

Coordination Compounds as Ligands: Binuclear Copper(II), Nickel(II) & Cobalt(II) Complexes

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o-N-(Salicylidene)aminobenzoylhydrazine, (LH₂), forms bi-metallic complexes of the formula M[M(LH)₂]X₂·nH₂O, where X = Cl, Br, I or ClO₄ for M = Ni(II) and Co(II), and X = Cl, Br or ClO₄ for M = Cu(II); n = 0, 2, 4 and 5. In these compounds, the complexing ligand M(LH)₂ binds the second metal ion through its two phenolic oxygen atoms placed *cis* to each other. Two heteronuclear compounds of nickel, having the formula Ni[Co(LH)₂]Cl₂ and Ni[Cu(LH)₂]Cl₂ have also been obtained from Co(LH)₂ and Cu(LH)₂ respectively. The C-O stretching frequency around 1525 cm⁻¹ in the complexing ligands M(LH)₂ is shifted to around 1550 cm⁻¹ in the bimetallic complexes, and this serves as an indication of the existence of tricovalent oxygen atoms in these complexes.

Metallic complexes of aliphatic and aromatic acidhydrazides¹⁻³ and of a large variety of schiff bases⁴⁻⁶ have been separately studied in considerable detail. But, very little work appears to have been done with ligands containing both these important catenating groups in a single molecule. The present paper deals with the preparation of one such ligand, viz. *o*-N-(salicylidene)aminobenzoylhydrazine and studies of its complexes with Co(II), Ni(II) and Cu(II). Striking difference in the complexing behaviour of the ligand in acidic and non-acidic media has been noticed. In acidic medium, oxygen-bridged complexes with 1:1 (metal:ligand) ratio are formed, where the complexes M(LH)₂, in which bonding from the schiff base part as well as the hydrazide part of the ligand takes place, act as the coordinating agents to form bimetallic complexes of the composition M(LH)₂, MX₂, nH₂O. The two metal atoms are connected by oxygen-bridge. Schiff base complexes of this type, where oxygen-bridging is present, have been reported earlier by some workers⁷⁻¹².

Materials and Methods

Preparation of *o*-aminobenzoylhydrazine

This was obtained in the form of white shining crystals through the reaction between methylanthranilate (0.2 mol) and hydrazine hydrate (0.3 mol).

Preparation of *o*-N-(salicylidene)aminobenzoylhydrazine

To an ethanolic solution of *o*-aminobenzoylhydrazine (30 g) was added freshly distilled salicylaldehyde (24 g) dropwise with constant shaking. The mixture was kept in an ice-bath for about 2 hr when an yellowish solid separated out. It was filtered and recrystallised from ethanol when a light yellow

crystalline solid, melting at 162°C was obtained. The compound is insoluble in water, but soluble in common organic solvents such as ethanol, methanol, acetone, etc.

Preparation of the metallic complexes:

(i) Cu(LH)₂·CuX₂ (X = Cl, Br, ClO₄)

A saturated solution of the ligand in ethanol was refluxed on a water bath with the ethanolic solutions of copper(II) halide or perchlorate in 1:1 molar proportions for about an hour. Dark green compounds separated out in all the cases. These were filtered, washed with cold water and acetone and dried in air.

(ii) Ni(LH)₂·NiX₂ (X = Cl, Br, I, ClO₄)

These compounds were prepared by methods analogous to that used for the copper(II) complexes mentioned above, using nickel(II) salts in place of Cu(II) salts. The amorphous green compounds that separated out were filtered, washed with ethanol and dried in air.

(iii) Co(LH)₂·CoX₂ (X = Cl, Br, I, ClO₄)

The binuclear Co(II) complexes were prepared from the mono-nuclear Ni(II) complex, Ni(LH)₂, which was obtained by warming the binuclear Ni(II) complexes with water. A suspension of the dry and finely powdered Ni(LH)₂ in ethanol was refluxed with excess of the halide or perchlorate of cobalt(II), when deep yellow or brown coloured amorphous compounds were obtained. These were filtered, washed with ethanol and dried in air.

(iv) M(LH)₂·NiCl₂ (M = Co²⁺ and Cu²⁺)

The starting materials for these two heterochelates were Co(LH)₂ and Cu(LH)₂ which were obtained by

warming aqueous suspensions of the bimetallic Co(II) and Cu(II) complexes described above. The suspension of each of the dry compounds in ethanol was refluxed with excess of nickel chloride for about 5 hr. Light green product was obtained in each case. The compounds were filtered, washed with ethanol and dried in air.

Nitrogen was estimated by Duma's method. The metals, halides and perchlorate were estimated by standard analytical procedures. Water was estimated by loss in weight on heating the compounds at 110°C. The analytical data of the compounds are given in Table 1.

