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Spectroscopical Investigations on Silver Sulfamides**

Alois Popitsch[a, *], **Edgar Nachbaur**[a], **Wolfgang Neißl**[b], and **Harald P. Fritzer**[b]

[a] Institute of Inorganic and Analytical Chemistry,
University Graz, A-8010 Graz, Austria

[b] Institute of Physical and Theoretical Chemistry,
Technical University Graz, A-8010 Graz, Austria

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Diffuse reflectance spectra (d.r.s.) of the diamagnetics $O_2S(NHAg)_2$ and $O_2S(NAg_2)_2$ have been measured in the region from 700 nm to 200 nm at 300 K and 77 K, respectively. Additionally, infrared spectra in the region of the SO and SN stretching mode have been recorded. The energetically low-lying d.r.s. bands of these substances have been assigned to charge transfer transitions. The shift of the SO stretching modes together with the thermal and mechanical instability is thought to be due to a transfer of charge from the $S=O$ bond region *via* the nitrogen atoms to the silver atoms.

(Keywords: Charge transfer transitions; Diffuse reflectance spectra; Infrared spectra; Silver sulfamides)

Spektroskopische Untersuchungen an Silbersulfamiden

Die diffusen Reflexionsspektren (im Bereich von 700 bis 200 nm bei 300 K und 77 K) sowie die IR-Spektren (im SO_2 und SN_2-Valenzschwingungsbereich) von $O_2S(NHAg)_2$ und $O_2S(NAg_2)_2$ werden mitgeteilt. Die niederenergetischen Banden in den diffusen Reflexionsspektren dieser diamagnetischen Verbindungen werden Charge-Transfer-Übergängen zugeordnet. Als Ursache für die Verschiebung der SO_2-Valenzschwingungen einerseits sowie für die thermische und mechanische Instabilität andererseits wird eine Ladungsverschiebung aus dem $S=O$-Bereich über die Stickstoffatome zu den Silberatomen angenommen.

Introduction

In this paper we report studies on the relationship between structure and optical and/or magnetic properties of coloured silver compounds respectively. For this purpose the sulfamide-silver system

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seems to be a suitable one because of the existence of well defined compounds of both known structure and increasing amount of Ag(I) in the lattice[1].

Former investigations[2–4] have shown that the hydrogen atoms in sulfamide, $O_2S(NH_2)_2$ (*SA*) can be stepwise replaced by metal ions. Whereas alkaline and alkaline earth ions produce colourless and readily hydrolyzable salts[2], silver ions generate various completely insoluble compounds of different colours varying with the silver content in the lattice. Disilversulfamide (Ag_2SA) appears colourless[2,4], Trisilversulfamide[3,3a] is yellow, whereas, Tetrasilversulfamide (Ag_4SA)[3] has a ruby colour. With increasing silver content an increasing thermal and mechanical instability is also recognized. Considering the d^{10} ground state configuration of Ag(I) the colours of these compounds cannot be explained on crystal field arguments. Therefore, other kinds of electronic transition mechanisms have to be taken into account.

Experimental

The substances were prepared and analysed by methods described previously[3,4]. Infrared spectra were recorded as Nujol mulls between cesium iodide plates on a Perkin Elmer 580B spectrometer and a Beckman IR 20A spectrometer. Diffuse reflectance spectra between 700 and 200 nm were obtained from microcrystalline samples using a Beckman DK-2A spectroreflectometer (equipped with an Oxford Instruments continuous-flow cryostate). "White reflectance quality" $BaSO_4$ (Eastman Kodak, Rochester, U.S.A.) was used as standard. The spectra were recorded in the RBW-technique (reference-beam-weakening) which is especially useful for heavily absorbing substances to obtain well resolved bands: The reference beam is attenuated by stainless steel nets of different mesh areas. Details of this technique are given elsewhere[5].

Results and Discussion

Diffuse Reflectance Spectra

The band maxima of the diffuse reflectance spectra recorded at 300 and 77 K are listed in Table 1.

$NaHN—SO_2—NH_2$ shows a strong maximum around 210 nm accompanied by a shoulder at ca. 230 nm. In contrary to these highly energetic transitions the spectra of Ag-substituted sulfamides are characterized by several transitions at lower energies (Figs. 1 and 2).

At 77 K the optical spectrum of Ag_2SA shows three bands peaking respectively at ca. 248, 298 and 351 nm (the latter band appears only after exposing the compound to light for several days). The crystal structure[6] for this compound shows that: (a) each silver atom is bonded to two nitrogen atoms from different O_2SN_2-tetrahedra; (b) the Ag—N distances (ranging from 2,12 to 2,20 Å) indicate that the Ag—N bond is partial covalent; (c) the silver atoms sharing a common nitrogen atom show a rather short Ag—Ag distance (3,09 Å). We assign the 248 nm band to an intramolecular transition in the *SA* anion. Because of the partial covalent Ag—N bond this band is shifted by ca. 2,600 cm^{-1} to lower energies compared to *SA*. The band at 298 nm with a pronounced decrease in intensity with decreasing temperature (Fig. 1) is related at present to a charge transfer transition (probably of the ligand to metal type). A further possibility, a vibrational electronic transition [*e.g.*, a parity-forbidden transition $4d^{10}$-$4d^9\,5s$, in Ag(I)] could be discussed.

