Inorganica Chimica Acta, 194 (1992) 105-112

Synthesis and structural characterization of incomplete cubanes derived from $[MS_4Cu_4Cl_4]^{2-}$ (M = Mo, W) anions

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(Received September 11, 1991; revised December 24, 1991)

Abstract

Reaction of $[Fe(bpy)_3]Cl_2$ upon $[MS_4Cu_4Cl_4]^{2-}$ (M = Mo, W) anions in acetonitrile-dichloromethane mixture gave incomplete cubanes. In the case of tungsten, $[WS_{3.4}O_{0.6}Cu_3(bpy)_2Cl]$ (**2a**) was obtained and structurally characterized; orthorhombic, *Pcab*, $a = 13.942(9)$, $b = 10.415(3)$, $c = 33.739(4)$ Å, $V = 4893(3)$ Å^3, $Z = 8$, $R = 0.059$ and $R_w = 0.064$. The overall geometry of **2a** is described as a cubane with a missing chloro-corner. Two copper atoms are tetrahedrally bound each of them being ligated to two sulfur and one bipyridine. The third copper has a trigonal environment, two sulfur atoms and a terminal chlorine. An oxygen-sulfur mixed occupancy was introduced for the terminal W=S bond, supported by IR data. In the molybdenum analogue **2b** the terminal double bond is pure Mo=O since the formula of **2b** is $[MoOS_3Cu_3(bpy)_2Cl]$. The product of oxidation of $[Febpy)_3]Cl_2$ found in the course of the preparation of **2a** was characterized as $[Fe(bpy)_3][Fe_2OCl_6]$ (**1**) by X-ray structure determination. The products of oxidation of copper(I) led to $[Cu(bpy)_2]_2[MS_4Cu_3Cl_3] \cdot CH_3CN$, M = W (**3a**), $a = 13.854(2)$, $b = 16.452(2)$, $c = 22.072(4)$ Å, $\beta = 97.06(1)°$, $Z = 4$, and M = Mo (**3b**), $a = 13.886(7)$, $b = 16.451(4)$, $c = 22.054(15)$ Å, $\beta = 96.84(5)°$, $Z = 4$, which were also characterized by X-ray structure determination.

Introduction

Step by step additions of CuCl on $[MS_4]^{2-}$ (M = Mo, W) anions resulted in the preparation of clusters of variable and controlled nuclearity; $[WS_4Cu_2Cl_2]^{2-}$ [1], $[MS_4Cu_3Cl_3]^{2-}$ [2-4], $[MS_4Cu_4Cl_4]^{2-}$ [5], $[MS_4Cu_5Cl_7]^{4-}$ [6]. In these compounds, terminal Cu-Cl bonds can be replaced by stronger nucleophilic ligands such as PhS^- [7], NCS^- [8], PPh_3 [9], phen [10], bpy [11] for example. For the given composition $Cu/MS_4 = 3$ two different geometries may be obtained.

(i) If three sulfur atoms are bound to three copper atoms, the remaining fourth S atom is involved in a terminal M=S double bond, and the structure is achieved by a chlorine atom which forms a cubane core, e.g. $[MS_4Cu_3(PPh_3)_3Cl]$ [22].

(ii) If four sulfur atoms are bound to three copper atoms the structure of the adduct is open, e.g. $[MS_4Cu_3Cl_3]^{2-}$ [2]. The addition of two Cu atoms is needed to obtain a cubane structure, e.g. $[MS_4Cu_5Cl_7]^{4-}$ [6].

Another way to obtain cubanes or cubane derivatives consists in eliminating a copper atom from the compound with the highest $Cu/MS_4 = 4$ composition. In this work we describe the reaction of Fe-bipyridine with $[MS_4Cu_4Cl_4]^{2-}$ anions to yield incomplete cubane structures.

Experimental

Preparations

All manipulations were carried out in air, except for $[Fe(bpy)_3]Cl_2$ which was prepared under argon. Solvents and chemicals were reagent grade and used as purchased. Chemical analyses were performed by the 'Service d'Analyses du CNRS, Solaize'. IR spectra were recorded on a Perkin-Elmer 580B spectrophotometer using KBr sampled pellets.

$[Fe(bpy)_3][Fe_2OCl_6]$ (1)

To a suspension of $[N(C_3H_7)_4]_2[WS_4Cu_4Cl_4]$ [5] (88 mg, 0.082 mmol) in a mixture of acetonitrile (20 ml) and dichloromethane (30 ml) was added under stirring $[Fe(bpy)_3]Cl_2$ (97 mg, 0.16 mmol). After 20 min at room temperature the resultant red solution was concentrated under reduced pressure until a solid was formed. Slow concentration of the filtrate by standing at room temperature for 48 h yielded deep-red crystals identified by X-ray determination as $[Fe(bpy)_3][Fe_2OCl_6]$ (**1**).

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$[WS_{3.4}O_{0.6}Cu_3(bpy)_2Cl]$ (2a)

After complete separation of **1** and standing for 6 days at room temperature, orange-red platelets deposited in the filtrate. They were shown by X-ray structure analysis to be $[WS_{3.4}O_{0.6}Cu_3(bpy)_2Cl]$.

$[MoS_3OCu_3(bpy)_2Cl]$ (**2b**) was obtained by the same route starting from $[N(C_3H_7)_4]_2$ $[MoS_4Cu_4Cl_4]$ and $[Fe(bpy)_3]Cl_2$.

$[Cu(bpy)_2Cl]_2[WS_4Cu_3Cl_3]\cdot CH_3CN$ (3a)

After stirring the previous suspension of $[WS_4Cu_4Cl_4]^{2-}$ and $[Febpy_3]Cl_2$ in acetonitrile–dichloromethane for 48 h and after filtering off compound **1**, crystals of $[Cu(bpy)_2Cl]_2[WS_4Cu_3Cl_3]\cdot MeCN$ (**3a**) deposited. *Anal.* Found: C, 34.25; H, 2.42; N, 8.55; Cl, 11.95; S, 8.44; Cu, 22.50; W, 10.80. Calc. for $C_{42}H_{35}N_9Cl_5S_4Cu_5W$: C, 34.24; H, 2.38; N, 8.56; Cl, 12.06; S, 8.69; Cu, 21.57; W, 12.50%. Compound **3a** was characterized by X-ray structure determination.

