

Polymeric Bipositive Metal Ion Complexes of Terephthalaldehyde bis-(isonicotinic acid hydrazone)

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Terephthalaldehyde bis-(isonicotinic acid hydrazone) (TBINH) has been synthesized by the condensation of terephthalaldehyde and isonicotinic acid hydrazone. TBINH yields complexes, $[\text{MLX}_2 \cdot x\text{H}_2\text{O}]_n$ [$M = \text{Mn(II), Co(II), Ni(II), Zn(II), Cd(II), UO}_2(\text{VI})$; $L = \text{C}_{10}\text{H}_8\text{N}_2\text{O}_2$; $X = \text{CH}_2\text{COO}^-$, NO_2^- and $x = 0, 1$ or 2], on refluxing a mixture of TBINH and metal salt in DMF medium in 1 : 1 ratio. Infrared and reflectance spectra, magnetic and thermogravimetric studies indicate that the complexes are polymeric having octahedral geometry. The order of thermal stability of the polymers is : $\text{Zn} > \text{Cd} > \text{Co} > \text{Mn} > \text{UO}_2 > \text{Ni}$.

TEREPHTHALALDEHYDE on reaction with carbazides yield Schiff bases, behaving as tetradentate coordinating ligands, which form polymeric coordination complexes¹⁻⁵. Metal-complexes⁶⁻¹² of Schiff bases with isonicotinic acid hydrazone, with aldehydes or ketones, have been of special interest in recent years, particularly in the context of the therapeutic value of the hydrazone and hydrazone. Coordination occurs both in keto^{6,12} as well as in enolic^{6,12} forms of the ligands with metal ions.

In the present communication, the synthesis of Schiff base, terephthalaldehyde bis-(isonicotinic acid hydrazone) (TBINH) and its complexes with Mn(II), Co(II), Ni(II), Zn(II), Cd(II) and UO₂(VI) are being described.

Experimental

Materials : Terephthalaldehyde (Koch Light) and isonicotinic acid hydrazone (Wilson Lab.) were used to synthesize the Schiff base. Mn(CH₃COO)₂·4H₂O, Zn(CH₃COO)₂·2H₂O, Cd(CH₃COO)₂·2H₂O (all BDH, AnalaR), Co(CH₃COO)₂·2H₂O (Sara-bhai M.), Ni(CH₃COO)₂·4H₂O (Veb Laborchemie) and UO₂(NO₃)₂·6H₂O (E. Merck) were used. The solvents were of reagent grade.

Preparation of Schiff base (TBINH) : Ethanolic solutions of 13.35 g (0.05 mole) isonicotinic acid hydrazone and terephthalaldehyde (6.7 g; 0.025 mole) were mixed and refluxed on a water bath for 2 hr. A white crystalline solid precipitated, which was filtered after allowing to stand for 2 hr, washed successively with water, ethanol and diethylether and dried (Yield 80%). TBINH obtained is insoluble in water, ethanol, chloroform, benzene, acetone, toluene, xylene, but soluble in dilute aqueous ammonia and DMF. Found : C, 64.61; H, 4.23; N, 22.35. Calcd. for C₂₀H₁₆N₂O₂ : C, 64.51; H, 4.33; N, 22.57%.

Preparation of metal-chelates : TBINH (0.01 mole) dissolved in DMF was gradually added to a

solution of the metal salt (0.01 mole) in DMF. Metal salts which are not soluble in DMF, were first dissolved in a minimum quantity of water and DMF was then added. The precipitation was instantaneous, but the reaction mixture was refluxed at ca 120° for 2 to 3 hr as necessary for completion of the reaction and left overnight. The precipitated mass was filtered, washed with DMF, ethanol and ether and dried (Yield ca 80%).

Properties : The 1 : 1 complexes (Table 1) are air stable and insoluble in water and in common organic solvents, viz., ethanol, acetone, benzene, chloroform, nitrobenzene, DMF and DMSO.

Spectral studies : IR spectra were recorded on Beckman Infrared spectrophotometer using KBr pellets in the range of 4000-400 cm⁻¹, DRS were obtained in the range 200-1000 nm using Carl-Zeiss spectrophotometer VSU-2.

Magnetic measurement : Magnetic susceptibility of the complexes were determined at 298°K by Faraday's method.

Thermogravimetry : TGA was done by heating the complexes upto 800° at a rate of 10° min⁻¹ in air.

Results and Discussion

The analytical data of the complexes agree with the general formula-(MLX₂·xH₂O)_n [where M = Mn(II), Co(II), Ni(II), Zn(II), Cd(II), UO₂(VI); L = C₂₀H₁₆N₂O₂; X = CH₃COO⁻, NO₂⁻; x = 0, 1 or 2].

Mn(II), Co(II) and Ni(II) complexes are paramagnetic with the observed magnetic moment values of 5.86, 4.98 and 2.94 B.M.* respectively. Various ligand field parameters such as ν_2/ν_1 , $10 D_q$, B' , β and β^0 have been calculated from electronic spectral data (Table 2). The magnetic moment values together with the spectral data show the octahedral geometry of the complexes.

