

NOTE

Synthesis and Characterization of Cd(II) Complex of S_4N_3Cl

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Cadmium(II) complex of S_4N_3Cl was prepared by refluxing the mixture of S_4N_3Cl and cadmium acetate in DMF. The chemical data assigned the complex as $(S_4N_3Cl)_2Cd(OOCCH_3)_2$. The spectroscopic data infer that the complex is quadridentate coordinated complex having triclinic geometrical structure.

Key Words: S_4N_3Cl , Cd(II), Complex.

$S_4N_3Cl^1$ is the most stable adduct of $S_4N_4^2$, out of its various halogenated derivatives^{3–11}. But, few complexes of these halogenated derivatives have been synthesised and reported^{12, 13}. In the present note we describe the synthesis of S_4N_3Cl and its spectral properties.

The complex of S_4N_3Cl with $Cd(OOCCH_3)_2$ is a light yellow coloured solid soluble in water and decomposes on heating. On the basis of its analytical data, % found (calcd.), S 39.72 (39.91), N 13.03 (13.10), Cl 11.02 (11.07), Cd 17.44 (17.50), CH_3COO^- 18.30 (18.40) and m.w. 644.5 (641.42), the complex has been formulated as $(S_4N_3Cl)_2 Cd(CH_3COO)_2$ which is also supported by its mass spectrum, showing mass fragments at m/z 289 for $(S_4N_3Cl-N-S-Cl)$ ($M+2$), 424 for $S_4N_3ClCd(CH_3COO)_2$ ($M+2$), 527 for $S_4N_3ClCd(CH_3COO)_2-S_2N_2$, 589 for $S_4N_3Cl-Cd(CH_3COO)_2-S_3N_4$ and 645 for $(S_4N_3Cl)_2Cd(CH_3COO)_2$ ($M+3$) fragments, suggesting that two molecules of S_4N_3Cl have linked to one molecule of $Cd(CH_3COO)_2$ forming quadridentate complex and confirming its above mentioned molecular formula.

The IR spectrum of the complex (Table-1) is compared to that of ligand vibrations at 435 cm^{-1} (w, b) for two $N-S \rightarrow Cd$ and 1066 (b, d) cm^{-1} for two $S-N \rightarrow Cd$ bands have been observed, explaining quadridentate complex ion of S_4N_3Cl ring to Cd^{2+} ions alongwith the presence of the frequencies at 1402 cm^{-1} for $N-S-Cl$, 1657 and 2343 (b) cm^{-1} for CH_3COO^- bands. The assignments in higher region for δ ($S-N$) bands have been found, expressing that the complex is Cd^{2+} ion bridged complex between two S_4N_3Cl rings possessing sandwich structure.

Further to expound the nature of the complex, its electronic spectrum was recorded. Two peaks at 200, 236 nm were observed. Out of them the former band is due to the charge transfer transition caused by Cd^{2+} and CH_3COO^- ions, while the latter assignment is on account of $p\pi-d\pi$ transitions of S_4N_3Cl ring. The value of oscillator strength 'f' is of the order of 10^{-5} for spin allowed Laport forbidden transition, i.e., for spin-orbital coupling, the coordination of S_4N_3Cl with Cd^{2+}

ion is occurring. No signal was observed in its EPR spectrum, suggesting its diamagnetic character.

TABLE-1
IR (cm^{-1}) SPECTRAL DATA OF $(S_4N_3Cl)_2Cd(OOCCH_3)_2$

Vibrations	Assignments	Force constants $K \times 10^{-5}$ dynes/cm ²
410 s	(S—Cl)	1.887
435 wb	(N—S→M)	0.858
617 s	(S—N free)	2.193
1066 b	(S—N→M)	6.549
1402 b	N—S—Cl	8.889
1657 b	—OOCCH ₃	—
2343 b	—OOCCH ₃	—
2825 w, s	δ (S—N)	45.957
2881 w, s	δ (S—N)	47.797
2927 s	δ (S—N)	49.342
2989 s	δ (S—N)	51.447
3039–3290 b	δ (S—N)	62.320

From the X-ray diffraction pattern of the complex, the values of 'd', ' d_{hkl} ', axial ratios and axial angles (Table-2) are calculated and it is inferred that the complex possesses triclinic geometrical structure (Fig. 1).

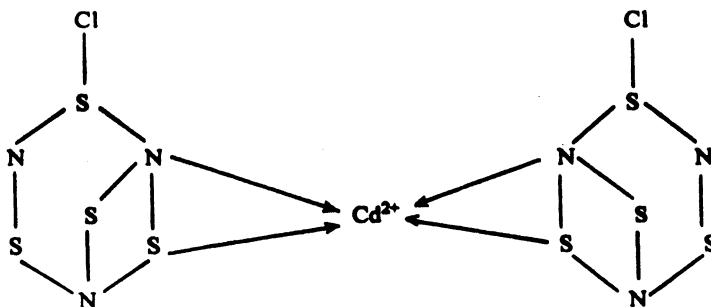


Fig. 1. Structure of $(S_4N_3Cl)_2Cd^{2+}$ Complex ion.

S_4N_4 and S_4N_3Cl were prepared by Jolly and Geohring's method^{14, 15}. The complex was synthesised by refluxing the mixture of S_4N_3Cl (0.5 g) and $Cd(CH_3COO)_2$ (0.5 g) in DMF for about 24 h. When the light yellow colour changed into orange, the product formed was separated, washed, dried and stored in vacuum desiccator over fused $CaCl_2$. The spectrometric investigations were carried out on Jeol SX 102 (FAB) mass spectrometer, Shimadzu 8201 P.C. IR and Hitachi 320 Perkin-Elmer-Lambda 15 UV/Vis spectrophotometers respectively, while XRD pattern was graphed on Debye-Flex 2002 diffractometer in 2θ range using $CuK\alpha$ as source of radiation.

TABLE-2
XRD PATTERN OF THE COMPLEX

Unit cell parameters	d (Å) (observed)	d _{hkl} (Å)
2θ(°) = 20.46, 22.85, 25.0,	4.3405	4.3405
26.69, 28.53, 33.76	3.8914	3.8915
37.25, 38.84, 41.63	3.5556	3.5556
43.97, 48.31, 52.24	3.3402	2.3623
a ₀ = 6.1499 Å	3.1285	2.2125
b ₀ = 5.0956 Å	2.6548	1.5328
c ₀ = 2.8585 Å	2.4139	1.3937
α = 124.193°	2.3184	1.1592
β = 107.770°	2.1693	1.0847
γ = 127.937°	2.0591	0.9209
Volume = 89.579 Å ³	1.8840	0.8426
Density = 11.946 g/cm ³	1.7510	0.7147

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