Volume 31
Number 26
December 23, 1992

Inorganic Chemistry

Communications

A Distorted $[Hg(SR)_4]^{2-}$ Complex with Alkanethiolate Ligands: The Fictile Coordination Sphere of Monomeric $[Hg(SR)_x]$ Complexes

Nandakumar Govindaswamy, Jayson Moy, Michelle Millar, and Stephen A. Koch*

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794-3400

Received August 28, 1992

Mononuclear Hg–cysteine coordination centers have been implicated for the proteins involved in bacterial mercury detoxification, which include mercuric reductase, organomercury lyase, and the metalloregulatory protein MerR.[1,2] The biological problems have directed interest to the characterization of monomeric Hg thiolate complexes.[3–6] We report the characterization of the first monomeric Hg tetrathiolate complexes with alkanethiolate ligands.

The reaction of $HgCl_2$ with 3 equiv of the lithium salt of 1,2-*trans*-cyclohexanedithiolate and 2 equiv of Ph_4PBr in water gives crystals of $[Ph_4P]_2[Hg(S_2\text{-cyclohexane})_2]\cdot 4H_2O$. The X-ray structure revealed well-separated monomeric $[Hg(S_2\text{-cyclohexane})_2]^{2-}$ anions (**1**) (Figure 1).[7] Previous studies with 1,2-ethanedithiolate (a less constrained chelate) had only given oligomeric compounds.[8] Three of the thiolates serve as hydrogen bond acceptors from water molecules. The water molecules occur as isolated molecules and as part of a centrosymmetric hexagonal $(H_2O)_6$ ring. The hydrogens on the water molecules could not be located in the X-ray structure, but the O···O and the S···O distances[9,10] are completely consistent with the hydrogen-bonding interactions that are indicated in Figure 1.

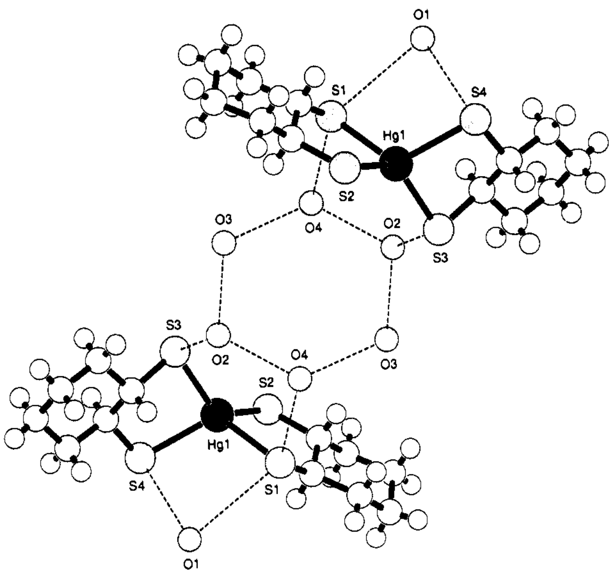

Figure 1. Structure of two $[Hg(S_2\text{-}1,2\text{-cyclohexane})_2]^{2-}$ anions (meso isomer) and the network of H_2O molecules. The cyclohexane ring of the ligand defined by S1 and S2 is 2-fold disordered; only one of the disordered rings is shown. Selected bond distances (Å) and angles (deg), with the metrical parameters of the isostructural Cd complex (**2**) given in brackets, are as follows: Hg–S1 = 2.570 (3) [2.535 (2)], Hg–S2 = 2.460 (2) [2.475 (2)], Hg–S3 = 2.509 (2) [2.522 (2)], Hg–S4 = 2.575 (2) [2.537 (2)], S1–O1 = 3.452 (7) [3.476 (6)], S1–O4 = 3.227 (8) [3.237 (6)], S3–O2 = 3.172 (8) [3.192 (5)], S4–O1 = 3.262 (7) [3.268 (6)], O2–O3 = 2.84 (1) [2.861 (8)], O2–O4 = 2.77 (1) [2.801 (8)], O3–O4 = 2.79 (1) [2.740 (8)], S1–Hg–S2 = 88.78 (8) [89.28 (6)], S1–Hg–S3 = 120.28 (8) [120.70 (6)], S1–Hg–S4 = 113.19 (8) [115.32 (6)], S2–Hg–S3 = 129.64 (8) [126.22 (6)], S2–Hg–S4 = 121.45 (8) [121.41 (6)], S3–Hg–S4 = 86.10 (7) [87.03 (5)], O3–O2–O4 = 118.2 (4) [117.0 (2)], O2–O3–O4 = 119.6 (4) [119.2 (2)], O2–O4–O3 = 121.9 (4) [123.5 (2)].

The large range in the Hg–S distances (2.460–2.575 Å) in **1** is unprecedented for a monomeric $[M(SR)_4]$ complex. In spite

---

(1) Walsh, C. T.; Distefano, M. D.; Moore, M. J.; Shewchuk, L. M.; Verdine, G. L. *FASEB J.* **1988**, *2*, 124. Helmann, J. D.; Shewchuk, L. M.; Walsh, C. T. *Adv. Inorg. Biochem.* **1990**, *8*, 33. Moore, M. J.; Distefano, M. D.; Zydowsky, L. D.; Cummings, R. T.; Walsh, C. T. *Acc. Chem. Res.* **1990**, *23*, 301.

