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Synthesis and structures of tetranuclear rhenium–cobalt mixed metal sulfide clusters [Re₃CoS₄Cl₆(PMe₂Ph)₄]

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Abstract

An isomeric pair of the title compounds have been prepared and characterized by NMR spectroscopy and X-ray crystallography. The major isomer contains three dimethylphenylphoshine ligands coordinated to rhenium atoms in the direction of the μ_3 -S atom in the starting trinuclear rhenium cluster complex, whereas the minor isomer has a dimethylphenylphosphine ligand in the opposite direction. The temperature of the preparative reactions controls the orientation of the phosphine ligands. © 2004 Elsevier Ltd. All rights reserved.

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1. Introduction

Recent development of the chemistry of sulfide and selenide cluster compounds of rhenium has been limited mostly to hexanuclear compounds [1,2]. Only a few trinuclear and tetranuclear rhenium chalcogenide cluster compounds are known [3,4] and mixed metal clusters are even rarer, a single example being a rhenium-nickel complex [Re₃NiS₄Cl₆(PEt₃)₄] [5]. Rhenium is a group 7 metal and its cations are isoelectronic with those of group 6 molybdenum or tungsten in one-electron lower oxidation states [3]. Since there are a number of mixedmetal sulfide clusters of Mo(IV) or W(IV) [6-8], it is anticipated that similar rhenium derivatives can be prepared using Re(V). The starting compounds to prepare rhenium cluster sulfide complexes are rare and Re₃S₇Cl₇ [9], isoelectronic with $Mo_3S_7Cl_4$ [10], is useful as a starting compound to lead to either trinuclear [11–13] or higher nuclear mixed-metal cluster compounds [5]. The present paper, describes the preparation of the first

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tetranuclear rhenium-cobalt mixed metal sulfide cluster complexes coordinated by dimethylphenylphosphine.

2. Experimental

2.1. Materials and methods

All experiments were performed under dinitrogen atmosphere. Solvents were dried and distilled by the reported methods. Electronic spectra were recorded on a JASCO Ubest-570 UV–Vis spectrometer. ¹H and ³¹P NMR spectra were measured in CDCl₃ with a JEOL GX-400 spectrometer.

Rhenium metal, PMe_2Ph and $(PPh_3)_2NCl$ were purchased from Aldrich, while $CoCl_2$ was from WAKO chemicals. These materials were used without further purification. $Re_3S_7Cl_7$ was prepared according to a literature method [9].

2.1.1. $[Re_3CoS_4Cl_6(PMe_2Ph)_4] \cdot (C_2H_5)_2O, 1$

 $[(PPh_3)_2N][Re_3S_4Cl_6(PMe_2Ph)_3] \cdot 3CH_2Cl_2 [14]: Re_3-S_7Cl_7 (1.03 g, 0.99 mmol) and PMe_2Ph (0.97 g, 7.02 mmol) in dichloromethane (30 mL) were reacted for 3$

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days at room temperature. The mixture was filtered and the solvent was removed by evaporation. The residue was washed twice with diethylether and dried. The product was dissolved in dichloromethane (10 mL), and (PPh₃)₂NCl (0.70 g, 1.21 mmol) was added to the solution. The dichloromethane solution was layered with diethylether (30 mL) and then left to stand for 3 days. The crystalline product was obtained by filtration.

A solution of $[(PP_3)_2N][Re_3S_4Cl_6(PMe_2^-Ph)_3]$. $3CH_2Cl_2$ (0.35 g, 0.16 mmol) in dichloromethane (20 mL) was treated with CoCl₂ (0.045 g, 0.34 mmol) and PMe₂Ph (0.1 g, 0.72 mmol) and stirred for 7 days at room temperature and then refluxed for 90 min. The solution was filtered, the solvent was evaporated and the residue was washed with diethylether. The product was dissolved in dichloromethane (10 mL), and diethylether (30 mL) was layered on the solution which was left for 7 days. A black crystalline compound was obtained in 38% yield. Anal. Calc. for C₃₂H₄₄CoCl₆P₄Re₃S₄. 0.4C4H10O: C, 25.95; H, 3.16. Found: C, 26.06; H, 3.29%. UV–Vis (CH₂Cl₂): 522 nm (ε 1123 M⁻¹ cm⁻¹), 771 nm (ϵ 456 M⁻¹ cm⁻¹). ¹H NMR (δ , CDCl₃): 1.71 (d, $\text{Re}-P(CH_3)_2(C_6H_5)$), 2.10 (dd, $\text{Co}-P(CH_3)_2(C_6H_5)$), 2.28 (d, Re-P(CH₃)₂(C₆H₅)), 7.22-7.87 (m, P(CH₃)₂ (C_6H_5)). ³¹P NMR (δ , CDCl₃, 15% H₃PO₄): -24.69 $(\text{Re}-P(\text{CH}_3)_2(\text{C}_6\text{H}_5)), 38.77 (\text{Co}-P(\text{CH}_3)_2(\text{C}_6\text{H}_5)).$

