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Silver Halide Complexes with N,N-Dimethylthioformamide

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N,N-Dimethylthioformamide (DMTF) was found to form the following complexes with silver halides: AgCl·2DMTF, AgBr·2DMTF and AgI·DMTF. These complexes have been studied in the crystalline state as well as in solution. The physical properties, NMR and IR spectra of these complexes have been determined and the constants for the dissociation of these compounds in N,N-dimethylthioformamide have been calculated from conductivity measurements.

Introduction

Studies on the polarographic behaviour of cations in dimethylthioformamide (DMTF)[1] as well as on the solvation of cations in this solvent[2,3] have shown that the interaction between silver ion and solvent is fairly strong. The surprisingly high solubility of silver chloride[1,3], silver bromide and silver iodide[1] has been observed independently by both research groups. This work has been undertaken to learn more about the nature of the interactions of silver halides with DMTF.

TABLE I. Physical Data of N,N-Dimethylthioformamide.

Dielectric constant (20°C)	51.2
Index of refration (20°C)	n_D^{20} 1.576
Density	D_4^{20}: 1.028 g/cm^3
Dipole moment	μ = 4.56 D
Viscosity (25°C)	η = 1.8276 cp
Specific conductance (25°C)	5.11 × 10^{-7} Ω^{-1} cm^{-1}

Experimental

DMTF was prepared and purified according to the procedure described recently[1].

Where they have been previously determined, the data presented in Table I agree well with the published values[4].

The silver chloride and silver bromide solvates were prepared by dissolving the silver salts in DMTF under nitrogen at 50°C and cooling the saturated solution to 0°C. The crystals were filtered and washed with absolute ethyl ether in a glove box under dry nitrogen.

The silver iodide solvate was prepared essentially in the same manner, but since this salt did not crystallize well from pure DMTF, small quantities of absolute ethyl ether were added.

The crystals obtained analyzed as follows:

		AgCl·DMTF	AgCl·2DMTF	AgCl·3DMTF
	% (found)	(theor.)	(theor.)	(theor.)
C:	22.17	15.50	22.41	26.32
H:	4.23	3.04	4.39	5.15
N:	8.63	6.03	8.71	10.23

		AgBr·DMTF	AgBr·2DMTF	AgBr·3DMTF
	% (found)	(theor.)	(theor.)	(theor.)
C:	19.51	13.01	19.69	23.75
H:	3.80	2.55	3.86	4.65
N:	7.65	5.06	7.65	9.23

		AgI · DMTF	AgI · 2DMTF
	% (found)	(theor.)	(theor.)
C:	11.26	11.12	17.45
H:	2.31	2.18	3.42
N:	4.22	4.32	6.78

From the above analysis it follows that the compounds obtained were: AgCl · 2DMTF, AgBr · 2DMTF, AgI · DMTF.

All are white crystals insoluble in hydrocarbons, ethers, acetone and CS_2. Decomposition was observed in water, alcohols, propylene carbonate, acetonitrile, dimethylformamide and nitromethane.

Silver fluoride and DMTF reacted to give a viscous brownish solution and a black precipitate, without any indications for the formation of a crystalline solvate.

All operations were carried out under an atmosphere of dry nitrogen.

Melting points and melting enthalpies were measured on a Perkin–Elmer DSC-1 differential scanning calorimeter; tin served as a reference. Densities were obtained pycnometrically employing nonane. Conductivity measurements were made by means of a Wayne Kerr B 642 Autobalance Universal bridge. An Ubbelohde viscosimeter was used to obtain the dynamic viscosity of DMTF. Infrared spectra were measured on a Perkin–Elmer 457 grating infrared spectrophotometer using thin films between KBr plates. Mulls with Nujol and polytrifluorochloroethylene were used to obtain the spectra of the silver halide solvates.

Results and Discussion

The densities, melting points, enthalpies and crystal systems of AgCl · 2DMTF, AgBr · 2DMTF and AgI · DMTF are summarized in Table II.

Infrared and NMR spectroscopy measurements were used to obtain information about the behaviour of silver halides in solution while X-ray analysis on single crystals performed by H. Kietaibl[5] yielded the crystal structure. Parts of the structural data have aided our interpretation and are briefly discussed with the author's permission.

AgCl · 2DMTF and AgBr · 2DMTF have similar structures. The silver atom in these compounds is tetrahedrically surrounded by three sulfur atoms from DMTF molecules and one halide atom forming a chain-like structure. One silver–sulfur distance is considerably longer than the other two.

The silver atom in AgI · DMTF is in the center of a distorted tetrahedron of three iodine and one sulfur atom, which creates a band-like structure in this compound.

The infrared spectrum of DMTF and the assignment of the peaks has been reported[6] in the range of 4000 to 250 cm^{-1} and spectra of AgCl (0.321*M*), AgBr (0.503*M*) and AgI (1.307*M*) in DMTF solutions did not show any measurable shift in the peak positions. Nujol and polytrifluorochloroethylene mulls of the solid silver solvates show a shift in the positions of three peaks, namely the C=S stretching (967 cm^{-1}), the C–N stretching (1530 cm^{-1}) and the C–H (915 cm^{-1}) out-of-plane bending (Table III, Figure 1).

The shift of the C=S stretching band to lower wavenumbers in conjunction with the structural data further supports the assignment of the bands. The effect is however not very pronounced, and it is therefore not surprising that no shift was observable in solution. A comparison of the ^1H NMR spectra of DMTF and of silver halides in DMTF shows only very minute shifts in the peak positions. These shifts (of the order of 1–2 Hz) indicate that the protons of the DMTF molecules are very weakly influenced by coordination of silver to the sulfur.

