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Crystal Structure of Bis(*N*,*N*-dimethylthioformamide)mercury(II) Iodide, Bromide, and Chloride and Solvation of the Neutral Mercury(II) Halide Complexes in *N*,*N*-Dimethylthioformamide, a Resonance-Induced Hydrogen-Bonding Solvent and Ligand

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The isostructural solvated mercury(II) halides $HgI_2(SCHN(CH_3)_2)_2$, $HgBr_2(SCHN(CH_3)_2)_2$, and $HgCl_2(SCHN(CH_3)_2)_2$ are by single-crystal X-ray diffraction methods found to crystallize in the monoclinic space group $P2_1/n$ (No. 14) with $Z = 4$ and the unit cell parameters $a = 9.757(1)$, $b = 15.546(3)$, $c = 10.416(2)$ Å and $\beta = 104.47(1)°$ for the iodide, $a = 9.406(2)$, $b = 15.208(3)$, $c = 10.226(2)$ Å and $\beta = 104.66(1)°$ for the bromide, and $a = 9.193(2)$, $b = 15.094(2)$, $c = 10.121(2)$ Å and $\beta = 105.10(1)°$ for the chloride. Discrete mercury(II) complexes with pseudotetrahedral coordination are held together in layers by weak intermolecular interactions. An intramolecular hydrogen bond between one halide and the −CHS group of an *N*,*N*-dimethylthioformamide ligand makes the two mercury−halide bond lengths significantly different with 2.762(1) and 2.724(1) Å for the iodide, 2.619(3) and 2.565(3) Å for the bromide, and 2.509(5) and 2.452(5) Å for the chloride compound. Large-angle X-ray scattering of a saturated HgI_2 solution in *N*,*N*-dimethylthioformamide shows $HgI_2(SCHN(CH_3)_2)_2$ complexes to be formed with the Hg−I bond length 2.740(8) Å. The vibrational mercury−halide stretching frequencies are used to discuss correlations between bond distances and strengths. Raman and infrared vibrational spectra of *N*,*N*-dimethylthioformamide ligands in zinc, cadmium, and mercury complexes show the shifts of the C−S and C−N vibrational frequencies to be useful indicators of the metal ion-sulfur bond strength. Calorimetric measurements give strongly exothermic heats of solvation of HgI_2 and $HgBr_2$ in liquid *N*,*N*-dimethylthioformamide, −146 and −156 $kJ{\cdot}mol^{-1}$, respectively. From the corresponding heat of solvation of HgI_2 and $HgBr_2$ by *N*,*N*-dimethylthioformamide in dilute benzene solution the enthalpy contribution from the resonance-induced C−H···S hydrogen bonding in liquid *N*,*N*-dimethylthioformamide is estimated to be about 12 $kJ{\cdot}mol^{-1}$. The overall stability constants for the addition of *N*,*N*-dimethylthioformamide ligands to HgX_2 in benzene solution are determined to be $\beta_1 = (2.9 \pm 0.8) \times 10^4$ and $(8.2 \pm 1.0) \times 10^4$ $mol^{-1}{\cdot}dm^3$ and $\beta_2 = (1.4 \pm 0.4) \times 10^7$ and $(3.6 \pm 1.2) \times 10^7$ $mol^{-2}{\cdot}dm^6$ for X = I and Br, respectively.

Introduction

The mercury atom in the neutral mercury(II) halide complexes HgX_2, with X = I, Br, and Cl, is a typical soft electron-pair acceptor and is strongly solvated by soft Lewis bases, L.[1] With an excess of the ligand L a large range of pseudotetrahedral complexes, HgX_2L_2, is formed both in solution and in the solid state, *e.g.* refs. 2−9, and the high stability of the HgX_2 entity allows the effect of very strongly coordinating electron-pair donor ligands to be studied. The shift of the Hg−Br symmetric stretching frequency of different $HgBr_2L_2$ species in solution, a measure of the change in the Hg−Br bond strength, has been used to construct the donor strength D_S scale for relative comparisons of the electron-pair donor ability of Lewis bases toward soft electron-pair acceptors.[1,10]

N,*N*-Dimethylthioformamide is an aprotic soft sulfur donor solvent, with the unusual additional property of being an efficient solvent also for ionic compounds because of its high dipole moment and permittivity, $\mu = 4.44$ D and $\epsilon = 47.5$, respectively.[11] Recent diffraction, vibrational spectroscopic, and transfer thermodynamic studies of *N*,*N*-dimethylthioformamide solvated mercury(II), cadmium, and zinc ions show strong metal−sulfur bonds to be formed, especially for mercury(II).[12−14] A special feature of the *N*,*N*-dimethylthioformamide molecule, $(CH_3)_2NCHS$, is the delocalization of π electrons over the NCS entity, [15,16] which leads to a high N−C rotation barrier, a planar C'_2−N−CH−S skeleton (C′ denotes methyl carbon), and a high polarizability of the sulfur atom explaining its unusually strong electron-pair donor properties. The donor strength value, D_S

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(1) Persson, I.; Sandström, M.; Goggin, P. L. *Inorg. Chim. Acta* **1987**, *129*, 183.

(2) Sandström, M. *Acta Chem. Scand., Ser. A* **1978**, *32*, 627.

(3) Bowmaker, G. A.; Clase, H. J.; Alcock, N. W.; Kessler, J. M.; Nelson, J. H.; Frye, J. S. *Inorg. Chim. Acta* **1993**, *210*, 107.

(4) Persson, I.; Sandström, M.; Goggin, P. L.; Mosset, A. *J. Chem. Soc., Dalton Trans*. **1985**, 1597.

(5) Canty, A. J.; Ralston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 15.

(6) Sandström, M.; Persson, I.; Goggin, P. L. *J. Chem. Soc., Dalton Trans.* **1987**, 2411.

(7) Fälth, L. *Chem. Scr*. **1976**, *9*, 71.

(8) Bell, N. A.; Dee, T. D.; Goggin, P. L.; Goldstein, M.; Goodfellow, R. J.; Jones, T.; Kessler, K.; McEwan, D. M.; Nowell, I. W. *J. Chem. Res. (S)* **1981,** 2; *J. Chem. Res. (M)* **1981**, 2.

(9) Bell, N. A.; Dee, T. D.; Goldstein, M.; McKenna, P. J.; Nowell, I. W. *Inorg. Chim. Acta* **1983**, *71*, 135.

(10) Sandström, M.; Persson, I.; Persson, P. *Acta Chem. Scand.* **1990**, *44*, 653.

(11) Diggle, J. W.; Bogsanyi, D. *J. Phys. Chem.* **1974**, *78*, 1018.

(12) Stålhandske, C. M. V.; Persson, I.; Sandström, M.; Kamienska-Piotrowicz, E., *Inorg. Chem.* **1997**, *36*, 3174.

(13) Stålhandske, C. M. V.; Stålhandske, C. I.; Sandström, M.; Persson, I. *Inorg. Chem.* **1997**, *36*, 3167.

(14) Chaudhry, M.; Dash, K. C.; Kamienska-Piotrowicz, E.; Kinjo, Y.; Persson, I. *J. Chem. Soc., Faraday Trans*. **1994**, *90*, 2235.

(15) Ferretti, V.; Bertolasi, V.; Gilli, P.; Gilli, G. *J. Phys. Chem.* **1993**, *97*, 13568.

(16) Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1995**, *117*, 2201.

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Table 1. Crystallographic Data for the *N,N*-Dimethylthioformamide-Solvated Mercury(II) Halides

chem formula	$[HgI_2(SCHN(CH_3)_2)_2]$	$[HgBr_2(SCHN(CH_3)_2)_2]$	$[HgCl_2(SCHN(CH_3)_2)_2]$
formula mass/au	632.72	538.72	449.82
space group	$P2_1/n$ (No. 14)[a]	$P2_1/n$	$P2_1/n$
a/Å	9.757(1)	9.406(2)	9.193(2)
b/Å	15.546(3)	15.208(3)	15.094(2)
c/Å	10.416(2)	10.226(2)	10.121(2)
β/deg	104.47(1)	104.66(1)	105.10(1)
ρ_{calcd}/g·cm^{-3}	2.747	2.528	2.203
ρ_{obsd}/g·cm^{-3}	2.78	2.54	2.22
V/Å^3	1530.0(4)	1415.2(4)	1356.0(5)
Z	4	4	4
T/°C	22	22	22
λ/Å	0.7107	0.7107	0.7107
μ/cm^{-1}	14.34	16.78	12.02
R[b]	0.040	0.051	0.043
wR[c]	0.043	0.076	0.060

[a] Monoclinic, cell choice 2.[20] [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma(w|F_o|)^2]^{1/2}$.