$[Cu(bpy)_2Cl]_2[MoS_4Cu_3Cl_3]\cdot CH_3CN$ (3b)

The same route carried out with $[MoS_4Cu_4Cl_4]^{2-}$ provided crystals of **1** and **3b** identified by IR spectra and characterized by unit cell dimensions determination. Compound **4** crystallized after separation of **1** and before crystallization of **3b**. Crystals are monoclinic, $a=21.677(9)$, $b=13.113(11)$, $c=31.738(15)$ Å, $\beta=97.16(4)°$, $V=8950$ Å^3. They slowly decomposed in air. Compound **3b** was also directly prepared from $[MoS_4]^{2-}$: a solution of $[NPr_4]_2$ $[MoS_4]$ (150 mg, 0.25 mmol) and CuCl (100 mg, 1 mmol) in 20 ml of acetonitrile was added to a solution of $[Fe(bpy)_3]Cl_2$ (297 mg, 0.5 mmol) in 60 ml of acetonitrile. After stirring for 48 h at room temperature, a red precipitate (**1**) was separated and the filtrate gave after a few days crystals of **3b** characterized by spectroscopic methods.

Crystal data

Suitable crystals of **1**, **2a** and **3** were obtained directly from synthesis solutions. A crystal was mounted and centered on an Enraf-Nonius CAD4 diffractometer. The orientation matrix and unit cell parameters with their standard deviations were determined by least-squares refinement of the setting angles of 25 reflections. Two standard reflections were measured every hour showing no intensity decay. Intensities were corrected

TABLE 1. Crystallographic data

	2a	3a	3b
Formula	$C_{20}H_{16}N_4O_{0.6}S_{3.4}ClCu_3W$	$C_{42}H_{35}N_9Cl_5S_4Cu_5W$	$C_{42}H_{35}N_9Cl_5S_4Cu_5Mo$
Molecular weight	840.90	1472.6	1384.7
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*Pcab*	$P2_1/n$	$P2_1/n$
a (Å)	13.942(9)	13.854(2)	13.886(7)
b (Å)	10.415(3)	16.452(2)	16.451(4)
c (Å)	33.739(4)	22.072(4)	22.054(15)
α	90	90	90
β (°)	90	97.06(1)	96.84(5)
γ (°)	90	90	90
V (Å^3)	4893(3)	4993(9)	5002(29)
Z	8	4	4
ρ (calc.) (g cm^{-3})	2.28	1.96	1.84
$F(000)$	2785.6	2872	2744
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Radiation	Mo Kα ($\lambda=0.71069$ Å)	Mo Kα ($\lambda=0.71069$ Å)	Mo Kα ($\lambda=0.71069$ Å)
μ (Mo Kα) (cm^{-1})	77.8	49,2	
Scan type	$\theta/2\theta$	$\theta/2\theta$	
Scan range	$0.9+0.345$ tgθ	$0.8+0.345$ tgθ	
θ limits (°)	1–25	1–20	
Octants collected	$+h, +k, +l$	$\pm h, +k, +l$	
No. data collected	4890	5034	
No. of unique reflections	4301	4645	
No. reflections used	2442	3260	
Criteria	$(F_o)^2>3\sigma(F_o^2)$	$(F_o)^2>3\sigma(F_o^2)$	
R (%)	5.9	3.3	
R_w (%)	6.4	4.1	
Absorption correction	Difabs	Difabs	
No. parameters	308	582	
Weighting scheme	Chebyshev	Chebyshev	
Using parameters	38.6, −21.0, 23.1	3.05, −0.57, 2.06	
Secondary extinction [27]	yes	yes	

for polarization and Lorentz effects. Absorption was corrected by Difabs [12].

Computations were performed by using CRYSTALS [13] adapted to a Micro Vax II. Atomic form factors for neutral W, Fe, Cu, C, N, O, S, Cl were taken from ref. 14. Structures were solved by interpretation of Patterson maps or by direct methods [15]. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Least-squares refinements were carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are observed and calculated structure factors. The weighting scheme used for **2a** and **3a** was $w = w'[1 - \Delta F/6\sigma(F_o)^2]^2$, where $w' = 1/\Sigma_1{}^3 \mathrm{ArTr}(x)$ with three Ar coefficients for the Chebyshev polynomial ArTr(x), $x = F_c/F_c(\max)$ [16]. Usual reliability factors were $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Crystallographic data and other pertinent informations are given in Table 1 for compounds **2a, 3a, 3b**; see also 'Supplementary material'.

Results and discussion

[Fe(bpy)$_3$][Fe$_2$OCl$_6$] (1)

The structure of **1** was first established by Weiss and Strähle [17]. As **1** was obtained as a by-product in the preparation of **2**, some structural results allowing its identification are given. The structure of **1** was solved by direct methods, all atom parameters were refined anisotropically to $R = 0.049$ and $R_w = 0.052$. Hydrogen atoms were omitted. The highest peak in the final difference map was 0.6 e Å^{-3} near C(10). See 'Supplementary material'. The geometry of $[\mathrm{Fe_2OCl_6}]^{2-}$ represented in Fig. 1 is very similar to that previously reported for [Fe(phen)$_3$][Fe$_2$OCl$_6$] [18], [Fe(η-C$_5$H$_5$)$_2$]$_2$ [Fe$_2$OCl$_6$] [19], [C$_5$H$_6$N]$_2$ [Fe$_2$OCl$_6$] [20] and [Fe(bpy)$_3$] [Fe$_2$OCl$_6$] [17]. Iron atoms are nearly tetrahedrally surrounded with angles ranging from 106.5(1) to 110.7(3)°. Both FeCl$_3$ moieties are bridged by an oxygen atom with short Fe–O distances independent of the nature of the counter-ion. The strong Fe–O π-bonding is probably the origin of the lengthening of Fe–Cl bonds, 2.206(3)–2.221(3) Å in **1**, with respect to corresponding distances of 2.180–2.186(2) Å observed in the $[\mathrm{FeCl_4}]^{2-}$ anion [21]. The Fe–O–Fe angle is significantly different in the four reported structures, probably a consequence of crystal packing effects.

