

5-Cyano-6-(4-pyridyl)-2-thiouracil as a building block in transition metal bipyridyl chemistry

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Multifunctional ligand 5-cyano-6-(4-pyridyl)-2-thiouracil (LH_2) has been prepared and used in the synthesis of polymeric complexes. The general compositions of the complexes $(M \text{ bpy}LH_2 Cl_2)_n$ [$M = Cu(II)$ and $Zn(II)$] have been assigned on the basis of their elemental analysis and spectroscopic (IR, NMR, UV-visible and EPR) data. FAB mass data recorded upto 1000 range also support higher composition of the complexes. Powder X-ray diffraction, optical microscopic and scanning electron microscopic (SEM) studies have also been carried out. Force field calculations have been carried out to simulate the energy minimized structures of the dimeric unit of the complexes. The geometry around each $Cu(II)$ centre has been found to be distorted octahedral whereas $Zn(II)$ complexes possess octahedral geometry. Solid state conductance has also been measured at room temperature as well as at higher temperatures.

Metallomacrocycles obtained by the assembly of organic ligands and transition metal ions¹⁻¹⁰ have become a major field of modern chemical research. These studies have been found quite useful in the identification of key building blocks that may allow the construction of efficient and controlled metallosupramolecular structures¹¹. Zinc showed its ability to adopt co-ordination number of 4, 5 or 6 in its complexes which may easily vary with the change in its co-ordination geometry¹². Thus, much synthetic efforts were made to develop macrocyclic structures with better selective recognitions¹³. In this direction, binuclear complexes have been found very conducive as metal co-ordination may provide an efficient route for the construction of macrocyclic systems. Several approaches using metal ions^{14,15} and organometallic complexes have recently been exploited¹⁶⁻¹⁸.

Copper(II) and zinc(II) complexes of 2,2'-bipyridines were chosen as chelating units due to their well characterized coordination chemistry¹⁹⁻²³. Metal bipyridyls have been assembled with a multifunctional ligand 5-cyano-6-(4-pyridyl)-2-thiouracil (LH_2) bearing several binding sites on its skeleton²⁴⁻²⁷.

Materials and Methods

$M \text{ (bpy)} Cl_2$ [$M = Cu(II)$ and $Zn(II)$] were prepared by the reported procedure²⁸ in which 2,2'-bipyridine

(0.156 g, 0.1 mmol) in methanol (10 ml) was added separately to a solution of $CuCl_2 \cdot 2H_2O$ (0.017 g, 0.1 mmol) and $ZnCl_2$ (0.013 g, 0.1 mmol) dissolved in (5 ml) of methanol and stirred for 4 h. The solids thus obtained were filtered and washed with methanol followed by diethyl ether and then dried *in vacuo*.

Preparation of $Cu(II)$ and $Zn(II)$ bipyridyl complexes containing LH_2

Solutions of $Zn(bpy)Cl_2$ (0.29 g, 0.1 mmol, 5 ml) in dimethyl sulphoxide (DMSO) and $Cu(bpy)Cl_2$ (0.029 g, 0.1 mmol, 5 ml) in DMSO were added separately to a solution of LH_2 (0.023 g, 0.1 mmol, 10 ml) in methanol²⁹. After stirring for 6 h colourless solid for $Zn(II)$ complexes and yellowish green solid for $Cu(II)$ complex, were obtained. They were filtered, washed with water and methanol followed by diethyl ether and then dried *in vacuo*.

