Heterobimetallic Aggregates of Copper(I) with $(WS_4)^{2-}$. Synthesis and Characterization of $(PPh_4)_2$-$Cu_2Cl_2WS_4$

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Tetrathiometallates $(MS_4)^{2-}$, (M = Mo, W), were extensively studied for their ligand properties. Besides transition metals [1], small neutral molecules such as CuCN [2, 3] or CuX (X = Cl, Br) [4–6] can be coordinated to $(MS_4)^{2-}$ to form heterobimetallic aggregates. Different structures are observed for dinuclear $[CNCuMS_4]^{2-}$ [2, 3], trinuclear $[(CNCu)_2MoS_4]^{2-}$ [2, 3] and tetranuclear $[X_3Cu_3MS_4]^{2-}$ species [4–6]. The present paper reports the synthesis of the di- and tri-nuclear complexes of $(WS_4)^{2-}$ with CuCl, including structural characterization of the latter. Furthermore, in an attempt to prepare other compounds, we obtained an orange crystalline material which analyzed satisfactorily for $[Cu_{2.5}Cl_{2.5}WS_4]^{2-}$. The structural data are in agreement with the predicted formula.

Experimental

Chemicals and solvents were used as purchased. Reactions were carried out under atmosphere. Elemental analyses were performed by the 'Service Central d'Analyses du CNRS'.

UV–Vis spectra were recorded on an Uvikon 810 spectrophotometer; crystals were dissolved in DMF. IR spectra were obtained for KBr pellet samples with a Perkin-Elmer grating spectrophotometer in the range of 4000–250 cm^{-1}.

Electrochemical experiments were done using a Tacussel PRT-1X fast rise time potentiostat equipped with a TP-PRT pilot signal and an Ifelec XY-recorder. Experiments were carried out with a three-electrode cell using DMF as solvent and $[(C_2H_5)_4N](ClO_4)$ as supporting electrolyte. The reversible one-electron $Fe(C_5H_5)_2^+/Fe(C_5H_5)_2$ and $[Ni(WS_4)_2]^{2-}/[(Ni-$

$(WS_4)_2]^{3-}$ redox couples [9] were used as external reversible standards. No IR compensation drop was used.

Preparation of $(PPh_4)CuWS_4$, 1

CuCl (0.025 g, 0.25 mmol) was dissolved in 10 ml of acetonitrile. To this solution was added with stirring a solution of $(PPh_4)_2WS_4$ (0.25 g, 0.25 mmol) in 15 ml of MeCN (Cu/W = 1). After 20 min of stirring, the orange–red precipitate formed was isolated by filtration and washed with 20 ml of ether. *Anal.* Calc.: C, 40.3; Cu, 8.9; S, 17.9; W, 25.8. Found: C, 39.7; Cu, 8.5; S, 16.9; W, 27.6%. No tungsten is present in the filtrate after elimination of 1.

Preparation of $(PPh_4)_2Cu_nCl_nWS_4$ (n = 2 to 3)

