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Crystal Structure of *N,N*-Dimethylthioformamide Solvates of the Divalent Group 12 Ions with Linear Coordination Geometry for Mercury(II), Tetrahedral for Zinc(II), and Octahedral for Cadmium(II)

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The crystalline solvates of the divalent group 12 metal ions with the soft sulfur donor *N,N*-dimethylthioformamide display an unusual variation in coordination number and geometry with two, four, and six ligands attached to the mercury(II), zinc(II), and cadmium(II), ions, respectively. Bis(*N,N*-dimethylthioformamide)mercury(II) perchlorate precipitates from acetonitrile solution when adding less than 2 equiv of *N,N*-dimethylthioformamide, while the zinc and cadmium solvates crystallize from saturated *N,N*-dimethylthioformamide solutions. The disolvate $[Hg(SCHN(CH_3)_2)_2](ClO_4)_2$ crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with $a = 6.208(1)$ Å, $b = 15.239(7)$ Å, $c = 8.681(2)$ Å, $\beta = 99.30(3)°$, and $Z = 2$. Centrosymmetric mercury(II) complexes with strong collinear bonds to two *N,N*-dimethylthioformamide molecules, Hg−S 2.350(2) Å, are joined by double bridges of perchlorate ions in chains along the *a*-axis by four weak interactions between the mercury and the perchlorate oxygen atoms, mean Hg−O distance 2.84 Å. Tetrakis(*N,N*-dimethylthioformamide)zinc trifluoromethanesulfonate, $[Zn(SCHN(CH_3)_2)_4](CF_3SO_3)_2$, crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a = 10.487(3)$ Å, $b = 12.910(3)$ Å, $c = 13.489(5)$ Å, $\alpha = 68.800(4)°$, $\beta = 69.260(4)°$, $\gamma = 74.06(1)°$, and $Z = 2$, with the zinc ions tetrahedrally surrounded by four *N,N*-dimethylthioformamide ligands, mean Zn−S distance 2.34 Å. Also the cadmium solvate of corresponding composition, $[Cd(SCHN(CH_3)_2)_4(CF_3SO_3)_2]$, crystallizes in the space group $P\bar{1}$, with $a = 8.670(1)$ Å, $b = 9.529(1)$ Å, $c = 10.685(1)$ Å, $\alpha = 75.20(1)°$, $\beta = 66.97(1)°$, $\gamma = 65.31(1)°$, and $Z = 1$, although the structure comprises centrosymmetric tetrakis(*N,N*-dimethylthioformamide)bis(trifluoromethanesulfonato)cadmium(II) complexes in which four Cd−S bonds (mean 2.65 Å) and two weaker Cd−O bonds at 2.470(2) Å to the trifluoromethanesulfonate ions give rise to a pseudo-octahedral coordination around the cadmium ion. When using perchlorate instead as counterion, hexakis(*N,N*-dimethylthioformamide)cadmium perchlorate, $[Cd(SCHN(CH_3)_2)_6](ClO_4)_2$, crystallizes in the space group $P2_1/n$ with $a = 12.757(1)$ Å, $b = 7.4681(6)$ Å, $c = 19.732(2)$ Å, $\beta = 96.31(1)°$, and $Z = 2$. The mean Cd−S bond distance increases to 2.715 Å in the fully solvated cadmium ion with almost regular octahedral coordination geometry to its six centrosymmetrically related ligands. The effect of the weak internal hydrogen bonding occuring between the hydrogen atom of a -CHS group and the sulfur atom of neighboring *N,N*-dimethylthioformamide ligands is discussed.

Introduction

N,N-Dimethylthioformamide has high dipole moment, $\mu = 4.44$ D, and permittivity, $\epsilon = 47.5$,[1] and is therefore a good solvent for metal salts. This is an unusual property for sulfur donor solvents, which in general are soft and strong electron-pair donors with values of the donor strength parameter D_S about 40 for *e.g.* thioethers[2] but often with poor solubility of ionic compounds. A special feature of the *N,N*-dimethylthioformamide molecule is the delocalization of π-electrons over the N−C−S entity, giving a high barrier for rotation around the N−C bond,[3] a planar $C_2N-CH-S$ skeleton, and enhanced electron-pair donor properties of the sulfur atom; the D_S value of the solvent is 52.[2] When the solvation of the divalent ions of group 12 in *N,N*-dimethylthioformamide solution is compared, the significance of this softness becomes evident for the metal ion−sulfur coordination. The zinc and mercury(II) ions are found to have four solvent ligands, while the cadmium ion of intermediate size is six-coordinated in solution.[4]

All three metal ions form six-coordinated solvates with the hard oxygen donor solvents water, methanol, and dimethyl sulfoxide,[5−10] as well as with the relatively soft ($D_S = 38$)[2] nitrogen donor pyridine.[11,12] It has been shown in previous studies that the zinc and mercury(II) ions have higher heat of solvation for these solvents,[13,14] and also higher symmetric

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Table 1. Crystallographic Data

