

Thermal, Spectral and Magnetic Studies of Complexes of Sebacic Acid Bis-hydrazide and Sebacic Acid Bis-2,4-Dinitrophenyl Hydrazide with Transition Metal Ions

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Present paper describes the work on the synthesis of sebacic acid bis-hydrazide [SABH] and sebacic acid bis-2,4-dinitrophenyl hydrazide and their complexes with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The characterisation of these newly synthesised complexes have been done on the basis of elemental analysis and structural aspects have been studied using spectral, magnetic and thermochemical techniques. All these complexes have been found to have 1 : 1 composition and are insoluble in almost all the organic solvents. The position of chelate loop has been suggested on the basis of infrared spectral studies. Electronic spectral and magnetic studies provided information on the geometry of the complexes formed while thermal studies indicate comparatively high thermal stability associated with these complexes.

INTRODUCTION

The present work deals with the preparation and characterisation of some new complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with sebacic acid bis-hydrazide [SABH] and sebacic acid bis-2,4-dinitrophenyl hydrazide [SABDNPH] which appear to be polymeric in nature.

EXPERIMENTAL

All chemicals used as starting material in the synthesis of ligands and coordination complexes were of chemically pure quality. Solvents used were distilled before use.

Carbon, hydrogen and nitrogen in these compounds were estimated using Coleman's analyser. Infrared spectra were recorded in 4000-400 cm^{-1} region on a Perkin-Elmer infrared spectrophotometer. Reflectance spectra using magnesium carbonate as reference material were recorded on Shimadzu-240. Magnetic susceptibility measurements of complexes were determined by Gouy's method and thermal studies were carried out by maintaining a heating rate of 5°C/min.

Preparation of Ligands: Sebacic acid bis-hydrazide [SABH] and sebacic acid bis 2,4-dinitrophenyl hydrazide [SABDNPH] were prepared by the standard methods^{1,2}.

Preparation of complexes: The ligand (0.1 M), metal acetate (0.1 M) and dimethyl formamide [DMF] were taken in round-bottomed flask and heated on water bath for 2 h. The insoluble coordination complexes formed were filtered and thoroughly washed several times with DMF and absolute alcohol till free from unreacted reactants. The purified sample was then derived in *vacuo*. The

complexes were obtained as amorphous powder and were found to be insoluble in almost all the organic solvents. The results of elemental analysis, decomposition temperature and magnetic moments for these coordination complexes are given in Table-1. The composition (assigned to these complexes) are also shown in Table-1.

TABLE-1
ELEMENTAL ANALYSIS, DECOMPOSITION TEMPERATURE AND MAGNETIC
MOMENT OF LIGANDS AND COORDINATION COMPLEXES

Proposed composition (Dec. temp. °C)	Elemental analysis found (Calcd.), %				μ_{eff} (B.M.)
	C	H	N	Metal	
SABH (186)	51.93 (52.71)	9.93 (9.56)	24.16 (24.34)	—	—
SABDNPH (227)	47.18 (46.97)	4.29 (4.62)	20.23 (19.92)	—	—
{[MnX]2H ₂ O} _n (348)	40.89 (42.40)	7.30 (7.06)	19.79 (19.78)	20.11 (19.40)	5.58
[Co(X)(H ₂ O) ₂] _n (328)	38.91 (37.15)	7.11 (7.43)	18.46 (17.34)	18.56 (18.24)	4.92
[Ni(X)(H ₂ O) ₂] _n (392)	39.12 (37.25)	7.94 (7.43)	18.59 (17.35)	19.43 (18.19)	3.35
[Cu(X)(H ₂ O) ₂] _n (440)	35.91 (36.63)	6.58 (6.10)	17.98 (17.09)	20.45 (19.39)	1.90
{[Zn(X)]2H ₂ O} _n (392)	36.01 (36.43)	6.32 (6.07)	16.91 (17.00)	20.51 (19.84)	—
{[Mn(Y)]2H ₂ O} _n (380)	39.89 (40.55)	4.19 (4.30)	16.73 (17.20)	8.79 (8.43)	6.12
[Co(Y)(H ₂ O) ₂] _n (400)	39.35 (40.18)	4.16 (4.26)	17.23 (17.04)	8.24 (8.97)	5.56
[Ni(Y)(H ₂ O) ₂] _n (428)	38.73 (40.20)	3.97 (4.26)	18.05 (17.05)	8.51 (8.94)	2.93
[Cu(Y)(H ₂ O) ₂] _n (412)	39.13 (40.02)	4.07 (4.24)	16.21 (16.98)	10.21 (9.63)	1.96
{[Zn(Y)]2H ₂ O} _n (352)	39.15 (39.91)	4.22 (4.23)	17.21 (16.93)	10.08 (9.88)	—