2.1.2. $[Re_3CoS_4Cl_6(PMe_2Ph)_4]$ 2

Α solution of $[(PPh_3)_2N][Re_3S_4Cl_6(PMe_2Ph)_3]$. 3CH₂Cl₂ (0.52 g, 0.24 mmol) in dichloromethane (20 mL) was stirred with CoCl₂ (0.067 g, 0.56 mmol) for 4 days, following which PMe₂Ph (0.072 g, 0.53 mmol) was added and the mixture was stirred for 3 days at room temperature. The solution was filtered, the solvent was evaporated and the residue was washed with diethylether. The product was dissolved in dichloromethane (10 mL) and chromatographed on a silica gel column with dichloromethane and acetone as eluents. Crystals obtained from the dichloromethane eluate were identical with the cluster 1 and those from the acetone eluate were crystallized from dichloromethane/diethylether to give black crystals 2 in 19% yield. Anal. Calc. for C₃₂H₄₄ CoCl₆P₄Re₃S₄: C, 25.43; H, 2.93. Found: C, 25.36; H, 2.95%. UV–Vis (CH₂Cl₂): 520 nm (ε 1259 M⁻¹ cm⁻¹), 768 nm (ε 452 M⁻¹ cm⁻¹). ¹H NMR (δ , CDCl₃): 1.85, 1.87, 2.37 (d, Re-P(CH₃)₂(C₆H₅)), 1.92 (d, Co-P(CH₃)₂-(C₆H₅)), 7.34–8.06 (m, P(CH₃)₂(C₆H₅)). ³¹P NMR (δ , CDCl₃, 15% H₃PO₄): -24.80, -26.89, -30.92 (Re- $P(CH_3)_2(C_6H_5))$, 33.10 (Co– $P(CH_3)_2(C_6H_5))$.

2.1.3. Crystal structures of 1 and 2

Crystals suitable for X-ray crystallography were obtained by recrystallization of the products from dichloromethane and diethylether over a week. Data were collected on a Bruker Smart APEX CCD system with a sealed molybdenum source and graphite monochro-

Table 1	
Crystallographic data for 1 and 2	

	1	2
Formula	C ₃₆ H ₅₄ Cl ₆ -	C ₃₂ H ₄₄ Cl ₆ -
	$CoOP_4Re_3S_4^{a}$	CoP ₄ Re ₃ S ₄
Formule weight $(g \text{ mol}^{-1})$	1585.14	1511.02
Crystallographic color	black	black
Crystallographic size (mm ³)	$0.40 \times 0.10 \times 0.10$	$0.12 \times 0.04 \times 0.02$
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a (Å)	17.7793(7)	18.5585(8)
b (Å)	11.5586(5)	11.4916(5)
c (Å)	25.6951(11)	20.6682(8)
α (°)	90	90
β (°)	102.943(1)	96.476(1)
γ (°)	90	90
$V(Å^3)$	5146.3(4)	4379.7(3)
Z	4	4
<i>T</i> (°C)	-100	-100
Radiation (Mo Ka) (Å)	0.71069	0.71069
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	2.046	2.292
$\mu (\mathrm{mm}^{-1})$	7.977	9.365
θ Range (°)	1.18-28.32	1.10-28.28
hkl Index ranges	-20/23	-24/19
	-15/15	-15/12
	-34/23	-23/27
Goodness-of-fit on F^2	1.055	1.039
R indices $[I > 2\sigma(I)]$	$R_1 = 0.0283,$	$R_1 = 0.0396$,
	$wR_2 = 0.0807$	$wR_2 = 0.0744$
R (all data)	$R_1 = 0.0345$,	$R_1 = 0.0505,$
	$wR_2 = 0.0859$	$wR_2 = 0.0790$
Largest differential peak and hole (e $Å^{-3}$)	3.207 and -0.858	1.847 and -0.929

