

Synthesis and Characterization of Some Cobalt(III) Complexes Containing Heterocyclic Nitrogen Donor Ligands

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Received 27 November 2001

Accepted for publication 3 December 2002

A number of mixed-ligand complexes of the type *trans*-[Co(DH)₂LCl] where DH = dimethylglyoximate anion, L = heterocyclic nitrogen donor ligand (pyridine, piperidine, quinoline, isoquinoline, triazole, indole, benzimidazole, benzotriazole, carbazole) have been synthesized and characterized. These complexes are not soluble in ordinary organic solvent but highly soluble in dimethylsulfoxide. The conductivity data show the nonelectrolytic nature of the complexes. The IR spectra reveal the coordination from nitrogen of ligand to central cobalt atom and intramolecular hydrogen bonding. ¹H NMR data of dimethylglyoxime and its Co(III) complexes are in agreement with the *trans* structure. The ¹³C NMR spectra of the complexes show a sharp signal for carbon atom in the methyl group. So the four methyl groups in the Co(III) complexes are equivalent and are situated in a plane. The thermal decomposition studies indicate the absence of water of crystallization or association of solvent molecules. This fact is supported by IR measurement. The loss of heterocyclic nitrogen donor ligands does not take place up to 215 °C. The ligand and chlorine atom are bonded strongly. The last product of decomposition is Co₃O₄ or CoO.

Recent literature on the chemistry of cobaloximes indicates that not much attention has been paid to the possibility of studying pyridine, piperidine, quinoline, isoquinoline, triazole, indole, benzimidazole, benzotriazole, carbazole-containing cobaloximes. Cobaloximes [1] contain a bisdimethylglyoximatecobalt(III) moiety - Co(DH)₂⁺ (DH = monoanion of dimethylglyoxime). They are known to stimulate the reactions of vitamin B₁₂ and are important in vitamin B₁₂ model chemistry [2]. The X-ray crystal structure of alkylcobaloxime [3] shows a higher positive charge on cobalt, thus developing a strong bond from a base or from an anion along the axial direction. The above-mentioned heterocyclic nitrogen donor ligands are of considerable interest, as they play important roles in many biological systems. These ligands provide a potential binding site for metal ions.

For proper understanding of interactions between the biologically important cobaloxime and heterocyclic nitrogen donor ligand, we have initiated a program of synthesizing and characterizing the complexes of cobaloxime containing chloride as an axial ligand.

EXPERIMENTAL

All chemicals, including ligands, were anal. grade.

Cobalt [4] and chlorine [5] were determined by reported methods. Elemental analyses were carried out by using an Erba instrument. The UV spectra ($\lambda = 200$ to 500 nm) were taken by Hitachi-320 Perkin—Elmer Lambda-15 instrument in DMSO solution and IR spectra in the $\tilde{\nu}$ region 400—4000 cm⁻¹ were recorded by Perkin—Elmer 783 spectrophotometer by the KBr pellet technique. ¹H NMR and ¹³C NMR spectra in DMSO-*d*₆ were obtained on a Bruker DRX-300 (300 MHz) FT NMR spectrometer using TMS as internal reference. The conductances of the complexes in DMSO solution were measured at room temperature by employing a Systronic 321 conductivity bridge.

Thermal decompositions of the complexes were carried out by using NETZSCH thermal analyzer. Measurements were carried out in an atmosphere of nitrogen by using a platinum crucible with a sample mass of 100 mg in the temperature range of 25—1000 °C. The rate of temperature increase of 10 °C

Table 1. Analytical Data and other Physical Properties of [Co(DH)₂LCl] Complexes I—IX

