Syntheses, crystal structure and spectroscopic properties of sulfur-bridged trinuclear complexes, $[\{Ru(TMP)_4\}_2(\mu\text{-}MS_4)](PF_6)_2$ (M = Mo,W; TMP = $P(OMe)_3$)

Takaya Matsumoto, Kazuko Matsumoto*
Department of Chemistry, Waseda University, Tokyo 169 (Japan)

and Toshio Sato
Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University, Aramaki Aoba, Aoba-ku, Sendai 980 (Japan)

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Abstract

Sulfur-bridged trinuclear compounds, $[\{Ru(TMP)_4\}_2(\mu\text{-}MS_4)](PF_6)_2$ (M = Mo, W; TMP = $P(OMe)_3$), have been synthesized and the crystal structure of the compound with M = W has been determined with single-crystal X-ray diffraction analysis. The crystal is monoclinic, space group $P2_1/c$ with $a = 15.980(4)$, $b = 19.921(3)$, $c = 21.651(4)$ Å, $\beta = 107.02(2)°$ and $Z = 4$. Least-squares refinement of the structure resulted in the final $R = 0.0863$ ($R_w = 0.0924$). The Ru–W distances are 2.988(2) and 3.002(2) Å.

Introduction

Recently tetrathiometalates (MS_4^{n-}; M = Mo, W, V) have been studied as ligands for various transition metals [1–9]. The iron compounds with MoS_4^{2-} as the ligand have been above all noted because of their relevance to the functional and structural models for the active sites of nitrogenase enzymes. The authors have reported the syntheses of sulfur-bridged trinuclear compounds, $[\{(Ru(L)(CO)(PPh_3)\}_2(\mu\text{-}MS_4)]$ (M = Mo, W; L = PhNCHS, $CH_2CH_2(C_5H_4N)$, $CH_2CH_2C(O)OMe$) [10]. Among the compounds synthesized, $[\{Ru(PhNCHS)(CO)(PPh_3)\}_2(\mu\text{-}MS_4)]$ exhibits a CO elimination reaction by Me_3NO and a novel trinuclear compound with a five-coordinated Ru atom, $[\{Ru(PhNCHS)(PPh_3)\}(\mu\text{-}MS_4)\{Ru(PhNCHS)(CO)(PPh_3)\}]$ has been isolated. The sixth vacant site is, contrary to our expectation, too resistant to coordination and, in spite of our extensive attempt to coordinate various ligands (N_2H_4, diphenylacetylene, CH_3CN or Et_3N) to the sixth vacant coordination site, only pyridine has so far been successfully coordinated to the coordinatively unsaturated Ru atom. We thought this poor reactivity of the compound would be due to the blocking effect of the adjacent bulky PPh_3 ligand, and attempted to replace PPh_3 in $[\{Ru(PhNCHS)(CO)(PPh_3)\}_2(\mu\text{-}MS_4)]$ with less bulky $P(OMe)_3$ (TMP). The result is that a trinuclear compound, $[\{Ru(TMP)_4\}_2(\mu\text{-}MS_4)](PF_6)_2$ (M = Mo, W) was unexpectedly obtained. We report here the crystal structure and the spectroscopic properties of these trinuclear compounds.

