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Spectral Studies of Some Transition Metal Chelates with Thiolactic Anilide and Thiolactic-*p*-Toluidide, Part-II†

MIRU SRIVASTAVA, BIRENDRA KUMAR, RAMDEO PRASAD, NIRMALA KUMARI and SACHCHIDA NAND PRASAD*
Department of Chemistry, Magadh University, Bodh-Gaya-824 234, India

To assign geometrical features to transition and pseudo transition metal(II) complexes with thiolactic anilide (H-TLA) and thiolactic-*p*-toluidide (H-TLPT), IR spectral studies were carried out. The IR spectra of the NI(II) and Cu(II) indicate that the metal ions are coordinated through imino nitrogen of the ligand, whereas Co(II), Hg(II), Pb(II) and Ag(I) are coordinated through oxygen of (C=O) group of the ligand. The disappearance of thiol absorption of bond SH stretching vibration reveals that thiol initially deprotonates and then coordinates with metal through S. Electronic spectral studies of transtion metal complexes corroborate with the findings of magnetic studies, *i.e.*, Co(II), Ni(II) and Cu(II) compounds are basically of octahedral geometry.

INTRODUCTION

A series of transition and pseudo-transition metal(II) complexes with thiolactic anilide (H-TLA) and thiolactic-*p*-toluidide (H-TLPT) were prepared[1]. The compounds were characterised on the basis of their elemental analysis which showed that the complexes have their metal : ligand ratio as 1 : 2. In order to assign specific geometry to these compounds, the dentate behaviours of the ligands with reference to their donor sites were conducted on the basis of IR spectral studies and also the electronic spectral studies of transition metal compounds to confirm their symmetries.

EXPERIMENTAL

The infrared spectra of the compounds as well as of the ligands were recorded in KBr disc. The shift or disappearance of IR frequencies of groups or atoms of ligands involved in coordination, suggests the donor sites and consequently their nature whether they behave as monodentate or bidentate. In case the ligands are bidentate and two of its molecules are attached with metal, the complex will be either tetrahedral or square planar. The complexes may also be octahedral but it

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will be only possible when two of the valencies of metals are satisfied by two other monodental molecules.

RESULTS AND DISCUSSION

IR Spectral studies

The sharp absorption bands located at 3265 and 3272 cm^{-1} are due to ν(NH) vibrations of the ligands, shift to lower frequencies by about 20 cm^{-1} in IR spectra of the complexes of nickel(II) and copper(II). It indicates the involvement of >N—H group coordination with the metal ions through imino nitrogen atom.

The confirmation of N-bonding with the metals in the complexes is obtained by the appearance of low frequency absorption bands formerly not present in the ligand spectra due to ν(M—N) interaction in the range 425–380 cm^{-1}. The absorption bands in the range 425–380 cm^{-1} are tentatively assigned to ν(M—N) vibrations.[2-5]

The absorption bands at 3265 and 3270 cm^{-1} in the ligands are raised in the complexes of Co(II), Hg(II), Pb(II) and Ag(I) by about 10 cm^{-1}. This indicates non-involvement of nitrogen atom of >NH group in the complexes of these metal ions.

The sharp absorption band appearing at 1650 cm^{-1} due to ν(C=O) vibrations in the IR spectra of the ligands is shifted to lower frequencies by about 25–15 cm^{-1} in the spectra of the complexes of Co(II), Hg(II), Pb(II) and Ag(I). This indicates the involvement of >C=O group in coordination with these metal ions in complexes through oxygen. The involvement of carbonyl oxygen in coordination is supported by the appearance of low frequency spectral absorption due to ν(M—O) in the range 500–480 cm^{-1}. The new absorption bands appearing in the region 500–480 cm^{-1} in the spectra of the complexes of these mentioned metal ions are tentatively attributed to ν(M—O).

However, the band located at 1650 cm^{-1} in the spectra of ligands remains unaltered in cases of nickel and copper compounds and indicates the non-involvement of >CO group in formation of coordination compounds.

