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A Spectroscopic and Electrochemical Study of Some Copper(II) Tetraaza Macrocyclic Complexes

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Infrared, electronic, electron spin resonance and d.c. polarographic data for some copper(II) tetraaza macrocyclic complexes, involving a novel cyclam type ligand, are reported and are interpreted in terms of the structure of the complexes and the influence of *Jahn-Teller* distortion effects and cation-anion interactions.

(Keywords: Electron spin resonance; Polarography; Ir; Electronic spectra; Cyclam type ligand).

Eine spektroskopische und elektrochemische Untersuchung einiger makrocyclischer Kupfer(II)-Komplexe

Es wird über Infrarot-, Elektronenanregungs-, Elektronenspinresonanz- und D.C. Polarographie-Daten einiger tetraaza-makrocyclischer Kupfer(II)-Komplexe einschließlich eines neuen Cyclam-Typs als Ligand berichtet. Die Befunde werden hinsichtlich der Strukturen der Komplexe, dem Einfluß von *Jahn-Teller*-Verdrillungseffekten und Kation-Anion-Wechselwirkungen interpretiert.

Introduction

Copper(II) compounds exhibit a wide variety of structures primarily as a result of *Jahn-Teller* distortion effects [1–16]. In this context, copper(II) tetraaza macrocyclic complexes are of particular significance, because additional and unusual structural features are apparent. For example, a recent field desorption mass spectrometric study [17] of [6,6,7,12,13,13-hexamethyl-1,4,8,11-tetraazacyclotetradeca-7,11-diene] copper(II) perchlorate, showed that, in a vacuum, these type of complexes exhibit various types of interaction between cation, anion and water of hydration with the formation of cluster-ions.

This paper reports the synthesis of several new copper(II) tetraaza macrocyclic complexes incorporating a cyclam-type ligand with *α-cis*-geminal methyl and *cis*-diene configurations. The physicochemical data (infrared, UV-visible, e.s.r. and d.c. polarography) for these complexes are interpreted in terms of structure, inter-related *Jahn-Teller* distortion effects and possible cluster-ion formation. Also, these data are compared with corresponding data for a structurally similar copper(II) macrocyclic complex with the ligand exhibiting *β-trans*-geminal methyl and *trans*-diene configurations.

Experimental

Infrared data in the range 4000–250 cm^{-1} were obtained on a Perkin-Elmer 457 Grating Infrared spectrophotometer; the KBr disc method was used. All vibrational bands were calibrated relative to polystyrene. Electronic spectral data in the range 190–900 nm were recorded on a Shimadzu UV-240 Recording spectrophotometer with a Shimadzu PR-1 Graphic Printer attachment, using 1 cm path length matched quartz cells. Electron spin resonance data were recorded on a Varian E-9 spectrometer system (9 GHz, X-Band) with a Varian E-101 Klystron microwave bridge. All samples were analysed in *DMSO* at a concentration of $2 \cdot 10^{-3}$ *M*. *DPPH* served as the standard marker. Direct Current Polarography (DCP) was carried out using an AMEL 471 Multipolarograph jacketted to allow thermostatting at 25 ± 0.2°. The three electrode system was used, and in the closest and most favourable electrode configuration to minimise the uncompensated i.r. potential. A dropping mercury electrode (DME) and a 15 cm coiled platinum wire served as the working electrode and counter electrode, respectively. A PAR model K 77 saturated calomel electrode (SCE) was used as the reference electrode, rendering all $E_{1/2}^{red}$ potentials relative to the SCE reference electrode. The SCE was isolated from the test solution by employing an AMEL model 303–90/NS reference electrode bridge with N 12 ground-glass joint, terminated by a frit-glass junction, and filled with 0.1 *M* LiCl in millipore water. A second bridge with luggin capillary separated the reference electrode bridge from the test solution; this luggin capillary bridge contained chromatographic grade acetonitrile-190 and 0.1 *M* tetrabutylammonium perchlorate. All samples were at $2 \cdot 10^{-3}$ *M* concentration in acetonitrile-190, with 0.2 *M* tetrabutylammonium perchlorate as supporting electrolyte and 60 μl Triton X-100 surface active agent. All test solutions were deoxygenated by bubbling high purity nitrogen through the test solution for 10 minutes before measurements were made.