	$[Zn(SCHN(CH_3)_2)_4](CF_3SO_3)_2$	$[Cd(SCHN(CH_3)_2)_6](ClO_4)_2$	$[Cd(SCHN(CH_3)_2)_4(O_3SCF_3)_2]$	$[Hg(SCHN(CH_3)_2)_2](ClO_4)_2$
fw	720.18	846.28	767.20	577.81
space group	$P\bar{1}$, No. 2 (triclinic)	$P2_1/n$, No. 14 (monoclinic)	$P\bar{1}$, No. 2	$P2_1/n$, No. 14
T/ °C	25	25	25	−123
a/Å	10.487(3)	12.757(1)	8.670(1)	6.208(1)
b/Å	12.910(3)	7.4681(6)	9.529(1)	15.239(7)
c/Å	13.489(5)	19.732(2)	10.685(1)	8.681(2)
α/deg	68.800(4)	90	75.20(1)	90
β/deg	69.260(4)	96.31(1)	66.97(1)	99.30(3)
γ/deg	74.06(1)	90	65.31(1)	90
$\rho_{calcd}{}^{a}$/g cm^{-3}	1.524	1.504	1.736	2.368
$\rho_{obsd}{}^{b}$/g cm^{-3}	1.52	1.51	1.74	2.33
V/Å	1569.7(8)	1868.6(2)	733.6(2)	810.5(8)
Z	2	2	1	2
R^{c}	0.058	0.032	0.021	0.027
$R_w{}^{d}$	0.068	0.043	0.033	0.036
μ(Mo K$_\alpha$)^{e}/cm^{-1}	12.50	10.91	12.23	101.1

[a] Calculated density. [b] Experimental density (see text). [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum(w|F_o|)^2]^{1/2}$. [e] Mo K$_\alpha$ radiation (λ = 0.710 69 Å) used in all cases.

stretching force constant of the metal-solvate bonds, than the cadmium ion.[6] Therefore, it seems reasonable that the bond character and structure of the strongly solvated zinc and mercury(II) ions in *N,N*-dimethylthioformamide solution are affected more than for the cadmium ion. Generally, zinc has a very flexible coordination geometry. Four coordination is found in the majority of crystal structures in which zinc is coordinated to sulfur atoms of organic ligands, while five coordination is most common for nitrogen donor atoms and six coordination dominates for oxygen donors.[15]

The only previously published X-ray crystal structure of a metal ion solvated with *N,N*-dimethylthioformamide is the iron(II) compound $[Fe(SCHN(CH_3)_2)_6](ClO_4)_2$.[16] The iron(II) ion binds six *N,N*-dimethylthioformamide ligands octahedrally with an average Fe−S distance of 2.54 Å. An EXAFS study shows that also the smaller nickel(II) ion coordinates six *N,N*-dimethylthioformamide ligands in solution with a Ni−S bond distance of 2.45 Å.[17] The ionic radii of six-coordinated nickel, zinc, and high-spin iron(II) ions are 0.69, 0.74, and 0.78 Å,[18] respectively. Thus, the change to four coordination found for the solvated zinc ion with the same ligand cannot be due to increasing ligand-ligand repulsion.

In order to get a better understanding of how the balance between steric and electronic factors influences the change in coordination number of the solvated zinc, cadmium, and mercury(II) ions, and to provide models for the solution structure studies,[4] the X-ray crystal structures of four solid solvates with *N,N*-dimethylthioformamide are determined in the present work.

Experimental Section

Preparation of Solvent. *N,N*-Dimethylthioformamide was prepared by adding phosphorus pentasulfide to a mixture of benzene and *N,N*-dimethylformamide (Merck) following the procedure described by Gutmann *et al.*[19] The purity of the twice distilled product was checked with ^{1}H-NMR, and no trace of unreacted *N,N*-dimethylformamide was found.

Preparation of Crystals. The anhydrous trifluoromethanesulfonate salts of zinc and cadmium, prepared as described previously,[20] were dissolved to saturation in *N,N*-dimethylthioformamide at about 40 °C and cooled in a refrigerator until crystalline solvates precipitated.

Hexakis(*N,N*-dimethylthioformamide)cadmium(II) perchlorate crystals were prepared from an acetone solution of cadmium perchlorate hexahydrate (G. F. Smith), in a similar way as for the corresponding dimethyl sulfoxide solvate.[21] 2,2-Dimethoxypropane (Merck) was added to react with the water from the hydrate, and after the mixture was shaken for 2 h, 6 equiv of *N,N*-dimethylthioformamide was added. After further shaking of the mixture for 30 min, the solvent was partly evaporated, and upon cooling in freezer, white crystals were formed, which were recrystallized first from acetone and finally from *N,N*-dimethylthioformamide.

Bis(*N,N*-dimethylthioformamide)mercury(II) perchlorate crystals were prepared from a solution of 0.32 g of mercury(II) perchlorate trihydrate (G. F. Smith) in 10 mL of acetonitrile, acidified by a few drops of concentrated perchloric acid. After addition of slightly less than 2 equiv of *N,N*-dimethylthioformamide white crystals precipitated either directly or upon standing in room temperature. We have not been able to obtain crystals from mercury(II) solutions containing more than 2 equiv of *N,N*-dimethylthioformamide.

Caution: *Organic solvates of metal perchlorates are powerful explosives, and especially when direct metal ion−perchlorate bonding occurs as for mercury(II) perchlorate a violent and unpredictable reaction is easily triggered.*[21−23] In order to eliminate the risk of explosions it is often recommended to use trifluoromethanesulfonate as a "noncoordinating" anion instead of perchlorate, but a black precipitate, probably mercury(II) sulfide, forms when anhydrous mercury(II) trifluoromethanesulfonate is added to *N,N*-dimethylthioformamide.

Crystal Density Determination. The flotation method with the crystals suspended in an inert liquid mixture was used to obtain the crystal density experimentally (Table 1).[24a] For the solvates of zinc and cadmium trifluoromethanesulfonate a benzene−dibromobutane mixture was used, for the cadmium perchlorate solvate hexane−tetrachloromethane, and for the solvate of mercury(II) perchlorate dibromomethane−diiodomethane. The density of the liquid mixture was measured (except for the mercury compound) by means of an Anton Paar DMA 35 densitometer.

