Synthesis and structural characterization of [Ni$_{12}$(S$_2$)$_6$S$_8$]$^{3-}$: a novel Ni–S cluster with a distorted cuboctahedral core

Christopher L. Cahill,[a] Kemin Tan,[b] Rachayl Novoseller[c] and John B. Parise*[a,b]

[a] *Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794, USA*
[b] *Department of Earth and Space Sciences, State University of New York at Stony Brook, Stony Brook, NY 11794, USA*
[c] *Department of Physics, Barnard College, New York, NY 10027, USA*

A novel nickel sulfide cluster comprised of an M$_{12}$E$_8$ core is synthesized.

Molecular clusters of metal–chalcogenide species exhibit considerable structural diversity.[1] For this reason, such compounds are of interest to a variety of scientific communities. Physicists have studied semiconducting materials of this type, as their transport and optical properties have been shown to vary as a function of cluster size.[2] Inorganic chemists and biochemists have long studied such materials, in particular metal–sulfur complexes, since they further our understanding of active sites in metalloproteins and metal–sulfide heterogeneous catalysis.[3] In this publication, we report the synthesis and structural characterization of a novel Ni–S molecular cluster, [NEt$_4$]$_3$[Ni$_{12}$(S$_2$)$_6$S$_8$] **1**.

Compound **1** can be formed from hydrothermal synthesis utilizing a variety of starting materials. Nickel sources include nickel acetate, chloride and sulfate; sulfur sources include elemental sulfur as well as germanium sulfide. The preparation from which a single crystal suitable for X-ray diffraction was chosen contained GeS$_2$, Ni(OAc)$_2$·4H$_2$O, 40% [NEt$_4$]HCO$_3$ and water in the approximate molar ratio 10 : 1 : 17 : 243. The reaction slurry had a initial pH of 7.3 before being sealed in a Pyrex® tube. The mixture was kept static for 7 days under autogeneous pressures at 120 °C. The resultant product, a black powder, was collected and washed in ethanol and in water. Black octahedral crystals up to 300 μm on edge were then isolated for study. Qualitative electron probe microanalysis (EPMA) of the crystals revealed the presence of nickel, sulfur and nitrogen, but no germanium. Powder X-ray diffraction indicated that the germanium is present in the powdered form as either GeS$_2$ or as GeO$_2$. Each batch typically produced 1 or 2 large crystals, with a total yield of approximately 70% as estimated from powder diffraction.

Structure determination† from single-crystal X-ray data showed that **1** contains discrete clusters of [Ni$_{12}$(S$_2$)$_6$S$_8$]$^{3-}$ (Fig. 1). The symmetry of these anions is D_2. Nickel and sulfur approximately define a cube, the corners of which contain sulfur atoms, whereas the midpoints of each edge are occupied by nickel in roughly square-planar coordination with sulfur. The faces of the cube are each capped by a μ-disulfide anion. This distorted cuboctahedral framework (Fig. 2) or M$_{12}$E$_8$ structure[1] upon which the disulfides reside, is quite similar to previously reported [Cu$_{12}$S$_8$]$^{4-}$ and [NaAu$_{12}$Se$_8$]$^{3-}$ clusters.[4,5] In these materials, copper and sulfur and gold and selenium respectively define cubes in the same fashion that nickel and sulfur do in our material. However, the faces of the [Cu$_{12}$S$_8$]$^{4-}$ and the [NaAu$_{12}$Se$_8$]$^{3-}$ clusters remain free of bridging anions.

The stoichiometry of **1** has been assigned as [NEt$_4$]$_3$[Ni$_{12}$(S$_2$)$_6$S$_8$]. As seen in Fig. 1, the nickel atoms are in square-planar coordination, implying a formal charge of 2+ on each. The average oxidation state of the nickel atoms, 2.08, indicates the possibility of a mixed-valence Ni^{2+}/Ni^{3+} formulation. Preliminary UV–VIS spectroscopy (in dmf) supports this notion, as the spectra contain a broad feature in the range 1500–1100 nm, ascribed to an intervalence transfer (IT)

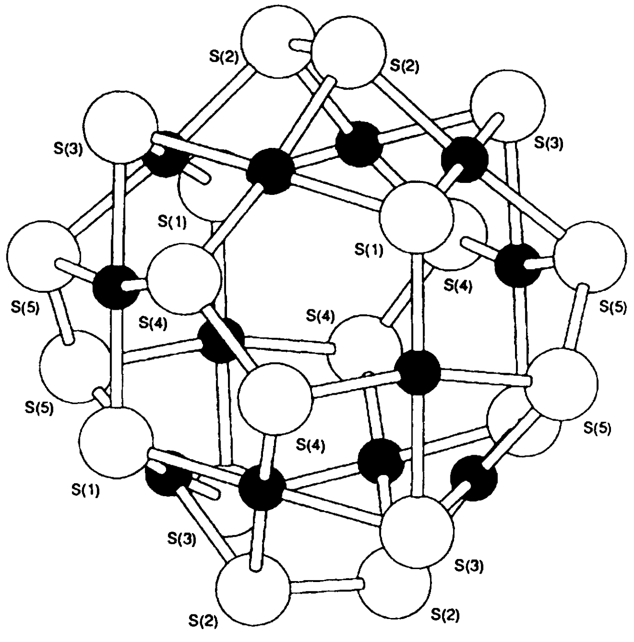

Fig. 1 The [Ni$_{12}$(S$_2$)$_6$S$_8$]$^{3-}$ anion of **1** exhibiting D_2 symmetry. See text for details.

