Sodium Triethanolamine Complex with Extend 3-D Network Structure

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Reaction of $(NH_4)_3VS_4$ with triethanolamine in the presence of NH_2Na has given novel metal TEA complex $\{[NaN(CH_2CH_2OH)_3]_2S_6\}_\infty$ which has unlimited coordination chains $\{[Na(TEA)]^+\}_x$ together with S_6^{2-} linkage forming 3-D network by the O-H···S hydrogen bond.

Being a very useful tetracoordinating ligand and protein-like ligand, triethanolamine (TEA) has attracted increased interest in metal coordination chemistry. It has been extensively used to prepare metal alkoxides including those of vanadium,[1] iron,[2] alkali and alkali-earth metal[3] for the multifarious purposes, such as biological activities of vanadium enzymes,[1b] supramolecular chemistry[2b] and low-temperature MOCVD techniques[4] etc. The structure type reported for the metal complexes contain monomeric tricyclic structure,[1b,d] metallacrown ethers[2b] and sheet structure.[3a] Here we report a novel sodium TEA complex $\{[NaN(CH_2CH_2OH)_3]_2S_6\}_\infty$ (**1**) with new structural feature.

To 7.5 mmol of TEA in 25 ml of CH_3OH solution, $(NH_4)_3VS_4$ (0.23 g, 1 mmol) was added in the presence of NH_2Na (0.12 g, 2.5 mmol) with stirring for 48 h. After filtration, the filtrate was concentrated under reduced pressure to *ca.* 10 ml. The resultant solution was allowed to stand for several days to produce orange-red prism crystals[5] of **1** (yield 39.3% based on $(NH_4)_3VS_4$). Interestingly, when similar procedure was carried out with the use of CH_3ONa instead of NH_2Na, we have also separated the other metal TEA complex in 25.7% yield, which is a vanadium-containing metallacrown $[Na\subset V_6O_6\{N(CH_2CH_2O)_2(CH_2CH_2OH)\}_6]_2S_6$[6] with the same V_6O_6 backbone to Fe_6O_6 backbone of $[Na\subset Fe_6\{N(CH_2CH_2O)_3\}_6]^+$ [2b] and the characterization of the V_6O_6 complex is in progress.

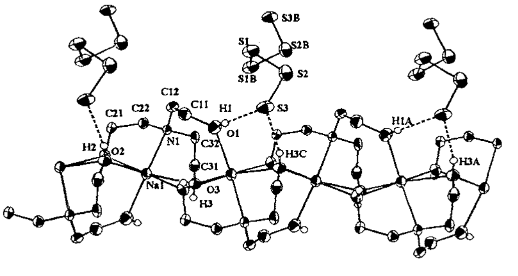

Figure 1. A ORTEP representation of $\{[NaN(CH_2CH_2OH)_3]_2S_6\}_\infty$ in 50% possibility. All H atoms in CH_2 groups are omitted. Selected bond distances (Å): S(1)—S(2) 2.034(1), S(1)—S(1A), 2.059(1), S(2)—S(3) 2.0428(8), Na(1)—O(2) 2.453(2), Na(1)—O(3) 2.481(2), Na(1)—O(2A) 2.419(1), Na(1)—O(3A) 2.426(2), Na(1)—N(1) 2.573(2), Na(1)—O(1A) 2.384(2).

In the participation of TEA, displacement of the sulfur atoms from $(NH_4)_3VS_4$ was observed. Complex **1** contains S_6^{2-} group in the molecule indicating where the sulfur has gone in the reaction. Meanwhile, accompanying with the production of the V_6O_6 cluster, sulfur element in S_8 format has also been separated, implying the self-redox process of VS_4^{3-} to afford V^{4+} and S^0. There are three examples of $Na(TEA)^+$ complexes reported, $Na(TEA)I$,[3c] $Na(TEA)ClO_4$[3a] and $Na(TEA)Cl$,[3b] which contain simple anion and O-H···O hydrogen bonding in molecules to form various structure. Complex **1** is the first example containing O-H···S hydrogen bonding and S_6^{2-} group for the TEA complexes, though S_2^{2-}, S_4^{2-} and S_5^{2-} have been found in other metal clusters.

The structure[7] of **1** contains a basic unit of $[NaN(CH_2CH_2OH)_3]_2S_6$, and the local coordination geometry is given in Figure 1. The structure consists of two relatively independent parts $[Na(TEA)_3]^+$ and S_6^{2-}. The first part has an unlimited chain structure via $Na(\mu\text{-}OH)_2Na$ bridges, wherein the sodium ion is coordinated by five oxygen atoms and a nitrogen

