Cr(III) Complexes of Tetraazamacrocycles Derived

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Cr(III) Complexes of Tetraazamacrocycles Derived from α-Diketones and Diaminoalkanes

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Template condensation of α-diketones such as 2,3-butanedione or benzil with diaminoalkanes such as 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane or 1,12-diaminododecane in the presence of Cr(III) results in the formation of complexes of the type $[CrLX_2]X$ (where L=tetraazamacrocycle having 12 to 32-membered ring and $X = NO_3^-$ or Cl^-). The complexes have been characterized by elemental analyses, magnetic measurements and IR and diffuse reflectance spectra.

Introduction

Fe(II), Co(III), Ni(II) and Cu(II) complexes of 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (TIM), a 14-membered N_4 macrocycle, have been synthesized by 2+2 condensation of 2,3-butanedione and 1,3-diaminopropane using metal ion templates[1-4]. Co(II) complexes of a similar macrocycle with C_6H_5 substituents was synthesized using the same procedure[5]. Cu(II) complexes of a 12-membered N_4 macrocycle derived from benzil and 1,2-diaminoethane were also prepared by template procedure[6]. Cr(III) complexes of such macrocycles have not been reported so far. However, Cr(III) complexes of saturated N_4 macrocycles have been reported[7-9]. Earlier, Zn(II) and Cd(II) complexes of tetraazamacrocycles containing two α-diimine groups were reported from our laboratores[10-12] and in the present paper Cr(III) complexes of the following tetraazamacrocycles(I) are described.

2,3,8,9-Tetramethyl-1,4,7,10-tetraazacyclododeca-1,3,7,9-tetraene (L^1); 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (L^2); 2,3,10,11-tetramethyl-1,4,9,12-tetraazacyclohexadeca-1,3,9,11-tetraene (L^3); 2,3,12,13-tetramethyl-1,4,11,14-tetraazacycloeicosa-1,3,11,13-tetraene (L^4); 2,3,14,15-tetramethyl-1,4,13,16-tetraazacyclotetracosa-1,3,13,15-tetraene (L^5) and 2,3,18,19-tetramethyl-1,4,17,20-tetraazacyclodotriaconta-1,3,17,19-tetraent (L^6) and corresponding tetra-phenyl derivatives (L^7-L^{12}).
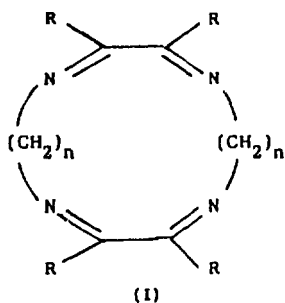
	R	n
L^1 - L^6	CH_3	2,3,4,6,8,12
L^7 - L^{12}	C_6H_5	2,3,4,6,8,12

Experimental

Materials. 1,2-Diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane and 2,3-butanedione were obtained from Fluka and distilled before use. 1,8-Diaminooctane (Fluka) and 1,2-diaminododecane (Fluka) were used as such. Benzil (Sisco, India) was recrystallized from hot n-butanol. $Cr(NO_3)_3 \cdot 9H_2O$ (Fluka) and $CrCl_3 \cdot 6H_2O$ (Fluka) were of GR grade.

Analytical Methods and Physical Measurements. Carbon and hydrogen were determined on Coleman C, H Analyser Model-33. Chromium was determined volumetrically using potassium dichromate, nitrogen by Kjeldahl's method and chlorine gravimetrically as AgCl. IR spectra were recorded as KBr pelletes in the region 4000 to 200 cm^{-1} on Perkin Elmer-577 Grating Infrared spectrophotometer. Magnetic measurements were carried out on Gouy Balance using $Hg[Co(CNS)_4]$ as a calibrant and reflectance spectra of the solid compounds suitably diluted with MgO were measured on Beckman-DU Spectrophotometer with standard Beckman reflectance attachment at S.P. University, Vallabh Vidyanagar (Gujrat).

