Five coordinate complexes of 2,6-bis(N, N-diethylaminomethyl)pyridine with Co(II), Ni(II) and Cu(II)

M M Mahajan*† & Gurdev Singh

Department of Chemistry, Panjab University, Chandigarh 160 014

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The title compound 2, 6-bis(N, N-diethylaminomethyl)pyridine (abbreviated as damp) forms a series of complexes corresponding to the composition M(damp)X2, where M = Co(II), Ni(II) or Cu(II) and X = Cl, I, NCS or SeCN. The results of IR studies indicate that in all these complexes damp behaves as a tridentate ligand coordinating to the metal through its NNN donor sequence. Molar conductance values and molecular weight data suggest that these complexes are essentially non-ionic monomers. Magnetic moment and electronic spectral data support five coordinate structure for all these complexes, except Ni(damp)(NCS)2 which is assigned a binuclear (dimeric) bridged structure containing both bridging and terminal NCS groups.

Penta coordinate metal complexes of multidentate ligands have been the subject of considerable interest over the past few years; Nelson et al.1, synthesised P,N,P donor ligands derived from 2,6-disubstituted pyridine and found them to form five coordinate complexes with Fe(II), Co(II) and Ni(II). The compound 2,6-bis(NN-diethylaminomethyl)pyridine(I) contains three nitrogen donor and hence is a potential tridentate ligand. It forms 1:1 (metal:ligand) complexes in preference to 2:1 complexes because of the steric hindrance caused by the ethyl substituents on the terminal nitrogen atoms. The present note describes the synthesis and characterization of some five coordinate complexes of Co(II), Ni(II) and Cu(II) with damp.

Preparation of M(damp)Cl2 where M = Co(II), Ni(II) or Cu(II)

To a hot solution of appropriate anhydrous metal chloride (0.01 mol) in 20 cm3 of absolute ethanol, was added 0.01 mol of the ligand. The reaction mixture was refluxed for 4 hr and allowed to stand overnight in a freezing mixture. A crystalline product separated which was filtered, washed with small quantity of absolute ethanol and dried in vacuo over P4O10.

Preparation of M(damp)(NCS)2 where M = Co(II), Ni(II) and Cu(II)

A solution of the appropriate metal chloride (0.01 mol) in 20 cm3 of dry ethanol was mixed with an ethanolic solution of KCNS (0.02 mol). The precipitated KCl was filtered off and 0.01 mol of ligand was added to the filtrate. The reaction mixture was kept in freezing mixture for 2 hr. A crystalline product separated, which was washed with ethanol and finally dried in vacuo.

Preparation of Co(damp)(SeCN)2

To a solution of anhydrous CoCl3(0.005 mol) in absolute ethanol (20 cm3) was added an ethanolic solution of potassium selenocyanate (0.01 mol). The reaction mixture was kept in ice, and KCl thus precipitated was filtered off. The ligand solution (0.005 mol)

Experimental

The IR spectra of the ligand and the complexes were recorded on a Perkin Elmer 621 spectrophotometer in the region 4000-200 cm⁻¹. Diffuse reflectance spectra of powdered samples were recorded on a Unicam SP 700 A UV-visible spectrophotometer. For solution spectra, the samples were scanned over the range 200-800 nm on a Specord UV-Vis spectrophotometer. Molar conductances were measured on a Toshniwal conductivity bridge type C 1-01/02A. The magnetic moments of the complexes were determined at room temperature by the Gouy method. Cryoscopic method was employed for determining molecular weights of the complexes. Microanalyses for C, H and N were performed at the Microanalytical Laboratory, Department of Chemistry, Panjab University, Chandigarh.

† Present address: J. N. Government College, Port Blair 744 101 (Andamans)
Table 1—Analytical and molecular weight data of complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour (m.p., °C)</th>
<th>Calc. (Found) %</th>
<th>Mol. wt. ratio obs./calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(damp)Cl₂</td>
<td>green (170-171)</td>
<td>C 47.50 N 11.09 H 7.13 M 15.54 X or S, Se 18.75</td>
<td>0.93</td>
</tr>
<tr>
<td>Co(damp)(NCS)₂</td>
<td>grey (150-152)</td>
<td>C 48.12 N 16.51 H 6.36 M 13.89 X or S, Se 15.09</td>
<td>0.90</td>
</tr>
<tr>
<td>Co(damp)(NCSe)₂</td>
<td>dark green (154-156)</td>
<td>C 39.40 N 13.52 H 5.21 M 11.34 X or S, Se 30.52</td>
<td>—</td>
</tr>
<tr>
<td>Ni(damp)Cl₂</td>
<td>yellow (210-212)</td>
<td>C 47.53 N 11.09 H 7.13 M 15.50 X or S, Se 18.84</td>
<td>0.89</td>
</tr>
<tr>
<td>Ni(damp)I₂</td>
<td>reddish brown (148-149)</td>
<td>C 32.04 N 7.47 H 4.80 M 10.45 X or S, Se 45.21</td>
<td>—</td>
</tr>
<tr>
<td>Ni(damp)(NCS)₂</td>
<td>greenish yellow (180-182)</td>
<td>C 48.15 N 16.51 H 6.37 M 13.85 X or S, Se 15.11</td>
<td>—</td>
</tr>
<tr>
<td>Cu(damp)Cl₂</td>
<td>green (145-146)</td>
<td>C 46.93 N 10.05 H 7.04 M 16.57 X or S, Se 18.51</td>
<td>0.84</td>
</tr>
<tr>
<td>Cu(damp)(NCS)₂</td>
<td>dark green (162-163)</td>
<td>C 47.61 N 16.34 H 6.30 M 14.82 X or S, Se 14.93</td>
<td>0.88</td>
</tr>
</tbody>
</table>

was added dropwise to the above filtrate. The reac‐
tion mixture was allowed to stand for 4 hr in freezing
mixture when the coloured crystalline product separ‐
ated, which was filtered, washed with dry petroleum
ether and dried in vacuo.

