Polyhedron Vol. 9, No. 22, pp. 2717–2720, 1990
Printed in Great Britain

0277-5387/90 $3.00+.00
© 1990 Pergamon Press plc

PREPARATION AND ^{199}Hg NMR STUDY OF SOME MERCURY(II) THIOLATE COMPLEXES

LAURENCE CARLTON* and **DAVID WHITE**

Department of Chemistry, University of the Witwatersrand, Johannesburg, Republic of South Africa

(*Received* 14 *March* 1990; *accepted* 5 *July* 1990)

Abstract—Mercury-199 NMR parameters are reported for the complexes $Hg(SPr^i)_2$, $Hg(SPh)_2$, $Hg(SCH_2CH_2OH)_2$, $Hg(SCH_2CO_2H)_2$, $Hg(SCH_2CH_2CO_2H)_2$ and $Hg(Sbt)_2$ (Sbt = benzthiazole-2-thiolate) which are readily prepared in moderate to good yield by the reaction of HgO with the free thiol. The ^{199}Hg chemical shift of $Hg(SPr^i)_2$ in a variety of solvents falls in a range −723 to −884 ppm; possible modes of interaction of the solvent with the metal are discussed.

The properties of mercury thiolate complexes are relevant to the study of biochemical systems that interact with the metal[1–3] and the development of antidotes to mercury poisoning.[4–6] Mercury-199 NMR spectroscopy has a potentially useful contribution to make in these areas but, as yet, few studies have reported ^{199}Hg NMR data.[7]

The isotope ^{199}Hg, spin 1/2, occurs in 16.84% natural abundance; relaxation processes (principally chemical shift anisotropy[8] at high magnetic field strengths) are effective and NMR data acquisition can be fairly rapid. The sensitivity of the ^{199}Hg nucleus to changes in its chemical environment is reflected in the observed chemical shift range of over 3000 ppm.[9] This makes ^{199}Hg NMR well suited to the detection of changes in the bonding and conformation of mercury complexes.

EXPERIMENTAL

Reagents were obtained from various sources and used without further purification. THF, pyrrolidine, benzene and toluene were distilled from sodium, dichloromethane was distilled from phosphorus pentoxide, acetone was distilled from potassium carbonate, pyridine, pyrrole, DMF, acetonitile and ether were distilled from calcium hydride and DMSO, n-hexane, isopropylamine, diisopropylamine and triethylamine were dried over calcium hydride. Other solvents were of the highest available purity and used without further treatment. Complexes were prepared under nitrogen.

NMR spectra were recorded at 22°C on a Bruker AC 200 FT spectrometer operating at 200.13 MHz (^{1}H), 50.32 MHz (^{13}C) and 35.84 MHz (^{199}Hg). ^{199}Hg spectra were obtained using a spectral width of 50,000 Hz and acquisition time of 0.33 s.

Preparation of $Hg(SPr^i)_2$[10]

A mixture of mercuric oxide (3.22 g, 14.9 mmol) and isopropyl thiol (2.26 g, 30 mmol) in dichloromethane (80 cm^3) at room temperature was stirred for 2 days. The solution was concentrated and an excess of hexane was added. On standing at −20°C for 12 h bis(isopropylthiolato)mercury was obtained as colourless needles (3.81 g, 10.9 mmol, 73%) Found: C, 20.0; H, 4.0. $C_6H_{14}HgS_2$ requires: C, 20.5; H, 4.0%. ^{1}H NMR (DMSO) δ 3.57 (sept, 1H, J 6.6 Hz), 1.31 (d, 6H, J 6.6 Hz). ^{13}C NMR (DMSO) δ 33.9, 31.0 ppm.