(2) (a) Ralston, D. M.; O'Halloran, T. V. *Adv. Inorg. Biochem.* **1990**, *8*, 1. (b) Wright, J. G.; Natan, M. J.; MacDonneil, F. M.; Ralston, D. M.; O'Halloran, T. V. *Prog. Inorg. Chem.* **1991**, *38*, 323.

(3) Gruff, E. S.; Koch, S. A. *J. Am. Chem. Soc.* **1990**, *112*, 1245.

(4) Santos, R. A.; Gruff, E. S.; Koch, S. A.; Harbison, G. S. *J. Am. Chem. Soc.* **1991**, *113*, 469.

(5) Watton, S. P.; Wright, J. G.; MacDonnell, F. M.; Bryson, J. W.; Sabatt, M.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1990**, *112*, 2824.

(6) Natan, M. J.; Millikan, C. F.; Wright, J. G.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1990**, *112*, 3255.

(7) $[Ph_4P]_2[Hg(1,2\text{-}S_2\text{-cyclohexane})_2]\cdot 4H_2O$, $HgS_4P_{22}C_{60}O_4H_{68}$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 13.685\ (2)$ Å, $b = 18.290\ (2)$ Å, $c = 13.307\ (1)$ Å, $\alpha = 110.445\ (8)°$, $\beta = 111.292\ (8)°$, $\gamma = 69.157\ (9)°$, $V = 2806\ (1)$ Å^3, and $Z = 2$. Final least-squares refinement using 5220 unique reflections with $I > 3\sigma(I)$ gave $R\ (R_w) = 0.043\ (0.043)$. The cyclohexane ring of the ligand (defined by S1 and S2) is disordered. A model was successfully refined in which there is 50% occupancy of both the *d* and *l* enantiomers of this cyclohexane ring. The other ligand (defined by S3 and S4) shows an ordered cyclohexane ring. A crystallographic model in the noncentrosymmetric space group $P1$ also showed disordered ligands.

(8) Henkel, G.; Betz, P.; Krebs, B. *J. Chem. Soc., Chem. Commun.* **1985**, 1498.

(9) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley & Sons: New York, 1988.

(10) Mereiter, K.; Preisinger, A.; Zellner, A.; Mikenda, W.; Steidl, H. *J. Chem. Soc., Dalton Trans.* **1984**, 1275.

0020-1669/92/1331-5343\$03.00/0

of the distortions in **1**, the average Hg–S distance (2.529 Å) is (as expected)[11] in good agreement with the distance in more symmetric $[Hg(SR)_4]^{2-}$ complexes with arenethiolate ligands.[12,13] The shortest Hg–S bond is associated with the thiolate that is not engaged in hydrogen bonding with the H_2O molecules. Although the unsymmetric pattern of the S···H_2O hydrogen bonding is the principal cause of the distortions in the Hg–S bonds, the large magnitude of this distortion is an intrinsic property of the Hg^{2+} atom. The Cd analog of **1** is isomorphous and isostructural.[14] The Cd–S bonds ($Cd–S_{av}$ = 2.518 Å) in **2** are distorted in a parallel fashion to the corresponding Hg–S bonds. However, the range in the Cd–S bonds (2.475–2.537 Å) is substantially smaller. It has already been noted that the M–S bonds in low-symmetry $[Hg(SR)_3]^-$ complexes are observed to be more distorted than isostructural $[Cd(SR)_3]^-$ complexes.[4] Although $[Hg(SR)_x]^{n-}$ (x = 3, 4) centers can have symmetric structures,[4,5,13] small (low energy) effects (i.e., intra- and intermolecular packing forces or hydrogen-bonding interactions) can result in large distortions in Hg–S distances.

These observations help present a general picture of the chemistry of monomeric $Hg(SR)_x$ complexes. Hg is unique among the transition metals in that it readily forms two-, three-, and four-coordinate monomeric compounds with the same ligand type.[3,4,2b] The interaction of Hg^{2+} with thiolate ligands is highly favored thermodynamically; however, this stability can be achieved by a number of structures of nearly equal energies which have widely different coordination numbers and coordination geometries. When one bond in a $Hg(SR)_x$ center increases, the remaining Hg–S bonds counterbalance by becoming shorter and a new stable structure results. In the case of an extreme deformation, the loss of a ligand, the Hg center is compensated by a substantial decrease of ~0.1 Å in the average length of the remaining Hg–S bonds.[3] The ease of distortion of $Hg(SR)_x$ complexes suggests that the energy barriers separating the different species are low; $Hg(SR)_x$ complexes are known to be extremely labile with respect to ligand-exchange reactions.[15] The fictile[16] nature of the $Hg(SR)_x$ coordination sphere inherent in monomeric centers finds expression in the complicated structures of polymeric and oligomeric Hg thiolate compounds.[2b]