X = SABH, Y = SABDNPH

RESULTS AND DISCUSSION

Reflectance Spectra and Magnetic Properties: A band appearing around 26.31 kK in the coordination complexes of Mn(II) formed with SABH and SABDNPH is assigned to ${}^6A_1 \rightarrow 4E(D)$ transition in tetrahedral field. Magnetic moment value of Mn(II) SABH and Mn(II) SABDNPH chelates also support tetrahedral geometry of these complexes.³

Co(II) complexes of SABH and SABDNPH show a broad band in the region 18.51 kK and 10.23 kK respectively which is assigned to ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$

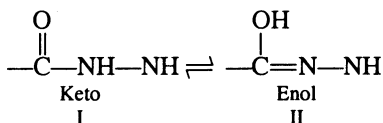
transition³, indicative of octahedral nature of these complexes. The octahedral nature of these complexes are also supported by magnetic study.

In case of Ni(II)-complexes of SABH and SABDNPH, the bands appearing at 15.5 kK and 26.15 kK are assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition in octahedral field in SABH and SABDNPH respectively. Magnetic moment values of these solid complexes also support octahedral geometry for these coordinations⁴.

A broad band which appears in the region of 14.80 kK in SABH and 16.62 kK in SABDNPH chelates of Cu(II) is assigned to ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition, indicating a distorted octahedral geometry. The magnetic moment values of Cu(II) complexes were found to be in the range of 1.90–1.96 B.M., supporting the conclusion drawn from the electronic spectral studies.

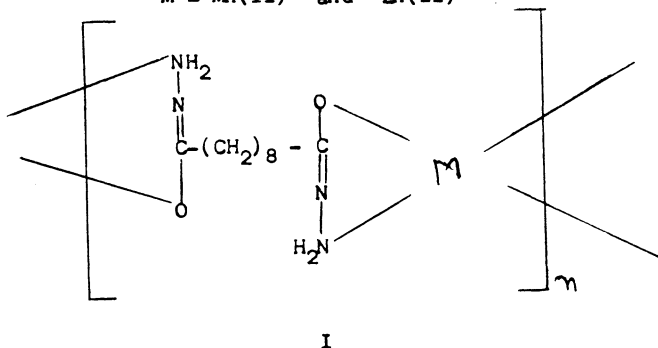
Infrared Spectral Studies: Infrared bands observed around 3100 cm^{-1} in SABH and 3200 cm^{-1} in SABDNPH have been assigned due to N—H stretching band in these bis-hydrazides². The sharp band of C=O stretching [amide-II] is observed at 1680 cm^{-1} in case of SABH and at 1620 cm^{-1} in SABDNPH. A strong band around 1500 cm^{-1} in SABH has been observed which may be due to N—H vibrational and C—N stretching mode [amide-II]. The amide (II) band is merged with Nujol-bands in case of SABDNPH since the spectra was recorded by Nujol-mull technique. Two bands appearing at 2680 cm^{-1} and 2560 cm^{-1} are assigned to —CH₂ stretching mode in both the ligands.

The C—NO₂ stretching vibration band is observed at 1450 cm^{-1} in SABDNPH. It has been found that bis-hydrazide undergoes keto-enol tautomerism during polymerisation as follows:

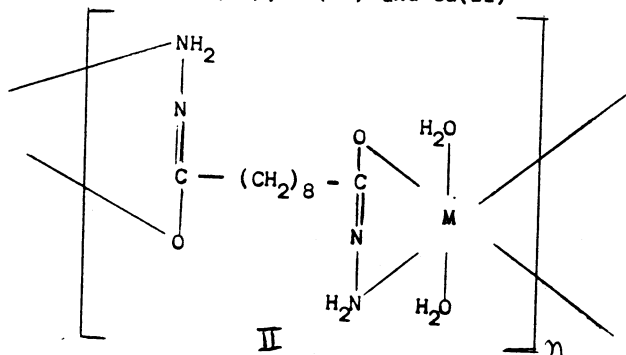


This has been proved by the fact that the band observed around $1680\text{--}1620\text{ cm}^{-1}$ due to C=O stretching mode [amide-I] in case of ligands, disappears and a new band is observed around $1560\text{--}1550\text{ cm}^{-1}$ in complexes which clearly indicates that the amide-I band (C=O) disappears due to formation of C=N (as shown in structure (I) as a result of enolization.