= 52, is higher than for most other sulfur and nitrogen donor solvents.[1,10]

Previously, structure studies of the neutral mercury(II) iodide and bromide complexes in dimethyl sulfoxide,[2] pyridine,[4] and tetrahydrothiophene[6] solutions and of some solid HgX_2L_2 solvates show the decreasing X−Hg−X angle to be correlated with the shift of the X−Hg−X stretching frequency toward lower wavenumbers for increasing donor strength of the solvent, $D_S = 28$, 38, and 43, respectively.[1] For tetrahydrothiophene, the correlation unexpectedly indicates a weaker coordination in solution than in the solid state.[10,17] One purpose of this study is to introduce an even more strongly coordinating sulfur donor solvent which can be used also for concentrated electrolyte solutions; another is to find reasons for possible differences in the effective donor ability of sulfur ligands in solution and in the solid state. By using the neutral mercury(II) halide molecules as acceptors of somewhat different strength, the properties of *N,N*-dimethylthioformamide are further explored in the present investigation, and it is shown that vibrational spectra of the *N,N*-dimethylthioformamide ligands can be used to indicate the relative bond strength in the complexes.

The hydrogen-bonding ability of the *N,N*-dimethylthioformamide molecule has been shown to influence the structure of the solvated ions.[12,13] No such bonds of the type C−H···S seem to have been described previously, and we propose that the unexpectedly strong hydrogen bond ability of the thioformyl group is resonance-induced due to the π-electron delocalization. Similar resonance-assisted O−H···O and N−H···O hydrogen bonding has previously been encountered in many systems with delocalized π-electrons.[18]

Experimental Section

Preparation of Solvent. *N,N*-Dimethylthioformamide was prepared by reacting phosphorus pentasulfide with *N,N*-dimethylformamide (Merck) in benzene, according to the procedure described by Gutmann *et al.*[19] After repeated distillations ^{1}H-NMR showed no trace of unreacted *N,N*-dimethylformamide.

Preparation of Crystals and Solutions. Colorless crystals were obtained by cooling saturated *N,N*-dimethylthioformamide solutions of mercury(II) iodide, bromide, and chloride (Merck, analytical reagent). The crystals of the chloride compound showed tendency for twin formation, and careful testing by X-ray photographic methods was necessary before a single crystal suitable for data collection was found. The density (Table 1) was determined by the flotation method with dibromomethane−diiodomethane mixtures.[20]

Only mercury(II) iodide gives a saturated solution concentrated enough, 0.235 mol·dm^{-3} at 25 °C, to allow a precise determination of the mercury−halide bond distances in the solvated complex by large-angle X-ray scattering, LAXS. The solubility of mercury(II) bromide is 0.11 mol·dm^{-3} at 25 °C. The density of the saturated mercury(II) iodide and bromide solutions is 1.12 and 1.061 g·cm^{-3}, giving linear absorption coefficients for Mo Kα radiation (0.71069 Å) of 10.4 and 7.9 cm^{-1}, respectively.[20] A saturated mercury(II) chloride solution, ca 0.07 mol·dm^{-3}, has been used for vibrational spectroscopic studies.

Crystallographic X-ray Data Collection and Processing. The intensity data were collected at room temperature (22 ± 2 °C) by means of a Syntex $P2_1$ four-circle single-crystal diffractometer using graphite-monochromatized Mo Kα radiation, from crystals sealed into Lindemann capillaries. Isomorphous monoclinic unit cells were found for the three compounds with decreasing size from iodide to chloride (Table 1). The cell parameters were refined from 25 independently centered high-angle reflections, $2\theta > 25°$. The $\omega/2\theta$ scan method was used with variable scan speed from 0.3 to 8°/min. Three check reflections were sampled regularly. Almost linear and isotropic crystal decay (16, 6, and 10% for the iodide, bromide, and chloride, respectively) was corrected for during data processing. A semi-empirical ψ-scan absorption correction method was applied.[21]

Atomic positions were obtained by means of direct methods followed by normal heavy atom procedures and finally full-matrix refinements with all non-hydrogen atoms anisotropic. The hydrogen atoms were included in calculated positions with isotropic temperature factors assuming an apparent C−H bond distance of 0.96 Å. The SHELXTL PLUS program system in Siemens PC-version was used for the data treatment.[22] Crystallographic data are given in Table 1, and further conditions for the data collection and treatment, in Table S1 (Supporting Information). The interatomic distances and angles are summarized in Table 2, and the refined atomic parameters are reported in Tables S2−S4 (Supporting Information).

Solution X-ray Data Collection and Treatment. A $\theta-\theta$ diffractometer, described previously,[23] was used to measure the scattered Mo Kα X-ray intensity from the free surface of the solution, which was enclosed within a half-cylindrical X-ray shield with a beryllium window. At 400 discrete θ-values, distributed with 0.1° interval over the range $1 < \theta < 25°$ and 0.25° for $25 < \theta < 70°$, 10^5 counts were recorded twice. After absorption correction,[24] the further data treatment was performed by means of the KURVLR and STEPLR programs,[25,26] in the same way as described elsewhere.[12] The scattering factors, f, for neutral atoms, including corrections for anomalous dispersion, $\Delta f'$ and

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(17) Persson, I.; Landgren, M.; Marton, A. *Inorg. Chim. Acta* **1986**, *116*, 135.

(18) Bertolasi, V.; Gilli, P.; Ferretti, V.; Gilli, G.: (a) *Chem. Eur. J.* **1996**, *2*, 925; (b) *Acta Crystallogr., Sect. B* **1995**, *51*, 1004.

(19) Gutmann, V.; Danksagmüller, K.; Duschek, O. *Z. Phys. Chem., Neue Folge (Frankfurt)* **1974**, *92*, 199.

(20) *International Tables for Crystallography*, Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995; Vol. C.

(21) North, A. C. T.; Phillips, D. C.; Scott Mathews, F. *Acta Crystallogr., Sect. A* **1964**, *24*, 351.

(22) Sheldrick, G. M. *SHELXTL PLUS 1992, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany.

(23) Johansson, G. *Acta Chem. Scand.* **1971**, *25*, 2787; **1966**, *20*, 553.

(24) Milberg, M. *J. Appl. Phys.* **1958**, *29*, 64.

(25) Johansson, G.; Sandström, M. *Chem. Scr.* **1973**, *4*, 195.

(26) Molund, M.; Persson, I. *Chem. Scr.* **1985**, *25*, 197.

Table 2. Interatomic Distances (Å) and Angles (deg) for the $HgX_2(SCHN(CH_3)_2)_2$ Structures (X = I, Br, and Cl), with Estimated Standard Deviations

mercury(II) coord		HgI_2L_2	$HgBr_2L_2$	$HgCl_2L_2$
		Intermolecular Bonds		
Hg−X	Hg − X(1)	2.762(1)	2.619(3)	2.509(5)
	Hg − X(2)	2.724(1)	2.565(3)	2.452(5)
Hg−S	Hg − S(1)	2.572(4)	2.544(7)	2.527(5)
	Hg − S(2)	2.584(4)	2.541(8)	2.536(6)
X−Hg−X	X(1)−Hg−X(2)	113.2(1)	112.4(1)	111.8(2)
X−Hg−S	X(1)−Hg−S(1)	107.0(1)	106.0(1)	105.0(2)
	X(1)−Hg−S(2)	112.2(1)	109.7(4)	107.7(2)
	X(2)−Hg−S(1)	111.9(1)	112.7(2)	114.2(2)
	X(2)−Hg−S(2)	108.8(1)	108.4(2)	108.7(2)
S-Hg−S	S(1)−Hg−S(2)	103.3(1)	107.5(2)	109.1(2)
Hg−S−C	Hg−S(1)−C(1)	99.2(5)	98.6(8)	99.4(7)
	Hg−S(2)−C(4)	105.9(6)	104.4(9)	103.2(7)
		Intermolecular Interactions		
X···S	X(1)···S(1)	4.062(4)	4.017(6)	4.013(7)
	X(1)···S(2)	3.968(4)	3.953(8)	4.008(7)
X···Hg	X(1)···Hg	4.241(1)	4.089(3)	4.031(5)
Hg−X···S	Hg−X(1)···S(1)	138.9(1)	140.5(1)	141.6(2)
	Hg−X(1)···S(2)	133.4(1)	134.8(1)	134.7(2)
Hg−X···Hg	Hg−X(1)···Hg	125.6(1)	128.6(1)	129.5(1)
		Hydrogen Bonds		
X···C(internal)	X(1)···C(1)	3.78(2)	3.64(2)	3.54(2)
X···C(external)	X(2)···C(4)	4.05(2)	3.89(3)	3.81(2)

