ChemComm

$^1J(^{199}Hg^{199}Hg)$ values of up to 284 kHz in complexes of $[Hg–Hg]^{2+}$ with crown ethers: the largest indirect coupling constants

Richard Malleier, Holger Kopacka, Walter Schuh, Klaus Wurst and Paul Peringer*

Institut für Allgemeine, Anorganische und Theoretische Chemie, Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria. E-mail: paul.peringer@uibk.ac.at

Received (in Cambridge, UK) 18th September 2000, Accepted 14th November 2000
First published as an Advance Article on the web

The values of the $^1J(^{199}Hg^{199}Hg)$ coupling constant in solution of the asymmetric dimercury(2+) complexes with the stoichiometries Hg_2^{2+}/18-crown-6 and Hg_2^{2+}/18-crown-6/15-crown-5 are 220 300 and 284 100 Hz, respectively, representing the largest scalar couplings measured.

Very large scalar coupling constants have been observed between heavy metal nuclei and have been attributed to relativistic effects. The largest value known at present is the one-bond $^{199}Hg^{199}Hg$ coupling in the polycation $[Hg–Hg–Hg]^{2+}$ **1** with a magnitude of 139 600 Hz.[1] The largest coupling constant between two different nuclei is a 71 060 Hz $^1J(^{195}Pt^{205}Tl)$ coupling observed for the compound $[(NC)_5Pt–Tl]$.[2]

The use of solid-state ^{199}Hg NMR for the determination of the $^{199}Hg^{199}Hg$ coupling of $[Hg–Hg]^{2+}$ salts involving magnetically inequivalent mercury atoms, has been proposed,[3] but appears not to have been carried out. We report here on the synthesis of asymmetric dimercury(2+)–crown ether complexes which are kinetically stable on the NMR time scale at low temperatures and provide straightforward access to the $^{199}Hg^{199}Hg$ coupling constants.

Treatment of $[Hg–Hg]^{2+}$ with 1 equiv. of 18-crown-6 in CH_2Cl_2 produces the dimercury(2+) complex **2** in which one Hg is complexed to the macrocyclic crown ether.† The mixed ligand complex $[Hg_2$(18-crown-6)(15-crown-5)-$(Me_2SO)](O_3SCF_3)_2$ **3a** containing one 18-crown-6 and one 15-crown-5 co-ordinated to dimercury(2+) was formed upon reaction of **2** with 1 equiv. of 15-crown-5.†

The ^{199}Hg NMR spectra of **2** and **3** consist of a superposition of the patterns of the two isotopomers with one ^{199}Hg nucleus (abundance 14.00% each) and the isotopomer containing two ^{199}Hg nuclei (abundance 2.84%). The latter arises from an AB spin system. The outer transitions of the AB system could not be observed because of very low probabilities (*e.g.* 0.3% of the inner transitions as calculated for **3b**) and because of linewidths of *ca.* 60–80 Hz for **2** and **3**, which are attributed to chemical shift anisotropy (CSA) relaxation. The coupling constant is readily derived from the distances of the inner lines of the AB system and of the shifts ν_a and ν_b which are obtained from the patterns of the isotopomers containing one ^{199}Hg nucleus. The value of the $^1J(^{199}Hg^{199}Hg)$ coupling constant in **2** is 220 300 Hz. An even larger $^{199}Hg^{199}Hg$ coupling constant (263 200 Hz) is observed for the mixed 18-crown-6/15-crown-5 complex **3a** in CH_2Cl_2. The ^{199}Hg NMR spectrum of a solution of **3a** in MeOH at 223 K shows the presence of two asymmetric dimercury(2+) complexes. The parameters of one of these species correspond to those of $[Hg_2$(18-crown-6)(15-crown-5)$(Me_2SO)](O_3SCF_3)_2$ **3a** in CH_2Cl_2, the other species is assigned to $[Hg_2$(18-crown-6)(15-crown-5)$(MeOH)](O_3SCF_3)_2$ **3b**, which is thought to be formed according to the equilibrium (1).

$$\underset{\mathbf{3a}}{[Hg_2(\text{18-crown-6})(\text{15-crown-5})(Me_2SO)]^{2+}} + MeOH \rightleftharpoons \underset{\mathbf{3b}}{[Hg_2(\text{18-crown-6})(\text{15-crown-5})(MeOH)]^{2+}} + Me_2SO \qquad (1)$$

The size of the Hg–Hg coupling constant of **3b** is 284100 Hz, and we believe that this represents the largest scalar coupling constant recorded so far. The ^{199}Hg shifts of the mercury atoms complexed to 18-crown-6 macrocycles appear at low frequencies compared with the Hg atoms coordinated by 15-crown-5 or bridging Me_2SO.

