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Synthesis and Characterization of the Complex of S_4N_3Cl with $Ni(CH_3COO)_2{\cdot}4H_2O$

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On the basis of its mass, IR and XRD spectra, the complex of S_4N_3Cl with $Ni(CH_3COO)_2{\cdot}4H_2O$ synthesized, is found to be a quadridentately coordinated complex, having triclinic geometrical array.

Key Words: Synthesis, Ni(II) complex, S_4N_3Cl.

INTRODUCTION

Jolly *et al.*[1] reported the formation of S_4N_3Cl by the reaction of S_2Cl_2 or acetyl chloride with S_4N_4. The complex ion reaction of S_4N_3Cl with $HgCl_2$ has also been reported[2]. The studies of complex of S_4N_3Cl with $Ni(CH_3COO)_2{\cdot}4H_2O$ are being reported.

RESULTS AND DISCUSSION

For the complex of S_4N_3Cl with $Ni(CH_3COO)_2{\cdot}4H_2O$, prepared:

Analytical data %: found (calcd.): S 28.18 (28.21), N 9.26 (9.24), H 3.08 (3.086); Cl 7.81 (7.82), C 10.56 (10.58), O 28.28 (28.21), Ni 12.91 (12.93) and molecular weight 454.21 (459.17) g/mol are according to its molecular formula $S_4N_3Cl{\cdot}Ni(CH_3COO)_2.4H_2O$.

The mass spectrum of the complex possesses mass peak at m/z ratio 198 for $SNCl{\cdot}NiCH_3COO^-$ (m + 1), 202 for $SN_3Cl{\cdot}Ni$, 213 for $SN_2Cl{\cdot}NiCH_3COO^-$, 253 for $SN_3{\cdot}Ni(CH_3COO)_2$, 257 for $SNCl{\cdot}Ni(CH_3COO)_2$ (m + 1) and 262 for $SN_3Cl_2{\cdot}NiCH_3COO^-$ (m + 1) indicate that S_4N_3Cl has linked to $Ni(CH_3COO)_2{\cdot}4H_2O$ during the refluxion, forming its complex.

Being non-available in lower region, the frequencies for metal ions could not be detected while the mass spectrum shows the presence of metal cations along with their anions. The vibrations at 459 cm^{-1} and 559.3 cm^{-1} for S—N → M indicate that the two N-atoms of S_4N_3Cl ring have coordinated to nickel atom and 621 and 740 cm^{-1} for N—S → M. It means S_4N_3Cl ring has coordinated quadridentately to Ni^{2+} through two N-coordinated S—N and two S-coordinated N—S bonds as shown in Fig. 1. The vibrations for S—N ring and N—S—Cl band are observed in the IR spectrum (Table-1) along with frequencies for CH_3COO^-, S—N—S and O—H groups. The ionic state due to Cl^- and CH_3COO^- is also expounded by its electronic spectrum which possesses only two bands

200 nm for charge transfer transition, showing ionic nature on account of CH_3COO^- and 232.72 nm for $p\pi$-$p\pi$ transition due to S_4N_3Cl ring. The low values of D_q (702.99 cm^{-1}) and band gap energy (ΔE_g = 0.88 Ev) suggested the exchange of electrons forming coordinated complex.

TABLE-1
IR SPECTRAL DATA OF COMPLEX $S_4N_3Cl{\cdot}Ni(CH_3COO)_2{\cdot}4H_2O$

S.No.	Vibrations (cm^{-1})	Assignments of bands	Force constant
1.	459	S—N → M	1.101
2.	559	S—N → M	1.636
3.	621	N—S → M	2.016
4.	740	N—S → M	2.868
5.	985	S—N ring	5.080
6.	1099	N—S—Cl	5.934
7.	1402	N—S—Cl	8.884
8.	1633	CH_3COO^-	24.456
9.	2081	S—S—Cl	5.397
10.	3114	O—H	—