Synthesis of Cr(III) Complexes of Tetraazamacrocycles Derived from 2,3-Butanedione. $Cr(NO_3)_3 \cdot 9H_2O$ or $CrCl_3 \cdot 6H_2O$ (3.0 mmol) was dissolved in 30 ml n-butanol. 2,3-Butanedione (6.0 mmol) in 20 ml n-butanol was added. To this, a solution of the diamine (6.0 mmol in 20 ml n-butanol) was added dropwise with constant stirring. A solid appeared during the addition and stirring was continued for 3-4 hrs. The precipitate was filtered, washed with n-butanol and dried *in vacuo*.

Synthesis of Cr(III) Complexes of Tetraazamacrocycles Derived from Benzil. $Cr(NO_3)_3 \cdot 9H_2O$ or $CrCl_3 \cdot 6H_2O$ (3.0 mmol) was dissolved in 35 ml hot n-butanol and benzil (6.0 mmol) dissolved in 25 ml hot n-butanol was added. To this, a solution of the diamine (6.0 mmol in 20 ml hot n-butanol) was added dropwise with constant stirring. A solid appeared during the addition and the stirring was continued for 3-4 hrs maintaining the temperature at 60-70 °C. The contents were then refluxed gently for 3-4 hrs. The precipitate was filtered while hot, washed with hot n-butanol and dried *in vacuo*.

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Results and Discussion

The reactions of $Cr(NO_3)_3 \cdot 9H_2O$ or $CrCl_3 \cdot 6H_2O$ with 2,3-butanedione or benzil and different diaminoalkanes viz., 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane or 1,12-diaminododecane in 1 : 2 : 2 molar ratios result in the formation of Cr(III) macrocylic complexes(II) according to the following general scheme.

R = CH₃, C₆H₅   X = Cl, m = 6

= NO₃, m = 9   n = 2,3,4,6,8,12
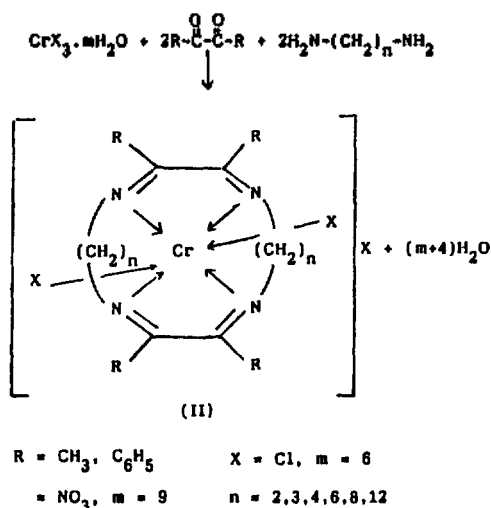
The resulting macrocyclic complexes are green solids except the complex $[Cr(Me_4[12]tetraene\ N_4)\ (NO_3)_2]NO_3$ which is brown. These are insoluble in water, methanol, acetone, carbon tetrachloride, acetonitrile, dimethylsulphoxide and nitrobenzene except a few complexes derived from lower diamines which are soluble in water and DMSO. Their characteristics and analyses are given in Table 1.

For tetraazamacrocycles ideal ring sizes of metal ions have been investigated and M-N distances for which the strain energy in the macrocycle is minimum have been calculated[13-15]. A larger or smaller metal ion would require a change in M-N distance with an accompanying increase in the strain energy of the ligand causing distortion. The M-N bond lengths for transition metal complexes of 12- to 16-membered saturated tetraazamacrocycles range from 1.8-2.4 Å and hence many macrocycles of varying ring sizes coordinate readily transition metal ions to give stable complexes[16]. There will be greater flexibility in the larger ring due to which metal ions smaller than the macrocyclic ring size can also be conveniently accomodated resulting in the formation of stable complexes. Formation constants and molecular mechanics calculations have shown that chelate ring size is important in controlling metal ion size-based selectivity than the macrocyclic ring size and there is very small effect of macrocyclic ring size on the stability of the complexes due to the flexibility of large ring macrocycles[17-20].

