Effects of Macrocyclic Ligand Structure and Axial Ligation on the Ligand-field Spectra of Tetra-azamacrocyclic Copper(II) Complexes in Co-ordinating Solvents†

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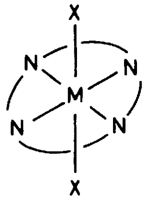
Four closely related 14-membered tetra-azamacrocyclic copper(II) complexes have been synthesized, and their ligand-field spectra in water, methanol, dimethylformamide, and dimethyl sulphoxide have been studied. In these solutions all the complexes contain tetragonal copper(II), and are of the general formula $[CuL(solv)_2]^{2+}$ (L = macrocyclic ligand, solv = solvent). The equatorial ligand-field strength is affected by the macrocyclic ligand structure; on the other hand, the axial ligand-field strength is affected by the donor ability of the co-ordinating solvent. Linear relationships between the *d–d* transition energies for the complexes and the donor numbers of the solvents were obtained.

Complexes of macrocyclic ligands having structure (I) are ideally suited to the study of the effects of tetragonal ligands on the electronic states of metal ions.[1] In our laboratory, four closely related 14-membered tetra-azamacrocyclic copper(II) complexes have been prepared as their perchlorate salts and characterized.[2–6] The crystal structure determinations of these four salts have recently been completed.[7–10] Their structures consist of six-co-ordinate monomeric $CuL(ClO_4)_2$ units in which the copper(II) ions have tetragonally distorted octahedral geometry, with the macrocyclic ligand equatorial and the perchlorate ions axial. The configurations of the macrocyclic ligands are shown in the Figure. In basic solvents, the four nitrogens of the macrocyclic ligand retain their planar or very slightly distorted planar co-ordination, but the axially co-ordinated perchlorate ions are replaced by the basic solvent molecules.[7,11]



(I)

This note concerns the ligand-field spectra of these complexes in co-ordinating solvents containing oxygen donors. Water, methanol, dimethylformamide (dmf), and dimethyl sulphoxide (dmso) are suitable for dissolution of these ionic macrocyclic complexes, and were used in this study. Like the spectra of copper(II) complexes of open-chain polyamines,[12,13] there are three *d–d* electronic transitions, the frequencies of which are strongly dependent on the field experienced by the *d* orbitals. The equatorial ligand-field strength is affected by the macrocyclic ligand structure; on the other hand, the axial ligand-field strength is affected by the donor ability of the co-ordinating solvent. Thus these systems provide an ideal opportunity to study the ligand-field spectra of elongated tetragonal octahedral CuN_4O_2 chromophores.

Experimental

Reagents.—The macrocyclic complexes were prepared as described earlier.[9,10,14] The water used was distilled and deionized. All other chemicals used were of GR grade from Merck.

Instrumentation.—Cary 17 and Lambda 5 spectrophotometers with thermostatted cell compartments were used to record absorption spectra. The temperature was maintained at 25.0 ± 0.1 °C. A CDC Cyber-172 computer was used to analyse the electronic spectra into their Gaussian components.

Results and Discussion

The absorption spectra of the complexes as their perchlorate salts dissolved in various co-ordinating solvents at 25 °C are available as SUP 56570. In all cases, a minimum of three Gaussian components was required to obtain a reasonable fit, and to give a consistent sequence of band intensities. The results of this analysis are given in the Table.

In these solvents, the four nitrogen donors of the macrocyclic ligand retain their 'planar' co-ordination but the axially co-ordinated ClO_4^- are replaced by solvent molecules.[7,11] Thus, the complexes are of pseudo-D_{4h} symmetry having 4 + 2 co-ordination (elongated tetragonal octahedral). The electronic energy levels of elongated tetragonal octahedral copper(II) complexes have been reported by Hathaway.[13] Three *d–d* electronic transitions are possible in a tetragonal complex: $d_{xz},d_{yz} \longrightarrow d_{x^2-y^2}(\nu_1)$; $d_{xy} \longrightarrow d_{x^2-y^2}(\nu_2)$; and $d_{z^2} \longrightarrow d_{x^2-y^2}(\nu_3)$. The frequency of these transitions is strongly dependent upon the field experienced by the various *d* orbitals. The equatorial ligand-field strength is affected by the macrocyclic ligand structures, generally decreasing as the Cu–N bond lengths increase and as the displacements of copper and nitrogen atoms from the CuN_4 plane increase. The Cu–N bond lengths increase in the order $[CuL^1]^{2+}$, $[CuL^2]^{2+}$ <

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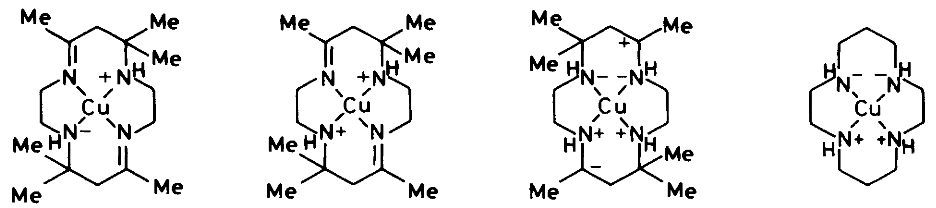
† *Supplementary data available* (No. SUP 56570, 7 pp.): Gaussian analyses of electronic spectra. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx.