Metal complexes were analyzed gravimetrically for their metal content using standard procedure³⁰ after decomposing them in aqua regia. The micro analysis was done on Carlo Erba analyzer, where as FAB mass data were obtained from JEOL SX 102/DA-6000 mass spectrometer using *m*-nitrobenzyl alcohol (NBA) as a matrix both at CDRI, Lucknow, India. IR spectra (KBr pellets) were recorded on JASCO 5300, while ¹H NMR (DMSO-*d*₆) spectra were recorded on JEOL FX-90 Q FT NMR spectrometer using $Si(CH_3)_4$ as an internal reference. The UV-visible spectra of the complexes were recorded on Cary 2390 spectrometer. ESR spectra of the $Cu(II)$ complex were recorded

both in solid and solution states at room temperature and at liquid nitrogen temperature (LNT) using Varian E-109X-band ESR spectrometer at Indian Institute of Technology, Mumbai, India. Powder X-ray diffraction data were collected from PW1717 and optical microscopic study was done using Leitz optical microscope whereas, scanning electron micrographs (SEM) were obtained on Philips model XL20. Electrical conductance of the pressed pellets (diameter 0.5 cm) was measured by a conventional two-probe method in the temperature range 305–373 K with contact mode on the pellet surface using silver paste. Keithley 236 source measure unit was employed for this purpose.

Results and Discussion

Elemental analysis, FAB mass and UV-visible spectral data ($\lambda_{\max}$, $\epsilon_{\max}$) and physical properties of the complexes are shown in Table 1. Composition of the complexes as shown in Table 1 were supported both by their elemental analysis and FAB mass data which gave mass up to dimer. Furthermore, poor solubility and high thermal stability of the complexes also indicated their polymeric nature.

IR spectra

Peaks observed at 2216 cm^{-1} ($\text{C}=\text{N}$) and 1601 cm^{-1} (pyridyl) in the spectrum of free ligand (LH_2) remained constant in the spectra of its metal complexes, indicating that these groups do not bind with the metal ion. However, $\nu\text{C}=\text{O}$ and $\nu\text{C}=\text{S}$ of the free ligand observed at 1633 and 1128 cm^{-1} respectively shifted to 1684 , 1110 cm^{-1} as well as 1682 , 1111 cm^{-1} in the spectra of $\text{CubpyLH}_2\text{Cl}_2$ and $\text{ZnbpyLH}_2\text{Cl}_2$ respectively. This indicated that the $\text{>C}=\text{O}$ and $\text{>C}=\text{S}$ groups of the ligand (LH_2) are involved in the bonding with metal ions. The νNH observed at 3209 cm^{-1} in the spectrum of free ligand remains constant in the spectra of both complexes.

^1H and ^{13}C NMR spectra

^1H NMR spectrum indicated that NH and pyridyl protons of the free ligand observed at $\delta 12.0$ and 8.9 – 7.9 ppm respectively remained constant in the spectrum of $\text{ZnbpyLH}_2\text{Cl}_2$. In order to get further structural support, ^{13}C NMR spectrum of both free ligand and $\text{ZnbpyLH}_2\text{Cl}_2$ were compared which showed that $\text{>C}=\text{O}$ and $\text{>C}=\text{S}$ groups of the free ligand observed at $\delta 183.55$ and 162.25 ppm shifted to $\delta 182.53$ and 170.005 ppm respectively in the spectrum of $\text{ZnbpyLH}_2\text{Cl}_2$ complex. Additionally, $\text{C}=\text{N}$ and pyridyl carbons of the free ligand observed at $\delta 118.21$ and 122.38 ppm remained constant in the spectrum of $\text{ZnbpyLH}_2\text{Cl}_2$.

UV-visible spectra

The UV-visible spectrum of the complex $\text{CubpyLH}_2\text{Cl}_2$ recorded in DMSO (10^{-3} M) showed a broad peak at $\lambda_{\max}$ 728 nm assigned as d - d transition whereas the peak observed at $\lambda_{\max}$ 384.5 nm is assigned to charge transfer transition between metal ion and ligand. Similarly peaks observed at $\lambda_{\max}$ 365.5 and 282.5 nm in the case of $\text{ZnbpyLH}_2\text{Cl}_2$ (10^{-5} M , DMSO) were assigned to charge transfer and intra-ligands transitions respectively. Details of spectral data are shown in Table 1.

