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Derivatives of Tetrathiometallates. Synthesis and Structural Characterization of $WS_4(Cu(phen))_2$ and $WS_4Pt(dppm)$

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Our recent contributions to the coordination chemistry of the tetrathiotungstate anion WS_4^{2-} have shown the ability of WS_4^{2-} to function as ligand forming tri- [1,2], tetra- [3] and penta-nuclear [4] heterobimetallic anionic species. Some organic derivatives of thiometallates have been previously structurally characterized [5–10]. In the present paper we report the synthesis and structural description of neutral bi- and tri-nuclear complexes of WS_4^{2-} with organometallic derivatives.

Experimental

Chemicals and solvents were used as purchased. $PtCl_2(dppm)$, [dppm = 1,2 bis(diphenylphosphino)-methane)] was prepared by the usual literature methods [11,12]. Elemental analysis were performed by the 'Service Central d'Analyses du CNRS'.

Preparation of $WS_4(Cu(phen))_2$ (1)

Reactions were carried out under nitrogen or argon atmosphere. $(PPh_4)_2WS_4$ (0.250 g, 0.25 mmol) was stirred for 30 min with CuCl (0.0375 g, 0.375 mmol) in 25 ml of acetonitrile. The orange precipitate first formed was eliminated [2]. A solution of phen (phen = 1,10 phenanthroline) (0.050 g, 0.25 mmol) in 5 ml of CH_3CN was carefully poured on the top of the filtrate. After 2 h at room temperature pure orange needles were deposited. *Anal.* Calc.: C, 36.0; H, 2.0; N, 7.0; S, 16.0; Cu, 15.9; W, 23.0. Found: C, 36.0; H, 2.3; N, 7.4; S, 13.8; Cu, 13.7; W, 21.2%. The compound is insoluble in all the usual solvents.

Preparation of $WS_4Pt(dppm)$ (2)

$PtCl_2(dppm)$ (0.162 g, 0.25 mmol) was dissolved in 50 ml of CH_3CN at 35–40 °C. After cooling to ambient temperature, addition of $(PPh_4)_2WS_4$ (0.25 g, 0.25 mmol) previously dissolved in 25 ml of CH_3CN led to the precipitation of a yellow crude product (0.193 g) which analysed as complex 2. *Anal.* Calc.: C, 33.7; P, 6.9; S, 14.4; Pt, 21.9; W, 20.6. Found: C, 33.9; P, 7.2; S, 14.2; Pt, 20.9; W, 20.8%. Suitable crystals for X-ray diffraction were obtained by slow diffusion of an acetonitrile solution of $PtCl_2$(dppm) in a CH_2Cl_2 solution of $(PPh_4)_2WS_4$.

Crystal Structure Determination

Diffraction experiments were performed on a Philips PW 1100 diffractometer at 20 °C using Mo Kα radiation. Cells constants and other pertinent data are presented in Table I. The data were processed by using the SHELX-76 program package. Absorption correction was applied for 2. The two structures were solved by normal heavy atom Patterson and Fourier procedures and refined by full-matrix least-squares methods.

$WS_4(Cu(phen))_2$ (1)

Anisotropic temperature factors were used for the refinements of W, Cu and S atoms while isotropic factors were used for C and N atoms. Riding isotropic hydrogen atoms were included in the refinement subject to the constraints: C–H = 1.08 Å, $U(H) = 1.1\ U_{eq}(Ci)$, where $U_{eq}(Ci)$ is the equivalent isotropic thermal parameter of a carbon atom.

$WS_4Pt(dppm)$ (2)

Final atomic positional parameters are obtained with anisotropic temperature factors for W, Pt, S, P and C atoms. Hydrogen atoms have calculated C–H distances (1.08 Å) and fixed $U(H) = 1.1\ U_{eq}(Ci)$.

