An *X*-Ray Structural and Thermodynamic Investigation of the Blue and Red Forms of (C-*meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradecane)copper(II) Perchlorate

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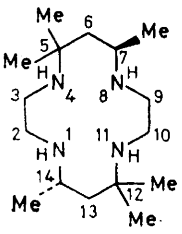
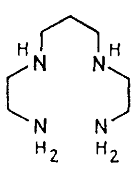
Copper(II) forms two products with C-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (L^1), a red and a blue complex. The crystal structures of both complexes (as perchlorates) have been determined. The red complex [Monoclinic, space group $P2_1/c$, a = 8.47(1), b = 9.26(1), c = 16.61(2) Å, β = 112.3(3)°] has been solved by heavy-atom methods and refined to R = 0.048. It contains tetragonally distorted octahedral coordination for the copper atom (Cu–N 2.02, 2.06; Cu–O 2.59 Å). The blue complex [Monoclinic, $P2_1$, a = 8.71(1), b = 15.68(2), c = 9.44(1) Å, β = 107.98(2)°] is pseudosymmetric and could not be completely refined (R = 0.22). It is likely that it is also octahedral, the main difference from the red complex being the inversion of the chiral nitrogen atom at N(8). The enthalpy difference between the two complexes has been determined (14.9 kJ mol^{-1}) and compared to the difference in stability constants. Thermodynamic, conductimetric, and spectral data are considered in the light of the likely structures for both complexes.

THE ' macrocyclic effect ' was first reported by Cabbiness and Margerum in 1969 [1] who noted the extra stability of metal complexes involving macrocyclic ligands over those with non-cyclic counterparts. Considerable attention has been focused on this area since that time by several groups to probe the thermodynamic origins of the extra stability.[2-5]

In the original communication,[1] the authors reported stability-constant data for copper(II) complexes with the macrocyclic ligand (I) C-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (L^1) and the non-cyclic counterpart (II) 3,7-diazanonane-1,9-diamine (L^2), in which the ring sequence is the same. They further noted that Cu^{II} forms two complexes with L^1, a blue form stable in acid solutions (log K 20) and a thermodynamically more stable red form (log K 28) into which the blue form can be converted at high pH. With L^2 only one complex is formed (log K 23.9). No suggestions were made as to the nature of these complexes, although subsequently the red form has been assumed to contain a symmetrical CuN_4 plane [6] whilst the blue form has been speculatively described as ' folded ' [7,8] or pyramidal.[7,9] In view of the historic importance of these complexes and the large free-energy difference between the red and blue forms (46 kJ mol^{-1}), we decided to attempt to characterise them more fully by a crystal-structure determination of the perchlorates and by related solution studies.



(L^1)



(L^2)

EXPERIMENTAL

Reagents.—The ligand C-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane dihydrate ($L^1\cdot 2H_2O$) was prepared as described by Hay *et al.*[10]

$[CuL^1][ClO_4]_2$, *Red complex*. The ligand $L^1\cdot 2H_2O$ (0.2 g, 0.62 mmol) and copper(II) acetate (0.12 g, 0.62 mmol) were dissolved in ethanol (12 cm^3) by heating on a water-bath. To this solution was added sodium perchlorate (0.3 g, 2.5 mmol) dissolved in ethanol (5 cm^3) and the resulting solution was covered and allowed to stand. Very well formed maroon crystals were slowly formed over a few days and were filtered off, washed with ethanol, and dried *in vacuo* over K[OH] pellets, yield 0.3 g (Found: C, 35.2; H, 6.70; N, 9.95. Calc. for $C_{16}H_{36}Cl_2CuN_4O_8$: C, 35.15; H, 6.65; N, 10.25%).

