

As shown by the present investigations, the spectra of  $0^- \rightarrow 0^+$  transitions of  $^{144}\text{Ce}$ ,  $^{144}\text{Pr}$  and

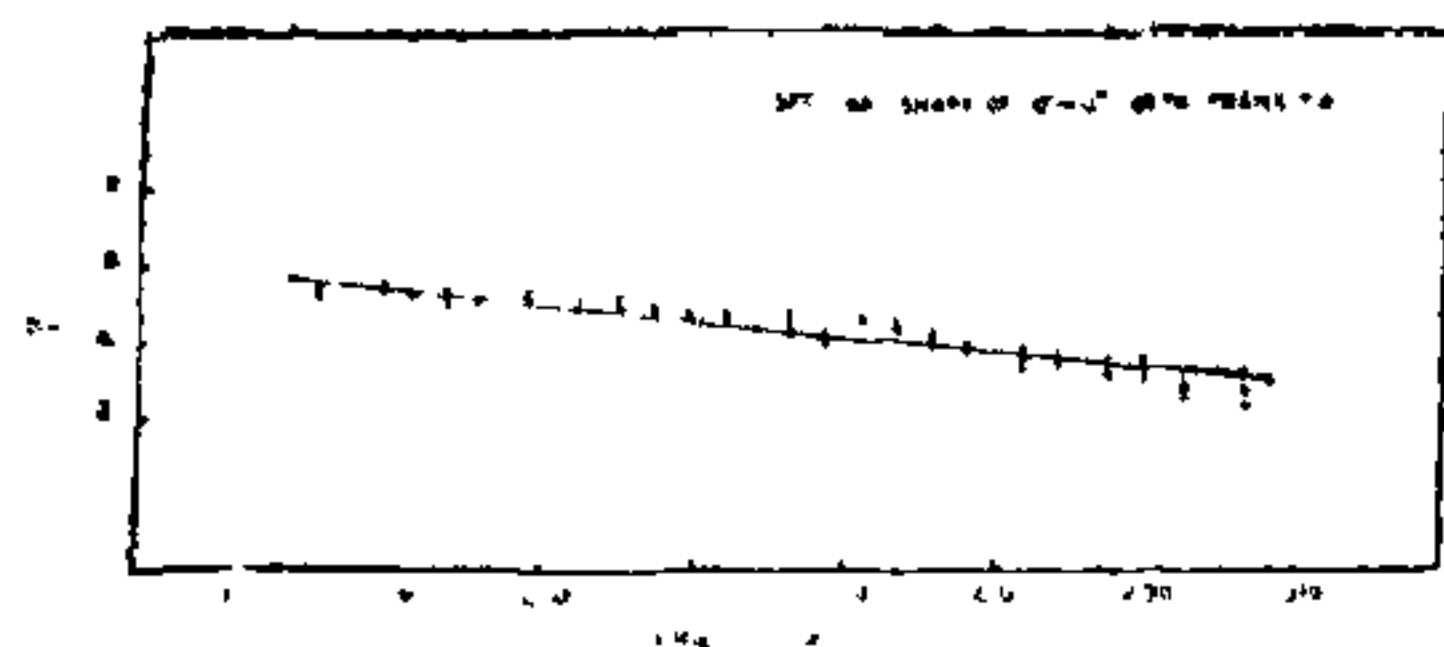


FIG. 1. Shape factor plot for the  $0^- \rightarrow 0^+$  beta Transition of  $^{144}\text{Ce}$ . Solid line is the least square fit for  $C(W) = (1 + aW)$  with  $A = -0.537 \pm 0.023$  and  $W_0 = 320 \text{ KeV}$ .

$^{166}\text{Ho}$  are not at all statistical. These results do not support the concept of a partially conserved axial vector current theory as suggested by Tadic<sup>1</sup>.

One of the authors (Ramaniah) acknowledges the financial assistance through a Post-Doctoral Fellowship by the C.S.I.R. of India.

1. Nagarajan, T., Ravindranath, M. and Venkata Reddy, *Nuovo Cim.*, 1971, 3 A, 699.
2. Tadic, D., *Phys. Letts.*, 1964, 12, 116.
3. Nagarajan, T., *Ph.D. Thesis*, Andhra University.
4. Daniel, H. and Kaschl, G., *Th. Nucl. Phys.*, 1966, 76, 97.
5. Nagarajan, T., Ravindranath, M. and Venkata Reddy, K., *Nucl. Inst. Meth.*, 1969, 67, 77.
6. —, — and —, *Ibid.*, 1970, 80, 217.