TABLE I. Results of the Crystal Structure Analysis

Compound	$WS_4(Cu(phen))_2$ (1)	$WS_4Pt(dppm)$ (2)
Space group	$P2_1/c$	$C2/c$
a (Å)	7.261	15.952
b (Å)	9.773	10.304
c (Å)	34.686	17.159
β (°)	94.87	108.31
U (Å^3)	2452.4	2677.6
Z	4	4
2θ max. (°)	50	70
No. reflections	5032	6152
Independent data with $F_o^2 > 3\sigma(F_o^2)$	2923	2984
μ (cm^{-1})	51.7	100.7
Transmission factors		0.45–0.90
Final parameters varied	176	151
Final R	0.045	0.052

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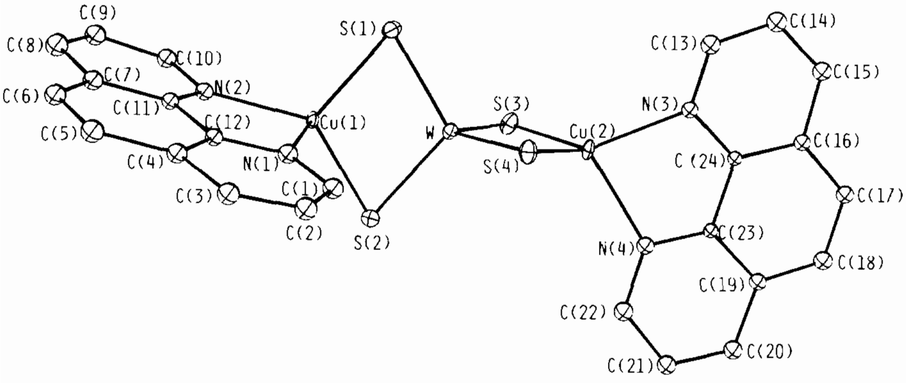

Fig. 1. ORTEP drawing of the $WS_4(Cu(phen))_2$ anion and the atomic numbering scheme employed.

Results and Discussion

The crystal structure of **1** consists of isolated molecules containing a WS_4 unit acting as a bidentate ligand towards two copper atoms. These latter have four neighbours in a distorted tetrahedron formed by two nitrogen atoms from the phen ligand and two sulfur atoms from the WS_4 core (Fig. 1).

However as indicated by the dihedral angles between the phen ligand and the WS_2Cu moiety, the distortion about the copper atoms is different. For Cu(2) the dihedral angle of 88° between the organic ligand and the WS_4Cu plane is significantly greater than that found for Cu(1) (dihedral angle of 75°). As a consequence of this distortion the Cu–N distances about each copper atom are unequal. The N–Cu–S bond angles subtended by the shorter Cu–N bond lengths are appreciably larger than the others (Table II). Similar trends have also been observed for related phen copper(I) complexes [13]. The phen ligands are reasonably planar, only the Cu(2) atom lies significantly out of its associated ligand skeleton (by 0.3 Å). The two CuS_2W planes meet with a normal dihedral angle while the two phen planes display a dihedral angle of 75°. The phen planes around Cu(1) are arranged in parallel stacks (Fig. 2) and separated by interplanar distance not significantly different from the sum of van der Waals radii. In contrast as a manifestation of the dihedral angle between the two aromatic ligands, the parallel stacking appears to be loose for the phen planes around Cu(2). There are no unusual features in the bond lengths or angles of the phen planes. The molecule involves short Cu...W...Cu distances and a Cu...W...Cu angle of 167° close to those previously reported.

The crystal structure of 2 is composed of the packing of four well-separated molecules in the unit cell. Figure 3 displays the molecular structure of 2 and the labelling scheme. $WS_4Pt(dppm)$ consists of an approximately WS_4 tetrahedron with an edge bridging (dppm) moiety. The W, Pt atoms and the C atom of the dppm chelate ring lie on a twofold axis. As expected the bridging sulfur atoms form longer bonds to W than the terminal sulfur atoms (2.239(3) and 2.145(3) Å respectively). The platinum atom is in the center of the approximately square planar arrangement of two phosphorus and two bridging sulfur atoms. The deviations of P atoms from the PtS_2 plane are ±0.093 Å. The Pt–S separation is 2.348(3) Å in reasonable agreement with other literature data [9]. The Pt–P bond lengths (2.257(2) Å) are also in the range observed for other similar platinum complexes [9]. The Pt–W separation of 2.8622(7) Å is slightly smaller than that mentioned in the $WS_4Pt(Et_3P)_2$ complex [9]. The formation of the PtP_2C chelate ring is ideal planar as required by symmetry. Consequently and in contrast with the homologous square planar $Pd(dppm)Cl_2$ complex [14], no puckering of the four membered chelate ring is observed. The P–C–P′ (93.0(7)°) and the P–Pt–P′ (73.7(1)°) angles are in the range reported in a compilation of data for structures containing chelating dppm [15]. The δ carbon atoms of the phenyl groups form an approximate square with edges 7.92 and 7.37 Å as in the flattest chelate ring analysed by Corfield *et al.* [15]. Within the chelate ring the Pt–P–C(phenyl) angles are larger than tetrahedral while the C(phenyl)–P–C(phenyl) and the C(phenyl)–P–C angles are in the range 107°–108° slightly less than tetrahedral. The P–C(phenyl) distances lie in the expected range 1.80–1.86 Å. The dihedral angle between the two phenyl groups is about 87°.