During the template synthesis of Fe(II), Co(III) and Ni(II)

Table 1. Analyses and Physical Characteristics of Cr(III) Tetraazamacrocyclic Complexes

Complex	Colour and decomposition Temp.(°C)	Yield (%)	Analysis(%) Found (Calcd.)				
			C	H	N	Cr	Cl
1	2	3	4	5	6	7	8
[Cr(Me₄[12]tetraene N₄) (NO₃)₂]NO₃	Brown	120	65	31.49(31.44)	4.24(4.39)	12.38(12.22)	11.51(11.34)	—
[Cr(Me₄[14]tetraene N₄) (NO₃)₂]NO₃	Green	110	61	35.16(35.57)	4.67(4.97)	11.62(11.51)	10.89(10.69)	—
[Cr(Me₄[16]tetraene N₄) (NO₃)₂]NO₃	Green	155	52	36.13(37.35)	6.11(5.48)	10.89(10.80)	10.25(10.10)	—
[Cr(Me₄[20]tetraene N₄) (NO₃)₂]NO₃	Green	178	67	41.19(42.10)	7.07(6.36)	9.73 (9.81)	9.32 (9.11)	—
[Cr(Me₄[24]tetraene N₄) (NO₃)₂]NO₃	Green	166	61	47.03(46.01)	7.73(7.07)	9.01 (8.94)	8.36 (8.29)	—
[Cr(Me₄[32]tetraene N₄) (NO₃)₂]NO₃	Green	150	64	51.18(52.02)	7.79(8.18)	7.74 (7.58)	7.12 (7.04)	—
[Cr(Me₄[12]tetraene N₄)Cl₂]Cl	Green	115	63	37.73(38.06)	5.17(5.32)	14.74(14.79)	13.93(13.73)	27.93(28.08)
[Cr(Me₄[14]tetraene N₄)Cl₂]Cl	Green	126	58	40.78(41.34)	6.26(5.94)	13.81(13.77)	12.92(12.78)	26.27(26.15)
[Cr(Me₄[16]tetraene N₄)Cl₂]Cl	Green	145	66	44.44(44.20)	7.03(6.49)	13.01(12.88)	12.20(11.95)	24.56(24.46)
[Cr(Me₄[20]tetraene N₄)Cl₂]Cl	Green	138	77	47.71(48.93)	8.22(7.39)	11.22(11.11)	10.77(10.59)	21.48(21.66)
[Cr(Me₄[24]tetraene N₄)Cl₂]Cl	Green	160	64	51.99(52.68)	8.51(8.10)	10.32(10.24)	9.74 (9.50)	19.57(19.44)
[Cr(Me₄[32]tetraene N₄)Cl₂]Cl	Green	152	69	58.04(58.30)	9.27(9.17)	8.32 (8.49)	8.05 (7.88)	15.96(16.13)
[Cr(Ph₄[12]tetraene N₄) (NO₃)₂]NO₃	Green	142	53	53.76(54.39)	4.23(3.99)	7.92 (7.86)	7.43 (7.35)	—
[Cr(Ph₄[14]tetraene N₄) (NO₃)₂]NO₃	Green	165	57	55.16(55.58)	4.83(4.39)	7.53 (7.62)	7.24 (7.07)	—
[Cr(Ph₄[16]tetraene N₄) (NO₃)₂]NO₃	Green	135	66	56.63(56.69)	4.70(4.75)	7.25 (7.34)	7.01 (6.81)	—
[Cr(Ph₄[20]tetraene N₄) (NO₃)₂]NO₃	Green	184	64	57.13(58.67)	6.22(5.41)	6.83 (6.84)	6.49 (6.34)	—
[Cr(Ph₄[24]tetraene N₄) (NO₃)₂]NO₃	Green	205	43	60.07(60.40)	5.95(5.99)	6.53 (6.40)	6.03 (5.94)	—
[Cr(Ph₄[32]tetraene N₄) (NO₃)₂]NO₃	Green	172	54	63.08(63.27)	7.25(6.94)	5.78 (5.67)	5.31 (5.26)	—
[Cr(Ph₄[12]tetraene N₄)Cl₂]Cl	Green	135	46	61.66(61.30)	4.72(4.50)	8.95 (8.93)	8.44 (8.29)	17.18(16.96)
[Cr(Ph₄[14]tetraene N₄)Cl₂]Cl	Green	146	48	61.76(62.34)	5.21(4.92)	8.41 (8.55)	8.09 (7.93)	16.17(16.24)
[Cr(Ph₄[16]tetraene N₄)Cl₂]Cl	Green	180	50	63.89(63.30)	5.81(5.31)	8.17 (8.20)	7.67 (7.61)	15.72(15.57)
[Cr(Ph₄[20]tetraene N₄)Cl₂]Cl	Green	155	48	65.98(64.99)	7.25(6.01)	7.51 (7.57)	7.21 (7.03)	14.52(14.28)
[Cr(Ph₄[24]tetraene N₄)Cl₂]Cl	Green	194	51	66.27(66.45)	6.71(6.59)	7.15 (7.04)	6.62 (6.53)	13.44(13.37)
[Cr(Ph₄[32]tetraene N₄)Cl₂]Cl	Green	210	56	67.57(68.82)	7.39(7.55)	6.28 (6.19)	5.94 (5.72)	11.83(11.72)

