Dielectrometric titrations were carried out with a Tangens dielectrometer by the heterodyne technique. The operating conditions were: cell capacity 20 pF, frequency 1 MHz, temperature 25 ± 0.1°. Dipole moments were calculated by the Hedestrand method(20).

The e.s.r. spectra were obtained at room temperature using a 3-cm band Varian E-3 radiospectrometer operating at high frequency modulation, 100 kHz. The g-factor values, calculated using $Mn^{+2}$/MgO as standard, are believed to be accurate to within ± 0.001.

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# Divalent Nickel, Cobalt and Copper Complexes of a Tetradentate $N_6$ Macrocyclic Ligand

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### Summary

Divalent nickel, cobalt and copper salts react with 2,6-diaminopyridine and acetylacetone to form complexes containing a 16-membered $N_6$ tetradentate macrocyclic ligand. The complexes are characterised as distorted octahedra of the $M(TML)X_2$ type where M = nickel(II), cobalt(II) and copper(II); TML = tetradentate macrocyclic ligand and X = Cl, Br, $NO_3$ or NCS. The ligand coordinates through all the four azomethine nitrogen atoms which are bridged by acetylacetone moieties. Pyridine nitrogen does not participate in coordination, a fact supported by far i.r. studies. The magnetic, electronic and i.r. spectral studies indicate that the complexes have lower symmetries and the amounts of distortion calculated in terms of DT/DQ applying normalised spherical harmonic Hamiltonian theory indicate that these complexes are moderately distored.

### Introduction

Condensations between carbonyl compounds and primary amines are primarily responsible for a major part of the process leading to the formation of a macrocyclic ligand(1). Many macrocyclic ligands have been synthesised by the reaction of amines with 2,6-diacetylpyridine(2), however very few(3) have been prepared from aromatic diamines and dicarbonyl compounds. In continuation of studies of syntheses of macrocyclic ligands(4, 5), we report the preparation of a novel type of $N_6$ macrocyclic ligand from 2,6-diaminopyridine and acetylacetone. The macrocycle was isolated as its metal chelates by template reactions in the presence of nickel, cobalt and copper salts. Attempts to isolate the free ligand were, however, unsuccessful. The complexes were characterised by elemental analyses, conductance, magnetic, i.r. and electronic spectral studies.

### Experimental

*Synthesis of the ligand*

2,6-Diaminopyridine (0.02 mole) and acetylacetone (0.04 mole) were refluxed in dry MeOH for 6 h and the mixture was stored in a vacuum dessicator for 3 days. The resulting light yellow hygroscopic solid was recrystallised from EtOH. Yield *ca.* 80%, m.p. 83–86°. The product is soluble in MeOH, $H_2O$, EtOH and DMF. (Found: C, 66.0; H, 6.8; N, 15.0. $C_{15}H_{19}N_3O_2$ calcd: C, 65.9; H, 6.95; N, 15.4%).

*Synthesis of the complexes*

2,6-Diaminopyridine (0.02 mole) dissolved in a minimum quantity of MeOH was mixed with a solution of acetylacetone

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(0.02 mole) in MeOH (50 cm$^3$). A MeOH solution of the metal salt (0.01 mole) was added and the mixture boiled under reflux on a water bath. Glacial HOAc (2 cm$^3$) was added and the mixture was boiled under reflux for 16 h, then concentrated to half vol. and set aside for 3 days. The dark crystals which separated were filtered, washed with MeOH, Me$_2$CO, Et$_2$O and dried *in vacuo*. For copper complexes, a precipitate appeared after 4 h. at the reflux temperature: Yield *ca.* 35%.

Nickel and copper complexes are stable up to 200° but cobalt complexes decompose above 175°. The nickel and cobalt complexes are soluble in H$_2$O, MeOH and DMF whereas copper complexes are only partially soluble in these solvents.

The nitrato complexes were prepared from metal nitrates. Bromo and thiocyanato salts were prepared by stirring and adding slowly KBr and NH$_4$CNS solutions to an EtOH solution of metal chloride and filtering off the KCl or NH$_4$Cl. The metal contents were determined by EDTA titrations using Erichrome Black-T as indicator while halides were estimated by Volhard's method and nitrate as nitron salt.

### *Magnetic and spectral measurements*

The magnetic susceptibility measurements were carried out using Guoy's method and CuSO$_4$ · 5 H$_2$O as calibrant.

