A Crystallographic Study of a Red and a Blue Complex of Copper(II) formed with Different Geometric Isomers of a Reinforced Macrocycle†

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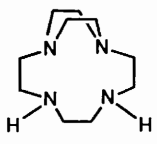
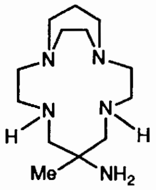
Two complexes of copper(II), one red and one blue, with the macrocyclic ligand L^3, have been prepared (L^3 occurs as both the *syn* and *anti* form of 6-methyl-6-nitro-1,4,8,11-tetraazabicyclo-[9,3,2]hexadecane). A structural study of the two complexes shows the blue one to be [CuL^3(NO$_3$)]ClO$_4$ and the red one to be [CuL^3(H$_2$O)][ClO$_4$]$_2$. In the blue complex the nitro group on the ligand is *syn* to the ethylene part of the double bridge, while in the red complex it is *anti*. The structural study shows, further, that the co-ordination geometry around the copper is different in the two complexes: mean Cu–N distance (blue) 2.00 Å, (red) 1.99 Å; Cu–O to the axial oxygen 2.20 (blue), 2.34 Å (red); the copper atom lies out of the plane of the four N-donors by 0.34 (blue), 0.25 Å (red). The difference in colour is related to the difference in co-ordination geometry. The crystals of both complexes were orthorhombic, space group *Pnma*, with $Z = 4$. Other details: (red) $a = 18.683(2)$, $b = 8.897(1)$, $c = 13.558(2)$ Å and final conventional R factor of 0.0531; (blue) $a = 20.417(5)$, $b = 9.033(4)$, $c = 10.870(2)$ Å and R 0.0941.

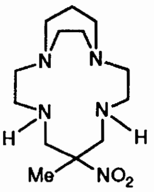
We have in the past concluded[1–5] that the saturated tetra-azamacrocycles are too flexible to show genuine size-match selectivity, and have accordingly synthesized a variety of *reinforced* macrocycles.[6–10] These reinforced macrocycles, the first examples of which were synthesised by Wainwright and Ramasubbu,[11,12] show much greater rigidity than do their non-reinforced analogues. This is seen in the considerable compression[6] of the square-planar nickel(II) ion by the ligand L^1, or very considerable stretching of the Cu–N bond in the complex of Cu^{II} with L^4.[10] The ligand-field strengths of the complexes of L^2 and L^3 with low-spin Ni^{II} were[9] higher than any previously reported, for low-spin Ni^{II} with four saturated nitrogen donors. This was attributed[9] to the near-exact fit of Ni^{II} into the cavity of the ligand, coupled with the tertiary nature of the nitrogen donors of the bridge. Ligands of the type L^2 have been synthesised by the template method of Lawrance and co-workers.[13] This is a synthetically attractive route to reinforced macrocycles. We used this route in order to synthesise the copper(II) complex of L^3 and obtained a mixture of red and blue crystals. The ligand L^7 gives red and blue crystals with Cu^{II},[14] and the reason for this has to date not been altogether satisfactorily resolved because of the difficulty of solving[14] the structure of the blue crystals. We report here the synthesis and a crystallographic study of the red and blue crystals of the complex of Cu^{II} with L^3.