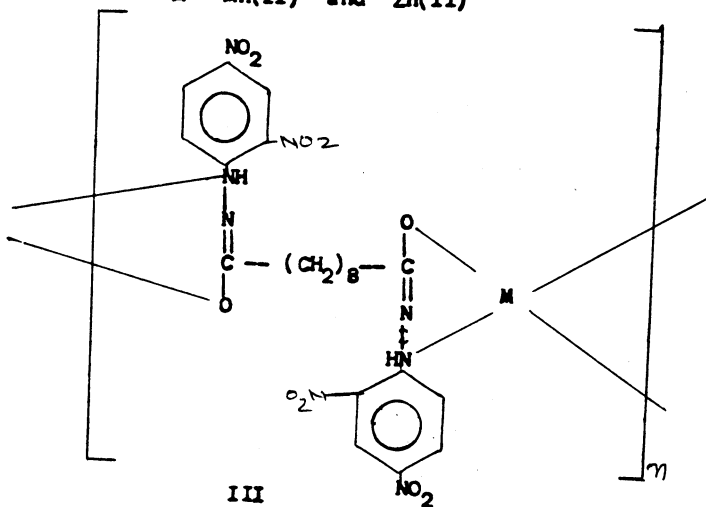
M = Mn(II) and Zn(II)



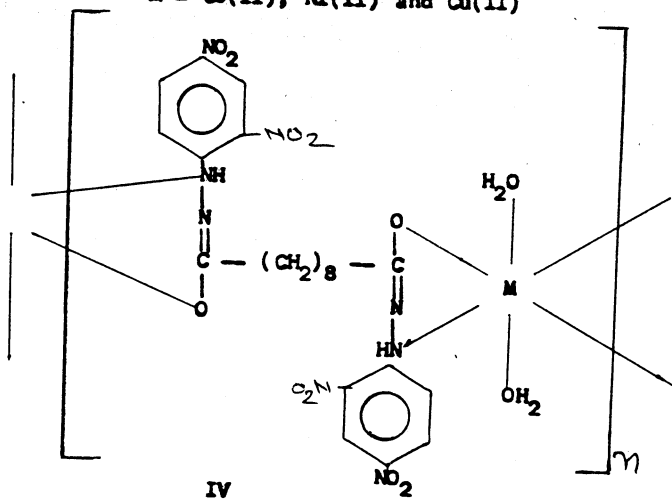
M = Co(II), Ni(II) and Cu(II)



M = Mn(II) and Zn(II)

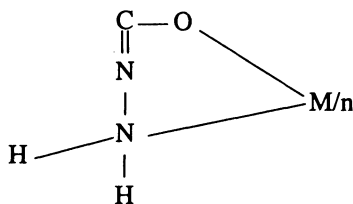


M = Co(II), Ni(II) and Cu(II)



This is further supported by the appearance of the C=O band around 1100 cm^{-1} in case of complexes.

Thus, it is appropriate to suggest that the bis-hydrazide reacts with the metal ions to form coordination complexes of the following type:



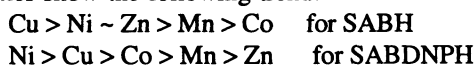
Due to the formation of N—N→M coordinate bond, the N—H band is found



to have been shifted towards lower frequency.

Medium bands appearing in the region of $880\text{--}650\text{ cm}^{-1}$ in the chelate complexes of Co(II), Ni(II) and Cu(II) may be assigned due to $\pi\text{--H--O--H}$ mode of coordinated water. The bands appearing at $615\text{--}460\text{ cm}^{-1}$ in polymers are assigned due to (M—O) bond interaction⁵ while the presence of band around $540\text{--}420\text{ cm}^{-1}$ is assigned to (M—N) band.

Thermal Studies of Coordination Complexes: The TG curves of Mn(II) and Zn(II) chelate complexes show that there is a loss of water of hydration between 100 to 120°C and then no weight loss is observed up to 200°C which indicates the absence of water of coordination. However Co(II), Ni(II) and Cu(II) chelates show loss in weight between $140\text{--}180^\circ\text{C}$ which may be assigned due to loss of two molecules of water of coordination. The decomposition temperatures in coordination complexes show the following trend:



Proposed Structure

On the basis of the results obtained on elemental analysis, IR, electronic spectra and thermal studies, structures I and II are proposed for the chelate complexes of Mn(II) and Zn(II) SABH and Co(II), Ni(II) and Cu(II) SABH, while structures III and IV are proposed for the monomeric unit of Mn(II) and Zn(II) SABDNPH and Co(II), Ni(II) and Cu(II) complexes of SABDNPH respectively.

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