Syntheses and structures of two rhenium–sulfur–copper cubane-like cluster compounds with the bridging sulfate anions

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ABSTRACT

Treatment of $[Et_4N][ReS_4]$ with three equivalents of $CuSO_4 \cdot 5H_2O$ in the presence of three equivalents PPh_3 gave a tetranuclear cubane-like cluster compound $[(\mu_3\text{-}SO_4)(\mu_3\text{-}ReS_4)Cu_3(PPh_3)_3] \cdot 2dmf$ (**1**·2dmf) in which a ReS_4Cu_3 core is capped by a $\mu_3\text{-}SO_4^{2-}$ moiety, leaving a S=O double bond. A similar reaction of $[Et_4N][ReS_4]$ with three equivalents of $CuSO_4 \cdot 5H_2O$ in the presence of two equivalents of PPh_3 gave rise to isolation of a neutral one-dimensional polymeric cubane-like cluster compound $[(\mu_4\text{-}SO_4)(\mu_3\text{-}ReOS_3)\text{-}Cu_3(PPh_3)_2]_n$ (**2**) in which the $ReOS_3Cu_3$ cores are bridged by the $\mu_4\text{-}SO_4^{2-}$ anions. Both cluster compounds were characterized by single-crystal X-ray diffraction along with the spectroscopic methods.

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1. Introduction

Heterobimetallic cubane-like cluster compounds containing central $[MS_4]^{n-}$ (M = Mo, W, $n = 2$; M = V, $n = 3$) cores and copper atoms have attached much interest because of their postulated implication in biological systems [1], their ability to serve as precursors of catalysts [2,3] and their potential application in nonlinear optical characteristics [4–10]. There are quite few examples of rhenium-related species based upon the $[ReS_4]^-$ central core. Actually, the $[ReS_4]^-$ ligand was expected to demonstrate a significantly different coordination behavior compared with the $[MS_4]^{2-}$ (M = Mo, W) anions which have a higher charge density [11]. This is even more remarkable in that, owing to the strongly reducing S^{2-} ligands at the Re^{VII} center, the $[ReS_4]^-$ ligand should exhibit interesting coordination chemistry [12]. Müller and others have studied interactions of $[ReS_4]^-$ with copper(I) halides and reported successively a series of rhenium–sulfur–copper cluster anions including binuclear linear complex $[(ReO_2S_2)CuI]^-$ [13], tetranuclear cubane-like clusters $[(ReOS_3)Cu_3Cl_4]^{2-}$ [11] and $[(ReS_4)Cu_3\text{-}X_4]^{2-}$ (X = Cl, I) [14], tetranuclear butterfly cluster $[(ReS_4)Cu_3Cl_5]^{3-}$ [14], hexanuclear double cubane-like clusters $[(ReS_4)Cu_5X_7]^{3-}$ (X = Cl, Br) [4,15], one-dimensional polymeric clusters $[(ReS_4)Cu_3I_4]_n^{2n-}$, $[(ReS_4)Cu_4I_5]_n^{2n-}$ and $[(ReS_4)Cu_5I_6]_n^{2n-}$ [16,17], and three-dimensional polymeric clusters $[(ReS_4)Cu_2(NCS)_2]_n^{2n-}$, $[(ReS_4)Cu_3(NCS)_4]_n^{2n-}$ and $[(ReS_4)_2Cu_2(NCS)_2]_n^{2n-}$ [5]. We report herein the syntheses and molecular structures of neutral cubane-like cluster compound $[(\mu_3\text{-}SO_4)(\mu_3\text{-}ReS_4)Cu_3(PPh_3)_3]\text{-}\cdot 2dmf$ (**1**·2dmf) and neutral one-dimensional polymeric cubane-like cluster compound $[(\mu_4\text{-}SO_4)(\mu_3\text{-}ReOS_3)Cu_3(PPh_3)_2]_n$ (**2**) with the bridging sulfate anions and triphenyl-phosphine ligands.

2. Experimental

2.1. Materials and measurements

All syntheses were performed in oven-dried glassware under a purified nitrogen atmosphere using standard Schlenk techniques. The solvents were purified by conventional methods and degassed prior to use. $[Et_4N][ReS_4]$ was prepared by the literature method [18]. Electronic absorption spectra were obtained on a Shimadzu UV-3000 spectrophotometer. Infrared spectra were recorded on a Digilab FTS-40 spectrophotometer with use of pressed KBr pellets. Positive FAB mass spectra were recorded on a Finnigan TSQ 7000 spectrometer. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300 and 121.5 MHz for ^1H and ^{31}P, respectively, and chemical shift (δ, ppm) were reported with refer-

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ence to SiMe$_4$ (1H) and H$_3$PO$_4$ (^{31}P). All elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer.