$\Delta f''$,[20] and for Compton scattering,[27] were used to derive the structure-dependent reduced intensity function, $i(s)$, which was normalized to a stoichiometric unit of volume containing one mercury atom. A Fourier transformation gave the radial distribution function in the form $D(r) - 4\pi r^2\rho_0$; cf. Figure 1. Theoretical intensity values for all pairwise interactions between the atoms p and q within the proposed molecular models were calculated according to the following expression:[25]

$$i_c(s) = \Sigma\Sigma[f_p(s)f_q(s) + \Delta f''_p\Delta f''_q](\sin sd_{pq})(sd_{pq})^{-1}\exp(-{}^1/_2 l_{pq}^{\,2}s^2)$$

The scattering variable is $s = (4\pi/\lambda)\sin\theta$. The exponent of the Debye−Waller factor contains the mean square variation l_{pq}^2 of the interatomic distance d_{pq} assuming a Gaussian distribution. Least-squares refinements of some model parameters were performed by fitting the experimental and calculated $s{\cdot}i(s)$ functions above $s = 4.2$ Å^{-1}, where the contributions from diffuse intermolecular interactions in the solution were found to be negligible. Prior to the refinements a better alignment of the experimental $i(s)$ curves was achieved by removing spurious nonphysical peaks below $r = 1.5$ Å by a Fourier back-transformation procedure.[28] The parameters obtained from the fitting procedure are given in Table 3. The *N*,*N*-dimethylthioformamide ligand and the solvent molecules are described with the model used for the pure liquid including contributions from weak S···H−C intermolecular hydrogen bonding (about 70%) and corresponding intermolecular S···S and S···C distances in the solvent.[29]

Calorimetry. The heat of solution of crystalline mercury(II) iodide and bromide in *N*,*N*-dimethylthioformamide, $\Delta_{sln}H°$, was determined at 25.000 ± 0.002 °C by means of an ampule calorimeter described elsewhere.[30] Varying amounts of the mercury(II) halides (0.01−0.025 g) were added to the glass ampules, which were weighed before and after the addition and sealed by burning. The dissolution of the salt in 3 or 4 ampules, one by one, in 80 cm^3 *N*,*N*-dimethylthioformamide was completed in a few minutes. Six experiments in agreement were performed for each system. The heat of solution was found to be independent of the mercury(II) halide concentration.

Titration calorimetry to determine the heat of complex formation between the HgI_2 or $HgBr_2$ species and *N*,*N*-dimethylthioformamide in benzene solution was performed by means of a ThermoMetric 2277 TAM microcalorimeter. The titration vessel, 3.5 cm^3, was rhodium-

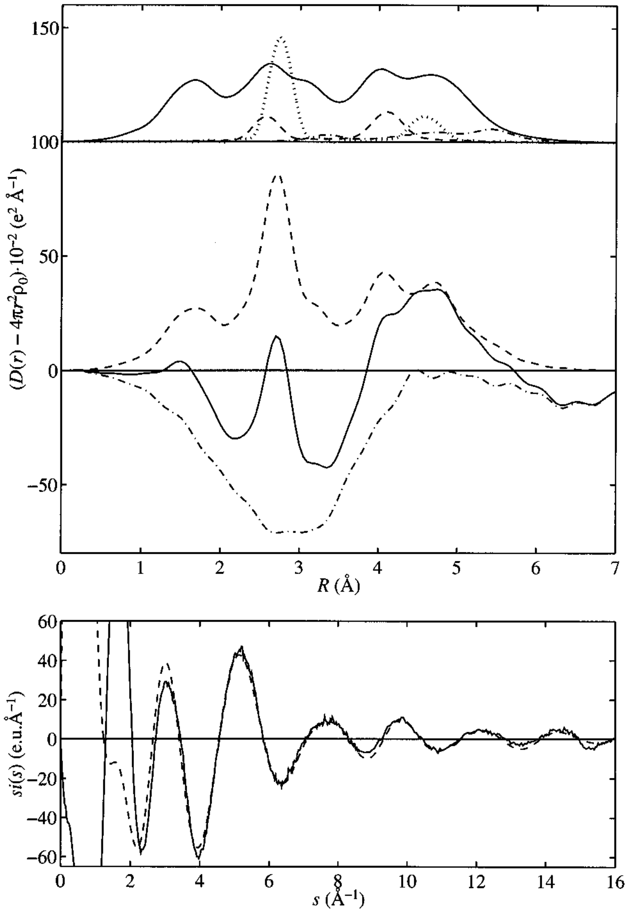

Figure 1. LAXS radial distribution curves for 0.235 mol·dm^{-3} HgI_2 in *N*,*N*-dimethylthioformamide. Top: Separate model contributions (Table 3) [Hg−I and I···I (dots); Hg−S and I···S (dashes); remaining distances between Hg and the atoms of the $HgI_2(SCHN(CH_3)_2)_2$ complex (dash−dots); *N*,*N*-dimethylthioformamide solvent (solid line)]. Middle: Experimental $D(r) - 4\pi r^2\rho_0$ (solid line); model (dashes); difference (dash-dots). Bottom: Reduced LAXS intensity functions, $i(s)$ (solid line = experimental; dashed = calculated), multiplied by the scattering variable, s.

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(27) Cromer, D. T.; Mann, J. B. *J. Chem. Phys.* **1967**, *47*, 1892; Cromer, D. T. *Ibid.* **1969**, *50*, 4857.

(28) Levy, H. A.; Danford, M. D.; Narten, A. H. *Data Collection and Evalution with an X-ray Diffractometer Designed for the Study of Liquid Structure*; Report ORNL-3960; Oak Ridge National Laboratory: Oak Ridge, TN, 1966.

(29) Stålhandske, C. M. V.; Borrman, H.; Persson, I.; Sandström, M. Unpublished results.

(30) Kullberg, L. *Acta Chem. Scand., Ser. A* **1974**, *28*, 979.

Table 3. LAXS Model Parameters for Selected Intramolecular Interactions of $[HgI_2(SCHN(CH_3)_2)_2]$ and $[HgBr_2(SCHN(CH_3)_2)_2]$ Complexes in *N*,*N*-Dimethylthioformamide Solution (Distance, *d*/Å, Displacement Parameter, *l*/Å, and Number of Distances, *n*), with Estimated Standard Errors Given within Parentheses for Parameters Varied in the Least-Squares Refinements

Hg−I	*d*	2.740(8)	Hg−Br	*d*	2.57(3)[a]
	l	0.05(2)		*l*	0.1
	n	2.0		*n*	2.0
I−I	*d*	4.58	Br−Br	*d*	4.20
	l	0.126		*l*	0.14
	n	1.0		*n*	1.0
Hg−S	*d*	2.56(3)	Hg−S	*d*	2.57(3)[a]
	l	0.077(13)		*l*	0.1
	n	2.0		*n*	2.0

[a] Refined together as one parameter.

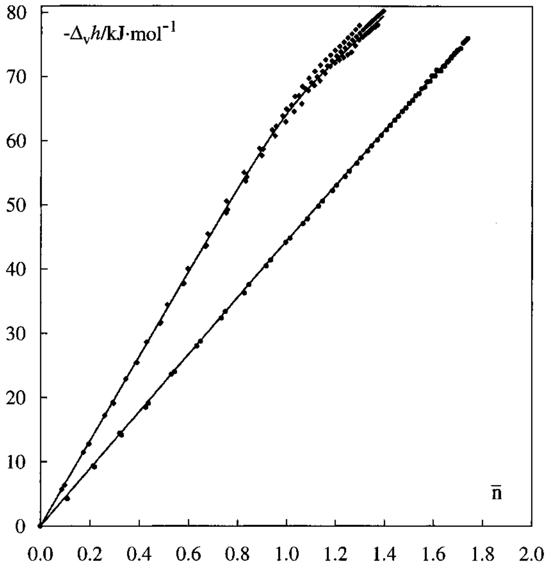

Figure 2. Total molar enthalpy change, $\Delta_v h$, as a function of ligand number, $\bar{n}$, at the complex formation between mercury(II) iodide and bromide molecules and *N*,*N*-dimethylthioformamide in benzene solution. The filled diamonds and circles represent experimental values for mercury(II) bromide and iodide, respectively; the solid lines are calculated from the derived β_i and $\Delta_{\beta i}H°$ values, Table 4.

plated for chemical inertness, and the stirrer was a KEL-F cylinder on a gold axis. Titrations of 3.0 cm^3 portions of 3.0 mmol·dm^{-3} mercury(II) iodide or 1.0 mmol·dm^{-3} mercury(II) bromide solutions in benzene were performed with a 0.200 or 0.050 mol·dm^{-3} solution of *N*,*N*-dimethylthioformamide in benzene. In each titration series 30 portions of 5.0 μL were added through a very thin gold capillary by a computer-controlled pump driving a microliter syringe. At least three titration series were performed for each system. Heats of dilution in benzene were measured for the HgX_2 and *N*,*N*-dimethylthioformamide solutions. The total molar enthalpy change, $\Delta_v h$, when adding *N*,*N*-dimethylthioformamide to HgI_2 or $HgBr_2$ in benzene solution is shown in Figure 2. The stability constants and the corresponding enthalpy changes have been calculated by means of the least-squares program KALORI,[17,31] and the results are given in Tables 4 and 5.

