



Synthesis, characterization and thermal kinetics of multiligand homobinuclear complex of Cobalt(II) with monoethanolamine as a bridging ligand

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ABSTRACT

Multiligand homobinuclear complex of Cobalt (II) has been synthesized and characterized on the basis of elemental analysis, FTIR, TA and DSC. The complex has been assigned empirical formula as $[\text{Co}(\text{Phen})_2(\text{MEOA})\text{Cl}_4]\text{H}_2\text{O}$. Presence of chloride, monoethanolamine (MEOA), 1,10- phenanthroline (phen.) and metal-metal bond is verified by FTIR absorption peaks. The appearance of ν (M-O), ν (M-N) and ν (M-O-H) bending mode supports the coordination of monoethanolamine via both oxygen and nitrogen, hence acting as a bidentate bridging ligand between two cobalt (II) centers. The coordination of 1, 10-phenanthroline has been proved by antisymmetric vibrations besides fundamental vibrations of coordinated 1,10-phenanthroline. Thermal kinetics of the complex has been studied by TG and DSC techniques. Thermal analysis shows the expulsion of water molecules in the first step below 150°C, which verifies the presence of water as lattice water. The thermal analysis has been carried out in nitrogen atmosphere up to 800°C. Thermograms obtained confirm FTIR data and hence supports the empirical formula. On the basis of thermal data, thermal decomposition mechanism has been proposed for the complex. Thermodynamic parameters like activation energy (E_a), pre-exponential factor (A) and entropy of activation (ΔS^\ddagger) has been calculated for each decomposition step, using Dolye's, Coats and Redfern and Arrhenius method. The trend of these parameters is found to be same for all the methods involved. The reaction enthalpy is obtained from DSC technique. It shows both exothermic and endothermic peaks. The structure as depicted by empirical and FTIR spectroscopy is also proposed.

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Introduction

A lot of work has been carried out on the ethanolamine and mixed ligand complexes of Cu(II), Ni(II), Co(II) and V(IV) (1-2). Complexes of cobalt with moieties like carbaboranes, porphyrins, aspirin, polyaminophenols, polycarboxylates, triazolyl derivatives, terpyridine-bipyridine ligands have got extensive applications as a result of magnetic, electrical, anti-tumour, catalytic, polymer and redox properties (3-8). Cobalt has got an extensive cluster chemistry in forming, homo, hetero, mono, bi- and trinuclear complexes with macrocyclic ligands like 1,10-phenanthroline, dipyrindyl, anthraquinones, dihydroxynaphthalene, anthranilic acid, o-aminophenol, bipyrimidines etc with exciting applications (9-13). Metal complexes of the type $[\text{M}(\text{LL})_3]^{n+}$ where LL is either 1,10-phenanthroline (phen.) or a modified phenanthroline ligand are particularly attractive species for developing new diagnostic and therapeutic agents that can recognize and cleave DNA (14). The ligands or the metal in these complexes can be varied in an easily controlled manner to facilitate an individual application, thus providing an easy access for understanding details involved in DNA bonding and cleavage (15).

Ethanolamine complexes have also been investigated in view of its tremendous applications in various fields like catalysis, inhibitors, ion exchangers, electroplating, dyes etc. The formation, structure and thermal stability of green colored complex of CoCl_2 with monoethanolamine $\text{Co}(\text{MEOA})_2\text{Cl}_2$ has already been reported (1). The comparative thermal stability of complexes of mono, di and tri- ethanolamines with various

metal salts has also been investigated (16). Keeping in view the extensive cluster chemistry of cobalt to form different types of complexes, here we report the synthesis of multiligand complex of cobalt with monoethanolamine and 1,10-phenanthroline. The choice of ligands is as a consequence of the capacity of various sites on ligands for coordination besides possessing multiple technical, industrial, biological and pharmaceutical applications. The empirical formula has been proposed by elemental analysis. The insertion of ligands into the complex has been ascertained by FTIR. The possible structure has also been proposed. The thermal kinetics is also reported.