Compound	L	Formula	M_r	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$					$\Lambda/(\text{S cm}^2 \text{ mol}^{-1})$	M.p. °C
				Co	Cl	C	H	N		
I	py	CoC ₁₃ H ₁₉ N ₅ O ₄ Cl	403.5	14.60	8.73	38.51	4.63	17.32	7.21	>240
				14.62	8.79	38.66	4.7	17.34		
II	pi	CoC ₁₃ H ₂₃ N ₅ O ₄ Cl	409.5	14.35	8.64	38.12	6.18	17.08	11.34	>240
				14.40	8.66	38.09	6.10	17.09		
III	qui	CoC ₁₇ H ₂₁ N ₅ O ₄ Cl	453.5	13.12	7.80	44.72	5.53	15.44	5.25	>240
				13.00	7.82	44.98	5.63	15.43		
IV	isoqui	CoC ₁₇ H ₂₁ N ₅ O ₄ Cl	453.5	13.12	7.80	44.72	5.53	15.44	6.51	>240
				13.00	7.82	44.98	5.63	15.43		
V	tria	CoC ₁₀ H ₁₇ N ₇ O ₄ Cl	393.5	14.54	8.75	30.01	4.32	24.23	21.31	>240
				14.62	8.79	29.73	4.21	24.28		
VI	ind	CoC ₁₆ H ₂₁ N ₅ O ₄ Cl	441.5	13.26	8.71	43.47	4.71	15.75	14.51	>240
				13.36	8.04	43.48	4.75	15.8		
VII	bmz	CoC ₁₅ H ₂₀ N ₆ O ₄ Cl	442.5	13.41	8.06	40.51	4.55	18.78	17.01	>240
				13.33	8.02	40.67	4.51	18.98		
VIII	btz	CoC ₁₄ H ₁₉ N ₇ O ₄ Cl	443.5	13.25	8.13	38.07	4.31	22.21	15.31	>240
				13.30	8.00	37.88	4.28	22.09		
IX	car	CoC ₂₀ H ₂₂ N ₅ O ₄ Cl	491.5	12.06	7.14	48.72	4.63	14.18	13.32	>240
				12.01	7.23	48.87	4.68	14.25		

min⁻¹ was chosen for the measurement. The equipment records TG and DTA simultaneously.

Chloro Cobaloximes [Co(DH)₂LCl] I—IX

To a warm EtOH solution (25 cm³) of CoCl₂·6H₂O (0.5 g; 2 mmol) dimethylglyoxime (DH) (0.5 g; 4.2 mmol) was added. The solution was warmed and stirred for 2—3 min. Then it was cooled and a heterocyclic ligand (2 mmol) (pyridine (py), piperidine (pi), quinoline (qui), isoquinoline (isoqui), triazole (tria), indole (ind), benzimidazole (bmz), benzotriazole (btz), carbazole (car)) was added. It was again warmed and stirred for 2 min. It was then cooled and a steady stream of air was passed through it for 1—3 h (depending on base and substituent). A dark brown solid deposited at the bottom of the flask. The mixture was set aside for 1 h, after which the product was collected on a sintered glass and washed successively with small amounts of EtOH, Et₂O and finally dried *in vacuo*.

RESULTS AND DISCUSSION

All the compounds reported in this work are presented in Table 1 along with their analytical data, melting point and conductivity values Λ at room temperature. The chloro(ligand)cobaloximes are stable and show sign of loss of indole or any other ligand and nonelectrolyte in the different solution (10⁻³ mol dm⁻³) of dimethylsulfoxide, conductances being in the range of 7—21 S cm² mol⁻¹.

The ligand field spectra of complexes in MeOH show a peak of weak to moderate intensity [6] at $\tilde{\nu} \approx 18000$ —20000 cm⁻¹. This is the spin-allowed

Table 2. Prominent IR Bands of *trans*-[Co(DH)₂LCl] Complexes

L	$\tilde{\nu}_i/\text{cm}^{-1}$		
	$\nu(\text{N—O})$	$\nu(\text{Co=O})$	$\nu(\text{Co—N})$
py	1245, 1090	1570	530, 425
pi	1247, 1092	1575	532, 430
qui	1247, 1095	1577	520, 430
isoqui	1245, 1090	1582	525, 432
tria	1235, 1090	1565	525, 430
ind	1224, 1108	1607	507, 446
bmz	1230, 1095	1580	525, 445
btz	1241, 1091	1562	513, 430
car	1248, 1095	1585	528, 430

