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Communication

Synthesis of $Im_3[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_9]Br$ (Im = 1-Ethyl-3-methylimidazolium) by Means of an Ionic Liquid

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Reaction of $[Re_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Cl_6]Cl$ with an ionic liquid composed of 1-ethyl-3-methylimidazolium bromide (ImBr) and aluminum bromide ($AlBr_3$) formed a new trinuclear rhenium sulfide cluster compound $Im_3[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_9]Br$ with nine terminal bromo ligands.

Rhenium chloride $Cs_3Re_3Cl_{12}$ is the first Re cluster compound characterized by X-ray crystallography[1,2] in 1963. Both solid-state and molecular chemistry of trinuclear rhenium halides has attracted interest for the last 43 years,[3−5] but only $Re_3Y_7X_7$ (Y = S or Se; X = Cl, Br, or I)[6−8] and $[Re_3YCl_9]^{2-}$ (Y = S, Se, or Te)[9] are fundamental trinuclear rhenium chalcohalide cluster compounds so far reported. Recent reports on the synthesis of trialkylphosphine derivatives with the $[Re_3S_4Cl_6(PR_3)_3]^-$ framework[10,11] and their conversion to heterometallic cubane clusters[12−14] suggest that more chemistry will develop if other fundamental Re_3S_4 structures are prepared. There has been extensive chemistry of Mo and W cluster compounds with the $M^{IV}{}_3Y_4$ (M = Mo or W; Y = S, Se, or Te) skeletons,[15] and the isoelectronic $Re^{V}{}_3Y_4$ compounds are promising starting materials for new cluster syntheses.[16]

Ionic liquids have been used extensively as new solvents for synthesis and catalysis,[17] but they have not been much applied to metal cluster compounds except for electrochemistry.[18−21] Hughbanks et al. have studied the excision of nonmolecular hexanuclear zirconium halide clusters to prepare soluble halide clusters and found the exchange of bromides to chlorides and alkali-metal cations to imidazolium cations by using the $ImCl-AlCl_3$ (Im = 1-ethyl-3-methylimidazolium cation) solvent system.[22,23] We attempted to prepare $Re_3S_7Br_7$ from $Re_3S_7Cl_7$ by means of an $ImBr-AlBr_3$ ionic liquid and unexpectedly found that the reaction formed a new type of cluster compound $Im_3[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_9]Br$ that must have resulted by S atom abstraction from the μ-S_2 ligand as well as by halide exchange.

Treatment of $Re_3S_7Cl_7$[6] with a 1:1 mixture of ImBr and $AlBr_3$ at 70 °C for 2 days followed by refluxing in acetonitrile for 5 days gave a viscous solution. After cooling, the mixture was filtered and diethyl ether was layered to precipitate black solids, which were washed with propan-2-ol and dried to give a black product **1** with 60% yield.[24] ^1H NMR spectra (CD_3CN, TMS) indicate imidazolium protons at 7.33, 7.38, and 8.53 ppm and peaks due to $N-CH_2CH_3$ (4.19 and 3.83 ppm) and $N-CH_3$ protons (1.46 ppm). UV−vis spectra (CH_3CN) show a band at 895 nm (ϵ 732 M^{-1} cm^{-1}).

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(24) $Im_3[Re_3S_4Br_9]Br$. Anal. Calcd for $C_{18}H_{33}Br_{10}N_6Re_3S_4$: C, 11.88; H, 1.83; N, 4.62. Found: C, 11.72; H, 1.81; N, 4.47.

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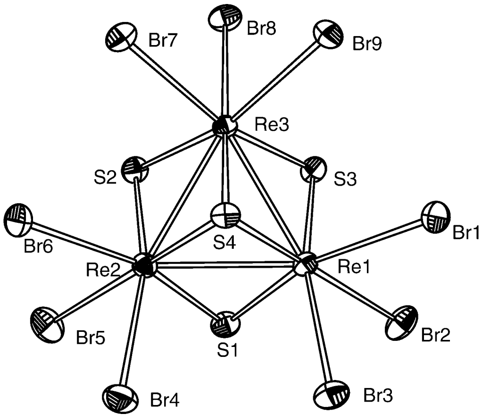

Figure 1. ORTEP view of cluster anion $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_9]^{2-}$. Selected distances (Å) and angles (deg): Re1−Re2 2.7504(3), Re2−Re3 2.7469(3), Re3−Re1 2.7298(3), Re1−S1 2.2432(14), Re1−S3 2.2393(13), Re1−S4 2.3228(13), Re1−Br1 2.5621(6), Re1−Br2 2.6241(6), Re1−Br3 2.5839; Re3−Re1−Re2 60.164(8), S1−Re1−S3 91.11(5), Br1−Re1−Re3 98.547(16), Br1−Re1−Br2 82.50(2), Re1−S4−Re2 72.51(4), Re1−S1−Re2 75.46(4).

