Pergamon

PII: S0277-5387(96)00544-X

Polyhedron Vol. 16, No. 13, pp. 2229–2232, 1997

0277-5387/97 $17.00+0.00

Synthesis and characterization of bivalent metal complexes of a tetradentate N_6 macrocyclic ligand

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(Received 11 October 1996; accepted 31 October 1996)

Abstract—Bivalent cobalt, nickel and copper salts react *in situ* with 2,6-diacetylpyridine and 1,2-diaminobenzene to form complexes containing a 18-membered N_6 tetradentate macrocyclic ligand. The complexes were characterized as distorted octahedral of the type: $[M(TML)X_2$; where M = Co^{II}, Ni^{II} or Cu^{II}; X = Cl, Br, NO_3 or NCS; TML = tetradentate macrocyclic ligand. The ligand coordinates through all the six nitrogen atoms. The molar conductance measured in DMF show that these chelates are 1 : 2 electrolytes. The test for anions are positive directly without decomposing the chelates, showing their presence outside the coordination sphere. The magnetic, electronic, IR and far-IR spectral studies are also discussed. © 1997 Elsevier Science Ltd

Keywords: macrocyclic ligand; bivalent metal complexes; magnetic, electronic and IR spectra.

Complexes of metal ions with synthetic macrocyclic ligands are of great importance, in part because of their resemblance to many natural systems, e.g. porphyrins and cobalamines. The publication of several reviews and books covering various aspects of synthetic macrocyclic ligands is witness to the great importance attached to them [1–3]. Most of the metal chelates have been derived from aliphatic or aromatic diamines and aliphatic dicarbonyl compounds. However, no work has been initiated on the metal chelates of macrocyclic compounds derived from aromatic dicarbonyl and aromatic diamine. In the present paper, the bivalent cobalt, nickel and copper complexes derived from 2,6-diacetylpyridine and 1,2-diaminobenzene are discussed.

EXPERIMENTAL

Isolation of metal chelates

A 20 cm^3 methanolic solution of 2,6-diacetylpyridine (~0.01 mol) was refluxed with 100 cm^3 methanolic solution of recrystallized 1,2-diaminobenzene (~0.01 mol) for 2 h. Divalent cobalt, nickel or copper salt (0.055 mol) dissolved in a minimum quantity of methanol (20 cm^3) was added to the refluxing mixture. A few drops of glacial acetic acid were also added to the mixture and refluxing continued for 6–10 h, depending upon the metal salt (6 h in case of nickel and copper and 10 h in case of cobalt salt). The mixture was concentrated to half of its volume and kept in a desiccator for 2 days. The complexes were filtered, washed with methanol, acetone and ether, dried *in vacuo* over P_4O_{10}; yield ~30%.

The complexes of nitrates were synthesized using metal nitrates. The bromide and thiocyanate complexes were prepared by the metathesis process. The metal chloride solution in methanol was treated with either lithium bromide or ammonium thiocyanate and stirred for 2 h. Lithium chloride or ammonium chloride was filtered and the filtrate was used to isolate the bromide or thiocyanate complexes.

The complexes are soluble in dimethylformamide and dimethylsulfoxide, but are insoluble in common organic solvents and water. They are thermally stable up to ~250°C.

RESULTS AND DISCUSSION

The analytical data of the metal chelates are given in Table 1, which show that chelates may be rep-

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Table 1. Analytical data of divalent cobalt, nickel and copper complexes

