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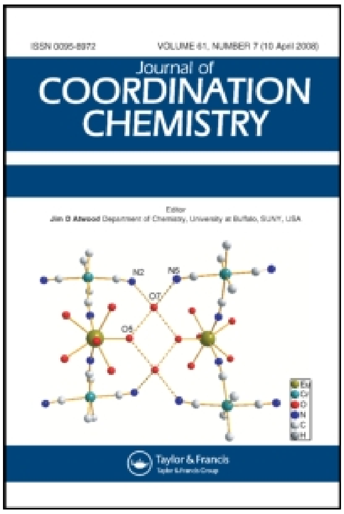

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Wahid U. Malik[ab]; Ramesh Bembi[a]; Randhir Singh[ab]
[a] Department of Chemistry, University of Roorkee, Roorkee, India [b] Vice-Chancellor, University of Kashmir, Srinagar, J&K, India

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STUDIES ON SOME TRANSITION METAL COMPLEXES CONTAINING QUADRIDENTATE NITROGEN DONOR MACROCYCLIC LIGAND

WAHID U. MALIK,† RAMESH BEMBI and RANDHIR SINGH†
Department of Chemistry, University of Roorkee, Roorkee 247672 India

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Macrocyclic complexes of Cu(II), Co(II) and Ni(II) have been synthesised by the template process using *m*-phenylene-diamine and the selected diketone in the presence of anhydrous metal salts. These macrocyclic complexes have been characterised by their elemental analysis, molar conductance, magnetic susceptibility, electronic and infrared spectra. The infrared spectral studies suggest that these complexes are of distorted octahedral geometry.

INTRODUCTION

The multifarious roles of transition metals in biochemistry suggest that considerable potential exists for the development of new chemistries with these metals in other suitably designed ligand systems.[1-3] Most published work has involved 14-membered macrocycles. Recent studies on the effects of varying ring size, charge and degree of unsaturation on the structures of such transition metal complexes have yielded some interesting results.[4] Macrocyclic complexes of copper have been shown to have widely differing geometries about the central metal atom.[5] Thus it was considered desirable to investigate the causes of differing geometries in the macrocyclic complexes. The macrocyclic ligand derived from the metal template condensation of *m*-phenylenediamine with 1, 3-diphenyl-1, 3-propanedione is grossly distorted from planarity due to the steric interactions of the phenyl groups with the benzenoid rings.[6] In this paper the synthesis and characterisation of 16-membered macrocycles are reported.

EXPERIMENTAL

The compounds employed were reagent grade B.D.H. products and were used without further purification. The compound 1, 3-diphenyl-1, 3-propanedione was prepared in the laboratory by a literature method,[7] and recrystallised twice from methanol.

Synthesis of Complexes

m-Phenylenediamine (0.02 mol) dissolved in the minimum quantity of MeOH was mixed with a methanolic solution of anhydrous metal salt (0.01 mol) and then 1, 3-diphenyl-1, 3-propanedione (0.02 mol) dissolved in methanol was added. The mixture was refluxed on a water bath for about 6 h. After adding 1 cm^3 of conc. hydrochloric acid and refluxing again for 4 h, the mixture was concentrated to half of its volume on a rotary evaporator and kept for 2 days as such. The dark greenish crystals formed were filtered off by suction, successively washed with methanol, acetone and ether and dried *in vacuo*. These complexes are soluble in DMF, CH_3CN and DMSO.

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†Present Address: Prof. Wahid U. Malik, Vice-Chancellor, University of Kashmir, Serinagar (JFK) India.

The nitrato-complexes were prepared from the metal nitrates. Bromo-, and thiocyanato-complexes were prepared by dissolving the chloro-complex in the minimum quantity of a suitable solvent and adding NaBr or NH_4CNS solution slowly to a stirred solution of the complex and then cooling the reaction mixture in an ice bath. Before cooling the NaCl or NH_4Cl formed was filtered off.

The complexes with CH_3CN as an axial ligand were prepared by using a slightly different procedure. A methanolic solution of CH_3CN was added to the reaction mixture (*m*-phenylenediamine, anhydrous metal salt and 1, 3-diphenyl-1, 3-propanedione) while refluxing it.

Analysis

The metal contents of the complexes were determined by standard spectrophotometric methods. Halides were estimated by Volhard's method and nitrate using nitron salt. The complexes were analysed for C, H and N in the laboratory of the Chemistry Department, University of Roorkee, Roorkee, India (Table I).