The i.r. spectra in the 4000–650 cm$^{-1}$ range in KBr pellets were recorded on a Perkin Elmer-621 instrument and in Nujol mull in the 650–200 cm$^{-1}$ range on a Beckmann IR-12 spectrophotometer. The electronic spectra (DMF solutions) were recorded on a Cary-14 recording spectrophotometer. A Toshniwal type CL-01/01 conductivity bridge was used for conductivity measurements. The molecular weights of soluble complexes were determined cryoscopically.

## Results and Discussion

The analytical data (Table 1) show that the complexes can be represented as [M(C$_{20}$H$_{22}$N$_6$)X$_2$] where M = Ni$^{II}$, Co$^{II}$ or Cu$^{II}$, and X = Cl, Br, NO$_3$ or NCS. The conductivity measurements show their nonelectrolytic nature and the molecular weights of nickel and cobalt complexes are consistent with monomers. The presence of anions is evident only after decomposition of the complexes, perhaps due to their presence in coordination sphere.

### *Infrared spectra*

The i.r. spectra of the condensation product of these compounds show various pyridine ring(6–8), azomethine(9) and acetylacetone moiety(7) vibrations. The bands at the *ca.* 1590, *ca.* 1570, *ca.* 1460 and *ca.* 1435 cm$^{-1}$ regions are assigned to four $\nu$(C=C) and $\nu$(C=N) skeletal frequencies(10). The other bands appearing at *ca.* 990, *ca.* 800, *ca.* 610 and *ca.* 410 cm$^{-1}$ may be assigned to ring breathing mode, out-of-plane C–H deformation and out-of-plane and in-plane C–C deformation modes of pyridine ring, respectively(11). The strong frequencies of *ca.* 1580–1555 cm$^{-1}$ are usually associated to $\nu$(CN) coupled with phenyl ring vibrations(9). By comparing the spectra with amines, a strong band at *ca.* 1625 cm$^{-1}$ with a shoulder at *ca.* 1610 cm$^{-1}$ may be assigned to symmetric and antisymmetric $\nu$(C=N) vibrations(6, 7), respectively. The absence of bands *ca.* 3300–3200 cm$^{-1}$ in the ligand show that amino groups of 2,6-diaminopyridine have condensed with acetylacetone molecules. This contention is supported by the presence of bands at *ca.* 2920, *ca.* 1350, *ca.* 1265, *ca.* 1190 and *ca.* 680 cm$^{-1}$ characteristic of the acetylacetone moiety and may be assigned to $\nu$(CH$_3$), $\delta$Sym(CH$_3$, $\nu$(C–CH$_3$), $\delta$(CH) + $\nu$(C–CH$_3$) and ring deformation modes(12), respectively. Further, the appearance of bands at *ca.* 1680–1670, *ca.* 1550, *ca.* 670 cm$^{-1}$ assignable to $\nu$(C=O) and $\nu$(CO) + $\nu$(C=C) or $\Pi$(CH$_3$–C) indicate the presence of the acetylacetone moiety in the free ligand(12).

Conspicuous changes are, however, observed in the spectra of all the complexes. The i.r. spectra do not show any change in pyridine ring vibrations and, interestingly enough, it appears that in these complexes, pyridine nitrogen does not participate in coordination(6, 7).

Various vibrations of free or coordinated acetylacetone at *ca.* 1680–1700 or *ca.* 1550 and *ca.* 670 cm$^{-1}$ are not observed in the spectra of complexes, however, the presence of new bands at *ca.* 1275, *ca.* 1190 and *ca.* 1030 cm$^{-1}$ assignable to $\nu$(C–CH$_3$) + $\nu$(C=C), $\delta$(CH) + $\nu$(C–CH$_3$) and $\varrho_\tau$(CH$_3$) show that acetylacetone moiety is present in the complexes. Thus, it appears that both the amino groups of 2,6-diaminopyridine react with oxygen atoms of acetylacetone forming a three carbon atom bridge between the two amino groups, similar to those reported in coordinated amines(3). The absence of stretching and bending (C–O) group vibrations at *ca.* 1525 and *ca.* 1280 cm$^{-1}$ also indicate the absence of (C–O) group in these complexes(12). The changes in $\nu$(C=N) vibrations indicate coordination through this site(9). The bands at *ca.* 1640

