Assembly of Heterometallic $V_2M_2S_4$ Cubane-like Clusters. Syntheses and Structures of $[Et_4N]_2[V_2M_2S_4(OC_4H_8dtc)_2(SPh)_2]$ (M = Cu, Ag; dtc = dithiocarbamate)

Yu Yang, Qiutian Liu,* Liangren Huang, Beisheng Kang and Jiaxi Lu

Fuzhou Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China

Two $V_2M_2S_4$ cubane-like cluster dianions (M = Cu, Ag) in which each distorted square pyramidal vanadium atom is chelated by a $O(CH_2CH_2)_2NCS_2$ group (OC_4H_8dtc) (dtc = dithiocarbamate) and each four-coordinate M atom linked by a terminal PhS group are prepared from an assembly system including VS_4^{3-}, CuCl [or $Ag(PPh_3)_2^+$], $OC_4H_8dtc^-$ and PhS^- and are structurally characterized.

Immense interest in heterometallic vanadium thiocubane clusters in recent years has stemmed from the discovery of vanadium-containing nitrogenase.[1] It has led to the isolation and characterization of a series of VFe_3S_4 cubane clusters.[2] The focus of our research is the development of cluster

containing the dialkyldithiocarbamate (R_2dtc) ligand. Extension of this research to include VS_4^{3-} has been successful. Herein are reported the syntheses and structures of $[Et_4N]_2[V_2Cu_2S_4(OC_4H_8dtc)_2(PhS)_2]$ **1** and $[Et_4N]_2[V_2Ag_2S_4(OC_4H_8dtc)_2(PhS)_2]$ **2** which are the first examples, respec-

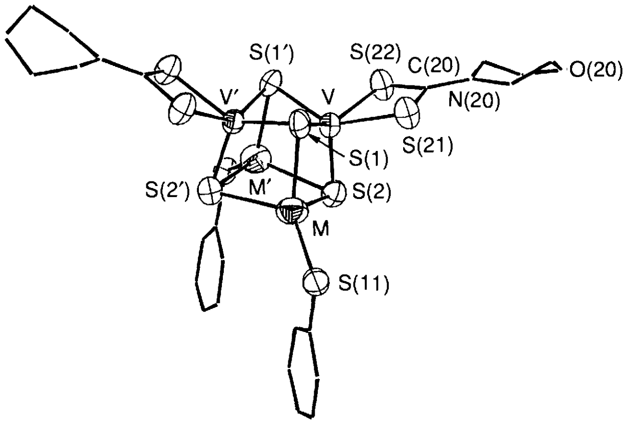

Fig. 1 Structure of $[V_2M_2S_4(OC_4H_8dtc)_2(PhS)_2]^{2-}$ (M = Cu or Ag). Selected interatomic distances (Å) are as follows: for **1**, V–V′ 2.787(4), Cu–V 2.791(3), Cu–V′ 2.772(3), Cu–S(1) 2.258(4), Cu–S(2) 2.431(4), Cu–S(2′) 2.426(4), Cu–S(11) 2.224(4), V–S(1) 2.263(4), V–S(1′) 2.303(4), V–S(2) 2.156(4), V–S(21) 2.425(4), V–S(22) 2.459(4). For **2**, V–V′ 2.793(7), Ag···V 3.038(4), Ag···V′ 3.014(4), Ag–S(1) 2.480(5), Ag–S(2) 2.670(5), Ag–S(2′) 2.670(6), Ag–S(11) 2.391(5), V–S(1) 2.264(5), V–S(1′) 2.293(7), V–S(2) 2.138(6), V–S(21) 2.403(6), V–S(22) 2.450(7).

$(NH_4)_3VS_4$ (0.55 g, 2.36 mmol), CuCl (0.70 g, 6.11 mmol), OC_4H_8dtcNa (1.66 g, 9.61 mmol), and NaPhS (1.20 g, 9.08 mmol) in dimethylformamide (DMF) in the presence of Et_4NCl (1.50 g, 9.05 mmol) under a dinitrogen atmosphere at room temp. for 24 h. The brown precipitate formed was filtered off and acetonitrile–acetone (v/v ratio 1 : 1) added to the concentrated filtrate, to give 0.4 g (yield 29.2%) of black crystals of **1**.† Compound **2** was obtained by the same procedure with the use of $Ag(PPh_3)_2NO_3$[5] instead of CuCl, but its yield was very low, a large amount of intractable amorphous precipitates occurred in the preparative solution after separation of the crystals of **2**. Single crystals of **1** and **2** were selected and used for structural characterization.‡ Almost identical crystal data of **1** and **2** showed them to be isostructural. The structure of the anion of **1** or **2** is shown in Fig. 1.