All copper(II) tetraaza macrocyclic complexes were prepared according to a previously reported procedure [17].

$[Cu(Me_6trans[14]7,14\text{-diene}N_4)](ClO_4)_2$ (**1**) was obtained as brick-red crystals (yield: 0.91 g; 66.6%). Found: C 35.60, H 6.23, N 10.54. $C_{16}H_{32}Cl_2CuN_4O_8$ requires: C 35.40, H 5.94, N 10.32%.

$[Cu(Me_6cis[14]7,11\text{-diene}N_4)](ClO_4)_2$ (**2**) was obtained as purple crystals (yield: 1.29 g; 62.3%). Found: C 34.21, H 6.12, N 9.81%. $C_{16}H_{32}Cl_2CuN_4O_8, 2\,H_2O$ requires: C 34.14, H 6.45, N 9.95%.

$[Cu(Me_6cis[14]7,11\text{-diene}N_4)](BF_4)_2$ (**3**) was obtained as purple powder (yield: 1.13 g; 52%). Found: C 35.32, H 6.89, N 10.12%.

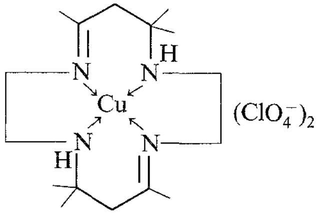
$B_2C_{16}CuF_8H_{32}N_4$, H_2O requires: C 35.88, H 6.39, N 10.46%.

[Cu(*Me*$_7$*cis*[14]7,11-dieneN$_4$)]$(BF_4)_2$ (**4**) was obtained as purple crystals (yield: 1.0 g; 44.6%). Found: C 35.01, H 6.27, N 9.26%.
$B_2C_{17}CuF_8H_{34}N_4$, 3 H_2O requires: C 34.86, H 6.88, N 9.56%.

[Cu(*Me*$_8$*cis*[14]7,11-dieneN$_4$)]$(BF_4)_2$ (**5**) was obtained as purple crystals (yield: 0.73 g; 31.7%). Found: C 37.05, H 6.19, N 9.05%.
$B_2C_{18}CuF_8H_{36}N_4$ requires: C 37.16, H 6.93, N 9.63%.

Results and Discussion

The copper(II) tetraaza macrocyclic complexes (Table 1) are characterised by secondary amine ν(N—H) vibrations in the region 3 220–3 320 cm^{-1} [3, 7, 14, 18, 19] and a single imine ν(C=N) vibration at ca. 1 660 cm^{-1} [18]. A broad ν(O—H) band in the spectrum of the *cis*[14]dieneN$_4$ species at ca. 3 520 cm^{-1} is attributed to hydration water. A weak ν(O—H) band at 3 420 cm^{-1} for the *trans*[14]dieneN$_4$ species is attributed to moisture on the KBr disc surface. The presence of ν(C=N), ν(Cu—N) and ν(N—H) bands, and *gem*-Me δ(C—H) bands are indicative of complex formation. The decreased ν(N—H) frequencies in the region 3 180–311 cm^{-1} for [Cu(*trans*[14]dieneN$_4$)]$(ClO_4)_2$ and [Cu(*Me*$_6$*cis*[14]dieneN$_4$)]$(X)_2$ ($X = ClO_4$, BF_4) indicate various extents of hydrogen-bonded interactions [18] between the secondary amine ligand functions and counterions. Similar 6-membered chelate ring conformations are suggested for the *trans*[14]dieneN$_4$ species as indicated