ESR spectra

ESR spectrum of the complex $\text{CubpyLH}_2\text{Cl}_2$ recorded in the solid state at room temperature showed anisotropic effect and corresponding g tensors (g_1 , g_2 and g_3) were found as 2.55 , 2.34 and 2.09 respectively. However, no significant change was observed at liquid nitrogen temperature (LNT) except that three peaks were observed to be more distinct. The spectrum of the same complex in solution (DMSO) at room temperature gave very weak peak giving g_{iso} at 2.16 . This solution spectrum got resolved at liquid nitrogen temperature showing four peaks due

Table 1—Physical properties, elemental analysis, FAB mass and UV-visible spectral data for the complexes

Complexes	FAB mass data (m/z) Calc. (Found) along with their assignments	Yield % Colour	Calc. (Found %)			$\lambda_{\max}$ nm	$\epsilon_{\max} \times 10^{-3}$ $\text{dm}^3\text{ mol}^{-1}$
			C	H	N		
$\text{CubpyLH}_2\text{Cl}_2$	520.5 (520) [$\text{CubpyLH}_2\text{Cl}_2$] $^+$	65	46.10	2.68	16.14	728	0.1611
$\text{C}_{20}\text{H}_{14}\text{N}_6\text{OSCl}_2\text{Cu}$	970 (970) [$\text{CubpyLH}_2\text{Cl}_2$] $^+_2$ -2Cl	Bluish green	(46.16)	(2.48)	(16.36)	384.5	0.388
$\text{ZnbpyLH}_2\text{Cl}_2$	522.3 (522) [$\text{ZnbpyLH}_2\text{Cl}_2$] $^+$	68	45.95	2.68	16.08	365.5	21.0
$\text{C}_{20}\text{H}_{14}\text{N}_6\text{OSCl}_2\text{Zn}$	973.6 (973) [$\text{ZnbpyLH}_2\text{Cl}_2$] $^+_2$ -2Cl	Colourless	(46.06)	(2.68)	(16.48)	282.5	109.9

to ^{63}Cu nucleus ($I=3/2$) and corresponding $g_{\parallel}$, $g_{\perp}$ and $A_{\parallel}$ values were found to be 2.31, 2.06 and 160G. Furthermore, half-field signals observed in the solid at room temperature and in the solution (DMSO) at LNT at 1100 and 1580G respectively, may be due to polymeric nature of the complex³¹ which is also corroborated by its lower magnetic moment value (1.4 BM).

Molecular structure optimization

Molecular structure simulation and isomeric analyses were carried out using chem 3D ultra (Ver. 6.0) programme package³² which employs a modified version of Allinger's MM2 force field³⁵ (in which a few additional terms like charge-dipole interaction, torsional and nonbonded constraints etc. have been incorporated) for force field calculations. The simulated structures of the complexes are shown in Figs 1 and 2. In the copper complex, Cu1 centre is separated from Cu2 by 8.97Å (Table 2). The geometry around each Cu(II) centre is distorted octahedral. It is interesting to note that in the energy

minimized structure the two LHz units coordinating Cu1 occupy *cis* position, the S1Cu1O2 angle being 102.0°. The two Cl atoms are also *cis* to each other (Cl1 Cu1 Cl2 = 90.8°). The extent of distortion is evinced by *trans* angles varying from 153.4° to 169.2°. The Cu1 donor atom distances are as expected and comparable to those in reported structures³⁴. The orientations of ligands in Cu2 is twisted with respect to those in Cu1. The Cl1 Cu1, Cl3 Cu2 and Cl1 Cu1, Cl4 Cu2 dihedral angles are 140.3° and 63.8°, respectively.

The structure of Zn(II) complex is similar that of the Cu(II) complex and the two LHa units are *cis* (within S1Zn1O2 angle of 98.5°) and are the two Cl atoms (Cl1Zn1Cl2 = 87.1°). The *trans* angle varies from 151.7° to 172.2° while the *cis* angle ranges from 76.1 to 111.1°. The CHZn1, Cl3Zn2 and Cl1Zn1, Cl4 Zn2 dihedral angles are 153.0° and 109.1°, respectively.