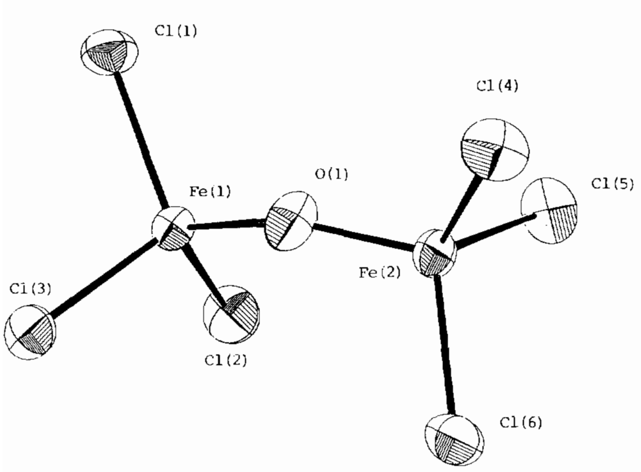

Fig. 1. ORTEP drawing of $[\mathrm{Fe_2OCl_6}]^{2-}$ with 50% thermal ellipsoids.

TABLE 2. Fractional atomic positional parameters for $(\mathrm{C_{10}H_8N_2})_2\mathrm{WS_{3.4}O_{0.6}Cu_3Cl}$

Atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
W(1)	0.33435(4)	0.34283(6)	0.12383(2)	0.0294
S(1)	0.4930(3)	0.3555(4)	0.1372(1)	0.0384
S(2)	0.2650(3)	0.2177(4)	0.1698(1)	0.0406
S(3)	0.3173(3)	0.2456(5)	0.0647(1)	0.0430
S(4)[b]	0.269(2)	0.524(3)	0.121(1)	0.0354
O(4)[b]	0.282(4)	0.500(5)	0.124(2)	0.0317
Cu(1)	0.4250(2)	0.2386(2)	0.18594(6)	0.0426
Cu(2)	0.4764(1)	0.2394(2)	0.08175(6)	0.0405
Cu(3)	0.2525(2)	0.1172(2)	0.11160(8)	0.0445
Cl(3)	0.1979(4)	−0.0741(5)	0.1038(2)	0.0624
N(11)	0.410(1)	0.278(1)	0.2470(5)	0.0417
N(12)	0.518(1)	0.108(1)	0.2093(4)	0.0398
N(21)	0.567(1)	0.268(1)	0.0358(5)	0.0417
N(22)	0.524(1)	0.051(1)	0.0722(5)	0.0456
C(10)	0.350(2)	0.363(2)	0.2628(6)	0.0590
C(11)	0.321(2)	0.362(2)	0.3031(7)	0.0659
C(12)	0.366(2)	0.266(2)	0.3274(7)	0.0627
C(13)	0.433(2)	0.179(2)	0.3118(7)	0.0609
C(14)	0.451(1)	0.188(2)	0.2690(6)	0.0392
C(15)	0.520(1)	0.100(2)	0.2481(6)	0.0412
C(16)	0.582(1)	0.018(2)	0.2713(7)	0.0564
C(17)	0.638(1)	−0.063(2)	0.2462(8)	0.0600
C(18)	0.639(2)	−0.056(2)	0.2059(8)	0.0714
C(19)	0.576(1)	0.031(2)	0.1889(6)	0.0481
C(20)	0.583(1)	0.382(2)	0.0193(6)	0.0496
C(21)	0.634(1)	0.393(2)	−0.0173(7)	0.0519
C(22)	0.169(1)	0.222(2)	−0.0338(7)	0.0547
C(23)	0.154(1)	0.336(2)	−0.0164(7)	0.0508
C(24)	0.600(1)	0.165(2)	0.0187(5)	0.0247
C(25)	0.578(1)	0.039(2)	0.0394(5)	0.0356
C(26)	0.610(1)	−0.081(2)	0.0281(6)	0.0460
C(27)	0.594(1)	−0.185(2)	0.0474(7)	0.0535
C(28)	0.535(2)	−0.178(2)	0.0800(7)	0.0580
C(29)	0.500(1)	−0.055(2)	0.0920(7)	0.0547

[a] $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$. [b] Statistical occupation; 0.4 S(4) + 0.6 O(4), see text.

[WS$_{3.4}$O$_{0.6}$Cu$_3$(bpy)$_2$Cl] (2a)

The *Pcab* group was unambiguously identified from systematic extinctions. A patterson map showed up the tungsten atom and remaining atoms were seen on Fourier difference maps. Parameters were refined isotropically. The value of the S(4) isotropic thermal parameter was quite high. A careful examination of a difference map revealed some residual electron density near S(4) which was assigned to the presence of oxygen on this site (see IR Section). This means that the crystal contains two species, one with a W=S bond and one with a W=O bond resulting from oxidation by air of the W=S one. Refinement of occupancy factors of both sites converged to 0.4 for S(4) and 0.6 for O(4). Hydrogen atoms were not introduced in refinements; all atom parameters were refined anisotropically to $R=0.059$ and $R_w=0.064$. After the last refinement, the highest residual electron density was 1.6 e Å^{-3} near the tungsten atom. Atomic coordinates with equivalent isotropic thermal parameters are given in Table 2.