A solution of CuCl (0.050 g, 0.5 mmol) in 10 ml of acetonitrile was added to a solution of $(PPh_4)_2$-WS_4 (0.25 g, 0.25 mmol) in 15 ml of MeCN (Cu/W = 2). The mixture was stirred for 20 min. The precipitate of 1 which formed was filtered off, and the filtrate was concentrated to 5 ml by rapid evaporation under vacuum. Electronic spectra of the crystals obtained from various preparations appeared quite different (Fig. 1), showing absorptions ranging from 424 and 295 nm for the original filtrate to 432 and 308 nm for the tetranuclear $(PPh_4)_2Cu_3Cl_3WS_4$, 5, complex [6]. Elemental analyses on crystals obtained from these different preparations led to Cu/W ratios varying from 2 to 3.
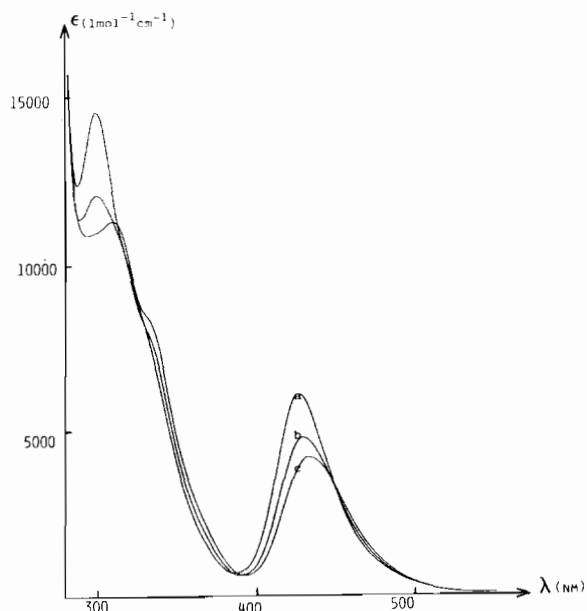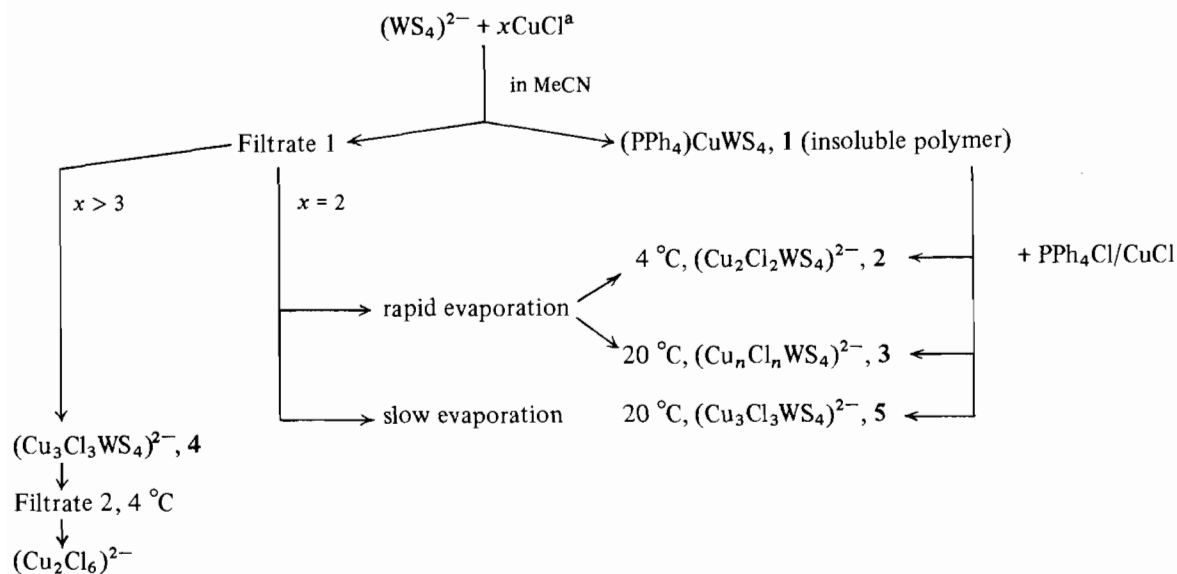

Fig. 1. Electronic spectra of $(PPh_4)_2(Cu_nCl_nWS_4)$ in DMF (a) $n = 2$, (b) $n = 2.5$, (c) $n = 3$.