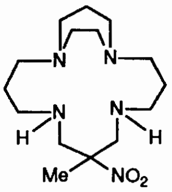
L^1



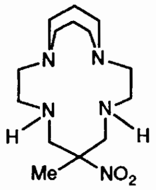
L^2



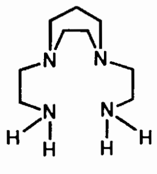
L^3



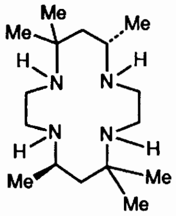
L^4



L^5



L^6



L^7

Experimental

Synthesis of the Complexes.—The ligand L^6 was synthesised as described previously.[15] The copper complexes of L^3 were synthesised using the nitroethane/formaldehyde route of Lawrance and co-workers.[13] This gave a mixture of red and blue crystals, which were separated manually: [CuL^3(H$_2$O)]-[ClO$_4$]$_2$ (red), UV/VIS (aqueous solution) $\lambda_{max} = 524$ nm, $\varepsilon = 343$ dm^3 mol^{-1} cm^{-1} (Found: C, 27.50; H, 5.10; N, 12.35. Calc. for $C_{13}H_{29}Cl_2CuN_5O_{11}$: C, 27.60; H, 5.15; N, 12.40%). [CuL^3(NO$_3$)]ClO$_4$ (blue), UV/VIS (aqueous solution) $\lambda_{max} = 524$ nm, $\varepsilon = 692$ dm^3 mol^{-1} cm^{-1} (Found: C, 30.70; H, 5.20; N, 16.20. Calc. for $C_{13}H_{27}ClCuN_6O_9$: C, 30.60; H, 5.35; N, 16.45%).

X-Ray Crystallographic Studies.—Crystals suitable for X-ray crystallography were selected from those obtained as described above for the blue and red complexes of Cu^{II} with L^3. The densities were determined by flotation in mixtures of chloroform and 1,2-dibromoethane. The data were collected at room

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Details of the crystallographic analysis of the complexes*

	$[CuL^3(H_2O)][ClO_4]_2$	$[CuL^3(NO_3)]ClO_4$
Formula	$C_{13}H_{29}Cl_2CuN_5O_{11}$	$C_{13}H_{27}ClCuN_6O_9$
M	565.85	510.39
Crystal colour	Red	Blue
a/Å	18.683(2)	20.417(5)
b/Å	8.897(1)	9.033(4)
c/Å	13.558(2)	10.870(2)
U/Å^3	2253.65	2004.72
D_c	1.67	1.69
D_m	1.66(2)	1.68(2)
μ/cm^{-1}	11.98	12.13
$F(000)$	1164	1052
Transmission coefficient (%)	94.8–99.8	85.7–99.7
Reflections measured	2390	2044
Unique reflections	2124	1879
Reflections used	1784 ($F > 3\sigma F_o$)	1236 ($F > 4\sigma F_o$)
Parameters refined	170	150
Maximum shift/e.s.d.	1.149	0.492
Maximum, minimum residual electron density (e Å^{-3})	1.01, −0.87	1.57, −0.83
R_{int}	0.0085	0.0000
Final R	0.0531	0.0941

* Details in common: orthorhombic, space group *Pnma* (no. 62); $Z = 4$; $1 < \theta < 25°$.

Table 2 Fractional coordinates ($\times 10^4$) for $[CuL^3(H_2O)][ClO_4]_2$ (red)

Atom	x	y	z
Cu	1 846.1(5)	2 500	11 024.5(6)
C(1)	4 380(5)	2 500	10 470(8)
C(2)	3 559(4)	2 500	10 480(6)
C(3)	3 299(3)	1 045(7)	10 967(5)
N(1)	2 520(2)	780(5)	10 886(3)
C(4)	2 264(4)	−318(6)	11 635(5)
C(5)	1 460(4)	−446(7)	11 554(5)
N(2)	1 138(2)	1 042(6)	11 567(3)
C(6)	459(4)	1 025(12)	10 985(6)
C(7)	47(6)	2 500	11 112(10)
C(8)	1 020(3)	1 618(6)	12 584(4)
N(3)	3 338(4)	2 500	9 394(5)
O(1)	3 262(3)	1 289(6)	8 989(3)
O(2)	1 629(4)	2 500	9 324(5)
Cl(1)	2 897(1)	2 500	3 982(1)
O(11)	2 291(2)	2 500	4 618(3)
O(12)	2 663(3)	2 500	2 982(2)
O(13)	3 315(2)	1 190(5)	4 162(3)
Cl(2)	5 485(1)	2 500	7 808(2)
O(21)	5 306(6)	2 500	6 762(4)
O(22)	6 260(2)	2 500	7 921(9)
O(23)	5 190(4)	1 156(8)	8 267(5)
O(24)	4 711(2)	2 500	7 925(11)
O(25)	5 821(7)	2 500	8 778(6)
O(26)	5 702(5)	1 156(9)	7 274(5)

