

Cr(III), Fe(III), and Co(II) Complexes of Tetraazamacrocycles Derived from 2,3-Butanedione or Benzil and 1,8-Diamino-3,6-diazaoctane

P. K. Rai* and R. N. Prasad

Department of Chemistry, University of Rajasthan, Jaipur 302004, India

Summary. Template condensation of α -diketones such as 2,3-butanedione or benzil with 1,8-diamino-3,6-diazaoctane in the presence of Cr(III), Fe(III) and Co(II) results in the formation of macrocyclic complexes of the type $[\text{MLX}_2]\text{X}$ and $[\text{CoLX}]\text{X}$ (where $\text{M} = \text{Cr(III)}$, Fe(III) , $\text{L} = \text{N}_4$ macrocycle and $\text{X} = \text{NO}_3^-$ or Cl^-). The complexes have been characterized by elemental analyses, conductance and magnetic measurements, molecular weight determinations, infrared and diffuse reflectance spectral studies.

Keywords. Tetraazamacrocycles; Cr(III), Fe(III) and Co(II) Complexes; Magnetic measurements; Diffuse reflectance spectra.

Cr(III)-, Fe(III)- und Co(II)-Komplexe mit Tetraazamacrocyclen aus 2,3-Butandion oder Benzil und 1,8-Diamino-3,6-diazaoctan

Zusammenfassung. Kondensation von α -Diketonen wie 2,3-Butandion oder Benzil mit 1,8-Diamino-3,6-diazaoctan in Gegenwart von Cr(III), Fe(III) und Co(II) resultiert in der Bildung von macrocyclischen Komplexen vom Typ $[\text{MLX}_2]\text{X}$ und $[\text{CoLX}]\text{X}$ mit $\text{M} = \text{Cr(III)}$, Fe(III) , $\text{L} = \text{N}_4$ -Macrocyclus und $\text{X} = \text{NO}_3^-$ oder Cl^- . Die Komplexe wurden mittels Elementaranalyse, Leitfähigkeits- und magnetischen Messungen, Molekulargewichtsbestimmung und Infrarot- bzw. diffuser Reflexions-Spektren charakterisiert.

Introduction

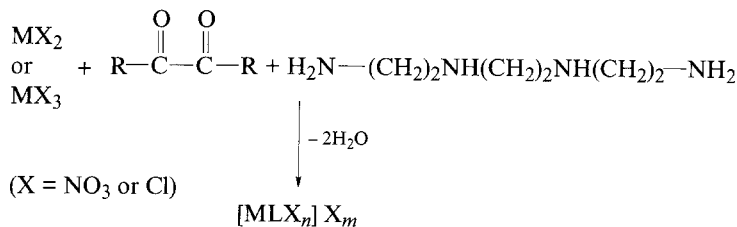
Interest in the complexes of macrocycles developed rapidly due to their biological relevance. Fe^{II} and Co^{III} complexes of the macrocycle derived from 2,6-diacetylpyridine and 3,3'-diaminodipropylamine have been used as models for biomolecules [1, 2]. Busch and coworkers [3, 4] have studied the redox properties of a number of macrocyclic complexes of transition elements with a view to understand the catalytic role of heme protein in various reactions. The decomposition of hydrogen peroxide to water and oxygen by catalase has attracted considerable attention and a Fe^{III} complex of the macrocycle 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene has been reported as a model for catalase [5]. Recently there has been a great deal of activity in the field of macrocyclic chemistry, which is due to the recognition of commercial values of macrocycles and their complexes. Reichgott and Rose [6] have reported the role of $\text{Fe}^{\text{II}}\text{TIM}$ complexes ($\text{TIM} = 2,3,7,10$ -tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) as catalyst in the oxidation of methanol. The electro-chemical and

spectrophotometric studies of Fe^{III} complexes of the macrocycles derived from 2,6-diacetylpyridine and 1,8-diamino-3,6-diazaoctane with their possible use in electrochemical devices have been reported [7].

