

NOTE

Synthesis and Characterization of Copper(II) Complexes with Tetrathioazoic Acid

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Copper(II) complex of tetrathioazoic acid (S_4N_3H) was prepared by refluxing the equimolar mixture of S_4N_3H and copper carbonate in DMF. The spectrometric data expound that the complex, assigned as $[(S_4N_3H)_2 \cdot CuCO_3]_{6.76}$ is quadridentated polymerized complex having Cu^{2+} bridged geometry.

Key Words: Synthesis, Characterization, Complex, Cu(II), Tetrathioazoic acid.

Various hydrides of $S_4N_4^1$ have been reported^{2–6} but the tetrathioazoic acid, neither reported nor its complex, have been synthesized. Therefore, S_4N_3H is used to prepare the complex of Cu(II) and its studies are being presented.

S_4N_3H was prepared by using S_4N_4 as starting material. S_4N_4 was prepared by passing dry ammonia gas into the solution of S_2Cl_2 in CCl_4 kept at $0^\circ C$. S_4N_4 was treated with acetyl chloride to get S_4N_3Cl . The brownish yellow product formed dissolved in benzene and was reduced by Sn/HCl . The bright yellow mass formed was separated, washed with benzene, ethanol and ether successively, dried and stored in vacuum.

To prepare the complex of S_4N_3H with copper carbonate, equimolar mixture of 0.5 g of each was dissolved in DMF and refluxed for about 12 h. The dark blackish-green product formed was separated, washed, dried and stored in a vacuum desiccator over fused $CaCl_2$. The spectrometric investigations were carried out on Jeol SX-102 (FAB) mass spectrometer, Perkin-Elmer RXI ($4000–450\text{ cm}^{-1}$) IR, Perkin-Elmer Lambda-15 (200–800 nm) UV/Vis and Bruker DRX-300 (300 MHz, FT-NMR) 1H NMR spectrometers at room temperature.

The chemical data of the complex: % found (calcd.): S 55.04 (54.34), N 18.07 (18.07), H 0.43 (0.43), Cu 13.64 (13.66), C 2.58 (2.58), O 10.23 (10.32) and m.w. 3141.6 (3142.23) g/mol, formulated it as $[(S_4N_3H)_2 \cdot CuCO_3]_{6.76}$ which is supported by mass spectrum showing mass lines at m/z 207 for $S_4N \rightarrow Cu(M+1)$, 465 due to $(S_4N_3H)_2CuCO_3$ and 994 for $[(S_4N_3H)_2 \cdot CuCO_3 \cdot S]_2$ fragment suggesting that two molecules of S_4N_3H have linked with copper carbonate. The mass lines m/z at 1361 due to $[(S_4N_3H)_2 \cdot CuCO_3]_3 \cdot S(M-2)$, 1532 for $[(S_4N_3H)_2 \cdot CuCO_3]_3 \cdot S \cdot S_4N_3H$ and 1683 for $[(S_4N_3H)_2 \cdot CuCO_3]_4 \cdot S_2(M-1)$ infer polymeric form of the complex and its molecular formula.

The IR spectrum of the complex is compared to that of ligand (Table-1).