Table 3 Fractional coordinates ($\times 10^4$) for $[CuL^3(NO_3)][ClO_4]$ (blue)

Atom	x	y	z
Cu	1 027.3(10)	2 500	1 464.4(19)
C(1)	736(8)	2 500	−1 867(15)
C(2)	1 483(8)	2 500	−1 447(15)
C(3)	1 676(6)	1 095(13)	−753(11)
N(1)	1 272(5)	831(10)	353(8)
C(4)	1 617(7)	−267(14)	1 188(11)
C(5)	1 219(8)	−404(14)	2 339(13)
N(2)	1 093(5)	1 075(12)	2 875(8)
C(6)	504(7)	1 087(18)	3 669(13)
C(7)	439(10)	2 500	4 395(20)
C(8)	1 677(6)	1 676(14)	3 568(11)
N(3)	1 918(10)	2 500	−2 555(17)
O(1)	1 712(16)	2 006(46)	−3 525(27)
O(2)	2 484(14)	2 118(55)	−2 395(31)
N(4)	−373(9)	2 500	733(20)
O(3)	20(10)	1 769(23)	1 067(18)
O(4)	−905(13)	2 500	350(22)
O(5)	−241(10)	950(24)	861(18)
Cl(1)	3 390(3)	2 500	11 092(5)
O(11)	3 258(11)	2 500	9 809(6)
O(12)	2 790(6)	2 500	11 753(18)
O(13)	3 757(4)	1 220(4)	11 404(12)
O(14)	3 716(38)	2 500	9 939(38)
O(15)	3 858(32)	2 500	12 056(55)
O(16)	2 989(4)	1 221(4)	11 187(47)

temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å). The cell dimensions were obtained from least-squares refinement of 25 high θ reflections. An ω–2θ scan mode was used with a scan width of $0.6 + 0.35 \tan \theta$ and a variable scan speed. Three standard reflections were monitored and showed no significant variation over the data collection. Lorentz polarization and absorption corrections were applied to the data according to the method of North *et al.*[16] Crystal data and data collection parameters are given in Table 1. The structures were determined by using Patterson and Fourier techniques with the program SHELX.[17] Unit weights were used for both refinements. The structure of the red complex refined smoothly and presented no problems. However, that of the blue complex showed very considerable disorder of the nitrate co-ordinated to the axial site of the copper and also of the nitro group on the macrocyclic ring. The refinement showed at least two nitrate and nitro orientations to be present, with site occupancy factors of 50% each. The two individual nitrates so resolved were not very satisfactory as far as bond angles and lengths are concerned, but this situation was not improved by considering more extensive disorder with more than two individual nitrates present. This poorly resolved disorder prevented refinement of the structure to an R factor lower than 0.094. Fractional atomic coordinates for the structures of the red and blue complexes are given in Tables 2 and 3, and bond lengths and angles in Tables 4 and 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Table 4 Bond lengths (Å) and angles (°) for $[CuL^3(H_2O)][ClO_4]_2$ (red)