Ideal ring sizes of tetraazamacrocycles for metal ions have been investigated and it has been observed that many macrocycles of varying ring sizes coordinate readily to transition metal ions to give stable complexes [8–11]. The effect of the chelate ring size in controlling metal ion size-based selectivity has been studied by a comparison of formation constants [12–14]. Busch and coworkers [15, 16] have reported the synthesis and characterization of Fe^{III} and Co^{II} complexes of the macrocycle 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18)-2,12,14,16-pentaene. Ni^{II} and Cu^{II} complexes of the macrocycle derived from 2,4-pentanedione and 1,8-diamino-3,6-diazaoctane have also been synthesized [17–18]. However, the macrocyclic complexes derived from more rigid molecules such as α -diketones and tetraamines such as 1,8-diamino-3,6-diazaoctane have not been reported so far. Several tetraazamacrocyclic complexes have been synthesized in our laboratory [19–21] and in this paper the synthesis and characterization of Cr^{III}, Fe^{III} and Co^{II} complexes of the macrocycles 2,3-dimethyl-1,4,7,10-tetraazacyclododeca-1,3-diene and 2,3-diphenyl-1,4,7,10-tetraazacyclododeca-1,3-diene are reported with a view that these may have some possible use in electrochemical devices and as biologically active compounds.

Results and Discussion

The reactions of metal nitrate or chloride with 2,3-butanedione or benzil and 1,8-diamino-3,6-diazaoctane in 1:1:1 molar ratios and in butanolic solution result in the formation of complexes with 12-membered tetraazamacrocycle(L) as ligand.

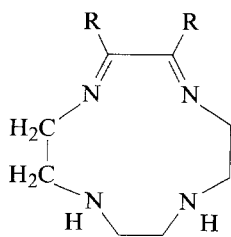


M = Cr^{III}, $n = 2$, $m = 1$; X = NO₃, Cl

M = Fe^{III}, $n = 2$, $m = 1$; X = NO₃

M = Co^{II}, $n = 1$, $m = 1$; X = NO₃, Cl

L = 12 membered tetraazamacrocycle



(L)

R = CH₃, C₆H₅

Table 1. Physical characteristics and analysis of tetraazamacrocyclic complexes

S.No.	Complex	Colour and decomposition temp. (°c)	Yield (%)	Analysis (%)		N found (calcd.)	Metal found (calcd.)	Cl found (calcd.)	Mol.Wt. found (calcd.)
				C found (calcd.)	H found (calcd.)				
1.	[Cr(Me ₂ [12]diene N ₄)(NO ₃) ₂][NO ₃	brown 125	67	27.74 (27.65)	4.51 (4.64)	12.91 (12.90)	12.11 (11.97)	—	415 (434)
2.	[Cr(Me ₂ [12]diene N ₄)Cl ₂][Cl	brown 115	65	33.93 (33.86)	5.57 (5.68)	15.63 (15.79)	14.76 (14.66)	30.07 (29.98)	370 (354)
3.	[Cr(Ph ₂ [12]diene N ₄)(NO ₃) ₂][NO ₃	brown 128	43	43.17 (43.01)	4.26 (4.33)	10.11 (10.03)	9.41 (9.31)	—	527 (558)
4.	[Cr(Ph ₂ [12]diene N ₄)Cl ₂][Cl	brown 138	38	50.06 (50.17)	5.13 (5.05)	11.89 (11.70)	10.98 (10.85)	22.12 (22.21)	454 (478)
5.	[Fe(Me ₂ [12]diene N ₄)(NO ₃) ₂][NO ₃	brown 105	68	27.37 (27.41)	4.52 (4.60)	12.71 (12.78)	12.87 (12.74)	—	450 (438)
6.	[Fe(Ph ₂ [12]diene N ₄)(NO ₃) ₂][NO ₃	brown 115	28	42.76 (42.72)	4.22 (4.30)	9.81 (9.96)	10.05 (9.93)	—	575 (562)
7.	[Co(Me ₂ [12]diene N ₄)NO ₃][NO ₃	brown 146	74	31.81 (31.67)	5.25 (5.31)	14.68 (14.77)	15.51 (15.53)	—	358 (379)
8.	[Co(Me ₂ [12]diene N ₄)Cl][Cl	brown 126	48	36.97 (36.82)	6.27 (6.18)	17.24 (17.17)	18.16 (18.07)	21.68 (21.74)	340 (326)
9.	[Co(Ph ₂ [12]diene N ₄)NO ₃][NO ₃	brown 130	38	47.83 (47.72)	4.71 (4.80)	11.14 (11.13)	11.86 (11.70)	—	524 (503)
10.	[Co(Ph ₂ [12]diene N ₄)Cl][Cl	brown 125	42	53.27 (53.34)	4.51 (4.37)	12.34 (12.44)	13.16 (13.08)	15.83 (15.74)	435 (450)