TABLE-1
IR SPECTRAL DATA OF THE COMPLEX $[(S_4N_3H)_2 \cdot CuCO_3]_{6.76}$

S.No.	Vibrations (cm^{-1})		Bands assigned	Force constant ($K \times N \ m^2 \ s^{-1}$)
	Ligand	Complex		
1.	461.9 (s)	—	S—N	1.229
2.	—	505.4 (b, d)	S—N→M	1.471
3.	—	585.3 (s)	S—N→M	1.973
4.	668.2 (s)	—	S—N	2.572
5.	—	749.7 (s)	S—N	3.237
6.	831.5	—	S—N-ring	3.982
7.	—	817.4 (s)	S—N	3.348
8.	—	878.4 (s)	S—N	4.444
9.	—	1045.5 (s)	S—N—H	25.830
10.	—	1097.9 (s)	S—N—H	28.485
11.	1103.6 (b)	—	S—N—H	28.781
12.	1397.5	—	S—N—H	46.152
13.	—	1391.5 (s)	S—N—H	45.760
14.	1623.6 (s)	—	N—H	15.738
15.	—	1492.3	CO ₃ ²⁻	52.630
16.	2092.1 (b)	—	N—H	26.130
17.	—	2138.6 (b)	N—H	27.305
18.	2361.0 (s)	—	N—H	33.279
19.	—	2355.3 (s)	N—H	33.119
20.	—	2909.6 (b)	N—H	50.541
21.	—	3317.0 (b)	N—H	65.686
22.	—	3376.2 (s, w)	N—H	68.051
23.	3411.0 (s)	—	N—H	69.461
24.	—	3531.2 (s)	N—H	74.443
25.	—	3715.0 (b, d)	N—H	82.395
26.	—	3795.4 (s, w)	N—H	85.999
27.	—	3931.1 (s, w)	N—H	92.259

The frequency at 461.9 (w) cm^{-1} found in the ligand diminished in the complex showing the coordination of the ligand as S—N→Cu while peaks at 668.2 cm^{-1} found in the ligand have also diminished showing the occurrence of N—S→Cu bands and the other frequencies are 817.4 (s), 878.4 (s) cm^{-1} for S—N ring, 1045.5 (s), 1391.5 (s) for S—N—H bands, 1492.3 (s) cm^{-1} for CO₃, 1634.2 (s), 2183.6 (b) for N—H and 3317.0 (s) 3531.2 (s), 3715.0 (b, d) due to δ (N—H) band, which has coordinated to Cu²⁺ ion.

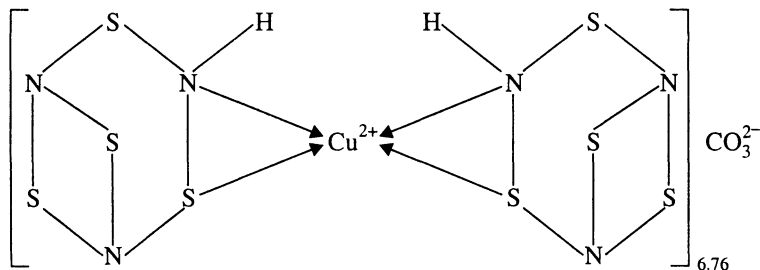


Fig. 1. Proposed Structure of the complex, $[(S_4N_3H)_2CuCO_3]_{6.76}$

Further, to expound the nature of the complex, its electronic spectrum recorded shows four peaks at 262.2, 334.4, 390.4 and 649.6 nm out of which the band 262.2 nm is due to the charge transfer, which is also supported by frequency ratio $\nu_1/\nu_2 < 2$ and the band 334.4 nm which can be attributed to ${}^2T_{2g} \leftarrow {}^2E_g$ transition as Cu^{2+} complex, while the 390.4 and 649.6 nm bands are corresponding to σ and π bands of S—N ring of S_4N_3H , coordinated to $CuCO_3$.

The value of band gap energy in the range of 0.26–0.63 eV and the number of conductive electron (ηc) in the range of $0.40\text{--}7.4 \times 10^5$ are according to the powerful conductive nature of the complex.

1H NMR spectrum of the ligand possesses 12 signals at 6.955–7.610 ppm due to N atom N—H band, reduced to five signal and shifted at the range 7.07–8.02 ppm in the complex, showing the coordination of N—H band to Cu^{2+} ion. The other signals in the ligand appear 5.660 and 5.668 (doublet) due to H atom are diminished in the complex and the range 3.624–4.353 ppm observed in the ligand has also shifted down 0.20–4.22 in the complex, inferring and stretching in the S—N ring due to attachment of N atoms to the Cu^{2+} ion indicating that out of three N atoms of S_4N_3H , two N atoms are coordinated to Cu^{2+} ion. But the appearance of signals is of symmetrical nature suggesting the symmetrical linkage of two S_4N_3H molecules to $CuCO_3$ by forming quadridentated polymeric complex of Cu^{2+} bridged geometry.

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