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$(WS_4)^{2-} + xCuCl^a$

in MeCN

Filtrate 1 ⟵ ⟶ $(PPh_4)CuWS_4$, **1** (insoluble polymer)

$x > 3$　　　$x = 2$

4 °C, $(Cu_2Cl_2WS_4)^{2-}$, **2** ⟵　⟵ + $PPh_4Cl/CuCl$

⟶ rapid evaporation

20 °C, $(Cu_nCl_nWS_4)^{2-}$, **3** ⟵

⟶ slow evaporation　　20 °C, $(Cu_3Cl_3WS_4)^{2-}$, **5** ⟵

$(Cu_3Cl_3WS_4)^{2-}$, **4**

↓

Filtrate 2, 4 °C

↓

$(Cu_2Cl_6)^{2-}$

Scheme 1. [a] x is the CuCl:$(PPh_4)_2WS_4$ ratio.

$(PPh_4)_2Cu_2Cl_2WS_4$, 2

After standing 15 min at 0 °C, the orange crystals formed in the filtrate (Scheme 1) were isolated by filtration, washed with 20 ml of ether and dried. *Anal.* Calc.: C, 48.00; Cu, 10.10; S, 9.9; Cl, 6.5; W, 14.5. Found: C, 48.48; Cu, 10.69; S, 10.8; Cl, 6.0; W, 15.5%.

$(PPh_4)_2Cu_{2.5}Cl_{2.5}WS_4$, 3

After standing for 30 min at room temperature, the crystals were isolated from the filtrate by filtration, washed with 20 ml of ether and air dried. The formula was determined from X-ray measurements.

Crystal Structure Determination

Cell constants and other pertinent data are presented in Table I. Absorption corrections were applied. The two structures were solved by normal heavy atom Patterson and Fourier procedures and refined by full-matrix least-squares methods. Values of the atomic scattering for all atoms were obtained from the usual source.

$(PPh_4)_2Cu_2Cl_2WS_4$, 2

The structure was successfully solved in the non-centrosymmetric space group $P2_1$. The W, Cu, S, Cl and P atoms were assigned anisotropic temperature

TABLE I. Results of the Crystal Structure Analysis

Compound	$(PPh_4)_2Cu_2Cl_2WS_4$ (2)	$(PPh_4)_2Cu_{2.5}Cl_{2.5}WS_4$ (3)
Space group	$P2_1$	$C2/c$
a (Å)	9.228(9)	22.786(5)
b (Å)	20.157(3)	13.441(3)
c (Å)	14.540(3)	17.077(4)
β (deg)	106.76(5)	96.63(3)
U (Å^3)	2589.7	5195.1
Z	2	4
Diffractometer	Nonius CAD4	Philips PW1100
Radiation (Mo Kα) (Å)	0.71069	0.71069
2θ max (deg)	60	50
Number of reflections	7200	5772
Independent data with $F_o^2 > 3\sigma(F_o^2)$	3073	3256
μ (cm^{-1})	43.1	42.3
Transmission factors	0.48–0.72	0.74–0.81
Final parameters varied	291	277
Final R	0.05	0.063

factors. The carbon atoms were refined with isotropic thermal parameters. Correct absolute configuration has been determined.

$(PPh_4)_2Cu_{2.5}Cl_{2.5}WS_4$, 3

After location of the W atom, a difference Fourier map revealed the positions of Cu, S, Cl atoms in general positions. The remaining Cu and Cl atoms were introduced in special positions on the twofold axis at 0, y, 1/4 with partial occupancy factors. Refinement of the site occupancies verified the assumed 0.25 factors. The final model for the structure was refined with anisotropic temperature factors assigned to all non-hydrogen atoms.

Results and Discussion

Syntheses

Our various procedures of synthesis are summarized in Scheme 1. PPh_4WS_4Cu, 1, was isolated under polymeric form as the ammonium homologues NH_4MS_4Cu (M = Mo [7], W [8]). Compound 2 could be prepared via an alternative route. Addition of PPh_4Cl and CuCl to a suspension of 1 in MeCN allows the isolation of 2. Similar procedures have been described for the cyano parent complex [3]. For $x > 3$ proportions of $CuCl:(PPh_4)_2WS_4$, the

orthorhombic form [4] of $(Cu_3Cl_3WS_4)^{2-}$, 4, was obtained by allowing the filtrate to stand at 4 °C after removing the insoluble 1. At this stage, the orange orthorhombic crystals 4 were filtered off and the filtrate kept at 4 °C in order to obtain other polynuclear species. Attempts to isolate the $(Cu_4Cl_4WS_4)^{2-}$ anion failed, but the solution deposited orange–red crystals which were identified by X-ray diffraction methods and characterized as $(PPh_4)_2Cu_2Cl_6$ [12].

