Angewandte Addendum

In this Communication, the authors reported the crystal structure of the glyoxal bis(amidiniumhydrazone) (GBAH) sulfate salt, whose synthesis was first reported by Thiele and Dralle in 1898.[1] The structure showed the sulfate crystallized as extended $[SO_4(H_2O)_5^{2-}]_n$ clusters. As an important part of this study, it was demonstrated for the first time that competitive crystallization of GBAH sulfate from aqueous solutions can be used as a basis for selective sulfate separation. The effectiveness of this crystallization-based sulfate separation method stems from the relatively low aqueous solubility of GBAH sulfate ($K_{sp} = 3.2 \times 10^{-7}$),[2] comparable with that of $SrSO_4$.
In the interest of completeness, the authors note that observations of the relatively insoluble nature of the sulfate salts of GBAH or other analogs had been previously made,[3] though no solubility values had been reported. Single-crystal X-ray structural studies of GBAH analogues showed that the sulfate anion can crystallize with variable numbers of water molecules (from zero to six).[4] However, due to the limited structural and solubility data available, it is not clear at this point the extent to which the included water molecules contribute to the low solubility of these salts and to the sulfate crystallization selectivity. Future structure–solubility relationship studies of bis(amidiniumhydrazone) sulfate salts offer the prospect for understanding the various factors controlling the crystallization efficiency of this intriguing class of compounds.[5]

[1] J. Thiele, E. Dralle, *Justus Liebigs Ann. Chem.* **1898**, *302*, 275.
[2] The solubility product was calculated from the measured solubility of GBAH sulfate of 7.2 $\times 10^{-4}$ M, and taking into account the corresponding activity coefficient of 0.78, estimated by the Debye–Huckel limiting law.
[3] a) P. Seppanen, R. Fagerstrom, L. Alhonen-Hongisto, H. Elo, P. Lumme, J. Janne, *Biochem. J.* **1984**, *221*, 483; b) H. Elo, *Spectroscopy Lett.* **1989**, *22*, 123; c) H. Elo, *Spectroscopy Lett.* **1989**, *22*, 161.
[4] a) P. O. Lumme, I. Mutikainen, H. O. Elo, Acta Cryst. **1986**, C*42*, 1209; b) H. Elo, I. Mutikainen, L. Alhonen-Hongisto, R. Laine, J. Jänne, P. Lumme, *Z. Naturforsch.* **1986**, *41c*, 851; c) H. Elo, I. Mutikainen, *Z. Naturforsch.* **1988**, *43c*, 601; d) M. Koskinen, I. Mutikainen, H. Elo, *Z. Naturforsch.* **1996**, *51b*, 1161; e) M. Koskinen, I. Mutikainen, J. T. Koskinen, H. Elo, *Z. Naturforsch.* **1997**, *52b*, 1114.
[5] R. Custelcean, N. J. Williams, C. A. Seipp, A. S. Ivanov, V. S. Bryantsev, *Chem. Eur. J.* DOI: 10.1002/chem.201504651.

Aqueous Sulfate Separation by Crystallization of Sulfate-Water Clusters

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