Derivatives of Tetrathiometallates. Synthesis of $[MS_4M'(bpy)_2]$ (M = Mo, W; M′ = Co, Ni, Mn, Ru) Complexes. Structural Characterization of $[Ni(bpy)_3][(WS_4)_2Pd]$

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(Received November 21, 1988; revised February 4, 1989)

Abstract

Reaction of $M'Cl_2(bpy)_2$ (M′ = Co, Ni, Mn) with $(PPh_4)_2MS_4$ (M = Mo, W) affords $MS_4M'(bpy)_2$. Crystals of $WS_4Co(bpy)_2,\frac{1}{2}$dmf are monoclinic space group $P2_1/n$ ($a = 12.458$, $b = 21.862$, $c = 10.164$ Å and $\beta = 100.0°$, $Z = 4$, $R = 0.039$ for 5414 independent data). The coordination geometry around the cobalt atom is octahedrally distorted with two bipyridyl groups and two sulfur atoms being *cis* to each other. Reaction of $M'Cl_2(bpy)_2$ with $[NEt_4]_2[(MS_4)_2M'']$ (M″ = Pd, Pt) gives $[M'(bpy)_3][(MS_4)_2M'']$. Crystals of $[Ni(bpy)_3][(WS_4)_2Pd]$ are triclinic, space group $P\bar{1}$ ($a = 12.771$, $b = 14.838$, $c = 12.077$ Å, $\alpha = 72.9$, $\beta = 116.9$ and $\gamma = 96.1°$, $Z = 2$, $R = 0.042$ for 3842 independent data). In the anionic species, the central palladium atom is coordinated by two chelating WS_4^{2-} anions leading to a distorted PdS_4 square plane moiety, the W...Pd...W core being nearly linear (173.72(6)°). Synthesis of new ruthenium complexes $[WS_4Ru(bpy)_2]$ and $[WS_4(Ru(bpy)_2)_2][PF_6]_2$ are also reported.

Introduction

Work on the coordination chemistry of MoS_4^{2-} and WS_4^{2-} has focused almost exclusively on coordination compounds with inorganic ligands [1–3]. Only a few complexes with organic ligands derived from the tetrathiometallate anions have been prepared and structurally characterized [4–9]. This paper describes an extension of this synthetic work to include binuclear complexes $MS_4M'(bpy)_2$ (M = Mo, W; M′ = Co, Ni, Mn, Ru) and the X-ray characterization of the representative $WS_4Co(bpy)_2,\frac{1}{2}$dmf.

In order to force the formation of polymetallic systems we have exploited the reactivity of $M'Cl_2(bpy)_2$ with $MS_4M'(bpy)_2$. Only a ruthenium–tungsten complex $[WS_4(Ru(bpy)_2)_2]^{2+}$ was obtained most likely comparable to the molybdenum analogues recently reported [10]. In addition we investigated the reaction between $M'Cl_2(bpy)_2$ and the tetrathiometallate complexes $[(MS_4)_2M'']^{2-}$ (M″ = Ni, Pd, Pt) prepared by Müller *et al.* [11, 12] and studied by Callahan and Piliero [13]. We report here on our attempts to obtain polymetallic complexes and on the X-ray crystal structure of $[Ni(bpy)_3][(WS_4)_2Pd]$.

Experimental

Chemicals and solvents were used as purchased. $M'Cl_2(bpy)_2$ (M′ = Co, Ni, Mn; bpy = 2,2′-bipyridine) were prepared by the usual literature methods [14, 15]. $RuCl_2(bpy)_2$ was synthesized according to the procedure of Meyer *et al.* [16]. $[(MS_4)_2M'']^{2-}$ (M″ = Pd, Pt) were obtained as in ref. 13.

Elemental analyses were performed by the 'Service Central d'Analyses du CNRS'. The possibility of occluded solvent molecules is not considered in the analytical results.

Preparation of $MS_4M'(bpy)_2$ (1) (M = Mo, W; M′ = Co, Ni, Mn)

$(PPh_4)_2WS_4$ (0.2 mmol) was dissolved in 20 ml of CH_3CN. Addition of $M'Cl_2(bpy)_2$ previously dissolved in 5 ml of CH_3OH led to the precipitation of a brown crude product which was collected by filtration, dried *in vacuo* and analysed as $MS_4M'(bpy)_2$.