An ORTEP representation of **2a** is given in Fig. 2 with the atomic labelling scheme. Selected distances are presented in Table 3. See also 'Supplementary material'. The coordination geometry around the tungsten atom is nearly tetrahedral with S–W–S angles ranging from 107.8(2) to 112.6(8)°. The terminal W=S(4) double bond, 2.10(3) Å, is shorter than single bonds engaged in W–S–Cu bridges, 2.244(4) to 2.258(4) Å. The W=S(4) distance as well as the short W=O(4) bond equal to 1.79(5) Å are in good agreement with W=X (X=O, S) values reported for related compounds, 2.131(4) Å in [$WS_4Cu_3(PPh_3)_3Cl$] and 1.754(11) Å in [$WOS_3Cu_3(PPh_3)_3Cl$] [22]. Cu(1) and Cu(2) atoms have a highly distorted tetrahedral surrounding with angles ranging from 79.4(6) to 130.4(4)°. On the contrary, Cu(3) has a trigonal planar environment with angles in the 107.9(2)–127.2(2)° range and a short Cu(3)–Cl(3) bond equal to 2.149(5) Å. The W S(2) S(3) Cu(3) Cl(3) moiety is planar, with a maximum deviation to the least-squares plane equal to 0.067 Å for W. S–Cu–S angles are quite similar, 106.5(2)–107.9(2)° and the W Cu(1) Cu(2) Cu(3) S(1) S(2) S(3) core has the approximate C_{3v} symmetry. The overall arrangement of the WS_3Cu_3 fragment can be viewed as a distorted cube with a missing corner, that is a cubane structure WS_3Cu_3Cl with a removed chloro corner. This missing eighth position of the cube is a consequence of the poor ability of Cu(I) to form five-coordinated compounds. An additional effect is the high electronic density of bipyridine which prevents the fixation of the Cl^- anion. Cu(1) and Cu(2) are located out of the bipyridine planes by 0.239 and 0.193 Å, respectively. These deviations indicate that d-electrons of both copper atoms do not participate to bipyridine aromaticity. The dihedral angle between bipyridine planes is 41.9°.

In a recent work [11] we described [$WS_4Cu_4(bpy)_2Cl_2$] represented on Fig. 3. It can be considered as resulting from the formal addition of a CuCl group to **2a**. The result of the addition of CuCl on the W=S double bond is a cubane with the same missing corner and an additional face. The adduct is polymerized through

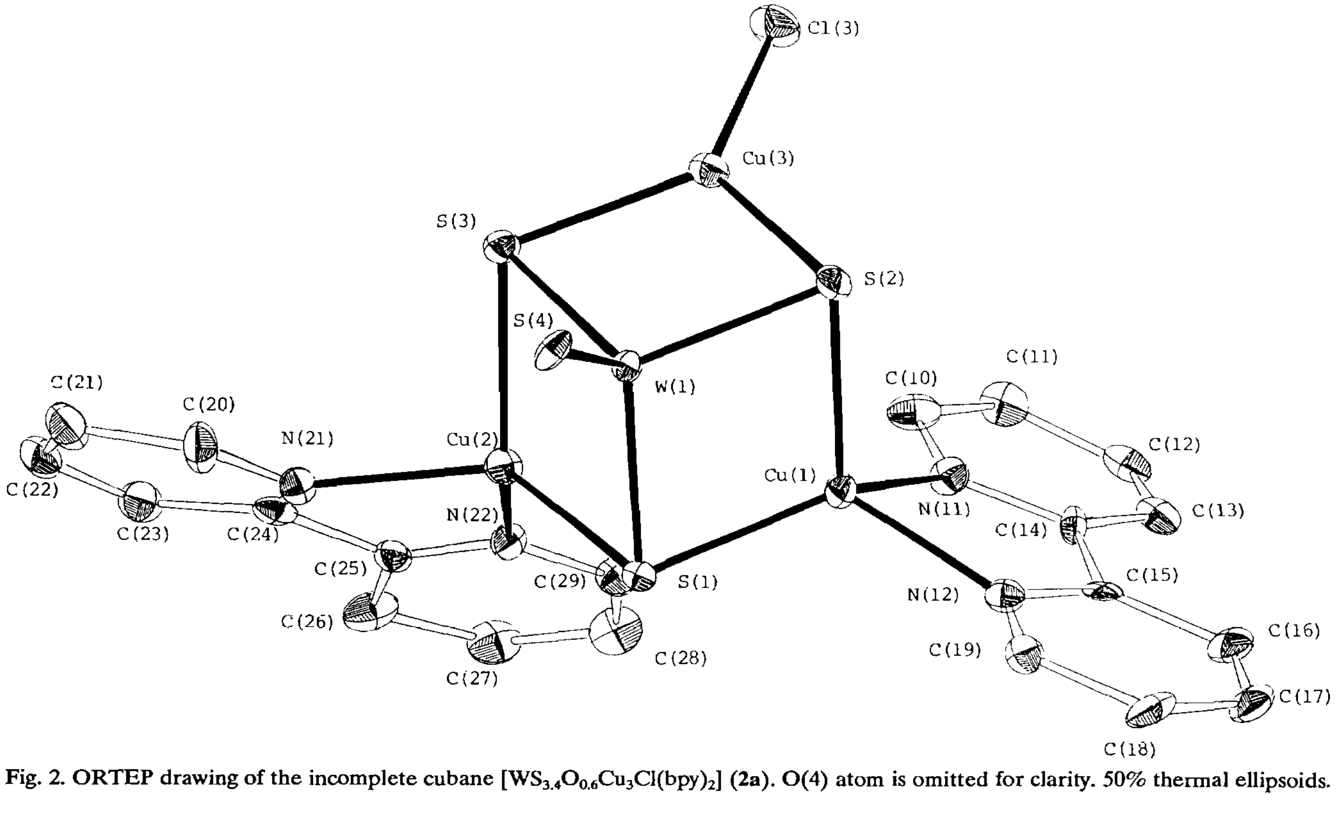

Fig. 2. ORTEP drawing of the incomplete cubane [$WS_{3.4}O_{0.6}Cu_3Cl(bpy)_2$] (**2a**). O(4) atom is omitted for clarity. 50% thermal ellipsoids.

