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Synthesis and characterization of Ni(II), Cu(II) and Co(III) complexes with polyamine-containing macrocycles bearing an aminoethyl pendant arm

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Abstract: Reaction of $[M(ppn)_2]X_2$ (where M = Cu(II), Ni(II), Co(II) and ppn = 1,3-diaminopropane) with formaldehyde and ethylenediamine in methanol results in the ready formation of a 16-membered macrocyclic complex. The complexes were characterized by elemental anlysis, IR, EPR, electronic spectral data, magnetic moments and conductance measurements. The Cu(II), Ni(II) and Co(III) complexes are coordinated axially with both pendant groups of the hexadentate macrocycle. These pendant donors are attached to the macrocycle by a carbon chain. The electrical conductivities of the Cu(II) and Ni(II) chelates indicated them to be 1:2 electrolytes whilst those of Co(III) is a 1:3 electrolyte in DMSO. The EPR spectrum of the copper complex exhibited G at 3.66, which indicates a considerable exchange interaction in the complex. Spectroscopic evidence suggests that in all of the complexes the metal ion is in an octahedral environment.

INTRODUCTION

The interest in the study of macrocyclic complexes with pendant arms is still growing on account of their unique coordination and structural properties, their utility as bio-inorganic models for cobalamine[1] and catalysis, and their rapidly growing applications as radio pharmaceuticals and magnetic resonance imaging reagents.[2]

Schiff base type macrocycles are readily accessible and versatile platforms that give rise to a variety of structural motifs, including mono- and di-compartmental cycles, sterically enforced macrocycles and ligands with additional functional groups attached to the macrocycles.[3]

In the last decade, Schiff base macrocyclic ligands have received more attention mainly because of their wide application in the field of synthesis and catalysis.[4] The attraction is still growing, so that a considerable research effort is today devoted to the

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synthesis of new Schiff base complexes with transition[5] and main group metal ions[6] to further develop applications in both catalysis and material chemistry.[7]

Recently a one step synthesis of Schiff base macrocyclic complexes bearing a primary amino group in the pendant arm *via* a template condensation has been reported.[3] However, its outcome depends on the nature of the metal template.

The metal directed synthesis of macrocyclic ligands by reaction of polyamines, formaldehyde and methylamine or nitroalkane and Cu(II) or Ni(II) as a labile metal ion has been studied in some detail.[8,9] The chemistry is usually facile and has been extended to polyamines. In general, it appears that the presence in the precursor complex of a pair of *cis*-disposed primary amines is the main requirement for the reaction. The chemistry may offer one of the most facile routes to new macrocyclic ligands.

We have attempted the synthesis of a 16-membered saturated hexaaza macrocyclic ligand containing a pendant arm and its complexes with Cu(II), Ni(II) and Co(III) ions. Effort was made to determine if the pendant group is also hooked to the metal ion.

EXPERIMENTAL

Materials

1,3-Diaminopropane, formaldehyde (Merck), 1,2-diaminoethane and hydrated $CoCl_2$, $NiCl_2$ and $CuCl_2$ (BDH) were used as received.

Analytical methods and physical measurements

Elemental analysis (C, H, N) was carried out with a Carlo Erba 1106 analyser. The metal was determined by complexometric titration[10] and chlorine was determined gravimetrically.[11] The IR spectra (4000–600 cm^{-1}) were recorded on a Perkin Elmer 621 spectrometer as KBr discs. The conductivity measurements were carried out on a CM-82T Elico conductivity meter in DMSO and MeOH. The UV-Vis spectra were recorded on a Carl-Zeiss VSU2P spectrophotometer in DMSO and MeOH. The magnetic susceptibility measurements were done with a 155 Allied Research vibrating sample magnetometer at room temperature. The EPR spectrum of a polycrystalline sample was recorded on a RE-2X Jeol EPR spectrometer fitted with 100 KHz field modulation.

Synthesis of $[Cu(L)](ClO_4)_2$

To a methanolic solution of $[Cu(ppn)_2]Cl_2$ (5 mmol, 1.4 g) in a 100 ml round bottom flask was slowly added 36 % formaldehyde (20 mmol, 1.6 ml). The mixture was refluxed for 30 min, 99 % ethylenediamine (10 mmol, 0.7 ml) was then added to the hot mixture and the reflux was continued for a further 5 to 6 h. After cooling to room temperature and acidification with perchloric acid, the mixture was left overnight in a refrigerator. The obtained sky blue complex was washed thrice with ether and dried under vacuum. Yield 45 %.