## SILVER (I) COMPLEXES OF SULFATHIAZOLE, SULFADIAZINE, SULFAMERAZINE AND SULFAMETHAZINE

K. K. NARANG AND J. K. GUPTA

Chemistry Department, Banaras Hindu University, Varanasi 221005

### ABSTRACT

Silver (I)-Sulfadruge complexes of the type,  $\text{AgD}$  and  $\text{Ag}(\text{HD})\text{NO}_3$  where HD = sulfathiazole, sulfadiazine, sulfamerazine and sulfamethazine, have been prepared and characterized. The complexes are white, insoluble in water and organic solvents and decompose without melting well below the melting points of the drugs. The drug molecules co-ordinate in anionic or neutral form.

### INTRODUCTION

IN our recent publications<sup>1-3</sup>, we have reported the preparation and characterization of the complexes of sulfadruge with Cu (II), Zn (II), Cd (II) and Hg (II). Since the sulfadruge are known for their bacteriostatic properties and their interactions with metal ions are not well understood, we are presently reporting their reactions with Ag(I) in aqueous and in ammoniacal media.

### EXPERIMENTAL

Silver (I) chloride, nitrate and sulphate, B.D.H., A.R. Grade were used for the preparation of the complexes. Purity of the drugs was judged from their melting points and were used as such. Ag(I) chloride and sulphate complexes were prepared by adding hot ammoniacal solution of metal salt (0.01 M) to the hot solution of sulfadruge (0.01 M) in dilute ethanol keeping the drug slightly in excess while Ag(I) nitrate complexes were prepared by mixing aqueous solution of the metal-salt (0.01 M) in minimum amount of water to the hot ethanolic solution of sulfadruge (0.01 M) keeping silver nitrate in excess. The reaction mixtures were heated for about  $\frac{1}{2}$  hr. The complexes were filtered, washed free from the sulfadruge or silver nitrate with dilute ethanol and dried in a desiccator.

Metal part and sulphur in the complexes were estimated gravimetrically and nitrogen microanalytically,

using a Coleman Nitrogen Analyzer. I.R. and electronic spectra were recorded on Perkin-Elmer-257 and Cary-14 respectively. The analytical data and some general characteristics of the complexes are summarized in Table I. Some important i.r. bands are given in Table II.

### RESULTS AND DISCUSSION

The sulfadruge form 1:1 complexes with Ag(I) both in water and ammoniacal solutions. The original anion is present in the complexes isolated from aqueous solution while it is absent in those isolated from ammoniacal solution. In the former case the sulfadruge act as neutral coordinating ligand while in the latter case they act as anionic coordinating ligands. The complexes are white and insoluble in water and organic solvents. They decompose in the range 228–289°C. In the case of silver (I) chloride or sulphate complexes with drugs, the course of reaction may be as follows :

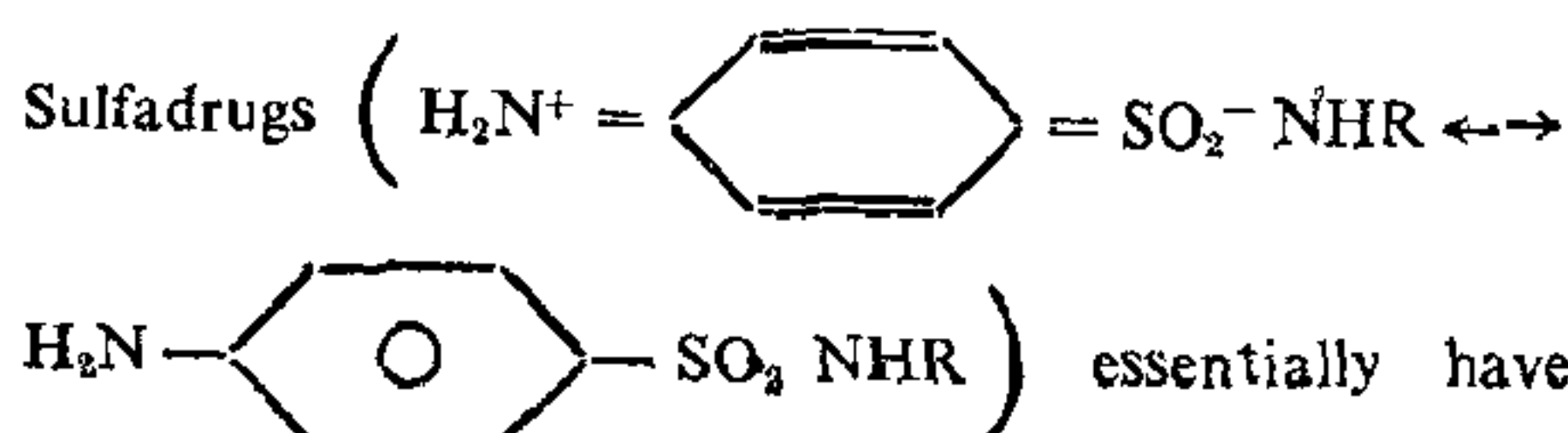
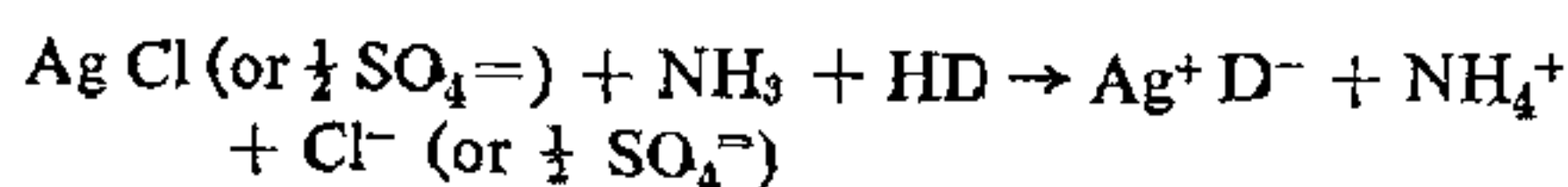