S. No.	Complexes	Color	Found (calc.) % M	C	H	N	X	$\Lambda_{M\ \mathrm{Mhos}}$ ($cm^{-2}\ mol^{-1}$)	Mol. wt
1.	$[Co(C_{30}H_{26}N_6)]Cl_2$	Reddish	9.9 (9.8)	60.1 (60.1)	4.4 (4.3)	14.2 (14.0)	11.5 (11.8)	152	600
2.	$[Co(C_{30}H_{26}N_6)]Br_2$	Brownish	8.5 (8.6)	52.2 (52.2)	3.5 (3.8)	12.5 (12.2)	23.1 (23.2)	158	689
3.	$[Co(C_{30}H_{26}N_6)](NO_3)_2$	Dark brown	9.0 (9.0)	55.3 (55.1)	3.9 (4.0)	17.2 (17.1)	18.6 (19.0)	154	653
4.	$[Co(C_{30}H_{26}N_6)](NCS)_2$	Brownish red	9.2 (9.1)	55.6 (55.8)	4.1 (4.0)	17.4 (17.4)		164	645
5.	$[Ni(C_{30}H_{26}N_6)]Cl_2$	Dark green	9.0 (9.1)	59.4 (59.9)	4.4 (4.3)	13.9 (14.0)	11.4 (11.8)	142	601
6.	$[Ni(C_{30}H_{26}N_6)]Br_2$	Green	8.8 (8.7)	52.2 (52.2)	3.8 (3.8)	13.8 (14.0)	12.2 (12.2)	149	690
7.	$[Ni(C_{30}H_{26}N_6)](NO_3)_2$	Blackish green	9.1 (9.2)	55.1 (55.0)	3.9 (4.0)	17.5 (17.1)	18.9 (19.0)	152	654
8.	$[Ni(C_{30}H_{26}N_6)](NCS)_2$	Dark green	9.2 (9.3)	59.5 (59.1)	5.0 (4.0)	17.4 (17.3)	— —	149	646
9.	$[Cu(C_{30}H_{26}N_6)]Cl_2$	Brown	10.6 (10.5)	59.1 (59.5)	4.3 (4.3)	13.9 (13.9)	12.0 (11.7)	137	604.5
10.	$[Cu(C_{30}H_{26}N_6)]Br_2$	Dark brown	9.1 (9.1)	51.8 (51.9)	3.8 (3.7)	12.2 (12.1)	23.1 (23.1)	141	693.5
11.	$[Cu(C_{30}H_{26}N_6)](NO_3)_2$	Dark brown	9.7 (9.6)	54.6 (54.7)	3.9 (3.9)	17.1 (17.0)	19.0 (19.1)	138	657.5
12.	$[Cu(C_{30}H_{26}N_6)](NCS)_2$	Blackish brownish	9.8 (9.8)	59.7 (59.6)	4.0 (4.0)	17.4 (17.4)	— —	144	644.5

resented by the formula $[M(C_{30}H_{26}N_6)]X_2$. The measurements of molar conductance in DMF show that these chelates are 1 : 2 electrolytes. The tests for anions are positive directly without decomposing the chelates showing their presence outside the coordination sphere.

IR spectra

The IR spectra of all the complexes do not exhibit any bands in the region at *ca* 3400–3200 cm^{-1}, the characteristic frequency of the free—NH_2 group. There is no absorption ~1700 cm^{-1} due to the free carbonyl group [4]. The absence of stretching and bending vibrations of the (C—O) group at *ca* 1525 and 1280 cm^{-1} substantiate the absence of this group [5]. The strong bands appearing as doubles at *ca* 1595–1629 cm^{-1} may be assigned to $\nu_{(C=N)}$ vibrations and point towards the coordinated azomethine groups [6,7]. Therefore, it is clear from the IR spectra that both the NH_2 groups of 1,2-diaminobenzene have condensed with both the carbonyl groups of 2,6-diacetylpyridine to give rise to an N_6 arrangement of four azomethine and two pyridine nitrogen atoms equally suitable for coordination. 2,6-Disubstituted pyridine derivatives show various bands at *ca* 1585–1615, 1570–1590, 1455–1490 and at *ca* 1440–1445 cm^{-1} can be assigned to four $\nu_{(C=C)}$ skeletal frequencies and designated as bands I, II, III and IV of pyridine rings, respectively [6–8]. The spectra also exhibit a ring breathing mode at *ca* 990 cm^{-1}, an out-of-plane (C—H) deformation at *ca* 800 cm^{-1}, an in-plane (C—C) deformation at *ca* 615 cm^{-1} and an out-of-plane (C—C) deformation at *ca* 405 cm^{-1}, respectively. The two strong bands at *ca* 785 and 740 cm^{-1} are assigned to γ(C—H) and ϕ(C—C) vibrations [9], respectively.

The spectra of the chelates exhibit a downward shift in the location of bands I, II, III and IV. The bands at *ca* 990 cm^{-1} disappear and are replaced by a band at *ca* 1015–1025 cm^{-1}. The band assigned γ(C—C) splits into two at *ca* 725 and 740 cm^{-1}, while γ(C—H) appears at *ca* 785 cm^{-1} as a single band. These changes point towards the involvement of the pyridine nitrogen in coordination. Furthermore, the bands assignable to an in-plane (C—C) deformation (~605 cm^{-1}) and an out-of-plane (C—C) deformation (~410 cm^{-1}) undergo an upward shift to 15–20 cm^{-1} in the spectra of chelates, which is consistent with the coordination of pyridine–nitrogen to the metal atom [10]. This mode of coordination is further supported by the far-IR spectra of complexes.

