



Study of formation of complex Salts, [Co(o-phen)₃][Zn(ecda)₂] and [Ni(bipy)₃][Cd(ecda)₂] Via Ligand Exchange Reaction

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(Received: September 28, 2011; Accepted: November 14, 2011)

ABSTRACT

Complex salts [Co(o-phen)₃][Zn(ecda)₂] and [Ni(bipy)₃][Cd(ecda)₂] have resulted by interaction of [Zn(o-phen)₃]²⁺ and [Co(ecda)₂]²⁻ ion; [Cd(bipy)₃]²⁺ cation and [Ni(ecda)₂]²⁻ dianion, where ecda=1-ethoxycarbonyl-1-cyanoethylene-2,2-dithiolate. Magnetic susceptibility measurement of the complex [Co(o-phen)₃][Zn(ecda)₂] suggest presence of octahedral cobalt II ion. Presence of octahedral environment around Ni II in complex, [Ni(bipy)₃][Cd(ecda)₂] has been supported by electronic spectral data and magnetic susceptibility measurement. IR spectra show presence of prominent groups and coordination of metal ions with ligand. Molar conductance measurements show extensive ion pairing in solution. Formation of these complexes take place presumably via ligand exchange reaction occurring during course of their formation.

Key words: Complex salts, Dithiolate, Ecda.

INTRODUCTION

Voluminous literature has been built up so far describing synthesis characterization and properties of transition metal dithiolate complexes¹⁻⁴. Still there is upsurge of interest in these complexes owing to their wide spread applications, such as, molecular conductors, NLO materials, photosensitization, catalysis and biological importance along with various other interesting physicochemical properties. Ability of 1,1- and 1,2-dithio ligands to form transition metal complexes in usual and unusual oxidation state of metal ion, heterobimetallic complexes, complex salts and

clusters are well documented. Their monodentate, bidentate chelating, bridging behaviour, along with electronic and structural properties have been exploited for design of various kinds of molecular materials. Recently, Singh and coworkers have reported synthesis characterization and solid state properties of some metal dithiolate complexes^{5,6}.

The ligand potassium 1-ethoxycarbonyl-1-cyanoethylene-2,2-dithiolate (K₂ecda) is highly conjugated, electron rich 1,1-dithiolate. Eisenburg and coworkers⁷ has reported interesting luminescence properties of some mixed ligand complexes formed with this ligand. Synthesis

characterization and solid state electrical conductance behaviour of some bimetallic complexes and organoheterobimetallic complex formed with this ligand has been reported earlier⁸.

Well known entity $[\text{Zn}(\text{o-phen})_3]^{2+}$ with $[\text{Co}(\text{ecda})_2]^{2-}$ both generated in situ yielded complex $[\text{Zn}(\text{o-phen})_3][\text{Co}(\text{ecda})_2]$. Similarly interaction of $[\text{Cd}(\text{bipy})_3]^{2+}$ and $[\text{Ni}(\text{ecda})_2]^{2-}$ has afforded $[\text{Ni}(\text{bipy})_3][\text{Cd}(\text{ecda})_2]$ instead of complex salt $[\text{Cd}(\text{bipy})_3][\text{Ni}(\text{ecda})_2]$. Formation of these complexes take place presumably via ligand exchange reaction. Result of investigation is reported herein.

EXPERIMENTAL

Materials and Physical Measurement

All the chemicals used were of analytical reagent grade. Metals were estimated following standard gravimetric procedures after destruction of organic matters by fusion with aquaregia. Sulfur was estimated as BaSO_4 .

Solution conductivity of 10^{-3} M solution of complexes in acetone was measured on WTW type conductivity meter. Magnetic susceptibility was measured on cahn-Faraday balance using $\text{Co}[\text{Hg}(\text{SCN})_4]$ as calibrant. Melting points were taken in an open capillary and are uncorrected. IR spectra were recorded on JASCO FTIR-5300 ($400\text{--}4000\text{ cm}^{-1}$) and PE 983 ($200\text{--}400\text{ cm}^{-1}$) spectrophotometer. UV-Vis absorption spectra were recorded on Shimadzu 160A and Cary-14 spectrophotometer.