The results of conductometric measurements are shown in Figure 2.

TABLE II. Physical Data of Silver Halide Solvates.

	AgCl · 2DMTF	AgBr · 2DMTF	AgI · DMTF
$Density_{exp}$[g/cm^3]	1.837	2.005	2.734
$D_{calc.}$[g/cm^3][5]	1.822	1.996	2.727
M.p. [°C]	59.1	51.3	94.3
Spec. melt. enthalpy [cal/g]	25.99	19.94	14.58
Mol. melt. enthalpy [kcal/mol]	8.358	7.299	4.723
Crystal system[5]	rhomb.	rhomb.	monocl.

TABLE III. IR Spectroscopy Data on Silver Halide DMTF Solvates (cm^{-1}).

Vibrational Mode	DMTF	AgCl·2DMTF	AgBr·2DMTF	AgJ·DMTF
	(Thin Film)	(Paraffine and Polytrifluorochloroethylene Mull)		
C–N stretching	1530	1553	1550	1550
C=S stretching	967	955	956	944
C–H out-of-plane bending	915	933	933	915

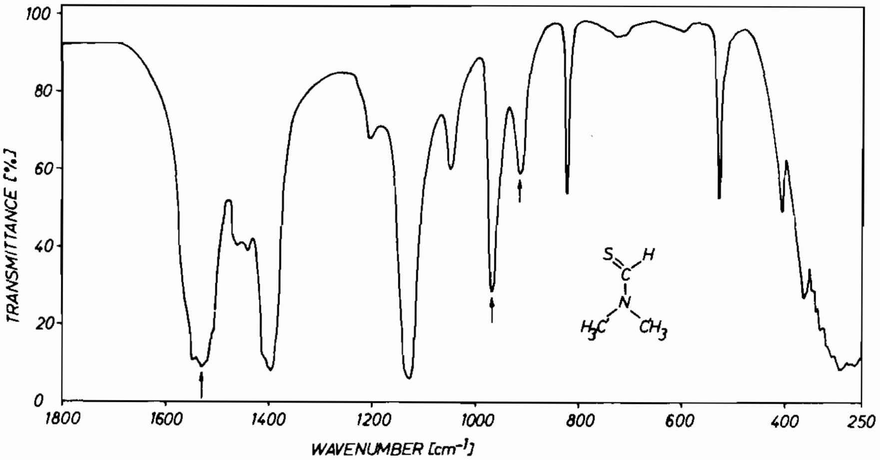

Figure 1. Infrared spectrum of N,N-dimethylthioformamide.

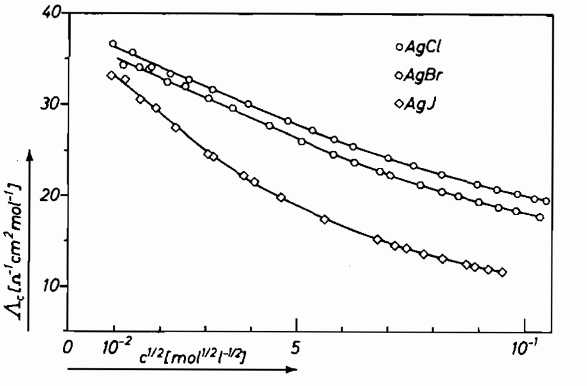

Figure 2. Conductivity data of AgCl, AgBr and AgI in N,N-dimethylthioformamide.

Dissociation constants of the solvated silver halides were calculated on the basis of the classical iteration procedure of Fuoss and Krauss[7,8] with the assumption of the equilibrium:

$$Ag(DMTF)_nX \rightleftharpoons Ag(DMTF)_n^+ + X^-$$

The calculations were made by means of a computer program employed previously in the calculation of dissociation constants in nonaqueous solvents[9]. An extrapolated value of Λ_0 was used as a starting value for Λ_0.

Three values for the distance of closest approach for each compound were used: (i) the bond distance Ag–X obtained from crystallographic measurements[5], (ii) the sum of the ionic radii and (iii) a value of 8.00 Å. The value of 8 Å has been added to account for

TABLE IV. Dissociation Constants and Calculated Λ_0 Values of Silver Halides in DMTF.

R[Å]	AgCl			AgBr			AgI		
	2.54	3.07	8.00	2.66	3.21	8.00	2.83	3.46	8.00
$\Lambda_0[\Omega^{-1}\ cm^2\ mol^{-1}]$	37.08	37.06	36.90	36.59	36.57	36.43	36.56	36.52	36.30
$K(3)^a \times 10^{+2}$	0.6822	0.6873	0.7286	0.5163	0.5197	0.5459	0.1359	0.1367	0.1419

[a] K(3) means the dissociation constant after the 3rd iteration step.

the possibility of formation of solvent separated ion pairs. The value of the dielectric constant reported for 25 °C (47.8) was used[4]. Only minute changes in the dissociation constants were observed as seen from Table IV. The existence of solvent separated ion pairs can be excluded, however, because the equilibrium constants are insensitive to the interatomic distances chosen. The dissociation constants are only correct to two digits, the four digits in Table IV being used only to show the variation with the distance. The following dissociation constants were obtained: $AgCl \cdot 2DMTF$: 0.68×10^{-2}, $AgBr \cdot 2DMTF$: 0.52×10^{-2}, $AgI \cdot DMTF$: 0.14×10^{-2}.

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