Cu–N(1)	1.990(4)	Cu–N(2)	1.994(4)
Cu–O(2)	2.342(6)	C(1)–C(2)	1.534(12)
C(2)–C(3)	1.532(7)	C(2)–N(3)	1.529(10)
C(3)–N(1)	1.479(7)	N(1)–C(4)	1.488(7)
C(4)–C(5)	1.510(10)	C(5)–N(2)	1.454(8)
N(2)–C(6)	1.494(8)	N(2)–C(8)	1.487(7)
C(6)–C(7)	1.531(10)	C(8)–C(8′)	1.570(11)
N(3)–O(1)	1.217(5)	Cl(1)–O(11)	1.424(2)
Cl(1)–O(12)	1.424(2)	Cl(1)–O(13)	1.424(2)
Cl(2)–O(21)	1.457(3)	Cl(2)–O(22)	1.455(3)
Cl(2)–O(23)	1.456(3)	Cl(2)–O(24)	1.455(3)
Cl(2)–O(25)	1.457(3)	Cl(2)–O(26)	1.456(3)
N(1)–Cu–N(2)	87.4(2)	N(1)–Cu–N(1′)	100.5(3)
N(2)–Cu–N(2′)	81.2(3)	N(1)–Cu–N(2′)	162.7(3)
N(1)–Cu–O(2)	91.0(2)	N(2)–Cu–O(2)	104.4(2)
C(1)–C(2)–C(3)	108.7(4)	C(1)–C(2)–N(3)	105.2(7)
C(3)–C(2)–N(3)	109.3(4)	C(3)–C(2)–C(3′)	115.3(7)
C(2)–C(3)–N(1)	114.5(5)		
Cu–N(1)–C(3)	119.5(4)	Cu–N(1)–C(4)	103.7(3)
C(3)–N(1)–C(4)	111.7(5)		
N(1)–C(4)–C(5)	108.6(6)	C(4)–C(5)–N(2)	110.0(5)
Cu–N(2)–C(5)	108.2(4)	Cu–N(2)–C(6)	112.0(4)
C(5)–N(2)–C(6)	109.6(6)	Cu–N(2)–C(8)	102.5(3)
C(5)–N(2)–C(8)	112.8(5)	C(6)–N(2)–C(8)	111.6(5)
N(2)–C(6)–C(7)	111.0(7)	C(6)–C(7)–C(6′)	118.0(9)
N(2)–C(8)–C(8′)	110.2(5)		
C(2)–N(3)–O(1)	117.7(4)	O(1)–N(3)–O(1′)	124.6(8)
O(11)–Cl(1)–O(12)	109.4(1)	O(11)–Cl(1)–O(13)	109.4(1)
O(12)–Cl(1)–O(13)	109.4(1)	O(13)–Cl(1)–O(13′)	109.8(4)
O(21)–Cl(2)–O(22)	109.3(2)	O(21)–Cl(2)–O(23)	109.2(2)
O(22)–Cl(2)–O(23)	109.4(2)	O(23)–Cl(2)–O(23′)	110.4(7)
O(24)–Cl(2)–O(25)	109.3(2)	O(24)–Cl(2)–O(26)	109.4(2)
O(25)–Cl(2)–O(26)	109.2(2)	O(26)–Cl(2)–O(26′)	110.4(7)

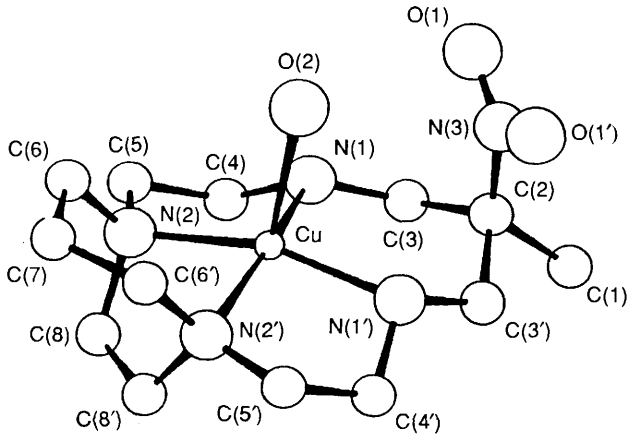


Fig. 1 PLUTO[18] drawing of the complex $[CuL^3(H_2O)][ClO_4]_2$ (red) showing the numbering scheme

Spectroscopy.—The electronic spectra of the copper(II) complexes of L^3 were recorded in aqueous solution on a Cary 2300 spectrophotometer.