Experimental

Synthesis of $[\{Ru(TMP)_4\}_2(\mu\text{-}WS_4)](PF_6)_2$

A benzene solution (50 cm^3) of $[\{Ru(PhNCHS)(CO)(PPh_3)\}_2(\mu\text{-}WS_4)]$ (1.37 g, 1.0 mmol) and $P(OMe)_3$ (10 cm^3) was refluxed for 30 min and the resulting solution was condensed to 1/10. Small amounts of methanol and NH_4PF_6 (0.65 g, 4.0 mmol) were added to the solution and a mixture of ether/THF (2:1) was added until precipitation occurred. The precipitate was recrystallized from acetone and orange plate crystals were obtained by an ether diffusion method. The yield was 41%. *Anal.* Found: C, 16.36; H, 4.09. Calc. for $[\{Ru(TMP)_4\}_2(\mu\text{-}WS_4)](PF_6)_2$: C, 16.04; H, 4.04%. UV–vis (CH_2Cl_2): λ_{max} 319.0 ($\epsilon = 13.43 \times 10^3$), 441.5 nm ($\epsilon = 8.27 \times 10^3$ M^{-1} cm^{-1}). ^{31}P NMR ($CDCl_3$): δ 129.91 (2P, t, $^2J(P\text{–}P) = 58.0$ Hz), 115.61 (2P, t, $^2J(P\text{–}P) = 57.0$ Hz), −147.16 (2P, septet, $^1J(F\text{–}P) = 711.8$ Hz). IR (KBr): 3008(w), 2960(m), 2852(w), 1636(vw), 1462(w), 1448(w), 1180(w), 1122(w), 1050(vs), 844(vs), 804(s), 780(s), 724(s), 560(s), 462(m), 410(w), 322(w) cm^{-1}. Mass (FAB): *m/e* 1653 $(M - PF_6)^+$, 1528 $(M - PF_6 - TMP)^+$,

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*Author to whom correspondence should be addressed.

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1404 $(M-\mathrm{PF}_6-2\mathrm{TMP})^+$, 1279 $(M-\mathrm{PF}_6-3\mathrm{TMP})^+$, 629 1/2 $(M-2\mathrm{PF}_6-2\mathrm{TMP})^{2+}$.

Synthesis of $[\{\mathrm{Ru(TMP)_4}\}_2(\mu\text{-}\mathrm{MoS_4})](\mathrm{PF_6})_2$

The compound was obtained as red plate crystals in the same way as for $[\{\mathrm{Ru(TMP)_4}\}_2(\mu\text{-}\mathrm{MoS_4})](\mathrm{PF_6})_2$ by using $[\{\mathrm{Ru(PhNCHS)(CO)(PPh_3)}\}_2(\mu\text{-}\mathrm{MoS_4})]$ instead of its tungsten analogue as the starting material. The yield was 48%. *Anal.* Found: C, 17.44; H, 4.23. Calc. for $[\{\mathrm{Ru(TMP)_4}\}_2(\mu\text{-}\mathrm{MoS_4})](\mathrm{PF_6})_2$: C, 16.87; H, 4.24%. UV–vis ($\mathrm{CH_2Cl_2}$): λ_{max} 352.5 ($\epsilon = 11.40 \times 10^3$), 530.0 nm ($\epsilon = 9.23 \times 10^3$ $\mathrm{M^{-1}\ cm^{-1}}$). ^{31}P NMR ($\mathrm{CDCl_3}$): δ 130.96 (2P, t, ^2J(P–P) = 57.0 Hz), 114.68 (2P, t, ^2J(P–P) = 57.0 Hz), −147.16 (2P, septet, ^1J(F–P) = 711.9 Hz). IR (KBr): 3000(w), 2956(m), 2852(w), 1630(vw), 1462(w), 1448(w), 1180(m), 1050(vs), 844(vs), 804(s), 780(s), 724(s), 560(s), 476(m), 412(w), 322(w) $\mathrm{cm^{-1}}$. Mass (FAB): *m/e* 1564 $(M-\mathrm{PF}_6)^+$, 1441 $(M-\mathrm{PF}_6-\mathrm{TMP})^+$, 1317 $(M-\mathrm{PF}_6-2\mathrm{TMP})^+$, 1191 $(M-\mathrm{PF}_6-3\mathrm{TMP})^+$, 585 1/2 $(M-\mathrm{PF}_6-2\mathrm{TMP})^{2+}$.

Physical measurements

IR spectra were recorded as KBr disks using a Hitachi I-3000 spectrophotometer and electronic spectra were measured on a Shimadzu UV-3101PC spectrometer using a 1 cm quartz cell. Resonance Raman spectra were measured as $\mathrm{CH_2Cl_2}$ solutions on a Spex Ramalog 6 double monochromator. The excitation sources were the 457.9 and 476.5 nm lines from an $\mathrm{Ar^+}$ laser and the 647.1 nm line from a $\mathrm{Kr^+}$ laser. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra were recorded on a JEOL GSX400 by using $\mathrm{CDCl_3}$ as the solvent. The chemical shifts are expressed in ppm referenced to an external standard of 85% $\mathrm{H_3PO_4}$. FAB mass spectra were obtained on a JEOL JMS-HX110. The samples were measured as nitrobenzylalcohol solutions.

