

Studies on Spectral Properties of Co(II), Ni(II) and Cu(II) Complexes with Ninhydrine and Ninhydrine Oximes

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A series of complexes of the type $ML^{1-3}Cl_2, ML^{1-3}Cl_2Y_2$, where $M = Co(II), Ni(II)$ and $Cu(II)$, $L^1 =$ ninhydrine, $L^2 =$ ninhydrine monoxime, $L^3 =$ ninhydrine dioxime, $Y = NH_3$ or pyridine, have been synthesised and characterised by elemental analysis, molar conductivity, electronic absorption spectra and infrared spectra. On the basis of experimental data the complexes of the type $ML^{1-3}Cl_2$ are found to be square planar whereas complexes of the type $ML^{1-3}Cl_2Y_2$ are found to be octahedral. The complexes are found to be non-electrolytic in nature on the basis of molar conductivity value.

INTRODUCTION

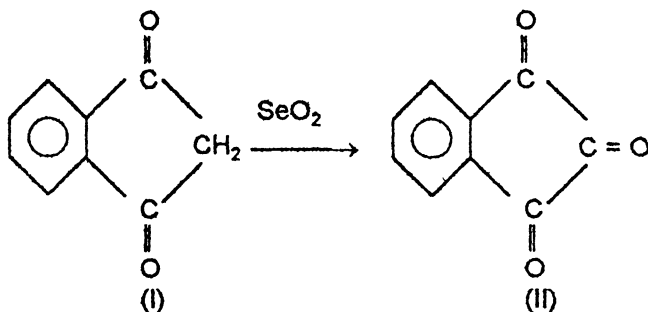
Organic chelating ligands containing oxime functional group have been extensively used in analytical chemistry for the detection and separation of metals¹⁻⁵. Extensive research done⁶⁻¹¹ on metal complexes with oximes and related ligands has been done in recent years but there seems to be no report on complexes with ninhydrine and related ligands. The present research paper deals with Co(II), Ni(II) and Cu(II) complexes with ninhydrine and related ligands.

EXPERIMENTAL

All the chemicals and solvents used for synthesis are LR Grade.

Preparation of Ninhydrine, L^1

Ninhydrine was prepared by applying Teeters and Shriner method¹². The only method of preparation by Ryhermann¹³ was laborious, expensive and required starting materials which were not readily available. In the present method it was found that diketohydrinedene(I) prepared from diethyl phthalate and ethylacetate according to the method mentioned by Wislicenus¹⁴ could be readily oxidised to ninhydrine(II) by means of selenium dioxide.



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A thorough study of this oxidation reaction was made and the maximum yields obtainable were found to be 31–33%. Variations in the order of mixing the reagent, solvents, temperatures and use of selenium acid instead of sublimed SeO_2 failed to increase the yield. The low yield was apparently due to bimolecular product formed by the combination of two molecules of diketohydrinedene or by the combination of one of the latter with one of the triketohydrinedenes. Similar bimolecular products were formed by the action of H_2O_2 on 1,3-diketohydrinedene. This byproduct did not cause any difficulty in the procedure and the ninhydrine was easily isolated in the pure state.

Since the 1,3-diketohydrinedene is readily prepared from the expensive starting materials which are available commercially, the low yield in the oxidation step is not serious and ninhydrine can now be considered as a potentially cheap reagent. The L^2 and L^3 ligands are prepared by the conventional method for the preparation of oximes and dioximes.

RESULTS AND DISCUSSION

Infrared spectra of complexes have been recorded in the frequency region $4000\text{--}400\text{ cm}^{-1}$. Vibrational bands of structural significance recorded in Table-1 have been analysed for elucidation of the structures and bonding of the complexes. Although the infrared spectra of the complexes are quite complex, structurally important vibrational bands such as (C—O) stretch, (O—H) stretch, N—OH scissoring, (C \equiv N) stretch and (N—O) stretch are quite discernible and provide unequivocal evidences concerning the nature of the bonding of the ligands with the metal ion. Apart from this, there has been found an overall similarity in the spectra indicating similarity in structures and mode of coordination in the complexes.

The infrared spectra of ninhydrine shows no band in the region above 3000 cm^{-1} whereas spectrum of ninhydrine monoxime shows a broad and strong absorption peak at 3200 cm^{-1} which can be assigned to the $\nu(\text{O—H})$ of N—OH group of the oxime.

In the spectra of the metal complexes of the type ML^2Cl_2 and ML^3Cl_2 the above mentioned peak persists, indicating ligands coordination in unchanged state.

Spectra of all the ligands show a strong intense peak at 1700 cm^{-1} which can be assigned to the $\nu(\text{C=O})$. This persists with red shift indicating coordination of nitrogen of the (C—N) group of oxime with the metal ion. The band at 1100 cm^{-1} in the spectra of the ligands L^2 and L^3 as well as in the spectra of the complexes can be assigned to $\nu(\text{N—O})$, indicating non-involvement of oxygen atom of (N—O) group in coordination.

Some additional bands appear in the spectra of the complexes in comparison to that of the ligand in the far infrared region which arises due to (M—N) and (M—X) linkage.