Magnetic susceptibilities of the compounds were measured at room temperature ($\sim 30^\circ\text{C}$) using a Gouy balance and $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant.

Diamagnetic corrections were applied using Pascal's constants¹³. In the binuclear complexes containing the same metal, the magnetic moment value was calculated per g-atom of the metal, but when two different metals were present in a molecule of the complex, the same values were calculated per mole of the compound.

The IR spectra of the complexes were recorded in nujol mull on a Perkin-Elmer Infracord spectrophotometer. The visible spectra of the solid complexes were recorded in nujol on a MOM-21 (Hungarian) spectrophotometer¹⁴. Electrical conductivities of the complexes were measured in doubly-distilled dimethylformamide. The PMR spectrum of the ligand was recorded in CDCl_3 solution using TMS as the standard.

Table 1—Analytical Data of the Complexes

Compound	Colour	Found (calc.), %			
		Metal	N	Anion	H ₂ O
Ni(LH) ₂	Yellow	10.45 (10.40)	14.82 (14.88)	—	—
Ni(LH) ₂ NiCl ₂ ·4H ₂ O	Green	15.38 (15.32)	10.98 (10.96)	9.38 (9.26)	9.40 (9.39)
Ni(LH) ₂ NiBr ₂ ·5H ₂ O	Green	13.40 (13.46)	9.64 (9.62)	18.29 (18.34)	10.20 (10.31)
Ni(LH) ₂ NiI ₂ ·4H ₂ O	Yellowish green	12.40 (12.37)	8.91 (8.87)	26.82 (26.75)	7.43 (7.58)
Ni(LH) ₂ Ni(ClO ₄) ₂ ·5H ₂ O	Green	12.85 (12.86)	9.26 (9.20)	21.78 (21.80)	9.90 (9.86)
Co(LH) ₂	Yellowish brown	10.48 (10.42)	14.83 (14.87)	—	—
Co(LH) ₂ CoCl ₂ ·4H ₂ O	Yellow	15.41 (15.36)	10.98 (10.95)	9.31 (9.26)	9.46 (9.38)
Co(LH) ₂ CoBr ₂ ·4H ₂ O	Reddish brown	13.81 (13.77)	9.80 (9.81)	18.78 (18.70)	8.48 (8.41)
Co(LH) ₂ CoI ₂ ·4H ₂ O	Reddish brown	12.45 (12.40)	8.90 (8.84)	26.78 (26.74)	7.45 (7.58)
Co(LH) ₂ Co(ClO ₄) ₂ ·4H ₂ O	Reddish brown	13.21 (13.17)	9.41 (9.38)	22.32 (22.24)	8.10 (8.04)
Cu(LH) ₂	Green	11.20 (11.15)	14.81 (14.75)	—	—
Cu(LH) ₂ CuCl ₂ ·4H ₂ O	Green	16.42 (16.35)	10.85 (10.82)	9.25 (9.15)	9.41 (9.28)
Cu(LH) ₂ CuBr ₂ ·2H ₂ O	Green	15.16 (15.31)	10.20 (10.14)	19.38 (19.31)	4.28 (4.34)
Cu(LH) ₂ Cu(ClO ₄) ₂	Green	15.31 (15.25)	10.10 (10.09)	23.99 (23.92)	—
Co(LH) ₂ CoCl ₂	Light green	8.46 (8.45)* 8.49 (8.47)†	12.15 (12.09)	10.28 (10.22)	—
NiCl ₂ ·Cu(LH) ₂	Green	8.40 (8.35)* 9.15 (9.08)‡	12.09 (12.01)	10.25 (10.16)	—

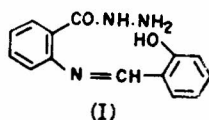
*Ni analysis, †Co analysis, ‡Cu analysis.

Results and Discussion

Structure of the ligand

The condensation of *o*-aminobenzoylhydrazine with salicylaldehyde in 1:1 molar proportion may result in two different products depending upon whether the azomethine linkage is established at the ring -NH_2 or the hydrazine -NH_2 site. The spectral data of the ligand indicate that the ring amino group is involved in the condensation to produce *o*-N-(salicylidene)amino-benzoylhydrazine. The IR spectrum of the ligand shows all the hydrazide bands¹⁵, viz. the bands at 1660, 1527, 1240, 1618, 1350, 1110 and 960 cm^{-1} . Further support of such condensation is obtained by comparing the PMR spectrum of the ligand with those of benzoylhydrazine and *o*-aminobenzoylhydrazine. The PMR spectrum of benzoylhydrazine shows two signals at δ 1.2 ppm (1H) and δ 1.6 (2H), which may be assigned to the amino protons of the hydrazine group. The present ligand also shows the same signals with the same chemical shifts. So, it is clear that the free hydrazide grouping is present in the ligand molecule. In *o*-aminobenzoylhydrazine, another broad band, besides those δ 1.2 and δ 1.6, is present at δ 4.0, which shows the existence of ring amino group; but, this band is absent in the present ligand, indicating the absence of nuclear primary amino group in it.