XRD

Lattice parameters for the complexes were calculated using Ito's method³⁵. The X-ray powder diffraction peaks of Cu(II) and Zn(II) complexes have been indexed based on the basis of tetragonal cell in all the cases. The values of the lattice parameters are reported in Table 3 from which it could be noted that complexes belong to tetragonal systems. The indexing of the different peaks has been done based on

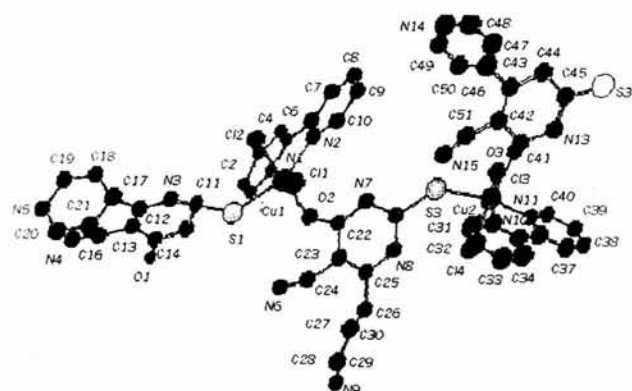


Fig. 1—Simulated structure of $(\text{CubpyLH}_2\text{Cl}_2)_2$ (Hydrogens are omitted for clarity).

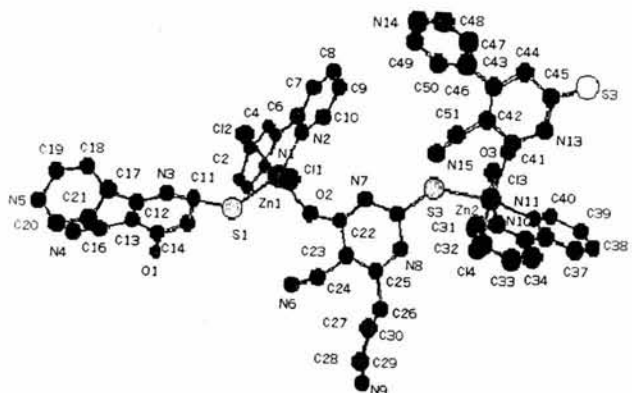


Fig. 2—Simulated structure of $(\text{ZnbpyLH}_2\text{Cl}_2)_2$ (Hydrogens are omitted for clarity).

Table 2—Selected bond angles(°) and bond lengths (Å)

Bond angles (°)	M1-Cu1	M1-Zn1
SIMIC11	82.8	82.7
SIMIC12	78.5	77.7
SIMINI	98.1	98.1
SIMIN2	153.4	151.7
SIMIO2	102.0	98.5
O2MIC12	169.2	163.2
C11M1C12	90.8	87.1
NIMIN2	83.9	81.8
N2MIO2	102.4	108.0
NIMIO2	103.4	111.1
C11M1O2	78.6	76.1
C11MINI	169.8	172.4
Bond lengths (Å)		
M1-M2	8.97	9.16
C16-N4	1.18	1.18
O1-C14	1.22	1.22
O2-C22	1.28	1.28
S1-M1	2.43	2.48
Cl2-M1	2.22	2.29
C11-M1	2.20	2.28
N1-M1	1.99	2.03
N2-M1	1.96	2.05
O2-M1	1.97	2.04

Table 3 — Lattice parameters of the complexes

Complexes	Root mean square deviation of d values ('R')	Crystal system and lattice parameter (Å)	θ (Angle at maximum intensity for the phase)	β (Half width at half maximum $\times 10^{-3}$ (radian))	T(Coherently scattering domain size) (Å)
CubpyLH ₂ Cl ₂	8.6	Tetragonal $a=11.76$ $b=11.76$ $c=9.81$	5.49	6.4	217
ZnbpyLH ₂ Cl ₂	4.7	Tetragonal $a=12.72$ $b=12.72$ $c=8.60$	5.13	4.5	309

respective unit cells in each case. Table 4 gives the values of $1/d^2_{\text{cal}}$ and $1/d^2_{\text{obs}}$. The root mean square deviation of d values (R)³⁶ calculated from these data are reported in Table 3 along with an estimate of coherently scattering domain size (t) in Å.