Vibrational Spectroscopy. Far-IR spectra were recorded as an average of 10^4 scans at a resolution of 4 cm^{-1} with a Perkin-Elmer 1760X spectrometer, equipped with a deuterated triglycine sulfate (DTGS) detector. Solids were contained in polyethylene disks, and a cell with silicon windows and a 0.012 mm Teflon spacer was used for the solutions. Mid-IR spectra were obtained by means of a Perkin-Elmer 1720X spectrometer, with the solid samples in a KBr matrix and the solutions between KBr windows at 2 and 4 cm^{-1} resolution, respectively. Raman spectra were recorded in 90° scattering geometry using photon counting with a DILOR Z24 triple monochromator at a spectral bandwidth of 4 cm^{-1}. The light source was the premonochromated 514.5 nm line of a Coherent Radiation Laboratories Innova 90-5 argon ion laser with an effective power of approximately 500 mW at the sample. From calibration measurements the band positions are estimated to be accurate within ±1 cm^{-1}.

Table 4. Overall Stability Constants, β_1/mol^{-1}·dm^3 (=K_1) and β_2/mol^{-2}·dm^6 (=K_1K_2), Corresponding Standard Reaction Enthalpies, $\Delta_{\beta i}H°$ (kJ·mol^{-1}), for the Addition of *N*,*N*-dimethylthioformamide to Mercury(II) Iodide or Bromide Molecules in Benzene Solution at 25 °C with Estimated Standard Errors (3σ), Derived Standard Reaction Quantities for Stepwise Additions, $\Delta G_i°$ and $T\Delta S_i°$ (kJ·mol^{-1})

	HgI_2	$HgBr_2$
β_1	$(2.9 \pm 0.8) \times 10^4$	$(8.2 \pm 1.0) \times 10^4$
β_2	$(1.4 \pm 0.4) \times 10^7$	$(3.6 \pm 1.2) \times 10^7$
$-\Delta_{\beta 1}H°$	44.6 ± 0.3	66.3 ± 0.3
$-\Delta_{\beta 2}H°$	87.3 ± 0.7	100.1 ± 1.0
K_2	4.6×10^2	$4.2 \cdot 10^2$
$-\Delta G_1°$	25.5 ± 0.7	28.0 ± 0.3
$-\Delta G_2°$	15 ± 1	15 ± 1
$T\Delta S_1°$	−19.1	−38.3
$T\Delta S_2°$	−28	−19

Table 5. Standard Reaction Enthalpies for HgI_2 and $HgBr_2$ in kJ·mol^{-1}, Heat of Solution of HgX_2(s) in *N*,*N*-Dimethylthioformamide, $\Delta_{sln}H°$, Heat of Sublimation, $\Delta_{sub}H°$,[36] Heat of Solvation of HgX_2(g) in Neat *N*,*N*-Dimethylthioformamide (L*), $\Delta_{sv}H°(L^*) = \Delta_{sln}H° - \Delta_{sub}H°$, and in Benzene, $\Delta_{sv}H°$(Bz), Heat of Complex Formation with *N*,*N*-Dimethylthioformamide in Dilute Benzene Solution, $\Delta_{\beta 2}H°$, and Heat of Solvation of HgX_2(g) with *N*,*N*-Dimethylthioformamide in Benzene Solution, $\Delta_{sv}H°$(L,Bz)[a]

std enthalpy	HgI_2	$HgBr_2$
$\Delta_{sln}H°$	-57.6 ± 0.8	-71.9 ± 1.1
$\Delta_{sub}H°$	88.2	84.1
$\Delta_{sv}H°(L^*)$	−145.8	−156.0
$\Delta_{sv}H°$(Bz)	−70	−68.4
$\Delta_{\beta 2}H°$	-87.3 ± 0.7	-100.1 ± 1.0
$\Delta_{sv}H°(L,Bz)$	−157	−168
$\Delta_{dil}H°$	−11	−12

[a] The difference $\Delta_{dil}H° = \Delta_{sv}H°(L,Bz) - \Delta_{sv}H°(L^*)$ provides a measure of the hydrogen bond enthalpy in liquid *N*,*N*-dimethylthioformamide.

The spectra were analysed by means of the Lab Calc program package.[32] The spectral features of the complexes in solution were isolated by solvent subtraction, and the depolarization ratios, $\rho_p = I_{vh}/I_{vv}$, were derived from polarization measurements with the polaroid analysator in parallel (I_{vv}) and perpendicular (I_{vh}) position relative the vertically polarized laser beam, with intensity calibrations according to a previously determined instrument efficiency curve. The Raman and infrared spectra are shown in Figure 3 in a limited range, 100−450 cm^{-1}, and vibrational frequencies for the solvated mercury(II) iodide, bromide, and chloride complexes both in solution and the solid state up to 1650 cm^{-1} are given in Table 6.

Results and Discussion

Crystal Structures. The three isostructural halides are built up from discrete $HgX_2(SCHN(CH_3)_2)_2$ complexes in layers perpendicular to the *a* axis of the unit cell; see Figure 4. The coordination at the mercury atom is pseudotetrahedral to two halide and two sulfur atoms. The Hg−X(1) bond is significantly longer than Hg−X(2). The difference is 0.038, 0.054, and 0.057 Å for X = I, Br, and Cl, respectively (cf. Table 2), and reflects the different interatomic interactions of the two halide ions. Several possible intermolecular contact distances with the X(1) ligand are listed in Table 2 (see also Figure 5), but only the I(1)···S(2) distance, 3.968(4) Å, is found to be slightly shorter than the corresponding sum of the estimated van der Waals radii (I 2.15, Br 1.95, Cl 1.81, C and S 1.85 Å,[33] Hg 1.7−2.0 Å[34]). The largest difference between the two Hg−X bond distances

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(31) Karlsson, R.; Kullberg, L. *Chem. Scr.* **1976**, *9*, 54.

(32) Lab Calc· Galactic Industries Corp., 395 Main Street, Salem, NH 03079-9891.

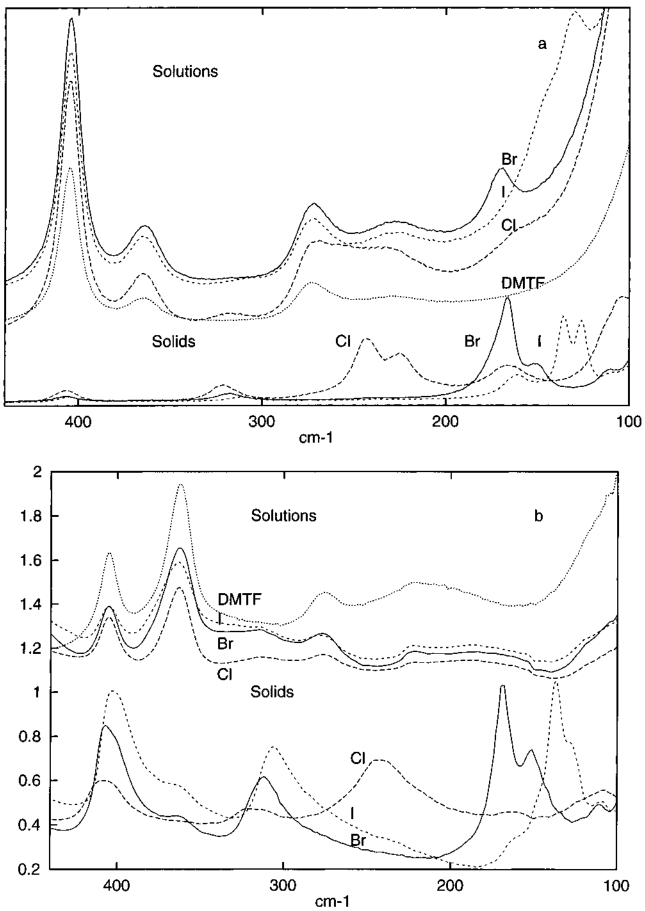

Figure 3. Vibrational spectra (100−450 cm^{-1}) of the [$HgX_2(SCHN(CH_3)_2)_2$] complexes, X = I, Br, and Cl, in the solid state and in *N,N*-dimethylthioformamide solution: (a) Raman spectra; and (b) far-IR spectra.

is found for the chloride structure. Figure 5 shows the hydrogen atom of the −CHS group of one *N,N*-dimethylthioformamide ligand to be in a position to form an internal hydrogen bond with the X(1) halide atom at an X(1)···H(1)−C(1) angle of about 145−150°. The strongest hydrogen bonding is expected for chloride, in accordance with the long Hg−Cl(1) bond length. The only interaction with the X(2) halide atom seems to be a very weak intermolecular hydrogen bond, X(2)···H(4)−C(4), to the second *N,N*-dimethylthioformamide ligand (Figures 4 and 5 and Table 2; cf. the vdW radii of C 1.85 Å and H 1.2 Å[33]).

