crystal structure; Sulfur; Tungsten

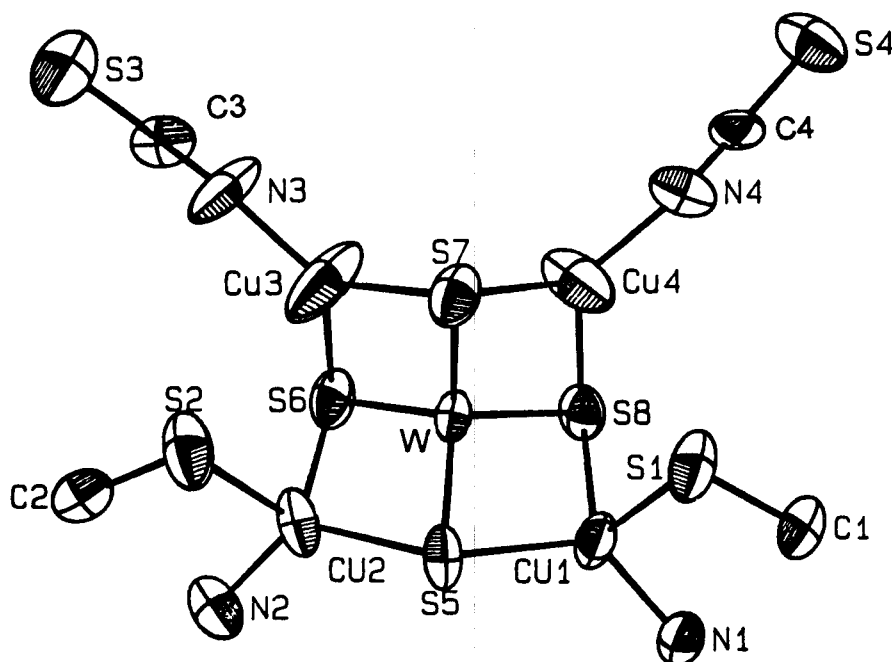


Figure 2. The structure of $[WS_4(CuNCS)_4]^{2-}$ ion

ulated structure factors is available.

Infrared Spectroscopy

Infrared spectrum of the cluster shows a doublet band at 2110 cm^{-1} due to the presence of the non-equivalent $\sqrt{2}$ ligands (bridging and N-bonding) in the $[WS_4(CuNCS)_4]^{2-}$ crystal. As expected, the $W=O$ stretch-frequency is absent in the IR spectrum of the $[WS_4(CuNCS)_4]^{2-}$ anion.

Crystal Structure

The crystal structure consists of $[PPh_4]^+$ cations (Fig. 1) discrete $[WS_4(CuNCS)_4]^{2-}$ anions (Fig. 2).

The bond lengths (Table 2) and bond angles (Table 3) of the $[PPh_4]^+$ ions indicate that the phenyl rings are essentially hexagonal, in other words, there is no significant deviation from planarity observed in the phenyl rings. Each tungsten atom of the structure (Fig. 2) is at the center of an essentially tetrahedral WS_4 unit [8], in which the mean $W-S$ bond length is $2.228(5)\text{ \AA}$ and the $S-W-S$ angles lie between $108.0(2)$ and $110.5(2)^\circ$. Four copper atoms are bonded to the WS_4 core, two of the Cu atoms [Cu_3 and Cu_4] show trigonal-planar coordinated by two sulfur groups and one NCS- group bonded to the Cu^+ ion through the N-atom. The other two Cu atoms [Cu_1 and Cu_2] show distorted tetrahedral coordination. The fourth coordination atom being S of an NCS- ion of neighbouring $[WS_4(CuNCS)_4]^{2-}$ anion. The bonds involving fourth coordinated Cu are somewhat longer than those of third coordinated Cu. The $W-Cu$ distances [$2.614(3)$ to $2.639(3)\text{ \AA}$]

are sufficiently closed to permit a direct metal-metal interaction. The angles around Cu_3 and Cu_4 ranging from $107.5(2)$ to $126.8(5)^\circ$ are those of the distorted trigonal-planar coordination geometry. The angles around Cu_1 and Cu_2 ranging from $99.8(2)$ to $127.5(5)^\circ$ are those of the distorted tetrahedral geometry. The $CuNCS$ linkages are essentially linear at C and only slightly bent at N. For the S-bonded mode, the $Cu-S-CN$ angles are bent due to the presence of two lone pairs of electrons on the S atom, with the bond angles ranging from $94.7(6)$ to $97.2(6)^\circ$.

Supplementary Material Available

Details of crystal data collection (Tables 1 to 3) and a listing of observed structure factors (Fig. 1). These materials can be obtained from the corresponding authors.

References

1. Mills, C.F. *Philos. Trans. R. Soc. London, Ser B*, **51**, 288, (1979).
2. Beheshti, A. and Garner, C.D. *J. Sci. I.R. Iran*, **1**, (4), (1990).
3. Beheshti, A. and Garner, C.D. *Iran J. Chem. and Chem. Eng.*, **10**, (2), (1991).
4. Potvin, C. and Manoli, J.M. *Inorganica Chimica Acta*, **83**, L19-L21, (1984).
5. *International tables for X-ray crystallography*. Vol. IV, 99, 149, Kynoch Press, England, (1974).
6. MoIEN: Crystal analysis programs, Enraf Nonius, (1991).
7. Boschen, I.P., Krebs, B., Muller, A., Ahlborn, E.K., Dornfeld, H. and Schulz, H. *Inorg. Chem.*, **17**, 1440, (1978).
8. Nicholson, J.N., Abrahams, I.L., Clegg, W. and Garner, C.D. *Ibid.*, **24**, 1092-1096, (1985).