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LETTER

The crystal and molecular structure of a diprotonated planar pentadentate macrocyclic ligand obtained from the transient template condensation of 2,9-bis(α-methylhydrazino)-1,10-phenanthroline with 2,6-pyridinedialdehyde

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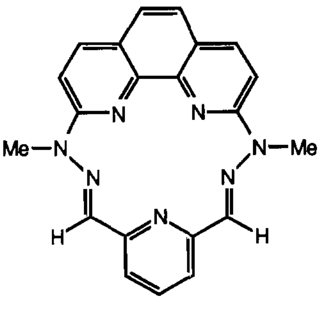
We have demonstrated that complexes of planar pentadentate macrocyclic ligands incorporating 2,2′-bipyridine [1–13], 1,10-phenanthroline [1, 3, 14–28], 2,2′:6′,2″-terpyridine [4, 29–34] or other heterocyclic moieties [35] may be prepared by the template condensation of suitable dicarbonyl compounds with bis(hydrazino)-substituted heterocyclic compounds. Template condensations are very satisfactory methods for the preparation of macrocyclic complexes, but are notoriously dependent upon the metal ion which is used to direct the reaction. More recently, we have demonstrated that a judicious choice of metal ion and reactants may allow the formation of metal-free macrocyclic ligands, and we have termed this process a transient template reaction [1, 3, 30, 31, 34]. The availability of the free macrocyclic ligands allows the preparation of a range of metal complexes with metal ions which are not effective as templates. To date, we have described the crystal and molecular structures of free macrocyclic ligands prepared by the transient template condensation of 6,6′-bis(α-hydroxyethylhydrazino)-2,2′-bipyridine with 2,6-pyridinedialdehyde [3] and of 6,6″-bis(α-methylhydrazino)-4′-phenyl-2,2′:6′,2″-terpyridine with glyoxal [30], and in this paper we wish to report the crystal and molecular structure of the macrocyclic ligand obtained from the transient template condensation of 2,9-bis(α-methylhydrazino)-1,10-phenanthroline with 2,6-pyridinedialdehyde. This structural determination provides the confirmation that the free macrocyclic ligands are obtained from transient template condensations involving all three of the α,α′-diimine moieties which we have investigated.

Experimental

2,9-Bis(α-methylhydrazino)-1,10-phenanthroline was prepared as described previously [3].

Preparation of [H_2L]Cl_2

2,6-Pyridinedialdehyde (0.405 g, 3 mmol) was added to a solution of 2,9-bis(α-methylhydrazino)-1,10-phenanthroline (0.804 g, 3 mmol) and [$Cr(H_2O)_4Cl_2$]$Cl\cdot 2H_2O$ in boiling water (500 cm^3), and the mixture heated to reflux for 3 h. After this period, the deep red solution was concentrated *in vacuo* to 50 cm^3 volume, and then cooled, when red needles of the salt [H_2L]$Cl_2\cdot H_2O$ separated. *Anal.* Found: C, 55.1; H, 4.5; N, 21.3; Cl, 15.5. Calc. for $C_{21}H_{21}Cl_2N_7O$: C, 55.0; H, 4.6; N, 21.4; Cl, 15.5%.



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X-ray crystallography of [H_2L][$FeCl_4$]$_2$

An orange–red rectangular block obtained by repeated recrystallisation of [H_2L]$Cl_2\cdot H_2O$ from water was mounted in a glass capillary. Space group and unit cell dimensions were derived from preliminary Weissenberg (Cu Kα) photography.

The crystal was mounted on a Stoe-AED four-circle diffractometer and accurate unit cell dimensions obtained from the angular measurements of 38 strong reflections in the range $30 < 2\theta < 40°$. Lorentz and polarisation effects were allowed for on the 4737 recorded intensity data in the range $5.0 < 2\theta < 120.0°$ and a numerical absorption correction was applied. The crystal was bound by the planes $\{001\}$, $\{00\bar{1}\}$, $\{011\}$, $\{0\bar{1}\bar{1}\}$, $\{01\bar{1}\}$, $\{0\bar{1}1\}$, $\{10\bar{1}\}$ and $\{\bar{1}01\}$. Transmission factors ranged from 0.7042 to 0.6077 for the full data set. Equivalent reflections were averaged leaving 3200 unique observed reflections with $F \geqslant 3\sigma(F)$. Pertinent crystallographic data

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are given in Table 1. Calculations were carried out using the program SHELX [36] on the University of Cambridge IBM 370/165 computer.

All the non-hydrogen atoms were located by direct methods followed by Fourier difference syntheses. Methyl and aromatic hydrogen atoms were placed in idealised positions 1.08 Å from the relevant carbon atom. The methyl groups were treated as rigid bodies and each type of hydrogen in the molecule was assigned a common isotropic thermal factor. The protons within the macrocyclic cavity were not located. The final difference Fourier map had no peaks larger than 0.69 e/Å^3. Positional parameters are presented in Table 2 and bond distances and bond angles are given in Table 3.

