Asian Journal of Chemistry Vol. 16, No. (2) (2004), 853–856

Synthesis of the Complexes of $S_3N_3Cl_3$ with Cadmium(II) and Mercury(II)—Part I

SHUBHA RANI and S.P.S. JADON*
Department of Chemistry, S.V. College, Aligarh-202 001, India
E-mail: ad_sp@yahoo.com

The complexes of $S_3N_3Cl_3$ with Cd(II) and Hg(II), synthesized and analyzed, are assigned as $(S_3N_3Cl_3)_4Cd(CH_3COO)_2$ and $S_3N_3Cl_3 \cdot HgCl_2$, possessing paramagnetic nature due to $5sp^3d$ and $6sp^3$ hybridization in subsequent metals and forming quadridentated and bidentated complexes coordinated through Chlorine atom of $S_3N_3Cl_3$ ring to metal ions

Key Words: Trithioaryl trichloride, Synthesis, Cd^{2+}, Hg^{2+}, Paramagnetic, Semiconductive.

INTRODUCTION

The reactions of $S_3N_3^-$ ion and $S_3N_3Cl_3$ trithioazyl trichloride (TTTCl) with various aromatic derivatives have been reported[1–4]. Since TTTCl has a six-membered ring, having lone pairs on all atoms, it may act as a donor. The complexes of TTTCl with some metal compounds have been synthesized and studied[5–7]. In this sequence, the investigations of the complexes of $S_3N_3Cl_3$ with Cd(II) and Hg(II), prepared, are being reported here.

EXPERIMENTAL

Trithioazyl trichloride (TTTCl) was synthesized[8] by passing dry Cl_2 gas into CS_2 solution of S_4N_4[9] (4 g) kept at 0°C. The resulting blue solid was washed with CS_2, ethanol and ether successively. The complexes of $S_3N_3Cl_3$ with Cd(II) and Hg(II) were prepared by refluxing, equimolar solutions of $Cd(CH_3COO)_2$ (500 mg) and $HgCl_2$ (500 mg) with $S_3N_3Cl_3$ (500 mg) dissolved in DMF separately for 24 h. The coloured solid products formed were filtered, washed with DMF and ethonal followed by ether and stored in vacuum desiccator. Quantitative estimations for constituent elements were exercised gravimetrcally by well described methods[10]. Mass, IR, UV and EPR spectra of the complexes were carried out subsequently on Mass Jeol SX102/DA, 820/PC (KBr), Perkin-Elmer-Lambda-15 and Varians, E-109X band (3400–5000 G) spectrometers.

RESULTS AND DISCUSSION

The complexes of $S_3N_3Cl_3$ (TTTCl) with Cd(II) and Hg(II) are termed as SB_1 and SB_2 throughout the present work. The complex SB_1 is orange having % found (calcd.) as S 31.58 (31.80), N 13.80 (13.90), Cl 35.10 (35.25), C 3.95 (3.90), H 0.49 (0.50), O 5.30 (5.35), Cd 9.24 (9.30) and m.w. 1209.2 (1208.4) g mol^{-1} assigning it as $(S_3N_3Cl_3)_4 \cdot Cd(CH_3COO)_2$; while the complex SB_2 is black, possessing the % found (calcd.) as S 18.50 (18.60), N 8.10 (8.10), Cl 34.35 (34.40), Hg 39.10 (38.90) and m.w. 516.45 (516.10) g mol^{-1} which formulates it as $S_3N_3Cl_3 \cdot HgCl_2$.

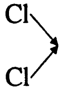
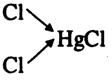
To confirm the molecular formulae of the complexes their mass spectra (Table-1) show some common mass lines (m/z); 107, 137, 242 and 273 for $S_3N_3^+$ ion, $S_3N_3Cl_3$ (M-2) and $S_3N_5Cl_3$ (polymeric form) respectively. The other m/z ratio in mass spectrum of SB_1 subsequently (m/z) 381, 424, 468 and 497 are corresponding to $S_3N_3Cl_3{\cdot}Cd(CH_3COO)$, $S_4N_4Cl_3{\cdot}Cd(CH_3COO)$ (M-2), $S_4N_3Cl_3{\cdot}Cd(CH_3COO)_2$ (M-3) and $S_4N_4Cl_4{\cdot}Cd(CH_3COO)$ fragments explaining the linkage of more than one $S_3N_3Cl_3$ ring to $Cd(CH_3COO)_2$ and inferring above mentioned molecular formula for the complex SB_1. The mass spectrum of SB_2 also possesses m/z 307, 443 and 518 beside the common m/z ratio; consequently for the  $\begin{matrix}\mathrm{Cl}\searrow\\ \mathrm{Cl}\nearrow\end{matrix}\mathrm{HgCl}$, $S_3N_3Cl_3{\cdot}Hg$ (M-1) and $S_3N_3Cl_3{\cdot}HgCl_2$ (M-3) fragments agreeing with the gravimetrical results and molecular formulae.