X-ray crystallography

An orange crystal of dimensions 0.3×0.3×0.2 mm was selected for the single-crystal X-ray diffraction analysis. Crystal data and the data collection parameters are given in Table 1. The relatively high *R* values are due to the insufficient quality of the crystal; in spite of our efforts, no better crystals were obtained in any solvent. The unit cell parameters were refined by least-squares procedures and 11 313 reflections were recorded at room temperature. The intensities of three reference reflections were measured at intervals of 100 reflections throughout the data collection and showed no significant variation. The empirical absorption correction was applied.

Structure solution and refinement

The coordinates of the metal atoms were found by the direct method, and a series of block-diagonal least-squares refinements followed by Fourier synthesis revealed all the remaining atoms. The structure was finally refined with anisotropic temperature factors for all the atoms to the final discrepancy index of $R = 0.086$ and $R_w = 0.092$, where $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$ and $R_w = [\Sigma w_i(|F_o| - |F_c|)^2/\Sigma w_i|F_o|^2]^{1/2}$ ($w_i = (1/\sigma^2(F))$). Atomic scattering factors and anomalous dispersion corrections were taken from ref. 11. All the calculations were performed with the program systems UNICS-III [12] and ORTEP [13]. The final positional and thermal parameters are listed in Table 2.

TABLE 1. Crystallographic data for $[\{(\mathrm{TMP})_4\mathrm{Ru}\}_2\mathrm{WS_4}](\mathrm{PF_6})_2$ ($\mathrm{TMP} = \mathrm{P(OMe)_3}$)

Chemical formula	$\mathrm{C_{24}H_{72}O_{24}P_{10}F_{12}S_4Ru_2W}$
Formula weight	1796,77
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
a (Å)	15.980(4)
b (Å)	19.921(3)
c (Å)	21.651(4)
β (°)	107.02(2)
V (Å^3)	6590(2)
Z	4
D_{calc} (g cm^{-3})	1.81
μ (cm^{-1})	26.79
T (°C)	23 ± 1
Crystal dimensions (mm)	0.3×0.3×0.2
Radiation	Mo Kα ($\lambda = 0.71068$ Å)
Diffractometer	Rigaku AFC-5R
Scan mode	$2\theta/\omega$
Scan width (°)	$\omega = 1.30 + 0.14\ \tan\theta$
Scan range (°)	$3.0 < 2\theta < 50.0$
Scan rate (°/min)	8.0 in 2θ
$\pm h$, $\pm k$, $\pm l$ collected	$-24 \leqslant h \leqslant 24$, $0 \leqslant k \leqslant 23$, $0 \leqslant l \leqslant 19$
Standard reflections	three standards measured every 200 observations, showing only random statistical fluctuations
No. unique reflections	6238 ($\lvert F_o\rvert > 3.5\sigma\lvert F_o\rvert$)
Data processing	Lorentz, polarization and absorption
R	0.0863
R_w[a]	0.0924
GOF[b]	1.94

[a] $w = 1/\sigma^2(F)$. [b] $GOF = [\Sigma\{\Delta F(h)/\sigma(h)\}^2/(n-m)]^{1/2}$.

Results and discussion

Synthesis

Contrary to our expectation that TMP would replace only the coordinated $\mathrm{PPh_3}$ in $[\{\mathrm{Ru(PhNCHS)(CO)(PPh_3)}\}_2(\mu\text{-}\mathrm{WS_4})]$, the reaction of TMP with the trinuclear compounds resulted in the replacement of all the ligands that had been coordinated to the Ru atoms, with the sulfur-bridged trinuclear structure retained. This sort of ligand substitution reactions in