Electronic and IR Spectra

The main IR absorptions in the range 600–250 cm^{-1} are for **1**: 468(sh), 447(vs), 423(sh) cm^{-1} and for 2: 545(s), 503(s), 495(vs), 440(m) and 370(m) cm^{-1}. For the former complex the triplet about 447(vs) is attributed to W–S bridging [16] but could also be assigned to the symmetric Cu–N-

TABLE II. Interatomic Distances and Angles in $WS_4[Cu(phen)]_2$ (1) and $WS_4Pt(dppm)$ (2)

$WS_4[Cu(phen)]_2$ (1)			
W–S(1)	2.199(3)	W–S(3)	2.214(3)
W–S(2)	2.208(3)	W–S(4)	2.208(4)
W...Cu(1)	2.640(2)	W...Cu(2)	2.628(2)
Cu(1)–N(1)	2.157(9)	Cu(2)–N(3)	2.064(9)
Cu(1)–N(2)	2.029(9)	Cu(2)–N(4)	2.151(9)
Cu(1)–S(1)	2.253(9)	Cu(2)–S(3)	2.251(4)
Cu(1)–S(2)	2.284(3)	Cu(2)–S(4)	2.236(4)
S(1)–W–S(2)	108.1(1)	S(2)–W–S(3)	110.8(1)
S(1)–W–S(3)	109.7(1)	S(2)–W–S(4)	109.8(1)
S(1)–W–S(4)	109.6(1)	S(3)–W–S(4)	109.8(1)
W–S(1)–Cu(1)	72.7(1)	W–S(3)–Cu(2)	72.1(1)
W–S(2)–Cu(1)	72.0(1)	W–S(4)–Cu(2)	72.5(1)
Cu(1)...W...Cu(2)	167.1(2)		
N(1)–Cu(1)–N(2)	79.7(3)	N(3)–Cu(2)–N(4)	79.6(4)
N(1)–Cu(1)–S(1)	118.8(3)	N(3)–Cu(2)–S(3)	118.1(3)
N(1)–Cu(1)–S(2)	102.5(3)	N(3)–Cu(2)–S(4)	123.6(3)
N(2)–Cu(1)–S(1)	116.4(3)	N(4)–Cu(2)–S(3)	113.8(3)
N(2)–Cu(1)–S(2)	132.9(3)	N(4)–Cu(2)–S(4)	112.9(3)
S(1)–Cu(1)–S(2)	103.7(1)	S(3)–Cu(2)–S(4)	106.5(1)
$WS_4Pt(dppm)$ (2)			
W–S(1)	2.239(3)	Pt–S(1)	2.348(3)
W–S(2)	2.145(3)	Pt–P	2.257(2)
W...Pt	2.8622(7)	P–C	1.87(1)
P–C(11)	1.81(1)	P–C(21)	1.807(9)
S(1)–W–S(2)	111.2(1)	S(1)'–W–S(2)'	111.2(1)
S(1)–W–S(2)' [a]	108.8(1)	S(2)–W–S(1)'	108.8(1)
S(1)–W–S(1)'	106.2(1)	S(2)–W–S(2)'	110.7(1)
P–Pt–S(1)	166.87(9)	P–Pt–S(1)'	93.50(9)
S(1)–Pt–S(1)'	99.4(1)	P–Pt–P'	73.7(1)
W–S(1)–Pt	77.2(1)	C(11)–P–C(21)	108.1(5)
C(11)–P–Pt	118.5(3)	C(21)–P–Pt	116.6(3)
Pt–P–C	96.7(3)	P–C–P'	93.0(4)
C(11)–P–C	107.2(3)	C(21)–P–C	108.5(4)

[a] Atoms related by the diad axis are primed.