Crystallography. The intensity data were collected by means of four-circle single-crystal X-ray diffractometers using graphite-monochromated Mo Kα radiation, 0.7107 Å, at ambient temperature, except for the mercury(II) salt which was kept at 150 K. The crystals were enclosed in Lindemann glass capillaries. For the zinc solvate a linear correction for crystal decay was applied prior to the data processing

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Table 2. Bond Distances in Å with Estimated Standard Deviations for the Solvated Metal Ions in the Crystal Structures of $[Zn(SCHN(CH_3)_2)_4](CF_3SO_3)_2$ (**1**), $[Cd(SCHN(CH_3)_2)_6](ClO_4)_2$ (**2**), $[Cd(SCHN(CH_3)_2)_4(O_3SCF_3)_2]$ (**3**), and $[Hg(SCHN(CH_3)_2)_2](ClO_4)_2$ (**4**)[a]

	1		2		3		4	
				Metal Coordination				
M−S	Zn−S1	2.333(3)	Cd−S1	2.698(1)	Cd−S2	2.6543(6)	Hg−S	2.350(2)
	Zn−S2	2.340(4)	Cd−S2	2.732(1)	Cd−S3	2.6466(7)		
	Zn−S3	2.342(3)	Cd−S3	2.714(1)				
	Zn−S4	2.343(3)						
M−O					Cd−O1	2.470(2)	Hg−O2	2.828(5)
							Hg−O3	2.857(4)
				N,N-Dimethylthioformamide Ligands				
S−C	S1−C1	1.65(1)	S1−C1	1.663(4)	S2−C2	1.673(3)	S−C1	1.703(6)
	S2−C2	1.68(1)	S2−C4	1.670(4)	S3−C5	1.672(3)		
	S3−C3	1.69(2)	S3−C7	1.671(4)				
	S4−C4	1.68(1)						
C−N	N1−C1	1.29(1)	N1−C1	1.297(5)	N1−C2	1.304(3)	N−C1	1.287(7)
	N2−C2	1.27(2)	N2−C4	1.289(5)	N2−C5	1.297(3)		
	N3−C3	1.28(2)	N3−C7	1.292(4)				
	N4−C4	1.29(2)						
N−C′	N1−C5	1.47(1)	N1−C2	1.456(6)	N1−C3	1.463(4)	N−C2	1.475(8)
	N1−C6	1.44(2)	N1−C3	1.444(7)	N1−C4	1.456(3)	N−C3	1.461(7)
	N2−C7	1.46(2)	N2−C5	1.461(6)	N2−C6	1.454(4)		
	N2−C8	1.47(2)	N2−C6	1.461(6)	N2−C7	1.459(3)		
	N3−C9	1.46(2)	N3−C8	1.465(6)				
	N3−C10	1.46(2)	N3−C9	1.455(5)				
	N4−C11	1.45(1)						
	N4−C12	1.43(2)						
C−H	C1−H1	0.77(8)	C1−H1	0.94(4)	C2−H1	0.91(3)	C1−H1	0.83(5)
	C2−H2	0.94(8)	C4−H8	0.95(4)	C5−H8	0.94(3)		
	C3−H3	0.80(12)	C7−H15	1.01(4)				
	C4−H4	0.89(8)						
				Coordinated Trifluoromethanesulfonate Ion				
O−S					S1−O1	1.444(2)		
					S1−O2	1.431(2)		
					S1−O3	1.428(2)		
S−C					S1−C1	1.826(3)		
C−F					C1−F1	1.328(3)		
					C1−F2	1.318(3)		
					C1−F3	1.317(3)		

[a] C′ denotes methyl carbon atoms in the *N,N*-dimethylthioformamide ligands.

based on the intensity decrease of the check reflections during the data collection (−10%), while no correction was needed for the other structures. The unit cell parameters were determined from at least 25 well-centered high-angle reflections.

The structures were solved by direct methods followed by normal heavy atom procedures and full-matrix least-squares refinements with all non-hydrogen atoms anisotropic. A semi-empirical absorption correction based on a series of ψ-scans was applied.[24b,25] The program packages used were SHELXTL PLUS for the zinc structure,[26] otherwise TEXSAN.[27] Details of the data collection and treatment procedures are given in Table 1 and in Table S1 (Supporting Information).

For all structures the position and isotropic temperature factors of the hydrogen atom of the −CHS group could be located from difference Fourier maps and refined, and this was also true for all methyl hydrogen atoms except for the zinc structure, where calculated methyl hydrogen atom positions were introduced by assuming an apparent C−H distance of 0.96 Å.[28] In the zinc structure one of the trifluoromethanesulfonate ions showed rotational disorder around the C−S bond. Its oxygen and fluorine atomic positions were described by assuming three equivalent orientations related by a rotation around the 3-fold C−S axis; see Figure S1 (Supporting Information).

Results and Discussion

Description of the Structures. The bond distances within the solvated metal ions in the four compounds $[Zn(SCHN(CH_3)_2)_4](CF_3SO_3)_2$, $[Cd(SCHN(CH_3)_2)_6](ClO_4)_2$, $[Cd(SCHN(CH_3)_2)_4(O_3SCF_3)_2]$, and $[Hg(SCHN(CH_3)_2)_2](ClO_4)_2$ are given in Table 2, and the interatomic angles, in Table 3. All the solvates show rather large anisotropy of some atomic positions, in particular of the methyl carbon atoms; see Figures 1−4. The perchlorate ion of the cadmium solvate performs large librational movements (Figure 2) which shorten the estimated apparent[28] mean Cl−O distance to 1.41 Å, while 1.44 Å is obtained from the more well-defined atomic positions of the perchlorate ion in the mercury(II) solvate (Figure 4).