TABLE 2. Coordinates and equivalent thermal parameters

Atom	x	y	z	B_{eq}[a]
W	0.77740(6)	0.34086(4)	0.09452(4)	4.19(2)
Ru(1)	0.87968(12)	0.45660(8)	0.16661(7)	5.15(6)
Ru(2)	0.67362(10)	0.22681(7)	0.01869(7)	4.15(5)
S(1)	0.7635(4)	0.3843(3)	0.1846(2)	6.2(2)
S(2)	0.8792(4)	0.3976(3)	0.0666(2)	5.2(2)
S(3)	0.6533(3)	0.3491(2)	0.0172(2)	4.9(2)
S(4)	0.8105(3)	0.2330(3)	0.1085(2)	5.0(2)
P(1)	0.9839(5)	0.3782(3)	0.2258(3)	7.2(2)
P(2)	0.8804(5)	0.5103(3)	0.2603(3)	7.0(2)
P(3)	0.9853(5)	0.5208(3)	0.1446(3)	7.1(2)
P(4)	0.7746(5)	0.5323(3)	0.1088(3)	6.8(2)
P(5)	0.7521(4)	0.2364(3)	−0.0565(2)	5.5(2)
P(6)	0.5472(4)	0.2177(3)	−0.0652(3)	6.6(2)
P(7)	0.6952(4)	0.1141(3)	0.0270(3)	5.5(2)
P(8)	0.5862(4)	0.2249(3)	0.0898(3)	5.8(2)
O(11)	1.0117(13)	0.3128(9)	0.1915(8)	11.1(8)
O(12)	1.0727(11)	0.4131(9)	0.2686(8)	10.4(7)
O(13)	0.9503(12)	0.3379(9)	0.2785(8)	10.7(8)
O(21)	0.9290(20)	0.5729(11)	0.2758(11)	18.9(14)
O(22)	0.7970(15)	0.5293(18)	0.2688(11)	22.2(16)
O(23)	0.9136(26)	0.4697(12)	0.3185(8)	25.2(20)
O(31)	1.0335(13)	0.5809(9)	0.1848(8)	11.8(9)
O(32)	0.9526(12)	0.5595(9)	0.0769(8)	11.0(8)
O(33)	1.0618(10)	0.4729(9)	0.1338(9)	10.4(8)
O(41)	0.8014(14)	0.6065(9)	0.1225(8)	11.4(9)
O(42)	0.6796(14)	0.5363(10)	0.1243(10)	13.3(10)
O(43)	0.7456(15)	0.5250(10)	0.0332(8)	14.6(10)
O(51)	0.7463(13)	0.1732(8)	−0.0998(7)	10.0(8)
O(52)	0.8518(11)	0.2568(10)	−0.0344(7)	10.0(7)
O(53)	0.7149(11)	0.2948(8)	−0.1109(7)	9.1(7)
O(61)	0.4767(10)	0.1692(9)	−0.0540(8)	10.4(7)
O(62)	0.4923(13)	0.2826(9)	−0.0939(9)	13.4(8)
O(63)	0.5688(11)	0.1861(9)	−0.1260(8)	10.6(8)
O(71)	0.7039(11)	0.0873(7)	0.0980(7)	8.4(6)
O(72)	0.7878(12)	0.0937(8)	0.0193(8)	10.0(8)
O(73)	0.6328(14)	0.0665(9)	−0.0150(9)	12.8(9)
O(81)	0.5379(10)	0.1568(7)	0.0905(7)	8.2(6)
O(82)	0.5094(10)	0.2792(8)	0.0721(8)	8.5(7)
O(83)	0.6289(10)	0.2443(9)	0.1657(8)	9.3(7)
C(11)	1.0697(19)	0.3093(18)	0.1470(15)	13(2)
C(12)	1.1456(21)	0.3750(18)	0.3123(18)	17(2)
C(13)	0.9675(26)	0.2714(14)	0.3025(16)	15(2)
C(21)	0.9353(26)	0.6313(15)	0.3137(16)	16(2)
C(22)	0.7199(20)	0.5205(15)	0.2804(16)	12(2)
C(23)	0.9372(28)	0.4713(20)	0.3845(13)	18(2)
C(31)	1.1062(19)	0.5720(18)	0.2469(13)	14(2)
C(32)	0.9753(22)	0.6295(14)	0.0619(17)	14(2)
C(33)	1.1278(20)	0.4937(21)	0.1047(19)	17(2)
C(41)	0.7540(31)	0.6688(14)	0.1098(20)	19(3)
C(42)	0.5994(21)	0.4998(19)	0.0918(20)	17(2)
C(43)	0.7136(28)	0.5610(23)	−0.0175(16)	21(2)
C(51)	0.7521(27)	0.1698(18)	−0.1628(12)	16(2)
C(52)	0.9300(17)	0.2163(16)	−0.0044(15)	12(1)
C(53)	0.7494(19)	0.3556(11)	−0.1182(11)	9(1)
C(61)	0.3856(18)	0.1680(18)	−0.0767(17)	14(2)
C(62)	0.5005(22)	0.3365(13)	−0.1297(14)	14(2)
C(63)	0.5056(27)	0.1806(21)	−0.1957(19)	20(2)
C(71)	0.6765(28)	0.0205(14)	0.1113(16)	16(2)
C(72)	0.8378(24)	0.0380(17)	0.0373(19)	16(2)
C(73)	0.6222(29)	0.0421(24)	−0.0727(18)	22(3)
C(81)	0.4659(16)	0.1468(14)	0.1234(13)	10(1)
C(82)	0.4832(21)	0.3301(16)	0.1056(15)	14(2)
C(83)	0.6867(20)	0.1919(16)	0.2106(13)	12(1)
P(9)	0.8225(5)	0.8305(4)	−0.0176(3)	8.5(3)
P(10)	0.4231(6)	1.0019(4)	−0.2780(4)	10.7(4)
F(1)	0.7479(12)	0.7796(10)	−0.0263(13)	19(1)
F(2)	0.7610(13)	0.8696(13)	−0.0703(10)	19(1)
F(3)	0.8609(15)	0.7887(14)	−0.0598(11)	22(1)
F(4)	0.8945(12)	0.8784(11)	−0.0065(11)	17(1)
F(5)	0.8763(13)	0.7899(11)	0.0365(9)	18(1)
F(6)	0.7871(13)	0.8663(12)	0.0319(10)	18(1)
F(7)	0.4691(20)	1.0080(13)	−0.2152(11)	28(2)
F(8)	0.4686(21)	1.0578(12)	−0.2908(11)	25(2)
F(9)	0.4115(25)	0.9827(14)	−0.3441(11)	28(2)
F(10)	0.4326(27)	0.9334(11)	−0.2682(13)	30(2)
F(11)	0.3299(15)	0.9832(15)	−0.2872(15)	25(2)
F(12)	0.3736(20)	1.0605(15)	−0.2616(19)	30(2)