Table 2. Characteristic IR bands and magnetic moments of tetraazamacrocyclic complexes

S.No.	Complex	IR bands (cm^{-1})							μ_{eff} (B.M.)
		$\nu\text{-NH}$	$\nu\text{C=N}$	NO_3 unidentate	NO_3 ionic	$\nu\text{M-Cl}$	$\nu\text{C=C}$		
1.	$[\text{Cr}(\text{Me}_2[12]\text{diene } \text{N}_4)(\text{NO}_3)_2]\text{NO}_3$	3360	1580	1510, 1270, 1020	1380, 820, 730	—	—	3.85	
2.	$[\text{Cr}(\text{Me}_2[12]\text{diene } \text{N}_4)\text{Cl}_2]\text{Cl}$	3240	1600	—	—	380	—	3.94	
3.	$[\text{Cr}(\text{Ph}_2[12]\text{diene } \text{N}_4)(\text{NO}_3)_2]\text{NO}_3$	3340	1580	1520, 1270, 1020	1400, 730	—	1560	3.92	
4.	$[\text{Cr}(\text{Ph}_2[12]\text{diene } \text{N}_4)\text{Cl}_2]\text{Cl}$	3180	1610	—	—	410	1560	3.91	
5.	$[\text{Fe}(\text{Me}_2[12]\text{diene } \text{N}_4)(\text{NO}_3)_2]\text{NO}_3$	3180	1580	1510, 1270, 1020	1380, 810, 720	—	—	5.95	
6.	$[\text{Fe}(\text{Ph}_2[12]\text{diene } \text{N}_4)(\text{NO}_3)_2]\text{NO}_3$	3200	1600	1510, 1270, 1020	1380, 820, 730	—	1560	5.76	
7.	$[\text{Co}(\text{Me}_2[12]\text{diene } \text{N}_4)\text{NO}_3]\text{NO}_3$	3260	1580	1510, 1260, 1020	1380, 810, 730	—	—	4.95	
8.	$[\text{Co}(\text{Me}_2[12]\text{diene } \text{N}_4)\text{Cl}]\text{Cl}$	3300	1600	—	—	400	—	5.08	
9.	$[\text{Co}(\text{Ph}_2[12]\text{diene } \text{N}_4)\text{NO}_3]\text{NO}_3$	3280	1580	1520, 1270, 1000	1380, 810, 720	—	1560	5.09	
10.	$[\text{Co}(\text{Ph}_2[12]\text{diene } \text{N}_4)\text{Cl}]\text{Cl}$	3340	1600	—	—	410	1560	6.23 (ferro-magnetic)	

The resulting macrocyclic complexes are brown solids and decompose on heating to 120–150 °C. Their characteristics and analyses are given in Table 1.

Infrared Spectra

Significant IR bands of the macrocyclic complexes are given in Table 2. No absorption band was observed at 1700 cm^{-1} indicating the absence of residual $>\text{C}=\text{O}$ group. Instead strong absorption bands are observed in region $3180\text{--}3360\text{ cm}^{-1}$ which can be assigned to coordinated $\nu\text{N-H}$. In Fe^{III} complexes of N_5 -macrocycles derived from 2,6-diacetyl pyridine and 1,9-diamino-3,7-diazanonane, Nelson and co-worker [22] have reported the band at 3240 cm^{-1} due to $\nu\text{N-H}$. For Pb^{II} complexes of macrocycles derived from 2,6-diacetyl-pyridine and 3,6-diazaoctane-1,8-diamine and 4,7-diazadecane-1,10-diamine two $\nu\text{N-H}$ bands have been reported in the region $3200\text{--}3400\text{ cm}^{-1}$ [23]. Fenton and coworkers [24] have reported $\nu\text{N-H}$ vibrations in the region $3100\text{--}3300\text{ cm}^{-1}$ for Co^{II} , Ni^{II} and Cu^{II} complexes of 15- to 19-membered oxygen-nitrogen donor macrocycles.