Anal. Calc. for $C_{20}H_{16}N_{14}WNiS_4$: C, 35.2; N, 8.2; S, 18.7; Ni, 8.6; W, 26.9. Found: C, 36.2; N, 7.2; S, 17.0; Ni, 7.6; W, 26.1%.

Calc. for $C_{20}H_{16}N_{14}MoNiS_4$: C, 40.4; N, 9.4; S, 21.5; Ni, 9.9; Mo, 16.1. Found: C, 41.1; N, 9.7; S, 20.4; Ni, 8.4; Mo, 16.2%.

Calc. for $C_{20}H_{16}N_{14}WMnS_4$: C, 35.4; H, 2.4; N, 8.25; S, 18.9; Mn, 8.1; W, 27.1. Found: C, 38.7; H, 2.6; N, 8.8; S, 17.1; Mn, 7.0; W, 25.8%.

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Suitable crystals for X-ray diffraction were obtained by slow diffusion of a methanol solution of $CoCl_2(bpy)_2$ (0.15 mmol in 2 ml) in a dimethylformamide (dmf) solution of $(PPh_4)_2WS_4$ (0.15 mmol in 5 ml).

A temperature dependent susceptibility was observed by the Faraday method in the 100–292 K range, the magnetic susceptibility obeys the Curie law. The magnetic moment corrected for diamagnetic contributions is calculated to be 4.41 μ_B; this value is consistent with the presence of three unpaired electrons as expected for monomeric high-spin d^7 complexes. The compounds are insoluble in all usual solvents except slightly in dmf with slow decomposition.

Preparation of $WS_4Ru(bpy)_2$

A filtered solution of $RuCl_2(bpy)_2$ (0.520 g, 1.0 mmol) in ethanol/water (4:1, vol./vol., 200 ml) was added to a solution of $(NH_4)_2WS_4$ (0.348 g, 1 mmol) in 100 ml of the same solvent. The mixture was stirred for 20 h at room temperature and filtered. The resulting precipitate was collected by filtration, washed with ethanol, water and diethylether and dried *in vacuo* to give a dark brown powder of $WS_4Ru(bpy)_2$ in a 60% yield.

Anal. Calc. for $C_{20}H_{16}N_4WRuS_4$: C, 33.1; N, 7.7; S, 17.7; Ru, 13.9; W, 25.3. Found: C, 33.6; N, 7.6; S, 16.4; Ru, 14.0; W, 25.3%.

This molecular complex is slightly soluble in dmf without decomposition.

Preparation of $[WS_4(Ru(bpy)_2)_2][PF_6]_2$

A mixture of $RuCl_2(bpy)_2$ (0.13 g, 0.25 mmol) and $WS_4Ru(bpy)_2$ (0.19 g, 0.25 mmol) was refluxed for 4 h in 50 ml of ethanol/water (4:1, vol./vol.) under argon atmosphere. The resulting solution was cooled and concentrated to *c.* 15 ml under reduced pressure. To the filtrate was added an aqueous solution (20 ml) of excess NH_4PF_6 (0.16 g, 1.0 mmol) to give a dark precipitate which was filtered off, washed with water and dried *in vacuo*. The yield was 65%.

Anal. Calc. for $C_{40}F_{12}H_{32}N_8WP_2Ru_2S_4$: C, 33.6; N, 7.8; P, 4.3; S, 9.0; Ru, 14.1; W, 12.9. Found: C, 35.1; N, 7.6; P, 3.7; S, 7.9; Ru, 14.2; W, 10.3%.

Preparation of $[M'(bpy)_3][(MS_4)_2M'']$ (2) ($M = Mo, W$; $M'' = Pd, Pt$; $M' = Ni, Co, Mn$)

Reactions were carried out by diffusion methods. A solution of $M'Cl_2(bpy)_2$ (0.15 mmol) in 2 ml of methanol was carefully poured on the top of a dmf solution (5 ml) of $[(MS_4)_2M''][NEt_4]_2$ (0.15 mmol). Microcrystalline products were obtained after 1–2 days at room temperature.

Anal. for $C_{30}H_{24}N_6PdWNiS_4$: C, 28.6; N, 6.7; S, 20.4; Pd, 8.5; Ni, 4.7; W, 29.3. Found: C, 28.3; N, 4.6; S, 22.1; Pd, 9.7; Ni, 3.1; W, 31.6%.

Suitable crystals for X-ray diffraction were obtained with $NiCl_2(bpy)_2$ and $[(WS_4)_2Pd][(NEt_4)_2]$.