Structures

Important bond distances and angles are given in Table II. The trinuclear anion 2 is represented in Fig. 2. The crystal structure of 2 consists of the discrete complex anion and PPh_4^+ cations, with $(WS_4)^{2-}$ acting here as a bidentate ligand towards Cu(I). In each anion the copper and tungsten atoms have essentially a trigonal planar and a tetrahedral coordination geometry, respectively. The two WS_2-CuCl moieties are planar. Bond lengths and angles are not significantly different from that of the tetranuclear $(Cu_3Cl_3WS_4)^{2-}$ [6]. The complex anion involves short Cu–W distances (2.614(4) and 2.625(4) Å) and an approximately linear Cu–W–Cu array (174.6(2)°), as previously observed [6].

Figure 3 shows the geometry of 3. The anion possesses crystallographically imposed C_2 symmetry

TABLE II. (a) Interatomic Distances and Angles in 2; (b) Interatomic Distances and Angles in 3

2			
W–S(1)	2.204(6)	W–S(3)	2.201(7)
W–S(2)	2.228(7)	W–S(4)	2.206(7)
W•••Cu(1)	2.614(4)	W•••Cu(2)	2.625(4)
Cu(1)–Cl(1)	2.153(8)	Cu(2)–Cl(2)	2.131(8)
Cu(1)–S(2)	2.240(9)	Cu(2)–S(1)	2.234(8)
Cu(1)–S(3)	2.221(9)	Cu(2)–S(4)	2.252(8)
S(1)–W–S(2)	108.5(3)	S(2)–W–S(3)	108.4(3)
S(1)–W–S(3)	109.7(2)	S(2)–W–S(4)	111.8(3)
S(1)–W–S(4)	109.0(3)	S(3)–W–S(4)	109.4(3)
Cl(1)–Cu(1)–S(2)	125.6(4)	Cu(1)•••W•••Cu(2)	174.6(2)
Cl(1)–Cu(1)–S(3)	127.2(4)	Cl(1)–Cu(1)•••W	175.5(4)
Cl(2)–Cu(2)–S(1)	125.6(3)	Cl(2)–Cu(2)•••W	175.0(3)
Cl(2)–Cu(2)–S(4)	127.7(3)		
3			
W–S(1)	2.206(1)	W–S(2)	2.234(5)
W•••Cu(1)	2.620(2)	W•••Cu(2)	2.567(2)
Cu(1)–S(1)	2.234(6)	Cu(1)–Cl(1)	2.143(5)
Cu(1)–S(2)	2.251(6)	Cu(2)–Cl(2)	2.091(2)
Cu(2)–S(2)	2.216(2)		
S(1)–W–S'(1)	111.8(4)	S(1)–W–S'(2)	109.2(2)
S(1)–W–S(2)	108.9(5)	Cu(1)–S(2)–Cu(2)	110.0(2)
Cl(1)–Cu(1)–S(1)	126.7(3)	Cl(2)–Cu(2)–S(2)	124.9(2)
Cl(1)–Cu(1)–S(2)	126.0(2)	Cl(1)–Cu(1)•••W	178.7(2)
W–S(1)–Cu(1)	72.3(2)	Cl(2)–Cu(2)•••W	180.0
W–S(2)–Cu(1)	71.5(2)	W–S(2)–Cu(2)	70.4(2)

