

Priority communication

The first heterotrinnuclear Pd–Cu cluster with two μ_3 -S bridging atoms
Synthesis and structure of $[\text{Pd}_2(\text{PPh}_3)_4(\mu_3\text{-S})_2(\text{CuPPh}_3)]_2(\text{W}_6\text{O}_{19})$

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Abstract

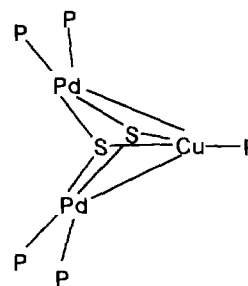
The compound $[\text{Pd}_2\text{CuS}_2(\text{PPh}_3)_5]_2(\text{W}_6\text{O}_{19})$ was prepared from the reaction of $\text{Pd}(\text{PPh}_3)_4$ and $\text{WCu}_2(\text{PPh}_3)_3\text{OS}_3$ in air. The structure of the $[\text{Pd}_2(\text{PPh}_3)_4(\mu_3\text{-S})_2(\text{CuPPh}_3)]_2(\text{W}_6\text{O}_{19})$ has been investigated by single crystal X-ray analysis. The cation is a heterotrinnuclear Pd_2Cu cluster bridged by two μ_3 -S atoms. Metal–metal interaction has been presented between copper and palladium atoms. The $\text{Pd}(1)\text{Cu}$ and $\text{Pd}(2)\text{Cu}$ distances are 2.789(3) and 2.889(2) Å, respectively. © 1997 Elsevier Science S.A.

Keywords: Palladium(II); Copper(I); Phosphine; Heterotrinnuclear; Structure; Hexatungstate

1. Introduction

Much attention has been directed toward the chemistry of heterometallic clusters in recent years. This stems from their possible biological importance [1,2], their structural chemistry [3–5] and their potential in catalytic processes [6] requiring multiple metal sites. $\text{Pt}_2(\text{PPh}_3)_4(\mu\text{-S})_2$, which is a very interesting metalloligand, was first prepared 26 years ago [7] and extensively studied by Briant et al. [8–10] and Bos et al. [11] and Hor [12]. It is air-stable and reacts rapidly with a variety of electrophiles, Lewis bases and halogenated solvents [13,14]. But the heterometallic chemistry of its homologue $\text{Pd}_2(\text{PPh}_3)_4(\mu\text{-S})_2$ has not, to our knowledge, been described. Accidentally we have made an unexpected cluster (Scheme 1) that contains the $[\text{Pd}_2(\text{PPh}_3)_4(\mu\text{-S})_2]$ fragment. X-ray crystallographic study on the compound has shown that the cation is a heterotrinnuclear Pd_2Cu cluster with metal–metal interaction. Metal–metal interaction is absent in derivatives of $[\text{Pt}_2(\text{PPh}_3)_4(\mu\text{-S})_2]$.

In this paper, we report $[\text{Pd}_2(\text{PPh}_3)_4(\mu_3\text{-S})_2(\text{CuPPh}_3)]_2(\text{W}_6\text{O}_{19})$ synthesized from $\text{Pd}(\text{PPh}_3)_4$ and $\text{WCu}_2\text{OS}_3(\text{PPh}_3)_3$ in air (Scheme 2).

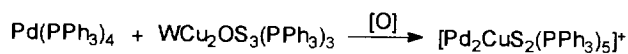


Scheme 1.

The compound $[\text{Pd}_2\text{CuS}_2(\text{PPh}_3)_5]_2[\text{W}_6\text{O}_{19}]$ was obtained as purplish-red crystalline solid.¹ Two singlet peaks in the $^{31}\text{P}\{^1\text{H}\}$ spectrum showed that the phosphorus nuclei are in two chemical environments. Both of them suggest that coordinated phosphines shifted to high frequency of H_3PO_4 (external standard) in CDCl_3 , the peak at δ 43.52 ppm is assigned to phosphorus

¹ 0.23 g (0.2 mmol) $\text{Pd}(\text{PPh}_3)_4$ was added to a solution of 1.55 g (1.2 mmol) $\text{WCu}_2\text{OS}_3(\text{PPh}_3)_3$ in 10 cm^3 CH_2Cl_2 . The mixture was stirred in dinitrogen atmosphere at room temperature for 1 h. After filtering, the solution was staying in air for 1 day, and gave purplish-red crystalline $[\text{Pd}_2\text{CuS}_2(\text{PPh}_3)_5]_2[\text{W}_6\text{O}_{19}]$ (0.18 g yield 76% according to Pd). Found: C, 45.02, H, 3.55, P, 6.22, Pd, 8.78, W, 24.57, Cu, 2.50, Calc.: C, 45.89, H, 3.21, P, 6.57, Pd, 9.04, W, 23.42, Cu, 2.70.

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Scheme 2.

atom attached to Pd atoms, and δ 29.76 ppm to these attached to the Cu atom. The following fingerprint absorption peaks were recorded in the FT-IR spectra: 973.9 ($\nu_{\text{W-O}_t}$), 445.5 ($\nu_{\text{W-O}_{br}}$), 552.6 ($\nu_{\text{Cu-P}}$), 509.1 ($\nu_{\text{Pd-P}}$), 464.8, 433.9 ($\nu_{\mu\text{-S}}$). The detailed structure was established by single crystal X-ray analysis.