The disappearance of weak absorption band at 2560 cm^{-1} in IR spectra of the ligands on account of ν(S—H) stretching vibration, however, indicates the deprotonation of thiol (—SH) group and its coordination with metal ions in complexes. The S-bonding with metals is further confirmed by appearance of low frequency spectral absorption[6] on account of ν(M—S) in the range 350–200 cm^{-1}. In the spectra of metal complexes under observation the absorption bands in the region 300–280 cm^{-1} are tentatively attributed to ν(M—S).

Electronic Spectral Studies

In view of the apparent coordination sites and ignoring the conclusion drawn earlier for explaining the magnetic values, the cobalt(II) complexes may be treated either of tetrahedral or octahedral symmetry. In the absence of the criteria, *i.e.*, high extinction coefficient of the bands recorded in this case, an absorption in the

infrared region and splitting of both the ν_2 and ν_3 bands, it is not plausible to attribute tetrahedral symmetry T_d to the present Co(II) complexes.

The doublets observed at 21,430 cm^{-1} and 20,410 cm^{-1} are attributed to the components of ν_3 band $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$. Such a splitting of ν_3 band is attributed either to the spin forbidden transition to doublet terms or to low symmetry ligand field components and is not uncommon[8]. The latter factor is of particular significance in the present case and the compounds exist possibly in distorted octahedral geometry.

Ligand field energy of splitting $10\,D_q$ and Racah interelectronic repulsion parameter B, were calculated and the values obtained for B and Dq of cobalt(II) complexes with the present ligands are found to be B ≈ 190, 22 and Dq = 3503 cm^{-1}.

The electronic spectrum of nickel(II) complex of TLPT shows bands at 12,660, 13,000 and 21,740 cm^{-1}. These are assigned to transitions.

$$\nu_1 = {}^3T_{2g} \leftarrow {}^3A_2g(12{,}660 \text{ and } 13{,}000\ cm^{-1})$$

and

$$\nu_2 = {}^3T_{1g} \leftarrow {}^3A_{2g}(21{,}740\ cm^{-1})$$

The ν_2/ν_1 ratio is evaluated to be *ca.* 1.7 and is well within the limits for octahedral symmetry of nickel(II) complexes; however, the value suggests distortion from the cubic field and hence the splitting of band ν_1. The most probable assignment for the split component can be suggested as

$$^3E_g \leftarrow {}^3B_{2g} : 12{,}660\ cm^{-1}$$

and

$$^3B_{2g} \leftarrow {}^3B_{1g} : 13{,}000\ cm^{-1}$$

The amount of splitting in ν_1 band is taken as measure($35/4D_t$) of degree distortion[10–12] and $D_t = 35\ cm^{-1}$ is evaluated. D_q as apparent is equal to 13,000 cm^{-1}.

Thiolactic anilide nickel complex being almost insoluble does not exhibit bands except one at 21,740 cm^{-1} and is attributed to

$$\nu_2 : {}^3T_{1g} \leftarrow {}^3A_{2g}$$

On the basis of the finding derived above and corroborating with that of the conclusion derived on values of magnetic moments, the complexes under consideration are concluded to have distorted octahedral geometries; however, the emphasis may be made that $Ni(TLA)_2{\cdot}2H_2O$ being insoluble may have polymeric behaviour[13].

In case of copper(II) complexes electronic spectra show only intense bands accountable to (C═O) and (C═S) groups and d-d bands are obscured. However, a very weak and broad symmetric band of both the complexes between 18,520 cm^{-1} and 16,670 cm^{-1} for $Cu(TLA)_2(H_2O)_2$ and 21,740 cm^{-1} and 20,410 cm^{-1} for $Cu(TLPT)_2(H_2O)_2$ are attributed to combination of $3B_{2g} \leftarrow {}^2B_{1g}$, $^2E_g \leftarrow {}^2B_{1g}$ and $^2A_{1g} \leftarrow {}^2B_{1g}$ transitions resulting from distorted tetragonal ligand field.

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