The reason that the HgX_2L_2 complexes are so easily distorted can be sought in the special bonding properties of mercury(II). As discussed previously, vibronic coupling mechanisms leading to d-orbital contributions in the bonds[35] give rise to pronounced distortions or "plasticity" effects for tetrahedrally coordinated mercury(II) complexes with sulfur donor ligands.[12] A possible reason for the relatively large distortions found in the present structures is then a combination of the weak specific interatomic interactions discussed above and deformations of the complexes due to packing effects. This "plasticity" or ease of deformation,[35] which previously has been observed for distorted $[Hg(SR)_4]^{2-}$ complexes with alkanethiolate ligands,[36] should be greatest for the chloride complex which has the smallest difference in donor strength between the halide and the sulfur donor ligands. The mean Hg−S bond distance decreases from the iodide to the chloride complex, 2.578, 2.542, and 2.532 Å, respectively, with the last value close to the mean Hg−S bond length, 2.527(6) Å, of the slightly distorted tetrahedrally solvated $[Hg(SCHN(CH_3)_2)_4]^{2+}$ ion in *N,N*-dimethylthioformamide solution.[12]

Within the pseudotetrahedral mercury(II) iodide, bromide and chloride complexes the X−Hg−X angle decreases, 113.2(1), 112.4(1), and 111.8(2)°, respectively, with a corresponding increase in the S−Hg−S angle, 103.3(1), 107.2(2), and 109.1(2)°; cf. Table 2. The X−Hg−X angles are intermediate to those found in the corresponding crystalline tetrahydrothiophene bis-solvates with bromide (117.5°) and chloride (115.4°) and those in the triphenylphosphine solvates, about 109°.[6,7] Previously, a correlation between increasing Hg−X bond distances and decreasing X−Hg−X angles has been found for a number of pseudotetrahedral bis-solvated mercury(II) dihalide complexes, HgX_2L_2.[1] This correlation, which is a result of the weakening of the Hg−X bonds, reflects the electron-pair donor ability of the ligands L toward the mercury atom in the HgX_2 molecules. The present results show that the donor strength of *N,N*-dimethylthioformamide as a ligand to mercury in the solid HgX_2L_2 complexes is intermediate to that of tetrahydrothiophene and triphenylphosphine, although the present nonsymmetrical distortion of the Hg−X bonds may influence the comparisons to some extent. Since the halide−halide distances in all cases are well above van der Waals contacts steric effects should be negligible.

The average amide carbon−nitrogen, C−N, distance, 1.30 Å, is much shorter than the mean nitrogen−methyl carbon, N−C′, distances, 1.46 Å. The bond angles around the thioformamide carbon and nitrogen atoms are close to 120° as expected for sp^2 hybridization. Both *N,N*-dimethylthioformamide ligands of the $HgX_2(SCHN(CH_3)_2)_2$ complexes are found to be planar with the mean deviation from a least-squares plane through the non-hydrogen atoms less than 0.011 Å for all three compounds. The mercury atom is only slightly outside the plane of the first ligand, 0.02, 0.06, and 0.07 Å, but deviates more for the second, 0.08, 0.23, and 0.28 Å, for the iodide, bromide, and chloride complexes (cf. Figure 6), respectively. The angle between the normals to the planes of the two *N,N*-dimethylthioformamide ligands is 80.4, 83.9, and 85.4°, in the three halides, respectively.

Large-Angle X-ray Scattering Studies. The radial distribution function, RDF, of mercury(II) iodide in *N,N*-dimethylthioformamide solution shows a dominating peak at 2.7 Å (Figure 1), which corresponds to the Hg−I bond distances 2.724(1) and 2.762(1) Å of the crystal structure (Table 2). For the solution, least-squares model refinements of the intensity data gave an intermediate bond length, Hg−I 2.740(8) Å (Table 3). Reliable values of the Hg−S and I···I distances are difficult to obtain because of the severe overlap with contributions from the solvent structure. The Hg−S bond distance is estimated to 2.56(3) Å which is similar to the mean Hg−S distance 2.578 Å of the $HgI_2(SCHN(CH_3)_2)_2$ structure. The I···I distance used in the model calculations is close to the solid state value, 4.58 Å, but cannot be precisely determined because of the overlapping Hg···N and S···C′ interactions in the complex and bulk solvent, respectively.

LAXS measurements were also performed on the 0.11 M mercury(II) bromide solution in *N,N*-dimethylthioformamide. The RDF shows a peak at 2.6 Å, which contains both the Hg−Br and the Hg−S bond distances of the complex. The distances are too close to be resolved and give, when refined together, a mean value of 2.57(3) Å, which corresponds to the mean of the distances found for the $HgBr_2(SCHN(CH_3)_2)_2$ complex in

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(33) Emsley, J. *The Elements*, 3rd ed.; Oxford University Press: Oxford, U.K., 1996.
(34) Canty, A. J.; Deacon, G. B. *Inorg. Chim. Acta* **1980**, *45*, L225.
(35) Bersuker, I. B. *Electronic Structure and Properties of Transition Metal Compounds*; Wiley-Interscience: New York, 1996; Chapters 7.3 and 9.4.
(36) Govindaswamy, N.; Moy, J.; Millar, M.; Koch, S. A. *Inorg. Chem.* **1992**, *31*, 5343.

Table 6. Vibrational Frequencies[a] Observed in IR Absorption and Raman Spectra of $[HgX_2(SCHN(CH_3)_2)_2]$ Complexes in the Solid State and in Solution and for Liquid *N*,*N*-Dimethylthioformamide (DMTF)[b]

DMTF		$[HgCl_2(SCHN(CH_3)_2)_2]$				$[HgBr_2(SCHN(CH_3)_2)_2]$				$[HgI_2(SCHN(CH_3)_2)_2]$				
		IR		Raman		IR		Raman		IR		Raman		
IR	Raman	solutn	cryst	solutn	cryst	solutn	cryst	solutn	cryst	solutn	cryst	solutn	cryst	assgnt[b]
					88 m				74 m				72 w	
			109 w		104 m		96 w		97 m				96 w	
							110 w		110 w		128 m	129[c] s	126 s	ν_s(Hg−I)
											137 s		134 s	ν_s(Hg−I)
												144 sh		ν_{as}(Hg−I)
							152 m		153 w					ν_s(Hg−Br)
							169 s	170[c] m	167 s					ν_s(Hg−Br)
			164 w	163 w	167 m				177 sh		162 w		162 m	ν_s (Hg−S), δ(C−S)
	224	222 w				222 w		226 w		222 w	238 vw	226 w	237 vw	$\tau(NCH_3)$
			220 w sh		225 m									ν(Hg−Cl)
			243 m	242[c] sh	243 s									ν(Hg−Cl)
275	273	277 w		272 w		277 w		272 m		276 w		272 w		δ(C−S), (NC'_2)[d]
		314 w	318 m	318 vw	321 w	314 w	311 m		319 w	315 w	306 m	308 vw	311 m	ν(Hg−S)
362	366	363 s		365 w	365 vw	363 s	363 w	364 w		363 s	364 w	365 m		$\gamma(C'_2N)$[d]
405	405	405 m	408 m	405 m	406 w	405 m	404 m	404 m	406 w	405 m	403 s	404 s	405 m	$\sigma(NC'_2)$, $\rho(NC'_2)$
521	522	521 w	512 m	521 m	518 w	521 w	514 m	520 m	516 w	521 w	513 m	521 s	515 w	$\sigma(NC'_2)$, δ(C−S)
			803 m						808 sh		795 sh			
824	824	824 w	823 m		825 m	824 w	822 m	823 s	825 w	824 w	822 w	824 vs	825 m	$\nu(NC'_2)$
			829 sh	828 s	833 sh									
917	917	917 w	941 w sh	916 vw	941 w sh	916 w	940 w sh	918 w	938 w	916 w	925 m	919 w	926 w	γ(CH)
			932 s		933 w		932 s		933 w		936 s		937 m	ν(C−S)
970	967	970 m	969 vw	967 s	968 m	969 m		966 s	966 w	969 m	970 vw	966 vs	967 w	ν(C−S)[d]
1052	1052	1050 w	1045 m	1051 vw	1058 vw	1052 w	1045 m		1052 w	1042 w				$\rho(CH_3)$
1094	1099	1094 vw	1099 vw	1098 w	1100 vw	1095 vw		1101 w	1095vw	1096 sh		1098 vw		$\rho(CH_3)$
1134	1134	1133 s	1140 s	1135 w	1143 m	1133 s	1141 s	1132 w	1141 w	1133 s	1137 s	1133 w	1139 m	$\rho(CH_3)$
1206	1207	1206 w	1195 w	1206 vw	1206 vw	1207 w	1196 w	1206 vw		1205 w	1198 w	1206 vw		$\nu_{as}(NC'_2)$
	1385	1398 s	1388 m	1385 s	1385 m	1385 sh	1386 m	1385 s	1379 w	1386 sh	1376 sh	1384 s	1377 s	$\delta_s(CH_3)$
						1398 s			1387 w	1400 s	1386 m		1388 s	$\delta(CH_3)$
1413	1410	1413 s	1407 s	1410 m	1410 s	1413 s	1407 s	1410 m	1404 w	1412 s	1403 s	1410 s	1404 m	$\delta(CH_3)$
			1417 sh				1417 m		1411 m		1416 w		1410 s	$\delta_s(CH_3)$
1442	1440	1441 w	1437 m	1439 w	1442 w	1441 m	1434 w	1440 w	1440 w	1441 m	1430 w	1440 m	1434 w	$\delta_{as}(CH_3)$
1465	1462	1465 w	1461 w	1463 w	1462 w	1464 m	1460 w	1463 w	1460 w	1465 m	1459 w	1463 m	1460 w	$\delta_{as}(CH_3)$
1542	1539	1540 s	1540 sh	1540 m	1539 w	1542 s		1538 m		1541 s	1542 sh	1539 m		ν(C−N)[d]
		1578 m	1568 s	1582 w	1570 m		1570 s	1578 w	1567 w	1574 sh	1565 s	1576 w	1565 m	ν(C−N)
			1591 s		1596 m	1581 sh	1590 s		1593 m		1583 s		1585 m	ν(C−N)
1645	1644	1645 vw	1639 w	1643 w	1640 vw	1644 vw		1642 vw	1635 vw	1647 vw		1643 vw		