**Table 1.** Analytical data of divalent nickel(II), cobalt(II) and copper(II) complexes

| Complex | Colour | Found (Calcd.) % | | | | |
|---|---|---|---|---|---|---|
| | | C | H | N | M | X |
| Ni(C$_{20}$H$_{22}$N$_6$)Cl$_2$ | greenish brown | 50.0(50.6) | 4.7(4.6) | 17.05(17.7) | 12.8(17.2) | 14.0(14.8)a) |
| Ni(C$_{20}$H$_{22}$N$_6$)Br$_2$ | greenish brown | 41.8(42.6) | 3.8(3.9) | 15.02(14.7) | 9.5(9.6) | 28.0(28.4)b) |
| Ni(C$_{20}$H$_{22}$N$_6$)(NO$_3$)$_2$ | greenish grey | 45.8(45.5) | 4.0(4.2) | 21.0(21.2) | 11.0(11.0) | 23.8(24.2)c) |
| Ni(C$_{20}$H$_{22}$N$_6$)(NCS)$_2$ | dark green back | – (50.8) | – (4.2) | 21.6(21.5) | 11.05(11.1) | – |
| Cu(C$_{20}$H$_{22}$N$_6$)Cl$_2$ | greenish brown | 51.0(50.1) | 4.8(4.6) | 16.8(17.5) | 12.9(13.2) | 14.2(14.6)a) |
| Cu(C$_{20}$H$_{22}$N$_6$)Br$_2$ | brownish green | – (42.2) | – (3.9) | 14.5(14.8) | 11.0(11.1) | 28.0(28.1)b) |
| Cu(C$_{20}$H$_{22}$N$_6$)(NO$_3$)$_2$ | brownish green | – (45.0) | – (4.1) | 21.0(21.0) | 12.0(11.9) | 22.9(23.2)c) |
| Cu(C$_{20}$H$_{22}$N$_6$)(NCS)$_2$ | greenish brown | 49.8(50.3) | 4.0(4.2) | 21.8(21.3) | 11.8(12.0) | – |
| Co(C$_{20}$H$_{22}$N$_6$)Cl$_2$ | bright green | 51.0(50.5) | 4.5(4.6) | 17.0(17.7) | 12.05(12.4) | 14.8(14.7)a) |
| Co(C$_{20}$H$_{22}$N$_6$)Br$_2$ | dark green | – (42.5) | – (3.9) | 14.2(14.9) | 10.8(10.4) | 27.05(28.3)b) |
| Co(C$_{20}$H$_{22}$N$_6$)(NO$_3$)$_2$ | greenish black | – (45.4) | – (4.2) | 21.8(21.2) | 12.0(11.2) | 22.8(23.4)c) |
| Co(C$_{20}$H$_{22}$N$_6$)(NCS)$_2$ | greenish black | 51.05(50.7) | 4.3(4.2) | 20.5(21.5) | 11.0(11.3) | – |

a) Chloride; b) bromide; c) nitrate

and *ca.* 840 $cm^{-1}$ may be assigned to NH deformation coupled with NH out-of-plane bending and may be due to the presence of this group in these complexes. Thus, in presence of metal salts, a quadridentate macrocycle is formed which coordinates through azomethine nitrogens while pyridine nitrogen does not take part in coordination. This seems in accord with the idea that quadridentate macrocycles are formed more easily than quinqui or hexadentate ligands(2). Moreover the azomethine nitrogen, being equally active, excludes coordination through pyridine nitrogen perhaps due to the formation of unstable four membered rings.

The far i.r. spectra of the chloro complexes reveal some new bands at *ca.* 300, *ca.* 285 and *ca.* 270 $cm^{-1}$ and are assignable to ν(Co–Cl) ν(Ni–Cl) and ν(Cu–Cl) vibrations(13), respectively. Similar bands in bromo-complexes are oberved at *ca.* 220 and *ca.* 215 $cm^{-1}$ for cobalt and nickel complexes and can be assigned to ν(Co–Br) and ν(Ni–Br) vibrational modes. The appearance of single bands and their regions are consistent with the *trans*-octahedral nature of the complexes(13).