$[CuL^1][ClO_4]_2$ *Blue complex*. A solution of $L^1\cdot 2H_2O$ (0.2 g, 0.62 mmol) in methanol (10 cm^3) was added slowly to a solution of copper(II) perchlorate hexahydrate (0.74 g, 2.0 mmol) in aqueous methanol (8 cm^3, 1 : 1). The intense blue solution was allowed to evaporate slowly when large very dark blue crystals separated. These were filtered off and recrystallised from the minimum quantity of aqueous methanol (1 : 1), yield 0.12 g (Found: C, 35.7; H, 6.65; N, 10.15. Calc. for $C_{16}H_{36}Cl_2CuN_4O_8$: C, 35.15; H, 6.65; N, 10.25%).

Crystal Structure Determinations.—(*a*) *Of* $[CuL^1][ClO_4]_2$, *red complex*. Deep red crystals (recrystallised from ethanol) were examined by precession and oscillation photography.

Crystal data. Monoclinic, a = 8.47(1), b = 9.26(1), c = 16.61(2) Å, β = 112.3(3)°, U = 1 204.5 Å^3, space group $P2_1/c$, D_m = 1.512, Z = 2, D_c = 1.507 g cm^{-3}, $F(000)$ = 570, crystal size *ca.* 0.4 × 0.35 × 0.2 mm, graphite-monochromated Mo-K_α radiation (λ 0.710 69 Å), μ = 11.09 cm^{-1}.

Reflection data were collected on a Stoe STADI-2 diffractometer for layers $h0$—$10l$, with $\theta_{max.}$ = 27.5° on $h0l$; of 2 548 data, 2 021 had $I > 3\sigma(I)$ and these were used in calculations. Lorentz and polarisation corrections (but none for absorption) were applied. The structure was solved by standard Patterson and Fourier techniques. Refinement was by full-matrix least squares, and in later cycles non-hydrogen atoms were given anisotropic temperature factors and a weighting scheme was used. Hydrogen atoms were placed in calculated positions and their positional parameters refined with fixed isotropic temperature factors; the N–H distance was constrained to 1.01 Å. Refinement converged at R 0.048 3 (R' 0.050 3).

Atomic positions are given in Table 1 and bond distances and angles in Tables 2 and 3. Structure factors and thermal parameters are listed in Supplementary Publication No.

TABLE 1

Fractional co-ordinates ($\times 10^4$) for the red isomer of $[CuL^1][ClO_4]_2$, with estimated standard deviations in parentheses (crystallographic numbering)

	x/*a*	*y*/*b*	*z*/*c*
Cu(1)	10 000	5 000	5 000
Cl(1)	3 297(1)	2 826(1)	4 570(1)
O(1)	1 889(5)	3 808(5)	4 268(3)
O(2)	4 133(5)	2 790(7)	3 996(2)
O(3)	4 405(6)	3 317(6)	5 394(3)
O(4)	2 565(8)	1 499(5)	4 672(6)
N(1)	7 884(3)	4 397(3)	3 980(2)
N(2)	9 972(4)	2 936(3)	5 462(2)
C(1)	8 267(5)	2 314(4)	4 932(2)
C(2)	7 832(5)	2 774(4)	3 999(2)
C(3)	7 659(5)	4 985(4)	3 100(2)
C(4)	5 989(6)	4 458(6)	2 404(3)
C(5)	7 686(5)	6 642(4)	3 127(2)
C(6)	10 594(5)	2 600(4)	6 414(2)
C(7)	10 914(7)	952(4)	6 553(3)
C(8)	9 283(6)	3 076(5)	6 794(3)
H(1)	8 311	1 151	4 980
H(2)	7 318	2 724	5 161
H(3)	6 577	2 390	3 592
H(4)	8 765	2 340	3 766
H(5)	8 706	4 592	2 941
H(6)	4 982	4 886	2 584
H(7)	5 866	3 298	2 341
H(8)	5 896	4 919	1 790
H(9)	6 858	6 971	3 454
H(10)	7 710	7 021	2 463
H(11)	11 167	674	7 222
H(12)	11 994	651	6 394
H(13)	9 792	382	6 131
H(14)	9 902	2 877	7 484
H(15)	8 184	2 379	6 z24
H(16)	8 879	4 190	6 687
H(17)	6 873	4 815	4 078
H(18)	10 786	2 335	5 294

Hydrogen-atom positions are calculated such that C–H 1.08, N–H 1.01 Å.