All the macrocyclic complexes show a strong absorption band in the region $1580\text{--}1610\text{ cm}^{-1}$ attributable to the coordinated $\text{C}=\text{N}$ group and indicating the condensation of carbonyl and amino groups. For Cu^{II} complexes of *TIM*, Maroney and Rose [25] have reported the $\nu\text{C}=\text{N}$ absorptions at $1600\text{--}1620\text{ cm}^{-1}$. In Co^{III} complexes of *TIM*, Busch et al. [26] have assigned a sharp band in the region $1550\text{--}1600\text{ cm}^{-1}$ to $\nu\text{C}=\text{N}(\text{sym})$ and a weak band at 1640 cm^{-1} to $\nu\text{C}=\text{N}(\text{asym})$.

Nitrate complexes exhibit intense absorption bands at $1510\text{--}1520$, $1260\text{--}1270$ and $1000\text{--}1020\text{ cm}^{-1}$ assigned to unidentate coordinated nitrate while free nitrate absorptions appear at $1380\text{--}1400$, $810\text{--}820$ $720\text{--}730\text{ cm}^{-1}$ [27]. In the chloro complexes a band at $\sim 400\text{ cm}^{-1}$ is observed which may be assigned to a coordinated chloro group [28]. Macrocyclic complexes derived from benzil show medium intensity bands at 1560 cm^{-1} due to $\nu\text{C}=\text{C}$ of the phenyl groups. Coltrain and Jackels [29] have assigned the bands at $1569\text{--}1590\text{ cm}^{-1}$ to $\nu\text{C}=\text{C}$ in Cu^{II} complexes of *MePhTIM*. The complexes exhibit absorptions at $740\text{--}770\text{ cm}^{-1}$ assignable to C-H out of plane bending of phenyl groups. All tetraazamacrocyclic complexes show an absorption band in the region $1200\text{--}1220\text{ cm}^{-1}$. This band is characteristic of the α -diimine moiety of macrocyclic complexes. It has been observed in several α -diimine containing tetraazamacrocyclic complexes regardless of the nature of metal ion present [25, 26, 29].

Conductances

Molar conductances of 10^{-3} M solutions of complexes in *DMSO* and water are given in Table 3. Molar conductances of Cr^{III} and Fe^{III} complexes are observed in the range $115\text{--}134\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ in *DMSO* and in the range $365\text{--}445\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ in water indicating their 3:1 electrolytic behaviour. The conductance data indicate that coordinated anions are rapidly displaced by solvent molecules. In *DMSO* $[\text{Co}(\text{Me}_2[12]\text{diene N}_4)\text{Cl}]\text{Cl}$ and $[\text{Co}(\text{Ph}_2[12]\text{diene N}_4)\text{Cl}]\text{Cl}$ are 1:1 electrolytes ($\Lambda_M = 39\text{--}42\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$) confirming the pentacoordination of Co^{II} . $[\text{Co}(\text{Me}_2[12]\text{diene N}_4)(\text{NO}_3)]\text{NO}_3$ and $[\text{Co}(\text{Ph}_2[12]\text{diene N}_4)\text{NO}_3]\text{NO}_3$ behave as 2:1 electrolytes in *DMSO* (Λ_M being $70\text{--}85\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$) indicating

Table 3. Molar conductances of tetraazamacrocyclic complexes (ca. $10^{-3} M$ solutions)

S.No.	Complex	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)	
		DMSO	H ₂ O
1.	[Cr(Me ₂ [12]diene N ₄)(NO ₃) ₂]NO ₃	130	395
2.	[Cr(Me ₂ [12]diene N ₄)Cl ₂]Cl	134	400
3.	[Cr(Ph ₂ [12]diene N ₄)(NO ₃) ₂]NO ₃	127	370
4.	[Cr(Ph ₂ [12]diene N ₄)Cl ₂]Cl	126	365
5.	[Fe(Me ₂ [12]diene N ₄)(NO ₃) ₂]NO ₃	120	445
6.	[Fe(Ph ₂ [12]diene N ₄)(NO ₃) ₂]NO ₃	115	420
7.	[Co(Me ₂ [12]diene N ₄)NO ₃]NO ₃	70	260
8.	[Co(Me ₂ [12]diene N ₄)Cl]Cl	42	270
9.	[Co(Ph ₂ [12]diene N ₄)NO ₃]NO ₃	85	250
10.	[Co(Ph ₂ [12]diene N ₄)Cl]Cl	39	240

