CROATICA CHEMICA ACTA CCACAA **60** (2) 303—308 (1987)

YU ISSN 0011-1643
CCA-1729 UDC 541.486
Original Scientific Paper

Copper(II) and Mercury(II) Complexes of Sulfamethazine, Succinylsulfathiazole and Phthalylsulfathiazole

Jai K. Gupta[+] *and Narandra K. Jha**

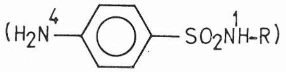
Department of Chemistry, Indian Institute of Technology, Delhi Hauz Khas,
New Delhi — 110016, India

Received July 2, 1986

Some new complexes of the types $MLCl_2$ (where M = Cu(II) or Hg(II) and L = sulfamethazine (SZ) or succinylsulfathiazole (SST) and ML_2Cl_2 [where M = Cu(II) or Hg(II) and L = phthalylsulfathiazole (PST) have been synthesized and their structures investigated by analyses, molar conductance, magnetic susceptibility, UV-visible and IR spectral measurements. Molar conductivities of the complexes indicate their non-electrolytic behaviour. Electronic, infrared and far IR-spectral studies suggest octahedral geometry for copper(II) complexes and tetrahedral geometry for mercury(II) complexes.

INTRODUCTION

Sulfadrugs, of general formula *I*, are of interest because of several donor atoms serving as potential sites for coordination with metal ions, and also because of their antimicrobial activity[1]. The antimicrobial activity of some metal complexes with sulfadrugs has also been reported[2–5]. Taking into account the increased antimicrobial action of many metal compounds of sulfadrugs, it was considered worthwhile to synthesize the complexes of copper(II) and mercury(II) chlorides with sulfamethazine ,succinylsulfathiazole and phthalylsulfathiazole to investigate various physico-chemical characteristics of these complexes.



I

EXPERIMENTAL

Copper(II) and mercury(II) chlorides BDH, AR Grade) and sulfadrugs (May and Maker, England) were used as such for the preparation of the complexes. The purity of the sulfadrugs was judged from their melting points compared to the literature values.[6]

Copper(II) and mercury(II) complexes were prepared by mixing a hot methanol solution (10 ml) of the metal(II) chloride (10 mmol) with a hot methanol solution

---

[+] Present Address: Additives Section, Petrochemistry Division Indian Institute of Petroleum, Dehradun-248001 (U. P.), India

* The author for correspondence.

(100 ml) of the sulfadrug (10 mmol). The reaction mixtures were refluxed for 2—3 hrs. Concentration of the solution to 10 ml and addition of 50 ml of ether led to separation of a stickly mass on standing for a few hours in a fridge. The sticky mass was washed with ether to obtain solid products which were dried in a vacuum desiccator.

The metal content, chloride and sulphur in the complexes were determined by following the standard literature procedures[7] and carbon microanalytically using a coleman C and H-analyzer. Molar conductances were measured in 10^{-3} M methanol solution of the complexes using the Toshniwal conductivity bridge at 25 °C. Magnetic measurements were made on a Faraday balance (Cahn Magnetic Susceptibility Apparatus) using $Hg[Co(NCS)_4]$ as the calibrant. Diamagnetic corrections were applied using Pascal's constants.[8] Electronic spectra were recorded in methanol solution of the compounds using a Unicam SP-700 spectrophotometer in the range 200—1000 nm. Infrared spectra were recorded as KBr pellets on a Unicam SP-1200 spectrophotometer in the range 4000—400 cm^{-1} and far IR spectra were obtained using a Perkin-Elmer-580B spectrophotometer in the range 500—200 cm^{-1}. The analytical, magnetic and electronic spectral data are listed in Table I. Some important IR spectral bands of the sulfadrugs and their complexes are given in Table II.

RESULTS AND DISCUSSION

The analytical data given in Table I show the formation of complexes having 1 : 1 and 1 : 2 (Metal:Sulfadrug) ratios. The Cu(II) complexes are dark green, light green or light brown, whereas the Hg(II) complexes are usually light yellow. All the complexes melt with decomposition in the temperature range 110—200 °C, which is much below the melting points of the corresponding sulfadrugs. All the 1 : 1 and 1 : 2 complexes are soluble in methanol, acetone, acetonitrile and dimethylsulfoxide but insoluble in water, ether, carbontetrachloride, benzene and chloroform. The molar conductivities of all the complexes in 10^{-3} M methanol solution lie much below the reported range[9], suggesting their non-electrolytic nature.