Experimental

A.R grades of cobalt chloride, monoethanolamine and 1-10 phenanthroline were used. Complex was prepared by the reaction of equimolar solution of CoCl_2 with a mixture of monoethanolamine and 1-10- phenanthroline. The mixture was added drop wise with constant stirring; the green color precipitate formed was kept overnight, filtered, washed with distilled water and dried in vacuum desiccator. Elemental analysis was done on Elementar Analysensysteme GmbH vario EL CHNS. The FTIR spectrum of the solid complexes was recorded on Perkin Elmer RXI IR spectrophotometer in the range of 200-4000 cm^{-1} using KBr disc techniques. Thermal analysis was carried on universal V4.1 DTA instrument. The instrument was made in a dynamic nitrogen atmosphere with a rate of 50 ml/min. between ambient temperature to 800 °C at a heating rate of 10 °C/min. DSC was taken on universal V4.1

DTA instrument. The temperature repeatability of the instrument is $\pm 0.1^\circ\text{C}$ and of ΔH is equal to ± 0.2 mW.

Results and Discussion

Complex was prepared by the reaction of equimolar solution of CoCl_2 with a mixture of monoethanolamine and 1-10-phenanthroline. The mixture was added drop wise with constant stirring, the green color precipitate formed was kept overnight, filtered, washed with distilled water and dried in vacuum desiccator. The complex was subjected to elemental analysis and FTIR. The thermal analysis of the complex was carried in an inert atmosphere.

Elemental Analysis:

On the basis of elemental analysis of C, H and N, the empirical formula assigned to the complex is : $[\text{Co}_2(\text{MEOA})(\text{Phen.})_2\text{Cl}_4] \cdot \text{H}_2\text{O}$ for which the observed values of C, H and N is 44.80, 3.61 and 10.80 against calculated values as 45.0, 3.49 and 10.64 respectively.

FTIR spectroscopic characterization:

The complex was subjected to FTIR spectroscopy and the spectra are shown in Fig.1 and Fig 2.

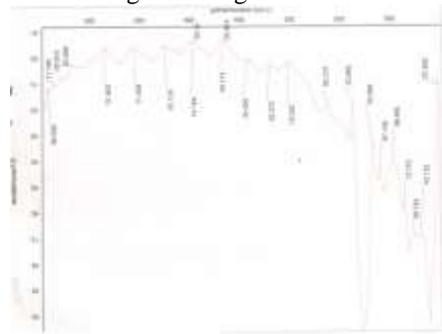


Fig.1. FTIR Spectral frequency range from 200-600 cm^{-1} for the complex $[\text{Co}_2(\text{MEOA})(\text{Phen.})_2\text{Cl}_4] \cdot \text{H}_2\text{O}$.

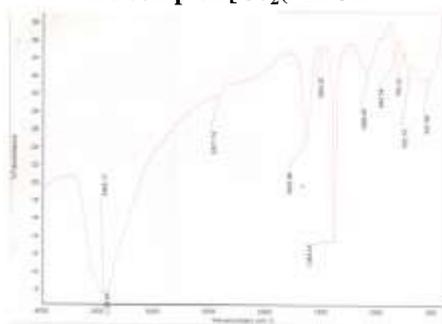


Fig.2. FTIR Spectral frequency range from 500-4000 cm^{-1} for the complex $[\text{Co}_2(\text{MEOA})(\text{Phen.})_2\text{Cl}_4] \cdot \text{H}_2\text{O}$.

The empirical formula of the complex suggests the presence of water, MEOA, 1, 10-phenanthroline and CoCl_2 , is supported by FTIR spectra. The presence of MEOA is confirmed by the appearance of absorption peaks at 3452 cm^{-1} , 1383 cm^{-1} , 1088 cm^{-1} and 840 cm^{-1} , which are because of $\nu(\text{O-H})$, $\nu(-\text{CH}_2)$, $\nu(-\text{C-O})$ and $\nu(\text{N-H})$ respectively being the characteristic peaks of MEOA (17-19). The presence of 1,10-phenanthroline is proved by the appearance of absorption peaks at 1635 cm^{-1} which is due to $\nu(\text{C=N})$ (20). The weak peak observed at 477 cm^{-1} , 447 cm^{-1} and 353 cm^{-1} are because of antisymmetric vibrations of phenanthroline ring (21). The presence of CoCl_2 in the complex is verified by the absorption peaks at 353 cm^{-1} , 313 cm^{-1} , 298 cm^{-1} which are because of $\nu(\text{Co-Cl})$ (1). The structure proposed for the complex is