Preparation of Ni(damp)I₂
An ethanolic solution of NiI₂ was obtained by trea‐
ting anhydrous NiCl₂ (0.005 mol) with KI (0.01 mol)
in ethanol and filtering off the precipitated KCl. To
the clear solution, the ligand (0.005 mol) was added
and the reaction mixture refluxed for 5 hr. The reac‐
tion mixture was kept in a freezing mixture overnight.
A red coloured crystalline product separated, which
was collected and dried in vacuo over P₄O₁₀.

Results and discussion
All the metal complexes listed in Table 1 are
crystalline and hygroscopic in nature. These com‐
plexes are soluble in water and most of the organic
solvents like chloroform, nitromethane and nitro‐
benzene. Elemental analysis indicated that these
complexes corresponded to the empirical formula
M(damp)X₂, where M = Co(II), Ni(II) or Cu(II), and
X = Cl, I, NCS or SeCN. Molar conductance values
(0.4-29.8 ohm⁻¹cm²mol⁻¹) of these complexes in dif‐
ferent organic solvents suggested that these com‐
plexes are non-electrolytes. The observed/calculated
molecular weight ratios of the complexes indicated
that these complexes were essentially monomers. The
slightly lower values of the observed molecular we‐
ights may be attributed to partial dissociation of the
complexes in polar solvents.

The IR spectrum of damp was compared with the
spectra of some closely related compounds such as 2,
6-dimethylpyridine, N, N, N',N'-tetraethylpyridine
2, 6-dicarboxamide and triethylamine. The bands
observed at 1585, 1570, 1455, 1445, 985 and 600 cm⁻¹
are attributable to pyridine ring vibrations, and, in
order of decreasing wave numbers, correspond to 8a,
8b, 19a, 19b, I and 6a modes. In the spectra of the
complexes 8a mode showed an upward shift by 10-20
cm⁻¹, mode I was observed between 1015 and 1030
cm⁻¹, while the 6a mode was located between 620 and
640 cm⁻¹. These shifts are suggestive of the coordina‐
tion of pyridine ring nitrogen in all the complexes.
Appearance of bands between 300 and 335 cm⁻¹
which are assigna ble to V,M - N further confirmed the
observation. The IR spectral behaviour of the thiocy‐
anato and selenocyanato complexes indicated that
the thiocyanate groups in Cu(II) and Co(II) com‐
plexes are bonded to the metal atom through nitrogen.
The splitting of the band indicated that thiocyanate
groups might be in different environments. In the
case of Ni(damp)(NCS)₂, the vCN band split into
three well defined peaks at 2120, 2085 and 2075 cm⁻¹.
The number and positions of these bands suggest that
the two thiocyanate groups are not only in different
environments but also differ in coordination behavi‐
our and it can be reasonably inferred that bridged as
as nitrogen bonded thiocyanate groups repn~s-
absorption band of strong intensity at 2050 cm\(^{-1}\) ind-
icated that selenocyanate group was bonded hrough
ent in the complex Ni(damp)(NCSh, The ne bands
v(M - NCS). In the complex Co( damp)(N Se b an
appearing around 250 cm\(^{-1}\) have been assi ned9 to
many a time, due to distortions from the idealised
structures, these bands are further split and 've bands
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The magnetic and electronic spectral data are listed
in Table 2. The observed room temperature magnetic
moments for these complexes are in the ran range expec-
gmentation is not possible on the basis of magn tic mom-
both these complexes are five coordinate onomers
or six coordinate dimers bridging through chlo ro, thi-
ocyanato or selenocyanato groups. Cbnclive evidc
from electronic spectral data both in solid and solut
Five coordinated Cu(II) complexes usually exhibit
two absorption bands which may be assigned to the transitions from \(^2A_1\) level to \(^2E\) and \(^2E''\) in \(D_{3h}\) sym-
metry but sometimes only one band is observed and
the shoulder is found to be missing. The solid state
spectral behaviour of the complexes Cu(damp)Cl\(_2\)
and Cu(damp)(NCS), compare well with the spectra of
some typical high spin Ni(II) five-coordinate complexes12-13. In the case of Ni(damp)(NCS), four absorp-
tion bands were observed at 15.4, 12.5, 9.3 and 7.4
kK. The region 22.0-18.0 kK was blank. Such a spect-
ral behaviour is suggestive of six coordinate structure
for the complex14. The IR spectral studies on this
complex have already indicated the presence of both
bridged and terminal NCS groups. Thus, all the avail-
able data support a six coordinate bridged structure
for the complex Ni(damp)(NCS). The complex also
does not retain its identity on dissolution in polar
solvents as indicated by the spectrum in the solution
state.

Five coordinated Cu(II) complexes usually exhibit
two absorption bands which may be assigned to the transitions from \(^2A_1\) level to \(^2E\) and \(^2E''\) in \(D_{3h}\) sym-
metry but sometimes only one band is observed and
the shoulder is found to be missing. The solid state
spectral behaviour of the complexes Cu(damp)Cl\(_2\)
and Cu(damp)(NCS), compare well with the spectra of
five coordinate Cu(II) complexes12-13-14.

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