Table 5 Bond lengths (Å) and angles (°) for $[CuL^3(NO_3)][ClO_4]$ (blue)

Cu–N(1)	1.995(9)	Cu–N(2)	2.007(10)
Cu–O(3)	2.20(2)	C(1)–C(2)	1.59(2)
C(2)–C(3)	1.528(14)	C(2)–N(3)	1.50(3)
C(3)–N(1)	1.478(14)	N(1)–C(4)	1.517(14)
C(4)–C(5)	1.50(2)	C(5)–N(2)	1.48(2)
N(2)–C(6)	1.48(2)	N(2)–C(8)	1.51(2)
C(6)–C(7)	1.51(2)	C(8)–C(8′)	1.49(3)
N(3)–O(1)	1.22(2)	N(3)–O(2)	1.22(2)
N(4)–O(3)	1.10(2)	N(4)–O(4)	1.16(3)
N(4)–O(5)	1.43(2)		
Cl(1)–O(11)	1.420(1)	Cl(1)–O(12)	1.420(1)
Cl(1)–O(13)	1.420(1)	Cl(1)–O(14)	1.420(1)
Cl(1)–O(15)	1.420(1)	Cl(1)–O(16)	1.420(1)
N(1)–Cu–N(2)	87.8(4)	N(1)–Cu–N(1′)	98.2(5)
N(2)–Cu–N(2′)	79.8(6)	N(1)–Cu–N(2′)	158.5(5)
N(1)–Cu–O(3)	83.6(6)	N(2)–Cu–O(3)	91.1(6)
O(3)–Cu–O(3′)	34.9(11)		
C(1)–C(2)–C(3)	112.8(9)	C(1)–C(2)–N(3)	109.7(14)
C(3)–C(2)–N(3)	104.2(10)	C(3)–C(2)–C(3′)	112.3(14)
C(2)–C(3)–N(1)	113.1(11)		
Cu–N(1)–C(3)	120.7(7)	Cu–N(1)–C(4)	104.4(7)
C(3)–N(1)–C(4)	109.4(9)		
N(1)–C(4)–C(5)	107.6(11)	C(4)–C(5)–N(2)	110.5(10)
Cu–N(2)–C(5)	106.8(7)	Cu–N(2)–C(6)	112.7(9)
C(5)–N(2)–C(6)	112.2(11)	Cu–N(2)–C(8)	101.7(7)
C(5)–N(2)–C(8)	112.5(11)	C(6)–N(2)–C(8)	110.4(10)
N(2)–C(6)–C(7)	112.5(13)	C(6)–C(7)–C(6′)	116(2)
N(2)–C(8)–C(8′)	111.1(5)		
C(2)–N(3)–O(1)	120(2)	C(2)–N(3)–O(2)	117(2)
O(1)–N(3)–O(2′)	123(2)		
O(3)–N(4)–O(4)	143.0(12)	O(3)–N(4)–O(5)	41.0(11)
O(4)–N(4)–O(5)	102.1(12)	O(3)–N(4)–O(3′)	73.6(13)
O(5)–N(4)–O(5′)	156(2)		
Cu–O(3)–N(4)	125(2)	Cu–O(3)–O(5)	144(2)
N(4)–O(3)–O(5)	89(2)		
N(4)–O(5)–O(3)	50(2)		
O(11)–Cl(1)–O(12)	109.5(1)	O(11)–Cl(1)–O(13)	109.5(1)
O(12)–Cl(1)–O(13)	109.6(1)	O(13)–Cl(1)–O(13′)	109.1(4)
O(14)–Cl(1)–O(15)	109.6(1)	O(14)–Cl(1)–O(16)	109.6(1)
O(15)–Cl(1)–O(16)	109.6(1)	O(16)–Cl(1)–O(16′)	109.0(4)