Results and discussion

The transient template condensation of 2,9-bis(α-hydrazino)-1,10-phenanthroline with 2,6-pyridinedialdehyde proceeded smoothly in aqueous conditions in the presence of $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ to yield a dark coloured solution containing the macrocyclic cation $[H_2L]^{2+}$. Concentration of this solution *in vacuo* followed by cooling resulted in the separation of long red needles of the salt $[H_2L]Cl_2 \cdot H_2O$. This same product was obtained when lithium chloride was substituted for chromium(III) chloride in the transient template reaction.

TALBE 1. Crystal data for $[H_2L][FeCl_4]_2$

Formula	$C_{21}H_{19}Cl_8Fe_2N_7$
Formula weight	764.75
Space group	$P2_1/n$
a (Å)	10.199(17)
b (Å)	11.688(16)
c (Å)	26.547(42)
β (°)	112.74(11)
V (Å^3)	2918.6
Z	4
$F(000)$	1528
D_{calc} (g/cm^3)	1.746
Crystal size (mm)	0.35 × 0.25 × 0.25
μ(Cu Kα) (cm^{-1})	147.96
Data collection instrument	Stoe AED
Radiation	Cu Kα ($\lambda = 1.5418$ Å)
Orientation reflections:	
no., range (2θ)	38, $30 < 2\theta < 40°$
Temperature (°C)	20
No. unique data	4737
Total with $F \geqslant 3\sigma(F)$	3200
R	0.0694
R'	0.0682
Weighting scheme	$w^{-} = 1.3469/[\sigma^2(F) + 0.001(F)^2]$
Largest peak (e/Å^3)	0.69

TABLE 2. Positional parameters ($\times 10^4$) and their e.s.d.s for $[H_2L][FeCl_4]_2$

	x	y	z
N(1)	3345(6)	4309(5)	1672(2)
C(1)	3670(8)	5145(6)	2051(3)
C(2)	4980(8)	5135(8)	2480(3)
C(3)	5935(9)	4264(8)	2498(3)
C(4)	5540(8)	3417(7)	2102(3)
C(5)	4235(8)	3434(6)	1693(3)
C(6)	3659(8)	2581(6)	1255(3)
N(2)	2434(6)	2780(5)	905(2)
N(3)	1761(6)	2085(5)	476(2)
C(7)	2418(9)	1028(6)	390(3)
N(4)	−31(6)	3383(5)	310(2)
C(8)	414(7)	2439(6)	150(3)
C(10)	−1844(8)	2321(7)	−615(3)
C(11)	2302(8)	3334(6)	−451(3)
C(12)	−1343(7)	3839(6)	21(3)
C(13)	−3652(8)	3880(7)	−716(3)
C(14)	3989(8)	4844(7)	−506(3)
C(15)	−3005(8)	5354(7)	−26(3)
C(16)	−1667(8)	4858(6)	239(3)
C(17)	−3225(9)	6361(7)	248(4)
C(18)	−2184(10)	6782(7)	714(4)
C(19)	−846(8)	6199(6)	939(3)
N(5)	−624(6)	5254(5)	703(2)
N(6)	285(7)	6561(5)	1395(3)
C(20)	281(12)	7581(7)	1727(4)
N(7)	1441(7)	5873(5)	1537(3)
C(21)	2582(9)	6008(6)	1966(3)
Fe(1)	7845(1)	6375(1)	4197
Cl(1)	5699(2)	5733(2)	4060(1)
Cl(2)	9187(2)	6303(2)	5066(1)
Cl(3)	7872(2)	8158(2)	3946(1)
Cl(4)	8717(2)	5315(2)	3721(1)
Fe(2)	175(1)	4123(1)	2557
Cl(5)	873(2)	3197(2)	1983(1)
Cl(6)	−1442(2)	5397(2)	2149(1)
Cl(7)	−612(2)	2835(2)	2975(1)
Cl(8)	2045(3)	4975(2)	3157(1)

The electron impact mass spectrum of the red crystalline salt exhibited a parent ion at *m/z* 367, and the partial elemental analysis (C, H, N, Cl) was fully in accord with the macrocyclic formulation. In order to confirm this, we determined the crystal and molecular structure of a salt of this cation.