Crystal Structural Determination

Diffraction experiments were performed on a Philips PW1100 diffractometer at 20 °C using graphite-monochromatized Mo Kα radiation and a θ–2θ flying-step scan technique. Specific parameters pertaining to the data collection are reported in Table 1. Absorption corrections were performed for 1 and 2. The structures were solved by normal heavy

TABLE 1. Experimental details of diffraction studies

Compound	$WS_4Co(bpy)_2,\frac{1}{2}dmf$	$[Ni(bpy)_3][(WS_4)_2Pd]$
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	12.458	12.772
b (Å)	21.862	14.838
c (Å)	10.164	12.077
α (°)	90.0	72.9
β (°)	100.0	116.6
γ (°)	90.0	96.0
Z	4	2
Crystal size (mm)	0.39 × 0.34 × 0.18	0.36 × 0.16 × 0.06
μ (cm^{-1})	48.7	76.4
Transmission factors	0.56–0.72	0.54–0.81
Scan range (2θ°)	2.0–60.0	2.0–40.0
Scan rate (° min^{-1})	0.025	0.02
Scan width (°)	1.20	1.20
No. reflections measured	8233	5103
No. data used ($F_o^2 > 3\sigma(F_o^2)$)	5414	3842
Final parameters varied	291	333 + 99
Final R	0.039	0.042
Final R_w	0.052	0.048

atom Patterson and Fourier procedures and refined by full matrix least-squares methods using Ibers' NUCLS program.

$WS_4Co(bpy)_2,\frac{1}{2}dmf$ *(1)*

Anisotropic temperature factors were used for refinement of all atoms. Final difference Fourier maps exhibit peaks attributed to a solvent molecule (dmf) which was introduced in subsequent refinement. The hydrogen atoms of 2,2′-bipyridine ligand were included in the calculations in idealized positions (assuming the appropriate geometries and a C–H distance of 0.95 Å). The thermal parameter for a given hydrogen atom was arbitrarily taken as 6 Å^2 and was kept fixed.

$[Ni(bpy)_3][(WS_4)_2Pd]$ *(2)*

Final atomic positional parameters are obtained with anisotropic temperature factors for all atoms. No hydrogen atoms were introduced in the refinement. The final model for the structure was refined in two blocks.

Results and Discussion

The crystal structure of **1** is depicted in Fig. 1. Four well separated molecules in the cell are formed of approximately tetrahedral WS_4 unit with an edge bridging $Co(bpy)_2$ moiety. Selected angles and distances are given in Table 2. The two independent W–S (terminal: S(2) and S(3)) bond distances are consistent with formal W–S double bonds [17] while the bridging sulfur atoms (S(1), S(4)) form longer bond lengths to tungsten. The distribution of ligands about the cobalt atom is distorted octahedral with two bipyridyl groups and sulfur atoms *cis* to each other. The Co–S (bridging) bond distances (2.450(2) and 2.462(2) Å) are considerably longer than expected on the basis of the values reported for similar bonds in $[(WS_4)_2Co]^{2-}$ [18] with a tetrahedral environment for cobalt. The axial Co–N bond distances (average 2.12 Å) agree well with the values found for such bonds in some other complexes containing $Co(bpy)^{2+}$ moieties [19]. On the other hand, the Co–N bond lengths *trans* to the bridging sulfur ligands show some lengthening. There are no unusual bond lengths and bond angles in the bipyridyl ligands. The two aromatic groups are planar (max. deviation: 0.056 Å for a carbon atom) and their mean planes display a dihedral angle of 82.9°. The W...Co separation

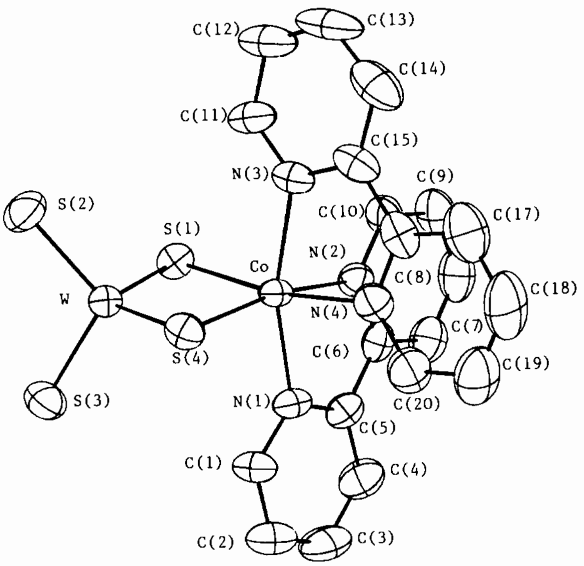

Fig. 1. ORTEP drawing of the $WS_4Co(bpy)_2$ molecule and the atomic numbering scheme employed.