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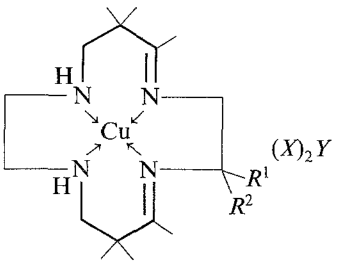

2 $R^1 = R^2 = H$, $X = ClO_4^-$, $Y = 2\,H_2O$
3 $R^1 = R^2 = H$, $X = BF_4^-$, $Y = H_2O$
4 $R^1 = CH_3$, $R^2 = H$, $X = BF_4^-$, $Y = 3\,H_2O$
5 $R^1 = R^2 = CH_3$, $X = BF_4^-$, $Y = 2\,H_2O$

Table 1. *IR data for the* Cu(II) *tetraaza complexes* **1–5**

Complex	ν(OH)	ν(NH)	ν(CH)	ν(C=N)	δ(NH)	δ(CH_2) scissor	δ(CH) C—CH_2 assym	δ(CH) gem-*Me*
1	3 420 s	3 180 s	2 950 s 2 900 mb	1 660 s		1 450 s	1 425 s	1 400 s 1 365 s
2	3 520 mb	3 315 s 3 250 s 3 230 s 3 115 s	2 975 s 2 945 s 2 940 s 2 880 s	1 683 s 1 623 s	1 580 s	1 473 s 1 460 s	1 430 s	1 390 m 1 355 s
3	3 520 mb	3 315 s 3 250 s 3 225 s	2 975 s 2 950 s 2 880 s	1 685 s 1 625 s	1 580 s	1 470 s 1 430 s	1 500 s	1 395 s 1 355 s
4	3 525 mb	3 305 s 3 220 s	2 960 s 2 930 s 2 870 s	1 685 s 1 625 s	1 575 s	1 465 s 1 455 s	1 430 s	1 395 s 1 355 s
5	3 520 mb	3 270 sb 3 240 sb 3 150 sb	2 950 s 2 865 s	1 685 s 1 610 sb	1 580 sb	1 470 s 1 430 m	1 500 m	1 395 s 1 355 s

Table 1 *(continued)*

Complex	$\delta(CH_2)$ twist	$\delta(CH_2)$ wag	$\delta(NH)$	$\delta(CH_2)$ rock	$\nu(Cl—O)$ or $\nu(B—F)$	$\nu(Cu—N)$	$\nu(Cu—OH_2)$ $\delta(Cu—OH_2)$
1	1 265 s		760 s, 985 s 965 s	890 w, 825 w 805 w	1 075 sb 615 s	570 m 525 s	450 w (δ) 420 w
2	1 270 s	1 370 s	742 s, 700 s 980 s, 925 s	875 s 835 s	1 080 sb, 620 s 1 195 s, 955 s 940 s, 460 m	575 s, 540 s 525 s, 510 s	390 s (ν) 480 m (δ) 450 m (δ)
3	1 275 s	1 370 s	760 s, 740 sb 705 s, 925 s	880 s, 835 s 810 w	1 080 sb, 620 s 520 s, 960 s 528 m, 465 m 355 m	578 s 540 s	395 s (ν) 480 s (δ) 455 m (δ)
4	1 265 s	1 365 s	762 s, 740 s 710 w, 990 s 930 s	885 s, 865 s 835 s, 825 s	1 090 sb, 620 s	582 s 572 m 550 s	390 m (ν) 480 s (δ) 440 s (δ)
5	1 275 m	1 370 s	735 s, 990 sb 700 s, 965 sb	850 w 830 w	1 090 sb, 620 s	570 m 550 m	380 m (ν) 475 s (δ) 455 m (δ)