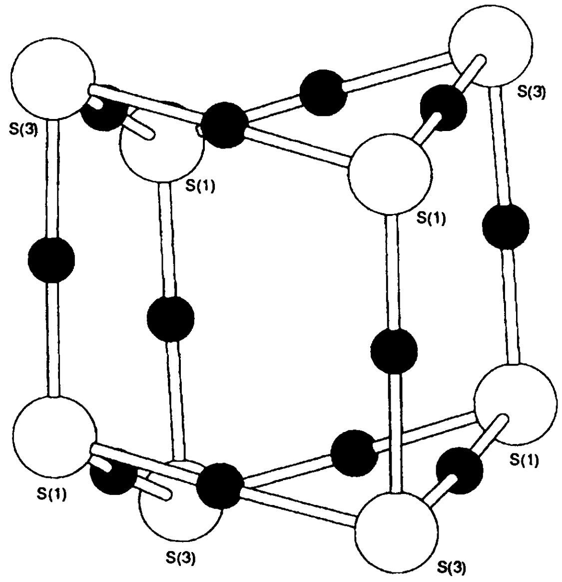

Fig. 2 The distorted cuboctahedral framework of **1**. Nickel atoms define the cuboctahedral core; S(3) and S(1) define the corners of a cube. The faces of the cube are then capped by disulfide anions, S(2), S(4) and S(5) to form the [Ni$_{12}$[S$_2$)$_6$S$_8$]$^{3+}$ anion shown in Fig. 1.

band. IT bands have been discussed previously,[6] as have mixed-valence nickel–sulfur compounds.[8] No attempt was made to assign integral oxidation states to individual metal centres. Although not located in this study, the presence of an S–H unit on the cluster is also possible. This would then not require mixed valence Ni. Magnetic measurements would be instructive as an all square-planar Ni^{2+} structure should be diamagnetic, whereas the presence of an Ni^{3+} site would give rise to a paramagnetic signal; such studies are planned in the future.

The Ni–Ni distances in **1** range from 2.763(2) to 2.915(2) Å, with an average value of 2.821 Å. This is approximately 0.33 Å larger than the average Ni–Ni distance in metallic nickel,[8] 0.02 Å shorter than found in Millerite,[9] and 0.30 Å longer than the Ni–Ni distance in Hazelwoodite.[10] The Ni–S distances range from 2.142(3) to 2.244(3) Å with an average of 2.190 Å as opposed to averages of 2.272 ans 2.306 Å in Hazelwoodite and Millerite respectively. The distortion of the $[Ni_{12}(S_2)_6S_8]^{3-}$ framework can be seen in the range of Ni–S–Ni bond angles, 77.0–105.8°, defining its corners.

This work was supported by the National Science Foundation (DMR 94-13003). The authors wish to thank M. Britton for help with sample preparation and S. A. Koch for useful discussions.

Footnote

† *Crystal structure data for* $[NEt_4]_3[Ni_{12}(S_2)_6S_8]$: tetragonal, space group $P\bar{4}2c$, $a = 11.092(1)$, $c = 21.733(1)$ Å, $U = 2673.9(5)$ Å^3, $Z = 2$, μ(Mo-Kα) = 49.1 cm^{-1}, Picker four-circle diffractometer, Mo-Kα radiation, graphite monochromator, ω–2θ scans, $2\theta_{max} = 62°$, 9833 reflections, 3257 with $I > 2.0\sigma(I)$; direct methods, Ni, C, N, S anisotropic; analytical absorption correction performed; $R = 0.065$, $R_w = 0.063$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/119.

References

1 I. Dance and K. Fisher, *Prog. Inorg. Chem.*, 1994, **41**, 637.
2 N. Herron, J. C. Calabrese, W. E. Farneth and Y. Wang, *Science*, 1993, **259**, 1426.
3 W. Tremel and G. Henkel, *Inorg. Chem.*, 1988, **27**, 3896 and references therein.
4 P. Betz, B. Krebs and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 311.
5 S.-P. Huang and M. G. Kanatzidis, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 787.
6 N. S. Hush, *Prog. Inorg. Chem.*, 1967, **8**, 357; M. B. Robin and P. Day, *Adv. Inorg. Radiochem.*, 1967, **10**, 247; C. Creutz, *Prog. Inorg. Chem.*, 1983, **30**, 1.
7 J. D. Franolic, PhD Dissertation, State University of New York at Stony Brook, 1993; T. Kruger, B. Krebs, G. Henkel, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 61.
8 B. J. Wuensch, *Rev. Mineral. Sulfide Mineral.*, 1976, **1**, 21.
9 V. Rajamani and C. T. Prewitt, *Can. Mineral.*, 1974, **112**, 248.
10 J. B. Parise, *Acta Crystallogr., Sect. B*, 1980, **36**, 1179.

Received, 29th March 1996; Com. 6/02213H