The anion contains a $V_2Cu_2S_4$ or $V_2Ag_2S_4$ cubane core, respectively, for **1** or **2**. A crystallographic C_2 axis passes through the centres of the V_2S_2 and M_2S_2 rhombic units. It is interesting to see that the subunit $V_2S_2(OC_4H_8dtc)_2$ in both anions exhibits the same structural features including similar bond lengths and angles. Three inorganic μ_3-S atoms and the S atoms of a dtc group complete the distorted square pyramidal coordination of each V centre which lies out of the equatorial plane toward the apical S(2) atom. A V–V distance of 2.787(4) Å for **1** or 2.793(7) Å for **2** is shorter than those seen in other $V_2M'_2S_4$ clusters [M′ = Fe, 2.95;[6] V, 2.873(3) and 2.854(5) Å[7]], and is comparable with those in certain V^{IV} dimers[8] [2.610(1) to 2.884(4) Å], which are believed to contain a V–V single bond. It may be reasonable to consider a V–V single bond with an oxidation state of +4 for each vanadium atom in **1** and **2**, since the $V–S_{dtc}$ bond distances ranging from 2.403(6) to 2.459(4) Å in **1** and **2** are slightly longer than (or near to) those in $VO(Et_2dtc)_2$[9] in which the V atom has an oxidation state of +4 and coordination number of five. The measurement of bulk magnetic susceptibility shows that **1** is diamagnetic and offers a support that $d^1–d^1$ electrons are spin-paired leading to a V–V single bond.

In anions of **1** and **2**, the copper and silver atoms are coordinated in a distorted tetrahedron [bond angle ranges from 90.1(1) to 125.8(1)° for Cu, 85.2(2) to 130.4(2)° for Ag] by three μ_3-S atoms and a PhS group occupying the terminal position. In order to investigate the Cu–SPh bonds [2.224(4) Å in anion **1**], comparison was made with a few Mo–Cu–S complexes containing trigonal copper coordination and a terminal PhS ligand. The Cu–SPh bond length in **1** is intermediate between those observed in $[PhSCuS_2MoS_2]^{2-}$ [2.188(2) Å][10] and $[Cu(SPh)_3]^{2-}$ [2.30(4) Å].[11] This difference can be attributed to the fact that an increase in the coordination number for a metal atom leads to the bond lengthening. Also this V–Cu–S complex may involve a transfer of charge from Cu^I to V^{IV}, similar to delocalisation from Cu^I to Mo^{VI}, suggested for Mo–Cu–S complexes by Garner,[10] which gives rise to the shorter Cu–SPh bond in **1** than in $[Cu(SPh)_3]^{2-}$ even though the copper of **1** is four-coordinate. The $Ag–SPh_{terminal}$ bond length of 2.391(5) Å has turned out to be the first datum reported so far since only a few crystal structure determinations for silver-thiolate(sulfide) compounds have been made. Nevertheless, we can use $[Ag_5(SPh)_7]^{2-}$,[12] in which all the PhS ligands doubly bridge the silver atoms, to make a rough comparison. The Ag–SPh bond length in **2** is obviously shorter than that in $[Ag_5(SPh)_7]^{2-}$ (av. 2.502 Å) even though the coordination number of silver is four in **2** rather than three in the latter, which may also imply a transfer of charge from Ag^I to V^{IV}. This supposition of partial charge redistribution is indirectly supported by the slightly shorter $V–S_{dtc}$ bonds in **1** and **2** than those in $VO(Et_2dtc)_2$ (see above).

Except for the V–V interaction, other types of intermetallic contacts are observed including V···Cu with distances of 2.772(3)–2.791(3) Å for **1**, which are longer than those in other V–Cu–S clusters [2.596(3)–2.680(2) Å],[13] and V···Ag with distances of 3.014(4)–3.038(4) Å for **2**, which may be too long for metal–metal bonds. The Cu···Cu [3.338(3) Å] and Ag···Ag [3.898(3) Å] separations are far greater than the Cu–Cu distance (2.55 Å) and Ag–Ag distance (2.88 Å) observed in copper and silver metals for direct M–M interaction, respectively.

The assembly of $V_2M_2S_4$ clusters from simple inorganic salts is complicated. Two other clusters V–Cu–S, $[(VS_4)Cu_4(SPh)_3(R_2dtc)]^{3-}$ [14] and V–S, $[V_3S_7(R_2dtc)_3]^-$ [14] have also been obtained from the reaction systems under slightly varied conditions. The discussion for the reaction mechanism at present is still difficult. However, it is noteworthy that phenylthiolate as both reducing agent and ligand reduces the vanadium(V) to vanadium(IV) and coordinates to copper or silver atoms. Interestingly, Cu^+ and Ag^+ ions being very soft acids and having a high tendency to form metal–sulfur bonds link only to a monodentate PhS group to satisfy its coordination, while vanadium is chelated by R_2dtc group to give five-coordinate geometry.