The complexes **2** and **3c** (all attempts to isolate **3a** gave **3c**) were characterised by single crystal X-ray diffraction:‡ as can be seen from Fig. 1, **2** exists as a dimer $\{[Hg_2(\text{18-crown-6})(Me_2SO)(\mu\text{-}Me_2SO)](O_3SCF_3)_2\}_2$ in the solid state. Curiously, the crystals of **3c** are built from two different complexes: the asymmetric unit contains one $[Hg_2$(18-crown-6)(15-crown-5)$(Me_2SO)](O_3SCF_3)_2$ and one $[Hg_2$(18-crown-6)(15-crown-5)$(H_2O)](O_3SCF_3)_2$ species which is shown in Fig. 2. In **2** and **3c** the coordination geometry of the mercury atoms complexed to a 18-crown-6 is hexagonal-bipyramidal with the other Hg atom and one oxygen of Me_2SO or H_2O in axial position and the crown oxygens in the equatorial sites. The 18-crown-6 ligands are located slightly off-centre with respect to the mercury atoms, presumably as a result of the steric demands of the Me_2SO ligand coordinated to the same Hg atom. The mercury atoms reside slightly off the 18-crown-6 plane which is shifted towards the terminal Me_2SO ligands. The 15-crown-5 macrocycle is coordinated in a 'half-sandwich' manner.

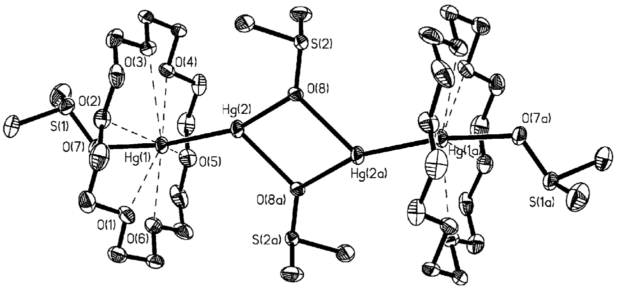

Fig. 1 Structure of $\{[Hg_2(\text{18-crown-6})_2(Me_2SO)(\mu\text{-}Me_2SO)]\}_2^{4+}$ (cation of **2**). Thermal ellipsoids are shown at the 20% probability level.

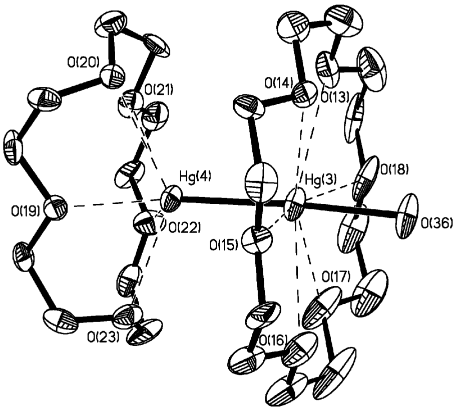

Fig. 2 Structure of $\{[Hg_2(\text{18-crown-6})(\text{15-crown-5})(H_2O)]^{2+}$ (part of **3c**). Thermal ellipsoids are shown at the 20% probability level.