complexes of MePhTIM Eggleston and Jackels[21] have ruled out the possibility of the formation of diazepine(III), a heterocyclic product of 1+1 condensation, on the basis of ^{1}H NMR studies. Henry *et al.*[5] have isolated and characterized a macrocyclic precursor 1,2,8,9-tetraphenyl-3,7-diazaduohepta-2,7-diene-1,9-dione (KIM, IV) during 2+2 cyclocondensation of benzil and 1,3-diaminopropane in the presence of $CoBr_2 \cdot 6H_2O$.

Infrared Spectra. Significant IR bands of the complexes are given in Table 2. No absorption band was observed at 1700 cm^{-1} and 3200-3400 cm^{-1} indicating the absence of unreacted$>$C$=$O or $-$NH$_2$ group[22].

All complexes show a strong absorption band in the region

(structure diagrams)

(III)
Diazepino

(IV)
KIM
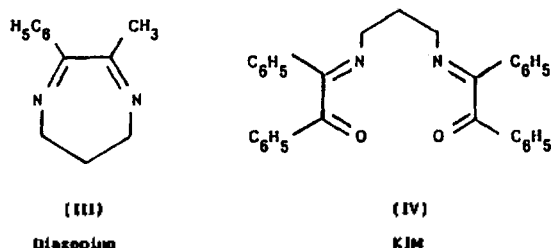
1600-1640 cm^{-1} attributed to the coordinated$>$C$=$N group. Busch *et al.*[2] have assigned the sharp band in the region 1550-1600 cm^{-1} to v (C$=$N) sym and weak band at 1640 cm^{-1} to v (C$=$N) asym in Co(III) TIM complexes. In Zn(MePhTIM) a band in the region 1610-1615 cm^{-1} has been assigned to v (C$=$N)[23].

Nitrate complexes exhibit intense absorption bands in the region 710-730, 810-820 and at 1380 cm^{-1} due to free nitrate while unidentate nitrate absorptions appear at 1000-1020, 1270-1280 and 1510-1520 cm^{-1}[24,25]. In the complex *trans*-[Cr (cyclam) $(NO_3)_2$]NO$_3 \cdot 2H_2O$ Maguire *et al.*[8] have assigned the bands at 1380 cm^{-1} to ionic nitrate and those at 1515 cm^{-1} and 1270 cm^{-1} to coordinated nitrate. In chloro complexes a band at 400 cm^{-1} may be assigned to coordinated chloro group[26]. Medium intensity bands in the region 1560-1580 cm^{-1} are attribute to v (C$=$C) of phenyl groups in the complexes derived from benzil[5]. We observe only two or in certain cases three absorption bands in the region 800-910 cm^{-1} suggesting *trans*-octahedral like structure for the chromium complexes. For the complex [(Co[14]ane N$_4$)X$_2$]$^+$ Poon[27] has shown that the *cis* and *trans* isomers can be differentiated on the basis of number and position of the bands in the CH$_2$ rocking region (800-910 cm^{-1}). Blinn *et al.*[7] have observed five bands in the region 800-910 cm^{-1} for *cis* isomer and two bands at 810 and 900 cm^{-1} for the *trans*-isomer of [(Cr[12])ane N$_4$)Cl$_2$] $\cdot$ H$_2$O.