Zinc Solvate. The structure of the solvated zinc ion, $[Zn(SCHN(CH_3)_2)_4]^{2+}$, is shown in Figure 1. The sulfur atoms of four *N,N*-dimethylthioformamide molecules surround the zinc ion tetrahedrally with a mean Zn−S bond distance of 2.34 Å and S−Zn−S angles in the range 101.7−111.7°. The mean Zn−S−C angle is 102.5°, and the displacement of the zinc atom from a least-squares plane through the non-hydrogen atoms of each of the four *N,N*-dimethylthioformamide ligands is between 0.09 and 0.30 Å. The thermal displacement ellipsoids for some of the methyl carbon atoms, C(5)−C(12), are rather elongated (Figure 1), and this applies also to the oxygen and fluorine atoms of the nondisordered trifluorometanesulfonate ion (Figure S1). This indicates large librational movements or most likely some

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Table 3. Interatomic Angles (deg) with Estimated Standard Deviations in the Metal Ion Complexes of the Crystal Structures of $[Zn(SCHN(CH_3)_2)_4](CF_3SO_3)_2$ (**1**), $[Cd(SCHN(CH_3)_2)_6](ClO_4)_2$ (**2**), $[Cd(SCHN(CH_3)_2)_4(O_3SCF_3)_2]$ (**3**), and $[Hg(SCHN(CH_3)_2)_2](ClO_4)_2$ (**4**)[a]

	1		2		3		4	
			Metal Coordination					
S−M−S	S1−Zn−S2	110.4(1)	S1−Cd−S2	86.70(4)	S2−Cd−S3	85.74(2)	S−Hg−S	180.00
	S1−Zn−S3	111.6(1)	S1−Cd−S3	85.80(3)				
	S1−Zn−S4	109.4(1)	S2−Cd−S3	94.63(3)				
	S2−Zn−S3	111.6(1)						
	S2−Zn−S4	101.7(1)						
	S3−Zn−S4	111.7(1)						
S−M−O					S2−Cd−O1	97.28(5)		
					S3−Cd−O1	91.44(5)		
M−S−C	Zn−S1−C1	102.3(3)	Cd−S1−C1	107.1(1)	Cd−S2−C2	101.91(8)	Hg−S−C1	101.4(2)
	Zn−S2−C2	103.1(2)	Cd−S2−C4	100.6(2)	Cd−S3−C5	108.12(8)		
	Zn−S3−C3	100.8(4)	Cd−S3−C7	106.0(1)				
	Zn−S4−C4	103.9(4)						
			N,*N*−Dimethylthioformamide Ligands					
S−C−N	S1−C1−N1	128.0(7)	S1−C1−N1	126.1(3)	S2−C2−N1	125.5 (2)	S−C1−N	122.9(5)
	S2−C2−N2	125.7(8)	S2−C4−N2	126.8(4)	S3−C5−N2	125.5(2)		
	S3−C3−N3	126.8(11)	S3−C7−N3	126.2(3)				
	S4−C4−N4	125.8(8)						
C−N−C′	C1−N1−C5	122.4(8)	C1−N1−C2	121.6(4)	C2−N1−C3	120.5(2)	C1−N−C2	121.5(5)
	C1−N1−C6	121.8(12)	C1−N1−C3	121.4(4)	C2−N1−C4	122.8(2)	C1−N−C3	123.0(5)
	C2−N2−C7	122.5(10)	C4−N2−C5	121.8(4)	C5−N2−C6	121.7(2)		
	C2−N2−C8	122.9(9)	C4−N2−C6	122.4(4)	C5−N2−C7	122.6(2)		
	C3−N3−C9	121.8(12)	C7−N3−C8	121.5(3)				
	C3−N3−C10	121.0(13)	C7−N3−C9	122.0(3)				
	C4−N4−C11	120.9(11)						
	C4−N4−C12	121.5(9)						
C′−N−C′	C5−N1−C6	115.9(9)	C2−N1−C3	117.0(4)	C3−N1−C4	116.7(2)	C2−N−C3	115.5(5)
	C7−N2−C8	114.6(11)	C5−N2−C6	115.7(4)	C6−N2−C7	115.7(2)		
	C9−N3−C10	117.2(9)	C8−N3−C9	116.4(4)				
	C11−N4−C12	117.6(11)						

[a] C′ denotes methyl carbon atoms in the *N*,*N*-dimethylthioformamide.

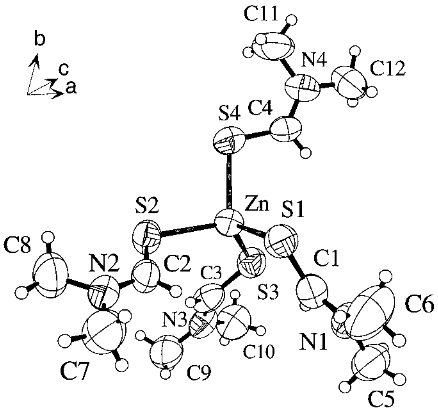

Figure 1. Tetrasolvated zinc ion in $[Zn(SCHN(CH_3)_2)_4](CF_3SO_3)_2$ with methyl hydrogen atoms in calculated positions. All non-hydrogen atoms are represented by 50% probability displacement ellipsoids.

disorder of these groups, as reflected in the relatively large standard deviation and apparent shortening of the corresponding interatomic bond lengths,[28] Table 2.