Some other characteristic bands of the ligand are observed in the IR region. Two bands at 3690 cm^{-1} (weak) and 3550 cm^{-1} (medium strong) are assigned to the enolic and phenolic hydroxyl groups respectively. (The enolic OH group originates from the slight keto-enol tautomerism in the hydrazide part of the ligand.) The relatively smaller lowering of the enolic νOH than that expected because of hydrogen bonding is due to the fact that the hydrogen bond formed by the enolic hydrogen with the nitrogen atom of the -NH_2 group is very weak. This may be due to the lack of conjugation in the five-membered ring formed and the consequent small resonance stabilisation of the ring. The frequency of the phenolic OH group is, however, considerably lowered, as it forms a strong hydrogen bond with the azomethine nitrogen. A sharp band at 1660 cm^{-1} is attributed to the $\nu\text{C}=\text{O}$ and/or $\nu\text{C}=\text{N}$. The bands in the region 3350-3000 cm^{-1} may be due to νNH and/or νNH_2 . Based on these facts, the ligand is represented by the structure (I):

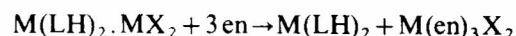


Action of water on the complexes

Each of the binuclear complexes underwent decomposition on warming its aqueous suspension,

forming the corresponding metal chloride (or perchlorate) in solution, together with an insoluble substance which was identified as $\text{M}(\text{LH})_2$, the complexing ligand in these cases. The original compound can, however, be re-formed on refluxing an alcoholic suspension of $\text{M}(\text{LH})_2$ with the corresponding metal halide or perchlorate. Such decomposition of the aqueous suspension of the binuclear complexes on warming suggests that the bonds between the complex ligand $\text{M}(\text{LH})_2$ and the second metal atom are quite weak, making them comparatively less stable.

The same conclusion as above is also drawn from the observation that, when an aqueous suspension of the binuclear compounds is treated with neutralised ethylenediamine (en), the metal ions bonded with $\text{M}(\text{LH})_2$ are detached to form the metal-tris(ethylenediamine) complexes. The following reaction takes place in such cases:



Conductance data

The molar conductance values of the binuclear complexes in dimethylformamide increase with time, giving finally steady values in the range 30-80 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. The gradual increase in the conductance values is most probably due to the partial solvolysis in DMF. These values are far below the molar conductance values for 1:2 type of electrolytes in this solvent, which are about 130-170 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$.

Magnetic moment data

The room temperature ($\sim 30^\circ\text{C}$) magnetic moment values of the complexes $\text{Ni}(\text{LH})_2$, $\text{Co}(\text{LH})_2$ and $\text{Cu}(\text{LH})_2$ are found to be 2.98, 4.20 and 1.76 B.M. respectively, which indicate octahedral or tetragonal crystal field around the metal atoms. The magnetic moment values per gram-atom of the metal in the binuclear nickel(II) complexes are found to be higher than 2.98 B.M. This suggests that the other nickel atom attached to the $\text{Ni}(\text{LH})_2$ ligand (through the *cis*-phenolic oxygen atoms) is either octahedral or tetrahedral, but not in square-planar environment, as the latter geometry would decrease the magnetic moment values due to the presence of diamagnetic nickel. The increase in the magnetic moment value from 2.98 B.M. in the parent compound to about 3.2 B.M. in the binuclear nickel complexes may be explained by assuming tetrahedral or pseudo-tetrahedral crystal-field around the other nickel atom. For tetrahedral nickel(II) complexes, having orbitally degenerate ground state, 3T_1 , large orbital contribution is obvious.

The magnetic moment value of $\text{Co}(\text{LH})_2$ is found to be 4.2 B.M. For octahedral $\text{Co}(\text{II})$ complexes, having

orbitally degenerate ${}^4T_{1g}$ ground state, large orbital contribution is possible. But, if appreciable distortion occurs in the octahedral complexes, thus lowering the cubic symmetry from O_h to D_{4h} , the degeneracy of the ground state term ${}^4T_{1g}$ will be lifted, and consequently, orbital contribution will be reduced. The lower magnetic moment value of $\text{Co}(\text{LH})_2$ clearly indicates that this compound is of distorted octahedral structure. The magnetic moment values of all the binuclear Co(II) complexes lie in the range 4.23-4.40 B.M., from which the geometry of the other cobalt atoms can not be ascertained definitely.