TABLE 2

Bond distances (Å) in the red isomer of $[CuL^1][ClO_4]_2$

Cu(1)–N(1)	2.022(2)	C(3)–C(5)	1.535(5)
Cu(1)–N(2)	2.063(3)	C(5)–C(6)	1.533(5)
Cu(1)–O(1)	2.594(5)	C(6)–C(7)	1.522(5)
N(1)–C(2)	1.504(4)	C(6)–C(8)	1.535(7)
N(1)–C(3)	1.502(5)	Cl(1)–O(1)	1.430(4)
N(2)–O(1)	1.492(4)	Cl(1)–O(2)	1.388(5)
N(2)–C(6)	1.497(5)	Cl(1)–O(3)	1.409(4)
C(1)–C(2)	1.511(6)	Cl(1)–O(4)	1.415(6)
C(3)–C(4)	1.527(5)		

TABLE 3

Bond angles (°) in the red isomer of $[CuL^1][ClO_4]_2$

N(1)–Cu(1)–O(1)	89.9(1)	C(3)–C(5)–C(6′)	118.2(3)
N(2)–Cu(1)–O(1)	82.9(1)	N(2)–C(6)–C(5′)	108.5(3)
N(1)–Cu(1)–N(2)	85.7(1)	N(2)–C(6)–C(7)	109.4(3)
Cu(1)–N(1)–C(2)	106.4(2)	N(2)–C(6)–C(8)	110.8(3)
Cu(1)–N(1)–C(3)	117.4(2)	C(5′)–C(6)–C(7)	107.3(3)
C(2)–N(1)–C(3)	112.9(3)	C(5′)–C(6)–C(8)	111.3(4)
Cu(1)–N(2)–C(1)	106.4(2)	C(7)–C(6)–C(8)	109.5(4)
Cu(1)–N(2)–C(6)	122.4(2)	O(1)–Cl(1)–O(2)	110.4(3)
C(1)–N(2)–C(6)	114.7(3)	O(1)–Cl(1)–O(3)	107.1(3)
N(2)–C(1)–C(2)	107.6(3)	O(1)–Cl(1)–O(4)	104.5(3)
N(1)–C(2)–C(1)	107.7(3)	O(2)–Cl(1)–O(3)	110.5(3)
N(1)–C(3)–C(4)	111.1(3)	O(2)–Cl(1)–O(4)	114.9(5)
N(1)–C(3)–C(5)	109.8(3)	O(3)–Cl(1)–O(4)	109.0(4)
C(4)–C(3)–C(5)	109.9(3)	Cl(1)–O(1)–Cu(1)	133.3(3)

SUP 22494 (14 pp.).* All calculations were carried out on the University of Stirling ICL 4130 with SHELX-76.[11]

(*b*) *Of* $[CuL^1][ClO_4]_2$, *blue complex*. Preliminary precession and Weissenberg photography showed the crystal to be monoclinic, apparently in space group $P2_1/a$. However, an overexposed *h*0*l* photograph showed very faint reflections for $h = 2n + 1$ and since the only definitely absent reflections were 0*k*0, $k = 2n + 1$, the space group is $P2_1$, but with pseudo-symmetry corresponding to $P2_1/a$.

Crystal data. Monoclinic, $a = 8.71(1)$, $b = 15.68(2)$, $c = 9.44(1)$ Å, $\beta = 107.98(2)°$, $U = 1\,240.1$ Å^3, space group $P2_1$, $D_m = 1.476$, $Z = 2$, $D_c = 1.465$ g cm^{-3}, $F(000) = 570$, graphite-monochromated Mo-K_α radiation (λ 0.710 69 Å), $\mu = 10.78$ cm^{-1}.