Other examples of tetrahedral four coordination of sulfur atoms around zinc are found for sphalerite, ZnS, with an average Zn−S bond distance of 2.34 Å,[29] zinc thiophenolate, 2.35 Å,[30] zinc ethyl xanthate, 2.36 Å,[31] and zinc diethyl dithiophosphate with Zn−S distances in the range 2.337−2.401 Å,[32] which are all similar to the present mean distance in the $[Zn(SCHN(CH_3)_2)_4]^{2+}$ complex, 2.34 Å; see Table 2. When precisely determined intramolecular bond distances from crystal structures are compared with corresponding values from solution studies, obtained e.g. by large-angle X-ray scattering (LAXS), a correction for the apparent shortening in the solid state due to thermal motion should be made.[28] A riding motion correction, S rides on Zn, for the solid $[Zn(SCHN(CH_3)_2)_4](CF_3SO_3)_2$ solvate resulted in a mean Zn−S bond distance of 2.35 Å, not significantly shorter than the Zn−S bond distance in *N*,*N*-dimethylthioformamide solution, 2.362(5) Å.[4] The same mean value of the S···S distances, 3.83 Å, is obtained for the $[Zn(SCHN(CH_3)_2)_4]^{2+}$ complex in solution and the solid state and shows that the tetrahedral coordination is retained in solution.[4]

Cadmium Solvates. The hexasolvated cadmium ion, $[Cd(SCHN(CH_3)_2)_6]^{2+}$, in the perchlorate salt has a centrosymmetric structure with the sulfur atoms of six *N*,*N*-dimethylthioformamide ligands forming an almost regular octahedron around cadmium (Figure 2). The mean Cd−S bond distance is 2.715 Å, with neighboring S−Cd−S angles in the range 85.8−94.6° and a mean Cd−S−C angle of 104.5° (Table 3). The displacement of the cadmium atom from the planes through each *N*,*N*-dimethylthioformamide ligand is less than 0.01 Å.

The $[Cd(SCHN(CH_3)_2)_4(O_3SCF_3)_2]$ complex where the sulfur atoms of two *N*,*N*-dimethylthioformamide ligands have been replaced by oxygen atoms from trifluoromethanesulfonate ions is also centrosymmetric; see Figure 3. The mean Cd−S and Cd−O bond distances are 2.65 and 2.47 Å, respectively, giving rise to a slightly distorted octahedral coordination geometry with the neighboring S−Cd−O and S−Cd−S angles in the range 85.7−97.3°, Table 3. The mean Cd−S−C angle is 105.0°, and the largest displacement for the cadmium atom is 0.01 Å from a least-squares plane through the *N*,*N*-dimethylthioformamide ligands. The atomic positions of the trifluoromethanesulfonate ion are well-defined and give bond distances (Table 2) in good agreement with other determinations.[12]

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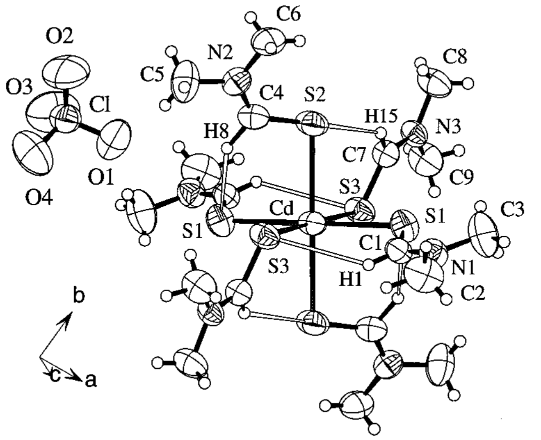

Figure 2. Hexasolvated cadmium ion and a perchlorate ion of the compound $[Cd(SCHN(CH_3)_2)_6](ClO_4)_2$ with the cadmium atom in a center of symmetry. The internal hydrogen bonding is shown by the open bonds. All non-hydrogen atoms are represented by 50% probability thermal ellipsoids.

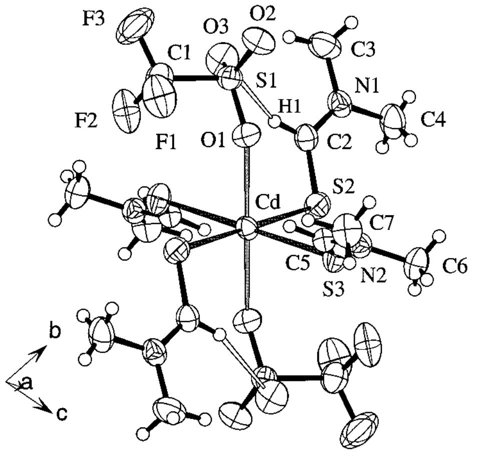

Figure 3. Centrosymmetric cadmium complex $[Cd(SCHN(CH_3)_2)_4(O_3SCF_3)_2]$, with 50% probability displacement ellipsoids except for the hydrogen atoms. The internal H1···O3 hydrogen bond to the trifluoromethanesulfonate ligand is shown by the open bond.

The mean Cd−S bond distance of the six-coordinated $[Cd(SCHN(CH_3)_2)_6](ClO_4)_2$ solvate is significantly longer, 0.065 Å, than the four Cd−S bonds in the $[Cd(SCHN(CH_3)_2)_4(O_3SCF_3)_2]$ complex; see Table 2. The Cd−O distance to the coordinated trifluorometanesulfonate ions, 2.470(2) Å, is much longer than the values reported for the six-coordinated cadmium ions in the crystal structures of $[Cd(H_2O)_6](ClO_4)_2$, 2.285 Å,[10b] and $[Cd(OS(CH_3)_2)_6](ClO_4)_2$, 2.29 Å.[8] This shows that the trifluoromethanesulfonate ions are much more weakly coordinated to cadmium than the *N,N*-dimethylthioformamide molecules, and it seems reasonable that the coordinated trifluoromethanesulfonate ions in the solid compound will be replaced by solvent molecules in *N,N*-dimethylthioformamide solution. Unexpectedly, the Cd−S bond distance of the hexasolvated cadmium ion, $[Cd(SCHN(CH_3)_2)_6]^{2+}$, in *N,N*-dimethylthioformamide solution, 2.69(1) Å,[4] was found to be slightly shorter than the corresponding mean distance in the solid hexasolvate, 2.715 Å, contrary to the apparent shortening expected due to thermal motion of the atoms of the solid structure (see above). The reason for the longer Cd−S bonds in the solid state is probably the weak internal hydrogen bonding between the −CHS proton and the sulfur atom of neighboring *N,N*-dimethylthioformamide ligands around the solvated cadmium ion (Figure 2), which is too weak to persist in solution (see Hydrogen Bonding below). A similar observation is made for the hexasolvated iron(II) ion. The crystal structure of $[Fe(SCHN(CH_3)_2)_6](ClO_4)_2$, which is isostructural with the present corresponding cadmium hexasolvate although reported with a different setting of its monoclinic unit cell,[16] also shows a slightly longer mean Fe−S distance, 2.54 Å, than that found in solution, 2.52(1) Å, from an EXAFS study.[17]