Magnetic Moments. The observed μ_{eff} values for Cr (III) macrocyclic complexe are recorded in Table 2. The μ_{eff} values at room temperature (298°K) range from 3.67-4.27 B.M indicating the high spin state of chromium(III) complexes. Blinn *et al.*[7] have reported the magnetic moments for Cr(III) tetraazamacrocyclic complexes in the range 3.8-3.9 B.M. μ_{eff} values for Cr(III) complexes of 6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane have been reported to be 3.87 B.M[28]. The observed magnetic moment values of

Table 2. IR and Magnetic Data of Cr(III) Complexes

Complex	IR bands (cm^{-1})					μ_{eff}(B.M.)
	VC$=$N	-NO$_3$(ionic)	-NO$_3$(unidentate)	vCr-Cl	vC$=$C	
[Cr(Me$_4$[12]tetraene N$_4$) (NO$_3$)$_2$]NO$_3$	1600	730, 810, 1370	1020, 1510	—	—	3.72
[Cr(Me$_4$[14]tetraene N$_4$) (NO$_3$)$_2$]NO$_3$	1610	720, 810, 1370	1020, 1510	—	—	3.81
[Cr(Me$_4$[16]tetraene N$_4$) (NO$_3$)$_2$]NO$_3$	1620	720, 820, 1380	1020, 1510	—	—	3.89
[Cr(Me$_4$[20]tetraene N$_4$) (NO$_3$)$_2$]NO$_3$	1630	720, 810, 1380	1020, 1510	—	—	3.93
[Cr(Me$_4$[24]tetraene N$_4$) (NO$_3$)$_2$]NO$_3$	1610	720, 820, 1370	1000, 1520	—	—	4.16
[Cr(Me$_4$[32]tetraene N$_4$) (NO$_3$)$_2$]NO$_3$	1630	720, 820, 1380	1020, 1510	—	—	4.26
[Cr(Me$_4$[12]tetraene N$_4$)Cl$_2$]Cl	1630	—	—	400	—	3.72
[Cr(Me$_4$[14]tetraene N$_4$)Cl$_2$]Cl	1640	—	—	410	—	3.71
[Cr(Me$_4$[16]tetraene N$_4$)Cl$_2$]Cl	1630	—	—	400	—	3.91
[Cr(Me$_4$[20]tetraene N$_4$)Cl$_2$]Cl	1620	—	—	400	—	3.67
[Cr(Me$_4$[24]tetraene N$_4$)Cl$_2$]Cl	1620	—	—	400	—	4.21
[Cr(Me$_4$[32]tetraene N$_4$)Cl$_2$]Cl	1640	—	—	410	—	4.22
[Cr(Ph$_4$[12]tetraene N$_4$) (NO$_3$)$_2$]NO$_3$	1610	710, 810, 1380	1020, 1280, 1510	—	1580	3.81
[Cr(Ph$_4$[14]tetraene N$_4$) (NO$_3$)$_2$]NO$_3$	1600	720, 810, 1385	1020, 1270, 1510	—	1560	3.95
[Cr(Ph$_4$[16]tetraene N$_4$) (NO$_3$)$_2$]NO$_3$	1610	720, 810, 1380	1010, 1510	—	1570	3.91
[Cr(Ph$_4$[20]tetraene N$_4$) (NO$_3$)$_2$]NO$_3$	1600	720, 810, 1385	1010, 1270	—	1560	4.22
[Cr(Ph$_4$[24]tetraene N$_4$) (NO$_3$)$_2$]NO$_3$	1620	720, 820, 1380	1020, 1510	—	1570	4.16
[Cr(Ph$_4$[32]tetraene N$_4$) (NO$_3$)$_2$]NO$_3$	1610	720, 820, 1380	1020, 1270	—	1570	4.21
[Cr(Ph$_4$[12]tetraene N$_4$)Cl$_2$]Cl	1620	—	—	410	1570	3.75
[Cr(Ph$_4$[14]tetraene N$_4$)Cl$_2$]Cl	1640	—	—	410	1570	3.73
[Cr(Ph$_4$[16]tetraene N$_4$)Cl$_2$]Cl	1630	—	—	410	1560	3.73
[Cr(Ph$_4$[20]tetraene N$_4$)Cl$_2$]Cl	1600	—	—	400	1580	4.13
[Cr(Ph$_4$[24]tetraene N$_4$)Cl$_2$]Cl	1640	—	—	400	1570	4.03
[Cr(Ph$_4$[32]tetraene N$_4$)Cl$_2$]Cl	1620	—	—	400	1560	4.27