1 567 Reflection data were collected on a Stoe STADI-2 two-circle diffractometer for layers 0—8*kl* with $3 < \theta < 22.5°$. There were 1 399 data with $I > 3\sigma(I)$ including most of the weak *h*0*l* reflections. Data were corrected for Lorentz and polarisation effects but not for absorption.

The weak *h*0*l* reflections show that the structure has a pseudo-centre of symmetry which must be near the copper atom. The Patterson function was solved in terms of the centrosymmetric arrangement: Cu (0.25, 0, 0) and two Cl at (0.42, 0.40, 0.15), (0.08, −0.40, −0.15). A Fourier synthesis was calculated phased on Cu and only one Cl in an attempt to break the pseudo-symmetry. Besides a peak at the second Cl position, peaks corresponding to most of the light atoms were found in the expected positions for a nearly centrosymmetric macrocyclic complex. A second Fourier synthesis and two cycles of full-matrix least squares with unit weights led to an *R* of 0.22 for a structure with all the atoms of the macrocycle and six of the eight perchlorate oxygen atoms. Atomic positions for this structure are given (without estimated standard deviations) in Table 4. However, all attempts to refine this structure further failed.

TABLE 4

Fractional co-ordinates ($\times 10^4$) for the blue isomer of $[CuL^1][ClO_4]_2$ at *R* 0.22. Two oxygen atoms are unlocated (crystallographic numbering)

	x/*a*	*y*/*b*	*z*/*c*
Cu	12 391	0	35
Cl(1)	9 257	956	1 519
Cl(2)	4 278	3 875	1 469
O(1)	8 888	592	2 497
O(2)	10 327	1 394	2 215
O(3)	8 400	1 293	386
O(4)	10 016	475	711
O(5)	3 045	3 606	546
O(6)	5 640	3 273	2 147
N(1)	11 247	−816	−1 620
N(2)	12 630	804	−1 411
N(3)	14 502	734	1 421
N(4)	13 001	−1 018	1 279
C(1)	10 686	−526	−3 039
C(2)	9 932	347	−3 472
C(3)	11 412	1 078	−2 849
C(4)	13 559	1 574	−621
C(5)	13 747	1 408	1 084
C(6)	14 421	579	3 195
C(7)	14 963	−393	3 157
C(8)	13 760	−1 055	2 971
C(9)	11 101	−1 593	713
C(10)	10 743	−1 634	−1 091
C(11)	9 283	−1 235	−4 073
C(12)	10 281	1 861	−3 286
C(13)	12 469	1 014	−3 816
C(14)	15 610	994	4 198
C(15)	14 400	−2 051	2 618
C(16)	12 667	−1 330	3 974

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

Calorimetry.—Calorimetric measurements were carried out in an LKB Batch Microcalorimeter (10 700—2) fitted with gold reaction cells. The thermal output was amplified by a KEITHLEY 150B microvolt amplifier and recorded on a Philips Integrating Recorder, from which the areas under the heat curves were directly obtained. The calorimeter was calibrated electrically and the absolute accuracy was checked by determining the enthalpy of formation of water (-55.2 kJ mol^{-1}).

A solution of the blue complex (0.002 mol dm^{-3}) was made up in HCl (0.001 mol dm^{-3}) in order to prevent the gradual change to the more thermodynamically stable red form. In the calorimeter 2 cm^3 of this solution was mixed with 1 cm^3 of 0.01 mol dm^{-3} Na[OH] solution. The heat liberated by the neutralisation of the acid was calculated and subtracted from the total heat output, together with a dilution correction, leaving the heat associated with the reaction $[CuL^1]^{2+}$ (blue) $\longrightarrow$ $[CuL^1]^{2+}$ (red). On completion of the reaction, the visible spectrum of the solution remaining in the calorimeter was determined. This confirmed that 100% conversion into the red complex had taken place, from both the total disappearance of the band with $\lambda_{max.}$ 636 nm and from the magnitude of the absorbance of the new band with $\lambda_{max.}$ 515 nm, associated with the red complex.