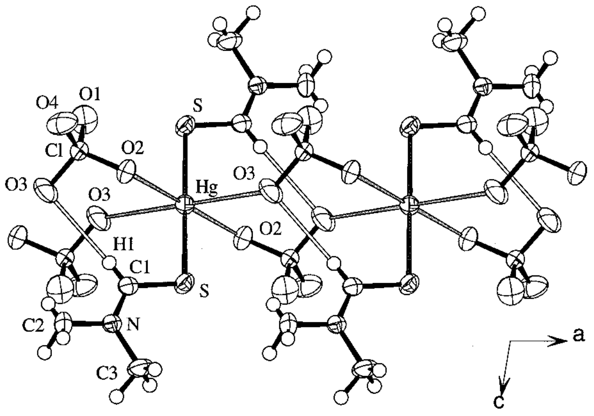

Figure 4. Mercury(II) coordination in $[Hg(SCHN(CH_3)_2)_2](ClO_4)_2$. Centrosymmetric bis(*N,N*-dimethylthioformamide)mercury(II) complexes are held together in chains along the *a*-axis by weak Hg−O bonds to perchlorate ions giving rise to double bridges. The proposed H1···O3 hydrogen bond is indicated (open bond), and the thermal ellipsoids (150 K) are scaled to enclose the non-hydrogen atoms with 70% probability.

Another six-coordinated cadmium complex is formed with the bidentate sulfur-donor ligand cyclohexyl trithiocarbonate with Cd−S bond distances in the range 2.667−2.722 Å.[33] Octahedral configuration is also found for some multidonor ligands containing sulfur,[34] including bis(thiosemicarbazide)-cadmium(II) sulfate, with a Cd−S distance of 2.514(2) Å, Cd−N 2.367(4) Å, and a weakly coordinated sulfate ion with Cd−O 2.525(5) Å in the less distorted *trans*-form of the complex.[35] However, a tetrahedral arrangement of sulfur atoms from multidentate ligands is frequently found around cadmium,[36] as *e.g.* in the cadmium ethyl xanthate and *n*-butyl xanthate compounds for which the mean Cd−S bond distances are considerably shorter, 2.56 and 2.59 Å,[37,38] respectively, than for the present six-coordinated complexes.

Mercury(II) Solvate. The structure and coordination of the mercury(II) compound, $[Hg(SCHN(CH_3)_2)_2](ClO_4)_2$, is shown in Figure 4. Two short and strong Hg−S bonds, of length 2.350(2) Å, are formed to centrosymmetrically related *N,N*-dimethylthioformamide molecules. The Hg−S−C angle is smaller, 101.4(2)°, than for the other solvates, and the displacement of the mercury atom from a least-squares plane through each ligand is less than 0.01 Å. Four distant equatorial perchlorate oxygen atoms around the linear S−Hg−S entity with Hg−O distances 2.828(5) and 2.857(4) Å, Table 2, give rise to a compressed octahedral configuration around mercury; see Figure 4.

The mercury(II)−thiosalicylic complex in bis(2-mercaptobenzoato-*S*)-mercury(II) monodioxane also has a linear S−Hg−S

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entity with Hg−S bonds of 2.361(7) Å and four distant oxygen atoms at about 3.1 Å from the mercury atom, although with a more irregular geometry.[39] The Hg−O distances in the six-coordinated dimethyl sulfoxide solvate, $[Hg(OS(CH_3)_2)_6](ClO_4)_2$, 2.34 Å,[7] are much shorter than the Hg−O interactions mentioned above. However, since the van der Waals radius for mercury(II) atoms has been estimated to about 1.73 Å, with an acceptable range from 1.7 to 2.0 Å,[40] the perchlorate ions are weakly coordinated in the present bis(*N*,*N*-dimethylthioformamide)mercury(II) perchlorate structure and form double bridges between the mercury(II) complexes giving rise to chains along the *a*-axis (Figure 4). The displacement ellipsoids of the perchlorate oxygen atoms are smaller than those of the noncoordinated anions in hexakis(*N*,*N*-dimethylthioformamide)cadmium perchlorate (Figure 2) or hexakis(dimethyl sulfoxide-*O*)mercury(II) perchlorate,[7] although this is partly due to the lower temperature, 150 K, at the structure determination of the present compound. Similar weak coordination of perchlorate oxygen atoms with Hg−O distances of 2.8 and 3.0 Å is found in the dimeric mercury(II) dimethyl sulfoxide solvate $[Hg_2(OS(CH_3)_2)_8](ClO_4)_4$.[41]

A much longer Hg−S bond distance, 2.527(6) Å,[4] is found for the solvated four-coordinated mercury(II) ion in *N*,*N*-dimethylthioformamide solution, but a corresponding solid tetrasolvate has not been possible to crystallize.

