

Complexes of the schiff base derived from phenylbiguanide and diacetyl monoxime with copper(II) and nickel(II)

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The imine-oxime ligand (H_2L) derived from phenyl biguanide and diacetyl monoxime forms 1:1 and 1:2 complexes with Cu(II) and only 1:2 complexes with Ni(II). In all these complexes the ligand acts in the tridentate uninegative form and is mostly protonated. Copper(II) forms complexes of the types $[Cu(HLH)X]X$ where $X = Cl^-$ or Br^- and $[Cu(HLH)_2]X_2$ where $X = Cl^-, Br^-, I^-$ or OH^- while nickel(II) forms complexes of the types $[Ni(HLH)_2]X_2$ where $X = Cl^-, Br^-$ or I^- and $[Ni(HL)_2]$. The 1:1 complexes are square-planar while the 1:2 complexes are distorted octahedral.

Biguanides¹⁻³ and schiff bases⁴⁻⁶ derived from them are well known for chelate formation with transition metal ions. The imine-oximes⁷ are schiff bases of α -carbonyl oximes and have two or more coordination sites depending on the amine used. The coordination chemistry of the imine-oxime (H_2L) derived from biguanide and diacetyl monoxime is of much interest because it has an additional oxime group as a potential donor site apart from the donor sites present in the biguanide unit, which is known to act as a uninegative bidentate donor. The aim of the present work is to investigate the effect of the substituents on the ligational property of this imine-oxime. The present study deals with the preparation and characterisation of copper(II) and nickel(II) complexes of H_2L which contains a phenyl group in the biguanide part.

Materials and Methods

Phenyl biguanide hydrochloride (1 mol) and sodium hydroxide (1 mol) were refluxed on a water-bath for 30 min in dry ethanol. The precipitated sodium chloride was filtered off. The filtrate containing free phenylbiguanide was mixed with diacetyl monoxime (1 mol) and the mixture was refluxed on a water-bath for 2 hours. The solution, on partial evaporation and cooling, gave a white crystalline solid (m.p. 235°C) which, from elemental analyses, IR spectra and PMR spectra, was characterised as the schiff base of phenylbiguanide and diacetyl monoxime (H_2L), $C_6H_5NHC(=NH)NHC(=NH)N=C(CH_3)C(CH_3)=NOH$. This compound (H_2L) was used to prepare different metal complexes.

Compounds of the type $[M(HLH)_2]Cl_2$ where $M = Cu(II)/Ni(II)$ were prepared by refluxing etha-

nolic solution of copper(II)/nickel(II) chloride (1 mol) and the ligand (2 mol) when the complexes precipitated. The precipitate was filtered, washed with ethanol and dried *in vacuo* over fused $CaCl_2$.

The complexes $[Cu(HLH)_2](OH)_2/[Ni(HL)_2]$ were prepared by warming together ethanolic solutions of $[M(HLH)_2]Cl_2$ (1 mol) and sodium hydroxide (2 mol) for some time. Precipitated sodium chloride was filtered off. The filtrate was partly evaporated and cooled when the solid complex separated. It was filtered, washed with ethanol and dried *in vacuo* over fused $CaCl_2$.

Complexes of the type $[Cu(HLH)_2]X_2$ where $X = Br^-/I^-$ were prepared by metathesis reaction between $[Cu(HLH)_2](OH)_2$ and NH_4Br/NH_4I in ethanolic medium.

Complexes of the type $[Ni(HLH)_2]X_2$ where $X = Br^-/I^-$ were also prepared by metathesis reaction between $[Ni(HL)_2]$ and NH_4Br/NH_4I in ethanolic medium.

For preparing $[Cu(HLH)X]X$ where $X = Cl^-/Br^-$, copper(II) chloride/copper(II) bromide and the ligand in 1:1 mole ratio were refluxed in ethanol when a crystalline solid precipitated. The precipitate was filtered, washed with ethanol and dried *in vacuo* over fused $CaCl_2$.

1:1 Ni(II) complexes could not be isolated. $[Cu(HLH)Cl]Cl$ on reaction with alkali in ethanol gave a precipitate of copper hydroxide and a pink solution which on concentration gave $[Cu(HLH)_2](OH)_2$. Elemental analyses of the ligand and its complexes and some of the physicochemical properties of the complexes are listed in Table 1.