All solutions were made up by weight and introduced into the two halves of the calorimeter cells by means of a weighed syringe. The calorimeter results are given in detail in Table 5.

Spectral and Other Measurements.—Conductivity measurements were made using a Portland P335 conductivity bridge (Table 6), visible spectra were recorded on a Perkin-Elmer 402 spectrophotometer ($\lambda_{max.}$ values in Table 7), and i.r. spectra on a Perkin-Elmer 577 spectrophotometer.

TABLE 5

Calorimetric results for the reaction

$[CuL^1]^{2+}$ (blue) $\longrightarrow$ $[CuL^1]^{2+}$ (red)

	Amount/mmol		Heat liberated (J)			
Experiment	Complex	HCl	Total	Due to acid	Dilution correction	ΔH/kJ mol^{-1}
(1)	0.003 621	0.001 939	0.162 3	0.108 5	0.000 4	-14.74
(2)	0.003 687	0.001 975	0.164 6	0.110 5	0.000 4	-14.56
(3)	0.003 734	0.001 967	0.168 1	0.110 0	0.000 4	-15.45
(4)	0.003 688	0.001 943	0.164 4	0.108 7	0.000 4	-14.99
					Mean value	-14.9 ± 0.4

TABLE 6

Conductivity data (S cm^2 mol^{-1}) for $[CuL^1][ClO_4]_2$ in various solvents

	Solvent			
Compound	Water	$MeNO_2$	$CHCl_3$	CH_2Cl_2
$[CuL^1][ClO_4]_2$ (red)	208	96	insoluble	insoluble
(blue)	214	93	0	0.21
$Cu[ClO_4]_2 \cdot 6H_2O$	254	170		
$[NBu^n_4][ClO_4]$			0.419	22.1

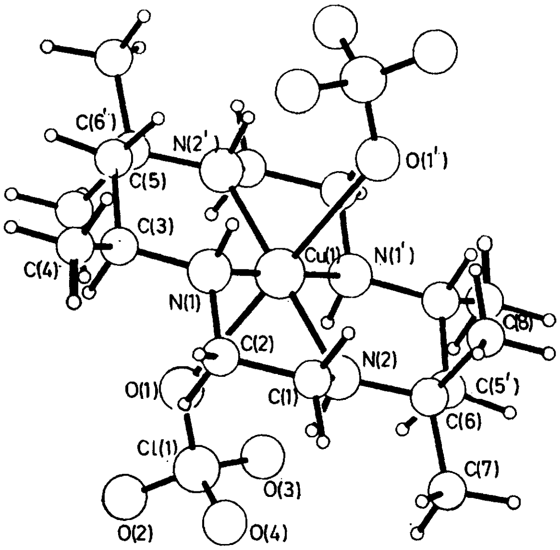
TABLE 7

Electronic spectra of $[CuL^1][ClO_4]_2$ complexes

	$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})			
Complex	Solid	Water	$MeNO_2$	$CHCl_3$
$[CuL^1][ClO_4]_2$ (red)	510	515 (146)	500	
(blue)	586	636 (174)	566	588

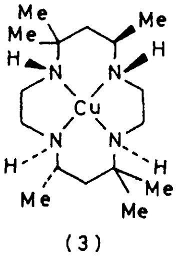
DISCUSSION

The structure of the red complex in the crystal is shown in the Figure, where it can be seen that the co-ordination about copper is a centrosymmetric tetragonally distorted octahedron. The stereochemistry of the complex corresponds to (3) [structure (16) of ref. 12] which is the most stable of the ten possible. The geometry is unremarkable and is virtually identical with that of (5) which differs only in the position of one methyl group and has chair forms for the six-membered rings and *gauche* for the five-membered rings.[13] The axial Cu–O lengths [2.594(5) Å] reflect the tendency of the structure to form a neutral complex (or a strong ion pair) in non-polar solvents.