(*continued*)

TABLE 2. (*continued*)

[a] The equivalent isotropic displacement parameter is defined as $4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

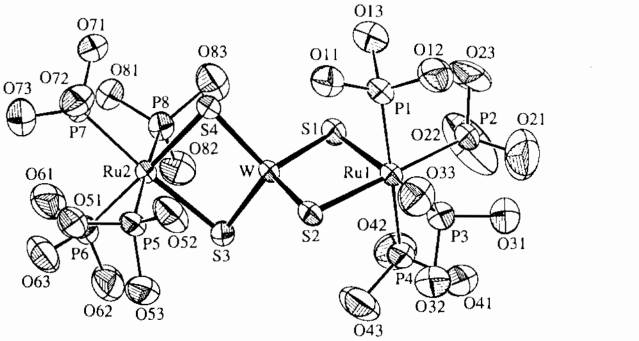

Fig. 1. Molecular structure of $[\{Ru(TMP)_4\}_2(\mu\text{-}WS_4)]^{2+}$. The methyl groups are omitted for clarity. The thermal ellipsoids are drawn at 30% probability level.

sulfur-bridged cluster compounds is very scarce and we know no precedent.

Structure of $[\{(Ru(TMP)_4\}_2(\mu\text{-}WS_4)](PF_6)_2$

The molecular structure of the cationic complex with the methyl groups omitted for clarity is shown in Fig. 1. The complex consists of a Ru–W–Ru trinuclear core with bridging sulfur atoms. Each Ru atom is coordinated by two sulfur atoms and four TMPs in an octahedron. The interatomic distances and angles are listed in Tables 3 and 4, respectively. The average Ru–W distance is 2.995 Å and those of Ru–S and W–S are 2.464 and 2.204 Å, respectively. The S–W–S angle is close to the tetrahedral angle.