In the spectra of complexes under study, a strong band at *ca* 1625 cm^{-1} with a shoulder at *ca* 1615 cm^{-1}

may be assigned to symmetric and antisymmetric stretching modes of the azomethine linkage [11] and the frequency concerned with the $\nu_{(C=N)}$ stretching mode shifted to lower range by 15–20 cm^{-1}, with a marginal loss of the intensity of the band. This lowering may be taken as an indication of the coordination of the nitrogen of the azomethine group to the metal atom [12].

The appearance of three bands at *ca* 1350, 1230 and 825 cm^{-1} assignable to NO_2 asymmetric stretching, symmetric stretching and bending modes, respectively, are found in the nitrato complexes of cobalt, nickel and copper. The position of these bands are compatible with the ionic nitrato group [13]. The fact is further substantiated by the presence of a sharp narrow band at *ca* 1765 cm^{-1} in these complexes, suggesting the ionic nature of nitrato group. The weak band at *ca* 2370 cm^{-1} and another strong band of these metals at *ca* 2110 cm^{-1} are depicted by the thiocyanato complexes of the metals. These bands are due to ν_{CN} of NCS group and suggest the ionic nature of thiocyanato group [14].

Magnetic properties and electronic spectral studies

The magnetic and electronic spectral data for these divalent metal chelates are recorded in Table 2.

The magnetic moments of divalent cobalt, nickel and copper complexes lie in the 4.46–4.64, 2.96–3.12 and 1.77–1.89 B.M. ranges, respectively, at room temperature and are close to the predicted values for octahedral geometry around the metal atom [15].

The solution spectra of cobalt(II) complexes exhibit absorption in the region at *ca* 8100–9100 (ν_1), 12,550–15,750 (ν_2) and 18,700–20,250 cm^{-1} (ν_3), respectively. The spectra resemble those reported to be octahedral [7]. The spectra of the complexes show a band in the visible region, which show a structure and is split due to the presence of low symmetry fields. Thus, assuming the effective symmetry to be D_{4h}, the various bands can be assigned to: ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$, ($\nu_1$) 8100–9100 cm^{-1}, ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$, ($\nu_2$) 15,250–15,750 cm^{-1}, ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$, ($\nu_3$), 18,700–20,250 cm^{-1}, respectively. It appears that the symmetry of these complexes is not idealized O_h, but is D_{4h}. The assignment of the first spin-allowed band seems plausible since the first band appears approximately at half the energy of the visible band [16]. This is evidence in view of the ν_2/ν_1 ratio which lies 1.72–1.89 and is consistent with the accuracy of assignment [17]. The values of various ligand field parameters, *Dq*, *B* and β are calculated and provided in Table 2.

The solution spectra of Ni^{II} complexes exhibit a well discernable band with a shoulder on the low energy side. The other two bands generally observed in the region at *ca* 16,650–17,050 (ν_2) and 27,800–28,250 cm^{-1} (ν_3) are assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3), respectively. The first two bands result from the splitting of one band, ν_1 and are in the range at *ca* 9700–10,300 and 11,750–12,300 cm^{-1}, which can be assigned to ${}^3B_{1g} \rightarrow {}^3E_g$ and ${}^3B_{1g} \rightarrow {}^3B_{2g}$, assuming the effective symmetry to be D_{4h} (component of ${}^3T_{2g}$ in O_h symmetry) [16]. The intense higher energy band at *ca* 34,500 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 distorted octahedral nature of these complexes and calculated *Dt*, *Dq*, *DT* and *DQ* values are given in Table 2. Thus,

Table 2. Magnetic and electronic spectral data of divalent cobalt, nickel and copper complexes