* 1 B.M. = 1 Bohr Magnetron = 9.273×10^{-24} m²A.

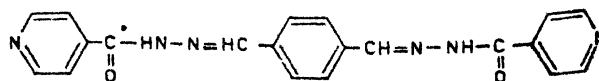
TABLE 1—COLOUR AND ANALYTICAL DATA OF THE COMPLEXES

| Complex | Colour | Elemental analyses(%) | | | |
|--|-----------------|-----------------------|---------------|-------------|---------------|
| | | Found | | (Calcd.) | |
| | | M | C | H | N |
| [MnLAc ₂ .H ₂ O] _n | Brownish yellow | 9.26 (9.77) | 50.89 (51.15) | 4.07 (4.26) | 14.67 (14.92) |
| [CoLAc ₂ .H ₂ O] _n | Reddish brown | 9.82 (10.09) | 50.68 (50.79) | 4.37 (4.23) | 14.14 (14.63) |
| [NiLAc ₂ .H ₂ O] _n | Yellow | 10.13 (10.09) | 49.28 (49.23) | 4.49 (4.44) | 14.63 (14.36) |
| [ZnLAc ₂ .2H ₂ O] _n | Yellow | 10.83 (11.17) | 48.45 (48.73) | 3.98 (4.39) | 14.07 (14.19) |
| [CdLAc ₂ .2H ₂ O] _n | Yellow | 17.31 (17.56) | 45.13 (45.15) | 3.83 (4.08) | 13.42 (13.18) |
| [UO ₂ L(NO ₃) ₂] _n | Yellow | 30.48 (30.84) | 31.81 (31.50) | 3.24 (3.04) | 10.18 (10.02) |

L=C₂O₂H₃N₂O₂; Ac=CH₃COO⁻

The ir spectrum (Table 3, wave number in cm⁻¹) of TBINH shows characteristic absorption bands at 3240, 1640, 1290, 750 and 670 assigned to be due to N-H stretching, C=O stretching, N-H in-plane bending, N-H bending, C=O in-plane deformation and C=O out-of-plane deformation, respectively^{21,22}. The bands at 1630 and 1600 are assigned to C=N and C=C stretching frequencies, respectively. The stretching vibrations due to nitrogen in pyridine ring are observed at 1490 and 1050. All these bands in the spectrum of TBINH

indicate that it is present in keto form, and the proposed structure I for the Schiff base may be more likely as,



I. TBINH

A comparative study of ir spectra of TBINH and its complexes reveals the mode of coordination of the ligand. The spectra show the characteristic bands of imino and amide groups, indicating that TBINH is coordinated in keto form. In the spectra of the complexes, amide I band i.e. C=O stretching, shifts to lower frequencies, while the amide II and amide VI bands shift to higher frequencies, but amide IV remains unchanged. These observations show the coordination of keto oxygen to metal ions²³⁻²⁵. The negative shift in C=N stretching and positive shift in N-N stretching suggest that the nitrogen of the azomethine group is coordinated to metal ions^{26,27}.

In acetato-complexes, two bands are observed near 1440 and 1340 which may be assigned to ν(COO) and δ(CH₃) respectively²⁸, and in nitrate-complex bands at 1360 and 840 are assigned to stretching frequency due to nitrate group²⁹. The

TABLE 2—ELECTRONIC SPECTRAL DATA AND LIGAND FIELD PARAMETERS OF THE COMPLEXES

| Complex with | Electronic Spectra | | ν ₂ /ν ₁ | 10 Dq | B' | β | β°(%) | Geometry |
|--------------|--------------------------|--|--------------------------------|--------|--------|------|-------|-----------------------------|
| | Band (cm ⁻¹) | Assignment | | | | | | |
| Mn(II) | 18,520 | *A _{1g} → ⁴ T _{1g} (G) | — | — | — | — | — | Octahedral ^{14,15} |
| | 21,740 | *A _{1g} → ⁴ T _{2g} (G) | | | | | | |
| | 23,260 | *A _{1g} → ⁴ E _g (G) | | | | | | |
| | 26,310 | *A _{1g} → ⁴ T _{1g} (D) | | | | | | |
| | 29,000 | *A _{1g} → ⁴ E _g (D) | | | | | | |
| Co(II) | 10,000 | *T _{1g} (F)→ ⁴ T _{2g} (F) | 2.13 | 11,300 | 901 | 0.93 | 7.21 | Octahedral ^{16,17} |
| | 21,300 ^a | *T _{1g} (F)→ ⁴ A _{1g} (F) | | | | | | |
| | 22,220 | *T _{1g} (F)→ ⁴ T _{1g} (P) | | | | | | |
| | 27,800 | *A _{1g} → ⁴ T _{1g} (F) | | | | | | |
| Ni(II) | 10,200 | *A _{1g} → ³ T _{1g} (F) | 1.48 | 10,200 | 13,900 | 0.87 | 12.93 | Octahedral ¹⁸⁻²⁰ |
| | 15,150 | *A _{1g} → ³ T _{1g} (F) | | | | | | |
| | 27,800 | *A _{1g} → ³ T _{1g} (P) | | | | | | |

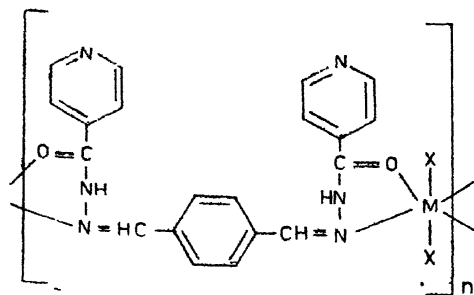
^a Calculated value (Method of Lever¹⁹).

