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NOTE

Spectral Characterization of the Co(II) Complex of $S_3N_2H_2$

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Spectral characterization of the Co(II) complex of $S_3N_2H_2$ reveals that the complex formulated as $(S_3N_2H_2)_3CoCl_2{\cdot}6H_2O$ is a hexadentated coordinated complex.

Key Word: Co(II), Complex, $S_3N_2H_2$. Hexadentated, Coordination.

S_4N_4[1] is reduced to form its hydrides such as $S_4N_4H_4$, $S_4N_4H_2$ or S_2N_2H, S_4N_3H, of which the metal complexes have been prepared[2–9]. A new ligand $S_3N_2H_2$ was prepared and its Co^{2+} complex was synthesized and characterized.

$S_3N_2Cl_2$ was prepared by the reaction of S_2Cl_2 on thiourea[10]. The green coloured mass deposited in condenser was separated by refluxing with CCl_4. The $S_3N_2Cl_2$ formed was washed with CCl_4, ethanol and ether and dried. It was dissolved into alcohol and reduced with Na/alcoholic solution. Light yellow coloured product obtained was refluxed in equimolar ratio with $CoCl_2$ in DMF for about 12 h. The brown coloured precipitat, produced was filtered, washed with DMF, ethanol and ether, dried successively and stored in a vacuum desiccator over fused $CaCl_2$.

The quantitative estimations for the constituent elements were done as described[11]. The molecular weight was determined by Rast's method using camphor as solvent.

IR and electronic spectra of the complex were carried out on Shimadzu 8201 PC (400–4000 cm^{-1}), Perkin-Elmer Lambda-15 (200–800 nm), respectively while the mass and ^1H NMR spectra recorded subsequently on Jeol SX-102 (FAB) and Bruker DRX-300 (300 MHz) at room temperature.

The complex is brown coloured solid soluble in chloroform (m.p. 160°C). The chemical data of the complex, % found S 46.46, N 13.55, H 2.90, Cl 11.45, Co 9.52 and m.w. 619.89 gm/mol assigned the complex as $(S_3N_2H_2)_3CoCl_2{\cdot}6H_2O$ which is supported by the mass lines observed in its mass spectrum (Table-1) at m/z 255, 273, 486, 510, 591 and 614 consequently for the $(S_3N_2H)CoCl_2(M+2)$, $(S_3N_2H){\cdot}CoCl_2{\cdot}H_2O$, $(S_3N_2H_2)_2$—$(S$—$N)_2$—$CoCl_2{\cdot}H_2O$, $(S_3N_2H_2)_3CoCl_2$-$(M+2)$, $(S_3N_2)_3$—$CoCl_2{\cdot}5H_2O(M-1)$ and $(S_3N_2H_2)_3$—$CoCl_2{\cdot}6H_2O(M - 2)$ fragments.

The vibrations found in its spectrum (Table-1) at 630, 747 and 984 cm^{-1} are due to N coordinated S—N bands, while the frequencies at 1099 and 1145 cm^{-1} are on account of S—N—H bands. The remaining peaks in higher region are corresponding to ν(N—H), δ(N—H) and ν(O—H) groups present in the complex, indicating that $S_3N_2H_2$ has linked only through its N atom, $CoCl_2$ forming hexadentated coordinated complex. The values of force constants are in support of the aforesaid opinion.

TABLE-1
MASS AND IR SPECTRA OF THE COMPLEX $(S_3N_2H_2)_2\ CoCl_2{\cdot}6H_2O$

Mass paramenters		IR spectral data		
m/z	Fragments	Vibrations (cm^{-1})	Bonds assigned	Force const. (kN/m^2)
149	(S_2N_2)—Co(M − 2)	630 (d)	ν(S—N→Co)	1.9661
209	(S_3N_2)—N_2—Co (M − 2)	747 (bw)	ν(S—N→Co)	2.7655
255	(S_3N_2H)—$CoCl_2$	984 (w)	ν(S—N→Co)	4.7901
273	(S_3N_2H)—$CoCl_2{\cdot}H_2O$	1099	ν(S—N—H)	0.6481
391	$(S_3N_2H)_2$—N—$CoCl_2$(M − 1)	1145	ν(S—N—H)	0.7036
460	$(S_3N_2H)_2$—S—N—$CoCl_2{\cdot}H_2O$	1401	ν(N—H)	1.0844
486	$(S_3N_2)_2$—$(S—N)_2$—$CoCl_2{\cdot}H_2O$	1629	ν(N—H)	1.4646
510	$(S_3N_2H_2)_3$—$CoCl_2$(M + 2)	265	δ(N—H)	3.0882
549	$(S_3N_2H_2)_2$—S—N—$CoCl_2{\cdot}6H_2O$(M − 1)	3251	ν(O—H)	13.3281
591	$(S_3N_2)_3$—$CoCl_2{\cdot}5H_2O$(M − 1)			
614	$(S_3N_2H_2)_3$—$CoCl_2{\cdot}6H_2O$(M − 2)			

Two bands occur in its electronic spectrum, at 200 and 222.4 nm. The former assignment is due to charge transfer transition, showing ionic environment caused by Co^{2+} ions. The latter band is for the p_π-d_π transition of $S_3N_2H_2$ ring. The absence of other transitions infers the coordination of $S_3N_2H_2$ to $CoCl_2$ without displacement reaction or emission of HCl during reflux.

This view gets weightage from its ^1H NMR spectrum recorded and compared to that of the ligand. ^1H NMR spectrum of the complex consists of signals in three different regions, *i.e.*, chemical shift δ 0.0–1.5, 2.5–3.5 and 7.5–8.1 ppm (Table-2). The first and last regions are due to two N—H groups as present in the ligand, while the middle region is caused by the N atoms of S—N ring of $S_3N_2H_2$. The intensity of the signals found in the ^1H NMR spectrum of the complex is reduced along with lowering of the region of the chemical shift, confirming the linkage of three $S_3N_2H_2$ molecules to one $CoCl_2$ molecule. The signals for water are suppressed and do not appear in the ^1H NMR spectrum of the complex.

TABLE-2
^{1}H NMR SPECTRAL DATA OF THE COMPLEX $(S_3N_2H_2)_2CoCl_2\cdot 6H_2O$

S. No.	Frequencies (Hz)	Chemical shift δ (ppm)	τ (10-δ)	J (Hz)
1.	0.08005	–0.0004	10.0004	—
2.	166.76916	0.8333	9.1667	166.8492
3.	251.24445	1.2554	8.7446	84.4753
4.	297.53475	1.4867	8.5133	46.2903
5.	519.34000	2.5950	7.4050	221.8052
6.	597.89140	2.9875	7.0125	78.5514
7.	666.57532	3.3307	6.6693	68.6850
8.	675.06200	3.3731	6.6269	0.4856
9.	687.13000	3.4334	6.5666	12.0679
10.	1515.35200	7.5718	2.4282	828.2221

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