TABLE 3. Selected bond lengths and angles for $(C_{10}H_8N_2)_2WS_{3.4}O_{0.6}Cu_3Cl$

W(1)–S(1)	2.258(4)	W(1)–Cu(1)	2.676(2)
W(1)–S(2)	2.244(4)	W(1)–Cu(2)	2.663(2)
W(1)–S(3)	2.249(4)	W(1)–Cu(3)	2.644(2)
W(1)–S(4)	2.10(3)		
W(1)–O(4)	1.79(5)		
S(1)–Cu(1)	2.254(5)	S(2)–Cu(3)	2.231(5)
S(1)–Cu(2)	2.239(5)	S(3)–Cu(2)	2.290(5)
S(2)–Cu(1)	2.304(5)	S(3)–Cu(3)	2.259(5)
S(4)–O(4)	0.33(7)		
Cu(1)–N(11)	2.11(2)	Cu(2)–N(21)	2.02(1)
Cu(1)–N(12)	2.04(1)	Cu(2)–N(22)	2.10(1)
Cu(3)–Cl(3)	2.149(5)		
S(2)–W(1)–S(1)	108.5(2)	S(4)–W(1)–S(3)	108.4(10)
S(3)–W(1)–S(1)	107.8(2)	O(4)–W(1)–S(1)	110.3(17)
S(3)–W(1)–S(2)	107.8(2)	O(4)–W(1)–S(2)	111.0(17)
S(4)–W(1)–S(1)	112.6(8)	O(4)–W(1)–S(3)	111.3(18)
S(4)–W(1)–S(2)	111.6(7)	O(4)–W(1)–S(4)	3.1(26)
Cu(1)–S(1)–W(1)	72.8(1)	Cu(1)–S(2)–W(1)	72.1(1)
Cu(2)–S(1)–W(1)	72.6(1)	Cu(3)–S(2)–W(1)	72.4(2)
Cu(2)–S(1)–Cu(1)	106.0(2)	Cu(3)–S(2)–Cu(1)	109.1(2)
Cu(2)–S(3)–W(1)	71.8(1)	O(4)–S(4)–W(1)	17.3(146)
Cu(3)–S(3)–W(1)	71.8(2)	S(4)–O(4)–W(1)	159.6(172)
Cu(3)–S(3)–Cu(2)	101.2(2)		
S(2)–Cu(1)–S(1)	106.5(2)	S(3)–Cu(2)–S(1)	107.1(2)
S(3)–Cu(3)–S(2)	107.9(2)		
Cl(3)–Cu(3)–S(3)	127.2(2)		

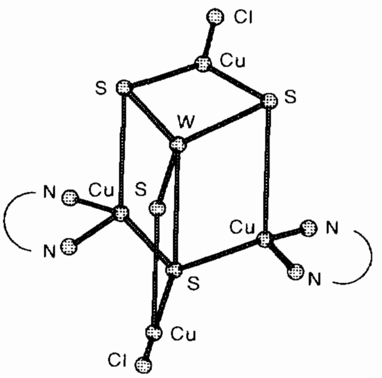

Fig. 3. Drawing of the incomplete cubane $[WS_4Cu_4Cl_2(bpy)_2]$, with an additional face.

both terminal CuCl groups. The presence of only one terminal CuCl group in **2a** prevents any linear polymerization through chloro bridges, at the utmost we might get a dimer.

$[Cu(bpy)_2Cl]_2[WS_4Cu_3Cl_3]$ (3a)

Coordinates of tungsten were obtained from the Patterson map interpretation with $P2_1/n$ space group. All non-hydrogen atoms were located on difference Fourier maps. In the last difference map, three isolated peaks were assigned to CH_3CN molecules. The occurrence of CH_3CN in the lattice was confirmed by ^1H NMR (80 MHz, solution in DMSO d6, $\delta CH_3CN = 1.95$ ppm). All atom parameters were refined anisotropically except C(100), C(101) and N(100) of the solvent molecule. After the last cycle of refinement, the maximum residual electronic density was 0.65 e/Å^3 near C(100). Contributions of hydrogen atoms were omitted. Crystal data are given in Table 1, atomic coordinates in Table 4 and selected bond distances and angles in Table 5. See also 'Supplementary material'. The molybdenum analogue **3b** is isostructural to **3a** as shown in Table 1.

$[Cu(bpy)_2Cl]^+$ cation

The geometry of the $[Cu(bpy)_2Cl]^+$ cation is a trigonal-bipyramid with chlorine located in the equatorial plane (Fig. 4). Axial bond lengths Cu(4)–N(42), Cu(4)–N(52), Cu(6)–N(61) and Cu(6)–N(72) are not significantly different (mean value 1.976(8) Å), but are quite different from the equatorial Cu(4)–N(41), Cu(4)–N(51)m Cu(6)–N(62) and Cu(6)–N(71) bond lengths (mean value 2.10(3) Å). Such a difference of 0.11 Å was previously observed for Cu(II) in a trigonal bipyramid environment [23]. Both equivalent Cu–N distances are slightly different, that is 2.071(8) and 2.139(8) Å, Cu–Cl distances in both cations being equal to 2.274(3) Å. The mean N–Cu–N angle between axial and equatorial bonds is 89(7)° including ligating atoms of bipyridines (79.9(5)°). The N(42)–Cu(4)–N(52) angle of 173.6(4)° and the N(61)–Cu(6)–N(72) angle of 171.8(3)° are close to 180°. In the equatorial plane, the distortion from ideal trigonal geometry is identical in both cations with three mean angles of 105, 120 and 135°. These values, together with the short Cu–Cl distance of 2.276(3) Å and long Cu(4)–N(41) and Cu(6)–N(71) bonds of 2.139(8) and 2.124(8) Å are in agreement with results reported for Cu(II)-distorted bipyramids [24].