All complexes indicated skeletal bands in the range 1 320–1 190 cm^{-1}

by the single imine $\nu(C=N)$ frequency at 1 660 cm^{-1}; whereas different 6-membered chelate ring conformations are apparent for the *cis*[14]dieneN_4 species, as indicated by imine bands at ca. 1 685 cm^{-1} and 1 625 cm^{-1}. The variability in frequency and number of $\nu(Cu—N)$ bands for the *cis*[14]dieneN_4 species suggests different Cu—N coordinate bond strengths within the macrocyclic cavity; which may be inferred to represent varying extents of tetragonal and/or tetrahedral distortion(s) of the copper(II) centre. Further, the constancy of the $\delta(CH)$ bands for the geminal-methyl groups of the *cis*[14]dieneN_4 species suggests similar geminal-methyl environments. The approximate constancy of the $\delta(CH_2)$ twisting and wagging deformation vibrations for the *cis*[14]dieneN_4 species suggests similar methylene environments, and therefore, similar 5-membered chelate ring conformations. Infrared data for the anions and water molecules tentatively suggest square planar geometry for the *trans*[14]dieneN_4 species and tetragonally distorted octahedral geometry for [Cu(Me_6*cis*[14]7,11-dieneN_4) (*X*) (H_2O)] (*X*-ClO_4^-, BF_4^-); [Cu(Me_7*cis*[14]7,11-dieneN_4) (H_2O_2] $(BF_4)_2$ and [Cu(Me_8*cis*[14]7,11-dieneN_4) $(H_2O)_2$] $(BF_4)_2$, in that it is evident (Table 1) that an anion and/or water molecule(s) is coordinated to the copper(II) ion. The proposed coordinated water in the Me_7*cis*[14]dieneN_4 and Me_8*cis*[14]dieneN_4 species suggests that the methyl substituents on the 5- and 6-membered chelate rings sterically hinder the axial approach of the bulky tetrafluoroborate ions toward the copper(II) ion.

Electronic spectral data for the copper(II) tetraaza macrocyclic complexes are recorded in Table 2 and are characteristic [18] of copper(II) tetraaza macrocyclic complexes, in that, a single, broad 'd-d' band near 38 461 cm^{-1} (ca. 5 000–8 000 $M^{-1}cm^{-1}$) [20] is exhibited, typical of square planar Cu(II) complexes. The broadness of the charge transfer bands is attributed to mixing of the $Cu \rightarrow L$ and $L \rightarrow Cu$ transitions [21, 22]. These copper(II) complexes with diene moieties exhibit a transition of the azomethine chromophore at ca. 50 000 cm^{-1} (11 000 $M^{-1}cm^{-1}$).

Previous studies of copper(II) macrocyclic complexes have shown that the energy of the 'd-d' band decreases with increasing degree of ligand unsaturation [4, 12, 23, 24]; the size of the macrocyclic ligand and metal ion size govern the structure of the macrocyclic complex and respective 'd-d' band energy; 7-membered chelate rings produce substantial distortions from square planar geometry [15] and induce ring strain into the N_4 plane, thus weakening the Cu—N interactions [8]; differences in *cis*- and *trans*-diene configuration contribute to the extent of distortion within the coordination sphere [15]; however these copper(II) tetraaza macrocyclic complexes exhibit (i) different diene configurations; (ii) different geminal-

Table 2. *UV-Vis data for the copper(II) tetraaza complexes* **1**–**5**

Complex	d-d (cm^{-1}) [$\varepsilon/M^{-1}cm^{-1}$]	C.T. (cm^{-1}) [$\varepsilon/M^{-1}cm^{-1}$]	$\pi \rightarrow \pi^*$ (cm^{-1}) [$\varepsilon/M^{-1}cm^{-1}$]	Dq_{xy} (cm^{-1})
1	20 000 (119)	38 461 (15 646)	49 020 (19 692)	2 000.0
2	18 553 (97.3)	38 314 (20 359)	51 546 (17 716)	1 855.3
3	18 416 (16)	38 314 (976)		1 841.6
4	18 553 (95)	38 241 (6 549)	52 083 (5 487)	1 855.3
5	18 587 (125)	37 736 (6 896)	51 813 (6 207)	1 858.7

methyl positions; (iii) different geometries; and (iv) different cation-anion interactions.