$[CuL^1]^{2+}$ $[CuL^2]^{2+}$ $[CuL^3]^{2+}$ (red form) $[CuL^4]^{2+}$

Figure. Configurations of the asymmetric centres of the complexes. A plus sign indicates that the hydrogen atom of the centre is above the plane of the macrocycle, and a minus sign that it is below

Table. Absorption bands of copper(II) macrocyclic complexes dissolved in various solvents at 25.0 °C*

Complex	Solvent	ν_1	$\varepsilon_{1,\max.}$	$\delta_{1,1/2}$	ν_2	$\varepsilon_{2,\max.}$	$\delta_{2,1/2}$	ν_3	$\varepsilon_{3,\max.}$	$\delta_{3,1/2}$
$[CuL^1]^{2+}$	Water	20 200	76	1 530	18 720	45	1 310	17 010	17	1 850
	MeOH	20 100	82	1 650	18 700	46	1 330	16 760	19	1 795
	dmf	19 880	86	1 480	18 680	48	1 340	16 450	21	1 640
	dmso	19 500	90	1 480	18 660	50	1 400	16 100	24	1 460
$[CuL^2]^{2+}$	Water	20 150	75	1 560	18 520	49	1 250	16 890	14	1 420
	MeOH	20 050	79	1 610	18 500	51	1 250	16 670	16	1 370
	dmf	19 800	80	1 520	18 480	53	1 280	16 390	18	1 370
	dmso	19 470	84	1 600	18 470	56	1 270	16 040	20	1 570
$[CuL^4]^{2+}$	Water	20 070	55.0	1 375	18 470	32.0	1 035	16 810	14.2	1 250
	MeOH	19 970	56.5	1 540	18 460	33.5	1 165	16 630	15.4	1 455
	dmf	19 760	60.8	1 625	18 440	39.0	1 335	16 340	17.0	1 580
	dmso	19 440	66.0	1 580	18 430	42.0	1 250	16 020	18.5	1 300
$[CuL^3]^{2+}$	Water	20 000	75	2 100	18 420	51.6	1 510	16 720	23.8	2 900
(red)	MeOH	19 900	76.2	2 670	18 410	53.1	1 525	16 600	25.9	2 580
	dmf	19 720	78.7	2 310	18 390	56.7	1 620	16 300	31.5	2 045
	dmso	19 400	80.1	1 945	18 380	58.1	1 640	16 000	37.5	2 070

* All frequencies and half-widths given in cm^{-1}; $\delta_{i,1/2}$ = half-width at $\varepsilon = \varepsilon_{\max.}/2$ for the band *i*; $\varepsilon_{i,\max.}$ given in $dm^3 mol^{-1} cm^{-1}$.

$[CuL^4]^{2+} < [CuL^3]^{2+}$ (red form);[7-10] the displacements of copper and nitrogen from the CuN_4 plane increase in the order $[CuL^1]^{2+} < [CuL^2]^{2+}$, $[CuL^4]^{2+}$ and $[CuL^3]^{2+}$ (red).[7-10] Therefore, the equatorial ligand-field strength is expected to decrease in the order $[CuL^1]^{2+} > [CuL^2]^{2+} > [CuL^4]^{2+} > [CuL^3]^{2+}$ (red). The sequence of the position of the band maximum is the same, lending support to this view. The axial ligand-field strength is affected by the donor abilities of the co-ordinating solvents.[15] The donor number of these solvents decreases in the order dmso > dmf > MeOH > water,[16] suggesting a decrease in axial field strength in the same order.

All of the *d*-orbital levels are affected by the equatorial ligand-field strength. The largest effect is on the $d_{x^2-y^2}$ level which is raised in energy, so that the transition energies of these three bands increase with increasing equatorial field. As shown in the Table, for each solvent the frequency of each transition increases with equatorial field strength in the order $[CuL^3]^{2+}$(red) $< [CuL^4]^{2+} < [CuL^2]^{2+} < [CuL^1]^{2+}$.

The donor number of the co-ordinating solvent as defined by Gutmann[16] can be used as a measure of the axial ligand-field strength. The correlation between the frequency of the transition and the donor number of the solvent is quite good. Upon addition of solvent molecules along the *z* axis, the $d_{x^2-y^2}$ and d_{xy} orbital levels are equally perturbed, and thus the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition energy is virtually unaffected or very slightly affected by axial ligation. The largest effect is on the d_{z^2} level which is raised in energy, so that the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition energy decreases with increasing axial field strength. A smaller shift to lower energy is expected for the $d_{xz},d_{yz} \longrightarrow d_{x^2-y^2}$ transition. The results listed in the Table substantiate these expectations.

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