The changes observed in the spectra of nitrato complexes show new bands at *ca.* 1260, *ca.* 1015 and *ca.* 865 $cm^{-1}$ consist with the monodentate nature of the nitrate group(12). The small splitting of $\nu_1 + \nu_4$ appearing at *ca.* 1760–1765 and *ca.* 1745–1755 $cm^{-1}$ again point to the monodentate nature of the nitrate group(14). In thiocyanato complexes, strong bands are observed at *ca.* 2115 ($\nu_1$) ν(C=N), *ca.* 480 ($\nu_2$)NCS bending and *ca.* 830 $cm^{-1}$ $\nu_3$, ν(C=S) of the NCS group, respectively are consistent with a monodentate N-bonded thiocyanato group. The coordination of nitrate and thiocyanate are further supported by the appearance of new bands at *ca.* 225–240 $cm^{-1}$ assignable to νM–O of nitrate group and *ca.* 260, *ca.* 285 $cm^{-1}$ assignable to ν(M–NCS) respectively in the far i.r. spectra of these complexes(12, 15).

The presence of bands in all the complexes in the 430–495 $cm^{-1}$ regions originate from νM–N (azomethine) vibrational modes and substantiates the involvement of azomethine nitrogen. However, the absence of various ν(M–py) vibrations supports the noninvolvement of pyridine nitrogen.

## *Magnetic and electronic spectral studies*

The magnetic moments of the complexes are reported in Table 2. Those of cobalt, nickel and copper lie in the 4.58–4.70, 3.15–3.30 and 1.75–1.82 B.M. ranges respectively at room temperature. The magnetic moments are well within the range reported for spin-free hexacoordinate complexes of these metal ions(16).

The solution spectra of nickel complexes show three strong bands in at *ca.* 10600–12350, 15000–17000 and 25000–28000 $cm^{-1}$ with a well discernable shoulder at *ca.* 8500–9500 $cm^{-1}$ on the low energy side of the first band. The spectral bands are well within the range for hexacoordinate octahedral complexes of nickel reported earlier(17). The first two bands result from the splitting of one band, $\nu_1$, and can be assigned to ${}^3B_{1g} \rightarrow {}^3E_g{}^a(\nu_1)$ and ${}^3B_{1g} \rightarrow {}^3B_{2g}(\nu_2)$, assuming the effective symmetry(17) to be $D_{4h}$ (components of ${}^3T_{2g}$ *in* $O_h$ symmetry). The other two higher bands can be assigned to ${}^3B_{1g} \rightarrow {}^2A_{2g}(F)$, ${}^3F_g{}^b(\nu_3)$ and ${}^3B_1g \rightarrow {}^3A_{2g}(P)$. The intense higher energy band at *ca.* 35000 $cm^{-1}$ may be due to a π–π* transition of the C=N group. Various bands do not follow any regular pattern and seem to be anion independent. The spectra are consistent with the distorted octahedral nature of the complexes(18, 19) and the calculated Dt, $Dq^{xy}$ and $Dq^z$ values are given in Table 2. Thus, all the complexes studied herein show pseudooctahedral geometry conforming to $D_{4h}$ symmetry. On the basis of symmetry arguments Lever *et al.*(20) have devised normalised spherical harmonic Hamiltonian theory applicable to molecules of $D_{4h}$. The newly developed NSH theory relates the classical ligand field parameters to NSH absolute ligand field parameters DQ, DS and DT. DQ is a measure of the average ligand field experienced by the metal ion unlike the classical Dq which is the measure of the in-plane ligand field. The DT/DQ ratio provides the amount of distortion of the molecule. The NSH parameters calculated are given in Table 2. The various values indicate that these complexes are moderately distorted and the distortion increases in the order: NCS > $NO_3$ > Br > Cl consistent with their order in the nephelauxetic series.

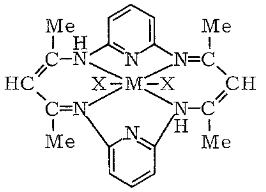
**Table 2.** Magnetic and electronic spectral data of nickel(II) and cobalt(II) complexes.