¹A_{1g} → ¹T_{1g} transition. The ¹A_{1g} → ¹T_{2g} of the *trans*-[Co(DH)₂LCl] complexes is marked by the intense charge-transfer bands. The band occurring at 28000 cm⁻¹ is due to heterocyclic ligand to cobalt metal transition (LMCT). The band [7] at 33.000 cm⁻¹ is due to $d\pi(\text{Co})-\pi^*(\text{DH})$ (MLCT) transition. A band at 40000 cm⁻¹ is due to intraligand $\pi-\pi^*$ transition of the coordinated dimethylglyoxime. The σ DH to σ^* Co(III) (LMCT) is marked by the intense short-wavelength bands of chloro(ligand)cobaloximes.

The free uncoordinated dimethylglyoxime has no band at 1240 cm⁻¹. In the Ni(DH)₂ complex, a band appears [8] at 1240 cm⁻¹ due to $\nu(\text{N—O})$ of the ionized (N—OH) group of dimethylglyoxime [9]. Here in all cobalt complexes, this band [10] is seen in the region of 1224 to 1248 cm⁻¹ and additional band $\nu(\text{N—O})$ appears at $\tilde{\nu} = 1090$ to 1108 cm⁻¹ (Table 2, see Fig. 1). From this it is evident that the N—O bonds of

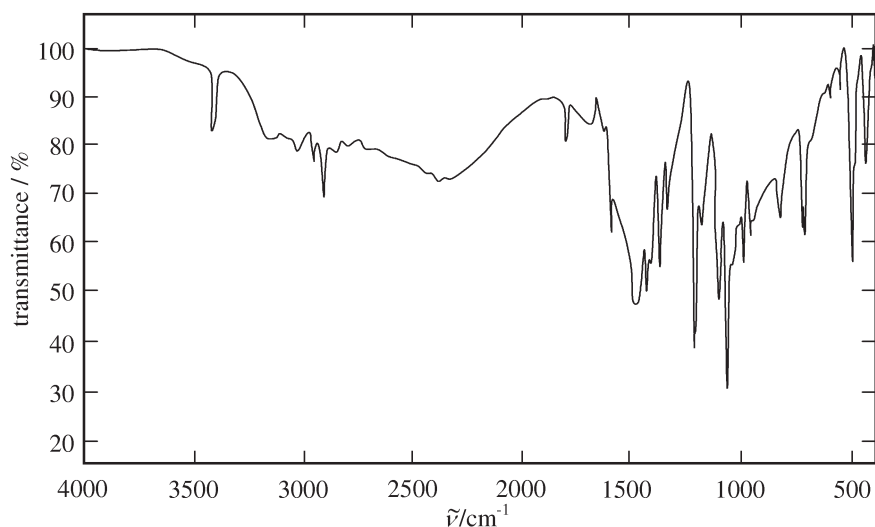


Fig. 1. Infrared spectrum of $[\text{Co}(\text{DH})_2\text{indCl}]$.

