

NOTE

Synthesis and Spectral Investigation of the Complex of S_4N_3Cl with $Fe(CH_3COO)_2 \cdot 4H_2O$

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On the basis of its mass, IR and XRD spectra, the complex of S_4N_3Cl with $Fe(CH_3COO)_2$ synthesized, is found to be a hexadentately coordinated complex, having triclinic geometrical array.

Key Words: Synthesis, Spectral, $Fe(CH_3COO)_2 \cdot 4H_2O$, S_4N_3Cl .

A variety of chlorine adducts of S_4N_4 such as $S_3N_3Cl_2$, S_3N_3Cl , $S_3N_4F_2$, $S_4N_4Br_4$, S_4N_3Cl and $SNCl$ etc. have been reported¹⁻⁸. Jadon^{9, 10} reported the formation of the complexes of $S_3N_3Cl_3$ with Cu^{2+} and $ThCl_4$ under varying conditions and suggested that complexes are metal bridged coordinated complexes, instead of ionic. The investigations of the complex of S_4N_3Cl with $Fe(CH_3COO)_2$ are being reported herewith.

The complex of S_4N_3Cl with $Fe(CH_3COO)_2$ is a red coloured solid, soluble in organic solvents and decomposes on heating. The chemical data, % found (calcd.) S 33.61 (33.78), N 11.03 (11.08), H 1.57 (1.58), Cl 9.32 (9.37), C 12.60 (12.67), O 14.70 (14.78), Fe 14.66 (14.74) and its molecular weight 380.8 (378.85) g/mol, lead to assign it as $S_4N_3Cl \cdot Fe(CH_3COO)_2$ which is confirmed by its mass spectrum. The peak at m/z 152 for $Fe(CH_3COO)_2$, 185 for $S_2N_2Cl \cdot Fe(M^{2+})$, 225 for $SNCl \cdot Fe(CH_3COO)_2$ and 262 for $S_4N_3Cl \cdot Fe$ found in its mass spectrum, indicate that S_4N_3Cl has linked to $Fe(CH_3COO)_2$ during the refluxion, forming its complex.

The frequencies found in its IR spectrum (Table-1) at 405, 416.6 and 457.1 cm^{-1} for three $S-N \rightarrow M$ indicate that three N-atoms of S_4N_3Cl ring have coordinated to iron atom. Vibrations at 561.2, 792.7 and 889.1 cm^{-1} for three $N-S \rightarrow M$ indicate that three S-atoms of S_4N_3Cl ring have also coordinated to iron atom, inferring that S_4N_3Cl has coordinated hexadentately to Fe^{2+} ion. Bands in 1126.4 cm^{-1} and 1629.7 cm^{-1} region are for $N-S-Cl$ groups.

The electronic spectra of the complex have two bands at 367.3 and 200 nm, out of which the former peak corresponds to $\pi\pi^*$ transition of S_4N_3Cl while the latter band at 50000 cm^{-1} is according to charge transfer transition caused by the presence of Fe^{2+} and Cl^- ions. The values of D_q 2277.2 cm^{-1} and band gap energy ($\Delta E_g = 1.415$ eV) suggest the exchange of electrons forming a coordinated complex.

From X-ray powder diffraction patterns of complexes, Miller indices, intensity

ratio and value of $d(\text{\AA})$ (Table-2) are determined. The values of axial distance a_0 9.468, b_0 8.345, c_0 9.251 \AA and axial angles α 121.12, β 117.26, γ 122.23 calculated, suggest that the complex has triclinic structure, while the intensity ratio I/I_0 explains its amorphous form. Hence the structure of the complex is as proposed in Fig. 1.

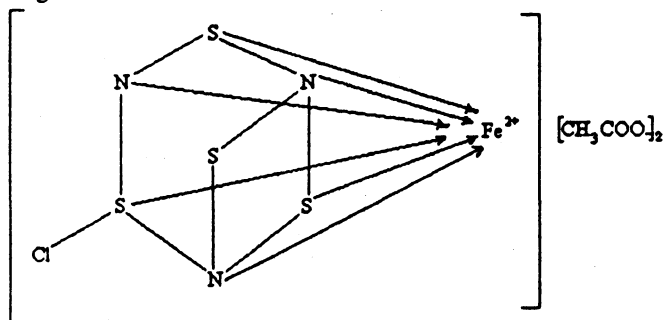


Fig. 1. Structure of $S_4N_3Cl \cdot Fe(CH_3COO)_2$

TABLE-1
IR SPECTRAL DATA OF COMPLEX $S_4N_3Cl \cdot Fe(CH_3COO)_2$

S.No.	Vibrations (cm^{-1})	Assignments of bands	Force constant $k \times 10^5$ (dyne/cm^2)
1.	405.0	S—N → M	0.805
2.	416.6	S—N → M	0.852
3.	457.1	S—N → M	1.025
4.	561.2	N—S → M	1.546
5.	617.2	S—N ring	1.870
6.	792.7	N—S → M	3.085
7.	889.1	N—S → M	3.881
8.	1126.4	N—S—Cl	5.733
9.	1629.7	N—S—Cl	12.001
10.	3141.8–3903	δ -S—N	5.491

S_4N_3Cl was prepared by boiling S_4N_4 with acetyl chloride in CCl_4 for 5 min. The light yellow product formed was separated. To synthesize the complex, S_4N_3Cl (1 g) and $Fe(CH_3COO)_2$ (1 g) were dissolved in DMF separately. After this both the solution were mixed and refluxed for 24 h. The mass deposited was separated, washed with DMF, ethanol and ether, subsequently dried and stored on fused $CaCl_2$ in a vacuum desiccator. The molecular weight was determined by Rast's method, using camphor as solvent. The complex was estimated gravimetrically as well as mass spectrometrically and recorded on Jeol SX 102/D. Mass spectrometer IR, UV and XRD spectra were carried out on Shimadzu-8201 PC, UV-Vis on Perkin-Elmer (200–800 nm) and Philips PW 3710 spectrometers using Cu_α as source of radiation ($\lambda = 1.542 \text{\AA}$) in 2θ range 3–80° respectively.

TABLE-2
X-RAY PATTERN OF COMPLEX $S_4N_3Cl \cdot Fe(CH_3COO)_2$

S.No.	2θ (degrees)	$\sin^2 \theta$	d (Å)
1.	3.935	0.001176	22.478
2.	15.075	0.0172	5.8810
3.	19.405	0.0284	4.5756
4.	21.550	0.0349	4.1252
5.	28.400	0.0602	3.1440
6.	29.420	0.0645	3.0367
7.	32.435	0.0780	2.7604
8.	34.195	0.0864	2.6224
9.	39.005	0.1114	2.3097
10.	49.105	0.1726	1.8556

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