Physical Measurements

Magnetic susceptibility measurements were carried out using a Princeton Applied Research Model 155 vibrating sample magnetometer incorporating a digital read out. The electromagnet was fed from a Polytronic Constant current regulator (Type CP 200). The instrument was calibrated using a pure nickel pellet and crosschecked against $Hg[Co(CNS)_4.]$

Absorbance measurements were carried out using a Carl Zeiss Specord spectrophotometer using 10 mm glass cells. Conductance measurements of 1.0 mM solutions were carried out using a Systronics Conductivity Meter Type 302 at 25 ± 1° using a "dip"-Type Conductivity Cell. Infrared spectra were recorded on a Beckmann IR 20 spectrophotometer in KBr pellets over the 4000 – 400 cm^{-1} range and in Nujol mull over the 650 – 200 cm^{-1} range with a Beckmann IR-12 spectrophotometer. The molecular weights of soluble complexes were determined cryoscopically.

RESULTS AND DISCUSSION

Chemical analysis data for the complexes are in accordance with the formulae $[M(Ph_4[16]$ tetraene-$N_4)X_2]$ where M = Cu(II), Co(II) and Ni(II) and X = Cl, Br, NO_3, NCS and CH_3CN. The electrical conductance measurements suggest that the complexes are non-electrolytic in nature except for the complexes with CH_3CN as an axial ligand. The molecular weight determinations of these complexes are consistent with their proposed formulae.

IR Spectra

The important infrared bands observed for the reported compounds are listed in Table II. The infrared spectra of all the compounds do not contain any bands that can be assigned to the C = O or NH groups.[8] Characteristic infrared bands due to phenyl groups are present in the spectra of all the complexes in the 700 – 770 cm^{-1} region. The strong bands appearing as doublets in the spectra of all the complexes around 1590 – 1620 cm^{-1} may be assigned to $\gamma_{C=N}$ vibrations and these bands indicate the presence of coordinated azomethine groups.[9] The absence of absorptions around 3400 cm^{-1} shows that amino

TABLE I
Analytical data

	Complexes	% C		% H		% N		% X		% M	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
I	$[Cu(C_{42}H_{32}N_4)Cl_2]$	69.4	69.1	4.4	4.1	7.7	7.6	9.8	9.7	8.7	8.6
II	$[Cu(C_{42}H_{32}N_4)Br_2]$	61.8	61.2	3.9	3.4	6.9	6.7	19.6	19.4	7.7	7.9
III	$[Cu(C_{42}H_{32}N_4)(NO_3)_2]$	64.7	64.1	4.1	4.0	7.2	7.3	15.9	15.2	8.1	8.4
IV	$[Cu(C_{42}H_{32}N_4)(NCS)_2]$			4.2	4.1	7.3	7.4	15.0	15.4	8.2	8.0
V	$[Cu(C_{42}H_{32}N_4)-$ $(CH_3CN)_2](Cl)_2$					10.8	10.7			8.1	8.5
VI	$[Co(C_{42}H_{32}N_4)Cl_2]$	69.8	69.9	4.4	4.3	7.8	7.6	9.8	9.6	8.2	8.0
VII	$[Co(C_{42}H_{32}N_4)Br_2]$	62.1	62.4	3.9	3.6	6.9	6.8	19.7	19.9	7.3	7.5
VIII	$[Co(C_{42}H_{32}N_4)(NO_3)_2]$			4.1	4.0	7.2	7.4	16.0	16.2	7.6	7.2
IX	$[Co(C_{42}H_{32}N_4)(NCS)_2]$	65.7	65.1			7.3	7.5			7.7	7.3
X	$[Co(C_{42}H_{32}N_4)(CH_3CN)_2](Cl)_2$	64.9	64.6	4.9	4.8	10.8	10.6			7.6	7.8
XI	$[Ni(C_{42}H_{32}N_4)Cl_2]$	69.9	69.1	4.4	4.2	11.7	11.5	9.8	9.6	8.0	8.2
XII	$[Ni(C_{42}H_{32}N_4)Br_2]$	62.2	62.0	4.0	3.7	6.9	6.8	19.8	19.6	7.2	7.0
XIII	$[Ni(C_{42}H_{32}N_4)(NO_3)_2]$	65.1	65.4			7.2	7.0			7.5	7.1
XIV	$[Ni(C_{42}H_{32}N_4)(NCS)_2]$					7.3	7.2	15.1	15.4	7.6	7.2
XV	$[Ni(C_{42}H_{32}N_4)(CH_3CN)_2](Cl)_2$	65.0	65.1	4.9	4.7	10.8	10.9			7.5	7.4

groups of the diamine have reacted with 1, 3-diphenyl-1, 3-propanedione. The phenyl ring absorptions[10] appear in the 1600 – 1400 cm^{-1} region. The absorption bands in the 900 – 700 cm^{-1} region give important information regarding the geometry of the complexes. The bands in this region can be exclusively assigned to the imine,-CH_2 absorptions of the macrocycle and the multiplicity of these bands is dependent on the geometry of these complexes. In these macrocycles the –CH_2 absorption shows two bands and this supports the proposed *cis* geometry of the complexes.