2. Crystal data

$\text{C}_{180}\text{H}_{150}\text{Cu}_2\text{O}_{19}\text{P}_{10}\text{Pd}_4\text{S}_4\text{W}_6$, $M = 4711.72$, triclinic, $a = 15.302(3)$, $b = 17.431(4)$, $c = 21.553(4)$ Å, $\alpha = 66.97(3)$, $\beta = 85.18(3)$, $\gamma = 68.75(3)^\circ$, $U = 4919.3$ (17) Å³ space group, $P-1$ (No. 2), $Z = 1$; $D_c = 1.59$ g/cm³, $F(000) = 2282$ electrons, $\mu(\text{Mo-K}\alpha) = 4.237$ mm⁻¹. Intensity data were collected at ca. 293 K on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation of 13660 unique reflections measured in the θ range 1–23°. Among them 10809 with $I \geq 2.0 \sigma(I)$ were used to solve (direct and Fourier methods) and refine (full matrix least squares) the structure on an INDY workstation using SHELXL 93 program [15] to a current R of 0.1002 ($R_w = 0.2769$).²

The cation $[\text{Pd}_2\text{CuS}_2(\text{PPh}_3)_5]^+$ illustrated in Fig. 1 shows that the heterotrinnuclear cluster has a 'Y-shape' structure. The two square faces containing palladium atoms are almost symmetrically distributed at the two sides of the Cu trigonal face.

A striking feature of the structure is the particularly short Pd–Cu distances (2.789(3) and 2.889(2) Å), which suggest the occurrence of significant interaction between copper and palladium atoms. The two Pd atoms are separated by 3.276(2) Å.

In the planes (1) (Pd(1), S(1), S(2), P(1), P(2)) and (2) (Pd(2), S(1), S(2), P(3), P(4)), the $\angle\text{S-Pd-S}$ angle (ave. 82.0(1)°) is slightly larger than that in $[(\text{PEt}_3)_6\text{Pd}_3\text{S}_3]^{2+}$ (ave. 79.3(2)°) [16], while $\angle\text{P-Pd-P}$ angle (ave. 101.2(2)°) is larger than that in the above cation (ave. 94.4(2)°), whereas *cis* $\angle\text{S-Pd-P}$ angles remain close to 90° (mean value 88.4(2)°). The dihedral angle between planes (1) and (2) is 136.5°. The copper atom is coordinated by two sulphidoligands of $[\text{Pd}_2\text{S}_2\text{Cu}(\text{PPh}_3)_5]^+$ fragment with PPh₃ in a trigonal plane. The copper atom is deviated 0.048 Å from plane

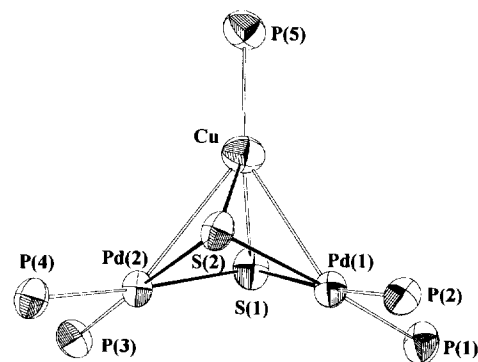


Fig. 1. The molecular structure of the $[\text{Pd}_2\text{CuS}_2(\text{PPh}_3)_5]^+$ cation. The phenyl rings have been omitted for clarity. Important bond lengths (Å) include: Pd(1)–Cu 2.789(3), Pd(1)–S(1) 2.326(4), Pd(1)–S(2) 2.357(4), Pd(2)–Cu 2.889(2), Pd(2)–S(1) 2.351(4), Pd(2)–S(2) 2.334(4), Pd(1)···Pd(2) 3.276(2), Cu–S(1) 2.251(4), Cu–S(2) 2.266(5), and bond angles (°): S(1)–Pd(1)–S(2) 82.02(14), S(1)–Pd(2)–S(2) 81.97(13), S(1)–Cu–S(2) 85.7(2), Pd(1)–Cu–Pd(2) 70.45(6).

(3) (Cu, S(1), S(2), P(5)). The Cu–(μ -S) bond lengths (ave. 2.258(4) Å) is slightly shorter than those in $[\text{Pt}_2\text{CuS}_2(\text{PPh}_3)_5]^+$ (ave. 2.286(5) Å). The angles $\angle\text{S(1)-Cu-S(2)}$ (85.7(2)°), P(5)–Cu–S(1) (135.0(2)°) and P(5)–Cu–S(2) (139.0(2)°) are approximately equal to those in its platinum analogue [17] (84.6(3), 139.4(4) and 135.7(2)°). The dihedral angles between plane (3) with planes (1) and (2) are 110.7 and 112.8°, respectively.

In the anion unit having cage structure, each W atom is surrounded by a distorted octahedron of oxygen atoms: one central O, one terminal and four bridging O atoms. The six W atoms form an octahedron with O(4) at the center [18].

Acknowledgements

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² The atomic coordinates for this work are available on request from the Directory the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 (Great Britain). Any request should be accompanied by a full literature citation for this communication.

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