Synthesis of $[Ni(L)]Cl_2$

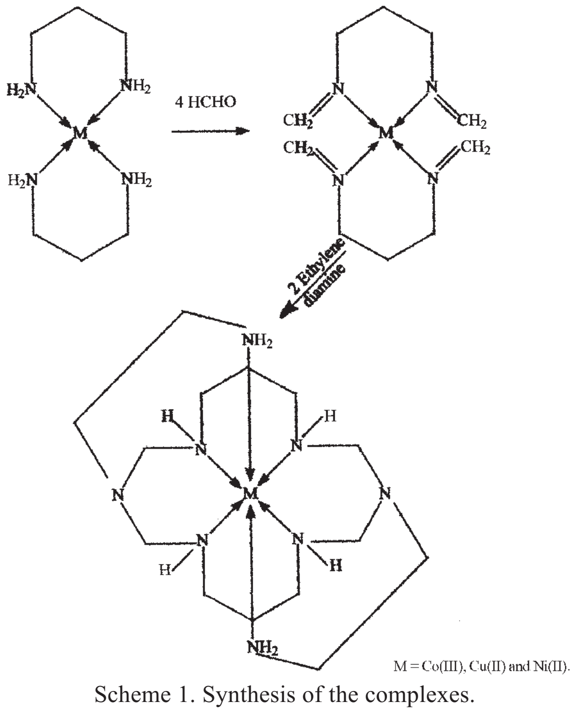
To $[Ni(ppn)_2]Cl_2$ (5 mmol, 1.6 g) in a 100 ml round bottom flask was added 36 % formaldehyde (20 mmol, 1.6 ml). The mixture was refluxed for 30 min. To the resulting mixture was added ethylenediamine (10 mmol, 0.7 ml) and the reflux was continued for a further 5 to 6 h. On cooling to room temperature, a violet complex was obtained, which was purified by washing with cold ether. Yield 55 %.

Synthesis of [Co(L)Cl$_3$]

[Co(ppn)$_2$]Cl$_2$ (5 mmol, 1.8 g) was dissolved in a 1:1 methanol–water mixture. It was aerated for nearly 10 h in order to oxidize Co(II) to Co(III). It was transferred to a 100 ml round bottom flask and 36 % formaldehyde (20 mmol, 1.6 ml) was added and refluxed for 30 min. To this resulting mixture was added 99 % ethylenediamine (10 mmol, 0.7 ml) and further refluxed for about 5 to 6 h. After cooling to room temperature, a yellowish orange product was obtained, which was purified by washing with cold ether. Yield 30 %.

RESULTS AND DISCUSSION

According to the Scheme 1, [Cu(ppn)$_2$]Cl$_2$ was allowed to react with formaldehyde under reflux. After about half an hour of reflux, ethylenediamine was slowly added and further refluxed for 5 to 6 h which yielded the product on cooling to room temperature.



M = Co(III), Cu(II) and Ni(II).

Scheme 1. Synthesis of the complexes.

Conductances

The molar conductance of a 1 mM solution of the Cu(II) complex measured in DMF falls in the range of a 1:2 electrolyte (Table I).

The molar conductance of a 1 mM solution of the Ni(II) complex measured in DMF corresponds to a 1:2 electrolyte. When it was analyzed by fusing the complex, two chloride ions per molecule were found.

The molar conductance of a 1 mM solution of the Co(III) complex measured in DMF was slightly below the range for a 1:3 electrolyte. It seems as if the third Cl ion is not fully ionized.[12]

TABLE I. Analytical data, melting points, colours and percentage yield of the complexes

Compound	Colour	M.p./ºC	Yield/%	% Analysis: Found (Calcd)					Molar conductance $\Omega^{-1}cm^2mol^{-1}$
				C	H	N	M	Cl	
$[Ni(L)]Cl_2$	Violet	183	45	29.4 (29.0)	5.8 (6.2)	19.6 (19.3)	11.0 (10.9)	– –	142
$[Co(L)]Cl_3$	Yellowish orange	>300	55	37.2 (37.6)	8.5 (8.1)	24.4 (25.1)	13.5 (13.1)	15.7 (15.9)	193
$[Cu(L)](ClO_4)_2$	Sky-blue	230	30	37.9 (37.6)	7.7 (7.4)	23.6 (23.2)	12.1 (12.2)	21.9 (22.0)	135

$$[Co(L)]Cl_3 \rightarrow [Co(L)]^{3+} + 3Cl^-$$

Electronic spectra

In the case of the Cu(II) complex, a broad low intensity band appears at 15570 cm^{-1} (626 nm) which is attributed to the d-d transition of the Cu(II) ion.[13] This band is of low molar absorptivity, ε, being Laporte forbidden[14] (Table II).