TABLE I  
Analytical data and general characteristics of silver (I) complexes with sulfadriugs

Compounds	Decompn. (°C)	Found (Calc.) %			Electronic spectral bands $\lambda_{\text{max}}$ , nm
		Metal	Nitrogen	Sulphur	
(a) Ag (ST-H)*	228 ST-200	29.29 (29.56)	11.53 (11.60)	18.05 (17.68)	275, 310 ST-260, 300
(b) Ag (SD-H)*	271 SD 253	29.66 (29.97)	15.65 (15.60)	9.25 (8.96)	260, 295 SD-275, 310
(c) Ag (SM-H)*	276 SM-234	28.53 (28.84)	15.01 (15.09)	9.10 (8.63)	260, 300 SM-270, 305
(d) Ag (SZ-H)*	280 SZ-197	27.41 (27.79)	14.26 (14.54)	7.95 (8.31)	265, 310 SZ-275, 305
(e) Ag (ST) NO <sub>3</sub>	237 ST-200	24.84 (25.23)	12.74 (13.20)	14.75 (15.09)	270, 305 ST-260, 300
(f) Ag (SD) NO <sub>3</sub>	281 SD-253	25.78 (25.53)	16.48 (16.70)	8.00 (7.63)	270, 300 SD-275, 310
(g) Ag (SM) NO <sub>3</sub>	285 SM-234	25.13 (24.71)	16.22 (16.16)	7.85 (7.39)	285, 310 SM-270, 305
(h) Ag (SZ) NO <sub>3</sub>	289 SZ-197	24.12 (23.93)	15.25 (15.66)	6.70 (7.16)	260, 290 SZ-275, 305

\* Prepared from Silver (I) Chloride and Sulphate.

Abbreviations : ST = Sulfathiazole, SD = Sulfadiazine, MS = Sulfamerazine, SZ = Sulfamethazine.

resonance stabilized structures<sup>4</sup> and the UV bands of the phenyl and SO<sub>2</sub> group merge to form a single strong absorption band around 260 nm<sup>5</sup>. In the solid state UV spectra of sulfadriugs in the present communication the maxima are shifted to longer wavelengths. The sulfadriugs in general show two bands, one due to

sulfanilamide part  $\left( \text{NH}_2 - \text{C}_6\text{H}_4 - \text{SO}_2\text{NH} - \right)$  in

the range 260–275 nm and the other due to R part in the range 300–310 nm. When the NH– proton is lost, the first band is affected while the coordination of R part affects the other band as well. If the drug acts simultaneously as an anion and coordinating ligand, both the bands are affected. This is observed in the Ag (I) complexes in the present case. The bands positions are considerably shifted from their original positions (Table I) indicating coordination of the neutral drug molecule or the drug anion to the metal.

Infrared spectra of silver (I)–sulfadriug complexes are compared with those of sulfanilamide<sup>6</sup> and substituted heterocyclic moieties<sup>7</sup> and nitrate ion<sup>7</sup>. Because of resonance stabilized NH<sub>2</sub> and NH groups in the drugs, the  $\nu$  NH bands shift to lower frequencies in sulfadiazine, sulfamerazine and sulfamethazine

