Asian Journal of Chemistry Vol. 19, No. 5 (2007), 4115-4117

NOTE

Synthesis and Characterization of Ni(II) Complex of $S_3N_2H_2$

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On the basis of quantitative estimations, mass IR, UV and ^{1}H NMR spectra, the complex of $S_3N_2H_2$ with Ni(II) compound, has been assigned as $(S_3N_2H_2)_2 \cdot NiSO_4 \cdot 6H_2O$, having quardidentated co-ordinated, Ni^{2+} ion bridged sandwich geometrical structure.

Key Words: Ni(II), $S_3N_2H_2$, Complex.

The complexes of hydride adducts of S_4N_4[1] have been synthesized and reported[2-9]. In continution of our previous work[10], the spectral investigations of the complex of $S_3N_2H_2$ with Ni(II) compound are being reported.

First of all $S_3N_2Cl_2$, as orange coloured solid, was prepared by action of thiourea with S_2Cl_2 by Roesky's method[11]. On Na/EtOH reduction $S_3N_2Cl_2$ was changed to bright yellow mass, confirmed as $S_3N_2H_2$ by its mass and IR spectra. The complex of $S_3N_2H_2$ with Ni(II) was synthesized by refluxing DMF solutions of $S_3N_2H_2$ and $NiSO_4$, for about 12 h. The dark green coloured product, was separated, washed subsequently with DMF, EtOH and ether, dried and stored in vacuum desiccator over fused $CaCl_2$.

Quantitative estimations for constituents were done as described[12], m.w. and m.p. were determined by well known methods (*loc.cit.*).

Mass IR, electronic and ^{1}H NMR spectra of the complex were carried out 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 FT-NMR) spectrometers.

The complex is green coloured solid, soluble in DMSO and melts at 120.2ºC. The chemical data of the complex; % found, S 43.90 (43.50), N 10.95 (10.87), H 3.14 (3.11), Ni 11.57 (11.46) and m.w. 509.80 (515.00) $gmol^{-1}$ leads to assign it as $(S_3N_2H_2)_2 \cdot NiSO_4 \cdot 6H_2O$, which is supported by the prominent mass lines observed at m/z, 149, 167, 178, 209, 232, 252, 279 and 308 subsequently for the (S_2N_2) - Ni (M-2), $(S_2N_2H_2)$-Ni-N, S_2N_2-Ni-N_2 (M-1), (S_3N_2)-Ni-N_2 (M-2), $(S_3N_2H_2)$-Ni-S-N (M+1), $(S_3N_2H_2)_2$,

$(S_3N_2)\cdot NiSO_4$ and $(S_3N_2)_2\cdot Ni$ (M+1) fragments in its mass spectrum (Table-1), suggesting that two molecules of $(S_3N_2H_2)$ have linked to one mol of $NiSO_4\cdot 6H_2O$ during the reaction, producing the quadridentated complex.

To confirm the nature of bonding, its IR spectrum (Table-1), recorded, is compared to that of ligand, $(S_3N_2H_2)$. The presence of bands, N—S→Ni, S—N→Ni, S—N—H, N—H, O—H and SO_4^{2-} ions are inferred by the consequent vibrations at 631 (d), 760 (bw), 1102 (sw), 1628, 3371, 984 (sw) cm^{-1}, explaining the $S_3N_2H_2$ has coordinated to Ni^{2+} ion through its both S and N atoms.

TABLE-1
MASS AND IR SPECTRA OF THE COMPLEX $(S_3N_2H_2)_2\cdot NiSO_4\cdot 6H_2O$

Mass parameters		IR spectra data		
m/z	Fragments	Vibrations (cm^{-1})	Bands assigned	Force const. K N / m
149	S_2N_2-Ni (M-2)	461ws	SO_4^{2-}	1.0512
167	$(S_2N_2H_2)$-Ni-N	631d	N—S→Ni	1.9723
171	(S_3N_2)-S-N (M+1)	760bw	S—N→Ni	2.8610
178	S_2N_2-Ni-N_2 (M+1)	–	–	–
197	(S_3N_2)-Ni—N	984ws	SO_4^{2-}	4.7881
209	(S_3N_2)-N_2-Ni (M-2)	1102d	S—N—H	0.6511
232	$(S_3N_2H_2)$-S-N-Ni	1401w	S—N—H	1.0837
252	$(S_3N_2H_2)_2$	1628b	N—H	3.0882
279	(S_3N_2)-$NiSO_4$	2365ds	δ N—H	3.0882
308	$(S_3N_2)_2$-Ni (M+1)	3371b	O—H	14.3275

Two peaks at 200 and 240 nm have occured in its electronic spectrum. The former band is due to ionic environment and charge transfer transition, caused by Ni^{2+} ions, while latter assignment is corresponding to d_π–p_π transitions of $S_3N_2H_2$ ring. The absence of other bands which generally appears for Ni^{2+} ions, expound the coordination of $S_3N_2H_2$ molecule to nickel sulphate.

If ionic displacement has occured during the reaction of $S_3N_2H_2$ with $NiSO_4$ librating H_2SO_4, the signals for N—H bands should not appear in its proton NMR spectrum, as observed at the chemical shift, δ 2.5153 to 2.985 ppm for N—H bands as found in amino compounds, expressing the quadridentative linkage of two $S_3N_2H_2$ molecule to nickel sulphate, without evaluation of H_2SO_4 or in its any form. Therefore, geometrical strucutre of $(S_3N_2H_2)_2\cdot NiSO_4\cdot 6H_2O$, may be shown as Fig. 1.

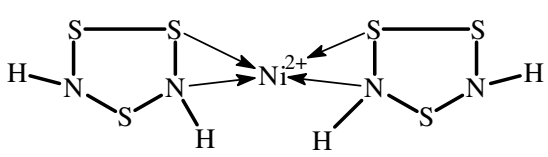

Fig. 1. Proposed structure of the complex $[(S_3N_2H_2)_2 \cdot Ni]SO_4 \cdot 6H_2O$

ACKNOWLEDGEMENT

Authors wish to express their thanks to Dr. K.P. Madhusudanan, CDRI, Lucknow, India for providing instrumental facilities.

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(*Received*: 14 March 2006; *Accepted*: 14 March 2007) AJC-5526