2.2. Preparation of [(μ$_3$-SO$_4$)(μ$_3$-ReS$_4$)Cu$_3$(PPh$_3$)$_3$]·2dmf (**1**·2dmf)

A solution of [Et$_4$N][ReS$_4$] (67 mg, 0.15 mmol) in DMF (10 mL) was added to a solution of CuSO$_4$·5H$_2$O (112 mg, 0.45 mmol) and PPh$_3$ (118 mg, 0.45 mmol) in MeOH-CH$_2$Cl$_2$ (1:1) (10 mL). The mixture was stirred at room temperature for 2 h, during which time the color gradually changed from purple to purple-red. A little precipitate was removed by filtration, and a clear filtrate was obtained. The purple-red filtrate was carefully layered with *i*-PrOH (15 mL). Purple-red needle crystals of [(μ$_3$-SO$_4$)(μ$_3$-ReS$_4$)Cu$_3$(PPh$_3$)$_3$] (**1**·2dmf) were obtained in three days. The product was washed with i-PrOH and Et$_2$O and dried under vacuum. Yield: 90 mg (39%). *Anal.* Calc. for C$_{54}$H$_{45}$O$_4$P$_3$S$_5$Cu$_3$Re·2(C$_3$H$_7$NO): C, 46.97; H, 3.88; N, 1.83. Found: C, 46.33; H, 3.85; N, 1.81%. UV–Vis (DMF, λ_{max}/ nm, $10^{-3}\varepsilon$/M^{-1} cm^{-1}): 266 (11.9), 295 (8.57), 437 (1.26). IR (KBr disc, cm^{-1}): ν(C–H) 3057 (m), ν(C=O) 1664 (s), ν(S=O) 1294 (s) and 1263 (s), ν(P–C) 1076 (s), ν(C–S) 693 (s), ν(Re–S) 522 (m), ν(Re–S) 451 (w), ν(Cu–P) 445 (w) and 436 (m). ^{1}H NMR (DMSO-d_6, ppm): δ 2.97 (s, 6H, *Me*$_2$NCHO), 2.88 (s, 6H, *Me*$_2$NCHO), 7.12– 7.59 (m, 45H, *Ph*), 8.01 (s, 2H, C*H*O). ^{31}P NMR (DMSO-d_6, ppm): δ 4.29 (s). MS (FAB): *m/z* 1388 (M$^+$), 1292 (M$^+$–SO$_4$).

2.3. Preparation of [(μ$_4$-SO$_4$)(μ$_3$-ReOS$_3$)Cu$_3$(PPh$_3$)$_2$]$_n$ (**2**)

A solution of [Et$_4$N][ReS$_4$] (67 mg, 0.15 mmol) in DMF (10 mL) was added to a solution of CuSO$_4$·5H$_2$O (112 mg, 0.45 mmol) and PPh$_3$ (79 mg, 0.30 mmol) in MeOH-CH$_2$Cl$_2$ (1:1) (10 mL). The mixture was stirred at room temperature for 1 h. A little precipitate was removed by filtration, and a clear filtrate was obtained. The red filtrate was carefully layered with Et$_2$O (10 mL). Purple-red block crystals of [(μ$_4$-SO$_4$)(μ$_3$-ReOS$_3$)Cu$_3$(PPh$_3$)$_2$]$_n$ (**2**) were obtained in a week. The product was washed with Et$_2$O and dried under vacuum. Yield: 53 mg (32%). *Anal.* Calc. for C$_{36}$H$_{30}$O$_5$P$_2$S$_4$Cu$_3$Re: C, 38.96; H, 2.72. Found: C, 38.87; H, 2.74%. UV–Vis (DMF, λ_{max}/nm, $10^{-3}\varepsilon$/M^{-1} cm^{-1}): 267 (12.4), 291 (9.38), 432 (2.01). IR (KBr disc, cm^{-1}): ν(S=O) 1272 (s), ν(P–C) 1073 (s), ν(Re=O) 935 (s), ν(C–S) 689 (s), ν(Re–S) 446 (w), ν(Cu–P) 449 (w) and 437 (w). ^{1}H NMR (DMSO-d_6, ppm): δ 6.85–7.38 (m, 30H, *Ph*). ^{31}P NMR (DMSO-d_6, ppm): δ 5.42 (s). MS (FAB): *m/z* 1109 (M$^+$), 1013 (M$^+$–SO$_4$).

2.4. X-ray crystallography

Crystallographic data and experimental details for [(μ$_3$-SO$_4$) (μ$_3$-ReS$_4$)Cu$_3$(PPh$_3$)$_3$]·2dmf and [(μ$_4$-SO$_4$)(μ$_3$-ReOS$_3$)Cu$_3$(PPh$_3$)$_2$]$_n$ are summarized in Table 1. Intensity data were collected on a Bruker SMART APEX 2000 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293(2) K. The collected frames were processed with the software SAINT [19]. The data was corrected for absorption using the program SADABS [20]. Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [21,22]. The metal, phosphorous, sulfur, selenium, and chloride atoms in the complexes were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C$_{sp3}$–H = 0.96 and C$_{sp2}$–H = 0.93 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon or nitrogen atoms before the final cycle of least-squares refinement. The largest peak in the final difference map had height of 1.978 e Å^{-3} in **1**·2dmf is in the vicinity of the rhenium atom. Atomic coordinates, complete bond distances and angles, and anisotropic thermal parameters of all non-hydrogen atoms for both two cluster compounds are available as supplementary materials.