^a Including a solvate molecule.

mator. Crystals were transferred to the goniostat where they were cooled to -100 °C for data collection. The data were collected using 15 s frames with an omega scan of 0.30° and corrected for Lorentz and polarization effects. Data were treated by the Bruker SAINT software and the structures were solved using SHELXTL [15] and Fourier techniques. All hydrogen atoms were placed in calculated positions and included in the final cycles of refinement. Four solvent (C₂H₅)₂O molecules were found in a unit cell of **1**. The final $R_1(wR_2)$ indices for **1** are 0.0345(0.0859) using 12,778 independent reflections. The final $R_1(wR_2)$ indices for **2** are 0.0505(0.0790) using 10,854 independent reflections. Crystallographic data are given in Table 1.

3. Results and discussion

3.1. Synthesis

Treatment of $[(PPh_3)_2N][Re_3(\mu_3-S)(\mu-S)_3Cl_6(PMe_2-Ph)_3]$ with anhydrous cobalt(II) chloride in dichloromethane in the presence of dimethylphenylphosphine formed isomeric rhenium–cobalt mixed metal cluster complexes, $[Re_3Co(\mu_3-S)_4Cl_6(PMe_2Ph)_4]$ 1 and 2. ¹H and ³¹P NMR spectra showed the presence of two types of cluster compounds in the products obtained from the reaction at room temperature which were isolated by silica-gel column chromatography using dichloromethane (compound 1) and acetone (compound 2) as eluents. Only the isomer 1 was obtained from the reaction at room temperature followed by reflux. Single crystals were obtained by slow diffusion of diethyl ether onto the dichloromethane solutions. Although coordination of three bridging sulfurs in the trinuclear rhenium complex to a hetero metal seems to be a facile reaction, only nickel [5] and copper [16] derivatives have been prepared and the present synthesis of the cobalt derivatives gives some clue to the difficulty of the preparation.

3.2. Structures

3.2.1. NMR spectra

¹H NMR spectra of **1** show methyl bands at 1.71 (d, $\text{Re-P}(CH_3)_2(C_6H_5)$, 2.10 (dd, $\text{Co-P}(CH_3)_2(C_6H_5)$) and 2.28 (d, Re–P(CH₃)₂(C₆H₅)) ppm with the intensity ratio of 3:2:3. The dimethylphenylphosphine coordinated to three rhenium atoms gives two kinds of methyl signals due to different conformations of the groups. The double doublet signals are assigned to the two methyl groups of dimethylphenylphosphine coordinated to a cobalt atom with slight difference of conformation. ³¹P NMR spectra of 1 show a band at -24.69 ppm assignable to dimethylphenylphosphine coordinated to rhenium and at 38.77 ppm assignable to the one coordinated to cobalt. ¹H NMR spectra of **2** show methyl bands at 1.85 (d, Re-P(CH₃)₂(C₆H₅)), 1.95 (dd, Re- $P(CH_3)_2(C_6H_5))$, 2.00 (d, $Co-P(CH_3)_2(C_6H_5)$) and 2.45 (d, Re–P(CH₃)₂(C₆H₅)) with the intensity ratio of 1:1:1:1. ³¹P NMR spectra of **2** show three bands at -30.92, -26.89 and -24.80 ppm assignable to dimethylphenylphosphine coordinated to rhenium and a band at 33.10 ppm assignable to the one coordinated to cobalt. ¹H and ³¹P NMR spectra indicate the different conformations of the methyl groups of the dimethylphenylphosphine ligands with respect to the Re₃ plane and μ_3 -S atom. The structures (vide infra) of the isomers indicate that the major isomer has three phosphines directed opposite to μ_3 -S and the minor isomer contains a dimethylphenylphosphine in the direction of μ_3 -S.

3.2.2. X-ray structures

The crystal of **1** contains a diethylether molecule as a solvate molecule. Both the major product (compound **1**) and minor product (compound **2**) have tetranuclear metal frameworks with three rhenium and one cobalt atom bonded together by four μ_3 -S atoms (Figs. 1 and 2).

The Re–Re, Re–Co, Re–S and Co–S interatomic distances in the two isomers are not appreciably different (Table 2).