[a] Intensites: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder. [b] Assignment of fundamentals (see ref 40): τ = torsion, ρ = rocking, σ = scissoring, δ = bending deformation, γ = out-of-plane deformation, ν_s = symmetric stretching, ν_{as} = asymmetric stretching, C′ denotes methyl carbon. [c] Polarized Raman band. [d] From free *N*,*N*-dimethylthioformamide molecules.

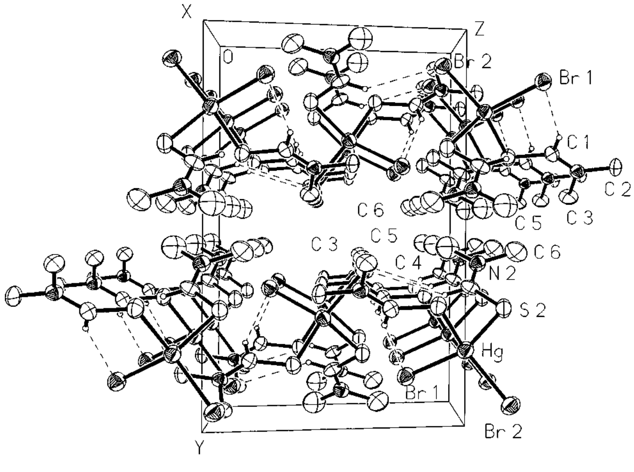

Figure 4. Unit cell view along the *a*-axis of the $HgBr_2(SCHN(CH_3)_2)_2$ compound. The hydrogen bonds are indicated by the dashed lines, and the thermal ellipsoids enclose 25% probability. Methyl hydrogen atoms are excluded for clarity.

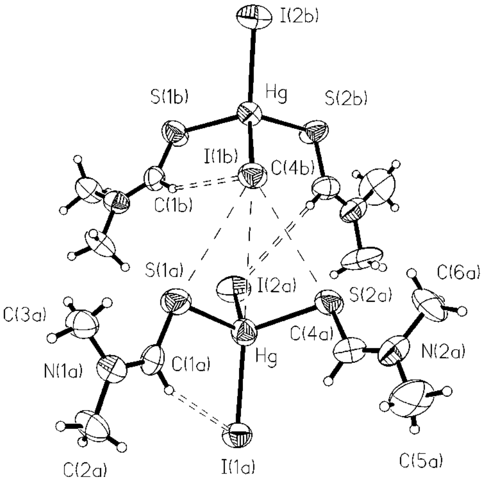

Figure 5. Hydrogen bonds (double dashed lines) and possible intermolecular interactions (single dashed lines) for two $HgI_2(SCHN(CH_3)_2)_2$ molecules. The thermal ellipsoids enclose 50% probability.

the crystal structure (Table 2) and is consistent with the formation of a similar complex in solution.

Calorimetry. The heat of solvation of HgI_2(g) and $HgBr_2$(g) in *N*,*N*-dimethylthioformamide, $\Delta_{sv}H° = -145.8$ and -156.0 kJ·mol^{-1}, respectively, was derived by combining the experimentally determined heat of solution, $\Delta_{sln}H° = -57.6 \pm 0.8$ and -71.9 ± 1.1 kJ·mol^{-1}, with the corresponding heats of sublimation, $\Delta_{sub}H° = 88.2$ and 84.1 kJ·mol^{-1};[37] cf. Scheme 1 and Table 5. These heats of solvation of mercury(II) halides are significantly more exothermic for *N*,*N*-dimethylthioformamide than for other sulfur donor solvents studied.[17]

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(37) Hepler, L. G.; Olofsson, G. *Chem. Rev.* **1975**, *75*, 585.

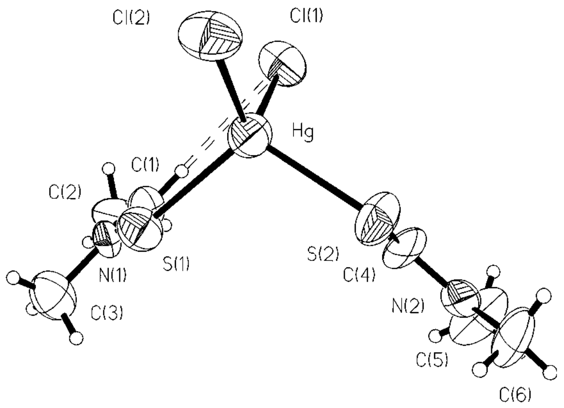
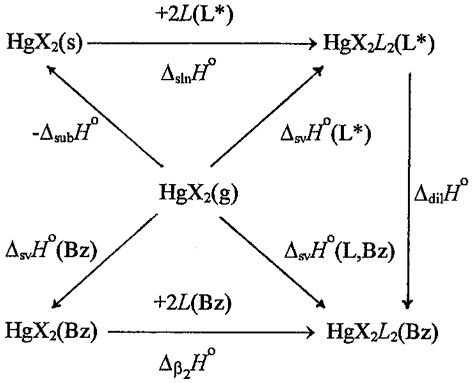


Figure 6. View of the $HgCl_2(SCHN(CH_3)_2)_2$ complex showing the planarity of the *N,N*-dimethylthioformamide ligands and the internal hydrogen bond (double dashed line) between H(1) and Cl(1). The thermal ellipsoids are shown at the 50% probability level.

Scheme 1. Relations between the Standard Molar Enthalpies for Mercury(II) Iodide and Bromide[a]



[a] Liquid *N,N*-dimethylthioformamide is denoted L*; benzene, Bz.

The stability constants and thermodynamics of the complex formation between *N,N*-dimethylthioformamide and mercury(II) bromide and iodide molecules in benzene solution are summarized in Table 4. A comparison of the $\Delta G°$ values for the stepwise addition of *N,N*-dimethylthioformamide ligands shows that the first ligand gives a more stable complex with mercury(II) bromide than with mercury(II) iodide, while the stability constants for the second addition, K_2, are similar. The first step in this complex formation is more strongly enthalpy driven for mercury(II) bromide (Table 4), as expected from the weaker mercury−halide bonding allowing a stronger Hg−S bond to be formed than in the iodide complex. The resulting distortion of the structure of the $HgBr_2$ entity is also more extensive than that for HgI_2 when the first *N,N*-dimethylthioformamide ligand coordinates, as shown by the high value of the opposing entropy term, $T\Delta S_1°$. For the second step opposite relations are found with the highest enthalpy and entropy terms for the iodide complex, showing that the largest structural change of the iodide complex occurs when its second *N,N*-dimethylthioformamide ligand coordinates.

The overall stability constants β_2 of the $HgX_2(SCHN(CH_3)_2)_2$ complexes show $HgBr_2$ to be a better acceptor of two *N,N*-dimethylthioformamide ligands than HgI_2 is (Table 4), consistent with the shorter Hg−S bonds formed in the $HgBr_2(SCHN(CH_3)_2)_2$ crystal structure (Table 2). The complex formation between HgX_2 and *N,N*-dimethylthioformamide is found to be weaker than for the corresponding tertiary phosphine complexes but much stronger than for tetrahydrothiophene and pyridine.[38] Both the stability constants and the exothermic enthalpy values increase with increasing donor strength of the ligand,[39] as expected for the soft electron pair acceptor mercury(II).