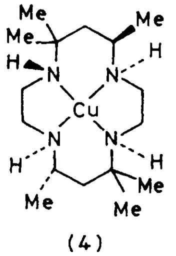


View of the red complex $[Cu^1][ClO_4]_2$ showing the crystallographic atom numbering scheme

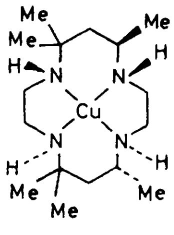
Despite the failure to satisfactorily refine the structure of the blue complex, it seems certain that the gross geometry is an approximately tetragonally distorted, octahedrally co-ordinated, copper with the macrocycle equatorial and perchlorates axial. Folded structures such as those found in (6) [14] and (7) [12] are definitely excluded. It is also very likely that the blue complex cannot have a centre of symmetry (or the structure would relax into $P2_1/a$) and that it must be a diastereoisomer of the red complex with one (or possibly more) of the nitrogen atoms having a different configuration.



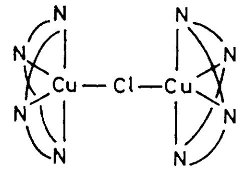
(3)
red complex



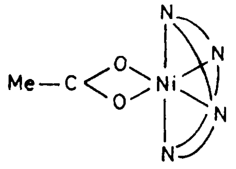
(4)
blue complex



(5)



(6)



(7)

Since some of the nitrogen-atom positions are not very well defined, models of the six different non-centrosymmetric diastereoisomers [12] were compared with the positions of Table 3 and one (4) [structure (13) of ref. 12] was found to fit much better than the others. Unfortunately, the refinement was too unstable (even with the use of distance and angle constraints) to gain any clearer picture of the exact structure of the molecule. The co-ordination of the copper also appears to be somewhat irregular with the metal slightly out of the plane of the N atoms and with one Cu · · · O bond (to the perchlorate) shorter than the other. However, the exact amount of distortion was very sensitive to the details of the refinement and it is impossible to say whether it is large enough to produce any change in the spectrum of the complex or to favour 1 : 1 or 1 : 2 ion pairing with the perchlorates. For this reason, no bond lengths and angles are given for the blue complex.

It seems that the essential difference between the structures of the red and blue complexes is the inversion of the nitrogen at N(8) * and although it is surprising that such a small change in geometry should cause such a dramatic change in spectral properties there is no evidence that the co-ordination around copper in the blue complex is very different from that in the red complex, although there may well be some distortions introduced by the ligand conformation. This difference in stereochemistry at a chiral nitrogen centre is supported by the kinetics for the blue ⟶ red conversion, following a rate law, Rate = $k[(CuL^1)^{2+}(\text{blue})][OH^-]$.[15,16] Despite a previous report on the blue complex occurring as a monohydrate,[16] all our analytical results, the density, and i.r. spectrum in CH_2Cl_2 solution are consistent with an anhydrous complex.

Conductivity data (Table 5), in various solvents, show that in aqueous solution both the red and the blue complexes have molar conductances typical of 2 : 1 electrolytes suggesting that both $[ClO_4]^-$ ions, which are co-ordinated in the solid, have been replaced by solvent molecules. However, in less-polar solvents it seems that $[ClO_4]^-$ ions may still be co-ordinated. In nitromethane solutions both the red and the blue complexes appear to have lost one $[ClO_4]^-$ ion and have conductances typical of 1 : 1 electrolytes, whereas in weakly polar solvents such as $CHCl_3$ and CH_2Cl_2 the blue form is a non-electrolyte indicating that both $[ClO_4]^-$ ions may still be co-ordinated. The red complex is not soluble in $CHCl_3$ or CH_2Cl_2.