Further studies on spectroscopic characterization and electrochemistry for these compounds are in progress.

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† Satisfactory elemental analyses were obtained.

‡ The data collection was completed on an Enraf-Nonius CAD4 diffractometer. All calculations to solve and refine the structures of **1** and **2** were performed on a VAX/785 computer using a SDP/VAX program. *Crystal data* for **1**: $C_{38}H_{66}Cu_2N_4O_2S_{10}V_2$, M_r = 1160.58, a = 20.219(10), b = 14.972(13), c = 18.027(9) Å, β = 109.03(4)°, V = 5158.7 Å^3, Z = 4, space group $C2/c$, R = 0.060 and R_w = 0.068 using 1797 reflections [$I > 3\sigma(I)$]: for **2**, $C_{38}H_{66}Ag_2N_4O_2S_{10}V_2$, M_r = 1249.24, a = 20.448(3), b = 15.086(2), c = 17.923(2) Å, β = 109.32(1)°, V = 5217.9 Å^3, Z = 4, space group $C2/c$, R = 0.068 and R_w = 0.073 using 1500 reflections with $I > 3\sigma(I)$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Though the possibility of site disorders in the Cu–V cluster cannot be ruled out on the evidence of the crystallography alone, the assignments of Cu–V are reasonable because elemental analyses and the coordination number of Cu and V (not more than four for Cu, and more than four for V) have strongly supported the assignments.

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References

1 B. J. Hales, E. E. Case, J. E. Morningstar, M. F. Dzeda and L. A. Mauterer, *Biochemistry*, 1986, **25**, 7251.

2 J. A. Kovacs and R. H. Holm, *Inorg. Chem.*, 1987, **26**, 702; J. A. Kovacs and R. H. Holm, *Inorg. Chem.*, 1987, **26**, 711.

3 Q. Liu, L. Huang, H. Liu, X. Lei, D. Wu, B. Kang and J. Lu, *Inorg. Chem.*, 1990, **29**, 4131; Q. Liu, X. Lei, L. Huang, W. Chen, K. Zhao, D. Chen, H. Liu and J. Lu, *Science in China* (*Ser. B*), 1990, **33**, 1446; Q. Liu, L. Huang, X. Lei, F. Wang, D. Chen and J. Lu, *Science in China* (*Ser. B*), 1991, **34**, 1036.

4 X. Lei, Z. Huang, Q. Liu, M. Hong and H. Liu, *Inorg. Chem.*, 1989, **28**, 4302; Z. Huang, X. Lei, B. Kang, J. Liu, M. Hong and H. Liu, *Inorg. Chim. Acta.*, 1990, **169**, 25.

5 E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc.*, 1972, **94**, 6386.

6 T. B. Rauchfuss, T. D. Weatherill, S. R. Wilson and J. P. Zebrowski, *J. Am. Chem. Soc.*, 1983, **105**, 6508.

7 J. Darkwa, J. R. Lockemeyer, P. D. W. Boyd, T. B. Rauchfuss and A. L. Rheingold, *J. Am. Chem. Soc.*, 1988, **110**, 141.

8 S. A. Duraj, M. T. Andras and P. A. Kibala, *Inorg. Chem.*, 1990, **29**, 1232; C. M. Bolinger, T. B. Rauchfuss and A. L. Rheingold, *J. Am. Chem. Soc.*, 1983, **105**, 6321; T. R. Halbert, L. I. Hutchings, R. Rhodes and E. I. Stiefel, *J. Am. Chem. Soc.*, 1986, **108**, 6437; Y. Yang, L. Huang, Q. Liu and B. Kang, *Acta Crystallogr. Sect. C*, 1991, **47**, 2085.

9 K. Henrick, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1976, 26.

10 S. R. Acott, C. D. Garner, J. R. Nicholson and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1983, 713.

11 D. Coucouvanis, C. N. Murphy and S. K. Kanodia, *Inorg. Chem.*, 1980, **19**, 2993.

12 I. G. Dance, *Aust. J. Chem.*, 1978, **31**, 2195.

13 A. Müller, J. Schimanski and H. Bögge, *Z. Anorg. Allg. Chem.*, 1987, **544**, 107; C. D. Scattergood, P. G. Bonney, J. M. Slater, C. D. Garner and W. Clegg, *J. Chem. Soc., Chem. Commun.*, 1987, 1749.

14 Y. Yang and Q. Liu, paper in preparation.