Carbon, hydrogen and nitrogen contents were measured by PE 240 elemental analyser and metals,

Table 1—Characterisation data of phenylbiguanido diacetyl imine-oxime (H₂L) and its copper(II) and nickel(II) complexes

Compound	Colour	Found (Calc), %						μ_{eff} (B.M.)	λ_{max} (nm)
		M	C	N	H	X	H ₂ O		
H ₂ L	White	—	55.14 (55.38)	32.00 (32.30)	6.22 (6.15)	—	—	—	—
[Cu(HLH)Cl]Cl	Bluish green	15.64 (16.09)	36.45 (36.50)	21.10 (21.29)	4.10 (4.05)	18.14 (17.99)	—	1.75	645
[Cu(HLH)Br]Br	Greenish blue	13.15 (13.00)	—	17.32 (17.33)	—	33.01 (33.20)	—	1.79	635
[Cu(HLH) ₂]Cl ₂	Rose red	9.56 (9.70)	43.50 (44.00)	25.40 (25.67)	4.88 (4.89)	11.60 (10.85)	—	1.90	560
[Cu(HLH) ₂]Br ₂	Rose red	8.60 (8.54)	—	22.30 (22.60)	—	22.00 (21.49)	—	1.86	560
[Cu(HLH) ₂]I ₂	Rose red	7.47 (7.58)	—	19.91 (20.06)	—	29.90 (30.31)	—	1.85	560
[Cu(HLH) ₂](OH) ₂	Pink	10.18 (10.28)	—	27.08 (27.21)	—	—	5.15 (5.83)	1.83	558
[Ni(HLH) ₂]Cl ₂	Orange red	9.20 (9.03)	42.91 (44.33)	24.67 (25.86)	4.96 (4.92)	10.57 (10.93)	—	Diamagnetic	450
[Ni(HLH) ₂]Br ₂	Orange	8.04 (7.95)	—	23.15 (22.75)	—	22.10 (21.64)	—	Diamagnetic	450
[Ni(HLH) ₂]I ₂	Orange	7.15 (7.05)	—	20.02 (20.18)	—	30.16 (30.49)	—	Diamagnetic	450
[Ni(HL) ₂]	Orange	11.00 (10.81)	—	28.87 (29.13)	—	—	—	Diamagnetic	450

M = Cu²⁺ / Ni²⁺, X = Cl⁻, Br⁻, I⁻, H₂L = C₁₂H₁₆N₆O

halogens and water were estimated⁸ by usual procedures. A Philips conductivity bridge, model GM 424, with a bottle type cell was used for conductivity measurements in water. Magnetic moments were measured using a PAR vibrating sample magnetometer (VSM), model 155. IR spectra were recorded in KBr/CsBr on a Beckman IR 20A instrument while a Shimadzu UV-240 UV visible spectrophotometer was used to record the electronic spectra in the range 400-800 nm in water/CCl₄. PMR spectra of the ligand and its diamagnetic nickel(II) complexes were recorded on a JEOL FX-100 instrument using DMSO-*d*₆ as solvent and TMS as internal standard.

Results and Discussion

All the complexes are soluble in ethanol. Except [Ni(HL)₂], they are also soluble in water. Only [Ni(HL)₂], unlike others, is freely soluble in CHCl₃ and CCl₄.

Molar conductances of [Cu(HLH)₂]Cl₂, [Ni(HLH)₂]Cl₂ and [Cu(HLH)Cl]Cl in aqueous solution are 154.5, 165.9 and 139 ohm⁻¹ cm² mol⁻¹ respectively suggesting them to be 1:2 electrolytes. Such electrolytic behaviour of the complexes is due

to monoprotation⁹ on the biguanide part of the ligand. The observed lower values of conductance are probably due to bulky complex cation. The behaviour of [Cu(HLH)Cl]Cl as 1:2 electrolyte is perhaps due to the ionization of its coordinatively bound chloride in addition to the salt type chloride forming the ions [Cu(HLH)(H₂O)]²⁺ and 2 Cl⁻ in solution. Although there is no direct proof of the occurrence of the complex cation [Cu(HLH)(H₂O)]²⁺, this formulation is necessary to maintain coordination number four which is much more common than coordination number three for Cu(II).

IR spectrum of diacetyl monoxime shows strong $\nu(\text{C}=\text{O})$ band at 1662 cm⁻¹, $\nu(\text{C}=\text{N})$ band at 1650 cm⁻¹ and a broad $\nu(\text{O}-\text{H})$ band at 3200 cm⁻¹ while the spectrum of phenylbiguanide shows $\nu(\text{N}-\text{H})$ bands at 3280 and 3310 cm⁻¹ and $\nu(\text{C}=\text{N})$ band at 1640 cm⁻¹. The spectrum of the ligand shows the absence of $\nu(\text{C}=\text{O})$ band and presence of a strong $\nu(\text{C}=\text{N})$ band at 1645 cm⁻¹ indicating formation of schiff base linkage. The $\nu(\text{C}=\text{N})$ band in the ligand shows a shoulder which may be due to the presence of different C=N groups. The ligand shows many other bands also, and in metal complexes, some of them show clear shifts charac-