TABLE II. Electronic spectra and their assignments

Compound	Transition cm^{-1}	Assignment	Magnetic moment B.M.	log ε L mol^{-1} cm^{-1}
$[Co(L)]Cl_3$	21367	${}^1T_{1g}\leftarrow{}^1A_{1g}$	5.25	1.66
	29239	$1T_{2g}\leftarrow{}^1A_{1g}$		
$[Ni(L)]Cl_2$	11325	${}^3T_{1g}(P)\leftarrow{}^3A_{2g}(F)$	3.7	1.62
	18416	${}^3T_{1g}(F)\leftarrow{}^3A_{2g}(F)$		
	29154	${}^3T_{2g}(F)\leftarrow{}^3A_{2g}(F)$		
$[Cu(L)](ClO_4)_2$	15974	${}^2T_{2g}\leftarrow{}^2E_g$	2.01	–
	33003	C.T. band		

Hathaway[15] has reported that octahedral CuN$_6$ chromophores have transitions in the region 15500–18500 cm^{-1} while square planar CuN$_4$ chromophores have transitions in the region 18000–20000 cm^{-1}, besides a charge transfer band. In the present work, the absorption band observed at 15570 cm^{-1} assigned to ${}^2T_{2g} \leftarrow {}^2Eg$ transition clearly indicates that the complex contains a CuN$_6$ chromophore. The chromophore is completed using the pendant arm as a donor site.

Further, the absorption at 15570 cm^{-1} may be ascribed to Cu(II) in an aminic site[16] and not in an iminic site. This indicates that the macrocycle is in a saturated state. The absorption at 33003 cm^{-1} may be due to ligand to metal charge transfer (LMCT) which is a characteristic of copper(II) complexes with amines.

In order to determine if the Cu(II) complex undergoes solvatochromic shifts in different solvents, the complex was dissolved in a variety of polar solvents, such as DMSO, DMF, THF, $CHCl_3$, $C_6H_5NO_2$, and their UV-Vis spectra were recorded. Since the spectra do not exhibit any variation in the absorption pattern as a function of solvent, it is suggested that binding of solvent to the Cu(II) ion does not occur. This means that geometry of the Cu(II) ion does not change in solution. However, the observed magnetic moment value is 2.01 B.M. which corresponds to an octahedral structure for the Cu(II) ion.[17]

Lawrance[18] found a correlation between the electronic spectrum of the $Co^{III}N_{6-n}Cl_n$ (n = 0,1 or 2) chromophore and its geometry. Co(III) complexes with N$_6$ macrocycles containing pendant group have been shown to split the ${}^1T_{1g}$ excited state into a ${}^1A_{2g}$ and a ${}^1E_g$ state under the influence of the tetragonally distorted ligand field where the pendant groups are not bonded. This pronounced splitting is indicative of a *trans*-octahedral geometry with two low energy maxima at 620 nm and

440 nm, which was also confirmed by the crystal structure.[18] If only one of the two pendant groups is coordinated to Co(III), a smaller splitting of the d-d band is observed.[18,19] When both the pendant groups are attached to the Co(III) ion in a macrocyclic complex, a symmetric absorption envelops for both the $^1T_{1g}\leftarrow{}^1A_{1g}$ and the $^2T_{1g}\leftarrow{}^1A_{1g}$ transitions, although the absorption occurs at slightly higher energy level.

Our results of the electronic spectrum for the Co(III) complex (Table II) are exactly identical to those reported by Lawrance.[18] It is, therefore, suggested that the prepared complex has pseudo octahedral geometry in which both the pendant groups are symmetrically bonded to the Co(III) ion.

The observed magnetic moment value for the Co(III) complex is 5.23 B.M. which is within the predicted high-spin value for an octahedral Co(III) complex with a considerable orbital contribution to the overall magnetic moment.[20]

Four sharp absorption bands for pseudo octahedral Ni(II) complexes with macrocyclic ligands have been reported in the visible range.[21] However, three distinct absorption bands are generally observed for an octahedral Ni(II) ion.[22] In our case, the electronic spectrum of the Ni(II) complex is compatible with an octahedral geometry. Three absorption bands were observed for the violet Ni(II) complex at 11325, 18416 and 29154 cm^{-1} corresponding to the $^3T_{1g}(P)\leftarrow{}^3A_{2g}(F)$, $^3T_{1g}(F)\leftarrow{}^3A_{2g}(F)$ and $^3T_{2g}(F)\leftarrow{}^3A_{2g}(F)$ transitions, respectively. On the basis of spectral bands, an octahedral geometry is therefore proposed for the Ni(II) ion. The values of ligand field parameters reflect that the M–L bond is quite strong, which in turn suggests sufficient overlapping of the metal orbitals with those of the ligand orbitals. The compounds are paramagnetic with a room temperature magnetic moment of 3.7 B.M. which is consistent with an $S = 1$ ground state in an octahedral field.

IR spectra

The IR spectra of the complexes are given in Table III. Generally, free primary amino groups exhibit two N–H stretching frequencies in the 3300 to 3500 cm^{-1} region which are shifted by about 100 to 200 cm^{-1} to lower wave number after coordination with a metal ion.[23,24] Since the prepared compounds contain both primary NH_2 and secondary NH groups, peaks corresponding to these groups appear in the IR spectra.