The heat of solvation of $HgX_2(g)$ in a dilute *N,N*-dimethylthioformamide solution in benzene, $\Delta_{sv}H°(L, Bz)$, *i.e.* for the formation of HgX_2L_2 complexes in benzene with discrete non-hydrogen-bonding *N,N*-dimethylthioformamide molecules, L, can be calculated by combining the overall heat of complex formation, $\Delta_{\beta_2}H°$, for the reaction

$$HgX_2(Bz) + 2L(Bz) \rightarrow HgX_2L_2(Bz)$$

with the heat of solvation of $HgX_2(g)$ in benzene, $\Delta_{sv}H°(Bz)$; cf. Scheme 1. There is a significant difference between the $\Delta_{sv}H°(L, Bz)$ values obtained in this way and the heat of solvation for liquid *N,N*-dimethylthioformamide, $\Delta_{sv}H°(L^*)$; cf. Table 5. This difference, $\Delta_{dil}H° = -11$ and -12 kJ·mol^{-1} for the bromide and iodide complex, respectively, shows that more energy is required to release a *N,N*-dimethylthioformamide molecule from the liquid than from a dilute benzene solution, if it can be assumed that differences in the heat of solvation of the $HgX_2(SCHN(CH)_3)_2$ complex in *N,N*-dimethylthioformamide and in benzene solution can be neglected. In view of the internal hydrogen bonding found to occur between the halide and *N,N*-dimethylthioformamide ligands in the crystal structure, and the single Hg−X distance and stretching frequency obtained for the $HgX_2(SCHN(CH)_3)_2$ complexes in *N,N*-dimethylthioformamide solution (Tables 3 and 6), it seems probable that both hydrogen atoms of the −CHS groups form internal hydrogen bonds within the complexes in solution and no hydrogen bonding to the solvent molecules is expected. The similarity of the $\Delta_{dil}H°$ values obtained for the iodide and bromide systems also indicates nonspecific solvent−halide interactions with the $HgX_2(SCHN(CH)_3)_2$ complexes. The $\Delta_{dil}H°$ values for the corresponding systems are very close to zero in such solvents as pyridine, triethylamine, and tri-*n*-butylphosphine with no hydrogen bonding between the solvent molecules.[17]

In liquid *N,N*-dimethylthioformamide weak intermolecular hydrogen bonds must be broken at the complex formation, while no such bonds are present in a dilute solution of *N,N*-dimethylthioformamide in benzene.[29] The comparison above of the heats of solvation shows that the electron-pair donor ability of an *N,N*-dimethylthioformamide molecule is slightly reduced in the liquid solvent by the competing intermolecular hydrogen bond formation than in dilute benzene solution and in solids. Structural evidence for the hydrogen bonding in crystalline and liquid *N,N*-dimethylthioformamide has been obtained by single-crystal X-ray diffraction and LAXS methods.[29]

Vibrational Spectroscopy. The vibrational spectra of the molecular $HgX_2(SCHN(CH_3)_2)_2$ species are complicated (Table 6), and detailed interpretations have to be based on previous assignments of characteristic frequencies of molecular motion. For this purpose the observed bands can be divided into two groups, those directly originating from the coordination of the halide and sulfur atoms to mercury(II) and the internal vibrations of the *N,N*-dimethylthioformamide molecules, which to some extent can shift at coordination.

Mercury−Ligand Frequencies. In most cases the X−Hg−X stretching frequencies of HgX_2L_2 complexes provide an easily comparable and sensitive measure of the change in Hg−X bond strength, assuming that the coupling with other ligand modes can be neglected, a reasonable approximation for pseudotetrahedral coordination geometry and light ligand atoms L.[1] Mostly

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[38] Graddon, D. P. *Rev. Inorg. Chem.* **1982**, *4*, 211 and references therein.

[39] Wei, L.; Inerowicz, H. D.; Persson, I. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2223.

the solution and solid-state frequencies agree well, but for tetrahydrothiophene there is a significant difference, also reflected in the X−Hg−X bond angles.[1,6] In the present case the difference in the Hg−X bond distances for the solid HgX_2L_2 solvates of *N,N*-dimethylthioformamide gives rise to another difficulty.

The Raman spectrum of the $HgI_2(SCHN(CH_3)_2)_2$ complex in solution shows a polarized band at 129 cm^{-1} and a weak band at 144 cm^{-1}, tentatively assigned as the in-phase and out-of-phase stretching modes, respectively, of a symmetric I−Hg−I entity. For the solid compound with two different Hg−I bond lengths both the Raman and far-IR spectra show two strong bands at about 126 and 137 cm^{-1} (Figure 3). Similarly, for the $HgBr_2(SCHN(CH_3)_2)_2$ complex in solution a polarized Raman band is found at 170 cm^{-1}, assumed to contain both the in-phase and out-of-phase modes, while in the solid state both the Raman and far-IR spectra show a double peak at about 152 and 169 cm^{-1}. The Raman spectrum of $HgCl_2$ in *N,N*-dimethylthioformamide solution displays a single polarized Hg−Cl stretching band at 234 cm^{-1}, but for the $HgCl_2(SCHN(CH_3)_2)_2$ complex in the solid state the Raman spectrum shows a double peak at 243 and 226 cm^{-1} and the far-IR spectrum a broad asymmetric band at about 243 cm^{-1}.

A simplified normal coordinate analysis was performed to investigate the coupling between the in-phase and out-of-phase stretching Hg−X frequencies and to estimate the relative bond strength of the Hg−X bonds in the asymmetric X−Hg−X entity in the solid iodide and bromide compounds. The solution frequencies were used to estimate the force constants of the Hg−X stretching and the stretch−stretch interaction by assuming C_{2v} symmetry for a symmetric HgX_2 entity with a mean Hg−X bond length according to the LAXS result and the X−Hg−X angle from the crystal structure and by neglecting the influence of the *N,N*-dimethylthioformamide ligands. This resulted in a stretching Hg−X force constant, $F = 0.88$ and 0.98, and a stretch−stretch interaction constant, $f = 0.25$ and 0.12 (in units of 10^2 $N{\cdot}m^{-1}$), for X = I, and Br, respectively (for the bromide $\nu_s = \nu_{as}$ was assumed). The same stretch−stretch interaction was then used for the solid-state systems which allowed two different Hg−X stretching force constants to be refined to fit the measured frequencies, using a program system developed by Mink.[40] This procedure gave for the two Hg−X bonds $F = 0.93$ and 0.84 for the iodide and $F = 0.94$ and 0.80 for the bromide complex. Even though the values obtained can only be regarded as semiquantitative, the potential energy distribution calculated in this way shows a fairly good separation (>80%) between the contributions from the two Hg−X bond stretching vibrations in the two bands, with the shorter and stronger Hg−X bond giving the dominating contribution to the higher frequency band.

The band assigned as Hg−S stretching is found at about 310−320 cm^{-1}, both in the Raman and IR spectra, see Figure 3. The wavenumber of the band increases from the iodide to the chloride complex indicating stronger Hg−S bonding (cf. Table 6), in accordance with the result from the crystal structure determinations. In the Raman spectrum of the tetrahedrally solvated mercury(II) ion in *N,N*-dimethylthioformamide solution, $[Hg(SCHN(CH_3)_2)_4]^{2+}$ with four Hg−S bonds, a polarized band with a strong Hg−S stretching contribution occurs at 323 cm^{-1},[12] only slightly higher than the 318 cm^{-1} Hg−S band found for the $HgCl_2(SCHN(CH_3)_2)_2$ complex. The small downward frequency shift of the Hg−S band when replacing two *N,N*-dimethylthioformamide ligands with chloride indicates that the Hg−Cl bond strength in the complex is only slightly stronger than Hg−S of the *N,N*-dimethylthioformamide ligands.

Internal Ligand Frequencies. There are 30 normal modes of an *N,N*-dimethylthioformamide molecule. A complete assignment based on *ab initio* calculations and normal coordinate analyses has been made recently[40] and provides the necessary basis to identify the internal vibrations of the *N,N*-dimethylthioformamide molecules and to interpret their shifts when coordinated; cf. Table 6. As a consequence of the planar geometry and the delocalized bonding, there are few pure group vibrations, and the interpretation in terms of molecular motion is not always straightforward.