The proposed structure is supported by the observations like MEOA acts as a bidentate ligand shows the coordination via both N and O as FTIR of the complex shows various absorption

peaks from $536\text{-}587 \text{ cm}^{-1}$ which are because of $\nu(\text{M-N})$, absorption peaks at 600 cm^{-1} besides in the range of $500\text{-}587 \text{ cm}^{-1}$ due to $\nu(\text{M-O-})$, which proves MEOA is coordinating through N and O (22). The absorption peak at 508 cm^{-1} as a result of $\nu(\text{M-O-H})$ also supports the coordination of MEOA through oxygen also (1).

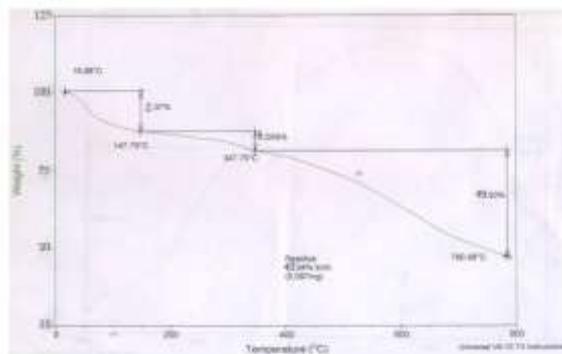


Fig.3. TG curve of the complex $[\text{Co}_2(\text{MEOA})(\text{Phen.})_2\text{Cl}_4] \cdot \text{H}_2\text{O}$.

Now this $\nu(\text{M-N})$ can be because of 1,10-phenanthroline also where the vibrations already mentioned supports the coordination of 1,10-phenanthroline. This coordination is further supported by the absorption peak at 722 cm^{-1} which has been reported for coordinated 1,10-phenanthroline ligand (23). This is further verified by the antisymmetric vibrations of 1,10-phenanthroline which appears at 477 cm^{-1} , 447 cm^{-1} and 355 cm^{-1} . The formation of homo binuclear complex is proved by the presence of M-M bond which is verified by the appearance of various absorption peaks in the range of $200\text{-}300 \text{ cm}^{-1}$ as a result of $\nu(\text{M-M})$. Since absorption peak at 3452 cm^{-1} can be as a result of $\nu(\text{H-O-H})$ which proves the presence of water. This single moiety of water remaining outside the coordination sphere is further supported by thermal analysis, by getting removed below 150°C . By means of metal-metal bond, the complex obeys EAN Rule or 18 electron rule, thus attains the sufficient stability by means of this linkage.

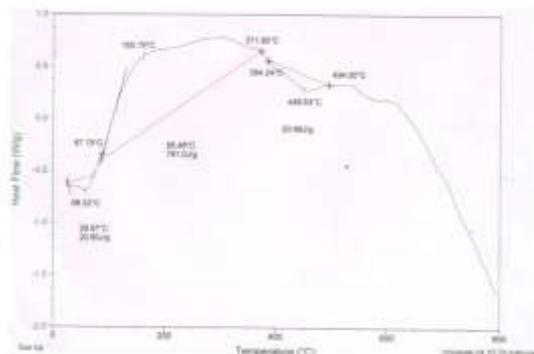
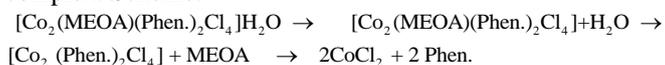


Fig.4. DSC curve of the complex $[\text{Co}_2(\text{MEOA})(\text{Phen.})_2\text{Cl}_4] \cdot \text{H}_2\text{O}$.

