

## Vibrational Spectra of $K_2[O(HgSO_3)_3]$ Containing a New Anionic Metallo-Oxonium Complex with a $OHg_3$ Core

D.K. Breiting<sup>1</sup>, G. Brehm<sup>2</sup>, M. Weil<sup>3</sup>, S. Baumann<sup>3</sup>

<sup>1</sup>*Institute of Inorganic Chemistry, University of Erlangen-Nürnberg, Egerlandstr. 1, D-91058 Erlangen, Germany,*

<sup>2</sup>*Institute of Physical Chemistry, University of Erlangen-Nürnberg,*

<sup>3</sup>*Institute of Chemical Technologies and Analytics, Vienna University of Technology, A-91060 Vienna, Austria*

Continuing recent work on sulfite complexes of mercury [1] we studied the systems  $HgX_2/K_2SO_3$  and  $HgO/K_2SO_3$  in aqueous solutions and the solid phases formed therein. In the latter case after dissolution of  $HgO$  in hot  $K_2SO_3$  solution and cooling crystals of the new compound  $K_2[O(HgSO_3)_3]$  were obtained. This compound crystallises in  $Pnma$  with  $Z = 4$ , with arrangement of both cations and anions into alternating layers parallel to (010) [2]. The distance between equivalent layers along the stacking direction  $b$  is about 10 Å. The anionic layers adopt the symmetry  $(a:c) \cdot m \cdot 2_1 - p2_1ma$  (cf. [2]),  $i e$  a two-dimensional non-centrosymmetric subgroup of  $Pnma$ , which is isomorphic to point group  $C_{2v} - mm2$ . The flat pyramidal anions  $[O(HgSO_3)_3]^{2-}$  with a central  $OHg_3$  core occupy crystallographic sites with symmetry  $C_s - m$ , but they are close to  $C_{3v} - 3m$ .

A factor group/unit-cell group analysis (UGA) for the whole cell-content was performed, also partly in internal coordinates. The UGA predicts much more species of specific vibrations, e.g.  $\nu_s(SO_3)$  or  $\delta_s(SO_3)$ , than found in both IR and Raman spectra. Further, most of the IR and Raman bands show near-coincidence of the wavenumbers and complementary intensities. The conclusion is that correlation coupling between the anionic layers and splitting of their vibrations does not take place anymore, due to the large inter-layer distance. Therefore, the symmetry analysis can be restricted to one of the two layers in the unit-cell. This means that only correlation coupling between two anions within one layer is still considered. Because of the non-centrosymmetry of the layers the mutual exclusion rule is no longer valid.

Assignment of the vibrations  $\nu_{as}(SO_3)$  (at least six components around  $1150\text{ cm}^{-1}$  in both spectra),  $\nu_s(SO_3)$  (quartet in IR around  $994\text{ cm}^{-1}$ ),  $\delta_s(SO_3)$  and  $\delta_{as}(SO_3)$  of the S-coordinated sulfite ligands is straightforward. As for the vibrations of the  $OHg_3$  core data for the mercurio-oxonium cations  $[O(HgCl)_3]^+$  [4],  $[O(HgCH_3)_3]^+$  [5] and  $[O(HgOH)(HgI)_2]^+$  [6] are of limited value as these are planar, in contrast to the pyramidal anion under discussion (average angle  $\alpha_{av}(Hg-O-Hg)$   $110.8^\circ$ ). Isolated medium to strong bands at  $560\text{ cm}^{-1}$  in both spectra are to be assigned to  $\nu_{as}(OHg_3)$ , without doubt, but the position of  $\nu_s(OHg_3)$  in the low-frequency part of the Raman spectrum, dominated by the very strong  $\nu(Hg-S)$  bands around  $230\text{ cm}^{-1}$ , is less evident. An approximate calculation of  $\nu_s(OHg_3)$  using  $\nu_{as}(OHg_3)$  and the above average bond angle in  $OHg_3$  gives  $285\text{ cm}^{-1}$ . In fact, there is an appropriate medium-to-weak, sharp band at  $267\text{ cm}^{-1}$ . But one has to be aware that  $\nu_s(OHg_3)$  (species  $A_1$  under idealised symmetry  $C_{3v} - 3m$ ) strongly mixes with  $\nu(Hg-S)$ , the bending mode  $\delta(O-Hg-S)$  (about  $100\text{ cm}^{-1}$ ), and even the rocking mode  $\rho(SO_3)$  ( $318\text{ cm}^{-1}$ ) of the same symmetry species.

[1] M. Weil, D.K. Breiting, G. Liehr, J. Zürgb, Z. Anorg. Allg. Chem. 633 (2007) 429-434.

[2] M. Weil, S. Baumann, D.K. Breiting, Acta Crystallogr. C64 (2008) i35-i37.

[3] A.V. Shubnikov, V.A. Koptsik, Symmetry in Science and Art, Plenum Press, New York-London, 1974, p. 195.

[4] W.P. Griffith, J. Chem. Soc. A 1969, 2270.

[5] J.H.R. Clarke, L.A. Woodward, Spectrochim. Acta 23 A (1967) 2077-2087.

[6] K. Köhler, G. Thiele, D.K. Breiting, Z. Anorg. Allg. Chem. 418 (1975) 79-87.

### Acknowledgment

Thanks to S. Hofmann, Institute of Inorganic Chemistry, Erlangen, for measuring IR spectra.