Asian Journal of Chemistry Vol. 16, Nos. 3–4 (2004), 1942–1944

NOTE

X-Ray Diffraction of Cobalt(II) Complex of S_4N_3Cl

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

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

Key Words: X-Ray diffraction, S_4N_3Cl, Co(II), Complex.

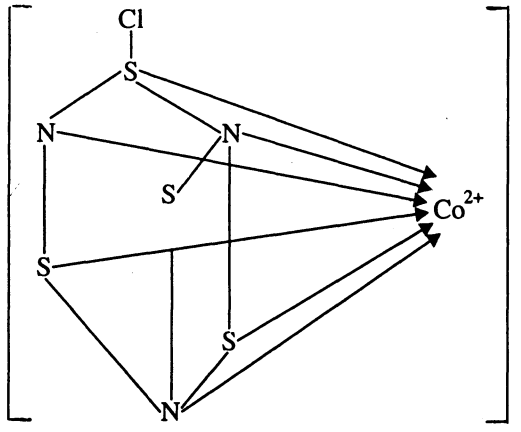
S_4N_4[1] forms a variety of halogenated derivatives[2–10] such as $S_4N_4X_4$, $S_3N_3X_3$ (X = F, Cl), $S_4N_2Cl_2$ and S_4N_3Cl[11, 12]. The complexes of $S_3N_3Cl_3$ with Th(IV), Zr(IV) and Cu(II) have been reported[13, 14]. The studies of complex of S_4N_3Cl with $Co(CH_3COO)_2{\cdot}4H_2O$, prepared, are being reported herewith.

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 $Co(CH_3COO)_2{\cdot}4H_2O$ (1 g) were dissolved in DMF separately. After that, both solutions 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, recorded on Jeol SX102/DA mass spectrometer, IR, UV and XRD spectra were carried out on Shimadzu 8201 PC, UV-Vis, Perkin-Elmer (200–800 nm) and Philips No. PW3710 spectrometers using Cu_α (X = 1.542 Å) as source of radiation in 2θ range 3–80° respectively.

The complex of S_4N_3Cl with $Co(CH_3COO)_2{\cdot}4H_2O$ is a pink coloured solid, soluble in organic solvents and decomposes on heating. The chemical data, found (calcd.): S 28.18 (28.20), N = 9.20 (9.25), Cl = 7.80 (7.82), C = 10.50 (10.55), Co = 12.95 (13.00), H = 3.10 (3.00) and its m.w. 454.20 (454.25) g/mol leads to assign it as $S_4N_3Cl{\cdot}Co(CH_3COO)_2{\cdot}4H_2O$, which is confirmed by its mass spectrum. The peaks at M/Z 200 for $SNCl{\cdot}CoCH_3COO^-$, 213 for $SN_2Cl{\cdot}CoCH_3OO^-$ (M-1), 257 due to $S_2N_3Cl{\cdot}Co(CH_3COO^-)$ and 262 for $S_4N_3Cl.Co$, found in its mass spectrum indicate that S_4N_3Cl has linked to $Co(CH_3COO)_2{\cdot}4H_2O$ during the refluxion, forming its complex.

The vibrations for three S—N → M, three N—S → M, S—N ring, N—S—Cl bands are observed in its IR spectrum (Table-1) along with frequencies for CH_3COO, δ-N—S and OH groups suggesting that S_4N_3Cl has coordinated to $Co(CH_3COO)_2{\cdot}4H_2O$, hexadentatedly through its three S and N atoms as express-

ed in Fig. 1. 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 229 nm for p_π-p_π transition due to S_4N_3Cl ring. The low values of Dq 633.18 cm^{-1} and band gap energy (ΔE_g = 0.79 eV) suggested the exchange of electrons forming coordinated complex.