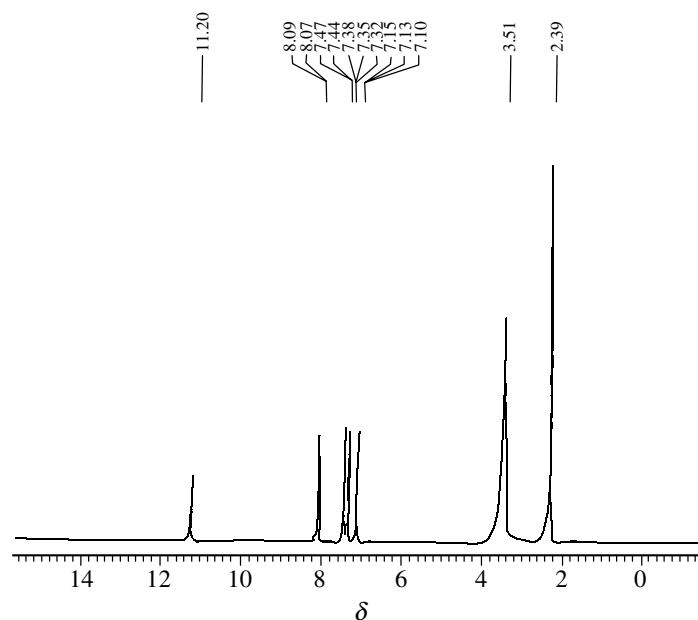


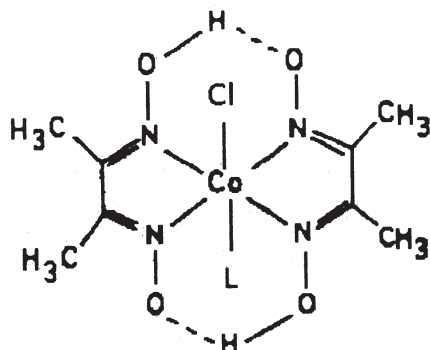
Fig. 2. Part of ^1H NMR spectra of $[\text{Co}(\text{DH})_2\text{carCl}]$.

coordinated dimethylglyoxime are not entirely equivalent. This observation is consistent with the result of X-ray diffraction analysis of $\text{Cu}(\text{DH})_2$ complexes in which two different $\text{Cu}-\text{N}$ distances are observed [11]. The stretching vibration of $\text{C}=\text{N}$ in the pyridine appears at 1590 cm^{-1} . Upon complex formation the peak shifts to higher frequencies, which is confirmed by the bond formation of metal with the nitrogen atom of the respective heterocyclic ring. The weak broad band appearing at around 3410 cm^{-1} belongs to the intramolecular hydrogen bonding and suggests the *trans* configuration [12, 13]. The oxime part ($\text{C}=\text{N}$) takes part in the chelate ring formation in cobalt complexes. The normal stretching vibration $\nu(\text{C}=\text{N})$ of free DH_2 is at $\tilde{\nu} = 1620\text{ cm}^{-1}$. In the present case this band in all

complexes shifted from 1562 to 1607 cm^{-1} . The characteristic band of $\nu(\text{Co}-\text{N}_{\text{DH}})$ appears at 513 cm^{-1} and $\nu(\text{Co}-\text{N}_{\text{ind}})$ band [14] appears at 446 cm^{-1} .

The band involving the metal and chlorine $\nu(\text{M}-\text{Cl})$ has been reported to appear around $\tilde{\nu} = 200$ to 300 cm^{-1} [15, 16]. Due to limitation of our IR instrument this particular band could not be observed. Many examples of such bonding between cobalt and chlorine are known [17, 18]. The ^1H NMR spectra of cobaloxime complexes clearly show that on coordination, the δ due to the CH_3 group of DH_2 at 1.91 undergoes a downfield shift by 0.43 to 2.33–2.41 (see Fig. 2). In all complexes δ appears as a singlet indicating the equivalent of four methyl groups and the presence of *trans* structure. The δ due to OH proton in

dimethylglyoxime appears at 11.33 (Fig. 3). This signal shifted upfield in the complexes appears at around 11.2. The indole proton or other ligand protons also undergo a considerable downfield shift.



The ^{13}C NMR shifts of the chloro cobalt complexes containing indole or other related axial ligand were assigned. The δ due to oxime CH_3 carbon in dimethylglyoxime appears at 9.2. This signal shifted downfield appears at 12.98 on coordination. The δ for imine carbon appears at 154 in free dimethylglyoxime. On coordination this signal shifted upfield appears at 151.5. The δ value of axial ligands in indole complexes generally shifted downfield appears at 39 to 40 (Fig. 4).

All of the observations show the *trans* structure of these indole complexes of the chlorocobaloxime $[\text{Co}(\text{DH})_2\text{indCl}]$. The indole or the other related ligands are bonded to the cobalt atom through their heterocyclic nitrogen.