$[WS_4Cu_3Cl_3]^{2-}$ anion

There are no unusual bond lengths or bond angles in the $[WS_4Cu_3Cl_3]^{2-}$ anion which is similar to that previously obtained by direct addition of CuCl to $[WS_4]^{2-}$ [2, 3]. A noticeable feature in the packing is the short Cu(1)–Cu(2) distance of 3.617(2) Å between two copper atoms of two neighbouring units related by an inversion centre. Nevertheless the corresponding chloro–copper distances, Cl(1)–Cu(2) = 4.786(3) Å and Cl(2)–Cu(1) = 4.840(3) Å are too long to be involved into both chloro bridges. Similarly related angles around Cu atoms are close to trigonal planar values preventing any polymerization through chloro bridges.

TABLE 4. Fractional atomic coordinates for $[CuCl(C_{10}H_8N_2)_2]_2[WS_4Cu_3Cl_3]MeCN$

Atom	x/a	y/b	z/c	U_{eq}
W(1)	0.15523(3)	0.07724(2)	0.00889(2)	0.0380
S(1)	0.1329(2)	0.0026(2)	−0.0770(1)	0.0484
S(2)	0.1849(2)	−0.0050(2)	0.0898(1)	0.0537
S(3)	0.0256(2)	0.1517(2)	0.0181(1)	0.0542
S(4)	0.2797(2)	0.1572(2)	0.0047(1)	0.0606
Cu(1)	0.0577(1)	0.07660(8)	0.10401(6)	0.0566
Cu(2)	0.1603(1)	−0.08479(8)	0.00435(6)	0.0606
Cu(3)	0.25544(9)	0.09065(8)	−0.08391(6)	0.0513
Cl(1)	0.0199(2)	0.1003(2)	0.1947(1)	0.0541
Cl(2)	0.2264(2)	−0.2058(2)	0.0045(2)	0.0652
Cl(3)	0.3313(2)	0.1112(2)	−0.1618(1)	0.0540
Cu(4)	0.98201(8)	0.57714(7)	0.16587(6)	0.0415
Cl(41)	1.1431(2)	0.5515(2)	0.1920(2)	0.0595
N(41)	0.9192(6)	0.5785(5)	0.0724(4)	0.0423
N(42)	0.9524(6)	0.4607(5)	0.1527(4)	0.0382
C(40)	0.9007(8)	0.6427(7)	0.0344(5)	0.0501
C(41)	0.8676(8)	0.6336(7)	−0.0271(5)	0.0551
C(42)	0.8529(7)	0.5546(8)	−0.0488(5)	0.0520
C(43)	0.8673(7)	0.4884(7)	−0.0119(5)	0.0451
C(44)	0.9004(6)	0.5025(7)	0.0506(5)	0.0346
C(45)	0.9186(6)	0.4379(6)	0.0958(5)	0.0353
C(46)	0.8989(9)	0.3551(7)	0.0816(6)	0.0557
C(47)	0.9175(8)	0.2975(7)	0.1276(7)	0.0565
C(48)	0.9528(8)	0.3226(7)	0.1861(6)	0.0594
C(49)	0.9709(7)	0.4062(7)	0.1974(5)	0.0464
N(51)	0.8642(6)	0.6034(5)	0.2119(3)	0.0338
N(52)	0.9976(6)	0.6961(5)	0.1733(4)	0.0422
C(50)	0.8017(8)	0.5509(6)	0.2307(5)	0.0433
C(51)	0.7215(7)	0.5757(7)	0.2581(4)	0.0457
C(52)	0.7084(8)	0.6594(7)	0.2662(5)	0.0514
C(53)	0.7752(8)	0.7135(7)	0.2469(5)	0.0441
C(54)	0.8521(7)	0.6831(7)	0.2197(4)	0.0317
C(55)	0.9269(7)	0.7360(6)	0.1989(4)	0.0341
C(56)	0.9292(9)	0.8213(7)	0.2050(5)	0.0470
C(57)	1.006(1)	0.8633(7)	0.1825(5)	0.0499
C(58)	1.0762(9)	0.8225(7)	0.1574(6)	0.0570
C(59)	1.0715(9)	0.7380(8)	0.1531(5)	0.0588
Cu(6)	0.48789(9)	0.36387(7)	0.12322(5)	0.0396
Cl(61)	0.6448(2)	0.3988(2)	0.1547(1)	0.0548
N(61)	0.5151(6)	0.2457(5)	0.1289(3)	0.0379
N(62)	0.3725(6)	0.3258(5)	0.1680(3)	0.0380
C(60)	0.5933(8)	0.2096(8)	0.1093(5)	0.0539
C(61)	0.6068(9)	0.1263(8)	0.1128(5)	0.0529
C(62)	0.540(1)	0.0784(8)	0.1391(5)	0.0601
C(63)	0.4578(9)	0.1160(7)	0.1569(5)	0.0555
C(64)	0.4479(7)	0.1988(6)	0.1520(4)	0.0308
C(65)	0.3658(7)	0.2442(7)	0.1711(4)	0.0354
C(66)	0.2873(9)	0.2068(7)	0.1940(6)	0.0599
C(67)	0.2149(8)	0.2566(9)	0.2135(6)	0.0680
C(68)	0.2258(9)	0.3405(8)	0.2125(6)	0.0660
C(69)	0.3047(8)	0.3729(7)	0.1885(5)	0.0431
N(71)	0.4362(6)	0.3626(6)	0.0286(4)	0.0432
N(72)	0.4418(6)	0.4773(5)	0.1122(4)	0.0396
C(70)	0.4370(8)	0.2999(7)	−0.0104(5)	0.0521
C(71)	0.395(1)	0.3069(9)	−0.0715(6)	0.0656
C(72)	0.3552(9)	0.380(1)	−0.0913(6)	0.0600
C(73)	0.3544(8)	0.4441(8)	−0.0509(5)	0.0499
C(74)	0.3961(7)	0.4348(7)	0.0096(5)	0.0370
C(75)	0.4012(7)	0.4991(6)	0.0558(5)	0.0386
C(76)	0.3658(7)	0.5766(8)	0.0435(6)	0.0535
C(77)	0.3684(8)	0.6317(7)	0.0901(7)	0.0526
C(78)	0.4110(9)	0.6121(8)	0.1487(6)	0.0647
C(79)	0.4476(8)	0.5314(7)	0.1577(5)	0.0506
C(100)	0.434(1)	0.9059(9)	0.0604(7)	0.102(5)
C(101)	0.414(1)	0.869(1)	0.1215(8)	0.108(5)
N(100)	0.404(1)	0.8376(9)	0.1625(7)	0.129(5)