Thermal Analysis:

The complex has been subjected to thermal decomposition in an inert atmosphere. The TG curve of the complex is shown in Fig.3. The TG curve can be explained by considering the three stages with three different maximum temperatures. Initiating from the initial temperature of 16.98°C to 147.79°C with maximum temperature of 66°C , complex shows a weight loss equivalent to 2.37% which is as a result of loss of external water moiety. The calculated weight loss for this moiety is 2.42%. The presence of water as lattice water confirmed from FTIR is supported by temperature range of thermal analysis at which

weight loss equivalent to water moiety occurs. The second thermal decomposition step is initiating from 147.79 °C to 347.79°C with DTG maximum of 324°C giving a weight loss of 8.20% against 8.10%, accounts for the removal of 1 mole of MEOA. The third decomposition step is initiating from 347.79°C to 780.98 °C with DTG maximum at 546 °C involves the weight loss of 48.54% against 49.50%, accounts for the removal of two moles of 1,10-phenanthroline. The curve shows incomplete decomposition, due to the presence of CoCl₂ the decomposition temperature of which is 1087°C (24). Since the temperature range of analysis is from ambient to 800°C, therefore the residue left at 800°C is 2CoCl₂, the calculated weight loss of which is 40.80% against observed weight loss of 40.34%. The thermo analytical data is given in table 1. DSC curve of this complex is shown in Fig. 4. It involves an endothermic peak in the temperature range of 26.67°C to 87.79 °C with maximum at 58.32 °C giving $\Delta H=20.60$ J/g. This peak is due to the release of H₂O molecule. The second peak is wide exothermic peak from 87.79°C to 371.80°C with maximum at 160.79°C, which is because of release of one mole of MEOA from the complex. The heat flow during the transition is 781.0 J/g. The third peak is wide being endothermic peak from 384.24°C to 494.0 °C with maximum at 448.63 °C, which is because of release of two moles of 1,10-phenanthroline from the complex. The heat flow during the transition is 50.66 J/g. On the basis of these results, following scheme is proposed for thermal decomposition of the complex. Scheme:



Three different methods viz. Doyle's ($-\log \alpha$ vs. $1/T \times 10^3$ K), Coats and Red fern ($-\log[-\ln(1-\alpha)/T^2]$ vs $1/T \times 10^3$ K) and Arrhenius($-\log K$ vs. $1/T \times 10^3$ K) were employed for evaluation of kinetic data (Table 2). Thermodynamic parameters like activation energy (E_a), pre- exponential factor (A) and entropy of activation (ΔS^\ddagger) for different decomposition steps of the complex were calculated and are given in Table 3.

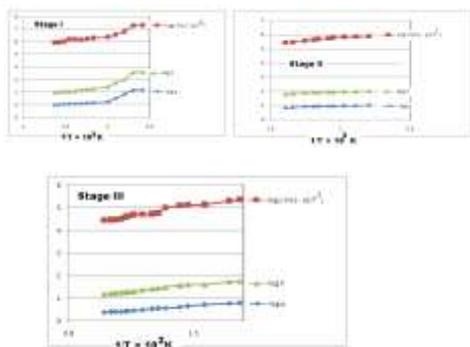


Fig.5. Plot of $-\log \alpha$, $-\log[-\ln(1-\alpha)/T^2]$ and $-\log K$ versus $1/T \times 10^3$ K for three stages of thermal decomposition of the complex $[\text{Co}_2(\text{MEOA})(\text{Phen.})_2\text{Cl}_4]\text{H}_2\text{O}$.

Lowest value of E_a and maximum value of (ΔS^\ddagger) for stage I corresponds to the release of water at the very onset of thermal decomposition process justifying the least bonding with central metal ion. The stage II corresponding to the release of one mole of MEOA. The third decomposition corresponding to the release of two moles of 1,10-phenanthroline gives the maximum value of E_a and lowest value of (ΔS^\ddagger) shows their strongest co-

ordination with cobalt. The same must be true for frequency factor according to Eyring's equation $A \propto e^{\Delta S^\ddagger/R}$ is verified from the data also (Table 3). After removal of one mole of MEOA and two moles of 1,10-phenanthroline, the rest four chloride moieties are present as two moles of cobalt chloride, the decomposition temperature of which is 1087°C which is beyond the analysis range, hence showing incomplete thermal decomposition and is present as residue (24). The thermal decomposition data using different methods is plotted in Fig.5 and it is evident that the trends is same for all the methods used and are linear, hence follow first order kinetics.