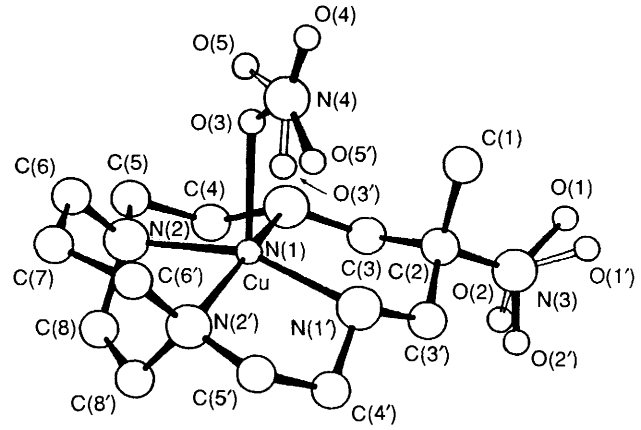
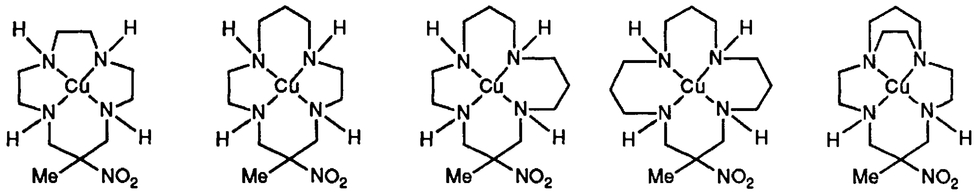


Fig. 2 PLUTO[18] drawing of the complex $[CuL^3(NO_3)][ClO_4]$ (blue) showing the numbering scheme

Results and Discussion

Drawings of the structures of the complexes $[CuL^3(H_2O)][ClO_4]_2$ (red) and $[CuL^3(NO_3)]ClO_4$ (blue) executed with the program PLUTO[18] are seen in Figs. 1 and 2. The red complex has the nitro group of the macrocyclic ligand *anti* to the ethylene part of the homopiperazine bridge of the ligand, while in the blue complex it is *syn* to it. This is probably not the cause of the colour difference, however. On dissolution in aqueous solution the two complexes are of identical colour and have similar electronic spectra. One assumes that in aqueous solution the nitrate ligand on the axial site of the blue complex in the solid state, which is usually weakly co-ordinated to copper(II), dissociates from the complex and is replaced by a water molecule. However, the crystallographic studies presented here show the bond lengths to the Cu^{II} to be rather different in the two structures. Thus, even allowing for the uncertainties introduced by the disorder of the axial nitrate in the blue complex, it seems that the Cu–O bond length in the blue complex (2.20 Å) is considerably shorter than Cu–O in the red



best-fit M–N length (Å):	1.91	2.07	2.22	2.38	1.91
v(d–d) (cm^{-1}):	18870	19570	17480	16560	19080

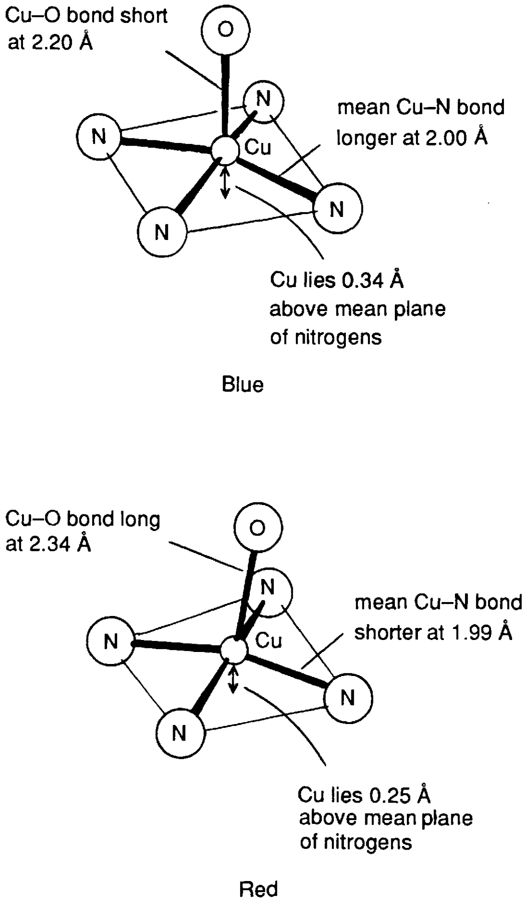


Fig. 3 Drawing of the co-ordination spheres of the red $[CuL^3(H_2O)]^{2+}$ and blue $[CuL^3(NO_3)]^+$ complex cations indicating the differences in co-ordination geometry