The spectra of nitrato-complexes exhibit bands at ~ 1240, 1010, and 870 cm^{-1} which are consistent with monodentate coordination of this group and this is substantiated by the small splitting of the bands appearing at ~ 1760 – 1750 cm^{-1}. Thiocyanato-complexes show bands at ~ 2110, 815 and 485 cm^{-1} assignable to γ_{CN}, γ_{CS} and NCS bending, respectively, and are in accord with the monodentate *N*-bonded nature of this group. The infrared spectra of the complexes V, X and XV show two very weak bands in the 2340 and 2385 cm^{-1} region due to $C \equiv N$ stretching vibrations of the axial acetonitrile ligands.

The IR spectra in the region 650 – 200 cm^{-1} show various bands characteristic of metal-ligand vibrations. The halogeno-complexes show bands at ~ 300, 280, 275 cm^{-1} due to γ_{Co-Cl}, γ_{Ni-Cl}, and γ_{Cu-Cl} stretches respectively, and at ~ 220 and 216 cm^{-1} assignable to γ_{Co-Br} and γ_{Ni-Br} vibrations, respectively. The appearance of single bands in this region is in accord with the distorted octahedral nature of these complexes.[11] The bands appearing at ~ 430 – 490 cm^{-1} in all the complexes indicate the γ_{M-N} (azomethine) vibration and confirms the coordination of these groups with the metal ion. The

TABLE II
Infrared spectral data for the macrocyclic complexes

	Complex formulae	C = N	Phenyl	CH_2	C ≡ N	Anions
I	$[Cu(C_{42}H_{32}N_4)Cl_2]$	1645	1600, 1585	805, 780		280
II	$[Cu(C_{42}H_{32}N_4)Br_2]$	1650	1610, 1580	800, 790		225
III	$[Cu(C_{42}H_{32}N_4)(NO_3)_2]$	1660	1630, 1590	810, 800		1250, 860 1020, 240
IV	$[Cu(C_{42}H_{32}N_4)(NCS)_2]$	1650	1620, 1575	800, 785		2120, 810 490, 285
V	$[Cu(C_{42}H_{32}N_4)(CH_3CN)_2](Cl)_2$	1680	1600, 1580	810, 790	2250	
VI	$[Co(C_{42}H_{32}N_4)Cl_2]$	1650	1600, 1570	805, 780		310
VII	$[Co(C_{42}H_{32}N_4)Br_2]$	1670	1610, 1590	805, 800		210
VIII	$[Co(C_{42}H_{32}N_4)(NO_3)_2]$	1640	1630, 1585	800, 785		1240, 1015 880, 220
IX	$[Co(C_{42}H_{32}N_4)(NCS)_2]$	1645	1605, 1590	810, 780		780
X	$[Co(C_{42}H_{32}N_4)(CH_3CN)_2](Cl)_2$	1670	1610, 1570	800, 790		
XI	$[Ni(C_{42}H_{32}N_4)Cl_2]$	1650	1630, 1580	810, 780		275 2260
XII	$[Ni(C_{42}H_{32}N_4)Br_2]$	1680	1610, 1590	805, 780		225
XIII	$[Ni(C_{42}H_{32}N_4)(NO_3)_2]$	1640	1620, 1575	800, 790		1250, 1010 870, 240
XIV	$[Ni(C_{42}H_{32}N_4)(NCS)_2]$	1660	1630, 1590	800, 785		2110, 820 490, 260
XV	$[Ni(C_{42}H_{32}N_4)(CH_3CN)_2](Cl)_2$	1670	1610, 1570	810, 790	2255	

coordination of nitrate and thiocyanate is supported by the bands appearing in the region at ~ 225 – 245 cm^{-1} assignable to γ_{M-O} of the ONO_2 group and at ~ 260 – 280 cm^{-1} to γ_{M-NCS} of the NCS group, respectively.