The 967 cm^{-1} band of the free molecules, which has its strongest contribution from C−S stretching, shifts toward lower wavenumbers for the ligands due to the weakening of the C−S bond and provides a useful indicator of the strength of the coordination. For the $HgX_2(SCHN(CH_3)_2)_2$ complexes in the solid state the smallest shift to 937 cm^{-1} occurs for the iodide which also has the longest Hg−S distances, while for the bromide and chloride the shifts are larger, down to about 932 cm^{-1}; cf. Table 6 The shift range found for other solid solvates is rather wide, and this band shifts to 949 cm^{-1} for the weakly coordinated ligands of the six-coordinated $[Cd(SCHN(CH_3)_2)_6](ClO_4)_2$ solvate, to 940 cm^{-1} for the tetrasolvate of zinc, $[Zn(SCHN(CH_3)_2)_4](CF_3SO_3)_2$, and down to 918 cm^{-1} for the strongly coordinated ligands in the linear bis-solvate $[Hg(SCHN(CH_3)_2)_2](ClO_4)_2$.[12] The tetrasolvated mercury(II) ion in solution, $[Hg(SCHN(CH_3)_2)_4]^{2+}$, was found to give a broad band at 931 cm^{-1} consistent with a slightly stronger Hg−S bonding than for the present $HgX_2(SCHN(CH_3)_2)_2$ solvates, as was also indicated by the Hg−S vibration frequency (see above).

The C−N stretching mode is also coordination-sensitive because of a strong charge transfer from the nitrogen to the sulfur atom but shifts to *higher* wavenumbers (see below).[29] The C−N stretching dominates the strong band at 1542 cm^{-1} in the IR spectrum (1539 cm^{-1} in Raman) of liquid *N,N*-dimethylthioformamide, which shifts considerably and splits for the two coordinated ligands of the $HgX_2(SCHN(CH_3)_2)_2$ solvates. The shifts are marginally larger for the chloride than for the bromide complex and are smallest for the iodide (Table 6). The solution spectrum of the solvated mercury(II) ion, $[Hg(SCHN(CH_3)_2)_4]^{2+}$, displays a broad C−N band at 1587 cm^{-1}, at slightly higher wavenumbers than the single solution bands of the $HgX_2(SCHN(CH_3)_2)_2$ solvates, 1582, 1578, and 1576 cm^{-1}, for X = Cl, Br, and I, respectively. This shift sequence implies the strongest Hg−S coordination in the tetrasolvated mercury(II) ion,[12] followed by that of the $HgX_2(SCHN(CH_3)_2)_2$ solvates in the above order, again in accordance with the results from the structure studies. The four-coordinated solvated Zn^{2+} ion gives a band at 1578 cm^{-1} in *N,N*-dimethylthioformamide solution, while for the six-coordinated solvated Cd^{2+} ion the shift is smaller and gives a shoulder at about 1565 cm^{-1} on the large solution band at 1542 cm^{-1}. For the corresponding solvates in the solid state the C−N stretching splits into two strong bands, at 1572 and 1592 cm^{-1} for $[Zn(SCHN(CH_3)_2)_4](CF_3SO_3)_2$ and at 1570 and 1589 cm^{-1} for $[Cd(SCHN(CH_3)_2)_6](ClO_4)_2$. The in-phase and out-of-phase C−N stretching bands of the linear bis-solvate of mercury(II), $[Hg(SCHN(CH_3)_2)_2](ClO_4)_2$, are shifted much more because of the strong coordination and are found at about 1592 and 1616 cm^{-1},[12] but split further probably due to Fermi resonance.

The band at 363 cm^{-1}, which is prominent in the IR spectra of the solutions (Figure 3b), is absent in the solids (the small remaining intensity corresponding to free molecules as also found for the C−S stretching mode is probably due to slightly "wet" samples). The normal coordinate analysis shows this

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(40) Stålhandske, C. M. V.; Mink, J.; Sandström, M.; Papai, I.; Johansson, P. *Vibrat. Spectrosc.* **1997**, *498*, 207 and references therein.

band to be the nitrogen out-of-plane deformation mode, $\gamma(C'_2N)$, of the dimethylamino group, which shifts upward and decreases in intensity for coordinated *N,N*-dimethylthioformamide molecules.[12,40] Theoretical calculations on thioformamide revealed considerable π charge transfer from the nitrogen atom over carbon to the sulfur atom, which stabilizes the planar form of the molecule and also restrains the out-of-plane bending of the amino group more than for formamide.[16] When an *N,N*-dimethylthioformamide molecule coordinates to mercury(II), back-bonding from the metal atom increases the C−N bond strength as shown by the upward shift observed for the C−N vibrational frequency and also from the shorter C−N bond in the bis-solvate, $[Hg(SCHN(CH_3)_2)_2](ClO_4)_2$.[12] The disappearance of the band at 363 cm^{-1} in the solid spectra thus corresponds to a hampering of the out-of-plane vibration, $\gamma(C'_2N)$. Also the band at about 275 cm^{-1} disappears for the solids. A lowering of this frequency, which is dominated by S−C deformation, δ(C−S),[40] is expected upon coordination.[12]

The out-of-plane vibration frequency, γ(CH), at 917 cm^{-1} in the liquid and at 940 cm^{-1} in crystalline *N,N*-dimethylthioformamide, is affected by the hydrogen bonding.[28,40] Its frequency is 925 cm^{-1} for the iodide complex and 938 and 941 cm^{-1} for the bromide and chloride complexes, respectively, indicating lower hydrogen bond strength for the iodide.

Conclusions

The crystal structures of the bis-solvates of the mercury(II) halides with *N,N*-dimethylthioformamide show the same type of discrete HgX_2L_2 complexes, X = Cl, Br, and I, as previously observed for a number of neutral ligands L.[1,10] The easily distorted pseudotetrahedral coordination geometry is affected by the donor strength of the ligands L, and the near tetrahedral angles in the present structures, X−Hg−X angles 111.8(2), 112.4(1), and 113.2(1)°, show that the *N,N*-dimethylthioformamide ligands are strongly coordinating. Comparisons of the Hg−S distance of the tetrahedrally solvated mercury(II) ion in *N,N*-dimethylthioformamide solution, Hg−S 2.527(6) Å, with the increasing mean Hg−S distance of the HgX_2L_2 complexes, 2.532, 2.542, and 2.578 Å for X = Cl, Br, and I, respectively, show increasing Hg−X bond strength in that order. The sulfur atoms are almost as strongly bonded as the chloride ligands in the $HgCl_2L_2$ complex, as also shown by the small shift of the Hg−S stretching vibration frequency from that of the HgL_4^{2+} complex. The shifts of the vibrational modes assigned as C−S and C−N stretching of the *N,N*-dimethylthioformamide ligands from previous normal coordinate analyses are shown to be useful indicators of the relative strength of the metal−sulfur bonds for a number of solvated metal ions.

The weak internal hydrogen bonding found between the −CHS group of one *N,N*-dimethylthioformamide ligand and one halide atom distorts the complexes with a significant lengthening of the corresponding Hg−X bond. The unexpectedly strong ability of the thioformyl group to form hydrogen bonds must be caused by the delocalization of the π electron system.[18,41] By means of thermochemical studies, the hydrogen bond enthalpy of the previously not described resonance-induced C−H···S hydrogen bond between *N,N*-dimethylthioformamide molecules in the liquid state could be estimated to about 12 kJ mol^{-1}. Also the stability constants of the $HgBr_2L_n$ and HgI_2L_n complexes with $n = 1$ and 2, determined in benzene solution, show the acceptor properties of the $HgBr_2$ species to be stronger than for HgI_2.

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Note Added in Proof. From a recent extensive survey of the hydrogen-bond *acceptor* ability of sulfur in uncharged C=S systems, it was concluded that resonance effects, owing to conjugative interactions between C=S and the lone pair of an N substituent, are in fact inducing and not only assisting the hydrogen-bond formation.[41] Unexpectedly, we have observed in this and another recent study[13] that the CHS group of *N,N*-dimethylthioformamide is also capable of acting as a hydrogen-bond donor. Results from theoretical and experimental comparisons of *N,N*-dimethylthioformamide and *N,N*-dimethylformamide show that also this hydrogen-bond *donor* ability of the thioformyl group is *resonance-induced*. Ab-initio calculations on the isolated molecules give charge distributions by Mulliken population analyses showing the hydrogen atom in the CHS group to be more positively charged than that in the corresponding CHO group, and the crystal and liquid structures of the pure compounds reveal *stronger* intermolecular hydrogen bonding for *N,N*-dimethylthioformamide than for *N,N*-dimethylformamide.[29]

Supporting Information Available: Listings of crystal properties, data collection and treatment procedures, complete atomic positional and isotropic and anisotropic displacement parameters including hydrogen atoms, intramolecular distances and angles and least-squares planes through the *N,N*-dimethylthioformamide ligands (Tables S1−S16) and ORTEP diagrams (Figures S1−S3) (20 pages). Ordering information is given on any current masthead page.

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(41) Allen, F. H.; Bird, C. M.; Rowland, R. S.; Raithby, P. R. *Acta Crystallogr., Sect. B* **1997**, *53*, 680.