TABLE III. Spectral Data for Complexes

Complex	IR [ν(W−S)][a]	UV−Vis[b]
$(NH_4)_2WS_4$	460	398(17.08),283(24.81)
$(nPr_4N)_2[(CN)CuWS_4]$[c]	490,482,450(sh),444,415	396(9.63),284(23.95)
$(nPr_4N)_2[(CN)_2Cu_2WS_4]$[c]	470,435	409(7.14),398(sh),291(24.2)
$(PPh_4)_2(Cu_2Cl_2WS_4)$	460	424(6.23),296(13.5)
$(PPh_4)_2(Cu_3Cl_3WS_4)$[d]	460,430	430(4.35),455(sh),308(11.9)

[a]Positions for ν(W−S) bands in cm^{-1}; spectra recorded as KBr pellets. [b]Wavelength in nm with molar absorptivities (10^{-3} M^{-1} cm^{-1}) in parentheses; DMF solutions. [c]Ref. 3. [d]Ref. 6.
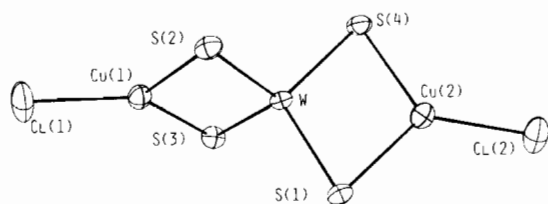
Fig. 2. ORTEP drawing of the $(Cu_2Cl_2WS_4)^{2-}$ anion and the atomic numbering scheme employed.

with the W, Cu(2) and Cl(2) atoms lying on the twofold axis. Distances and angles about the Cu(2) atom are significantly shorter than the corresponding ones in the related $(Cu_3Cl_3WS_4)^{2-}$ [6]. All the other salient dimensions in the two different anions are similar.

Electronic and IR Spectra

Electronic spectra for $(Cu_nCl_nWS_4)^{2-}$, ($n = 2, 2.5, 3$) and similar cyano complexes [3] are listed in Table III. All complexes absorb in the same energy regions as $(WS_4)^{2-}$. Molecular orbital calculations for $(MoS_4)^{2-}$ have recently been described [1, 10]. Similar conclusions can be drawn from comparison of the electronic spectra of $(MoS_4)^{2-}$ and $(WS_4)^{2-}$. The longest wavelength absorption at 398 nm can be attributed to the one-electron transition $\nu_1: 1t_1 \rightarrow 2e^*$. In addition, the absorption at 283 nm (ν_2) is assigned to both the $1t_1 \rightarrow 4t_2^*$ and $3t_2 \rightarrow 2e^*$ transitions. It can be seen from Table III that the addition of Cu(I) to $(WS_4)^{2-}$ shifts the spectra to lower energies. The ν_1 and ν_2 transitions are significantly lower, 34 and 25 nm, respectively, for $(Cu_3Cl_3WS_4)^{2-}$ in comparison to free $(WS_4)^{2-}$. The splitting of the ν_2 absorption band is possibly due to the lowering of symmetry, but there is no evidence of splitting of the ν_1 band, although additional shoulders at *ca.* 455 nm for the tetranuclear anion $(Cu_3Cl_3WS_4)^{2-}$ have not clearly been assigned.

Terminal W=S are characterized by absorption in the 480–515 cm^{-1} range of IR spectra, and sulfur–tungsten bridges by frequencies about 430–460 cm^{-1} [11]. The vibrational spectra of $(Cu_2Cl_2WS_4)^{2-}$ and $(Cu_{2.5}Cl_{2.5}WS_4)^{2-}$ reflect the different symmetries of the $(WS_4)^{2-}$ moieties. In **2** the sym-

metry of the WS$_4$ group is lowered from Td to the approximate point group *D2d* [11]. In this latter symmetry, the ν(W−S) stretching modes of e and b$_2$ symmetry are considered to be responsible for the infrared envelope centered at 460 cm^{-1} in the spectrum of **2**. With reference to the structure of $(Cu_3Cl_3WS_4)^{2-}$ of C_2 symmetry, four absorption bands are expected for the ν(W−S) vibrations. The IR spectrum shows only two bands (460 and 430 cm^{-1}); no assignment has been proposed. As expected the IR spectrum of **3** corresponds to the superposition of the spectra of **2** and **4**. The presence of absorption at 345 cm^{-1}, out of the range of ν(W−S) vibrations, has been attributed to the CuCl group since absorption is not observed in this range for the related cyano complexes.