TABLE 5. Selected bond distances and angles for $[CuCl(C_{10}H_8N_2)_2]_2[WS_4Cu_3Cl_3]MeCN$

$[CuCl(C_{10}H_8N_2)_2]_2$ cations			
Cu(4)–Cl(41)	2.275(3)	Cu(6)–Cl(61)	2.273(3)
Cu(4)–N(41)	2.139(8)	Cu(6)–N(61)	1.981(8)
Cu(4)–N(42)	1.973(8)	Cu(6)–N(62)	2.076(8)
Cu(4)–N(51)	2.071(8)	Cu(6)–N(72)	1.978(8)
Cu(4)–N(52)	1.973(8)	Cu(6)–N(71)	2.124(8)
N(41)–Cu(4)–Cl(41)	121.1(2)	N(61)–Cu(6)–Cl(61)	93.5(2)
N(42)–Cu(4)–Cl(41)	92.1(3)	N(62)–Cu(6)–Cl(61)	134.0(2)
N(42)–Cu(4)–N(41)	79.3(4)	N(62)–Cu(6)–N(61)	80.0(3)
N(51)–Cu(4)–Cl(41)	136.2(2)	N(71)–Cu(6)–Cl(61)	119.8(2)
N(51)–Cu(4)–N(41)	102.6(3)	N(71)–Cu(6)–N(61)	95.2(3)
N(51)–Cu(4)–N(42)	96.5(3)	N(71)–Cu(6)–N(62)	106.2(3)
N(52)–Cu(4)–Cl(41)	93.9(3)	N(72)–Cu(6)–Cl(61)	94.7(2)
N(52)–Cu(4)–N(41)	95.6(3)	N(72)–Cu(6)–N(61)	171.8(3)
N(52)–Cu(4)–N(42)	173.6(4)	N(72)–Cu(6)–N(62)	95.0(3)
N(52)–Cu(4)–N(51)	80.6(3)	N(72)–Cu(6)–N(71)	79.8(4)
$[WS_4Cu_3Cl_3]$ anion			
W(1)–S(1)	2.247(3)	S(1)–Cu(2)	2.295(3)
W(1)–S(2)	2.237(3)	S(1)–Cu(3)	2.251(3)
W(1)–S(3)	2.203(3)	S(2)–Cu(1)	2.268(3)
W(1)–S(4)	2.180(3)	S(2)–Cu(2)	2.288(3)
W(1)–Cu(1)	2.633(1)		
W(1)–Cu(2)	2.669(1)		
W(1)–Cu(3)	2.621(1)	S(4)–Cu(3)	2.231(3)
Cu(1)–Cl(1)	2.165(3)		
Cu(2)–Cl(2)	2.192(3)		
Cu(3)–Cl(3)	2.150(3)		
S(2)–W(1)–S(1)	109.6(1)	S(4)–W(1)–S(1)	108.8(1)
S(3)–W(1)–S(1)	110.6(1)	S(4)–W(1)–S(2)	109.3(1)
S(3)–W(1)–S(2)	109.5(1)	S(4)–W(1)–S(3)	109.1(1)
S(2)–Cu(1)–W(1)	53.69(7)	Cl(1)–Cu(1)–W(1)	160.4(1)
S(3)–Cu(1)–W(1)	52.85(8)	Cl(1)–Cu(1)–S(2)	121.0(1)
S(3)–Cu(1)–S(2)	106.4(1)	Cl(1)–Cu(1)–S(3)	129.2(1)
S(1)–Cu(2)–W(1)	53.19(7)	Cl(2)–Cu(2)–W(1)	157.0(1)
S(2)–Cu(2)–W(1)	52.97(8)	Cl(2)–Cu(2)–S(1)	126.8(1)
S(2)–Cu(2)–S(1)	106.2(1)	Cl(2)–Cu(2)–S(2)	120.0(1)
S(1)–Cu(3)–W(1)	54.29(7)	Cl(3)–Cu(3)–W(1)	175.1(1)
S(4)–Cu(3)–W(1)	52.64(8)	Cl(3)–Cu(3)–S(1)	127.1(1)
S(4)–Cu(3)–S(1)	106.8(1)	Cl(3)–Cu(3)–S(4)	126.0(1)

IR spectra

Compound 1

Characteristic absorptions of μ-oxodiiron(III) complexes are observed: an intense broad band located at 850 cm^{-1} attributed to the Fe–O–Fe antisymmetric stretching mode [19] and two bands for Fe–Cl stretching modes at 365 and 320 cm^{-1}.