Thermal decomposition studies indicate the absence of water of crystallization or association of solvent molecules. This fact is supported by IR measure-

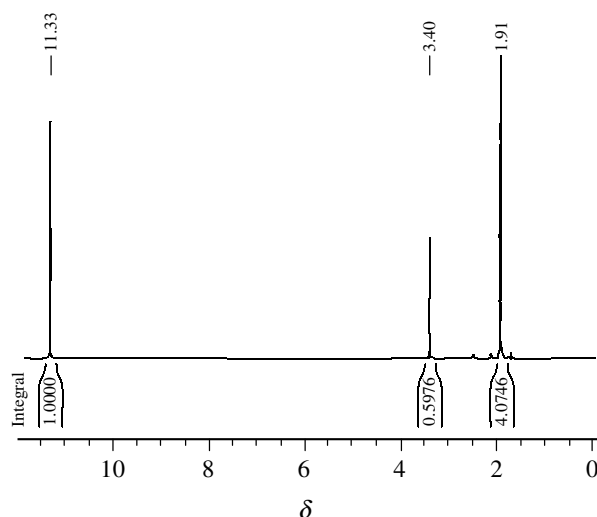


Fig. 3. ^1H NMR spectra of dimethylglyoxime in $\text{DMSO-}d_6$ solution using TMS as internal reference.

ments. The loss of indole, pyridine, *etc.* ligands does not take place up to 215°C . Both the ligand and chlorine are bonded strongly. The final product of decomposition is Co_3O_4 or CoO .

Thermal decomposition data on the compound VI are collected in Table 3. The thermal decomposition of the compounds is a multistage process, the final product of each case was Co_3O_4 . The results of the thermal decomposition of the complexes are compared with the literature results [19].

The TG and DTA curves for the decomposition of $[\text{Co}(\text{DH})_2\text{indCl}]$ are shown in Fig. 5 and other related thermal decomposition data are collected in Table 3. The TG curve indicates that it is thermally

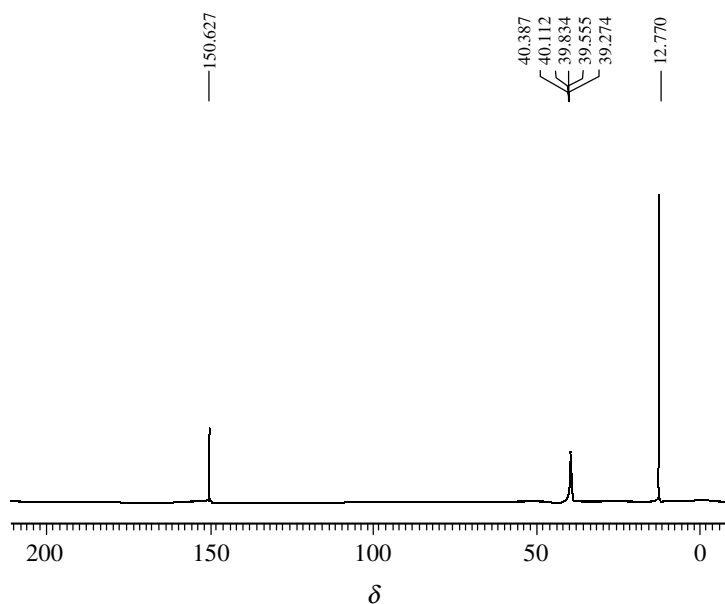
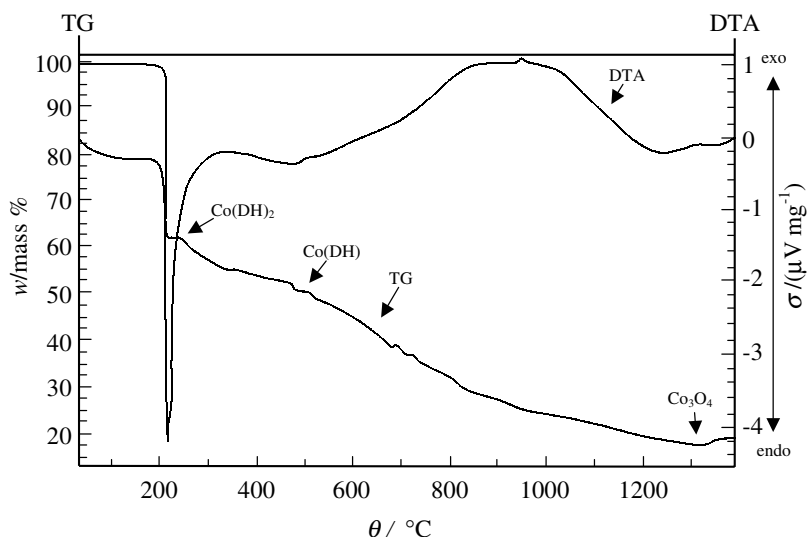