In square planar or tetragonally distorted octahedral copper(II) complexes, mixing of the three $a_{1g} \rightarrow b_{1g}$, $b_{2g} \rightarrow b_{1g}$ and $e_g \rightarrow b_{1g}$ ('d-d') transitions results in broad bands in the electronic spectra [5]. The appearance of a single broad 'd-d' band in the visible spectrum of square planar [3] or tetragonally distorted octahedral complexes containing neutral macrocyclic diimine ligands is common. *Anichini* et al. [12] and *Fabbrizzi* et al. [25] have approximated the λ_{max} of the single broad 'd-d' band for tetragonally distorted copper(II) complexes to be the value of the in-plane $10\,Dq_{xy}$. This approximation suggests that the $b_{2g} \rightarrow b_{1g}$ transition is the principal contributor to the energy of the broad band; where the $b_{2g} \rightarrow b_{1g}$ transition is equal to the difference in energies of the d_{xy} and $d_{x^2-y^2}$ orbitals, which is $10\,Dq_{xy}$. The decreased values of the 'd-d' energies (ca. $10\,Dq_{xy}$) for the *cis*[14]dieneN_4 species relative to the *trans*[14]dieneN_4 species suggests significant *Jahn-Teller* tetragonal distortion of the coordination sphere in the *cis*[14]dieneN_4 species, whereas the 'd-d' energy of the *trans*[14]dieneN_4 species (20 000 cm^{-1}) is indicative of a tetrahedrally distorted square planar geometry. Distortions of the CuN_4 plane reflect a much weakend Cu—N interaction, as reflected in the order of Dq_{xy}; for the copper(II) complexes studied, this order is:

[Cu(*Me*$_6$*cis*[14]dieneN_4)] $(BF_4)_2$ < [Cu(*Me*$_6$*cis*[14]dieneN_4)] $(ClO_4)_2$
≃ [Cu(*Me*$_7$*cis*[14]dieneN_4)] $(BF_4)_2$ < [Cu(*Me*$_8$*cis*[14]dieneN_4)] $(BF_4)_2$
< [Cu(*Me*$_6$*trans*[14]dieneN_4)] $(ClO_4)_2$.

This order of increasing Dq_{xy} for copper(II) macrocyclic complexes is opposite to the order of increasing ε for some structurally related nickel(II) macrocyclic complexes [26]. This order suggests that [Cu(*Me*$_6$*trans*[14]dieneN_4)] $(ClO_4)_2$ is the most stable complex within the series. It is proposed that the larger copper(II) ionic size, relative to the nickel(II) ionic size, distorts (destabilises) the *cis*[14]dieneN_4 macrocycle. The order [Cu(*Me*$_6$*cis*[14]dieneN_4)] $(BF_4)_2$ < [Cu(*Me*$_7$*cis*[14]dieneN_4)] $(BF_4)_2$ < [Cu(*Me*$_8$*cis*[14]dieneN_4)] $(BF_4)_2$ indicates an increasing Cu—N interaction with increasing methyl substitution of the 5-membered chelate ring bridging the two imino-methyl moieties. This feature reflects (i) the increasing inductive effect of the methyl groups on the imine nitrogen electronic environment, but more so (ii) the reduction in complex symmetry with increasing methylation. The decreasing charge transfer transition energies in the same order suggests little Cu → *L* transition, whereas the *L* → Cu transition possibly increases electron density on the Cu(II) ion. This suggestion is partly supported by the decreasing π-π^* transition energy of the azomethine moieties in the same order. The differences in 'd-d' band energies for the two [Cu(*Me*$_6$*cis*[14]dieneN$_4$)] (X_2) species [$X = ClO_4^-$: 18 553 cm^{-1}; $X = BF_4^-$: 18 416 cm^{-1}] but equivalent C.T. band energies (38 314 cm^{-1}) suggest equivalent Cu—N bond strengths and distinctly different *Jahn-Teller* distortions. This feature possibly reflects the differing steric and inductive effects of the perchlorato and tetrafluoroborato groups on the CuN$_4$ coordination sphere.