TABLE-1
MASS SPECTRA OF THE COMPLEXES

S.No.	Cd(II) TTTC		Hg(II) TTTC	
	Mass lines (M/e) ratio	Fragments	Mass lines (M/e) ratio	Fragments
1.	107	3Cl	107	3Cl
2.	138	S_3N_3	137	S_3N_3 (M-1)
3.	155	$(N{-}S{-}N)_2Cl$	157	$(N{-}S{-}N)_2Cl$
4.	227	$(S{-}N{-}S{-}Cl)_2$	273	$S_3N_5Cl_3$
5.	242	$S_3N_5Cl_3$	289	$S_4N_4Cl_3$
6.	273	$S_3N_5Cl_3$	307	 $\begin{matrix}\mathrm{Cl}\searrow\\ \mathrm{Cl}\nearrow\end{matrix}\mathrm{HgCl}$
7.	351	$S_3N_3Cl_2{\cdot}Cd(CH_3COO)$	391	$(N{-}S{-}N)_2Cl{\cdot}HgCl$
8.	381	$S_3N_3Cl_2{\cdot}Cd(CH_3COO)$		
9.	424	$S_4N_4Cl_2{\cdot}Cd(CH_3COO)$	443	$S_3N_3Cl_3{\cdot}Hg$
10.	468	$S_4N_3Cl_2{\cdot}Cd(CH_3COO)_2$	518	$S_3N_3Cl_3{\cdot}HgCl_2$
11.	497	$S_4N_4Cl_4{\cdot}Cd(CH_3COO)$		

Further, to expound the nature of linkage between $S_3N_3Cl_3$ ring and metal compounds, their IR spectra are elucidated. The vibrations at 410.8, 518 and 557.4 cm^{-1} for four N—S—Cl→Cd and 408 and 557.4 cm^{-1} due to two N—S—Cl→Hg bands in the IR spectra of SB_1 and SB_2 subsequently observed expressing quadridentated and bidentated coordination in them. The fequencies at 1109, 1155, 1314 and 1402.3 cm^{-1} in IR spectrum of SB_1 corresponding to N—S—Cl bands of $S_3N_3Cl_3$ ring have appeared, while assignments in the IR spectrum of SB_2 are found at 1103.2, 1157.2, 1300 and 340 cm^{-1} for N—S—Cl bands. Thus the molecular formulae of both complexes established by their mass spectra are corroborated by their IR spectra.

The electronic spectra (Table-2) of complexes show only one peak at 205.6 (SB_1) and 204.6 (SB_2) nm according to charge transfer transition of metal ions, Cd^{2+} and Hg^{2+} respectively. The absence of other transitions, mainly *pπ-pπ* which should appear due to $S_3N_3Cl_3$ ring, indicate the coordination of $S_3N_3Cl_3$ with metal ion as L →M. This view is also supported by the values of oscillator strength 'f' (1.01 and 1.1) × 10^{-4} and Dq × 10^{-3} as 2.50 and 2.30 for SB_1 and SB_2, consequently expressing sping-orbital coupling, *i.e.*, exchange of electrons from Ligand→Metal. The low values of band gap energy (ΔE 1.55 and 1.48 ev) and conducting electrons (Table-2), suggest that complexes are semiconductive.