DOI: 10.1039/b007581g

Notes and references

† *Synthesis and data*: for **2**: a mixture of $[Hg(Me_2SO)_6](O_3SCF_3)_2$[4] (0.1 mmol, 0.0968 g) in CH_2Cl_2 (0.5 mL) and elemental mercury (0.1 mL) was stirred vigorously for 2 h and 0.1 mmol (0.0264 g) of 18-crown-6 was then added. Colourless crystals were obtained from a 0.4 M solution in MeOH after 10 days at 277 K (0.060 g, 54%). Anal. Calc. for $C_{36}H_{72}F_{12}Hg_4O_{28}S_8$: C, 19.31; H, 3.24. Found C, 19.34; H, 3.26%. ^{199}Hg NMR (53.63 MHz, shifts relative to 2 mmol HgO in 1 ml 60% $HClO_4$, sweep width 50 kHz, time domain size 64 K, typical number of scans 20000, CH_2Cl_2, 243 K): δ 435 (Hg atom complexed to 18-crown-6), 944; $J(^{199}Hg^{199}Hg)$ 220300 (±790) (corresponding to an uncertainty of the difference of the two inner AB lines of ±4 data points).

For **3a**: a solution of 0.1 mmol (0.1120 g) of **2** in 0.5 mL of MeOH was treated with 0.1 mmol of 15-crown-5 (0.0220 g). All attempts to isolate **3a** gave **3c**: colourless crystals of **3c** were obtained upon standing of a solution of **3a** in MeOH for 3 weeks in contact with the atmosphere (0.070 g, 56%). Anal. Calc. for $C_{50}H_{96}F_{12}Hg_4O_{36}S_5 \cdot H_2O$: C, 24.20; H, 3.98. Found C, 24.08; H, 3.89%. ^{199}Hg NMR for **3a**, (CH_2Cl_2, 223 K): δ 304 (Hg atom complexed to 18-crown-6), 1023; $J(^{199}Hg^{199}Hg)$ 263200 (±570); i, (MeOH, 223 K): δ 317, 1032, $J(^{199}Hg^{199}Hg)$ 266600 (±590); **3b** (MeOH, 223 K): δ 345, 972, $J(^{199}Hg^{199}Hg)$ 284100 (±860).

‡ *Crystal data*: for **2**: $C_{36}H_{72}F_{12}Hg_4O_{28}S_8$, M = 2239.78, triclinic, space group $P\bar{1}$ (no. 2), a = 9.547(5), b = 11.836(2), c = 15.548(2) Å, α = 78.39(2), β = 77.21(4), γ = 83.79(2)°, V = 1674.5(9) Å^3, T = 213(2) K, Z = 1, Mo-Kα radiation (λ = 0.71073 Å), 5809 reflections collected, 4795 independent reflections (R_{int} 0.0274), 3457 reflections with $I > 2\sigma(I)$, $R1$ $[I > 2\sigma(I)]$ = 0.0373, $wR2$ (all data) = 0.0726, goodness-of-fit 1.021. The structure was solved by direct methods (SHELXS-86),[5] and refined by full-matrix least-squares methods on F^2 (SHELXL-93).[6]

For **3c**: $C_{50}H_{96}F_{12}Hg_4O_{36}S_5 \cdot H_2O$, M = 2481.94, triclinic, space group $P\bar{1}$ (no. 2), a = 12.289(2), b = 15.902(4), c = 21.254(4) Å, α = 92.25(2), β = 93.06(2), γ = 93.35(2)°, V = 4136.7(15) Å^3, T = 213(2) K, Z = 2, Mo-Kα radiation (λ = 0.71073 Å), 8498 reflections collected, 8004 independent reflections (R_{int} = 0.0508), 5405 reflections with $I > 2\sigma(I)$, $R1$ $[I > 2\sigma(I)]$ = 0.0566, $wR2$ (all data) = 0.1483, goodness-of-fit 1.032. The structure was solved and refined as for **2**.[5,6] CCDC 182/1851. See http://www.rsc.org/suppdata/cc/b0/b007581g/ for crystallographic files in .cif format.

1 R. J. Gillespie, P. Granger, K. R. Morgan and G. J. Schrobilgen, *Inorg. Chem.*, 1984, **23**, 887.
2 M. Maliarik, K. Berg, J. Glaser, M. Sandström and I. Tóth, *Inorg. Chem.*, 1998, **37**, 2910.
3 R. A. Santos and G. S. Harbison, *J. Am. Chem. Soc.*, 1994, **116**, 3075.
4 P. Peringer, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1501.
5 G. M. Sheldrick, SHELXS-86: program for crystal structure solutions. Universität Göttingen, 1986.
6 G. M. Sheldrick, SHELXL-93: program for refinement of crystal structures. Universität Göttingen, 1993.