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^{1}H NMR and X-ray Diffraction Investigations of the Complex of S_4N_3Cl with HgCl

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On the basis of ^{1}H NMR and X-ray diffractometric studies, the complex of S_4N_3Cl with HgCI, formulated as $(S_4N_3ClHgCl)_2$ is found to be a bidentate coordinated complex with a triclinic geometrical structure.

Key Words: **^{1}H NMR, XRD, Complex, S_4N_3Cl, HgCl**

INTRODUCTION

Out of various halogenated adducts[1–4] of S_4N_4,[5] thiotrithiazy monochloride was reported to be ionic in nature in solution. The molecular conformation as S_4N_3Cl has also been established as monochlroride, but its complexes with metal compounds have neither been synthesized nor studied. Both S and N atoms of S_4N_3Cl have the tendency to donate electron pairs; therefore a complex of S_4N_3Cl with HgCl has been prepared and investigated by ^{1}H NMR and X-ray diffraction.

RESULTS AND DISCUSSION

On the basis of chemical data the complex is formulated as $(S_4N_3Cl\cdot HgCl)_2$.[6] Since nuclear magnetic momenta 'I_n' of Cl(1/2) and N(1) are multiples of that of H(1/2), the ^{1}H NMR technique was used. Its ^{1}H NMR spectrum (Fig. 1) has a triplet at 1.119 ppm and doublet at 1.252 ppm indicating three N—S bands linked at a point N atom of S_4N_3Cl and to different S—Cl bands because only Cl shows spin along with the presence of S—Cl of S_4N_3Cl ring (Table-1). A broad peak at 3.456 ppm for the coordination of S_4N_3Cl ring with HgCl is found in ^{1}H NMR spectrum along with further repetition of peaks in high region expressing the presence of another S_4N_3Cl ring attached to the HgCl ring confirming its molecular formula and structure (Fig. 2). Because broadening of peak (+ν) by 51.747 Hz explains the exchange of electrons from ligand to metal (L → M) inferring the coordination of the ligand to metal. The values of spin-orbital coupling constant J (Table-1) also support the coordination of S_4N_3Cl with HgCl forming its complex. Theoretically for a compound having S—N and chlorine atom there must be seven singlets, a triplet and a doublet, due to N—S coordinated complex. Further, to confirm the structure of the complex, its X-ray diffraction spectrum was recorded and the values of hkl and d(A) (Table-2) were determined. From these the values of axial ratios and axial angles (Table-3) calculated, are according to the triclinic packing of the complex. The values of different bonds and bond

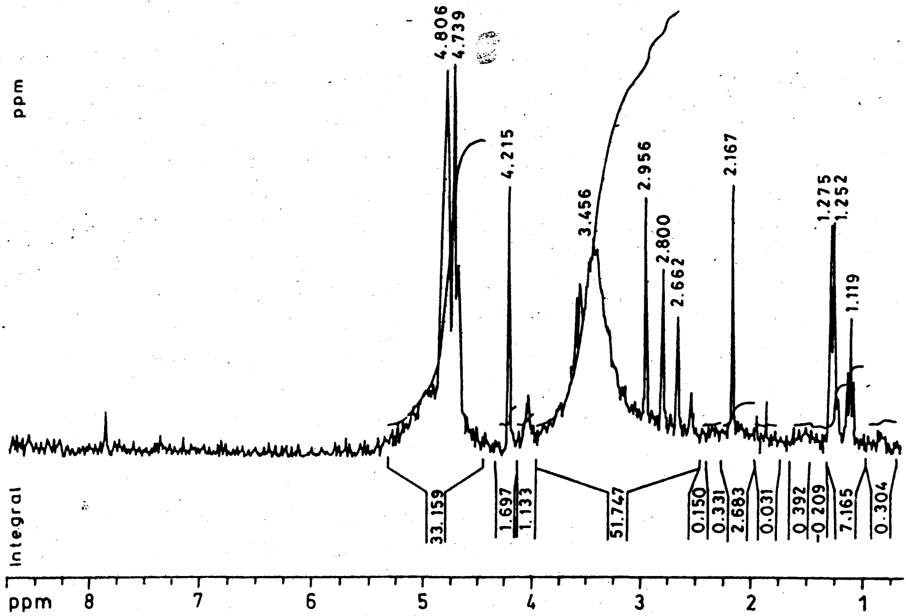

Fig. 1. ^{1}H NMR spectrum of the complex

TABLE-1
^{1}H NMR SPECTRAL DATA OF THE COMPLEX

S.No	Frequency (Hz)	Chemical shift δ (ppm)	τ (10 – δ)	J (Hz)
1.	282.942	1.119 (trip.)	8.881	40
2.	321.525	1.252 (doub.)	8.748	7
3.	334.386	1.275	8.725	268
4.	591.606	2.167	7.833	148
5.	745.938	2.662	7.338	41
6.	784.521	2.800	7.200	47
7.	823.104	2.956	7.044	150
8.	964.575	3.456	6.544	228
9.	1196.073	4.215	5.785	157
10.	1350.405	4.739	5.261	20
11.	1376. 127	4.806	5.194	—

angles are nearly approximate to the values given in the literature, supporting the geometrical structure of $(S_4N_3Cl{\cdot}HgCl)_2$ (Fig. 2).

