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NOTE

Mass and ^{1}H NMR Spectra of the Fe(II) Complex of $S_3N_2H_2$

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The complex of trithioazyl dihydride, ($S_3N_2H_2$) with Fe(II), prepared by refluxing the mixture of $S_3N_2H_2$ and ferrous sulphate in DMF, was analyzed quantitatively and spectrometrically. The chemical data assigned the complex as $(S_3N_2H_2)_2$ $FeSO_4 \cdot 7H_2O$. The spectroscopic data inferred that the complex is hexadentated coordinated complex.

Key Words: Trithioazyldihydride, Fe(II), Complex.

Some hydrides of $S_4N_4^1$ such as $S_4N_4H_4$, S_7NH and S_4N_3H and their complexes with metals have been reported[2–9]. No report is available in literature on $S_3N_2H_2$ and its metal complexes. Therefore it is proposed to prepare $S_3N_2H_2$ and its complex with Fe(II) compound and to investigate their nature, molecular composition and geometrical structure by spectroscopic methods.

$S_3N_2Cl_2$ was prepared by Roesky's method[10], although its formation was reported[11] by the reaction of S_2Cl_2 on S_4N_4 which was synthesized by Jolly's method[12]. On Na/alcoholic reduction, $S_3N_2Cl_2$ produced $S_3N_2H_2$. The complex of $S_3N_2H_2$ with Fe(II) was synthesized by refluxing DMF solution of $S_3N_2H_2$ and $FeSO_4$ separately and subsequently after mixing with $S_3N_2H_2$ solution for about 12 h. The light orange coloured mass, precipitated, was filtered, washed successively with DMF, ethanol and ether, dried and stored *in vacuo*.

Mass, IR, UV and ^{1}H NMR spectra of the complex were graphed consequently on Jeol Sx-102 (FAB), Shimadzu 8201 PC (400–4000 cm^{-1}), Perkin-Elmer Lambda-15 (200–800 nm) and Bruker DRX-300 (300 MHz) spectrometers from C.D.R.I. Lucknow.

The complex is light orange coloured solid, soluble in water and phenol. Its melting point is 154.2°C. The analytical data, % found (Calcd.): S 42.53 (42.26), N 10.63 (10.56), H 3.43 (3.40), Fe 10.63 (10.57) and m.w. 526.7 (530) g/mol, leads to assign it as $(S_3N_2H_2)_2 \cdot FeSO_4 \cdot 7H_2O$, which is confirmed by the mass lines m/z at 244 for $(S_3N_2H_2)$—S—N—N—Fe 273 due to $(S_3N_2)FeSO_4$ (M-3) 324 on account of $(S_3N_2H_2)$—S—N—$FeSO_4$ fragments along with other fragments found in its mass spectrum (Table-1), inferring that the ligand is coordinated to $FeSO_4$ without emiting its hydrogen atom during the reaction.

TABLE-1
MASS AND IR SPECTRA OF THE COMPLEX $(S_3N_2H_2)_2 \cdot FeSO_4 \cdot 7H_2O$

Mass parameters		I.R. Spectral data		
M/z	Fragments	Vibrations (cm^{-1})	Bonds assigned	Force const. kN/m^2
149	(S_2N_2)—Fe	621.2 (q)	ν(N—S→Fe)	1.8935
171	(S_3N_2H)—S—N	1089.1 (b)	ν(S—N→Fe)	5.8201
226	$(S_3N_2H_2)$—S—N—Fe(M-2)	1144.7 (b)	ν(S—N—H)	0.7027
244	$(S_3N_2H_2)$—S—N—N—Fe	1402.5 (s)	ν(N—H)	1.0856
258	(S_3N_2)—S_2N—Fe	1637.7 (b)	δ (N—H)	1.4802
273	$(S_3N_2)FeSO_4$(M-3)	2365.4 (d)	δ (N—H)	3.0880
308	(S_3N_2)—S—$FeSO_4$(M-2)	3168.6 (b)	ν(O—H)	12.6571
324	(S_3N_2)—S—N—$FeSO_4$			

To confirm the complex formation, its IR spectrum recorded is interpreted. The vibrations at 621 cm^{-1} a broad quadrant peak is for N—S→Fe band shifted from the lower region as found in ligand. The band at 1089 cm^{-1} is also for the S—N→Fe while the vibrations in high region (Table-1) are due to ν(S—N—H), δ (N—H) and ν(O—H) stretchings, suggessting that $S_3N_2H_2$ has coordinated to Fe atoms through both S and N atoms forming hexadentated complex with Fe bridged sandwich geometry (Fig. 1).

The two peaks at 200 nm (50000 cm^{-1}) due to charge transfer transitions caused by Fe^{2+} ions and 223.2 nm (44802 cm^{-1}) for the d_{π}-p_{π} transition of S_3N_2 ring have accrued in its electronic spectrum. The disapearance of the other bands expounds the coordinate linkage of $S_3N_2H_2$ to $FeSO_4$.

During the reaction of $S_3N_2H_2$ with $FeSO_4$ it may be possible that H_2SO_4 may be formed and it must be filtered off. Then the complex should not show any signals in its proton NMR spectrum but experimentally it is found that the proton NMR spectrum of the complex consists of two sets of four signals in the range of the chemical shift δ 1.216–2.1419 ppm in lower region and δ 6.4861–7.0399 ppm and higher region for N—H bands having these signals to each side of signals for the water molecule at the chemical shift δ 4.7972 ppm (959.43 H_2) main signal with 14 ether signals for 14 protons confirming the occurrence of two N—H groups on each side of $FeSO_4$, *i.e.*, two $S_3N_2H_2$ molecules have coordinative hexadentatively to Fe^{2+} ions (Fig. 1).

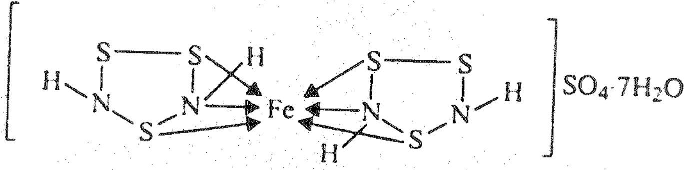

Fig. 1. Proposed structure of the complex $(S_3N_2H_2)_2 \cdot FeSO_4 \cdot 7H_2O$

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