that the coordinated nitrate is replaced by the solvent molecules but the coordinated chloro group is not replaced. Conductances in *DMSO* in the range 20–42 ohm⁻¹ cm² mol⁻¹ for 1:1 electrolytes and in the range 50–80 ohm⁻¹ cm² mol⁻¹ for 2:1 electrolytes have been reported [30, 31]. However, in aqueous solution both chloro and nitrate complexes behave as 2:1 electrolytes ($\Lambda_M = 240\text{--}270$ ohm⁻¹ cm² mol⁻¹) indicating that the coordinated chloro and nitrate groups are readily replaced by the solvent water molecules. A similar behaviour has been reported for Co(*CR*)(NO₃)₃·*n*H₂O [32]. (*CR* = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11,3,1]-heptadeca-1[17],2,11,13,15-pentaene).

Magnetic Moments

The μ_{eff} values for macrocyclic complexes are recorded in Table 2. The observed magnetic moments of Cr^{III} complexes (3.85–3.94 B.M.) are in accord with the spin only value for three unpaired electrons and are characteristic of high spin octahedral chromium(III) complexes [33]. The μ_{eff} values of Fe^{III} macrocyclic complexes range from 5.76 to 5.95 B.M. indicating high spin state of d⁵ Fe^{III} [22]. For d⁷, Co^{II} the magnetic moment should be somewhere between 3.88 and 5.20 B.M. as given by $\sqrt{[4S(S+1)]}$ and $\sqrt{[4S(S+1) + L(L+1)]}$ respectively (where *S* is the total spin angular momentum of $(3/2)h/2\pi$ and *L* is the total orbital angular momentum of $h/2\pi$). The ground term is ⁴F which splits into two orbital triplet sets and a singlet one. One of the triplets predominantly lies at the lowest ($d\varepsilon^5 dy^2$). If fields of less than cubic symmetry are present the orbital angular momentum of the ion, this results from orbital degeneracy or near degeneracy within this triplet. The actual value depends upon the amount of *L* remaining associated with the ground state orbital triplet. The magnetic moments of Co^{II} complexes are in the range from 4.95 to 5.09 B.M. except for the complex [Co(Ph₂[12]diene N₄)Cl]Cl which has the magnetic moment 6.23 B.M. indicating a little ferromagnetic behaviour. Thus it is

obvious that there is a large orbital contribution towards the magnetic moment for Co^{II} complexes [34].

It is interesting to note that these macrocyclic complexes are high spin in the presence of strong coordinating azomethine groups. This is probably due to the saddle shape of the macrocycles and the sitting atop of the metal ion with respect to the N_4 macrocyclic plane. The saddle shape arises from steric strain and the strain is relieved as a result of distortion of the N_4 planar ring through the twisting of the torsional angles about the C–N bonds on the N_4 ring which is most readily deformable site. In the saddle shape the nitrogen lone pairs are directed out of the N_4 plane as the metal sits atop and not inside the N_4 cavity. Macrocycles are folded in the complexes and metal ions are lying above the N_4 plane on the opposite side of the fold [35].