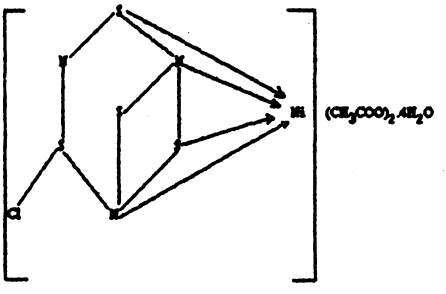

Fig. 1. Structure of $S_4N_3Cl{\cdot}Ni(CH_3COO)_2{\cdot}4H_2O$

From X-Ray powder diffraction patterns of complex, Miller indices, intensity ratio and value of d (Å) (Table-2), axial distances and axial angles {Table-3) have been calculated and it is found that the complex has triclinic geometrical structure, while the intensity ratio I/I_0 explains the amorphous form of the complex.

EXPERIMENTAL

S_4N_3Cl was prepared by Jolly's method[1] (*loc. cit.*). To synthesize the complex, S_4N_3Cl (1 g) and $Ni(CH_3COO)_2{\cdot}4H_2O$ (1 g) were dissolved in DMF and the resultant was refluxed for about 24 h. The change in colour of the solution indicated the complex formation; the green mass formed was filtered, washed with DMF followed by diethyl ether, dried and stored in *vacuo*.

TABLE-2
X-RAY PATTERN OF COMPLEX $S_4N_3Cl \cdot Ni(CH_3COO)_2 \cdot 4H_2O$

S.No.	2θ (degrees)	$\sin^2\theta$	d (Å)
1.	38.895	0.1108	2.3160
2.	40.990	0.1226	2.2022
3.	42.055	0.0287	2.1488
4.	43.805	0.1391	2.0670
5.	44.740	0.1448	2.0257
6.	45.820	0.1515	1.9809
7.	47.970	0.1652	1.8966
8.	49.075	0.1724	1.8569
9.	51.015	0.1854	1.7905
10.	53.170	0.2003	1.7229
11.	54.675	0.2109	1.6790
12.	57.055	0.2281	1.6146
13.	63.265	0.2750	1.4720
14.	70.270	0.3312	2.3278
15.	76.330	0.3818	1.2477

TABLE-3
AXIAL RATIOS AND AXIAL ANGLES OF THE COMPLEX $S_4N_3Cl \cdot Ni(CH_3COO)_2 \cdot 4H_2O$

S.No.	Axial ratios (Å)			Axial angles (degrees)		
	a_0	b_0	c_0	α	β	γ
1.	8.3627	27.0632	87.5814	151.13	104.20	104.70
2.	8.2660	26.7502	86.5684	95.42	103.50	161.00
3.	8.6201	27.8962	90.2771	100.34	101.00	158.65
4.	8.5143	27.5538	89.1690	37.33	168.34	154.34
5.	8.6201	27.8962	90.2771	38.40	165.40	156.00
6.	8.6744	28.0719	90.8457	153.46	106.70	99.86
7.	8.5143	27.5538	89.1690	143.16	84.70	132.30
8.	8.7299	28.2515	91.4269	126.60	124.30	109.27
9.	8.7864	28.4343	92.0185	165.40	169.20	25.46
10.	8.6201	27.8962	90.2771	121.27	102.56	136.18
11.	8.5667	27.7234	89.7179	139.42	76.90	143.70
12.	8.4123	27.0000	88.1008	128.75	146.40	84.86
13.	7.9103	25.5991	82.8433	108.25	119.82	132.00
14.	7.8283	25.3338	81.9847	126.20	136.24	97.56
15.	7.9949	25.8729	83.7293	136.66	100.35	123.00

Quantitative estimations of the complex was done gravimetrically as well as mass spectrometrically. The m.w. was determined by Rast's method. IR spectrum of the complex was recorded on Shimadzu-8201 PC (4000–400 cm^{-1}) at room temperature. Electronic and XRD spectra were graphed on UV-Vis Perkin-Elmer (200–800 nm) and on Philips PW3710 spectrometers using Cu_α as a source of radiation in 2θ range 3–80° respectively.

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