The electronic data collectively suggest a distorted square planar geometry for the *trans*[14]dieneN$_4$ species and varying degrees of tetragonally distorted octahedral geometry for the *cis*[14]dieneN$_4$ species. It is apparent that the methyl substituents on the 5-membered chelate rings, metal ion size and the counterions exert a significant influence on the copper(II) ion electronic environment and complex symmetry. Further, it is evident that the *trans*[14]dieneN$_4$ species is more structurally stable than the *cis*[14]dieneN$_4$ species, possibly reflecting a greater constrictive effect [20, 27] of the *cis*-diene macrocyclic ligands relative to the *trans*-diene macrocyclic ligand.

Electron spin resonance (ESR) parameters for some copper(II) tetraaza macrocyclic complexes are recorded in Table 3. The four line spectrum of these complexes indicates no line splitting due to N^{14}-hyperfine coupling or H^1-hyperfine coupling; with exception to the $\frac{1}{2}^+ \rightarrow \frac{1}{2}^+$ transition line for the frozen glass spectrum of [Cu(*Me*$_6$*cis*[14]7,11-dieneN$_4$)] (ClO$_4$)$_2$, which exhibits a three component split, attributed to N^{14}-hyperfine coupling; the existence of g_y and g_z tensors in the frozen-glass spectrum of this species is evident of *Jahn-Teller* tetragonal distortion. The solution and frozen-glass ESR spectra of [Cu(*Me*$_6$*cis*[14]7,11-dieneN$_4$)] (ClO$_4$)$_2$ are shown in Figs. 1 and 2, respectively.

Although the σ-covalency in many Cu(II) macrocyclic complexes has been evaluated by several ESR parameters [4, 28—30], the g_{11}-values are reported [4, 31] to be the most reliable and convenient measure of the in-plane Cu—N bond covalency in copper(II) tetraaza macrocyclic complexes: therefore, only the g_{11}-values will be considered. The ESR

Table 3. *ESR data for copper(II) tetraaza macrocyclic complexes* **1**, **2**, **4**, and **5**

Complex	[ ] (M)	Solvent	Spectra type	Tube temp. °C	ν(DPPH) GHz	ν GHz	g_x	g_y ($g_\perp$)	g_z ($g_\parallel$)
1	$1.47 \cdot 10^{-3}$	CH_3CN	Frozen	− 195.8	9.122	9.119	2.0577	1.9571	2.1597
2	$2 \cdot 10^{-3}$	*DMSO*	solution	22	9.512	9.503			
	$2 \cdot 10^{-3}$	*DMSO*	Frozen	− 195.8	9.200	9.170	2.0432	1.973	2.1915
			Powder	22	9.523	9.523			
4	$2.5 \cdot 10^{-3}$	CH_3CN	Frozen	− 195.8	9.122	9.119	2.059	1.975	2.1885
5	$4.0 \cdot 10^{-3}$	CH_3CN	Frozen	− 195.8	9.122	9.119	2.058	1.973	2.184

Complex	g_{Av}	A_z (G) ($A_\parallel$)	A_{Av} (G)	$-\frac{3}{2} \rightarrow -\frac{3}{2}$ (G)	$-\frac{1}{2} \rightarrow -\frac{1}{2}$ (G)	$+\frac{1}{2} \rightarrow +\frac{1}{2}$ (G)	$+\frac{3}{2} \rightarrow +\frac{3}{2}$ (G)	$A_z (\times 10^{-4})$ (cm^{-1})
1	2.058	212.56		2 697.99	2 910.49	3 104.49	3 293.24	204.2
2	2.112		77.5	3 099.15	3 173.65	3 253.15	3 331.65	
	2.069	186.75		2 709.57	2 896.32	3 087.82 3 142.07 3 178.32	3 273.32	180.4
	2.031							
4	2.074	197.25		2 681.24	2 878.49	3 084.98	3 249.99	191.0
5	2.072	195.49		2 689.99	2 885.48	3 086.99	3 252.49	189.1