The peak widths in almost all cases were found higher than those introduced by instrumental broadening in XRD data which clearly indicates size restriction on the coherently scattering domain. This is characteristic of the complexes with larger motifs. As such, system would require more idealized condition of growth for producing defects free grain.

Microstructural characterization

Figure 3(a,b) depicts the optical micrographs of representative section of CubpyLH₂Cl₂ and ZnbpyLH₂Cl₂ respectively. Specimens in the form of pellet of identical diameter (1 cm) and thickness ~1-3 mm were used and the usual technique for the preparation of surface for optical micrography has been adopted. These microstructures display changes with the addition of metal salts (Cu(II)/Zn(II)) in ligands. One of the significant features for CubpyLHsCl₂ complex in this system pertains to granular appearance separated by boundaries from their neighbourhood. Such characteristics are obviously missed in ZnbpyLH₂Cl₂ complex. These clearly indicate the distinct effect of the different metal ions on same ligand. The particle size seems to vary from region to region. The microstructural features as described above clearly display a distinct morphology of different complexes.

SEM

Scanning electron micrographs (SEM) of the both complexes taken at different magnification are shown in Fig. 4a,b. Marked change in the size and morphology could be seen. In this microstructure,

Table 4—XRD data for a representative complex ZnbpyLH₂Cl₂

Angle (2 θ)	d value (Å)	$1/d^2_{\text{obs}}$	$1/d^2_{\text{calc}}$	hkl
6.940	12.7268	0.006	0.006	100
10.270	8.6064	0.013	0.013	001
15.620	5.6686	0.031	0.030	210
17.375	5.0998	0.038	0.038	201
20.880	4.2510	0.055	0.055	300
22.455	3.9562	0.063	0.062	221
23.355	3.8058	0.069	0.069	301
27.990	3.1852	0.098	0.098	400
29.780	2.9977	0.111	0.111	330
36.020	2.4914	0.161	0.160	150
40.050	2.2495	0.197	0.197	440
44.935	2.0157	0.246	0.246	620
50.680	1.7998	0.308	0.308	710

several grains of different sizes are also visible. However, in a particular grain, one may notice uniformity in the surface morphology.

Solid state electrical conductivity

The temperature dependent (305-373 K) d.c. electrical conductivity behaviour of the metal complexes in solid state has been studied using a conventional two probe technique³⁷. Different voltages were applied and correspondingly produced current is measured by Keithley 236 to calculate the resistance. Complexes were compressed in the form of pellets (diameter 0-5 cm) at a load of 20 KM and silver paste was used to make the contacts on the pellet surface. Both Cu(II) and Zn(II) complexes showed conductivity at room temperature as $10^{-8} \text{ S cm}^{-1}$. The d.c. conductivity was found to increase with the temperature which support the semi-conducting nature of the complexes. As compared to reported³⁷ ranges of conductivity data