Electronic spectra and magnetic moment data of the complexes

The electronic spectral and magnetic moment data are recorded in Table-2.

The electronic spectra of all the Co(II) complexes of the type $ML^{1-3}Cl_2$ and $ML^{1-3}Cl_2Y_2$ exhibit a multiplet band structure in the region $20,500-18,500\text{ cm}^{-1}$ the band width spreading over 2000 cm^{-1} . The band can be assigned to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and ${}^2A_{1g} \rightarrow {}^2B_{1g}(d_{x^2-y^2})$ respectively.

The magnetic moment data of all the Co(II) complexes of the type $CoL^{1-3}Cl_2Y_2$ lie in the range of 4.7 to 5.2 B.M. which indicate the octahedral structure of these complexes. The magnetic moment data of the cobalt(II) complex of the type $ML^{1-3}Cl_2$ lie in the range of 2.0 to 2.4 B.M. and suggest planar structure for them.

The electronic spectra of the complexes of the type $NiL^{1-3}Cl_2Y_2$ are recorded in Table 2. The spectra consist of three bands, one in the region $14,000-13,000\text{ cm}^{-1}$, the next one in the range of $19,000-18,000\text{ cm}^{-1}$ followed by a strong intense band in the vicinity of $24,000\text{ cm}^{-1}$. These can be assigned to the transitions ${}^3A_{2g} \rightarrow {}^2T_{2g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ respectively in an octahedral field. Complexes of the type $[NiL^{1-3}Cl_2]$ are found to be diamagnetic and show two bands one in the region $16,000-15,000\text{ cm}^{-1}$ and another one in the range $20,000-19,000\text{ cm}^{-1}$. This suggests square planar geometry for the complexes and bands can be assigned to the transitions ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1B_{2g}$ respectively.

The electronic spectra of the Cu(II) complex of the type $CuL^{1-3}Cl_2$ gives one sharp band at about $17,500\text{ cm}^{-1}$. The electronic spectra of the complexes of the type $ML^{1-3}Cl_2Y_2$ give one sharp band at about $15,400\text{ cm}^{-1}$.

The magnetic moment values for the Cu(II) complexes of the type $CuL^{1-3}Cl_2$ lie in the range of 1.73–1.80 and the complexes of the type $CuL^{1-3}Cl_2Y_2$ [where $Y = NH_3$ or pyridine] are in the range 1.90 to 2.20 B.M.

On the basis of elemental analysis data, infrared spectra, electronic spectra and magnetic moment values we find that the complexes of the type $ML^{1-3}Cl_2$ are square planar in geometry whereas the complexes of the type $ML^{1-3}Cl_2Y_2$ are octahedral. A representative structure of both types has been shown in Figs. 1 and 2 respectively.