TABLE-2
X-RAY SPECTRAL DATA OF THE COMPLEX

S. No.	Intensity	$2\theta_{in}$(O)	$\sin^2\theta$	$(h^2 + k^2 + l^2) \times Q$	hkl	d(Å)$_{observed}$	d_{hkl}(Å)
1.	96.70	21.26	0.0340	0.0340 × (1)	100	4.179824	4.179824
2.	40.99	23.56	0.0417	0.0417 × (1)	100	3.776623	3.776623
3.	38.37	24.73	0.0459	0.0459 × (1)	100	3.599853	3.599853
4.	33.72	27.37	0.0560	0.0280 × (2)	110	3.258012	2.304110
5.	45.86	29.53	0.0650	0.0325 × (2)	101	3.025127	2.139410
6.	35.07	32.07	0.0763	0.0382 × (2)	011	2.790656	1.973589
7.	42.49	33.10	0.0811	0.0270 × (3)	111	2.706318	1.562539
8.	43.78	36.97	0.1006	0.0335 × (3)	111	2.431660	1.403961
9	32.08	48.03	0.1556	0.0331 × (5)	210	1.894326	0.847194
10.	27.81	51.06	0.1857	0.0310 × (6)	211	1.788654	0.730063
11.	27.96	59.68	0.2476	0.0310 × (8)	220	1.549418	0.547498

TABLE-3
AXIAL DISTANCE AND ANGLES OF THE COMPLEX

S. No.	a_0 (Å)	b_0 (Å)	c_0 (Å)	α_{in}(O)	β_{in}(O)	γ_{in}(O)
1.	4.177407	3.461280	1.941693	125.305	140.600	94.096
2.	3.772057	3.125418	1.753283	125.305	140.600	94.096
3.	3.595340	2.978996	1.671144	125.305	140.600	94.096
4.	4.603279	3.814145	2.139642	91.809	121.050	147.140
5.	4.272722	3.540255	1.985996	91.809	121.050	147.140
6.	3.941074	3.265461	1.831844	91.809	121.050	147.140
7.	4.687750	3.884135	2.178905	140.599	85.904	133.496
8.	4.208466	3.487014	1.956130	140.599	85.904	133.496
9.	8.467638	7.016042	3.935828	144.250	76.842	138.466
10.	8.749746	7.249789	4.066955	119.348	102.137	138.907
11.	8.749746	7.249789	4.066955	138.247	129.022	92.729

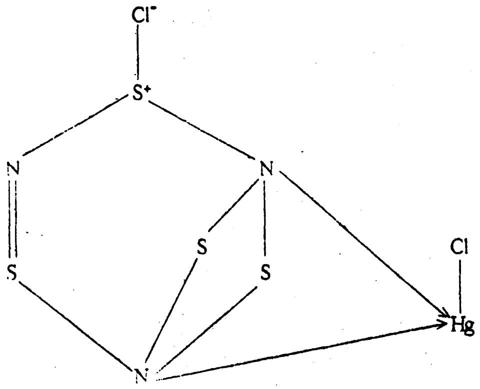

Fig. 2. Structure of complex $(S_4N_3Cl{\cdot}HgCl)_2$

EXPERIMENTAL

To synthesize S_4N_3Cl the S_4N_4, used as starting material, was prepared by passing dry ammonia gas into S_2Cl_2 solution as reported by Goehring and Jolly and others[7–12]. The orange needle-shaped crystalline solid (S_4N_4) was treated with acetyl chloride to get S_4N_3Cl. The change in orange color to light yellow indicates the formation of S_4N_3Cl, which was separated, washed with alcohol and ether successively and stored in a vacuum desiccator. On reaction with HgCl, S_4N_3Cl yielded $(S_4N_3Cl.HgCl)_2$. ^1H NMR spectrum was recorded on Bruker DRX300 NMR spectrometer and the X-ray diffraction pattern was graphed on ISO Debyeflex 2002 diffractometer in the 2θ range (10°–59°) using CuK_α as source of radiation (λ = 1.5414 Å).

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