The distances and angles of the present trinuclear compound are compared with those of the starting Ru compound and a similar trinuclear Ru–W–Ru compound, $[\{Ru(bpy)_2\}_2(\mu\text{-}WS_4)](PF_6)_2$ [8], in Table 5. The

TABLE 3. Interatomic distances (Å)

Metal–metal			
W–Ru(1)	2.988(2)	W–Ru(2)	3.002(2)
Coordination bond			
W–S(1)	2.204(6)	W–S(3)	2.194(5)
W–S(2)	2.205(6)	W–S(4)	2.212(5)
Ru(1)–S(1)	2.469(7)	Ru(2)–S(3)	2.456(5)
Ru(1)–S(2)	2.461(6)	Ru(2)–S(4)	2.468(5)
Ru(1)–P(1)	2.368(7)	Ru(2)–P(5)	2.335(7)
Ru(1)–P(2)	2.289(7)	Ru(2)–P(6)	2.294(6)
Ru(1)–P(3)	2.275(8)	Ru(2)–P(7)	2.271(5)
Ru(1)–P(4)	2.329(6)	Ru(2)–P(8)	2.364(7)
Ligand geometry			
P(1)–O(11)	1.62(2)	P(5)–O(51)	1.56(2)
P(1)–O(12)	1.61(2)	P(5)–O(52)	1.58(2)
P(1)–O(13)	1.61(2)	P(5)–O(53)	1.64(2)
P(2)–O(21)	1.46(2)	P(6)–O(61)	1.56(2)
P(2)–O(22)	1.45(3)	P(6)–O(62)	1.58(2)
P(2)–O(23)	1.46(2)	P(6)–O(63)	1.58(2)
P(3)–O(31)	1.55(2)	P(7)–O(71)	1.59(2)
P(3)–O(23)	1.60(2)	P(7)–O(72)	1.59(2)
P(3)–O(33)	1.62(2)	P(7)–O(73)	1.48(2)
P(4)–O(41)	1.54(2)	P(8)–O(81)	1.56(2)
P(4)–O(42)	1.65(3)	P(8)–O(82)	1.60(2)
P(4)–O(43)	1.57(2)	P(8)–O(83)	1.63(2)
O(11)–C(11)	1.52(4)	O(51)–C(51)	1.40(3)
O(12)–C(12)	1.48(4)	O(52)–C(52)	1.47(3)
O(13)–C(13)	1.42(3)	O(53)–C(53)	1.36(3)
O(21)–C(21)	1.41(4)	O(61)–C(61)	1.39(3)
O(22)–C(22)	1.34(4)	O(62)–C(62)	1.35(4)
O(23)–C(23)	1.37(3)	O(63)–C(63)	1.56(4)
O(31)–C(31)	1.51(3)	O(71)–C(71)	1.46(4)
O(32)–C(32)	1.50(3)	O(72)–C(72)	1.36(4)
O(33)–C(33)	1.44(5)	O(73)–C(73)	1.30(5)
O(41)–C(41)	1.44(4)	O(81)–C(81)	1.53(3)
O(42)–C(42)	1.46(4)	O(82)–C(82)	1.38(4)
O(43)–C(43)	1.29(4)	O(83)–C(83)	1.54(3)
Anion geometry			
P(9)–F(1)	1.53(2)	P(10–F(7)	1.35(2)
P(9)–F(2)	1.49(2)	P(10)–F(8)	1.40(3)
P(9)–F(3)	1.49(3)	P(10)–F(9)	1.44(3)
P(9)–F(4)	1.46(2)	P(10)–F(10)	1.38(2)
P(9)–F(5)	1.48(2)	P(10)–F(11)	1.49(3)
P(9)–F(6)	1.53(3)	P(10)–F(12)	1.51(3)

TABLE 4. Interatomic angles (°)

