

Nickel(II) & Copper(II) Complexes of the Schiff Base Derived from Phenylbiguanide & Benzil

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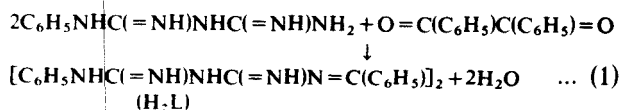
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The schiff base (H_2L) derived from the condensation of phenylbiguanide and benzil forms 1:1 complexes with Ni(II) and Cu(II). In these complexes, the ligand is tetradentate and can act in neutral, uninegative or binegative form depending on the pH. Nickel(II) forms complexes of the types $Ni(H_2L)Cl_2$, $NiLX_2$ and NiL while copper(II) forms complexes of the types $Cu(H_2L)Cl_2$, $Cu(HL)Cl$ and $Cu(HL)(X)Cl$ where $X = py$, α -pic, β -pic, or γ -pic.

Biguanides are well known as versatile complexing agents^{1,2} for different transition metal ions. Schiff bases derived from substituted biguanides have also been used³ to prepare different metal complexes. Reaction of the biguanides with β -diketones or β -ketonic esters, however, results in the formation of substituted pyrimidines^{4,5}, which also form metal complexes. In these condensation reactions, a substituted biguanide always behaves as a monoamine. A study of the condensation reaction of these biguanides with an α -diketone seems to be of interest as both the carbonyl groups of the diketone may condense with amine groups to give a planar tetradentate ligand. Such a view about the geometry of the ligand is supported by the fact that the biguanide moiety in metal complexes is planar as elucidated by X-ray studies⁶. The present note deals with the preparation and characterisation of nickel(II) and copper(II) complexes of the schiff base derived from the condensation of phenylbiguanide and benzil.

Phenylbiguanide hydrochloride (1 mol) and sodium hydroxide (1 mol) were refluxed for 15-20 min in dry ethanol. Sodium chloride, which was precipitated, was filtered off. The filtrate containing free biguanide was mixed with benzil (0.5 mol) and the mixture was refluxed on a water bath for 2 hr. This solution on partial evaporation on a water bath and cooling gave a white crystalline solid (m.p. 195°C) characterised as bis (phenylbiguanido)benzil (H_2L) (Eq. 1).



The metal complexes were prepared by adding ethanolic solution of nickel or copper chloride to

excess ligand in ethanol and refluxing the mixture. The precipitated complex was filtered, washed with ethanol and dried *in vacuo* over fused $CaCl_2$. Copper formed two complexes: a violet complex at pH 7-8 and a blue complex at pH 5.5-6.0 when more copper(II) was added to the violet one.

Pyridine and different picoline adducts of both nickel(II) and copper(II) complexes were prepared by adding ethanolic solution of metal chloride to an ethanolic solution of the ligand and pyridine/picoline mixed in 1:1 ratio and then refluxing the mixture. The complex, which was precipitated, was filtered, washed with ethanol containing a little pyridine/picoline followed by once with CCl_4 and then dried *in vacuo* over fused $CaCl_2$.

Each adduct of the nickel(II) complex was heated in an air-oven at 150-155°C for an hour to isolate another nickel complex, NiL .

Elemental analyses⁷ of the ligand and its complexes and some of the physicochemical properties of the complexes are listed in Table 1. A Philips conductivity bridge model GM 424 with a bottle type cell was used for conductivity measurements in DMSO. 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 PYECO UV-visible spectrophotometer was used to record electronic spectra in the range 400-800 nm in DMSO. TGA and DTA were recorded using a Shimadzu Thermal Analyser, DT-30.

All the complexes are soluble in DMSO; $Cu(H_2L)Cl_2$ is soluble in dry ethanol also. All of them are insoluble in water, but the blue complex, $Cu(H_2L)Cl_2$, on contact with water turns into the violet complex, $Cu(HL)Cl$.

Molar conductances of the complexes in DMSO at room temperature are in the range 2-36.5 $ohm^{-1} cm^2 mol^{-1}$ except for $Cu(H_2L)Cl_2$ (88.0 $ohm^{-1} cm^2 mol^{-1}$) indicating⁸ that all the complexes are nonelectrolytes except $Cu(H_2L)Cl_2$ which appears to be a 1:2 electrolyte.

IR spectra are relatively complicated because of overlap of different characteristic bands. However, a careful examination reveals that $\nu N-H$ and $\nu C=N$ bands⁹ are present both in ligand and metal complexes, but these are shifted to lower frequencies by 5-25 cm^{-1} in the spectra of complexes indicating involvement of $N-H$ and $C=N$ groups in complexation. The important bands of ligand and metal complexes and their assignment are entered in Table 2.

Table 1—Characterisation Data of Nickel(II) and Copper(II) Complexes with Bis(phenylbiguanido)benzil (H_2L)