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Table.1. Thermoanalytical data for the decomposition of the complex $[\text{Co}_2(\text{MEOA})(\text{Phen.})_2\text{Cl}_4] \cdot \text{H}_2\text{O}$

Temp. range in $^{\circ}\text{C}$	Max. Temp. in DTG $^{\circ}\text{C}$	Obsd. Wt. Loss%	Calc. wt. loss %	Remarks Removal of
16.98 – 147.79	66	2.37	2.42	1 mole of H_2O
147.79 – 347.79	324	8.10	8.20	1 mole of MEOA
347.79 – 780.98	546	49.50	48.54	2 moles of 1-10 phenanthroline

Residue is CoCl_2 Obsd.(40.34%), Calc.(40.80%)**Table.2. Thermal decomposition data of the complex $[\text{Co}_2(\text{MEOA})(\text{Phen.})_2\text{Cl}_4] \cdot \text{H}_2\text{O}$. using Doyle's, Coats and Redfern and Arrhenius methods****Stage-I**

$1/T \times 10^3 \text{K}$	$-\log \alpha$	$-\log (-\ln(1-\alpha)/T^2)$	$-\log K$
3.413	2.16	7.31	3.60
3.300	2.13	7.29	3.55
3.195	1.84	6.82	3.04
3.090	1.51	6.55	2.75
3.000	1.21	6.38	2.43
2.830	1.15	6.29	2.27
2.755	1.11	6.23	2.23
2.680	1.08	6.18	2.20
2.611	1.057	6.203	2.094
2.544	1.037	6.205	2.068
2.481	1.021	6.015	2.046
2.421	1.017	5.943	2.016
2.364	0.994	5.923	1.998

Stage-II

2.207	0.981	5.869	1.993
2.114	0.968	5.840	1.977
2.028	0.953	5.811	1.962
1.949	0.937	5.765	1.944
1.912	0.928	5.712	1.934
1.841	0.918	5.665	1.914
1.808	0.912	5.610	1.907
1.745	0.894	5.543	1.886
1.658	0.844	5.435	1.828
1.605	0.821	5.405	1.773

Stage-III

1.485	0.781	5.358	1.753
1.443	0.760	5.299	1.739
1.345	0.700	5.137	1.609
1.277	0.651	5.121	1.593
1.245	0.611	5.106	1.559
1.186	0.560	4.998	1.485
1.158	0.542	4.768	1.447
1.132	0.517	4.723	1.411
1.095	0.481	4.708	1.358
1.060	0.446	4.697	1.305
1.038	0.429	4.623	1.278
1.027	0.422	4.588	1.266
1.007	0.408	4.499	1.245
0.987	0.397	4.471	1.225
0.968	0.385	4.456	1.206
0.940	0.373	4.443	1.186

Table 3. Activation energy (E_a), pre-exponential factor (A) and entropy of activation (ΔS^\ddagger) for the complex $[\text{Co}_2(\text{MEOA})(\text{Phen.})_2\text{Cl}_4] \cdot \text{H}_2\text{O}$.

Stage	DTG max. in K	Parameters	Doyle	Coats and Redfern	Arrhenius
I.	339	E_a (KJmol^{-1}) A (S^{-1}) ΔS^\ddagger ($\text{JK}^{-1}\text{mol}^{-1}$)	22.3 1.4×10^{22} -174.0	22.0 1.9×10^{-5} -340.6	27.8 1.7×10^{26} -251.9
II	597	E_a (KJ mol^{-1}) A (S^{-1}) ΔS^\ddagger ($\text{JK}^{-1}\text{mol}^{-1}$)	49.2 3.7×10^{11} 230.6	45.4 1.8×10^{-7} -477.2	36.3 1.7×10^{12} -317.8
III	819	E_a (KJmol^{-1}) A (S^{-1}) ΔS^\ddagger ($\text{JK}^{-1}\text{mol}^{-1}$)	52.6 8.7×10^{10} -244.5	48.1 2.5×10^{-12} -480.1	41.0 4.6×10^{11} -330.5