It has been reported by Suh and Kang[25] that Ni(II) and Cu(II) complexes with macrocyclic ligands containing a secondary amino group show a single absorption at around 3200 cm^{-1}, indicating coordination of the secondary amino group. In the present work, absorption band was observed in 3122 – 3168 cm^{-1} region corresponding to ν(NH) of the secondary amino group, which is consistent with the work of Suh and Kang.[25]

The pendant amino group is made accessible for coordination to the metal ion only when it is attached to the macrocycle through a carbon chain. Since there is no sideways movement with the axial elongation as a result of the type of attachment of the pendant group to the macrocycle, it may account for the octahedral coordination of Cu(II) ion but distortion of the octahedron can not be ruled out.

TABLE III. Observed IR bands for the metal complexes

Compound	ν(NH)	ν(NH_2)	δ(NH)	ν(C–N)	ν(ClO_4)
$[Ni(L)]Cl_2$	3245 (*s*) (sym) 3293 (*s*) (anti)	3339 (*m*) (sym) 3400 (*m*) (anti)	1605 (*s*)	1330 (*m*)	–
$[Co(L)]Cl_3$	3201 (*s*) (sym) 3289 (*s*) (anti)	3356 (*m*) (sym) 3393 (*m*) (anti)	1580 (*s*)	1369 (*w*)	–
$[Cu(L)](ClO_4)_2$	3232 (*s*) (sym) 3300 (*s*) (sym)	3369 (*m*) (sym) 3405 (*m*) (anti)	1570 (*s*)	1363 (*w*)	1041 (*s*) 1101 (*s*) 975 (*m*) 625 (*w*)

In the case of $[Cu(L)](ClO_4)_2$, it is difficult to ascertain if the ClO_4^- ion is ionic or bonded to the Cu(II) ion.[26,27] However, it has been shown[26,27] that ionic perchlorate exhibits a single strong band in the 1085–1160 cm^{-1} region while a bonded ClO_4^- ion gives several absorption bands in the same region.[28] Two strong bands at 1041 and 1100 cm^{-1} were, however, observed, which is not conclusive because quite often these bands appear due to the crystalline state.[26] The molar conductance also supports the presence of ionic perchlorate.

EPR Spectrum

The EPR spectrum of the polycrystalline Cu(II) complex at room temperature exhibited a strong signal and its $g_{\|}$, $g_{\perp}$ and G values were calculated. The spectrum did not show hyperfine structure at room temperature, which may be attributed to strong dipolar and exchange interactions between the Cu(II) ions in the unit cell. The $g_{\|}$ (2.304) and $g_{\perp}$ (2.083) values suggest[29] that d_{x2-y2} may be the ground state as $g_{\|} > g_{\perp} > 2.04$. It has been reported that high $g_{\|}$ values are common for six coordinate Cu(II) complexes with ligands containing hard donors, such as nitrogen and oxygen.[30] Very high $g_{\|}$ values were observed for the copper complex, which is consistent with a six coordinated Cu(II) complex with N donor sets. The observed g values are characteristic[31] of an axially distorted octahedral Cu(II) ion such that the unpaired electron is present in the d_{x2-y2} orbital. The g values are related by the expression

$$G = \frac{g_{\|-2}}{g_{\perp-2}}$$

which measures the exchange interaction between the copper centers in the polycrystalline solid. If $G > 4$ exchange, the interaction is negligible and if $G < 4$ considerable exchange interaction occurs in solid complexes.[32] In the present case, G is 3.66 which indicates the occurrence of exchange interaction in the complex.

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ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА КОМПЛЕКСА Ni(II), Cu(II) И Co(III) СА МАКРОЦИКЛИМА СА ПОЛИАМИНОМ И АМИНОЕТИЛНИМ БОЧНИМ МОСТОМ

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Реаговањем M(ppn)$_2$X$_2$ (где је M = Cu(II), Ni(II), Co(II) а ppn = 1,3-диаминопропан) са формалдехидом и етилендиамином у метанолу лако се ствара 16-члани макроциклични комплекс. Комплекси су карактерисани елементалном анализом, IR и електронском спектроскопијом, као и мерењима магнетнх момената и електричне проводљивости. Комплекси Cu(II), Ni(II) и Co(II) координисани су аксијално са обе бочно везујуће групе хексадентантног макроцикла. Ови бочни донори повезани су за макроцикле угљеничним ланцем. Електричне проводљивости Cu(II) и Ni(II) хелата указују да су то 1:2 електролити, док је код Co(III) јона у питању 1:3 електролит у DMSO. EPR спектар комплекса бакра показао је *G* на 3,66, а што указује на значајну интеракцију размене у комплексу. Спектроскопски докази указују на то да комплекси имају октаедарско окружење око јона метала.

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