Compound	Colour	Found (Calc.), %					$\mu_{\text{eff.}}$ (B.M.)	λ_{max} (nm)
		M	C	N	H	Cl		
H_2L^*	White	—	67.75 (68.18)	26.50 (26.51)	5.61 (5.30)	—	—	—
$Ni(H_2L)Cl_2$	Bright red	8.78 (8.96)	54.30 (54.71)	20.95 (21.27)	4.52 (4.25)	10.52 (10.79)	Diamagnetic	500
$NiL(py)_2$	Light blue	7.78 (7.94)	—	22.40 (22.61)	—	—	2.76	480,716
$NiL(\alpha\text{-pic})_2$	Bluish violet	7.62 (7.65)	—	21.50 (21.78)	—	—	2.82	472,720
$NiL(\beta\text{-pic})_2$	Bluish violet	7.64 (7.65)	—	21.48 (21.78)	—	—	2.80	472,720
$NiL(\gamma\text{-pic})_2$	Light violet	7.62 (7.65)	—	21.52 (21.78)	—	—	2.86	472,720
NiL	Dull red	10.15 (10.08)	61.26 (61.53)	23.80 (23.93)	4.75 (4.44)	—	Diamagnetic	470
$Cu(H_2L)Cl_2$	Blue	9.70 (9.59)	54.06 (54.34)	20.85 (21.13)	4.61 (4.23)	10.90 (10.72)	2.04	618
$Cu(HL)Cl$	Violet	9.90 (10.15)	57.40 (57.50)	21.84 (22.36)	4.72 (4.31)	5.80 (5.67)	1.74	536
$Cu(HL)(py)Cl$	Violet	8.90 (9.01)	—	21.75 (21.84)	—	4.86 (5.03)	1.75	544
$Cu(HL)(\alpha\text{-pic})Cl$	Violet	8.72 (8.83)	—	21.10 (21.42)	—	4.82 (4.93)	1.80	540
$Cu(HL)(\beta\text{-pic})Cl$	Violet	8.70 (8.83)	—	21.20 (21.42)	—	5.00 (4.93)	1.82	540
$Cu(HL)(\gamma\text{-pic})Cl$	Violet	8.68 (8.83)	—	21.25 (21.42)	—	4.85 (4.93)	1.80	540

* H_2L stands for $C_{30}H_{28}N_{10}$.Table 2—Important IR Absorption Bands (in cm^{-1}) of Bis(phenylbiguanido)benzil (H_2L) and Its Nickel(II) and Copper(II) Complexes

Compound	$\nu N-H$	$\nu C=N$	$\delta N-H$
H_2L	3400, 3330 3220-3200	1690-1680 1615	1675-1665 1595
$Ni(H_2L)Cl_2$	3305	1670	1645, 1590, 1560
$Cu(H_2L)Cl_2$	3390	1670	1590, 1560
$Cu(HL)Cl$			

The Ni(II) complexes, $Ni(H_2L)Cl_2$ and NiL , are diamagnetic suggesting square planar geometry for them. Their electronic spectra show one band only at 500 and 470 nm respectively which may be assigned^{10,11} to the transition $^1B_{1g} \rightarrow ^1A_{2g}$, supporting the square planar geometry. However, the molar conductance value of $Ni(H_2L)Cl_2$ ($36.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) suggests that it may be present in the highly tetragonally distorted octahedral geometry. At room temperature, pyridine and picoline adducts of nickel(II) complex have $\mu_{\text{eff.}}$ values around 2.8 B.M. which are somewhat less than that expected for O_h symmetry suggesting a partial tetragonal distortion (D_{4h}). The electronic spectra of these adducts show two

bands around 475 and 720 nm which correspond respectively to the transitions $^1^3A_{2g} \rightarrow ^3T_{1g}(F)(v_2)$ and $^3A_{2g} \rightarrow ^3T_{1g}(P)(v_3)$ in O_h symmetry. The transition $^3A_{2g} \rightarrow ^3T_{2g}(v_1)$ also occurring in O_h symmetry splits into two components in D_{4h} symmetry; however, these bands may have escaped detection being in the range beyond 800 nm.

$\mu_{\text{eff.}}$ values for copper(II) complex and its adducts are around 1.9 B.M. which, together with analytical data and conductivity data, suggest square planar geometry for $Cu(H_2L)Cl_2$, square pyramidal for $Cu(HL)Cl$ and distorted octahedral geometry for the adducts. The electronic spectra of all the complexes show only a single, somewhat asymmetric and broad band. The band observed at 518 nm for $Cu(H_2L)Cl_2$ with D_{4h} symmetry covers the transitions $^1^3B_{1g} \rightarrow ^2A_{1g}(v_1)$ and $^2B_{1g} \rightarrow ^2B_{2g}(v_2)$ while the transition $^2B_{1g} \rightarrow ^2E_g(v_3)$, being in the higher energy region, has probably escaped detection. The bands around 540 nm for $Cu(HL)Cl$ and its different adducts which have a C_{4v} local symmetry may be due to the overlapping of the transitions¹⁴ $^2A_1 \rightarrow ^2B_1$ and $^2A_1 \rightarrow ^2E$ which are equivalent to transitions with a $d_{x^2-y^2}$ ground state.

TGA and DTA data of $NiL(py)_2$ reveal that the complex loses two molecules of pyridine at 120°C . The

decomposition product, NiL, remains stable upto 330°C beyond which it undergoes further decomposition resulting ultimately in the formation of a black solid, NiO. It has been found that all the adducts of nickel(II) complex on heating at 150-155°C give the complex, NiL. Under identical conditions, adducts of copper complex also undergo thermal decomposition resulting in Cu(HL)Cl. It may be mentioned that pyridine and picolines present in the adducts are only weakly bound¹⁵ as they are lost when the adduct is repeatedly washed with dry ethanol or ether. That the ligand bears a planar framework of the four ligational sites in its complexes is justified by the suggested stereochemistries of the different complexes.

Bis-(phenylbiguanido)benzil behaves as a tetradentate ligand in all its complexes, but it is not clear whether the coordinating N-atoms at the two ends of the molecule are from $-\text{C}=\text{NH}$ or $-\text{C}-\text{NH.C}_6\text{H}_5$ moiety. Although participation of $\text{C}=\text{NH}$ in coordination, where ligand remains neutral, cannot be ruled out, the coordination where ligand is uni- or bi-negative is definitely through N of $-\text{NH.C}_6\text{H}_5$ group because this is the only point of deprotonation of the ligand.

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