The magnetic moment values per gram-atom of copper in the binuclear copper complexes are in the range 1.95-2.05 B.M. The increase in the magnetic moment values from 1.76 B.M. in the complex ligand to about 2.0 B.M. in the binuclear complexes clearly indicates that the anions bonded to the other copper atoms are more or less tetrahedral.

The magnetic moment values of the two heteronuclear complexes, $\text{Ni}[\text{Co}(\text{LH})_2]\text{Cl}_2$ and $\text{Ni}[\text{Cu}(\text{LH})_2]\text{Cl}_2$ are found to be 4.85 B.M. and 3.20 B.M. respectively. These values are in agreement with the spin only values obtained from the equation¹⁶,

$$\mu_{\text{eff.}} = 2 \times \sqrt{\sum_{i=1}^m S_i(S_i + 1)}$$

Nothing can, however, be said conclusively regarding the stereochemistry of the other nickel atom from the magnetic moment values of the two heteronuclear complexes.

IR spectra

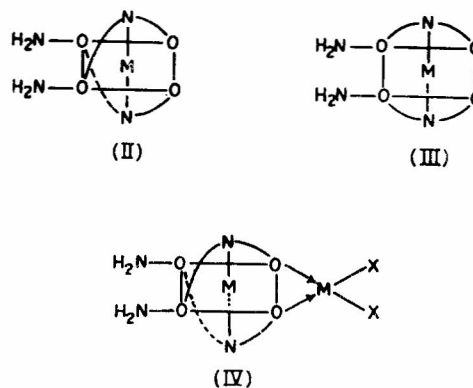
In the complexes $\text{M}(\text{LH})_2$, the 3550 cm^{-1} band is absent, indicating the bonding of the metal to the deprotonated phenolic $-\text{OH}$ group. In the $\text{M}(\text{LH})_2$ complexes, the 1660 cm^{-1} band of the ligand is lowered to about 1610 cm^{-1} , showing bonding from $\text{C}=\text{O}$ and $\text{C}=\text{N}$. The unchanged nature of the bands in the region $3350\text{--}3000\text{ cm}^{-1}$ in the above complexes eliminates the possibility of the involvement of the hydrazinic $-\text{NH}_2$ group in bond formation. These compounds also show bands around 1525 cm^{-1} , which may be assigned to the $\text{C}-\text{O}-\text{M}$ stretching frequency. In the IR spectra of the binuclear complexes, all the observed bands are similar in nature and position to those of the $\text{M}(\text{LH})_2$ complexes, except that the bands at 1525 cm^{-1} in the $\text{M}(\text{LH})_2$ complexes are shifted to $\sim 1550\text{ cm}^{-1}$ in the binuclear complexes. When tricovalent oxygen atoms are present in a compound, the $\nu\text{C}-\text{O}$ frequency must occur in higher wave-number region in comparison with the $\nu\text{C}-\text{O}$ frequency in the compounds where oxygen-bridging is absent.

Visible spectra

All the complexes show strong bands in the 25000 cm^{-1} region, which obviously arise from intra-ligand electronic transitions. The $\text{Ni}(\text{LH})_2$ and $\text{Co}(\text{LH})_2$ complexes show bands in the region 9000 , 10000 , $16,000$ and $24,000\text{ cm}^{-1}$. The presence of the two bands in $9,000\text{--}10,000\text{ cm}^{-1}$ region indicates tetragonal distortion in the complexes. The $\text{Cu}(\text{LH})_2$ complex shows a broad envelope at $16,000\text{ cm}^{-1}$ region, indicating octahedral or tetragonal crystal-field around the metal atom. In the binuclear complexes of Ni(II) and Co(II), sharp bands around $13,500\text{ cm}^{-1}$ occur, which suggest the presence of tetrahedral metal atoms in them. The binuclear Cu(II) complexes show sharp bands around $9,000\text{ cm}^{-1}$, which are most probably due to tetrahedral copper(II) ions. From the electronic spectra of the binuclear complexes, it is suggested that of the two metal atoms present in each of them, one is in tetragonal and the other is in tetrahedral crystal field.

Structures of the complexes

Considering the fact that both the phenolic oxygen atoms of the ligand in the complex $\text{M}(\text{LH})_2$ can take part in bridge formation, they must be placed at the *cis*-position to each other. So, the $\text{M}(\text{LH})_2$ complex should have either structure (II) or (III):



where $\text{H}_2\text{N}-\text{O}-\text{N}-\text{O}$ represents the mono-anion of the ligand. As much strain is involved in structure (III), structure II is more probable for $\text{M}(\text{LH})_2$. Consequently, the binuclear complexes should be represented by the structure (IV) shown below:

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