Table 2—Important IR absorption bands (in cm^{-1}) of the schiff base (H_2L), derived from phenylbiguanide and diacetyl monoxime and its metal complexes

Compound	$\nu(\text{N}-\text{H})$	$\nu(\text{O}-\text{H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{N})$	$\nu(\text{N}-\text{O})$
H_2L	3320	3170	1645	1320, 1290	933
$[\text{Cu}(\text{HLH})\text{Cl}]\text{Cl}$	3390, 3320	3220	1670, 1600	1260, 1240	910
$[\text{Cu}(\text{HLH})\text{Br}]\text{Br}$	3390, 3320	3220	1670, 1610	1265, 1250	910
$[\text{Cu}(\text{HLH})_2]\text{Cl}_2$	3460, 3360	3200	1710, 1670, 1610	1290, 1270	925
$[\text{Cu}(\text{HLH})_2]\text{Br}_2$	3465, 3370	3210	1710, 1670, 1610	1295, 1260	925
$[\text{Cu}(\text{HLH})_2]\text{I}_2$	3460, 3365	3210	1710, 1670, 1610	1290, 1265	925
$[\text{Cu}(\text{HLH})_2](\text{OH})_2$	3440, 3365	3200	1670, 1630 1600	1290, 1270	925
$[\text{Ni}(\text{HLH})_2]\text{Cl}_2$	3440, 3360	3220	1710, 1675 1610	1305, 1280	925
$[\text{Ni}(\text{HLH})_2]\text{Br}_2$	3440, 3365	3220	1710, 1670 1610	1305, 1280	925
$[\text{Ni}(\text{HLH})_2]\text{I}_2$	3440, 3360	3220	1710, 1675 1610	1305, 1280	925
$[\text{Ni}(\text{HL})_2]$	3440, 3320 3240	—	1625, 1595	1350	920

Table 3—PMR signals (in δ , ppm) of H_2L and its nickel(II) complexes

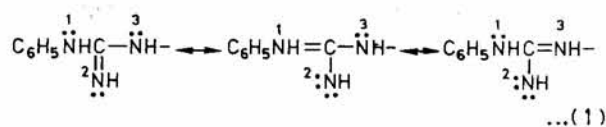
Compound	(CH_3)	(NH)	(C_6H_5)	($=\text{NOH}$)
H_2L	1.92 (s, 3H) 3.36 (s, 3H)	6.96-7.28	(cm, 9H)	9.98 (bs, 1H)
$[\text{Ni}(\text{HLH})_2]\text{Cl}_2$	1.88 (s, 3H) 3.88 (s, 3H)	5.80 (s, 4H)	7.18-7.22 (m, 5H)	9.76 (bs, 1H)
$[\text{Ni}(\text{HLH})_2]\text{Br}_2$	1.88 (s, 3H) 3.88 (s, 3H)	5.80 (s, 4H)	7.18-7.22 (m, 5H)	9.76 (bs, 1H)
$[\text{Ni}(\text{HLH})_2]\text{I}_2$	1.88 (s, 3H) 3.88 (s, 3H)	5.80 (s, 4H)	7.18-7.22 (m, 5H)	9.76 (bs, 1H)
$[\text{Ni}(\text{HL})_2]$	1.88 (s, 3H) 3.32 (s, 3H)	5.60 (s, 3H) 6.68 (d, 1H)	7.16-7.4 (m, 5H)	—

s = singlet, d = doublet, m = multiplet, cm = complex multiplet, bs = broad singlet
*Signals due to NH and C_6H_5 moieties overlapped to form a complex multiplet.

terising the mode of ligation. Important bands of structural significance and their possible assignments are listed in Table 2.

$\nu(\text{C}=\text{N})$ band in metal complexes, except the $[\text{Ni}(\text{HL})_2]$ complex, shows both red and blue shifts. The red shift clearly indicates that bonding to the metal occurs¹⁰ via oxime and imine ($\overset{5}{\text{N}}$) nitrogen atoms. The ligand in its complexes behaves in a uninegative tridentate manner indicating the presence of a third coordination site. The observed shift of $\nu(\text{C}=\text{N})$, whether it is both red and blue or only red, may be useful in deciding this point.