Visible spectra of the complexes were recorded in the solid and various solvents and $\lambda_{max.}$ values for the single broad band associated with the d^9 system are given in Table 5. The $\lambda_{max.}$ value of the band for the red complex is not strongly affected by ligand replacement, but for the blue large differences exist in different solvents. The value in $CHCl_3$, in which the blue complex is a non-electrolyte, is very close to the solid-state reflectance value. The less-symmetrical blue complex also has a slightly higher absorption coefficient in water, and a broader absorption band.

Infrared spectra (KBr discs) of both complexes indicate co-ordinated perchlorate by the presence of an intense band at 930 cm^{-1},[17] and *trans* co-ordination of the perchlorates by the presence of a single N–H stretching band at 3 205 cm^{-1}. In no case where a tetra-aza macrocyclic ligand is known to be folded, so that the four donor nitrogen atoms occupy *cis* positions, has a single N–H stretching frequency been reported.[18] However, this band in the spectrum of the blue complex is broader than that in the red and shows a slight shoulder at 3 260 cm^{-1}.

The calorimetric results (Table 4) show an overall enthalpy difference between the red and blue complexes of 14.9 kJ mol^{-1}. Originally, Cabbiness and Margerum reported log K values of 20 and 28 respectively [1] for the blue and red complexes which is equivalent to a free-energy difference of 45.7 kJ mol^{-1}. If these equilibrium data are correct they imply an entropy change of 103 J K^{-1} mol^{-1} for the conversion blue ⟶ red which is roughly equivalent to the entropy gain which would be associated with the release of between two and three ligand water molecules. This is difficult to reconcile with the slight structural difference between the two complexes in the solid [the inversion at N(8) *] and casts doubt on the accuracy of the equilibrium constants. Indeed, one might reasonably expect the entropy change associated with this conversion to be very small, making ΔH almost identical with ΔG. Further, with only a small structural difference between the red and blue complexes one would expect that the macrocyclic complex, even in the blue form, would be more stable than the equivalent complex with a non-cyclic ligand ($[CuL^2]^{2+}$; log K 23.9). It thus seems likely that it is the stability constant for the blue form which is in error. Unfortunately, due to the exceedingly low solubility of L^1, it is not possible to determine the enthalpy of formation of the copper complex by the established method.[4] It has recently been suggested that the linear relationship previously reported [19] for tetra-aza non-cyclic

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* Chemical numbering.

ligands between ΔH of the copper complexes and $\nu(d\text{–}d)$ can be extended to macrocyclic complexes,[4] provided the copper and four donor nitrogen atoms remain planar. Thus, one can make a reliable estimate of the enthalpy of formation of the red complex ($\lambda_{max.}$ 515 nm) of $\Delta H = 125$ kJ mol^{-1}. Further, the entropy change, ΔS, associated with the formation of copper macrocyclic complexes, has been shown, at least for non-substituted ligands containing 12—15-membered rings, to lie in the range 95—150 J K^{-1} mol^{-1}, and to decrease with increasing ring size. An estimate of 120 J K^{-1} mol^{-1} is appropriate for a 14-membered ring, giving rise to a free-energy term at 298 K of $\Delta G \simeq 160$ kJ mol^{-1} (log K 28) in excellent agreement with the experimental stability constant for the red complex. Using our value of ΔH for the blue-to-red conversion it is likely that the enthalpy of formation of the blue complex will be *ca.* -110 kJ mol^{-1} and log K *ca.* 25.5.

While our experimental enthalpy difference (14.9 kJ mol^{-1}) is smaller than the estimated difference between the two configurations according to Curtis[12] (36.4 kJ mol^{-1}), good agreement would have been fortuitous in view of the empirical nature of Curtis' method and the almost certain reduction in energy in the blue complex which will result from distortions away from the strictly planar CuN_4 model. It is nonetheless remarkable that what appears to be such a slight change in structure causes marked changes in spectra and solubility.

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