Preparation of $Hg(SPh)_2$[5]

A mixture of mercuric oxide (6.44 g, 29.8 mmol) and thiophenol (6.55 g, 60 mmol) in ethanol (80 cm^3) at room temperature was stirred for 12 h. The product was collected in a sinter, washed with ethanol and dried *in vacuo* to give bis(phenylthiolato)mercury as a white powder (10.51 g, 25.1 mmol, 84%) Found: C, 33.7; H, 2.3. $C_{12}H_{10}HgS_2$ requires: C, 34.4; H, 2.4%. ^{1}H NMR (DMSO) δ

---

* Author to whom correspondence should be addressed.

7.36 (mult, 2H), 7.11 (mult, 3H). ^{13}C NMR (DMSO) δ 136.9, 131.5, 128.4, 124.5 ppm.

Preparation of $Hg(SCH_2CH_2OH)_2$

A mixture of mercuric oxide (3.22 g, 14.9 mmol) and 2-mercaptoethanol (2.33 g, 30 mmol) in ethanol (80 cm^3) at room temperature was stirred for 12 h. The product was collected in a sinter, washed with ethanol and dried *in vacuo* to give bis(2-hydroxyethanethiolato)mercury as a white powder (1.61 g, 4.5 mmol, 31%) Found: C, 13.0; H, 2.8. $C_4H_{10}HgO_2S_2$ requires: C, 13.5; H, 2.8%. ^1H NMR (DMSO) δ 5.24 (s, 1H) 3.33 (t, 3H, *J* 5.9 Hz), 2.87 (t, 3H, *J* 5.9 Hz). ^{13}C NMR (DMSO) 63.3, 30.2 ppm.

Preparation of $Hg(SCH_2CO_2H)_2$[11]

A mixture of mercuric oxide (3.22 g, 14.9 mmol) and thioglycolic acid (2.78 g, 30 mmol) in ethanol (80 cm^3) at room temperature was stirred for 12 h. The product was collected in a sinter, washed with ethanol and dried *in vacuo* to give bis(acetic acid thiolato)mercury as a white powder (5.40 g, 14.1 mmol, 95%) Found: C, 12.7; H, 1.7. $C_4H_6HgO_4S_2$ requires: C, 12.6; H, 1.6%. ^1H NMR (DMSO) δ 11.75 (s, 1H) 3.67 (s, 2H). ^{13}C NMR (DMSO) δ 175.5, 29.4 ppm.

Preparation of $Hg(SCH_2CH_2CO_2H)_2$

A mixture of mercuric oxide (3.22 g, 14.9 mmol) and 3-mercaptopropionic acid (3.20 g, 30 mmol) in dichloromethane (80 cm^3) at room temperature was stirred for 12 h. The product was collected in a sinter, washed with dichloromethane and dried *in vacuo* to give bis(propionic acid-3-thiolato)mercury as a white powder (1.71 g, 4.2 mmol, 28%). Found: C, 16.9; H, 2.4. $C_6H_{10}HgO_4S_2$ requires: C, 17.5; H, 2.5%. ^1H NMR (DMSO) δ 12 (broad, 1H), 3.05 (t, 2H, *J* 6.8 Hz), 2.56 (t, 2H, *J* 6.8 Hz). ^{13}C NMR (DMSO) δ 174.1, 39.4, 22.1 ppm.

Preparation of $Hg(Sbt)_2$

A mixture of mercuric oxide (3.22 g, 14.9 mmol) and benzthiazole-2-thiol (4.98 g, 30 mmol) in dichloromethane at room temperature was stirred for 3 days. The product was collected in a sinter, washed with dichloromethane and dried *in vacuo* to give bis(benzthiazole-2-thiolato)mercury as a white powder (6.4 g, 12.0 mmol, 81%). Found: C, 29.8; H, 1.5; N, 4.9. $C_{14}H_8HgN_2S_4$ requires: C, 31.5; H, 1.5; N, 5.3%. ^1H NMR (DMSO) 7.88 (mult, 1H), 7.61 (mult, 1H), 7.30 (mult, 2H). ^{13}C NMR (DMSO) δ 167.5, 152.7, 137.0, 125.9, 123.8, 121.1, 120.0 ppm.