***N*,*N*-Dimethylthioformamide Ligands.** Closely planar structures are found for the *N*,*N*-dimethylthioformamide ligands in the present structures. The hydrogen atoms of the −CHS groups, all of which could be located from electron density maps, are also in the plane although the C−H distances with a mean value of 0.90 Å (Table 2) show the usual apparent shortening when using X-ray diffraction.[28] The average nitrogen−methyl carbon bond distance, N−C′ 1.46 Å, in the *N*,*N*-dimethylthioformamide molecules is much longer, 0.17 Å, than the formamide nitrogen−carbon bond, N−C 1.29 Å, (see Table 2), which is almost as short as the double N═C bond in oximes, 1.28 Å.[42] This is consistent with theoretical calculations on thioformamide, H_2NCHS, where the partial double-bond character of the N−C and C−S bonds, with a considerable transfer of π charge from the nitrogen to the sulfur atom, stabilizes the planar form of the molecule even more than for its oxygen analogue, formamide.[3] There are, however, some deviations in the interatomic angles within the molecular plane from the value 120° expected for sp^2 hybridization (Table 3). The different character of the nitrogen-carbon bonds is reflected also in the C′−N−C′ angle between the methyl groups (C′) which on the average is 5.7° smaller than the C−N−C′ angles. The S−C−N angles are in all cases larger than 120° (Table 3), due to the repulsion between the sulfur atom and the adjacent methyl group, which are in van der Waals contact. These intramolecular S···C′ distances are in the range 3.02−3.07 Å for all solvates in this study with the shortest value for the mercury(II) complex, much shorter than the sum of the van der Waals radii which are 1.85 Å for both the sulfur and carbon atoms.[43]

The S−C bond distance of the two strongly bound *N*,*N*-dimethylthioformamide ligands in the mercury(II) solvate, 1.703(6) Å, is significantly longer than for the solvated cadmium complexes, mean 1.67 Å. This could in part be due to interactions between the filled large $5d_\pi$-orbitals of the closely approaching mercury(II) atom and the π electrons of the C−S bond, thus reducing the charge transfer to the sulfur atom within the thioamide group. In the simple thioamide double-bond resonance picture this would correspond to a decrease in the double-bond character for the C−S bond[3] but an increase in the C−N bond which also seems to be slightly shorter for the mercury(II) compound; see Table 2. The S−C−N angle is also smaller, 122.9(5)°, in the mercury(II) complex than in the zinc and cadmium complexes (Table 3).

The M−S−C angles are in general smaller for the mercury(II) and also for zinc solvates, than for the isostructural cadmium and iron(II) hexasolvates, Table 3 (mean value for Fe−S−C 109.4°),[16] despite the weak hydrogen bond interaction between sulfur atoms and neighboring −CHS protons (see below) in the last two compounds. An increasing involvement of the lone pair of high p character of the sulfur atom,[3] resulting in a stronger σ bond to the metal atom in the mercury(II) and zinc complexes, would be consistent with this observation. However, the hydrogen bonding seems to have a minor influence on the M−S−C angle as can be seen by comparing the *N*,*N*-dimethylthioformamide ligands in the $[Cd(SCHN(CH_3)_2)_4(O_3SCF_3)_2]$ complex (Table 3), one of which is hydrogen bonded (see below) to an oxygen atom of the trifluoromethanesulfonate ion, Figure 3.

Hydrogen Bonding. Recently, weak almost linear C−H···S hydrogen bonds with S···H distances of 2.82 Å were found to join the *N*,*N*-dimethylthioformamide molecules in zigzag chains in solid *N*,*N*-dimethylthioformamide.[44] Internal C−H···X hydrogen bonding is also found in the crystal structures of the pseudotetrahedral bis-solvated mercury(II) halide complexes, $[HgX_2(SCHN(CH_3)_2)_2]$, X = Cl, Br, and I.[45] Even though weak, the hydrogen-bonding ability of the proton of the −CHS group is stronger than for its oxygen analogue *N*,*N*-dimethylformamide[44] and is also evident in some of the present structures. Most prominent is the hydrogen bonding in the $[Cd(SCHN(CH_3)_2)_6](ClO_4)_2$ hexasolvate where S···H distances between 2.76 and 2.93 Å with C−H···S angles of about 136° are found between the ligands of the complex and is probably the reason why the Cd−S distances are slightly longer than in solution.[4] Though not mentioned in the original paper,[16] there is hydrogen bonding of similar type in the isostructural hexasolvate of iron(II), $[Fe(SCHN(CH_3)_2)_6](ClO_4)_2$. No hydrogen atoms could be found in the determination of the reported structure and calculated positions assuming C−H 1.08 Å were introduced,[16] which result in S···H hydrogen bond distances between 2.7 and 2.9 Å.

Another indication of the hydrogen-bonding influence is the slightly (0.008 Å) but significantly longer Cd−S distance (Table 2) for the hydrogen-bonded *N*,*N*-dimethylthioformamide ligand (S2) of the $[Cd(SCHN(CH_3)_2)_4(O_3SCF_3)_2]$ complex; see Figure 3 (O3···H1 2.46 Å, C2−H1···O3 154°, C2···O3 3.30 Å). Even weaker possible hydrogen bond distances can be found for the mercury(II) solvate (O3···H1 2.65 Å, C1−H1···O3 171°, C1···O3 3.48 Å), see Figure 4, and the zinc solvate (Figure S1, Supporting Information), but seemingly without significant structural influence. Considering that the actual position of the proton of the −CHS groups is 0.1−0.2 Å more distant from the carbon atom than the apparent C−H bond length determined by X-ray diffraction (Table 2),[28] the O···H and S···H hydrogen