Table 1
Crystallgraphic data and experimental details for [(μ$_3$-SO$_4$)(μ$_3$-ReS$_4$)Cu$_3$(PPh$_3$)$_3$]·2dmf (**1**·2dmf) and [(μ$_4$-SO$_4$)(μ$_3$-ReOS$_3$)Cu$_3$(PPh$_3$)$_2$]$_n$ (**2**).

	1·2dmf	**2**
Formula	C$_{60}$H$_{59}$N$_2$O$_6$P$_3$S$_5$Cu$_3$Re	C$_{36}$H$_{30}$O$_5$P$_2$S$_4$Cu$_3$Re
Formula weight	1534.12	1109.60
a (Å)	19.263(11)	16.213(6)
b (Å)	12.982(7)	10.296(4)
c (Å)	25.776(15)	24.666(9)
α (°)	90	90
β (°)	92.496(11)	10.109(6)
γ (°)	90	90
V (Å^3)	6440(6)	4053(3)
Z	4	4
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
ρ_{calc} (g cm^{-3})	3.136	1.818
No. of reflections	18077	24674
No. of independent reflections	13023	9318
Goodness-of-fit (GoF)[a]	0.952	0.980
R_1[b], wR_2[c] ($I > 2\sigma(I)$)	0.0796, 0.1309	0.0458, 0.0786
R_1, wR_2 (all data)	0.0945, 0.1653	0.0666, 0.0909
Parameters	715	460

[a] GoF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.
[b] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
[c] $wR_2 = [\Sigma w^2(|F_o| - |F_c|)^2/\Sigma w^2 F_o|^2]^{1/2}$.

3. Results and discussion

Interaction of [Et$_4$N][ReS$_4$] with CuSO$_4$·5H$_2$O and PPh$_3$ in a 1:3:3 ratio in the mixed DMF/MeOH/CH$_2$Cl$_2$ solvents led to the isolation of the typical tetranuclear cubane-like cluster compound [(μ$_3$-SO$_4$)(μ$_3$-ReS$_4$)Cu$_3$(PPh$_3$)$_3$]·2dmf (**1**·2dmf) as purple-red needle crystals in 39% yield, while the similar reaction of [Et$_4$N][ReS$_4$] with CuSO$_4$·5H$_2$O and PPh$_3$ in a 1:3:2 ratio gave the polymeric tetranuclear cubane-like cluster compound [(μ$_4$-SO$_4$)(μ$_3$-ReOS$_3$)- Cu$_3$(PPh$_3$)$_2$]$_n$ (**2**) as purple-red block crystals in 32% yield. Obviously, treatment of CuSO$_4$·5H$_2$O with σ-donor ligand PPh$_3$ in MeOH-CH$_2$Cl$_2$ (1:1) solution resulted in the blue solution to gradually turn to the colorless solution, indicating that the Cu(II) ion was reduced to the Cu(I) ion. The resulting Cu(I)-specie may effectively bind to three ReS$_2$ edges of the [ReS$_4$]$^-$ anion, leading to the formation of the cubane-like skeleton core {ReS$_3$Cu$_3$(SO$_4$)}$^{2+}$, in which the SO$_4^{2-}$ fragment ligates three Cu(I) ions *via* three oxygen atoms. It is not difficult to understand that the single cubane-like cluster compound **1** formed due to three equivalents of PPh$_3$ ligands bound to three copper atoms in the cubane-like skeleton core. Moreover, the following self-assembly reaction of the [(μ$_3$-SO$_4$)(μ$_3$-ReS$_4$)Cu$_3$] intermediate may occur in the present system when two equivalents of PPh$_3$ ligands was used only: two copper atoms were terminally bonded by two PPh$_3$ ligands and the leaving one copper atom was coordinated by the oxygen atom of the terminal S=O moiety in the μ$_3$-SO$_4^{2-}$ [23], resulting in formation of polymeric cluster compound **2** with a one-dimensional zigzig chain. It is believed that the Re=O group in **2** formed due to the hydrolysis of the terminal Re=S group attached to the cubane-like core during the recrytallization. Hydrolysis of Re=S groups to give Re=O groups have been found for analogous thiomolybdate and thiotungstate systems previously [24,25].

The main features in the electronic absorption spectra in DMF solution at room temperature are structured bands at 266– 268 nm, to which aromatic $\pi \rightarrow \pi^*$ transitions make the major contribution. The relatively low energy absorption bands at 290– 295 nm which are probably assigned to $\pi(S^{2-}) \rightarrow d(Re^{VII})$ charge transfer arising from the [ReS$_4$]$^-$ or [ReOS$_3$]$^-$ moiety [26]. Absorption spectrum of the polymeric cluster compound **2** in DMF solution is shown in Fig. 1(up). The luminescent properties of the polymeric cluster compound **2** in the solid state have been