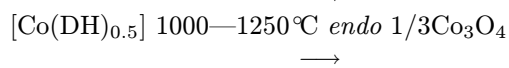
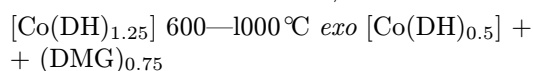
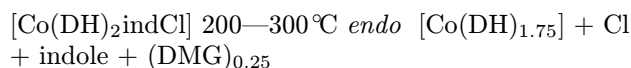
Fig. 4. Part of ^{13}C NMR spectra of $[\text{Co}(\text{DH})_2\text{indCl}]$.

Table 3. Thermal Decomposition Data of Compound $[\text{Co}(\text{DH})_2\text{indCl}]$

DTA $\theta_{\text{peak}}/\text{°C}$	TG $\theta_{\text{range}}/\text{°C}$	Mass loss/% found (calc.)	Loss of Cl, indole, 1/4DH	Composition of residue
216 <i>endo</i>	200—300	41.1 (41.5)		$[\text{Co}(\text{DH})_{1.75}]$
467.3 <i>endo</i>	300—600	13.14 (13.26)	0.5 (DH)	$[\text{Co}(\text{DH})_{1.25}]$
947 <i>exo</i>	600—1000	19.71 (19.81)	0.75 (DH)	$[\text{Co}(\text{DH})_{0.5}]$
1239.9 <i>endo</i>	1000—1250	8.85 (8.48)	Decomposition of DH	$1/3 \text{Co}_3\text{O}_4$

**Fig. 5.** TG and DTA curves of $[\text{Co}(\text{DH})_2\text{indCl}]$, sample mass 100 mg, heating rate 10°C min^{-1} , atmosphere: nitrogen.

stable up to 210°C showing the absence of water in crystal lattice. Afterwards, the TG curve shows four mass loss steps. The first step between 200 to 300°C is accompanied by 41.1% mass loss, attributed to the loss of chlorine atom, indole molecule and 25% of dimethylglyoxime molecules. The second step (300°C — 600°C) and the third step (600°C — 1000°C) are accompanied by mass loss 13.26% and 19.71% , respectively. These two steps may be due to the decomposition of dimethylglyoxime molecules. The last step (1000°C — 1200°C) is accompanied by 8.85% mass loss, at which the complex is converted to metallic oxide. The thermal decomposition reaction of the complex II $[\text{Co}(\text{DH})_2\text{indCl}]$ can be represented as



The DTA curve for the complex (Fig. 5) presents

three endothermic peaks at 200 — 300°C , 300 — 600°C , and 1000 — 1250°C corresponding to removal of chlorine atom of the indole molecule and decomposition of dimethylglyoxime with simultaneous formation of Co_3O_4 . There is an exothermic process at 600 — 1000°C corresponding to decomposition reaction of dimethylglyoxime.

Acknowledgements. The authors thank the authorities of the Regional Sophisticated Instrumentation Centre (RSIC) at IIT (Indian Institute of Technology), Madras for UV and IR spectra and thermogravimetric analysis. Thanks are due to the Regional Sophisticated Instrumentation Centre (RSIC), Lucknow for providing NMR and ^{13}C NMR spectra. One of us (S. C. Nayak) is thankful to the University Grants Commission (UGC), Kolkata Unit for financial support under a minor research project.

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