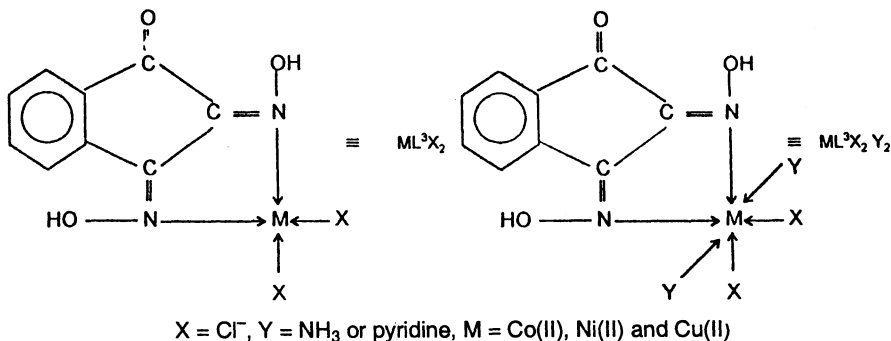


Fig. 1

Fig. 2

TABLE-1
 INFRARED SPECTRAL DATA OF LIGANDS L¹, L² & L³ AND THEIR
 COMPLEXES WITH Co(II), Ni(II) and Cu(II) METAL IONS

Ligands and Complexes	$\nu(\text{O—H})$	$\nu(\text{C=N})$	$\nu(\text{C=O})$	$\nu(\text{N—O})$
L ¹	—	—	1700s	—
L ²	3200b	1600s	1720s	1100m
L ³	3210b	1605s	1715s	1115m
[CoL ¹ Cl ₂]	—	—	1730s	—
[CoL ² Cl ₂]	3220b	1625s	1735s	1130m
[CoL ³ Cl ₂]	3218b	1630s	1732s	1115m
[CoL ¹ Cl ₂ (NH ₃) ₂]	3215b	1620s	1735s	1110m
[CoL ¹ Cl ₂ (Py) ₂]	3225b	1625s	1728s	1115m
[CoL ² Cl ₂ (NH ₃) ₂]	3225b	1615s	1730s	1115m
[CoL ² Cl ₂ (Py) ₂]	3215b	1630s	1735s	1120m
[CoL ² Cl ₂ (NH ₃) ₂]	3220b	1635s	1732s	1125m
[CoL ³ Cl ₂ (Py) ₂]	3225b	1630s	1730s	1120m
[NiL ¹ Cl ₂]	—	—	1725s	—
[NiL ² Cl ₂]	3220b	1630s	1730s	1115m
[NiL ³ Cl ₂]	3215b	1625s	1735s	1105m
[NiL ¹ Cl ₂ (NH ₃) ₂]	3230b	1630s	1725s	1115m
[NiL ¹ Cl ₂ (Py) ₂]	3220b	1620s	1735s	1110m
[NiL ² Cl ₂ (NH ₃) ₂]	3230b	1625s	1730s	1115m
[NiL ² Cl ₂ (Py) ₂]	3220b	1620s	1735s	1110m
[NiL ³ Cl ₂ (NH ₃) ₂]	3230b	1630s	1730s	1105m
[NiL ³ Cl ₂ (Py) ₂]	3235b	1625s	1735s	1120m
[CuL ¹ Cl ₂]	—	—	1730s	—
[CuL ² Cl ₂]	3200b	1605s	1725s	1115m
[CuL ³ Cl ₂]	3210b	1610s	1720s	1115m
[CuL ¹ Cl ₂ (NH ₃) ₂]	3215b	1605s	1730s	1120m
[CuL ¹ Cl ₂ (Py) ₂]	3215b	1620s	1715s	1115m
[CuL ² Cl ₂ (NH ₃) ₂]	3220b	1610s	1725s	1110m
[CuL ² Cl ₂ (Py) ₂]	3215b	1615s	1725s	1115m
[CuL ³ Cl ₂ (NH ₃) ₂]	3220b	1610s	1720s	1115m
[CuL ³ Cl ₂ (Py) ₂]	3215b	1600s	1725s	1120m

TABLE-2
ELECTRONIC SPECTRA (cm^{-1}) AND MAGNETIC MOMENT DATA (B.M.)
OF Co(II), Ni(II), AND Cu(II) COMPLEXES

Complexes	${}^4T_{2g}(F) \rightarrow {}^4T_{1g}(P)$			μ_{eff}
$[\text{CoL}^1\text{Cl}_2(\text{NH}_3)_2]$	18900			4.82
$[\text{CoL}^1\text{Cl}_2(\text{Py})_2]$	19700			4.90
$[\text{CoL}^2\text{Cl}_2(\text{NH}_3)_2]$	19200			4.85
$[\text{CoL}^2\text{Cl}_2(\text{Py})_2]$	19800			5.00
$[\text{CoL}^3\text{Cl}_2(\text{NH}_3)_2]$	19500			4.95
$[\text{CoL}^3\text{Cl}_2(\text{Py})_2]$	20200			5.15
Complexes	${}^2A_{1g} \rightarrow {}^2B_{1g}(dx^2 - y^2)$			μ_{eff}
CoL^1Cl_2	20400			2.20
CoL^2Cl_2	20300			2.30
CoL^3Cl_2	20200			2.40
Complexes	${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$	μ_{eff}
$[\text{NiL}^1\text{Cl}_2(\text{NH}_3)_2]$	13000	18700	24700	2.92
$[\text{NiL}^2\text{Cl}_2(\text{Py})_2]$	13800	18500	24800	2.87
$[\text{NiL}^2\text{Cl}_2(\text{NH}_3)_2]$	13000	19000	24600	2.92
$[\text{NiL}^2\text{Cl}_2(\text{Py})_2]$	13800	18000	24000	2.92
$[\text{NiL}^3\text{Cl}_2(\text{NH}_3)_2]$	14200	19000	24000	2.87
$[\text{NiL}^3\text{Cl}_2(\text{Py})_2]$	14100	18300	24700	2.92
Complexes	λ_{max} (electronic)			μ_{eff}
CuL^1Cl_2	17400			1.73
CuL^2Cl_2	17300			1.78
CuL^3Cl_2	17500			1.80
$\text{CuL}^1\text{Cl}_2(\text{NH}_3)_2$	15400			1.90
$\text{CuL}^1\text{Cl}_2(\text{Py})_2$	15300			1.92
$\text{CuL}^2\text{Cl}_2(\text{NH}_3)_2$	15200			1.93
$\text{CuL}^2\text{Cl}_2(\text{Py})_2$	15100			1.95
$\text{CuL}^3\text{Cl}_2(\text{NH}_3)_2$	15600			1.92
$\text{CuL}^3\text{Cl}_2(\text{Py})_2$	15500			2.10
Complexes	${}^1A_{1g} \rightarrow {}^1B_{1g}$		${}^1A_{1g} \rightarrow {}^1B_{2g}$	
NiL^1Cl_2	15300		19800	
NiL^2Cl_2	15400		19600	
NiL^3Cl_2	15200		19700	

Conductivities of the complexes of the type $ML^{1-3}Cl_2$ and $ML^{1-3}Cl_2Y_2$ were measured in the solvent dimethyl sulphoxide and all the complexes were found to be non-electrolytic in nature giving conductivity values in the range 10 to 20 $ohm^{-1} cm^2 mole^{-1}$. The conductivity value also supports the structure assigned on the basis of elemental analysis, infrared spectra, electronic spectra and magnetic moment data.

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