TABLE-2
ELECTRONIC AND E.P.R. SPECTRAL DATA OF THE COMPLEXES

	Complexes	
	Cd(II) TTTC	Hg(II) TTTC
Electronic Spectral Data		
Band assigned e (nm)	205.6	204.6
Oscillator f × 10^{-4}	1.01	1.11
Dq × 10^3 (cm^{-1})	2.50	2.38
ΔEg (ev)	1.55	1.48
$n_e \times 10^5$	1.34	1.76
E.P.R. Spectral Data		
Hs (Gauss)	4066.7	4040
g_{av}	1.66	1.674
μ_{eff} (B.M.)	2.07	2.10
$\chi_A \times 10^{-3}$	1.79	1.84
No. of unpaired	2	2

The broad peak of high intensity observed in the e.p.r. spectra of the complexes shows the paramagnetic character of both complexes of cadmium and mercury, which generally form diamagnetic complexes, while $S_3N_3Cl_3$ is also diamagnetic in nature. This abnormal behaviour of the complexes depicts the presence of two unpaired electrons on metal ions as defined by the values of μ_{eff}: 2.07 and 2.10 BM and $\chi_a \times 10^{-3}$: 1.79 and 1.84 for SB_1 and SB_2, and it can only be explained if $5sp^3d$ and $5sp^3$ hybridisation in Cd^{2+} and Hg^{2+} respectivly occurred, retaining two unpaired electrons in each metal ion after the quadrdentated and bidentated coordination of $S_3N_3Cl_3$ with Cd^{2+} and Hg^{2+}, inferring tetragonal pyramidal structure of SB_1 and distorted tetrahedral geometrical array of SB_2 as expressed by Figs. 1 and 2.

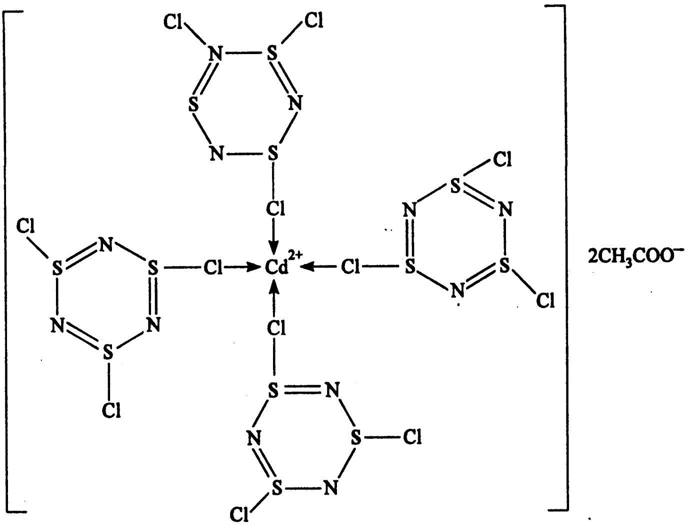


Fig. 1. Structure of $(S_3N_3Cl_3)_4 \cdot Cd(CH_3COO)_2$

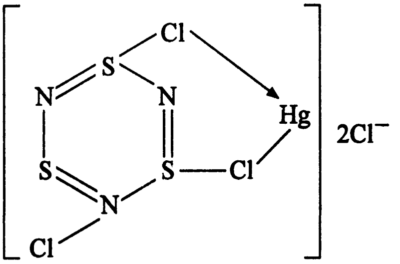


Fig. 2. Structure of $S_3N_3Cl_3 \cdot HgCl_2$

ACKNOWLEDGEMENTS

Authors thank the Director CDRI Lucknow, Chairman, Department of Chemistry, IIT Kanpur and Principal, S.V. College, Aligarh to provide instrumental and laboratory facilities.

REFERENCES

1. A.J. Banister, *J. Chem. Soc. Dalton Trans.*, 2793 (1990).
2. S. Shi, T.J. Katz, B.V. Yang and L. Liu, *J. Org. Chem.*, **60**, 1285 (1965).
3. T. Mohan, P. Senthival and M.N.S. Rao, *Indian J. Chem.*, **34A**, 961 (1995).
4. A. Sundermann and W.W. Schoellar, *Inorg. Chem.*, **38**, 6261 (1999).
5. S.P.S. Jadon, *Asian J. Chem.*, **12**, 1139, (2000); *J. Bangladesh Acad. Sci.*, **24**, 135 (2000).
6. A. Agrawal and S.P.S. Jadon, *Asian J. Chem.*, **13**, 1525 (2001).
7. S. Rani and S.P.S. Jadon, *J. Indian Chem. Soc.* (2003) (in press).
8. J. Nelson and H.G. Heal, *Inorg. Nucl. Chem. Lett.*, **6**, 429 (1970).
9. M.B. Goehring, *Quart. Rev.*, **10**, 437 (1956).
10. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, ELBS, London (1968).

(*Received*: 21 July 2003; *Accepted*: 12 December 2003) AJC-3281