Compounds 2a and 2b

In the 400–500 cm^{-1} region where ν(M–S) frequencies are expected [25], spectra of **2b** exhibit two bands at 420 and 440 cm^{-1}, consistent with the approximate T_d symmetry of the MX_4 core, while only one broad band is observed at 435 cm^{-1} for **2a**. The statistical occupancy

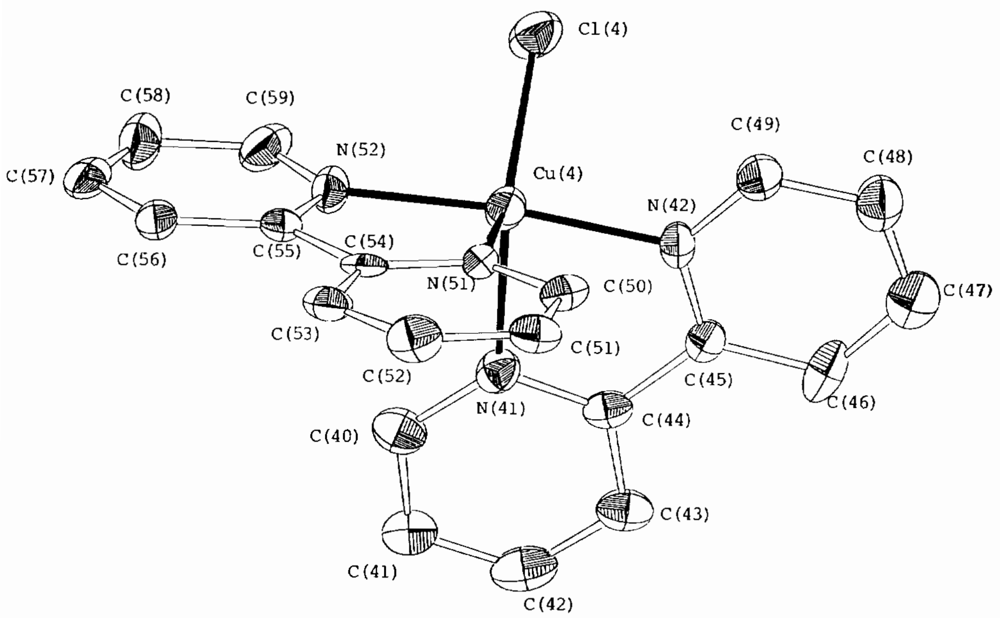

Fig. 4. ORTEP drawing of the $[CuCl(bpy)_2]^+$ cation in **3a** showing the copper square pyramidal surrounding and 50% thermal ellipsoids.

postulated in the X-ray section for **2a** is confirmed by the two absorptions observed: (i) at 505 cm^{-1} typical of a terminal W=S bond, (ii) at 925 cm^{-1} typical of a terminal W=O bond. The spectra of **2b** showed only one band at 920 cm^{-1} attributed to the terminal Mo=O vibration. On the contrary with **2a** the lack of absorption about 500 cm^{-1} confirmed that **2b** contains a pure Mo=O double bond according to the $[MoOS_3Cu_3(bpy)_2Cl]$ composition.

The main frequencies of the bipyridine ligand are observed in the 1700–600 cm^{-1} region. Among bands present in the spectra, the most interesting feature appeared at about 760 cm^{-1}. The single strong band observed in the spectra of free bipyridine at 755 cm^{-1} (νCH) split into two well-separated components at 760(s) and 740(m) cm^{-1} as a result of the coordination with copper.

Compounds 3

In compounds **3a** and **3b**, the C_2 local symmetry of the MS_4 group should lead to four IR active (M–S) frequencies. In the spectra of **3a** the four expected bands are observed at 480, 465, 440 and 425 cm^{-1} while only three are present for **3b** at 480, 450 and 425 cm^{-1}. In the region of expected ν(CuCl) frequencies [26], two bands are observed for both compounds at 365 and 325 cm^{-1}.

Compound 4

Though the structure of **4** was not determined, it appeared from IR data that **4** unambiguously contains the $[WS_4Cu_3Cl_3]^{2-}$ anion (absorptions at 475, 445, 425 and 345 cm^{-1}) probably associated with $[Cu(bpy)_2]^+$ cations (bands at 770, 740, 700, 665 and 650 cm^{-1}).

Synthesis

$[MS_4Cu_3(bpy)_2Cl]$ (**2a, 2b**) were obtained by substitution of monodentate Cl^- ligands by bidentate bipyridines in $[MS_4Cu_4Cl_4]^{2-}$. The substitution proceeded through a ligand transfer from iron to copper since direct addition of bipyridine to $[MS_4Cu_4Cl_4]^{2-}$ did not yield the expected compounds **2a** and **2b**.

In all the preparations described here, the first compound systematically isolated was $[Fe_2OCl_6]^{2-}$ resulting from oxidation of $[Fe(bpy)_3]Cl_2$. In $[Fe(bpy)_3]Cl_2$, the central Fe(II) ion is highly stabilized and protected against oxidation by the three bipyridine ligands since $[Fe(bpy)_3]Cl_2$ dissolved in a mixture of acetonitrile–dichloromethane recrystallized without evidence of oxidation of the Fe(II) metallic centre. Nevertheless oxidation of Fe(II) was readily obtained in the presence of $[MS_4Cu_4Cl_4]^{2-}$ giving $[Fe_2OCl_6]^{2-}$ (**1**) and $[MS_4Cu_3(bpy)_2Cl]$ (**2**), so revealing a transfer of bipyridine from iron to copper.

$$[Fe(bpy)_3]Cl_2 + [MS_4Cu_4Cl_4]^{2-} + \frac{1}{2}\,O_2 \longrightarrow$$

$$[Fe_2OCl_6][Fe(bpy)_3]\ (\mathbf{1}) + [MS_4Cu_3Cl(bpy)_2]\ (\mathbf{2})$$

$$+ [Cu(bpy)_2Cl] + 2Cl^- + 2\,bpy$$

Formation of $[Cu(bpy)_2Cl]$ might be postulated with respect to the evidence of its oxidized form $[Cu(bpy)_2Cl]^+$ (**3**) obtained by standing the reaction mixture in the air for 48 h. This oxidation is strictly similar to the oxidation of the analogous [Cu(phen)$_2$NCS] in [Cu(phen)$_2$NCS]$^+$ previously observed in the formation of [MS$_4$Cu$_2$(phen)$_2$] [28].

Supplementary material

Crystallographic data for compound **I** (Table S(I)), final atomic coordinates (Table S(II)), selected bond distances and angles (Table S(III)) and anisotropic thermal parameters for [Fe$_2$OCl$_6$]$^{2-}$ (Table S(IV)) and anisotropic thermal parameters of **2a** (Table S(V)) and **3a** (Table S(VI)) are available from the authors on request.

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