Electronic Spectra

The simple sulfanilamides have one single intense band around 260 nm[10] in neutral solution. The UV spectra of sulfadrugs studied presently reveal a single band at 260—265 nm in methanol solution. In the spectra of Cu(II) and Hg(II) complexes, there is a shifting and splitting in the bands of sulfadrugs indicating their coordination to the metal ion. An interesting feature of the electronic spectra of Cu(II) complexes is the appearance of a band in the range 425—450 nm (Table I)· Although a high energy band in the blue region has been related to binuclear nature of copper complexes[11,12], a careful observation reveals that this band is of similar intensity (high) to those of the other UV bands of sulfadrugs. This blue band in Cu(II) complexes may be a ligand to metal charge transfer band indicating the coordination of ligand to metal. Besides the UV bands, Cu(II) complexes show one band around at 900 nm which corresponds to the octahedral structure for all of these complexes[13]. Since Hg(II) is a d^{10} metal ion, no d—d transition bands are expected in the visible region in the Hg(II) complexes. However, information about the ligand coordination and stereochemistry of Hg(II) complexes can be obtained from infrared spectra.

TABLE I

Analytical, Magnetic and Electronic Spectral Data of Complexes

No.		Colour	Yield/%	M. P. (dec.) °C	Analyses : Found (Calc.)/%				μ_{eff}	Electronic spectral Bands in Methanol (λ_{max}/nm)
					Metal	Chloride	Carbon	Sulphur	(B. M.)	
1.	Cu(SZ)Cl_2	Dark Green	80	110 SZ-197	15.09 (15.39)	16.96 (17.21)	35.08 (34.90)	7.43 (7.75)	1.85	272, 425, 900 SZ-260
2.	Cu(SST)Cl_2	Light Green	75	125 SST-185	13.26 (12.97)	15.22 (14.50)	42.57 (31.86)	12.85 (13.07)	1.80	260, 285, 450, 900 SST-265
3.	Cu$(PST)_2Cl_2$	Light Brown	85	175 PST-260	7.02 (6.75)	7.28 (7.54)	43.10 543.38)	13.35 (13.60)	1.87	260, 290, 440, 900 PST-265
4.	Hg(SZ)Cl_2	Light Yellow	90	115 SZ-197	36.08 (36.42)	13.32 (12.93)	26.51 (26.22)	6.54 (5.82)	—	270 SZ-260
5.	Hg(SST)Cl_2	Light Yellow	80	120 SST-185	32.25 (31.94)	11.62 (11.34)	25.19 (24.92)	9.97 (10.22)	—	260, 290 SST-265
6.	Hg$(PST)_2Cl_2$	Light Yellow	85	200 PST-260	18.88 (18.57)	6.86 (6.59)	38.01 (37.58)	12.05 (11.88)	—	262, 295 PST-265

Abbreviations:
SZ = Sulfamethazine
SST = Succinylsulfathiazole
PST = Phthalylsulfathiazole

TABLE II

Important IR Spectral Bands (4000—200 cm^{-1}) of Sulfadrugs and Their Cu(II) and Hg(II) Complexes

Complex	$\nu C = 0$	Phenyl Ring Vibrations	Substituent Sensitive Aromatic Mode	ν as and νs (SO_2 groups)	νS—N	R (Heterocyclic group)	νM—N (Heterocyclic Ring N)	νM—Cl
SZ	1640m(a)	1595s 1510w	1090s	1330m 1160s	835m	1575m	—	—
SST	1680m	1600s 1500w	1100s	1340m 1155s	840m	1580m	—	—
PST	1720m	1500w 1600s	1095s	1320m 1150s	830m	1575m	—	—
$Cu(SZ)Cl_2$	1620m(a)	1600s 1510w	1090s	1330m 1160s	835m	1555w	270m	—
$Cu(SST)Cl_2$	1640m	1605s 1505w	1100s	1335m 1155s	840m	1560w	260m	—
$Cu(PST)_2Cl_2$	1720m	1600s 1500w	1095s	1330m 1155s	830m	1555w	265m	—
$Hg(SZ)Cl_2$	1615m(a)	1600s 1510w	1090s	1330m 1150s	840m	1550w	270m	310m
$Hg(SST)Cl_2$	1660m	1605s 1500w	1098s	1340m 1150s	840m	1545w	265m	300m
$Hg(PST)_2Cl_2$	1725m	1605s 1500w	1095s	1320m 1150s	830m	1540w	260m	305m