In the ligand, conjugation in the phenylamidine part of the type (1), lowers the $\nu(\text{C}=\text{N})$ band to 1645 cm^{-1} . If $\overset{1}{\text{N}}$ coordinates to the metal, $\nu(\text{C}=\text{N})$ band

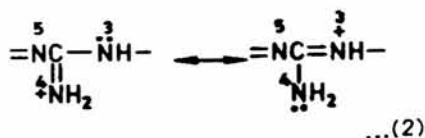


is expected to show a blue shift because this mode

hinders conjugation; but if $\overset{2}{\text{N}}$ coordinates, a red shift is expected. This system is analogous to urea where the observed shifts^{11,12} of $\nu(\text{C}=\text{O})$ band in its metal complexes have been used to decide the point of coordination. The observed blue shift of $\nu(\text{C}=\text{N})$

clearly indicates that $\overset{1}{\text{N}}$ takes part in coordination in all the complexes except $[\text{Ni}(\text{HL})_2]$ where the occurrence of only red shift of $\nu(\text{C}=\text{N})$ indicates coor-

dination through $\overset{2}{N}$. This conclusion is also supported by the observed lowering of $\nu(C-N)$ and $\nu(N-O)$ bands. The present ligand has two potential deprotonation centers, viz., the oxime proton and C_6H_5NH -proton and only one of the protons is lost in the complexes. As $\nu(O-H)$ band virtually remains unaffected around 3200 cm^{-1} , the complexes, except the $[Ni(HL)_2]$ complex, probably retain the oxime proton and lose C_6H_5NH -proton on coordination. This is also expected on the basis of the electron attracting behaviour of the adjacent phenyl group. It may be noted that frequencies of $\nu(N-H)$ bands in the complexes are consistently higher than that in the ligand. This may be due to the presence of an $-NH_2$ group¹³ which might have originated^{9,14} from the tautomerisation of NH proton to give NH_2 group at $\overset{4}{N}$. As the ligand in the complexes is monoprotonated, this protonation leaves $C=N$ group as such which exhibits blue shift of $\nu(C=N)$ band as pointed out earlier. But resonance interaction of the type (2), might again result in NH_2 group shifting the protonation to $\overset{3}{N}$.



PMR signals of the ligand and its nickel(II) complexes with their possible assignments, multiplicities and proton counts are listed in Table 3. From the results it is clear that the oxime proton is retained in the structures of $[Ni(HLH)_2]X_2$ where $X = Cl^-, Br^-, I^-$ but it is lost in $[Ni(HL)_2]$. This observation supports the conclusion arrived at from IR data. Since in $[Ni(HL)_2]$ coordination occurs through $\overset{2}{N}$ in place of $\overset{1}{N}$, loss of oxime proton is quite likely.

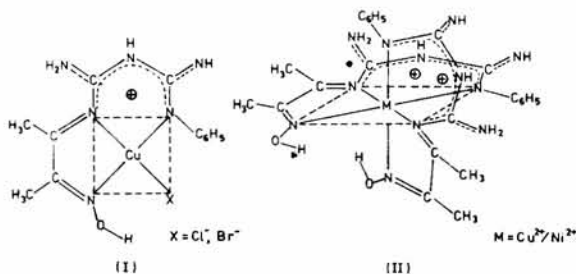
Room temperature magnetic moment of 1:1 Cu(II) complex is 1.75 B.M. This, in conjunction with the suggested coordination sites of the ligand indicates a square-planar geometry for the complex. This view is supported by the electronic spectra which show only a single, somewhat asymmetric band around 635-645 nm covering the transitions¹⁵, ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$; the transition ${}^2B_{1g} \rightarrow {}^2E_g$ being in the higher energy region, has probably escaped detection.

μ_{eff} values of 1:2 Cu(II) complexes at room temperature are around 1.9 B.M. which together with

the 1:2 (metal:ligand) stoichiometry suggest a distorted octahedral geometry for the complexes. The electronic spectra show a broad asymmetric band around 560 nm which, as in 1:1 complex, corresponds to identical transitions and supports a distorted octahedral geometry.

1:2 Ni(II) complexes are diamagnetic implying either a square-planar or a distorted octahedral geometry for the complexes. The electronic spectra show one band only at 450 nm which again suggests a similar geometry¹⁶ for the complexes. However, in view of the presence of three properly separated potential donor sites in the ligand molecule and participation of those donor sites in coordination as indicated from IR data, it may be assumed that the complexes probably possess a distorted octahedral geometry and the observed spectral band covers the transitions, ${}^1B_{1g} \rightarrow {}^1E_g$ and ${}^1B_{1g} \rightarrow {}^1A_{2g}$.

In the octahedral complexes, the ligand, because of its structural framework, probably spans meridionally rather than facially. In consonance with the reported structure¹⁴ of the biguanide moiety in metal complexes, 1:1 and 1:2 complex cations under study may be represented by the structures (I) and (II)



which show ligand with a delocalised π bond in the biguanide part and a positive charge for protonation inside the π ring.

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