Synthesis of complexes

$[\text{Co}(\text{o-phen})_3][\text{Zn}(\text{ecda})_2]$

Ligand K_2ecda was prepared by method reported in literature⁹. A greenish-brown solution of $\text{K}_2[\text{Co}(\text{ecda})_2]$ was generated by addition of 30 ml of an aqueous solution of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.248g, 1mmol) to about 30 ml of an aqueous-ethanolic 50:50(v/v) solution of K_2ecda (0.53 g, 2 mmol) with stirring. To this clear solution about 15 ml of an aqueous ethanolic solution of $[\text{Zn}(\text{o-phen})_3]^{2+}$ prepared by mixing 10 ml of an aqueous $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.219g, 1 mmol) and 5 ml of ethanolic o-phen (0.594 g, 3 mmol) was added dropwise with stirring. Reaction mixture was stirred for sometime and product was filtered off; washed

with water-ethanol 50:50(v/v) mixture followed by ethanol and ether, dried in vacuum over CaCl_2 . MP-210°, Colour-brown

Anal.Calc. for $\text{C}_{48}\text{H}_{34}\text{N}_8\text{O}_4\text{S}_4\text{CoZn}$; Co, 5.6, Zn, 6.3, S, 9.9 %; Found, Co, 5.4, Zn, 6.3, S, 9.6.

$[\text{Ni}(\text{bipy})_3][\text{Cd}(\text{edca})_2]$

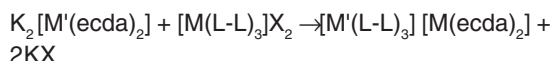
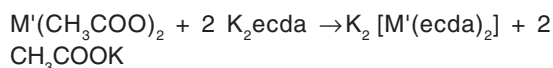
This complex formed similarly as above by interaction of blood red $\text{K}_2[\text{Ni}(\text{ecda})_2]$ solution generated in situ by reaction of the dithiolate ligand and nickel acetate as above and $[\text{Cd}(\text{o-phen})_3]\text{Cl}_2$ by stoichiometric amount of reacting salts and ligands. MP-230°, Colour-yellow

Anal.Calc. for $\text{C}_{42}\text{H}_{34}\text{N}_8\text{O}_4\text{S}_4\text{NiCd}$; Ni, 5.7, Cd, 11.1, S, 12.6 %; Found, Ni, 5.6, Cd, 11.1, S, 12.5.

RESULTS AND DISCUSSION

Treatment of $\text{K}_2[\text{M}'(\text{ecda})_2]$, generated in situ, with equimolar amount of $[\text{M}(\text{L-L})_3]^{2+}$ afforded $[\text{M}'(\text{L-L})_3][\text{M}(\text{ecda})_2]$ by substitution of coordinatively inert K^+ by coordinatively saturated $[\text{M}(\text{L-L})_3]^{2+}$ cation.

These complexes form via ligand exchange reaction as outlined below.



M' = NiII, CoII

M = CdII, ZnII

High propensity of ZnII and CdII ions for tetra coordination seem to have dictated the coordination environment in cationic and anionic moieties.

The complexes show low value of molar conductance in acetone (10^{-3} M) ($40.6/48\text{ cm}^2\ \Omega^{-1}\text{ mol}^{-1}$) indicating substantial degree of ion pairing and their falling short of 1:1 electrolytic behaviour.

Table 1: UV-Vis spectral data of the complexes

Complex	Solvent	λ_{\max} , nm (ϵ , l mol ⁻¹ cm ⁻¹)
[Co(o-phen) ₃][Zn(ecda) ₂]	Ethanol	228, 263, 325
	DMSO	341, 410, 625
	Acetonitrile	650
[Ni(bipy) ₃][Cd(ecda) ₂]	Methanol	210(5800), 240(3884), 295(5882), 306(5823), 330(1658), 433(905)
	DMSO	445, 480
	Acetonitrile	830