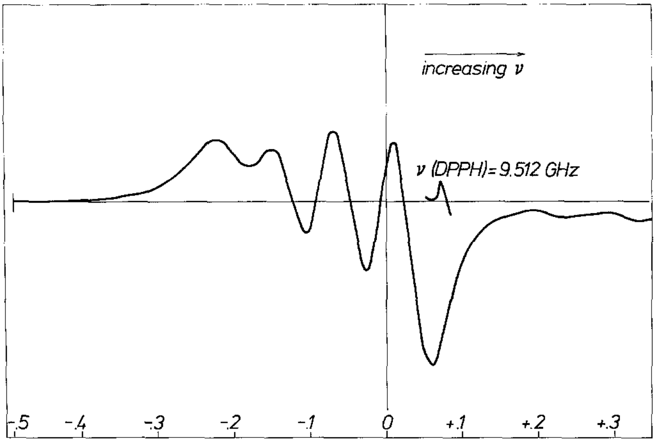

Fig. 1. Solution (*DMSO*) ESR spectrum of **2**

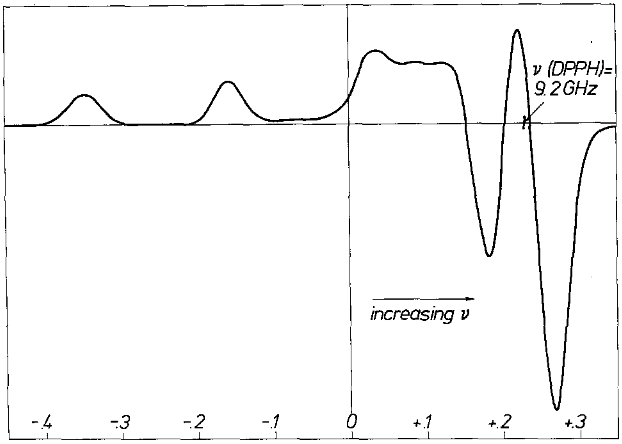

Fig. 2. Frozen-glass ESR spectrum of **2**

parameters for the complexes of the present study (Table 3) compare with the ESR parameters for some structurally related copper(II) complexes previously reported (Table 4), while the g-values and A-values are characteristic of copper(II) tetraaza macrocyclic complexes. The order of increasing g_{11}-values, and therefore of decreasing σ-covalency of the Cu—N bonds for these complexes (Table 3) is:

$[Cu(Me_6trans[14]7,14\text{-}dieneN_4)](ClO_4)_2$
$< [Cu(Me_8cis[14]7,11\text{-}dieneN_4)](BF_4)_2$
$< [Cu(Me_7cis[14]7,11\text{-}dieneN_4)](BF_4)_2$
$< [Cu(Me_6cis[14]7,11\text{-}dieneN_4)](BF_4)_2$.

Table 4. *ESR literature data for some copper complexes*

Complex	$g_\parallel$	$g_\perp$	$A_\parallel$ $(10^{-4}\,\mathrm{cm}^{-1})$	α^2
$[\mathrm{Cu}(Me_4[14]\mathrm{aneN}_4)](\mathrm{ClO}_4)_2$ [28]	2.21	2.058	206	0.85
$[\mathrm{Cu}(Me_4[14]\mathrm{dieneN}_4)](\mathrm{ClO}_4)_2$ [28]	2.20	2.029	198	0.81
$[\mathrm{Cu}(Me_4[14]\mathrm{tetraeneN}_4)](\mathrm{ClO}_4)_2$ [28]	2.156	2.047	201	0.77
$[\mathrm{Cu}(Me_4[14]\mathrm{hexaeneN}_4)]$ [28]	2.156	2.047	196	0.76
Cu-dibenzotetraaza[14]annulene [31]	2.127		207	
$\mathrm{Cu}[\mathrm{H}Ph\mathrm{H}(en)_2]$ [4]				0.79
$[\mathrm{Cu}(Me_6trans[14]7,14\text{-}\mathrm{dieneN}_4)](Bph_4)_2$ [4]	2.161		199	
Cu-*TPP* [4]	2.187		218	
Cu-phthalocyanine [4]	2.160		217	