TABLE 2. Selected interatomic distances and angles in 1 and 2

$WS_4Co(bpy)_2,\frac{1}{2}dmf$			
W–S(1)	2.216(2)	Co–S(1)	2.462(2)
W–S(2)	2.161(2)	Co–S(4)	2.450(2)
W–S(3)	2.160(2)	Co–N(1)	2.117(5)
W–S(4)	2.227(2)	Co–N(2)	2.158(5)
W...Co	2.9766(7)	Co–N(3)	2.123(5)
		Co–N(4)	2.153(5)
S(1)–W–S(2)	110.24(7)	S(2)–W–S(3)	110.72(9)
S(1)–W–S(3)	108.57(8)	S(2)–W–S(4)	109.58(8)
S(1)–W–S(4)	108.06(6)	S(3)–W–S(4)	109.62(7)
S(1)–Co–S(4)	94.12(6)	N(1)–Co–N(2)	76.1(2)
S(1)–Co–N(1)	95.7(2)	N(1)–Co–N(3)	163.9(2)
S(1)–Co–N(2)	89.6(1)	N(1)–Co–N(4)	92.2(2)
S(1)–Co–N(3)	95.3(2)	N(2)–Co–N(3)	92.2(2)
S(1)–Co–N(4)	170.9(2)	N(2)–Co–N(4)	88.0(2)
S(4)–Co–N(1)	95.1(2)	N(3)–Co–N(4)	76.0(2)
S(4)–Co–N(2)	170.8(1)	W–S(1)–Co	78.83(5)
S(4)–Co–N(3)	95.8(2)	W–S(4)–Co	78.91(6)
S(4)–Co–N(4)	89.5(1)		
$[Ni(bpy)_3][(WS_4)_2Pd]$			
W(1)–S(1)	2.236(4)	W(2)–S(4)	2.239(4)
W(1)–S(2)	2.157(4)	W(2)–S(5)	2.225(4)
W(1)–S(3)	2.235(4)	W(2)–S(6)	2.157(5)
W(1)–S(8)	2.145(5)	W(2)–S(7)	2.135(5)
W(1)...Pd	2.879(1)	W(2)...Pd	2.900(1)
Pd–S(1)	2.352(4)	Pd–S(4)	2.343(4)
Pd–S(3)	2.347(4)	Pd–S(5)	2.341(4)
S(1)–W(1)–S(2)	110.5(2)	S(4)–W(2)–S(5)	104.7(1)
S(1)–W(1)–S(3)	105.2(1)	S(4)–W(2)–S(6)	111.5(2)
S(1)–W(1)–S(8)	111.0(2)	S(4)–W(2)–S(7)	110.8(2)
S(2)–W(1)–S(3)	112.0(2)	S(5)–W(2)–S(6)	110.9(2)
S(2)–W(1)–S(8)	110.1(2)	S(5)–W(2)–S(7)	109.4(2)
S(3)–W(1)–S(8)	107.9(2)	S(6)–W(2)–S(7)	109.4(2)
S(1)–Pd–S(3)	98.2(1)	S(4)–Pd–S(5)	98.0(1)
S(1)–Pd–S(4)	83.2(1)	W(1)...Pd...W(2)	173.72(6)
S(3)–Pd–S(5)	81.8(1)		

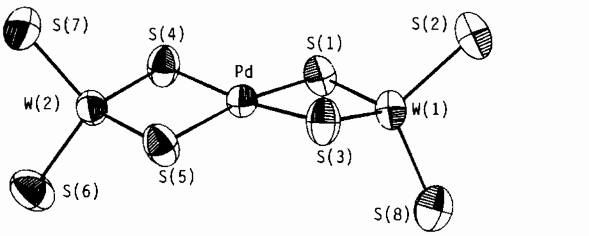

Fig. 2. Perspective view of the $[(WS_4)_2Pd]^{2-}$ dianion and the atomic numbering scheme employed.

of 2.9766(7) Å is 0.18 Å longer than that mentioned in $[(WS_4)_2Co]^{2-}$, it precludes any significant metal–metal interaction.