Table 1. *Diffuse reflectance spectra of solid sulfamides*

Compound	Temperature (K)	Absorption maxima (nm)
SA	300	233
	77	233
Na—*SA*	77	210, 230
Ag_2*SA*	300	300
	77	248, 298, (351)
Ag_4*SA*	300	290, 420, 483, 570
	77	285, 343, 400, 460, 545

In this connection it is worth mentioning that in Ag-activated metaphosphate glasses it was found that X-irradiation produces colour centres with band maxima at ca. 275, 315 and 365 nm, respectively. The well developed peak at 315 nm was assigned *via* ESR investigations to the presence of Ag_2^+[7].

The band at 351 nm in Ag_2*SA* (Table 1) which appears only after light exposure of the compound probably belongs to a Ag(O) species.

The optical spectrum of Ag_4*SA* shows three band systems in the visible and two in the near ultra violet region (Table 1 and Fig. 2). In comparison with the spectrum at 300 K all bands are shifted to higher energies at 77 K. This increase is not surprising and can be attributed to electrostatic effects of the lattice as a whole. A noticable change in intensity of these bands, however, is not evident.

In accordance with our interpretation above we assign the band at 285 nm to an intramolecular transition in the O_2SN_2 framework. A plausible starting explanation for the bands in the visible region would be to assign these bands to charge-transfer transitions too. But in contrast to Ag_2*SA*, we have to consider here a different Ag framework in which trinuclear and tetranuclear close-packed arrays exist around the nitrogen atoms[8]. This would point at energetically different charge-

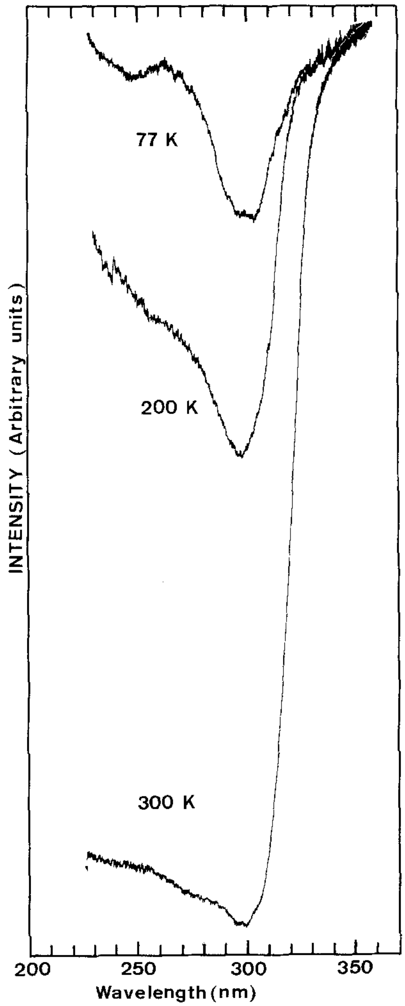

Fig. 1. Diffuse reflectance spectrum of Ag_2SA at various temperatures

transfer bands causing the remarkable colour shifts. For a more detailed interpretation further experiments, *e.g.* single crystal studies at low temperature, will be necessary.

In this context it might be interesting to recall the fact that thin silver layers show abnormal optical transmission behaviour. With increasing thickness of the layer colour changes from yellow to blue have been observed[9].

A charge-transfer process is obviously closely related to an oxidation-reduction process. In fact, with ligands of low electronegativity such redox reaction will lead to the formation of an excited anion as the first step. The subsequent dissociation of such anions can produce electrons in the conduction band (as is well known, for example, from the photochemistry of inorganic solid azides[10]), finally resulting in the formation of transient radicals followed by a decomposition of the whole compound.

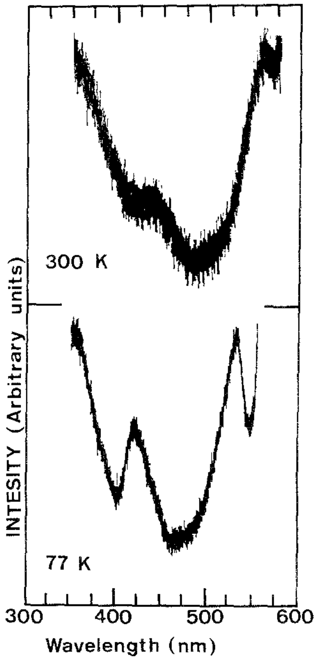

Fig. 2. Diffuse reflectance spectrum of Ag_4SA at 300 K and 77 K

In fact, Ag_4SA has the lowest lying electronic transitions (see Table 1) and is the most unstable member in our series of Ag-sulfamides too: The compound is extremely sensitive to thermal and mechanical energy and explodes easily on grinding and pushing (*Warning: Careful handling is necessary!*)

Infrared Spectra

The infrared spectra of *SA* and its Ag compounds in the SO and SN stretching mode region are shown in Fig. 3. Values of the SO and SN frequencies together with the bond lengths are listed in Table 2.