Abbreviations: Same as in Table I(a) δNH_2 of the Drug/Complex.

Magnetic Measurements

All the copper(II) complexes of sulfadrugs are normal paramagnetic and the μ_{eff} values lie in the range 1.80—1.90 B. M. in agreement with the observed values for one unpaired electron in copper(II) complexes[14].

Infrared Spectra

Because of resonance contributions from NH_2 and NH groups in the sulfadrugs, the ν NH bands at 3500—3300 cm^{-1} due to anilino NH_2 group[15] in sulfadrugs shifted to the lower or the higher frequency side in the complexes upon coordination cannot be assigned satisfactorily. Positive evidence of coordination through anilino NH_2/succinyl group, however, is provided by the $\delta NH_2/\nu C{=}O$ band, which shows a negative shift of about 20—40 cm^{-1} in the Cu(II) and Hg(II) complexes of sulfamethazine and succinylsulfathiazole. But $\nu C{=}O$ due to phthalyl group in the Cu(II) and Hg(II) complexes of phthalylsulfathiazole remains unshifted indicating that the phthalyl group does not take part in coordination.

The phenyl ring stretching vibrations[15] at ~1600 and 1500 cm^{-1} in suldrugs are unaffected or slightly shifted to higher frequencies in the complexes. The substituent-sensitive aromatic mode[16] appearing in sulfadrugs at 1100—1090 cm^{-1} is observed unchanged in all the complexes, which signifies that the phenyl group is not involved in bonding to the metal.

The asymmetric and symmetric —SO_2-group stretching vibrations in sulfadrugs are observed at 1340—1320 and 1160—1150 cm^{-1}, respectively[15,16]. The $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ vibrations are not appreciably altered in the spectra of the complexes. The ν S—N band[16] observed at 840—830 cm^{-1} in sulfadrugs remains unperturbed in the complexes. The above observations suggest that the sulphonyl group does not participate in coordination.

The heterocyclic ring stretching vibrations[17] appearing in sulfadrugs at 1580—1575 cm^{-1} shift to 1560—1540 cm^{-1} in all the complexes, showing coordination of heterocyclic ring nitrogen/sulphur to the metal. The C—S stretching frequency generally appears as a band of weak or moderate intensity in the 720—570 cm^{-1} range[18]. The ν C—S appearing in succinyl- and phthalylsulfathiazole at 730 cm^{-1} is observed unshifted in the complexes, suggesting that only the heterocyclic ring nitrogen is involved in coordination.

The ν Cu—N[19] and ν Hg—N[20] bands in Cu(II) and Hg(II) complexes (where ligand is a heterocyclic base) have been reported at 270—240 and 280—220 cm^{-1}, respectively. In view of the above assignments for ν M—N, the non-ligand bands in sulfadrug complexes occurring at 270—260 cm^{-1} have been attributed to ν M—N (heterocyclic ring nitrogen).

The ν Cu—Cl serves to distinguish between tetrahedral and octahedral complexes of the same stoichiometry, the ν Cu—Cl in pseudo-tetrahedral copper(II) complexes occurs at 305—319 cm^{-1}, [21] while for octahedral complexes it occurs below 200 cm^{-1}. In the present study, the absence of ν Cu—Cl in the range for pseudo-tetrahedral copper(II) complexes indicates a possibility of octahedral structure, which is further supported by the electronic spectra of the copper(II)- sulfadrug complexes discussed previously. In $HgCl_2$-sulfadrug complexes, the terminal ν Hg—Cl and bridging ν Hg—Cl are reported at 320—290 and 220 cm^{-1}, respectively[22,23]. The ν Hg—Cl observed at 310—330 cm^{-1} in the Hg(II)-sulfadrug complexes are in good agreement with the frequencies normally associated with terminal Hg—Cl stretching modes in tetrahedral structures. Thus, the structures of these Hg(II) complexes are tetrahedral.