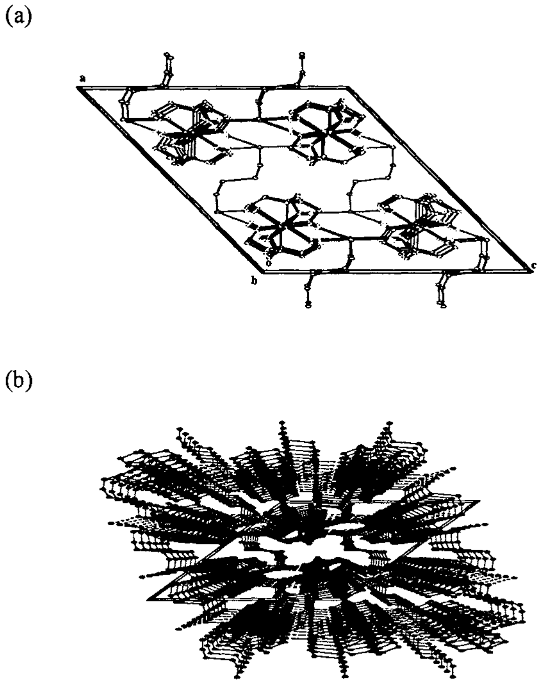

Figure 2. View of the extended 3-D structure. (a). Two ends of the S_6^{2-} linkage are linked to the two $\{[Na(TEA)_3]^+\}_x$ chains by three O-H···S hydrogen bonds. (b). The inner cavities in the structure are exhibited.

atom to form a distorted octahedral coordination geometry. These coordinate atoms come from three TEA molecules affording one O, two O and 2O + 1N atoms, respectively. The Na—O_{bridge} distances ranging from 2.419(1) Å to 2.481(2) Å are obviously longer than Na—$O_{terminal}$ distance of 2.384(2) Å, showing that the necessity of the bridged OH groups to share their electron density gives rise to the lengthening of the Na—O_{bridge} distance. In the vertical direction of the unlimited chain S_6^{2-} linkages are located, the two ends of which are linked to the two $\{[Na(TEA)_3]^+\}_x$ chains by three O-H···S hydrogen bonds to form 3D extended network structure as shown in Figure 2a. Here, the S···O distances of 3.17Å and 3.21Å are in the range of the O-H···S hydrogen bond.[8] Interestingly, there are two inner cavities in the structure as illustrated in the Figure 2b. The big cavity is enclosed by 30 atoms of two S_6 and two HOCCNCCOH linkages. The largest S···S separation of 12.85 Å and O···O separation of 9.14 Å were marked by opposite S atoms and O atoms, respectively. The small cavity is composed of 12 atoms including 4OH, 2Na and 2S with dimensions of 8.8 Å (Na···Na) and 7.8 Å (O···O). Variable-temperature conductance of powdered sample was determined in the range from 23 °C ($8.6 \times 10^{-6}\ \Omega^{-1}\cdot cm^{-1}$) to 80 °C ($7.6 \times 10^{-5}\ \Omega^{-1}\cdot cm^{-1}$), exhibiting a rising tend of the conductance with the rising of temperature. As expected, the ^1H and ^{13}C NMR spectra for complex **1** are close to those[9] of free TEA and are almost consistent to those of other metal TEA complexes.[3b,c]

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References and Notes

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5 $\{[NaN(CH_2CH_2OH)_3]_2S_6\}_\infty$, Anal. calcd for $C_{12}H_{30}N_2Na_2O_6S_6$: C, 26.85; H, 5.63; N, 5.22; S, 35.98%. Found: C, 27.47; H, 5.61; N, 5.32; S, 36.36%. IR (KBr, cm^{-1}) 258, 545 (S—S), 3154 (O—H); ^1H NMR (DMSO-d_6, ppm): δ 4.36 (OH), 3.40 (OCH_2), 2.54 (NCH_2). ^{13}C NMR (DMSO-d_6, ppm): δ 57.47, 59.54.

6 $[Na\subset V_6O_6\{N(CH_2CH_2O)_2(CH_2CH_2OH)\}_6]_2S_6\cdot 2CH_3OH$, Crystal data: $C_{74}H_{164}N_{12}Na_2O_{50}S_6V_{12}$, space group $P\bar{1}$ (No. 2), a = 14.374(3) Å, b = 14.486(3) Å, c = 15.152(3) Å, α = 73.94(2) °, β = 80.29(2) °, γ = 72.75(2) °, V = 2882.4(1) $Å^3$.

7 Crystal data for **1**: Enraf-Nonius CAD4 diffractometer, $C_{12}H_{30}Na_2N_2O_6S_6$, M_r = 536.74, a = 22.507(5) Å, b = 7.2826(3) Å, c = 16.464(3) Å, β = 119.96(2)°, V = 2338.1(3) $Å^3$, Z = 4, space group C2/c (No. 15), μ = 0.63 mm^{-1}, R = 0.0368, R_w = 0.0425 using 2445 reflections ($I > 3\sigma(I)$). Maximum and minimum residual peaks are 0.18 e/$Å^3$ and -0.03 e/$Å^3$, respectively.

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9 ^1H NMR (DMSO-d_6): δ 4.37 (3H, OH), 3.41 (6H, OCH_2), 2.54 (6H, NCH_2). ^{13}C NMR (DMSO-d_6): δ 59.19 (OCH_2), 55.98 (NCH_2).