The ^{199}Hg NMR spectra of **1** show two sharp ($\Delta\nu_{1/2}$ = 12 Hz) closely spaced singlets at −125.8 and −134.3 ppm (while the ^{113}Cd spectrum of **2** shows two resonances at 760.4 and 759.0 ppm ($\Delta\nu_{1/2}$ = 7 Hz)).[17a] Because the ligand exists as a racemic mixture, several isomers are possible for the tetrahedral $[M(S_2\text{-cyclohexane})_2]^{2-}$ complexes, a *dd/ll* pair of enantiomers and a meso (*dl*) isomer which has S_4 point group symmetry. Support for the assignments of the two resonances to the enantiomers and to the meso isomer comes from the ^{113}Cd NMR spectrum of **2** in an optically active solvent (4/1 (*S*)-(+)-2-butanol/MeOH). The low-field resonance splits by 8.1 Hz into two peaks of equal intensity, while the high-field resonance is unchanged.[17b] There is no evidence in any spectra for resolved ^3J coupling between the Cd and Hg and the SCH protons, which has been observed in ^{113}Cd NMR studies of $[Cd(Cys\text{-}S)_x]$ centers in proteins.[18,20b] This can be rationalized by the near orthogonal value of M–S–C–H torsion angles, which average 80.3°.[19] Although the ^{199}Hg and ^{113}Cd chemical shifts of species assumed to be $[M(S\text{-alkyl})_4]^{2-}$ complexes have been reported,[20] the values reported herein are the first chemical shifts from structurally characterized compounds.

Acknowledgment. This research was supported by grants from the National Institutes of Health to S.A.K. (GM 31849) and to M.M. (GM 36308). We thank Dr. G. Crull for assistance with the NMR studies.

Supplementary Material Available: ORTEP diagrams and tables of crystallographic parameters, atomic coordinates, thermal parameters, and bond distances and angles for **1** and **2** (36 pages). Ordering information is given on any current masthead page.

---

(11) Maelia, L. E.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1896.

(12) Choudhury, S.; Dance, I. G.; Guerney, P. J.; Rae, A. D. *Inorg. Chim. Acta* **1983**, *70*, 227.

(13) The $[Hg(SR)_4]^{2-}$ anion in $[Et_4N]_2[Hg(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]$ has crystallographic S_4 symmetry; see ref 4 and: Gebhard, M. S.; Koch, S. A.; Millar, M.; Devlin, F. J.; Stephens, P. S.; Solomon, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 469. Silver, A.; Koch, S. A.; Millar, M. *Inorg. Chim. Acta*, in press.

(14) $[Ph_4P]_2[Cd(1,2\text{-}S_2\text{-cyclohexane})_2]\cdot 4H_2O$ (**2**), $CdS_4P_{22}C_{60}O_4H_{68}$, crystallizes in the triclinic space group $P\bar{1}$ with a = 13.716 (1) Å, b = 18.306 (1) Å, c = 13.330 (1) Å, α = 110.511 (6)°, β = 111.133 (6)°, γ = 69.290 (5)°, V = 2823 (1) Å^3, and Z = 2. Final least-squares refinement using 5412 unique reflections with $I > 3\sigma(I)$ gave R (R_w) = 0.043 (0.049). The disorder of one of the thiolate ligands is similar to that in compound **1**.

(15) Cheesman, B. V.; Arnold, A. P.; Rabenstein, D. L. *J. Am. Chem. Soc.* **1988**, *110*, 6359.

(16) Cotton, F. A.; Jamerson, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 1273.

(17) (a) The ^{199}Hg NMR spectrum (44.80 MHz) was measured at 215 K in MeOD with respect to $Hg(Me)_2$. The ^{113}Cd NMR spectrum (55.48 MHz) was measured at 295 K in DMSO with respect to 0.1 M $[Cd(ClO_4)_2]_{aq}$. (b) A similar splitting has not been resolved in the analogous ^{199}Hg NMR experiment with **1**.

(18) Armitage, I. M.; Otvos, J. D. *Biol. Magn. Reson.* **1982**, *4*, 79.

(19) The ^{199}Hg and ^{113}Cd spectra of $[Ph_4P]_2[M(S_2\text{-norbornane})_2]$ show quintets: for Cd, δ = 794.01 ppm (at 295 K in $CDCl_3$), $^3J_{Cd-H}$ = 18 Hz; for M = Hg, δ = −34 ppm (at 295 K in $CDCl_3$), $^3J_{Hg-H}$ = 46 Hz. The average M–S–C–H torsion angle is estimated from a related structure to be 127°.

(20) (a) Carson, G. K.; Dean, P. A. W. *Inorg. Chim. Acta* **1982**, *66*, 157. (b) Carson, G. K.; Dean, P. A. W.; Stillman, M. J. *Inorg. Chim. Acta* **1981**, *56*, 59. (c) Summers, M. F. *Coord. Chem. Rev.* **1988**, *86*, 43 and references therein.