The data point at a pronounced trend towards a lowering of the SO stretching modes with increasing silver content of the compounds. It is also evident that there exists a relationship between the bond lengths and the SO stretching frequencies. The shift of the SN stretching modes is not as pronounced as that of the SO modes. The asymmetric and the symmetric modes separate with increasing Ag content in the lattice in connection with the increasing difference in the lenghts of the two SN bonds. A correlation with the NSN angles is not evident.

Table 2. *Bond lengths* (Å) *and stretching frequencies (cm^{-1}) for the* SO_2 *and* SN_2 *groups*

Compound	r_{SO} r_{SN}	ν_{as}, ν_s (SO_2) ν_{as}, ν_s (SN_2)
SA	1.39; 1.39[11] 1.60; 1.60	1358; 1156[12] 931; 904
Ag_2*SA*	1.45; 1.45[6] 1.61; 1.58	1185; 1088; 1058 875; 838
Ag_4*SA*	1.49; 1.48[8] 1.63; 1.57	1090; 937 898; 790

We interpret the lowering of the SO modes as a transfer of charge from the $S=O$ region *via* the sulphur and nitrogen atoms to the Ag atoms. This charge migration should lead to a lengthening of the SO distances and consequently to both a lowering of the force constant and the stretching frequencies of the SO bonds. A complete charge-transfer of this type would finally lead to the formation of reduced species, *e.g.*, Ag_2^+, Ag_3^{2+} etc.

As mentioned above the Ag atoms are connected solely to nitrogen atoms except in Ag_4*SA* where one short Ag—O was found. Therefore the mass of the Ag atoms should have an unimportant effect on the lowering of the SO stretching frequencies.

From a structural point of view one might predict high co-ordination numbers for d^{10} systems. Ag(I), however, shows a pronounced tendency to form linear, two co-ordinated systems indicating partial covalent bonding between silver and the ligand atoms. Single-crystal X-ray crystallographic studies[6,8] of the silversulfamides indicate that—besides two almost linearly arranged N—Ag—N short bonds—there exist also one or two short Ag—Ag bonds. The distances (ranging from 3.09 to 2.87 Å) between silver atoms bonded to the same nitrogen atom are close to that found in silver metal (2.88 Å) such that interactions between Ag atoms (*e.g.*, *via* formation of Ag-cluster) seem possible.

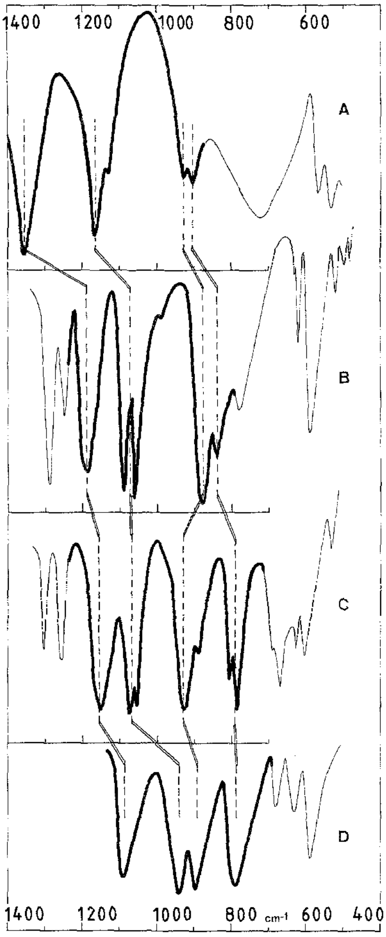

Fig. 3. IR-spectra of *SA* (*A*); Ag_2*SA* (*B*); Ag_3*SA* $\cdot NH_3 \cdot H_2O$ (*C*) and Ag_4*SA* (*D*) in the S—O and S—N stretching region

The formation of both metal—metal bonds together with two bonds to non-metal atoms seem to be an interesting feature of the structural chemistry for these compounds.

Preliminary magnetic measurements[13] on these compounds show that the overall magnetic properties are of the diamagnetic type since the values of the molar susceptibilities are negative. This is reasonable since Ag(I) has a closed shell configuration. Ag metal itself is also diamagnetic. Therefore independent evidence of metal—metal-bonding is not possible at present. But there is, however, a statistically significant field and temperature dependence of the susceptibility for both Ag compounds (Ag_2SA, Ag_4SA) such that the existence of cooperative interactions suggested above finds a reliable support.

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