Fig. 1. ORTEP representation of $[Re_3CoS_4Cl_6(PMe_2Ph)_4]$ 1 at the 50% probability level.



Fig. 2. ORTEP representation of $[Re_3CoS_4Cl_6(PMe_2Ph)_4]$ 2 at the 50% probability level.

As the Re–Re distances are larger than Re–Co distances, the shapes of the cluster frameworks are flattened tetrahedra. The tetranuclear cluster compounds

Table 2 Selected interatomic distances (Å) and bond angles (°) for 1 and 2

	1	2
Interatomic distances		
Re(1)–Re(2)	2.7720(3)	2.7711(3)
Re(1)-Re(3)	2.7683(3)	2.7647(4)
Re(2)-Re(3)	2.7679(3)	2.7738(3)
Re(1)-Co(1)	2.5970(6)	2.5954(8)
Re(2)-Co(1)	2.5992(6)	2.5990(8)
Re(3)-Co(1)	2.6014(7)	2.6045(8)
Re–S (av)	2.324	2.322
Co–S (av)	2.148	2.144
Re–P (av)	2.553	2.550
Co–P	2.185	2.187
Re-Cl (av)	2.438	2.437
Bond angles		
Re(3) - Re(1) - Re(2)	59.947(6)	60.140(9)
Co(1)-Re(2)-Re(3)	57.882(15)	57.884(19)
Re(1)-Co(1)-Re(3)	64.353(15)	64.238(19)
Co(1)-S(1)-Re(1)	70.68(4)	71.14(5)
Re(2)-S(1)-Re(1)	73.22(4)	73.25(4)
Re(1)-S(4)-Re(2)	73.01(3)	73.24(4)
P(1)-Re(1)-Re(3)	101.32(3)	146.48(4)
P(1)-Re(1)-Re(2)	143.04(3)	101.79(4)
P(4)-Co(1)-Re(3)	141.69(5)	145.96(6)
P(4)-Co(1)-Re(1)	136.27(4)	137.94(6)
Cl(1)-Re(1)-Cl(2)	83.96(4)	84.83(8)
P(1)-Re(1)-Cl(1)	78.41(4)	78.53(6)
P(1)-Re(1)-Cl(2)	79.70(4)	80.20(5)

1 and 2 have 60 valence electrons counted on the basis of neutral atoms (Re7, Co9, S4, Cl1, P2) and the number is common among tetrahedral cluster compounds [17]. The average Re-Re (2.769 Å) and Re-Co (2.599 Å) distances are close enough to invoke Re-Re and Re-Co metal-metal bonding interactions. They are a little shorter than Re-Re (2.806 Å) and Re-Ni (2.710 Å) interatomic distances in [Re₃NiS₄Cl₆(PEt₃)₄], which has 61 valence electrons [5]. The smaller total number of valence electrons (60 vs. 61 e) seems to have a slight influence upon shortening of the metal-metal distances in spite of the fact that different phosphines are coordinated. Each rhenium atom is coordinated by two chlorine atoms and one dimethylphenylphosphine ligand. Compound 1 has three dimethylphenylphosphine ligands in the direction of the original μ_3 -S atom in the starting trinuclear cluster, but compound 2 has one dimethylphenylphosphine ligand in the opposite direction. The steric influence of dimethylphenylphosphine ligands upon the capture of the cobalt atom seems to make formation of isomers with two or three dimethylphenylphosphine ligands in the direction opposite to the original µ₃-S atom in the trinuclear cluster less favorable. The cobalt atom is coordinated by a dimethylphenylphosphine ligand. Thus the rhenium atoms are hexa-coordinate and cobalt tetra-coordinate if metalmetal bonds are not taken into account.

The present synthesis of mixed metal Re_3Co sulfide cluster complexes indicates that the conformation of coordinated phosphines in the trinuclear rhenium cluster complex is important to facilitate coordination of μ -S atoms to a hetero atom like cobalt. The fact that the major product 1 contains three dimethylphenylphosphines in the opposite orientation to that in the starting cluster compound necessitates the change of the conformation of chlorine and phosphine ligands during the reaction. It is conceivable that 1, obtained under reflux, is thermodynamically more stable than 2.

4. Supplementary material

All the crystallographic data of 1 and 2 have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 232748 and 232749 for 1 and 2, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ conts/retrieving.html, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033.

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