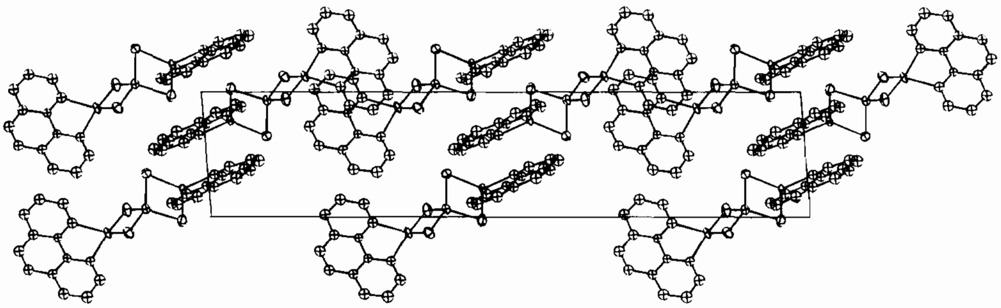

Fig. 2. Packing diagram for $WS_4(Cu(phen))_2$ showing the stack direction of one phen ligand. The origin of the unit cell lies at the lower left corner with a pointing upwards, c from left to right and b towards the reader.

(phen) stretching vibration [17]. For the platinum compound the absorption bands at 495 and 440 cm^{-1} are assigned to W=S terminal and W–S bridging vibrations respectively [16]. The remaining frequency at 370 cm^{-1} for 2 not observed in the IR spectra of $Pt(dppm)Cl_2$ could be attributed to Pt–S.

Owing to the poor solubility of 1 in the usual solvents a solid state electronic spectra was effected.

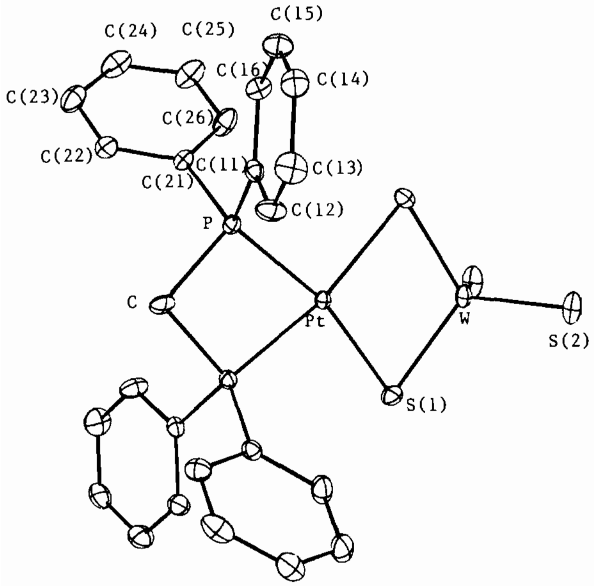

Fig. 3. View of the $WS_4Pt(dppm)$ complex with the atomic numbering scheme. Phenyl rings A(C(11) to C(16)) and B(C(21) to C(26)) are on the same side of the CP_2Pt plane. Atoms related by the diad axis passing through W, Pt and C are denoted by a prime.

The reflectance spectra of **1** shows bands at about 275, 410, 485 nm and a less defined shoulder at 725 nm. Bands at 275 and 410 nm are attributed to the charge transfer transitions of the WS_4^{2-} moiety [16] perturbed by coordination of two (phen)Cu groups. The shoulder at 725 nm already observed [10] is assigned to a $Cu(I) \rightarrow WS_4^{2-}$ transition. An additional band at 485 nm is tentatively assigned to a Cu(I) → ligand charge transfer transition, since Cu(2,9-dimethyl-1,10 $phen)_2^+$ has absorption near this energy [18]. The reflectance spectra of $WS_4(dppm)$ consists of bands at 270, 330, 380 and 425 nm. With reference to earlier comments the three bands to shorter wavelength are suggested to involve a charge transfer transition of the WS_4^{2-} unit.

Supplementary Material

Atomic coordinates, thermal parameters and mean planes are available from the authors on request.

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