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Disproportionation of Elemental Sulfur in Zeolite. Crystal Structure of Zeolite LTA Containing Two New Ions: Perthiosulfite, S_4^{2-}, and Trisulfur Cation, S_3^{2+}

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1 Introduction

Elements have been observed to disproportionate electronically into cations and anions upon sorption into zeolites.[1,2] Because anhydrous polar zeolites are polar media, this is akin to the dissociation of salts when they dissolve in polar solvents. Perhaps NO, an odd molecule, disproportionates into NO^+ and NO^- upon sorption into polar zeolites.[3] Zeolites A (LTA) and X (FAU) are examples of polar zeolites; they have very anionic frameworks due to their high aluminum contents and, to balance that negative charge, a high density of exchangeable cations. Here we report a third example of the disproportionation of an element upon sorption into a zeolite, sulfur sorbed at a high temperature into anhydrous zeolite A.

This work was undertaken simply to find the twelfth Na^+ ion in a sulfur sorption complex of Na_{12}-A; $Na_{12}Si_{12}Al_{12}O_{48}$ is its unit cell formula. Its structure, reported in 1972, was found to contain two S_8 rings per unit cell, but only 11 Na^+ ions could be found.[4] Now, with the availability of higher quality diffraction data, we wished to find that twelfth ion. We anticipated that it would be at the center of the large cavity, sandwiched between two parallel (non-planar) S_8 rings.

2 Experiment

A tube of sulfur flakes was attached as a side arm to a Pyrex reaction vessel. Another arm to this vessel ended with the capillary containing a hydrated Na-A single crystal. The complete vessel was then attached to a vacuum line for dehydration. After the crystal was dehydrated under vacuum at 623 K, the temperature of the sulfur-containing side arm was increased to 623 K and the sulfur was distilled *in situ* under dynamic vacuum. The crystal at 623 K was then exposed to 20 Pa of S(*g*) for 48 hours. It was then maintained at 333 K to remove any excess S from near or inside the crystal.

Synchrotron X-ray diffraction intensities for the single crystal were measured at the Photon Factory (PF), Tsukuba, Japan. The space group $Pm\overline{3}m$ (a = 12.192(1) Å), appropriate for zeolite A unless high precision is achievable, was used. Its crystal structure was refined with all unique data to the final error index $R_1 = 0.075$ for the 679 unique reflections for which $F_o > 4\sigma(F_o)$.

3 Results and Discussion

Elemental sulfur disproportionated electronically upon sorption into anhydrous Na_{12}-A at 623 K. The net reaction, and also the net reaction per 12.2- Å unit cell, is:

$$7S \rightarrow S_4^{2-} + S_3^{2+}.$$

The perthiosulfite anion, S_4^{2-}, the perthio form of SO_3^{2-}, is in the large cavity. It bonds to one 6-ring and three 8-ring Na^+ ions (S-Na = 2.83(6) Å, 2.80(5) Å, and 2.43(5) Å). It appears to be the first example of a branched polysulfide ion. Its geometry, S-S = 2.16(5) Å and S-S-S = 105.4(22)°, is in agreement with that calculated, 2.08 Å and 108.2°(Figure 1).[5] These calculations also indicate that the perthiosulfite ion is only about 10 kJ/mol less stable than the *n*-tetrasulfide ion,[5] suggesting that it could readily form in an environment that a zeolite might provide.

The electron deficient trisulfur cation, S_3^{2+} (S-S = 2.11(8) Å and S-S-S = 102.0(14)°), bonds to framework oxygen atoms in the sodalite cavity (S-O = 2.64(7) Å) (Figure 1).

Twelve Na^+ ions are found per unit cell at five crystallographic sites similar to, but different from, those in anhydrous Na-A. Eleven are near 6- and 8-rings, and the twelfth lies opposite a 4-ring in the sodalite cavity.

A mixture of sulfur species is present in the vapor phase at 623 K; S_2 and S_3 should easily be able to enter the zeolite structure. The reaction proceeded until the sodalite cavities (one per unit cell) became full with S_3^{2+}.

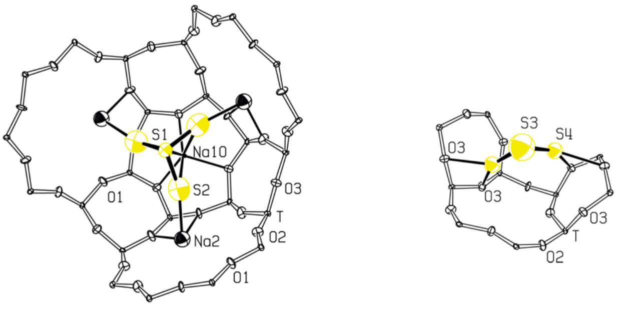

Fig. 1: The Perthiosulfite anion, S_4^{2+}, and the trisulfur cation, S_3^{2+}, in their coordination environments.

The two previous observations of the disproportionation of an element in a zeolite involved 3-coordinate Cd^{2+} ions.[1,2] These ions satisfied their coordinative unsaturation by making strong bonds to sulfide or iodide ions, and this was viewed as the principle driving force for those reactions. In this work, a zeolite in its Na^+ form is seen to be capable of disproportionating a substrate. Thus electronic disproportionation appears to be a general property of polar zeolites. It may be an important step in some intrazeolitic reaction mechanisms.

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References

[1] M. K. Song, Y. Kim; K. Seff, *J. Phys. Chem. B* **107**, 3117, (2003).
[2] M. K. Song, E. Y. Choi, Y. Kim; K. Seff, *J. Phys. Chem. B* **107**, 10709, (2003).
[3] C.-C. Chao, J. H. Lunsford, *J. Am. Chem. Soc*, **93**, 6794, (1971).
[4] K. Seff, *J. Phys. Chem.* **76**, 2601, (1972).
[5] R. Steudel, Y. Steudel, *Chem. Eur. J.* **107**, 10709, (2003).

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