Cyclic Voltammetry Experiments

Cyclic voltammetry of the $(WS_4)^{2-}$ ligand in DMF (*vs.* SCE) shows broad multistep irreversible reductions between −0.8 and −1.5 V. In comparison, **2** and **4** are electrochemically irreducible up to −2 V. Therefore, the central WS$_4$ core of the aggregates can be considered as protected against reduction by the addition of CuCl. On the other hand, free $(WS_4)^{2-}$ ligand underwent irreversible oxidation waves about 1 V. Cyclic voltammograms of each of the two anions **2** and **4** showed two anodic waves at
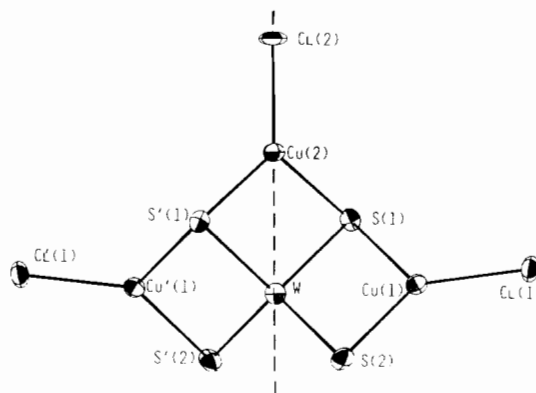

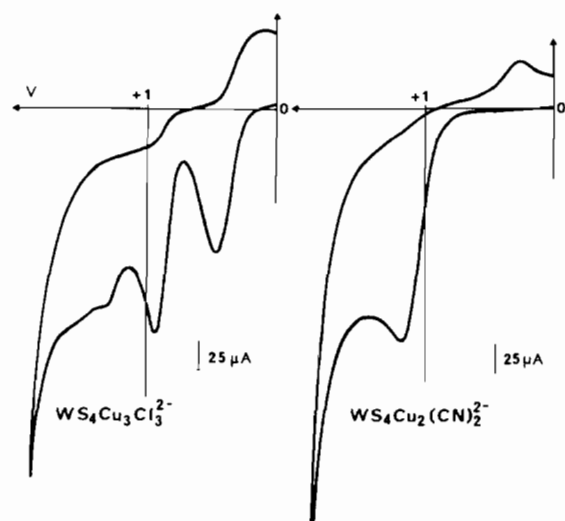Fig. 3. ORTEP drawing of $(Cu_{2.5}Cl_{2.5}WS_4)^{2-}$ and the atomic numbering scheme employed.

Fig. 4. Cyclic voltammograms of 2 mM solutions in 0.1 M tetraethylammonium perchlorate in DMF at platinum electrode. Scan rate 0.2 V s^{-1}.

0.45 V and 0.93 V (Fig. 4). In view of previous voltammetric trends [9] of $(WS_4)^{2-}$ and $[Ni(WS_4)_2]^{2-}$ anions, we assign the wave observed at 0.93 V to the irreversible oxidation of the WS_4 group. The former wave at 0.45 V was attributed to the irreversible oxidation of copper(I). This fact is consistent with: (i) the increasing intensity of the peak with the presence of copper atoms coordinated to $(WS_4)^{2-}$, (ii) the presence of the same anodic wave at the same potential for the isostructural $(Cu_3Cl_3MoS_4)^{2-}$ anion. In contrast, this anodic wave was absent for $[(CN)_2Cu_2WS_4]^{2-}$.

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