Electronic Spectra

Reflectance spectra of macrocyclic complexes have been recorded and the transition energies of the spectral bands are given in Table 4. The spectra of Cr^{III} complexes show three bands at 16393–17699, 20202–22727 and 24691–27777 cm^{-1} which may be assigned to ${}^4\text{B}_{1g} \rightarrow {}^4\text{E}_g(\nu_1)$, ${}^4\text{B}_{1g} \rightarrow {}^4\text{B}_{2g}(\nu_2)$ and ${}^4\text{B}_{1g} \rightarrow {}^4\text{A}_{2g}(\nu_3)$, respectively. The ν_1 and ν_2 bands are slightly broader and indicate some sort of splitting. This suggests distortion in the octahedral structure [33]. The splitting of the ${}^4\text{T}_{2g}$ band in *trans*-disubstituted Cr^{III} complexes due to the value of Dt (ligand field parameter) being larger than that for the corresponding monosubstituted derivatives, has been described. The splitting of second band (ν_2) has also been observed in many complexes having D_{4h} symmetry [36]. The wave lengths of the electronic transitions and the number of bands are reliable indicators for distinguishing *cis*- and *trans*-isomers of Cr^{III} complexes. In case of *cis*-complexes two bands have been reported while *trans*-complexes give three bands [37]. Thus the Cr^{III} macrocyclic complexes synthesized during the present investigations possess *trans*-octahedral structures.

Table 4. Electronic spectral data of tetraazamacrocyclic complexes

S.No.	Complex	Observed transition energies (cm^{-1})			
1.	$[\text{Cr}(\text{Me}_2[12]\text{diene N}_4)(\text{NO}_3)_2]\text{NO}_3$	16393	20202	24691	
2.	$[\text{Cr}(\text{Me}_2[12]\text{diene N}_4)\text{Cl}_2]\text{Cl}$	17391	21978	27397	
3.	$[\text{Cr}(\text{Ph}_2[12]\text{diene N}_4)(\text{NO}_3)_2]\text{NO}_3$	17094	22471	27777	
4.	$[\text{Cr}(\text{Ph}_2[12]\text{diene N}_4)\text{Cl}_2]\text{Cl}$	17699	22727	27397	
5.	$[\text{Fe}(\text{Me}_2[12]\text{diene N}_4)(\text{NO}_3)_2]\text{NO}_3$	10526	20000	26666	
6.	$[\text{Fe}(\text{Ph}_2[12]\text{diene N}_4)(\text{NO}_3)_2]\text{NO}_3$	10526	19801	25641	
7.	$[\text{Co}(\text{Me}_2[12]\text{diene N}_4)(\text{NO}_3)]\text{NO}_3$	9433	17241	21276	27777
			(i6000sh)		
8.	$[\text{Co}(\text{Me}_2[12]\text{diene N}_4)\text{Cl}]\text{Cl}$	9216	17857	20408	26666
9.	$[\text{Co}(\text{Ph}_2[12]\text{diene N}_4)(\text{NO}_3)]\text{NO}_3$	9132	17391	21739	27027
			(16000sh)		
10.	$[\text{Co}(\text{Ph}_2[12]\text{diene N}_4)\text{Cl}]\text{Cl}$	9302	17241	21739	27397
			(16000sh)		

The high spin octahedral Fe^{III} complexes are generally characterized by the presence of a broad band in the near infrared region which may be the combination of several transitions from ${}^6\text{A}_{1\text{g}}$ to ${}^4\text{T}_{1\text{g}}(\text{G})$, ${}^4\text{T}_{2\text{g}}(\text{G})$, and ${}^4\text{A}_{1\text{g}}$ and ${}^4\text{E}_{\text{g}}(\text{G})$ states. The spectra of Fe^{III} macrocyclic complexes exhibit strong charge-transfer bands in the wavelength region below 500 nm which obscure the observation of spin forbidden d-d transitions of very low intensity expected for the sextet state of Fe^{III} . However, a broad band at 10526 cm^{-1} is observed which may be due to the spin-forbidden transition and is assigned to ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{1\text{g}}(\text{G})$ [38].

The spectra of Co^{II} macrocyclic complexes exhibit three bands corresponding to d-d transitions and one charge-transfer band. Co^{II} in the complexes is pentacoordinated as evidenced by IR and conductance studies but the spectra are quite similar to those of octahedral complexes. Therefore, it might be possible that anions are coordinated to some extent giving distorted octahedral geometry. A similar behaviour has been reported in case of planar Co^{II} complexes [39]. Electronic spectra of Co^{II} macrocyclic complexes can be interpreted in terms of $\text{D}_{4\text{h}}$ symmetry and the bands at $9132\text{--}9433$, $17241\text{--}17857$ and $20408\text{--}21739\text{ cm}^{-1}$ can be assigned to ${}^4\text{T}_{1\text{g}} \rightarrow {}^4\text{T}_{2\text{g}}$, ${}^4\text{T}_{1\text{g}} \rightarrow {}^4\text{A}_{2\text{g}}$ and ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{1\text{g}}(\text{P})$ transitions, respectively. The band at $26666\text{--}27777\text{ cm}^{-1}$ is due to a charge-transfer transition [38]. The first two bands are broad, however, the second splits in two bands in most of the cases.