| Complex | Spectral bands ($cm^{-1}$) | $\mu_{eff}$. B. M. (300 K) | $Dq^{xy}$ | $Dq^z$ | Dt | DT | DS | DQ | $DQ^{xy}$ | $DQ^z$ | DT/DQ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $Ni(TML)Cl_2$ | 10700, 11710, 18180, 27836, 34850 | 3.30 | 1171 | 969 | 115 | 1560 | 11690 | 30353 | 32199 | 26661 | 0.051 |
| $Ni(TML)Br_3$ | 10720, 11760, 18220, 28200, 35000 | 3.25 | 1176 | 968 | 119 | 1615 | 11480 | 30427 | 32338 | 26605 | 0.053 |
| $Ni(TML)(NO_3)_2$ | 10650, 11780, 18280, 28320, 35200 | 3.15 | 1178 | 952 | 121 | 1640 | 11550 | 30450 | 32390 | 26568 | 0.054 |
| $Ni(TML)(NCS)_2$ | 10560, 11690, 18250, 28280, 34780 | 3.28 | 1169 | 943 | 129 | 1750 | 11480 | 30073 | 32144 | 25931 | 0.058 |
|  |  | $\mu_{eff}$. B. M. (300 K) | Dq | B | β | $\nu_2/\nu_1$ |  |  |  |  |  |
| $Co(TML)Cl_2$ | 8630, 15930, 18620, 21570 | 4.59 | 1078 | 810 | 0.83 | 1.85 |  |  |  |  |  |
| $Co(TML)Br_2$ | 8250, 16250, 18480, 21620 | 4.68 | 1031 | 820 | 0.84 | 1.97 |  |  |  |  |  |
| $Co(TML)(NO_3)_2$ | 8570, 15750, 18540, 21490 | 4.63 | 1071 | 808 | 0.83 | 1.84 |  |  |  |  |  |
| $Co(TML)(NCS)_2$ | 8750, 16120, 18460, 21500 | 4.57 | 1094 | 793 | 0.82 | 1.84 |  |  |  |  |  |

The solution spectra of cobalt complexes exhibit bands at *ca.* 8250–8750 cm$^{-1}$ ($\nu_1$) and 15750–16250 cm$^{-1}$ ($\nu_2$) with a broad band envelop *ca.* 21000 cm$^{-1}$ ($\nu_3$) showing almost two discernable bands at *ca.* 18500 and 21500 cm$^{-1}$. These spectra resemble those of cobalt(II) complexes reported to be distorted octahedral having effective $D_{4h}$ symmetry(17). The spectra of present complexes exhibit the bands in the visible region which show a structure and are split due to the presence of low symmetry fields. The splitting causes a band envelope due to considerable overlap and a broad collection of bands is observed in the spectra(17). Thus, assuming the effective symmetry to be $D_{4h}$, various bands can be assigned(17) to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, (*ca.* 8500), $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (*ca.* 1600) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (*ca.* 20000) cm$^{-1}$, respectively. The first band $\nu_1$ is observed approximately at half of the visible band, thus, the assignment of the visible band to $^4A_{2g}$ seems plausible and it can not be spin forbidden(17). This is true in view of the $\nu_2/\nu_1$ ratio which lies towards the lower side (Table 2) of 2.1 – 2.2 and is consistent with the accuracy of the assignment(17). The calculated Dq, B and $\beta$ values are given in Table 2.

The spectra of copper complexes in solution show a broad maxima at *ca.* 17700–19250 cm$^{-1}$ with a shoulder on the low energy side at *ca.* 14500–17000 cm$^{-1}$ which indicates that these complexes are distorted octahedral(21). The spectral bands shift to higher energy in the order: NCS > NO$_3$ > Br > Cl, *i.e.* in order of weakening interaction of the metal ion with the anions. Assuming tetragonal distortion in the molecule, the energy level sequence for these complexes may be: $x^2\text{-}y^2 > z^2 > xy > xz > yz$ and the shoulder can be assigned to $z^2 \rightarrow x^2\text{-}y^2$ ($^2B_{1g} \rightarrow {}^2B_{2g}$) and the broad band contains both the $xy \rightarrow x^2\text{-}y^2$ ($^2B_{1g} \rightarrow {}^2E_g$) and $xz$, $yz \rightarrow x^2\text{-}y^2$ ($^2B_{1g} \rightarrow {}^2A_{2g}$) transitions(22). The band separation of spectra of the complexes is of the order of 2500 cm$^{-1}$ which is consistent with proposed geometry of the complexes(23).

Thus, based on conductance, molecular weight, magnetic, electronic and i. r. spectral studies the following structure (*1*) may be proposed for these complexes:



(*1*)

M = Ni$^{II}$, Co$^{II}$ or Cu$^{II}$; X = Cl, Br, NO$_3$ or NCS

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