RESULTS AND DISCUSSION

The complexes $Hg(SR)_2$ are readily prepared in moderate to good yield by the reaction of HgO with the free thiol in dichloromethane or ethanol at room temperature. $Hg(SPr^i)_2$ is soluble in all common solvents except water while $Hg(SPh)_2$, $Hg(SCH_2CH_2OH)_2$, $Hg(SCH_2CO_2H)_2$, $Hg(SCH_2CH_2CO_2H)_2$ and $Hg(Sbt)_2$ are soluble only in DMSO and DMF.

Mercury-199 chemical shifts (Table 1) for the complexes in DMSO solution are found in the range −882 to −1206 ppm relative to $HgMe_2$. This upfield shift may result from the involvement of sulphur lone pair electrons in bonding to the metal. No spin–spin coupling is observed between ^{199}Hg and either hydrogen or ^{13}C, and all ^{199}Hg resonance lines appear as singlets.

From the similarity in the chemical shifts of $Hg(SPr^i)_2$ and $Hg(SCH_2CH_2OH)_2$ it is clear that in the latter the influence of the OH group over four bonds is negligible. For $Hg(SCH_2CH_2CO_2H)_2$, with carboxyl groups positioned a similar distance from the metal, the upfield shift of over 70 ppm relative to $Hg(SPr^i)_2$ must arise from diamagnetic through space shielding by the carbonyls. The closer proximity of the carbonyls to the metal in $Hg(SCH_2CO_2H)_2$ causes a further upfield shift. With aromatic rings positioned at a distance of two bonds from the metal in $Hg(SPh)_2$ and $Hg(Sbt)_2$, the effects of diamagnetic shielding are more pronounced, amounting in the case of Hg(Sbt) to an upfield shift of 324 ppm relative to $Hg(SPr^i)_2$.

Table 1. Mercury-199 spectral data for the complexes $Hg(SR)_2$[a]

	δ Hg[b]	$\nu_{1/2}$[c]	T_1 (Hg)[d]
$Hg(SCH_2CH_2OH)_2$	−882	15	0.10
$Hg(SPr^i)_2$	−884	5	0.15
$Hg(SCH_2CH_2CO_2H)_2$	−959	20	0.06
$Hg(SCH_2CO_2H)_2$	−985	65	0.07
$Hg(SPh)_2$	−1112	7.5	0.11
$Hg(Sbt)_2$	−1206	95	0.06

[a] Solvent DMSO: DMSO-d_6 (~ 20 : 1), concentration 0.1 M, temperature 22°C, 400–2400 transients recorded from each.

[b] Chemical shifts in ppm from neat $HgMe_2$ (external standard), negative values to high field.

[c] Line widths at half height in hertz.

[d] Spin–lattice relaxation times in seconds.

Table 2. The ^{199}Hg chemical shift of Hg(SPr^i)$_2$ in various solvents[a]

Solvent	δ Hg	Solvent	δ Hg	Solvent	δ Hg
Dimethylsulphoxide	−884	Pyrrole	−828	Diethyl ether	−789
Dimethylformamide	−871	Acetic acid	−822	Toluene	−783
Tetrahydrofuran	−845	Isopropanol[b]	−804	Benzene	−783
Acetonitrile	−836	Dichloromethane	−800	n-Hexane	−779
Methanol[b]	−834	Chloroform	−797	Diisopropylamine	−749
Nitromethane[b]	−834	Furan	−795	Pyrrolidine	−745
Acetone	−832	Thiophene	−794	Triethylamine	−733
Pyridine	−832	Isopropyl thiol	−791	Isopropylamine	−723

[a] Chemical shifts in ppm from neat HgMe$_2$ (external standard), negative values to high field; concentration 0.1 M; temperature 22°C.

[b] ~ 0.05 M (saturated).