TABLE 3—INFRARED SPECTRA OF TBINH AND ITS COMPLEXES (Wave numbers are in cm⁻¹)

| TBINH | Mn(II) | Co(II) | Ni(II) | Zn(II) | Cd(II) | UO ₂ (VI) | Assignment |
|-------|--------|--------|--------|--------|--------|----------------------|------------------------------------|
| — | 3400 | 3420 | 3400 | 3400 | 3450 | — | O-H(H ₂ O) stretching |
| 3240 | 3240 | 3240 | 3240 | 3240 | 3240 | 3240 | N-H stretching |
| 3050 | 3050 | 3050 | 3050 | 3050 | 3050 | 3050 | O-H stretching |
| — | 1665 | 1665 | 1675 | 1660 | 1660 | — | H ₂ O deformation |
| 1640 | 1590 | 1590 | 1595 | 1590 | 1590 | 1590 | C=O stretching |
| 1630 | 1620 | 1610 | 1620 | 1615 | 1620 | 1620 | C=N stretching |
| 1600 | 1600 | 1605 | 1600 | 1605 | 1605 | 1600 | C=C (aromatic) stretching |
| 1585 | 1550 | 1560 | 1560 | 1560 | 1560 | 1560 | C-N stretching and N-H deformation |
| 1490 | 1490 | 1495 | 1500 | 1490 | 1495 | 1490 | =N-(pyridine) stretching |
| 1295 | 1300 | 1295 | 1295 | 1300 | 1300 | 1300 | N-H deformation |
| 1050 | 1050 | 1045 | 1050 | 1045 | 1050 | 1050 | =N-(pyridine) stretching |
| 915 | 935 | 935 | 935 | 940 | 935 | 935 | N-N stretching |
| 750 | 750 | 750 | 750 | 750 | 750 | 750 | C=O in-plane deformation |
| 670 | 690 | 690 | 690 | 690 | 690 | 690 | C=O out-of-plane deformation |

bands observed in the regions of 3420-3380 and ca 1660 may be assigned to $\nu(\text{OH})\text{H}_2\text{O}$ and $\delta(\text{H}_2\text{O})$, respectively³⁰, and these indicate the presence of water in the complexes^{31,32}.

The metal and ligand ratio of 1:1 does not seem to permit a monomeric complex to exist, since the four coordinating groups of one ligand molecule cannot coordinate to a single metal ion due to steric factors and a polymeric structure II is formed by TBINH-metal linkages.



II. M = Mn(II), Co(II), Ni(II), Zn(II), Cd(II), UO₂(VI).
X = CH₃COO⁻, NO₂⁻.

The thermogravimetric analysis data (Table 4) of the complexes reveal that the rate of percentage loss in weight at lower temperatures is slow. The initial slopes in the curves may be due to the volatilization of water and low molecular weight moieties present in the compounds. The weight loss upto 180° corresponds to the water content of metal-chelates. The abrupt change in weight loss points to the commencement of decomposition of the complexes. The weights of the residue correspond to the formation of oxide of the respective metal. The order of thermal stability of the polymers is: Zn (420°) > Cd (400°) > Co (380°) > Mn (330°) > UO₂ (320°) > Ni (300°).

| Complex with | % weight loss of H ₂ O at 100-180° | | Temperature °C | | % weight of residue | |
|----------------------|---|-------------------|--------------------------------|-------------------------------|---------------------|--------|
| | Found | Calcd. | Commence-ment of decomposition | Comple-tion of decom-position | Found | Calcd. |
| Mn(II) | 3.54 | 3.19 ^a | 330 | 660 | 16.80 | 15.08 |
| Co(II) | 3.36 | 3.18 ^a | 380 | 780 | 15.73 | 14.65 |
| Ni(II) | 5.66 | 6.15 ^a | 300 | 520 | 12.27 | 12.87 |
| Zn(II) | 5.98 | 6.09 ^b | 420 | 600 | 14.56 | 13.70 |
| Cd(II) | 5.43 | 5.65 ^b | 400 | 520 | 22.86 | 20.07 |
| UO ₂ (VI) | — | — | 320 | 640 | 36.86 | 37.20 |

^a for 1H₂O; ^b for 2H₂O.

The geometry of the ligand, and composition, insolubility and high thermal stability of the complexes indicate their polymeric nature.

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