Single crystals for the X-ray structure determination were obtained by dissolving the solid **1** in acetonitrile and layered with diethyl ether.[25] The structure is illustrated in Figure 1 with selected distances and angles. The structure of the cluster anion comprises an almost equilateral triangle of Re atoms with a μ_3-S, three μ-S, and nine terminal Br ligands. Four cluster anions, 12 Im cations, and four Br anions are contained in a unit cell. The Re−Re distances (2.73−2.75 Å) are a little longer than those in $[Re^{V}_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_6]^+$ (2.69 Å).[7] The comparison of the structure with those of $Re^{III}_3Br_9$ (Re−Re 2.47 and 2.43 Å)[26] and $[Re^{III}_3(\mu\text{-}Cl)_3Cl_9]^{3-}$ (Re−Re 2.47 Å)[1] indicates that the Re^{V}_3 (3 × d^2, 6 e^-) clusters have much longer Re−Re distances than those in the Re^{III}_3 (3 × d^4, 12 e^-) clusters with Re−Re double-bond character.[4] The number of metal cluster electrons in Re^{V}_3 clusters is just enough for three Re−Re single bonds.[27]

It is noted that the μ-S ligands are very close to the outer-sphere bromide anion Br10 paired with one of the three imidazolium cations, as illustrated in Figure 2. The distances are S1−Br10 = 3.08 Å, S2−Br10 = 3.13 Å, and S3−Br10 = 2.78 Å, which are shorter than the sum (3.80 Å) of the van der Waals radii of S and Br.[28] The secondary bonding of the axial S atoms in μ-S_2 ligands with a halide anion is well-known in various trinuclear Mo and W clusters[29,30] and in $[Re_3(\mu_3\text{-}S)(\mu\text{-}S_2)Cl_6]Cl$,[6] and this is ascribed to the electrophilicity of the axial S atoms. However, the secondary bonding of μ-S ligands in $[M_3(\mu_3\text{-}S)(\mu\text{-}S)_3L_9]$-type clusters is very rare. Considerably strong interaction of the μ-S atoms in the dianionic cluster moiety of **1** with an anionic bromide suggests that their electrophilicity is significant, and this may be why an extra ImBr exists in the crystal.

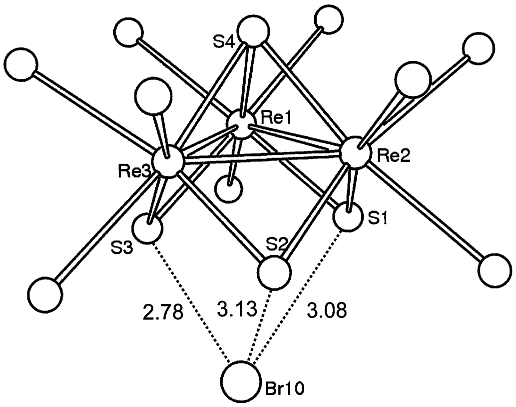

Figure 2. μ-S−Br10 secondary bonding.

The present synthesis has shown that the ionic liquid ImBr−$AlBr_3$ has an ability to remove one of the S atoms in the μ-S_2 ligands of $[Re_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Cl_6]Cl$, to exchange Cl to Br, and to coordinate three extra bromo ligands to the Re_3S_4 core. This type of reaction is comparable to that of PR_3[31] or KCN,[32] and ImBr−$AlBr_3$ is another reagent to change μ-S_2 to μ-S. Trinuclear M_3Y_4 (M = Mo, W, or Re; Y = S, Se, or Te) cluster compounds with nine terminal halogen ligands have not been reported,[15] and the cluster core $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_9]^{2-}$ is expected to give chemistry similar to that of trinuclear Mo or W cluster compounds.

Supporting Information Available: X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org. The data reported in this Communication have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 601320. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

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(25) Data: diffractometer, Bruker Smart Apex CCD system; Mo Kα (0.710 73 Å); T = 173 K; $Im_3[Re_3S_4Br_9]Br$; empirical formula, $C_{18}H_{33}Br_{10}N_6Re_3S_4$; space group, $P2_1/n$; a = 11.1803(4) Å, b = 19.2698(7) Å, c = 18.5815(7) Å, β = 96.672(1)°; Z = 4; data collection, 1.53−28.30°; R1 = 0.0308, wR2 = 0.0684 [$I > 2\sigma(I)$], R1 = 0.0422, wR2 = 0.0723 (all data).

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