Spin–lattice relaxation times, measured by the inversion-recovery method, are short and fall in a narrow range of 0.06–0.15 s. The dominant relaxation effects are likely to be spin-rotation and chemical shift anisotropy.[12] The broadening of the resonance lines of Hg(SCH$_2$CO$_2$H)$_2$ and Hg(Sbt)$_2$ suggests that in these compounds spin–spin relaxation processes are also operating; these might be expected to arise from conformational changes involving restricted rotation about the Hg—S or S—C bonds.

The ^{199}Hg chemical shift of Hg(SPr^i)$_2$ in a variety of solvents is shown in Table 2 and appears (with the exception of measurements in THF and methanol) to fall into four groups according to the nature of the solvent: (i) O- and N-donors in which the donor atom is involved in π-bonding (δ −822 to −884); (ii) O- and S-donors in which the donor atom is not π-bonded, Cl-donors (δ −789 to −804); (iii) aliphatic and aromatic hydrocarbons (δ −779 to −783); (iv) aliphatic amines (δ −723 to −749). Groups (i)–(iii) follow an order of decreasing dipole moment but the position of group (iv) on this scale is clearly anomalous. If the coordinating properties of hexane and its contribution to the ^{199}Hg chemical shift can be regarded as minimal (as found for HgMe$_2$[12]) it is possible to draw a number of conclusions.

The interaction between the solvents of group (i) and mercury favours an overall diamagnetic shielding by π-bonded groups of the solvent, i.e. the chemical shifts (relative to that measured in hexane) can be attributed to effects of solvent magnetic anisotropy. The fact that the increasing upfield shift roughly parallels the increase in dipole moment of the solvent suggests that electrostatic forces are involved in the ordering of the solvent in the region close to the metal.

Solvents of group (ii) provide a small diamagnetic shielding while for those of group (iii) there is no significant shielding. The data provide no evidence for an interaction of the π systems of benzene and toluene with the metal; the chemical shift in these solvents is only marginally different from that observed in hexane. This contrasts with the finding of Sens *et al.*[12] for dimethyl mercury, where a shift to high field of 56 ppm was observed on changing from hexane to benzene. The presence of sulphur would seem to discourage the interaction of the metal with the aromatic π system of a non-polar hydrocarbon.

Solvents of group (iv) contribute an overall paramagnetic shielding which is likely to arise from the mixing of atomic orbitals (i.e. nitrogen lone pair and mercury 6*p*) induced by a Lewis acid–base interaction.

Acknowledgement—We thank the University of the Witwatersrand for financial support.

REFERENCES

1. G. A. Neville and T. Drakenberg, *Can. J. Chem.* 1974, **52**, 616.
2. P. G. Schultz, K. G. Au and C. T. Walsh, *Biochemistry* 1985, **24**, 6840.
3. S. M. Miller, D. P. Ballou, V. Massey, C. H. Williams and C. T. Walsh, *J. Biol. Chem.* 1986, **261**, 8081.
4. G. Pouskouleli, P. Kourounakis and T. Theophanides, *Inorg. Chim. Acta* 1977, **24**, 45.
5. A. J. Canty and R. Kishimoto, *Inorg. Chim. Acta* 1977, **24**, 109.
6. D. L. Rabenstein, A. P. Arnold and R. D. Guy, *J. Inorg. Biochem.* 1986, **28**, 279.
7. G. K. Carson and P. A. W. Dean, *Inorg. Chim. Acta* 1982, **66**, 157.

8. J. D. Kennedy and W. McFarlane, *J. Chem. Soc. Faraday II* 1976, **72**, 1653.
9. R. Garth Kidd and R. J. Goodfellow, in *NMR and the Periodic Table* (Edited by R. K. Harris and B. Mann), p. 266. Academic Press, London (1978).
10. E. Wertheim, *J. Am. Chem. Soc.* 1929, **51**, 3661.
11. W. Stricks, I. M. Kolthoff and A. Heyndrickx, *J. Org. Chem.* 1954, **76**, 1515.
12. M. A. Sens, N. K. Wilson, P. D. Ellis and J. D. Odom, *J. Magn. Reson.* 1975, **19**, 323.