$(CH_3COO^-)_2 \cdot 4H_2O$

Fig. 1. Structure of $S_4N_3Cl \cdot Co(CH_3COO)_2 \cdot 4H_2O$

TABLE-1
IR SPECTRAL DATA OF THE COMPLEX

Vibrations (cm^{-1})	Assignment of bands	Force constant ($K \times 10^5$ dyne/cm)	Vibrations (cm^{-1})	Assignment of bands	Force constant ($K \times 10^5$ dyne/cm)
435	N—S → M	0.939	1429	N—S—Cl	9.230
455	N—S → M	1.024	1614	CH_3COO^-	
520	N—S → M	1.340	2135	δ-N—S	26.256
615	S—N → M	1.871	2370	δ-N—S	32.384
684	S—N → M	2.318	2484	δ-N—S	45.566
954	S—N → M	4.507	3155	O—H	5.538
983	S—N-ring	4.784	3346	O—H	6.229
1097	N—S—Cl	5.913	3766	O—H	7.892

Further, to illustrate the nature of the complex from its X-Ray diffraction spectrum recorded, the values of sin 2θ, hkl, d (Å) (Table-2), axial distances and axial angles (Table-3) have been calculated and it is found that the complex has triclinical geometrical structure, while the intensity ratio I/I_0 explains the amorphous form of the complex.

TABLE-2
XRD PATTERN OF THE COMPLEX

S.No.	θ (°)	$\sin^2\theta$	$q(h_2 + k_2 + l_2)$	hkl	d (Å)	I/I_0
1.	1.642	0.00082	1 × (0.0008)	100	26.9580	11.1
2.	10.250	0.03166	4 × (0.0079)	200	4.3390	18.9
3.	11.552	0.04010	6 × (0.0067)	211	3.8511	34.3
4.	24.710	0.17474	18 × (0.0097)	411	1.8444	18.9
5.	24.905	0.17733	19 × (0.0093)	331	1.8309	33.6
6.	28.087	0.22166	24 × (0.0092)	422	1.6376	21.5
7.	29.687	0.24528	25 × (0.0098)	500	1.5567	100

TABLE-3
AXIAL RATIOS AND AXIAL ANGLES OF THE COMPLEX

S.No.	a_0 (Å)	b_0 (Å)	c_0 (Å)	α (°)	β (°)	γ (°)
1.	27.2591	15.7366	9.0847	103.00	155.00	102.45
2.	8.6744	4.0885	1.9270	172.17	18.00	169.80
3.	9.4193	20.2474	43.5233	105.30	146.50	108.20
4.	7.8283	4.6897	2.8095	146.24	107.00	106.78
5.	7.9949	13.1719	21.7013	120.54	120.44	119.00
6.	8.0382	13.2433	21.81.89	108.12	146.65	105.40
7.	7.7883	12.8314	21.14.03	27.00	164.73	168.32

REFERENCES

1. M.B. Goehring, *Progr. Inorg. Chem.*, 1207 (1959).
2. R.N. Fordir and G.M. Shelderick, *J. Fluoride Chem.*, **1**, 13 (1971).
3. M.B. Goehring and H.P. Latscha, *Z. Naturforsch.*, **17B**, 125 (1962).
4. N. Logan and W.L. Jolly, *Inorg. Chem.*, **4**, 1508 (1965).
5. A.W. Cordes, R.F. Kruh and E.K. Gordon, *Inorg. Chem.*, **4**, 1 (1965).
6. R.P. Sharma and R.D. Verma, *J. Sci. Ind. Res.*, **40**, 3 (1981).
7. I. Zhorilova, P. Gebauer and J. Sternod, *Z. Chem.*, **19**, 255 (1979).
8. A. Lurowski, R. Appel, W. Sawodney and K. Malt, *J. Mol. Struct.*, **48**, 313 (1978).
9. T. Mohan, P. Senthival and M.N.S. Rao, *Indian J. Chem.*, **34A**, 961 (1995).
10. A. Sundermann and W.W. Schoellar, *Inorg. Chem.*, **38**, 6261 (1999).
11. S. Upadhyay and S.P.S. Jadon, *Asian J. Chem.*, **15**, 1065, 1181 (2003).
12. S.S. Yadav and S.P.S. Jadon, *J. Indian Chem. Soc.*, **79**, 751(2002).
13. S.P.S. Jadon, *J. Bangladesh Acad. Sci.*, **24**, 135 (2000); *Asian J. Chem.*, **12**, 1139 (2000).
14. A. Agrawal and S.P.S. Jadon, *Asian J. Chem.*, **13**, 1525 (2001).

(*Received*: 23 December 2003; *Accepted*: 10 June 2004) AJC-3474