complex (2.34 Å). It is usually observed[19] that co-ordination of ligands of higher ligand-field strength to the axial co-ordination site causes a shift of the d–d band to lower energy, as seen in $[Cu(NH_3)_4(H_2O)_2]^{2+}$ [v(d–d) 16 670 cm^{-1}] relative to $[Cu(NH_3)_5(H_2O)]^{2+}$ [v(d–d) 15 600 cm^{-1}]. It thus seems likely that the axial nitrate in the blue complex with its shorter Cu–O bond is exerting a higher ligand-field strength than the axial water in the red complex. Thus, co-ordination of nitrate to the axial site of the blue complex causes a shift of v(d–d) to lower energies than in the red complex where a water molecule occupies the axial site. Supporting this idea is the observation that (Tables 4 and 5) the mean Cu–N bond lengths in the red complex are slightly shorter than those of the blue complex. In addition, the Cu atom in the blue complex is 0.34 Å out of the mean plane of the nitrogen donors, whereas that in the red complex is only 0.25 Å out of the plane. The crystallographic study thus suggests that the difference in colour in the solid state arises from differences in co-ordination geometry, with relatively shorter axial Cu–O bond lengths and longer Cu–N bond lengths in the plane in the blue as compared to the red complex, with the copper also lying further out of the plane of the nitrogen donors in the blue as compared to the red complex. This is summarized in Fig. 3.

A puzzle is the origin of the nitrate co-ordinated to the blue complex. No nitrate was added to the reaction mixture at any stage, and one can only conclude that it originated in decomposition of some of the nitroethane. The preferential co-ordination of nitrate to the blue form of the complex may relate to steric effects. In the blue form the nitro group of the ligand lies away from the axial co-ordination site, and so there may be more room to accommodate the bulkier nitrate anion. In the red form the nitro group of the ligand lies adjacent to the axial co-ordination site, so that co-ordination of the smaller water molecule as compared to a bulky nitrate may be favoured here.

A point of interest here is how well the ligand L^3 fits the Cu^{II}. With Ni^{II} this ligand produces an extremely high ligand field,[9] which we have attributed to the presence of tertiary nitrogen donors on the ligand in a sterically efficient environment. If the ligand-field strengths for Cu^{II} in a variety of complexes of tetraazamacrocycles in aqueous solution are compared it is seen that for $[CuL^3]^{2+}$ this is not particularly high.

It would seem that the cavity in L^3 is a little small for copper(II), and that the copper is accommodated lying out of the plane of the donor atoms of the ligand. This is in accord with molecular mechanics calculations on L^3 complexes which suggest[9] that the best-fit M–N length for co-ordination to this ligand is 1.91 Å, as compared to the strain-free Cu–N bond length for square-pyramidal Cu^{II} of about 2.03 Å. A better fit for Cu^{II} would be with the ligand L^5, which we are currently attempting to synthesise in the hope of obtaining very high ligand-field strengths for Cu^{II}.

With regard to the red and blue forms of L^7, previous workers[14] were able to obtain an *R* factor of only 0.22 for the blue form, so that its structure was not determined with any certainty. We have examined[20] the blue crystals formed from copper(II) perchlorate and L^7, $[CuL^7][ClO_4]_2$, and found that the reason for the problems with the crystallography lies in the fact that the crystals are undergoing a slow solid-state isomerization to a form of the red complex crystallographically distinct from that reported previously.[14] The evidence suggests, however, that the blue form has an oxygen occupying the axial co-ordination site, whereas the red form is effectively square planar, accounting for the colour difference.

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