Experimental Part

$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fluka), $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (Fluka), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fluka), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fluka) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Fluka) were of G.R. grade. 2,3-Butanedione and 1,8-diamino-3,6-diazaoctane were obtained from Fluka and purified by distillation before use. Benzil was recrystallized from *n*-butanol.

Synthesis of Tetraazamacrocyclic Complexes Derived from 2,3-Butanedione

Metal salt (3.0 mmol) was dissolved in $\sim 30\text{ ml}$ *n*-butanol and 2,3-butanedione (3.0 mmol in $\sim 20\text{ ml}$ *n*-butanol) was added. To this, a solution of the diamine (3.0 mmol in $\sim 20\text{ ml}$ *n*-butanol) was added dropwise with constant stirring. A solid appeared during the addition and stirring was continued for 3–4 h. The precipitate was filtered, washed with *n*-butanol and dried in vacuo.

Synthesis of Tetraazamacrocyclic Complexes Derived from Benzil

Benzil (3.0 mmol) dissolved in $\sim 25\text{ ml}$ hot *n*-butanol was added to the metal salt solution (3.0 mmol in $\sim 35\text{ ml}$ hot *n*-butanol). To this, a solution of diamine (3.0 mmol in $\sim 20\text{ ml}$ hot *n*-butanol) was added dropwise with constant stirring. A solid appeared during the addition and the stirring was continued for 3–4 h maintaining the temperature at $60\text{--}70^\circ\text{C}$. The contents were then refluxed gently for 3–4 h. The precipitate was filtered while hot, washed with hot *n*-butanol and dried in vacuo.

Analytical Methods and Physical Measurements

Carbon and hydrogen were determined on a Coleman C,H-Analyser-33. Ring-Nitrogen was determined by Kjeldahl's method and Chlorine gravimetrically as AgCl . Chromium and iron contents were determined volumetrically using potassium dichromate while cobalt was determined using *EDTA*. Molar conductances of 10^{-3} M solutions of the complexes in different solvents were determined using a Systronics Direct Reading Conductivity Meter-304. Molecular weight determinations of the complexes which are sufficiently soluble in methanol were carried out by the cryoscopic method. I.R. spectra were recorded as KBr pellets in the region $4000\text{--}200\text{ cm}^{-1}$ on a Perkin Elmer 577 Grating

Infrared Spectrophotometer. Magnetic measurements were carried out on a Guoy balance using $\text{HgCo}(\text{SCN})_4$ as a calibrant and reflectance spectra of solid compounds suitably diluted with MgO were recorded on a Beckman-DU spectrophotometer with standard Beckman reflectance attachment at S. P. University, Vallabh Vidyanagar, Gujrat.