Metal–metal–metal			
Ru(1)–W–Ru(2)	178.40(5)		
Coordination geometry			
S(1)–W–S(2)	108.3(2)	S(2)–W–S(3)	109.1(2)
S(1)–W–S(3)	110.1(2)	S(2)–W–S(4)	111.7(2)
S(1)–W–S(4)	110.0(2)	S(3)–W–S(4)	107.7(2)
S(1)–Ru(1)–S(2)	93.0(2)	S(3)–Ru(2)–S(4)	92.5(2)
S(1)–Ru(1)–P(1)	88.4(2)	S(3)–Ru(2)–P(5)	90.3(2)
S(1)–Ru(1)–P(2)	86.7(2)	S(3)–Ru(2)–P(6)	89.2(2)
S(1)–Ru(1)–P(3)	176.9(2)	S(3)–Ru(2)–P(7)	176.4(2)
S(1)–Ru(1)–P(4)	90.3(2)	S(3)–Ru(2)–P(8)	85.6(2)
S(2)–Ru(1)–P(1)	89.0(2)	S(4)–Ru(2)–P(5)	90.7(2)
S(2)–Ru(1)–P(2)	179.3(2)	S(4)–Ru(2)–P(6)	178.3(2)
S(2)–Ru(1)–P(3)	84.0(2)	S(4)–Ru(2)–P(7)	84.7(2)
S(2)–Ru(1)–P(4)	91.2(2)	S(4)–Ru(2)–P(8)	92.5(2)
P(1)–Ru(1)–P(2)	90.5(2)	P(5)–Ru(2)–P(6)	89.0(2)
P(1)–Ru(1)–P(3)	92.1(3)	P(5)–Ru(2)–P(7)	92.1(2)
P(1)–Ru(1)–P(4)	178.7(3)	P(5)–Ru(2)–P(8)	174.9(2)
P(2)–Ru(1)–P(3)	96.4(3)	P(6)–Ru(2)–P(7)	93.6(2)
P(2)–Ru(1)–P(4)	89.4(2)	P(6)–Ru(2)–P(8)	87.9(2)
P(3)–Ru(1)–P(4)	89.2(3)	P(7)–Ru(2)–P(8)	92.1(2)

Ru–W distance of the present compound (2.886 Å) is significantly longer (0.11–0.15 Å) than those of the starting compound and of [{Ru(bpy)$_2$}$_2$(μ-WS$_4$)](PF$_6$)$_2$. This is probably because of the strong donating nature of TMP, which apparently exerts a strong *trans* influence to elongate the Ru–S bond *trans* to it. Furthermore, as a result of this elongation of the Ru–S distances, the W–S distances in the present compound are relatively short compared to those of the other two compounds. Regarding the Ru–N distance in [{Ru(bpy)$_2$}$_2$(μ-WS$_4$)](PF$_6$)$_2$, no significant difference was observed among the four Ru–N distances. This is probably because the *trans* influence of the sulfur atoms of WS$_4$$^{2-}$ and that of the bpy nitrogen atoms are comparable and therefore affect the Ru–N distances *trans* to them to the same extent. On the other hand, in the present compound the Ru–P distances *trans* to TMP are significantly longer than those *trans* to the sulfur atoms, which suggests that the *trans* influence of TMP is stronger than that of the sulfur atoms of WS$_4$$^{2-}$. The S–Ru–S angle of 92.8° in the present compound is closer to 90°, compared to those of the starting compound (97.0°) and [{Ru(bpy)$_2$}$_2$(μ-WS$_4$)](PF$_6$)$_2$ (98.5°). This would be because the angle strain caused by the chelate ligands in the latter two compounds is removed in the present compound.

Spectroscopic properties

The IR and UV–Vis bands in the present compounds and the starting compounds are listed in Table 6. In both the M = W and M = Mo cases, the ν(M–S) bands shift to higher wavenumbers if one compares the starting mononuclear compound with the corresponding trinuclear compound. This corresponds to the fact that the W–S distances are shortened by the trinuclear complex formation. The resonance Raman spectrum of the present compound with M = W shows a band at 469 cm^{-1} corresponding to ν(W–S), when λ_{ex} = 457.9 or 476.5 nm line was employed, however, the band was not observed when the excitation line was λ_{ex} = 647.1 nm. Furthermore, the band is more strongly enhanced by λ_{ex} = 457.9 nm, compared to λ_{ex} = 476.5 nm. From these facts, the UV–Vis absorption band at 441.5 nm of the compounds is assigned to LMCT (S–W). A similar LMCT UV–Vis band due to S–Mo and the corresponding ν(Mo–S) band in the resonance Raman