showing the involvement of NH<sub>2</sub> group in the coordination. Another evidence for the coordination of NH<sub>2</sub> group is the negative shift of  $\delta$  NH<sub>2</sub> band between 1640–1625 cm<sup>-1</sup>. The heterocyclic ring frequencies in the above drugs appearing around 1570 cm<sup>-1</sup> also show negative shift of about 15 cm<sup>-1</sup> indicating the coordination of ring nitrogen to the metal. In case of sulfathiazole, however, a positive shift in  $\nu$  NH and  $\delta$  NH<sub>2</sub> vibrations is observed but the thiazole ring frequencies at 1575 and 1532 cm<sup>-1</sup> are considerably reduced in intensity due to coordination from sulphur. C–S stretching ( $\nu$  C–S) at 730 cm<sup>-1</sup> shifts to 720 and 705 cm<sup>-1</sup> in Ag (I) complexes (Nos. a and e, Table II). Out of the two SO<sub>2</sub>-frequencies in the range 1330–1310 cm<sup>-1</sup> ( $\nu_{\text{as}}$ ) and 1155–1140 cm<sup>-1</sup> ( $\nu_{\text{s}}$ ), the former shows a slight negative or positive shift while the latter remains unshifted ruling out the possibility of coordination through SO<sub>2</sub> group. The nitrate group frequencies at 1370 and 820 cm<sup>-1</sup> correspond to unbonded nitrate<sup>7</sup>.

## ACKNOWLEDGMENT

The authors are thankful to Prof. O. P. Malhotra, Chemistry Department, Banaras Hindu University, Varanasi-221005, for providing laboratory facilities. One of us (J.K.G.) thanks Council of Scientific and



TABLE II  
Some important i.r. bands of drugs and their silver (I) complexes

Drugs and Complexes	$\nu$ NH	$\delta$ NH <sub>2</sub>	Phenyl Ring	SO <sub>2</sub> Asym. and Sym.	R Group	Nitrate Frequencies
ST	3320 (S) 3280 (M)	1625 (W)	1598 (S) 1500 (M)	1330 (S) 1140 (S)	1575 (S)	..
SD	3480 (S) 3380 (S)	1640 (M)	1598 (S) 1508 (M)	1310 (M) 1155 (S)	1570 (S)	..
SM	3485 (S) 3380 (S)	1640 (S)	1600 (S) 1505 (S)	1310 (M) 1155 (S)	1570 (S)	..
SZ	3440 (S) 3350 (S)	1640 (S)	1595 (S) 1510 (M)	1325 (M) 1150 (S)	1570 (M)	..
(a) Ag (ST-H)*	3405 (M) 3340 (M)	1640 (M)	1598 (M) 1505 (M)	1320 (M) 1140 (S)	..	..
(b) Ag (SD-H)*	3400 (S) 3340 (S)	1620 (W)	1600 (S) 1508 (M)	1325 (M) 1155 (S)	1560 (S)	..
(c) Ag (SM-H)*	3405 (M) 3340 (M)	1620 (M)	1600 (M) 1505 (M)	1330 (M) 1155 (S)	1560 (S)	..
(d) Ag (SZ-H)*	3425 (S) 3350 (S)	1610 (M)	1590 (S) 1510 (M)	1315 (W) 1150 (S)	1560 (M)	..
(e) Ag (ST) NO <sub>3</sub>	3390 (M) 3320 (M)	1635 (M)	1595 (M) 1500 (M)	1310 (M) 1140 (S)	..	1370 (S) 820 (M)
(f) Ag (SD) NO <sub>3</sub>	3370 (M) 3310 (M)	1630 (M)	1595 (S) 1508 (W)	1315 (W) 1150 (S)	1560 (S)	1370 (S) 820 (M)
(g) Ag (SM) NO <sub>3</sub>	3390 (M) 3330 (M)	1625 (M)	1595 (M) 1505 (W)	1320 (W) 1150 (S)	1555 (S)	1370 (S) 820 (M)
(h) Ag (SZ) NO <sub>3</sub>	3420 (S) 3350 (S)	1610 (M)	1590 (S) 1510 (M)	1310 (M) 1145 (S)	1560 (M)	1370 (S) 820 (M)

\* Prepared from Silver (I) Chloride and Sulphate.

Abbreviations: ST = Sulfathiazol, SD = Sulfadiazine, SM = Sulfamerazime, SZ = Sulfamethazime.

Industrial Research, New Delhi, for the financial assistance.

1. Narang, K. K. and Gupta, J. K., *Ind. J. Chem.*, 1975, 13, 705.
2. —, and —, *J. Inorg. Nucl. Chem.*, 1976, 38, 589.
3. —, and —, *Curr. Sci.*, 1976, 15, 536.
4. Commarata, A. and Martin, A. N., *Medicinal Chemistry*, (Edited by Burger, A). Wiley—Interscience, New York, 1970, p. 119.
5. Vandenberg, J. M. and Doub, D., *J. Am. Chem. Soc.*, 1944, 66, 1633.
6. Nakanishi, K., *Infrared Absorption Spectroscopy*, Nankodo Company Limited (1962), p. 216.
7. Rao, C. N. R., *Application of Infrared Spectroscopy*. Academic Press, New York and London, 1963, p. 323.