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References

- [1] Riley D. P., Merell P. H., Stone J. A., Busch D. H. (1975) *Inorg. Chem.* **14**: 490
- [2] Ochiai E., Long K. M., Sperati C. R., Busch D. H. (1969) *J. Am. Chem. Soc.* **91**: 3201
- [3] Busch D. H., Pillsbury D. G., Lovecchio F. V., Tait A. M., Hung Y., Jackels S., Rakowski M. C., Schamel W. P., Martin Y. L. (1977) In: *Electrochemical Studies of Biological Systems*, Vol. 38. American Chemical Society, Washington D.C.
- [4] Pillsbury D. G., Busch D. H. (1976) *J. Am. Chem. Soc.* **98**: 7836
- [5] Melnyk A. C., Kildahl N. K., Rendina A. R., Busch D. H. (1979) *J. Am. Chem. Soc.* **101**: 3232
- [6] Reichgott D. W., Rose N. J. (1977) *J. Am. Chem. Soc.* **99**: 1813
- [7] Chen Y. W. D., Bard A. J. (1984) *Inorg. Chem.* **23**: 2175
- [8] Collman J. P., Schneider P. W. (1966) *Inorg. Chem.* **5**: 1380
- [9] Geodken V. L., Molin-Case J., Cristoph G. G. (1974) *Inorg. Chem.* **12**: 2894
- [10] Hoard J. L., Hamor M. J., Hamor T. A., Gaughey W. S. (1965) *J. Am. Chem. Soc.* **87**: 2312
- [11] Martin L. Y., Dehayes L. J., Zompa L. J., Busch D. H. (1974) *J. Am. Chem. Soc.* **96**: 4046
- [12] Hancock R. D., Ngwenya M. P., Evers A., Wade P. W., Boeyens J. C. A., Dobson S. M. (1990) *Inorg. Chem.* **29**: 264
- [13] Thom V. J., Hancock R. D. (1985) *J. Chem. Soc. Dalton Trans.*: 1877
- [14] Hancock R. D., Ngwenya M. P. (1987) *J. Chem. Soc. Dalton Trans.*: 2911
- [15] Curry J. D., Busch D. H. (1964) *J. Am. Chem. Soc.* **86**: 592
- [16] Nelson S. M., Busch D. H. (1969) *Inorg. Chem.* **8**: 1859
- [17] Martin J. G., Wei R. M. C., Cummings S. C. (1972) *Inorg. Chem.* **11**: 475
- [18] Cummings S. C., Sievers R. E. (1970) *J. Am. Chem. Soc.* **92**: 215
- [19] Prasad R. N., Gupta A. K., Rai P. K. (1991) *J. Prakt. Chem.* **333**: 145
- [20] Prasad R. N., Gupta A. K., Rai P. K. (1991) *Ann. Chim. (Rome)* **81**: 85
- [21] Rai P. K., Gupta A. K., Prasad R. N. (1992) *Z. Naturforsch.* **47B**: 1701
- [22] Drew M. G. B., bin Othman A. H., McIlroy P. D. A., Nelson S. M. (1975) *J. Chem. Soc. Dalton Trans.*: 2507
- [23] Cook D. H., Fenton D. E., Drew M. G. B., Rodgers A., McCann M., Nelson S. M. (1979) *J. Chem. Soc. Dalton Trans.*: 414
- [24] Fenton D. E., Murphy B. P., Leong A. J., Lindoy L. F., Bashall A., Mcpartlin M. (1987) *J. Chem. Soc. Dalton Trans.*: 2583
- [25] Maroney M. J., Rose N. J. (1984) *Inorg. Chem.* **23**: 2252
- [26] Jackels S. C., Farmery K., Barefield E. K., Rose N. J., Busch D. H. (1972) *Inorg. Chem.* **11**: 2893
- [27] Alcock N. W., Curson E. H., Herron N., Moore P. (1979) *J. Chem. Soc. Dalton Trans.*: 1987
- [28] Nakamoto K. (1970) *Infrared Spectra of Inorganic and Coordination Compounds*. Wiley-Interscience, New York
- [29] Coltrain B. K., Jackels S. C. (1981) *Inorg. Chem.* **20**: 2032

- [30] Geary W. J. (1971) *Coord. Chem. Rev.* **7**: 81
- [31] Lewis J., O'Donoghue T. D. (1980) *J. Chem. Soc. Dalton Trans.*: 736
- [32] Long K. M., Busch D. H. (1974) *J. Coord. Chem.* **4**: 113
- [33] Swisher R. G., Brown G. A., Smierciak R. C., Blinn E. L. (1981) *Inorg. Chem.* **20**: 3947
- [34] Malik W. U., Bembi R., Singh R. (1983) *Polyhedron* **2**: 369
- [35] Weiss M. C., Goedken V. L. (1976) *J. Chem. Soc. Chem. Commun.*: 531
- [36] Perumareddi J. R. (1969) *Coord. Chem. Rev.* **4**: 73
- [37] House D. A., Garner C. S. (1966) *J. Am. Chem. Soc.* **88**: 2156
- [38] Lever A. B. P. (1968) *Inorg. Electronic Spectroscopy*. Elsevier, Amsterdam
- [39] Cotton F. A., Wilkinson G. (1988) *Advanced Inorganic Chemistry*, 5th Ed. Wiley-Interscience, New York

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