Table 3. Electronic Spectral Data of Cr(III) Complexes

Complex	Wave lengths (nm)		
	ν_1	ν_2	ν_3
[Cr(Me₄[12]tetraene N₄) (NO₃)₂]NO₃	595	440	365
[Cr(Me₄[14]tetraene N₄) (NO₃)₂]NO₃	585	450	380
[Cr(Me₄[16]tetraene N₄) (NO₃)₂]NO₃	590	445	365
[Cr(Me₄[20]tetraene N₄) (NO₃)₂]NO₃	575	445	360
[Cr(Me₄[24]tetraene N₄) (NO₃)₂]NO₃	575	435	355
[Cr(Me₄[32]tetraene N₄) (NO₃)₂]NO₃	595	430	360
[Cr(Me₄[12]tetraene N₄)Cl₂]Cl	565	440	365
[Cr(Me₄[14]tetraene N₄)Cl₂]Cl	580	435	370
[Cr(Me₄[16]tetraene N₄)Cl₂]Cl	570	450	375
[Cr(Me₄[20]tetraene N₄)Cl₂]Cl	585	445	365
[Cr(Me₄[24]tetraene N₄)Cl₂]Cl	590	430	370
[Cr(Me₄[32]tetraene N₄)Cl₂]Cl	575	440	360
[Cr(Ph₄[12]tetraene N₄) (NO₃)₂]NO₃	585	425	370
[Cr(Ph₄[14]tetraene N₄) (NO₃)₂]NO₃	575	410	380
[Cr(Ph₄[16]tetraene N₄) (NO₃)₂]NO₃	580	435	360
[Cr(Ph₄[20]tetraene N₄) (NO₃)₂]NO₃	570	430	375
[Cr(Ph₄[24]tetraene N₄) (NO₃)₂]NO₃	590	425	355
[Cr(Ph₄[32]tetraene N₄) (NO₃)₂]NO₃	575	430	360
[Cr(Ph₄[12]tetraene N₄)Cl₂]Cl	565	435	365
[Cr(Ph₄[14]tetraene N₄)Cl₂]Cl	580	450	370
[Cr(Ph₄[16]tetraene N₄)Cl₂]Cl	565	440	355
[Cr(Ph₄[20]tetraene N₄)Cl₂]Cl	570	435	360
[Cr(Ph₄[24]tetraene N₄)Cl₂]Cl	585	430	370
[Cr(Ph₄[32]tetraene N₄)Cl₂]Cl	575	440	375

Cr(III) macrocyclic complexes are in accord with the spin only value for three unpaired electrons and are characteristic of high spin octahedral chromium complexes. Slightly lower values for Cr(III) tetraazamacrocyclic complexes of lower diamines indicate metal-metal interaction while slightly higher values for the complexes derived from higher diamines suggest greater distortion from the normal octahedral geometry. The possibility of metal-metal interaction will be less in case of the complexes of macrocycles derived from higher diamines due to the crowding of ligands.

Electronic Spectra. λ_{max} values of the electronic spectral bands of Cr(III) macrocyclic complexes are recorded in Table 3. The wavelengths of the electronic transitions and the number of bands are usually reliable indicators for distinguishing the *cis-* and *trans-* isomers of Cr(III) complexes. Usually two bands are observed for *cis* chromium(III) complexes in the visible region and these bands are at lower energies than those for the corresponding *trans* isomers. Blinn *et al.*[7] have reported absorption maximum for *cis*-[Cr ([12]ane N₄)Cl₂]Cl·H₂O at 520 nm and for *cis*-[Cr([14]ane N₄)Cl₂]Cl at 532 nm while *trans*-[Cr([14]ane N₄)Cl₂]Cl exhibits the band at 582 nm and *trans*-[Cr([15]ane N₄)Cl₂]·2H₂O at 592 nm.