Magnetic and Electronic Spectral Studies

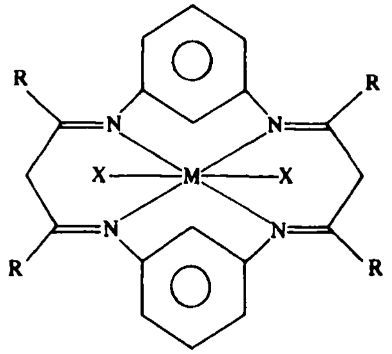
The magnetic moments of the macrocyclic complexes are given in Table III. The values are in accord with a high spin configuration (except for the CH_3CN complexes) and show the presence of a distorted octahedral environment about the metal ions.[13]

The observed absorption bands in the visible and ultra-violet region are listed in Table III. An examination of the electronic spectral data indicates that these macrocyclic complexes have distorted octahedral geometries and might possess D_{4h} symmetry.[12-14] The spectra do not show any regular pattern or splitting of the first band which is probably due to there being little difference between the ligand field strengths of the nitrogen atoms of azomethine, secondary amine and thiocyanate groups. The assignments for charge transfers may be given as follows.

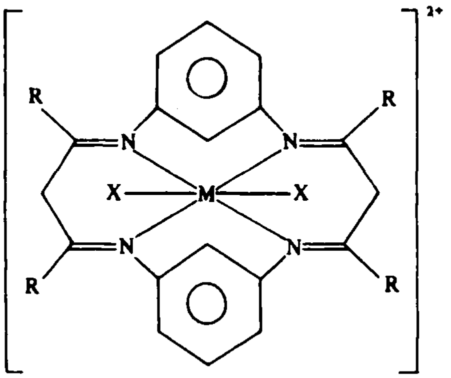
Nickel(II): $^3B_{1g} \rightarrow {}^3E_g$, $^3B_{1g} \rightarrow {}^3B_{2g}$, $^3B_{1g} \rightarrow {}^3A_{2g(F)}$, $^3B_{1g} \rightarrow {}^3A_{2g(P)}$; Cobalt(II): $^4T_{1g} \rightarrow {}^4T_{2g}$, $^4T_{1g} \rightarrow {}^4A_{2g}$, $^4T_{1g} \rightarrow {}^4T_{1g(P)}$; Copper(II): $^2B_{2g}$, $^2B_{1g} \rightarrow {}^2E_g$ or $^2A_{2g}$.

The band separations of about 15285 – 16230 cm^{-1} *is consistent with the proposed geo*metry of these macrocyclic complexes. All the macrocyclic complexes show strong absorption at ~ 30710 cm^{-1} which may be associated with intra-ligand charge transfer involving imine functions.

Thus, based on the results of chemical analysis, conductance measurements, molecular weights, electronic and IR spectra structures (I) and (II) are suggested for the complexes.



(I)



(II)

M = Cu(II), Co(II), Ni(II)
X = Cl, Br, NO_3, NCS, and CH_3CN
R = C_6H_5

X = CH_3CN

TABLE III

Magnetic and electronic spectral data for the macrocyclic complexes

	Complex formulae	Spectral data cm^{-1}	μ_{eff}(B.M.)
I	$[Cu(C_{42}H_{32}N_4)Cl_2]$	15325, 18290, 30650	1.81
II	$[Cu(C_{42}H_{32}N_4)Br_2]$	16210, 19000, 30620	1.70
III	$[Cu(C_{42}H_{32}N_4)(NO_3)_2]$	15560, 18620, 30610	1.75
IV	$[Cu(C_{42}H_{32}N_4)(NCS)_2]$	16010, 18720, 30750	1.85
V	$[Cu(C_{42}H_{32}N_4)(CH_3CN)_2](Cl)_2$	16000, 18730, 30760	
VI	$[Co(C_{42}H_{32}N_4)Cl_2]$	7950, 15660, 18550, 19320, 30650	4.90
VII	$[Co(C_{42}H_{32}N_4)Br_2]$	7940, 16380, 18010, 18860, 30740	5.10
VIII	$[Co(C_{42}H_{32}N_4)(NO_3)_2]$	8940, 17530, 16260, 19015, 30710	4.85
IX	$[Co(C_{42}H_{32}N_4)(NCS)_2]$	8210, 16060, 18330, 19200, 30600	4.80
X	$[Co(C_{42}H_{32}N_4)(CH_3CN)_2](Cl)_2$	8215, 16040, 18200, 19000, 30590	
XI	$[Ni(C_{42}H_{32}N_4)Cl_2]$	8120, 11000, 15390, 26320, 30710	3.20
XII	$[Ni(C_{42}H_{32}N_4)Br_2]$	8520, 10590, 16670, 26640, 30750	3.00
XIII	$[Ni(C_{42}H_{32}N_4)(NO_3)_2$	8210, 10290, 15870, 26300, 30710	3.70
XIV	$[Ni(C_{42}H_{32}N_4)(NCS)_2]$	8230, 10600, 16540, 26720, 30700	3.10
XV	$[Ni(C_{42}H_{32}N_4)(CH_3CN)_2](Cl)_2$	8215, 16030, 18210, 19000, 30600	

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