IR spectra

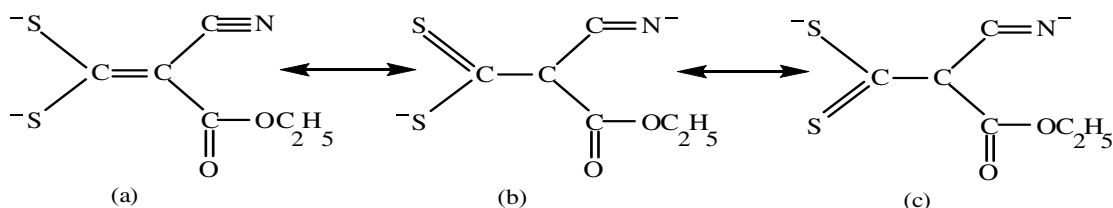
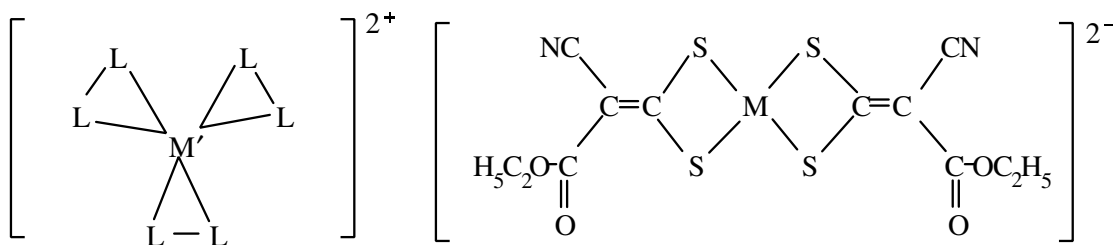
A characteristic $\nu(\text{C-S})$ band has been observed at around 1000 cm^{-1} in the complexes. This band is suggestive of bidentate mode of coordination of the ligand through its two sulfur atoms¹⁰. $\nu(\text{C=C})$ vibration observed in the range (1440-1450 cm^{-1}) is somewhat higher than that of ligand, K_2ecda . It suggests major contribution of resonance form (1a) in the complexes.

In metal dithiolate complexes of conjugated ligands containing C=C linkage, $\nu(\text{C=C})$ is generally observed at lower frequency because of conjugation present in molecule causing delocalization of C=C electrons. $\nu(\text{C=O})$ has also

been found at quite lower frequencies subject to the degree of conjugation present in the molecule and effect on carbonyl functional thereof. $\nu(\text{C}\equiv\text{N})$ in all the complexes have been observed at ~ 2200 cm^{-1} . In the ligand it has been reported at 2195 cm^{-1} . νCO is almost unchanged in complexes and ligand showing non involvement of this group in coordination. IR bands at 640 and 475 cm^{-1} shows coordination by o-phen and bipy with metal¹¹. In far IR region bands at ~ 360 and 235 cm^{-1} has been assigned to M-N and M-S stretching vibrations respectively.

Magnetic moment and electronic spectra

Room temperature magnetic moment of the

**Fig. 1: Some resonance structure of the ligand**

M = Zn II or Cd II

M' = Co II or Ni II

L-L = o-phen or bipy

complex salt, $[\text{Co}(\text{o-phen})_3][\text{Zn}(\text{ecda})_2]$ has been found 5.06 BM indicating presence of octahedral Co II ruling out formulation, like $[\text{Zn}(\text{o-phen})_3][\text{Co}(\text{ecda})_2]$ as might be expected by mode of preparation. From this structure magnetic moment corresponding to one unpaired electron of $[\text{Co}(\text{ecda})_2]^{2-}$ would have been expected. Electronic absorption spectra of this complex salt (tab 1) recorded in displays bands at 410 and 625/650 nm supporting octahedral geometry around cobalt, however lower energy band expected for this geometry could not be resolved.

For the complex salt, $[\text{Ni}(\text{o-phen})_3][\text{Cd}(\text{ecda})_2]$, m, has been observed 2.22 BM, lower than expected for octahedral nickel II with two unpaired electron.

From the structure, $[\text{Cd}(\text{o-phen})_3][\text{Ni}(\text{ecda})_2]$ of this complex diamagnetism is expected. Electronic absorption spectrum of this complex salt displays bands at 440, 478 and 830 nm assignable to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ transition of octahedral nickel¹². Further these band do not show splitting favouring symmetrical structure of the complex salt as proposed.

On the basis of foregoing discussions on earlier literature on metal dithiolate complexes, following structure is proposed tentatively.

ACKNOWLEDGEMENTS

Author is thankful to UGC New Delhi, India for financial assistance.

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