

Sulfito Mercurate Complexes in Solution Studied by ^{199}Hg NMR Spectrometry

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Recently, several crystalline sulfito complexes of mercury appropriate for X-ray structure analyses were obtained upon reaction of HgX_2 ($X = \text{Cl}, \text{Br}$) or HgO with sulfites M_2SO_3 ($M = \text{NH}_4, \text{Na}, \text{K}$) in aqueous solutions [1-3]. Some of these complexes in solution were already studied by Raman spectrometry. In order to get more insight into the composition of the solutions prior to crystallisation of solid reaction products we started ^{199}Hg NMR studies, also of redissolved crystalline reaction products. To our knowledge no pertinent ^{199}Hg NMR data have been published up to now.

In the chosen systems only atoms without magnetically active nuclei or with quadrupole nuclei (Cl, Br) are bound to mercury; thus, because of lack or suppression of heteronuclear coupling very simple single-line ^{199}Hg NMR spectra are expected.

First, solid $\text{K}_2[\text{Hg}(\text{SO}_3)_2] \cdot 2.25 \text{H}_2\text{O}$ (**1**) contains $[\text{Hg}(\text{SO}_3)_2]^{2-}$ anions (X-ray structure analysis [4]) which are still present after dissolution in H_2O (Raman spectrometry). The ^{199}Hg NMR spectrum of a solution of (**1**) in D_2O displays one single resonance at $\delta = -2152$ ppm *re neat* $\text{Hg}(\text{CH}_3)_2$; the very narrow NMR signal of HgCl_2 in D_2O appears at $\delta = -1556$ ppm. This means that the Hg nuclei in the anion are much more shielded than in solvated HgCl_2 . Further, the solution of HgCl_2 and $(\text{NH}_4)_2\text{SO}_3$ (molar ratio 1:1), from which $(\text{NH}_4)[\text{ClHgSO}_3]$ crystallises after some time (crystal structure in [1]), gives one NMR signal (-1550 ppm) close to that of HgCl_2 , but asymmetric and much broader than that of HgCl_2 . This signal is attributed to the polar $[\text{ClHgSO}_3]^-$ anions (probably linear Cl-Hg-S skeleton) with shielding of the Hg nuclei similar as in HgCl_2 , but with faster (spin-lattice) relaxation.

Finally, for the D_2O solution obtained upon reaction of HgO and K_2SO_3 in the heat, analogous to the preparation of the compound $\text{K}_2[\text{O}(\text{HgSO}_3)_3]$ with a new anionic metalloonium complex [2], a single signal is observed at $\delta = -1999$ ppm. This signal is appropriate and reasonable for the $[\text{O}(\text{HgSO}_3)_3]^{2-}$ anion, as shielding is expected to be lower with reference to $[\text{Hg}(\text{SO}_3)_2]^{2-}$ for the following reasons: The average negative charge in one Hg- SO_3 fragment is lower than in $[\text{Hg}(\text{SO}_3)_2]^{2-}$, the charge tends to shift to the periphery, and Hg is bound to the electronegative and formally positive central oxygen atom.

As a general result, in each of the solutions studied seemingly only one mercury-containing complex species is present.

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

[2] M. Weil, S. Baumann, D.K. Breitinger, *Acta Crystallogr. C* 64 (2008) i35-i37.

[3] M. Weil, S. Baumann, D.K. Breitinger, *Z. Anorg. Allg. Chem.*, in press.

[4] M. Weil, S. Baumann, D.K. Breitinger, to be published.

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