Table 5. *D.C. Polarographic data for* **1**, **2**, **4**, *and* **5**

Complex	D.C.P. $E_{1/2}$ (V) $II \rightarrow I$	Absorption Maxima (V)	Dq_{xy} (cm^{-1})
1	− 0.52	− 1.1	2000
2	− 0.42	− 0.75	1855.3
4	− 0.61	− 1.0	1855.3
5	− 0.81	− 1.1	1858.7

This sequence is consistent with the order proposed by the Dq_{xy} terms and the expression:

$$(1/[2 - g_{11}]) \simeq (5/4)(\lambda \alpha^2 \beta_1^2)^{-1} Dq_{xy}$$

which is derived from the Ligand Field Theory expression for g_{11} of Cu(II) complexes of axial symmetry:

$$g = 2[1 - (4\lambda K_{11}/[\Delta E(d_{x^2-y^2} - d_{xy})])]$$

and the approximation of $\Delta E(d_{x^2-y^2} - d_{xy})$ as the $10\,Dq_{xy}$ term. The abnormally low A_z for [Cu(*Me*$_6$*cis*[14]7,11-dieneN$_4$)] $(ClO_4)_2$ (186.75 G) and [Cu(*Me*$_8$*cis*[14]7,11-dieneN$_4$)] $(BF_4)_2$ (195.5 G) compared to ca. 200 G [32], is characteristic of tetrahedral distortion of the copper(II) environment in these complexes.

The D.C. Polarographic data for some copper(II) tetraaza macrocyclic complexes are recorded in Table 5. The $E^{red}_{1/2}$ reduction potentials for copper(II) are characteristic for copper(II) tetraaza macrocyclic complexes under these experimental conditions. The $E^{red}_{1/2}$ potential for the *trans*[14]diene species is within the range previously reported [21, 33]. It is evident from the DCP data that: a "spike" within the range − 0.75 → 1.8 V is associated with various adsorption processes involving the mercury electrode. Variation of surfactant agent (TRX-100) concentration does not eliminate these "spikes" (adsorption waves); sequential addition of a methyl group contributes − 195 mV to the $E^{red}_{1/2}$(II–I) potential; and change of diene configuration from *trans*-diene to *cis*-diene contributes + 100 mV to $E^{red}_{1/2}$. These data suggest that the methyl groups induce electrons into the Cu(II) electronic environment and that the *cis*-diene configuration destabilises complex stability. However, variation of the degree of tetragonal and/or tetrahedral distortion of the copper(II) coordination sphere causes no discernible contribution to the reduction potential, and variation of counter ion also appears to have little influence on the $E^{red}_{1/2}$.

Conclusion

The data collectively indicate tetragonally distorted octahedral structures for these copper(II) tetraaza macrocyclic complexes exhibiting *α-cis*-geminal-methyl and *cis*-diene ligand configurations. A degree of tetrahedral distortion is evident in the CuN_4 plane of $[Cu(Me_6cis[14]7,11\text{-}dieneN_4)](ClO_4)_2$ and $[Cu(Me_8cis[14]7,11\text{-}dieneN_4)](BF_4)_2$. The octahedral symmetry of the *cis*[14]dieneN_4 species results from coordination of anion and/or water molecule(s) as previously suggested [17]. It is apparent that increasing the degree of methylation decreases complex symmetry and exerts a significant influence on the CuN_4 environment. Further, it is evident that the *trans*[14]dieneN_4 species is structurally more stable than the *cis*[14]dieneN_4 species, by virtue of a significantly decreased ligand constrictive effect.

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