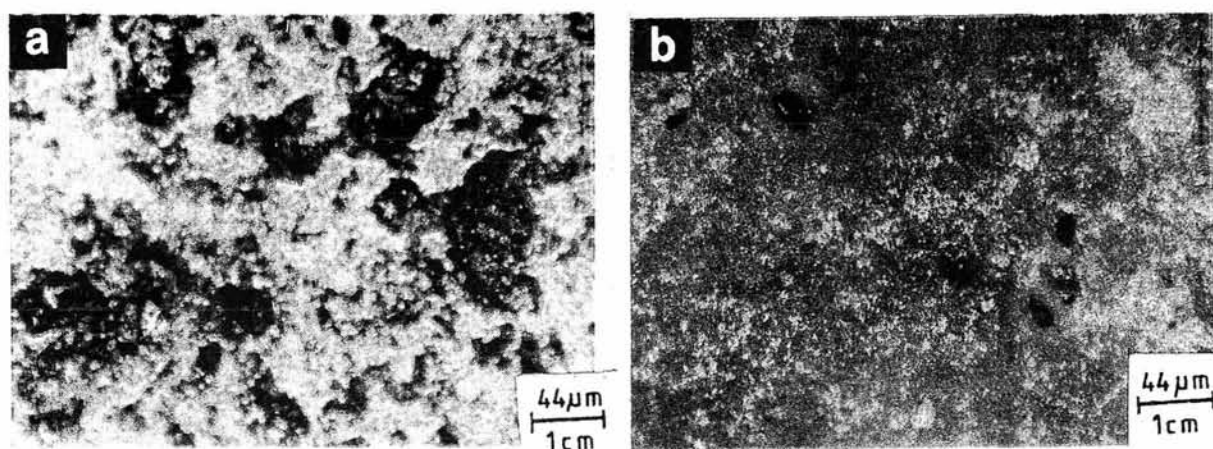


Fig. 3—Optical micrographs of the complexes [(a) CubpyLH₂Cl₂ and (b) ZnbpvLH₂Cl₂].

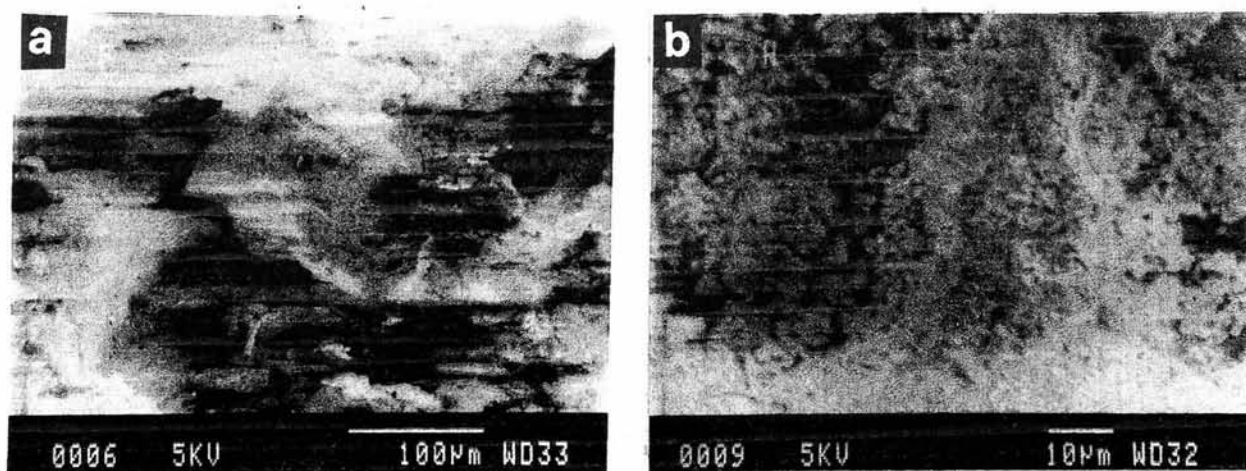


Fig. 4—Scanning electron micrographs of the complexes [(a) CubpyLH₂Cl₂ and (b) ZnbpvLH₂Cl₂].

(10^7 to 10^3 Scm^{-1} for metallic behaviour, 10^1 to 10^{-5} Scm^{-1} for semiconducting and 10^{-7} to 10^{-19} Scm^{-1} for insulator), it was found that present complexes possess room temperature value conforming to those of conventional insulators. After these broad observations, we now propose to understand the nature of conductivity versus temperature curve so that a possible correlation with respect to nature of electron transport in this class of materials could be arrived at. The $\log \sigma$ versus $1000/T$ and polynomial fit curve for representative complex CubpyLH₂Cl₂ show that there is remarkable change in the value of standard deviation for the 2nd order polynomial fit which display significant departure from linear relationship conventionally known for traditional semiconductors. It was also noted that similar but less

pronounced trend could also be observed from ZnbpvLH₂Cl₂.

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