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bond lengths discussed above should be shorter with a corresponding amount and consequently somewhat stronger than what appears from a direct comparison with the relevant van der Waals radii (O 1.40, S 1.85, and H 1.2 Å),[43] except for the $[Fe(SCHN(CH_3)_2)_6](ClO_4)_2$ structure for which calculated hydrogen atom positions were used.[16] Another comparison of the relative hydrogen bond strength can therefore be made on the basis of the more precisely determined C···S distances between the internally hydrogen bonded *N,N*-dimethylthioformamide ligands. The mean values are 3.54 and 3.64 Å for the hexasolvated iron(II) and cadmium structures, respectively, which can be compared to the nearly linear weak hydrogen bond with C···S 3.78 Å in the structure of solid *N,N*-dimethylthioformamide.[44]

Bonding in the Complexes. The increase in bond strength toward mercury(II) for comparable complexes of the divalent ions of group 12, which is noticeable already with relatively hard oxygen donor ligands,[6] is strongly enhanced with increasing softness of the ligand, *e.g.* pyridine[12] and *N,N*-dimethylthioformamide.[14] The main reason seems to be the high polarizability of the mercury(II) atom, allowing a significant contribution of its filled $5d_{z^2}$ atomic orbital to the valence shell s and p orbitals in the formation of the molecular orbitals of the complex.[46] The efficient overlap with the accessible lone pair of the sulfur atom in *N,N*-dimethylthioformamide then gives a stable complex already with two strongly bonded ligands for mercury(II). Also for the smaller and less polarizable zinc ion, the relatively low excitation energy of the $3d_{z^2}$ orbital allows a vibronic mixing into the bonding molecular orbitals, giving rise to a noticeable second-order Jahn−Teller effect.[46] For soft donors the destabilization of a regular octahedral σ-bonded coordination geometry increases, which in the present case results in a preferred tetrahedral coordination for zinc(II).

Only the tetrahedrally coordinated zinc atom, but not the cadmium and mercury atoms, shows some displacement from the planes through each *N,N*-dimethylthioformamide ligand. This is another indication of significant π back-bonding from the more accessible outer shell d-orbitals of the larger metal atoms, especially for mercury(II), into the π-system of the ligands.

For the intermediate cadmium ion in this group, the involvement of its d-orbitals into the σ-bonds is energetically less favorable, which results in less covalent bonding than for mercury(II) and zinc. The preferred coordination geometry remains octahedral for monodentate and not too bulky ligands, as expected for electrostatic reasons. The preference for soft sulfur relative to harder oxygen donors is so small, in contrast to mercury(II), that two of the *N,N*-dimethylthioformamide ligands around cadmium(II) are replaced by normally noncoordinating trifluoromethanesulfonate ions upon crystallization. However, the 0.065 Å shorter mean Cd−S distance in the tetrasolvated inner-sphere ion-paired complex $[Cd(SCHN(CH_3)_2)_4(O_3SCF_3)_2]$, as compared to that of the hexasolvated complex, shows the two Cd−O bonds formed to the trifluoromethanesulfonate ions to be weaker than the Cd−S bonds in the hexasolvate. In order to make such an exchange possible at the crystallization process despite the weaker bonding there must be a compensating energy gain from relatively strong interactions between the liberated solvent molecules and those in the bulk. Crystal and liquid structure determinations have shown significant hydrogen bonding between the *N,N*-dimethylthioformamide molecules,[44] and the strength in solution has been estimated by calorimetric measurements to about 12 kJ mol^{-1}.[45] However, the solvation increases more for the $CF_3SO_3^-$ ion than for ClO_4^- in a transfer from aqueous to *N,N*-dimethylthioformamide solution, as shown by transfer thermodynamic studies,[47] and would prevent inner-sphere ion-pair formation with the solvated cadmium ion in an *N,N*-dimethylthioformamide solution. The main balancing factor which enables trifluoromethanesulfonate ions, but not perchlorate, to replace two of the *N,N*-dimethylthioformamide ligands in the solid state is probably the somewhat stronger ability to coordinate metal ions, which is implied by the slightly stronger hydrogen bonds formed from trifluoromethanesulfonate than from perchlorate ions to water molecules in aqueous solution.[48,49] In addition, the lattice energy of the solid hexasolvate $[Cd(SCHN(CH_3)_2)_6](ClO_4)_2$ is expected to be slightly more favorable than for a corresponding compound with trifluoromethanesulfonate since the perchlorate anion is somewhat smaller. The energy required for breaking the internal hydrogen bonds between the *N,N*-dimethylthioformamide ligands in the hexasolvated $[Cd(SCHN(CH_3)_2)_6]^{2+}$ cadmium ion (Figure 2) is probably compensated for by the C2−H1···O3 hydrogen bond formed to the trifluoromethanesulfonate ligand within the $[Cd(SCHN(CH_3)_2)_4(O_3SCF_3)_2]$ complex (Figure 3). Thus, there are several energy contributions which together make the unexpected formation of two Cd−O rather than Cd−S bonds possible in a solid state inner-sphere complex with $CF_3SO_3^-$ ions, despite the excess of *N,N*-dimethylthioformamide ligands available during the crystallization process.

Acknowledgment. The financial support given by the Swedish Natural Science Research Council is gratefully acknowledged.

Supporting Information Available: Listings of crystal properties and data collection and treatment procedures and complete atomic positional, isotropic and anisotropic displacement parameters including hydrogen atoms, intramolecular distances and angles, and least-squares planes through the *N,N*-dimethylthioformamide ligands and Figure S1, showing the $[Zn(SCHN(CH_3)_2)_4](CF_3SO_3)_2$ complex with the atomic positions of all atoms including the disordered trifluoromethanesulfonate ion and the possible hydrogen bonds (50 pages). Ordering information is given on any current masthead page.

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