All the complexes show three spin allowed transitions in their electronic spectra. These energy bands occur in the region 565-595 nm (ν_1), 410-450 nm (ν_2) and 355-380 nm (ν_3). These can be assigned to $^4B_{1g}{\rightarrow}^4E_g$, $^4B_{1b}{\rightarrow}^4B_{2g}$ and $^4B_{1g}{\rightarrow}^4A_{2g}$ respectively[7]. In *trans*-[Cr(cyclam) (CH₃)₂](PF₆) (NO₃)₂·

1/2H₂O two spin allowed transitions have been reported $^4A_{2g}{\rightarrow}^4T_{2g}$ at 440 nm and $^4A_{2g}{\rightarrow}^4T_{1g}$ at 334 nm occurring at higher energy than their *cis*-analogues[8]. Bernhardt *et al.*[28] have assigned the transitions at 485 nm and 375 nm to $^4A_{2g}{\rightarrow}^4T_{2g}$ and $^4A_{2g}{\rightarrow}^4T_{1g}$ respectively in Cr(III) complexes of 6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane, in addition to two spin forbidden transitions. On the basis of the above facts the *trans* or folded octahedral configuration for Cr(III) tetraazamacrocyclic complexes may be assigned.

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Reactivity and Mechanism for Aryl Carbenic Anion Radicals

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Aryl carbenic anion radicals have been generated from the corresponding alkoxy-aryl diazo compounds by unimolecular decomposition reaction in various electrolyte/solvent systems. The electrochemical reductions of alkoxy-aryl diazo compounds in the electrolyte/solvent system are shown to initially be a one-electron process which affords the corresponding anion radicals. The unimolecular loss of nitrogen is favored at the propagation step and accelerated by the oxygen and carbon atoms of alkoxy group adjacent to the diazo function. The structure of the carbene anion radical in the termination is considered to be a resonance hybrid.

Introduction

Anion radicals of the carbene exist the intermediates in the electrochemical reduction of the diazoalkanes[1,2]. Diphenylcarbene anion radical could be produced *via* one unimolecular loss of nitrogen from the corresponding diazodiphenylmethane radical ion Eq. (1)[3]. Decomposition reaction of

$$Ph_2CN_2 \xrightarrow{e^-} Ph_2CN_2{}^- \xrightarrow{-N_2} Ph_2C:{}^{\cdot-} \qquad (1)$$
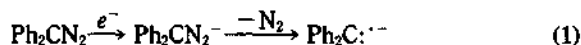
diazodiphenylmethane anion radical was of the first-order in acetonitrile and *N,N*-dimethylformamide[4]. The characteristic features of the unimolecular decomposition, (1), consist in that they have relatively high activation energies and take place only with extensive delocalization of a negative charge[4].

However, the decomposition of aryldiazoalkanes by an electron-transfer chain catalysis reaction gave a carbene cation radicals in the presence of copper(II) salts with non-nucleophilic anions in aprotic solvents[5].

$$Ph_2CN_2 \xrightarrow{-e^-} Ph_2CN_2{}^{\cdot+} \xrightarrow{-N_2} Ph_2C{}^{\cdot+}: \qquad (2)$$
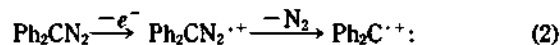
Those unimolecular decomposition reactions of aryldiazoalkanes could give different radicals depending upon the variation of the reaction conditions such as the presence of nucleophiles, the nature of electrolytes, and the presence of catalysts *etc.*.

While the point of the question still remains uncleared,

two independent studies have provided convincing kinetic evidences for the electrochemical generation of carbene anion radicals from the azibenzil[6] and diethyl diazomalonate[7]. It was concluded that the kinetic results were consistent with initial generation to give the carbene anion radical. This may suggest that localization of the charge in the anion radicals into the carbonyl oxygen, facilitates the loss of dinitrogen atoms.

We now examine the influence of the alkoxy group in the reactions of various alkoxy-aryldiazo compounds (I, II, and III) by detection of the radicals employing generation by the method of electrochemical decomposition. We also report here the kinetic results for the reaction of electrochemical decomposition of aryl carbene anion radicals in various solvents and electrolytes.

I

II

III