Complexes	Spectral bands (cm^{-1})	*Dq*	*Dt*	*DT*	*DQ*	*DT*/*DQ*	μ_{eff} (B.M.) (300 K)
[Ni(TML)]Cl_2	9000, 11,750, 17,100 28,150	1175	210	2857	28,926	0.08	2.97
[Ni(TML)]Br_2	10,050, 12,000, 16,700, 28,250	1200	220	3009	29,435	0.09	3.12
[Ni(TML)]$(NO_3)_2$	10,300, 12,300, 17,000, 27,800	1230	225	3087	30,165	0.09	3.06
[Ni(TML)](NCS)$_2$	9700, 12,200, 16,850, 28,000	1220	286	3860	28,975	0.12	2.95
		Dq	*B*		β	ν_2/ν_1	
[Co(TML)]Cl_2	8550, 12,550, 18,700	1068	817		0.83	1.77	4.64
[Co(TML)]Br_2	9100, 15,750, 19,650	1136	854		0.89	1.72	4.56
[Co(TML)]$(NO_3)_2$	8100, 15,250, 19,050	1015	862		0.88	1.89	4.50
[Co(TML)](NCS)$_2$	8700, 15.700, 20,250	1082	916		0.95	1.86	4.46
[Cu(TML)]Cl_2	15,300, 18,050	1530	—		—	—	1.81
[Cu(TML)]Br_2	14,550, 17,700	1455	—		—	—	1.89
[Cu(TML)]$(NO_3)_2$	16,000, 18,750	1600	—		—	—	1.77
[Cu(TML)](NCS)$_2$	15,850, 19,600	1585	—		—	—	1.86

TML = Tetradentate Macrocyclic Ligand.

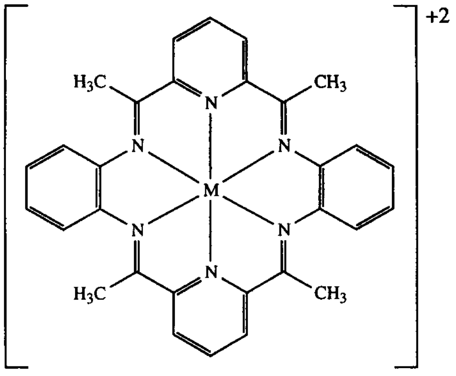
all the complexes studied herein show pseudo-octahedral geometry conforming to D_{4h} symmetry. On the basis of symmetry arguments Lever and coworkers [18] have devised normalized spherical harmonic Hamiltonian (NSH) theory applicable to molecules in D_{4h}. The NSH theory relates the classical ligand field parameters to NSH absolute ligand field parameters *DQ* and *DT*. *DQ* is a measure of the average ligand field experienced by the metal ion, unlike the classical *Dq* which is a measure of the in-plane ligand field. The *DT*/*DQ* ratio provides the amount of distortion of the molecule. 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 nephelauxetic series.

The absorption spectra of the copper complexes exhibit bands in the region *ca* 17,700–19,600 cm^{-1} with a shoulder on the low energy side at *ca* 14,550–16,000 cm^{-1}, and show that these complexes are distorted octahedral [7,16]. 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 *d*-orbital energy level sequence for these complexes may be: $x^2-y^2 > z^2 > xy > xz > yz$ and the shoulder can be assigned to: $z^2 \rightarrow x^2-y^2$ $(^2B_{1g} \rightarrow {}^2B_{2g})$ and the broad band contains both the $xy \rightarrow x^2-y^2(^2B_{1g} \rightarrow {}^2E_g)$ and $xz, yz \rightarrow x^2-y^2$ $(^2B_{1g} \rightarrow {}^2A_{2g})$ transitions [19]. The band separation of the spectra of the complexes is of the order 2500 cm^{-1}, which is consistent with proposed geometry of the complexes [19]. Therefore, it may be concluded that all the complexes formed by macrocycles with Cu^{II} metals are distorted octahedral.

Far-IR spectra

The far-IR spectra of the complexes show various bands in various regions assignable to pyridine ring and metal–nitrogen vibrations. The spectra of the complexes derived from 2,6-diacetylpyridine and 1,2-diaminobenzene show bands at *ca* 415 and 600 cm^{-1}, assignable to (C—C) out-of-plane and (C—C) in-plane deformations. The vibrations suffer significant shift towards higher frequencies and support pyridine–nitrogen coordination to the metal atom [20]. The spectra also exhibit various bands in the region at *ca* 260–280 cm^{-1}. In this region the various vibrations observed are at *ca* 260–270, 265–274 and 275–280 cm^{-1} and these may be assigned to ν(Co-py), ν(Ni-py) and ν(Cu-py) stretching vibrations, respectively [21]. The far-IR spectra also show various bands at *ca* 430–495 cm^{-1}, which implies ν(M—N) (azomethine) vibrational modes and confirms the involvement of the azomethine nitrogen.

Therefore, based on elemental analysis, conductance, magnetic, electronic and IR spectral studies the following structure may be proposed for the these complexes:



M =Co(II), Ni(III), or Cu(II)
X = Cl, Br, NO_3, or NCS.

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