TABLE 5. Comparison of the selected interatomic distances (Å) and angles (°)

Formula	Ru–W	W–S	Ru–S[a]	S–Ru–S[a]
$[\{Ru(TMP)_4\}_2(\mu\text{-}WS_4)](PF_6)_2$	2.988(2)	2.204(6)	2.469(7)	93.0(2)
	3.002(2)	2.205(6)	2.461(6)	92.5(2)
		2.194(5)	2.456(5)	
		2.212(5)	2.468(5)	
$[\{Ru(PhNCHS)(CO)(PPh_3)\}_2(\mu\text{-}WS_4)]$[d]	2.886(2)	2.213(5)	2.375(5)[b]	97.0(2)
		2.213(6)	2.411(4)[c]	
$[\{Ru(bpy)_2\}_2(\mu\text{-}WS_4)](PF_6)_2$[e]	2.838(1)	2.222(2)	2.376(2)	98.5(1)
		2.206(2)	2.369(3)	

[a]The sulfur atom of tetrathiotungstate. [b]*trans* to S. [c]*trans* to P. [d]Ref. 10. [e]Ref. 8.

TABLE 6. Comparison of the spectroscopic data

Formula	IR[a] ν(M–S) (cm^{-1})	UV–Vis[b]	
		λ_{max} (nm)	ϵ (M^{-1} cm^{-1})
$[\{Ru(TMP)_4\}_2(\mu\text{-}WS_4)](PF_6)_2$	462	319.0	13.43×10^3
		441.5	8.27×10^3
$[\{Ru(PhNCMS)(CO)(PPh_3)\}_2(\mu\text{-}WS_4)]$	447	339.5	19.34×10^3
		437.5	5.64×10^3
$[\{Ru(TMP)_4\}_2(\mu\text{-}MoS_4)](PF_6)_2$	476	352.5	11.40×10^3
		530.0	9.23×10^3
$[\{Ru(PhNCMS)(CO)(PPh_3)\}_2(\mu\text{-}MoS_4)]$	464, 426	367.5	21.57×10^3
		552.0	8.20×10^3

[a]KBr pellet. [b]CH_2Cl_2 solution.

spectrum were observed in the MoS_4-bridged trinuclear compound $[(PhNCHS)Ru(CO)(PPh_3)]_2(MoS_4)$ [10].

The ^{31}P NMR of the present compound with M = W in $CDCl_3$ shows triplet peaks at 115.6 (^2J(P–P) = 57.0 Hz) and 129.9 (^2J(P–P) = 58.90 Hz) ppm, which suggests that the trinuclear structure is retained in solution. The peak at 115.6 ppm is assigned to the P atom *trans* to TMP and the peak at 129.9 ppm, the P atom *trans* to the sulfur atom. These assignments are based on the Ru–P distances; since the P atom *trans* to TMP receives a stronger *trans* influence having longer Ru–P distance, the electron density at the P nucleus would be higher compared to that of the P atom *trans* to the sulfur atom, thus leading to the lower chemical shift. A similar assignment based on the coordination bond distances is reported for platinum compounds [14]. The compound with M = Mo also shows two triplets at 114.7 (^2J(P–P) = 57.0 Hz) and 131.0 (^2J(P–P) = 57.0 Hz) ppm.

Conclusions

Trinuclear compounds $[\{Ru(TMP)_4\}_2(\mu\text{-}MS_4)](PF_6)_2$ (M = Mo, W) have been synthesized from a novel ligand substitution of $[\{Ru(PhNCHS)(CO)(PPh_3)\}_2(\mu\text{-}MS_4)]$ by TMP. The crystal structure of the compound with M = W was solved and the sulfur-bridged trinuclear structure was elucidated. From the elemental, IR and NMR spectroscopic analyses, we conclude that the compound with M = Mo has also the same structure as that with M = W.

Supplementary material

Anisotropic thermal parameters, detailed bond angles and the F_o–F_c tables are available from the authors on request.

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