Acknowledgement. — One of the authors (J. K. G.) thanks the Council of Scientific and Industrial Research, New Delhi, for financial assistance.

REFERENCES

1. P. G. Stetcher, *The Merck Index of Chemicals and Drugs,* Merck and Co. Inc. Rahaway, New Jersey, U.S.A., 1960, pp. 992.
2. C. L. Fox, *Arch. Surg.* **96** (1968) 184.
3. C. L. Fox, S. M. Modak, and J. W. Stanford, *Surg. Cynecol. Obstet.* **142** (1976) 553.
4. C. L. Fox, S. M. Modak, and J. W. Stanford, *Burns.* **4** (1978) 233.
5. C. L. Fox, S. M. Modak, J. W. Stanford, and P. L. Fox, *Scand. J. Plast. Reconstr. Surg.* **13** (1979) 89.
6. A. Rose and E. Rose, *The Condensed Chemical Dictionary,* Reinhold Publishing Corporation, New York, 1966, pp. 903.
7. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis,* Longmans Green, London, 1962.
8. A. Earnshaw, *An Introduction to Magneto Chemistry,* Academic Press, London, 1968.
9. W. J. Geary, *Coord. Chem. Rev.* **7** (1971) 81.
10. J. M. Vandenbelt and L. Doub, *J. Am. Chem. Soc.* **66** (1944) 1633.
11. J. Lewis, Y. C. Lin, R. K. Royston, and R. C. Thompson, *J. Chem. Soc.* (1965) 6464.
12. I. G. Ross, M. L. Tonnet, and S. Yamada, *Trans Faraday Soc.* **60** (1964) 840.
13. T. M. Dunn, *Modern Coordination Chemistry, The Visible and Ultraviolet Spectra of Complex Compounds,* Edited by J. Lewis, Interscience, New York, 1960.
14. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry,* Interscience, New York, 1980.
15. K. Nakanishi, *Infrared Absorption Spectroscopy,* Nankodo Co. Ltd., 1962, pp. 216.
16. M. Goldstein, M. A. Russell, and H. A. Williams, *Spectrochim. Acta* **25A** (1969) 1275.
17. C. N. R. Rao, *Applications of Infrared Spectroscopy,* Academic Press, New York and London, 1963.
18. I. F. Trotter and H. W. Thompson, *J. Chem. Soc.* (1946) 481.
19. M. Goldstein, E. F. Mooney, A. Anderson, and H. A. Gebbie, *Spectrochim Acta* **21** (1965) 105.
20. I. S. Ahuja and A. Garg, *J. Inorg. Nucl. Chem.* **34** (1972) 1929.
21. R. J. H. Clark, *Halogen Chemistry,* Vol. III, Edited by V. Gutmann Academic Press, London, 1967.
22. G. E. Coates and D. Ridley, *J. Chem. Soc.* (1964) 166.
23. I. S. Ahuja and P. Rastogi, *J. Chem. Soc. (A),* (1970) 2161.

SAŽETAK

Kompleksi bakra(II) i žive(II) sa sulfametazinom, sukcinilsulfatiazolom i ftalilsulfatiazolom

J. K. Gupta i N. K. Jha

Pripravljeni su novi kompleksni spojevi tipa $MLCl_2$, gdje je M = Cu(II), Hg(II), a L = sulfametazin (SZ) ili sukcinilsulfatiazol (SST), kao i spojevi ML_2Cl_2, gdje je M = Cu, Hg(II), a L = ftalilsulfatiazol (PST). Spojevi su karakterizirani kemijskom analizom, molarnom vodljivošću, UV-vidljivom i infracrvenom spektroskopijom. Molarna vodljivost upućuje na neelektrolitsku prirodu spojeva, a elektronski i infracrveni spektri na oktaedarsku koordinaciju spojeva bakra(II) i tetraedarsku koordinaciju spojeva žive(II).