The crystal structure of 2 consists of isolated anions and cations in general positions in the cell. In the dianion shown in Fig. 2, the central palladium atom is coordinated by two bidentate chelating $WS_4{}^{2-}$ anions leading to a distorted PdS_4 square planar moiety comparable with the rigorously planar central NiS_4 group in $[(WS_4)_2Ni]^{2-}$ [20]. Other compounds of this series $[(WS_4)_2M]^{2-}$ with M = Co [18], Zn [21] have been structurally characterized but with a distorted tetrahedral environment for the central M atom.

Therefore, as a consequence of the strain in the PdS_4 group, all angles S–Pd–S (Table 2) have values significantly different from 90°, the central Pd atom being perfectly located in the mean plane of the bridged sulfur atoms. Within the WS_2PdS_2W group, significant differences between the Pd–S and the W–S bond distances are observed. The tungsten atom is involved in a distorted tetrahedral geometry with the S–W–S bond angles subtended by the W–S(bridging) bond lengths smaller than the tetrahedral value. The WS_2PdS_2W core is not truly planar since the dihedral angle between the planes defined by PdS(4)S(5) and W(2)S(4)S(5) atoms is 0.27° while the corresponding angle between the planes defined by PdS(1)S(3) and W(1)S(1)S(3) atoms is 12.15°. The two Pd...W separations are 2.879(1) and 2.900(1) Å, the W...Pd...W core is nearly linear (173.72(6)°).

The six nitrogen atoms in the tris(2,2′-bipyridyl)-nickel(II) cation form a distorted octahedron around the nickel atom with a mean Ni–N distance of 2.09(1) Å and average N–Ni–N bite angle of 78.7(5)°. The 2,2′-bipyridyl ligands are all planar within experimental accuracy. There are no significant differences in the bond lengths and angles of bipyridyl groups in $Ni(bpy)_3{}^{2+}$ in accordance with related complexes [22].

The vibrational spectra of $WS_4M'(bpy)_2$ and $[WS_4(Ru(bpy)_2)_2][PF_6]_2$ are given in Table 3. Bands attributed to the W–S stretching vibrations have been found in the region 422–516 cm^{-1} [23] but unfortunately the out-of-plane bipyridine deformations are observed in the same range [24]. Consequently no assignment is proposed. Our IR absorption data are in good agreement with those obtained for the high-spin $[WS_4Fe(bpy)_2]$ complex by Nakamoto *et al.* [25].

Electronic spectra are listed in Table 3. The $[WS_4M'(bpy)_2]$ (M′ = Co, Ni, Mn) compounds are insoluble in all usual organic solvents and cleave in dmf. However the electronic spectra of $[WS_4Ru(bpy)_2]$ and $[WS_4(Ru(bpy)_2)_2][PF_6]_2$ show absorption bands in the visible region. The absorptions at 524 nm may be associated with Ru to bipyridine charge transfer bands by reference to the assignments for the absorption spectrum of $[RuCl_2(bpy)_2]$ [26]. The remaining bands in the visible region involve the charge transfer transitions from sulfur to tungsten [1, 27] with additional contribution of the ruthenium to bipyridine charge transfer [26]. The ultraviolet region is dominated by intraligand (bipyridine) transitions with contribution of the charge transfer of the WS_4 moiety.

Supplementary Material

Atomic coordinates, thermal parameters, mean planes, complete bond distances and bond angles,

TABLE 3. Spectral data for complexes

Complex	IR [ν(W–S) and deformation of bpy]^a	UV–Vis^b
$WS_4Co(bpy)_2$	490(m)^c, 480(s), 475(sh), 442(s), 435(sh), 415(w)	
$WS_4Ni(bpy)_2$	485(sh), 480(s), 448(s), 435(sh), 412(w)	
$WS_4Mn(bpy)_2$	490(m), 478(s), 438(s), 410(w)	
$WS_4Fe(bpy)_2$	492(sh), 486, 443, 432^d	
$WS_4Ru(bpy)_2$	482(sh), 480(s), 445(m), 430(m)	556(4.03), 452(8.76), 348(sh), 288(40.59), 258(25.85)
$[WS_4(Ru(bpy)_2)_2][PF_6]_2$	470(m), 445(s), 430(sh)	524(12.09), 460(sh), 392(15.12), 288(70.56), 256(53.43)

^{a}Positions for 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}Abbreviations: s, strong; m, medium; w, weak; sh, shoulder. ^{d}Ref. 21.

and an ORTEP drawing for $[Ni(bpy)_3]^{2+}$ are available from the authors on request.

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