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Research Note

SYNTHESIS AND CRYSTAL STRUCTURE OF $[PPh_4]_2$ $[WOS_3(CuNCS)_3]$

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Abstract

The reaction of $[PPh_4]_2$ $[WOS_3]$ with CuCl and KSCN (1:3:3) in acetone produces the yellow crystals of $[PPh_4]_2$ $[WOS_3(CuNCS)_3]$. The crystals are triclinic, space group $P\bar{1}$(2), z=2, a=12.4823(7), b=12.9224(7), c=18.6395(10)Å, α=83.907(5), β= 73.152(4), γ= 65.194(4)°. The crystal structure was determined by single crystal X-ray diffraction methods (Mo-Kα) and refined by least-squares calculations to a final R-value of 0.062 (R_w= 0.081) for 1851 unique observed reflections $[F>3\sigma|F|]$. In $[WOS_3(CuNCS)_3]^{2-}$ anion the tungsten and copper atoms have essentially a tetrahedral and trigonal planar co-ordination geometry respectively.

We have already reported the synthesis and crystal structure of several clusters of molybdenum [1, 2] and tungsten [3] with thiocyanate ion. In continuing the studies of linkage isomerization, here the synthesis and structural characterization of $[PPh_4]_2[WOS_3(CuNCS)_3]$ is reported.

Experimental Section

Materials

H_2WO_4, KSCN and PPh_4Cl were obtained from Merck and used without further purification. $[PPh_4]_2[WOS_3]$ was prepared by the published method [4].

Physical Measurement

Infrared spectrum was recorded as KBr disk with a Shimadzu IR-470 spectrometer. UV/VIS spectrum was obtained on a Jasco 1850 spectrometer.

Preparation of $[PPh_4]_2$ $[WOS_3(CuNCS]_3]$

$[PPh_4]_2$ $[WOS_3]$ (0.4 g, 0.4 mmol) was suspended in acetone (100 ml) and solid CuCl (0.1219 g, 1.23 mmol) was added to this solution. After stirring for 2 hours at ambient temperature, the colour of the solution changed from green to bright orange. Stirring was discontinued and solid KSCN (0.1195 g., 1.23 mmol) was added to the solution. After stirring for 2 more hours the deep orange solution was filtered from the precipitate KCl and the filtrate was vacuum evaporated. The residue was redissolved in dichloromethane (30 ml) and filtrate to remove any insoluble material. The filtrate was vacuum evaporated to dryness, leaving a residue which was washed with dry n-pentane (2×3 ml) and vacuum dried. The compound was crystallized by vapour diffusion (a tube containing the cluster dissolved in CH_2Cl_2 was kept for 3 days at ambient temperature in a closed desiccator containing a tube of n-pentane).

Crystal Structure Determination

A freshly prepared crystal was carried out on a CAD4-diffractometer. Details about the crystal size, the lattice constants and the experimental parameters are collected in Table 1 and selected interatomic distances and angles are

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given in Tables 2 and 3. The programs Multan and MolEN [5] were used on a Vax 3100 computer.

The structure was solved using the Multan method and difference Fourier synthesis. No attempt was made to observe the position of the hydrogen atoms. The W, Cu, S and P atoms were refined with anisotropic N and C atoms with isotropic temperature coefficients. The least-squares refinement converged at R= 0.062 and R_w= 0.081.

The infrared spectrum of the complex exhibits a strong band at 2090 cm^{-1}, which indicates monodentate N-coordination of the SCN-anion to the Cu^+- ion, in contrast to the solid IR spectrum of the analogous cluster with the molybdenum [1] which shows two ν(CN) bands at 2112 cm^{-1} and 2076 cm^{-1} due to the bridging and N-bonded SCN ligands respectively. The appearance of the absorption band at 814 cm^{-1} in the IR spectrum indicates the presence of the terminal W= O bond in this complex.

The UV-visible spectrum of the complex (Fig. 1B) proves the existence of $[WOS_3]^{2-}$ [4] in the cluster by the internal transitions of this anion (Fig. 1A). The major peak in the electronic spectrum of $[WOS_3(CuNCS)_3]^{2-}$ (342 nm) anion is red-shifted from the position of this transition in the free $[WOS_3]^{2-}$ (334 nm) ion. The absorption band at 269 nm (Table 4) is characteristic of the $\pi \rightarrow \pi^*$ transitions of the $[PPh_4]^+$cation [7] in the complex.

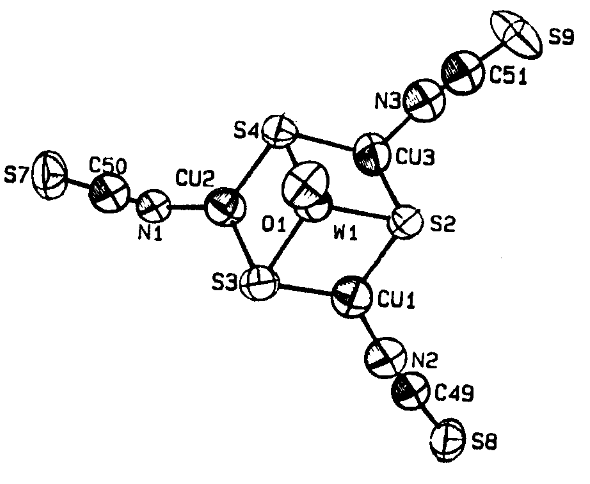

Figure 3. The structure of $[WOS_3(CuNCS)_3]^{2-}$ ion

The crystal structure consists of discrete $[WOS_3(CuNCS)_3]^{2-}$ and $[PPh_4]^+$ ions (Fig. 2). The bond lengths (Table 2) and angles (Table 3) in the $[PPh_4]^+$ ion indicate that the phenyl rings are essentially hexagonal; in other words, there is no significant deviation from planarity observed in the phenyl rings [8].

In the $[WOS_3(CuNCS)_3]^{2-}$ anion (Fig. 3), the three sulfur atoms are equivalent and μ_3-S bridging. In the central core, the tungsten, three sulfur and three copper atoms are arranged on seven of the vertices of a distorted cube of edge 2.222(8)Å; the eighth vertex opposite tungsten is vacant. All of the Cu atoms show trigonal planar coordination by two S^{2-} and one N-bonded SCN^- ligands. This arrangement is in contrast to that found in $[PPh_4]_2[MoOS_3(CuNCS)_3]$ [2], in which the coordination of copper ranging from distorted tetrahedral to trigonal planar and the $[MoOS_3(CuNCS)_3]^{2-}$ anions are linked by pairs of Cu-NCS-Cu bridges to form centrosymmetric dimers. The W= O bond length is 1.71(2)Å; W-S range from 2.191(9) to 2.222(8)Å; Cu-S from 2.220(1) to 2.227(9)Å; Cu-N from 1.83(3) to 1.95(2)Å and W...Cu from 2.631(4) to 2.673(6)Å. The CuNCS linkages are essentially linear at C and only slightly bent at nitrogen atom.

Supplementary Material Available

Details of crystal data collection (Tables 1 to 4) and a listing of observed structure factors (Fig. 3). These materials can be obtained from the corresponding authors.

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