The crystal and molecular structure of the macrocyclic cation is shown in Fig. 1, and bond lengths and angles are presented in Table 3. The crystal structural determination confirms the presence of the free macrocyclic ligand. The ligand is approximately planar, with the maximum deviation of any of the five nitrogen atoms N(1), N(2), N(4), N(5) and N(7) from the least-squares plane through them equal to 0.02 Å. The 1,10-phenanthroline and pyridine heterocyclic systems are each close to planar (maximum deviation of any atom from the least-squares

TABLE 3. Bond distances (Å) and bond angles (°) for $[H_2L][FeCl_4]_2$

N(1)–C(1)	1.350(10)	N(1)–C(5)	1.354(10)
C(1)–C(2)	1.380(9)	C(1)–C(21)	1.452(12)
C(2)–C(3)	1.397(13)	C(3)–C(4)	1.385(12)
C(4)–C(5)	1.354(9)	C(5)–C(6)	1.472(10)
N(2)–C(6)	1.257(8)	N(2)–N(3)	1.349(7)
N(3)–C(7)	1.465(10)	N(3)–C(8)	1.375(8)
N(4)–C(8)	1.323(10)	N(4)–C(12)	1.367(8)
C(8)–C(9)	1.417(9)	C(9)–C(10)	1.379(10)
C(10)–C(11)	1.403(12)	C(11)–C(12)	1.387(9)
C(11)–C(13)	1.431(10)	C(12)–C(16)	1.419(11)
C(13)–C(14)	1.359(13)	C(14)–C(15)	1.413(10)
C(15)–C(16)	1.396(10)	C(15)–C(17)	1.446(12)
C(16)–N(5)	1.360(8)	C(17)–C(18)	1.372(11)
C(18)–C(19)	1.433(12)	C(19)–N(5)	1.332(10)
C(19)–N(6)	1.376(9)	C(20)–N(6)	1.484(12)
N(6)–N(7)	1.354(9)	N(7)–C(21)	1.286(9)
Fe(1)–Cl(1)	2.207(3)	Fe(1)–Cl(2)	2.183(2)
Fe(1)–Cl(3)	2.192(3)	Fe(1)–Cl(4)	2.187(3)
Fe(2)–Cl(5)	2.201(3)	Fe(2)–Cl(6)	2.174(2)
Fe(2)–Cl(7)	2.198(3)	Fe92)–Cl(8)	2.194(2)
Cl(1)–Fe(1)–Cl(2)	109.7(1)	Cl(1)–Fe(1)–Cl(3)	113.6(1)
Cl(1)–Fe(1)–Cl(4)	108.1(1)	Cl(2)–Fe(1)–Cl(3)	106.4(1)
Cl(2)–Fe(1)–Cl(4)	111.1(1)	Cl(3)–Fe(1)–Cl(4)	107.9(1)
Cl(5)–Fe(2)–Cl(6)	112.2(1)	Cl(5)–Fe(2)–Cl(7)	107.0(1)
Cl(5)–Fe(2)–Cl(8)	107.6(1)	Cl(6)–Fe(2)–Cl(7)	111.5(1)
Cl(6)–Fe(2)–Cl(8)	109.3(1)	Cl(7)–Fe(2)–Cl(8)	109.2(1)
C(1)–N(1)–C(5)	123.3(6)	N(1)–C(1)–C(2)	119.3(7)
N(1)–C(1)–C(21)	115.8(6)	C(2)–C(1)–C(21)	124.9(7)
C(2)–C(3)–C(4)	120.0(7)	C(3)–C(4)–C(5)	120.4(8)
N(1)–C(5)–C(4)	118.7(7)	N(1)–C(5)–C(6)	115.0(6)
C(4)–C(5)–C(6)	126.4(7)	C(5)–C(6)–N(2)	116.0(7)
C(6)–N(2)–N(3)	123.2(6)	N(2)–N(3)–C(7)	121.7(5)
N(2)–N(3)–C(8)	114.1(6)	C(7)–N(3)–C(8)	124.2(5)
C(8)–N(4)–C(12)	121.8(6)	N(3)–C(8)–N(4)	115.6(6)
N(3)–C(8)–C(9)	125.5(7)	N(4)–C(8)–C(9)	118.9(6)
C(8)–C(9)–C(10)	119.4(7)	C(9)–C(10)–C(11)	121.5(6)
C(10)–C(11)–C(12)	115.8(6)	C(10–C(11)–C(13)	126.6(6)
C(12)–C(11)–C(13)	117.6(7)	N(4)–C(12)–C(16)	115.5(6)
N(4)–C(12)–C(11)	122.5(7)	C(11)–C(12)–C(16)	122.1(6)
C(11)–C(13)–C(14)	121.0(6)	C(13)–C(14)–C(15)	121.0(7)
C(14)–C(15)–C(16)	119.6(8)	C(14)–C(15)–C(17)	127.0(7)
C(16)–C(15)–C(17)	113.3(6)	C(12)–C(16)–C(15)	118.7(6)
C(12)–C(16)–N(5)	115.5(6)	C(15)–C(16)–N(5)	125.8(7)
C(15)–C(17)–C(18)	121.9(7)	C(17)–C(18)–C(19)	119.0(8)
C(18)–C(19)–N(6)	124.0(7)	N(5)–C(19)–N(6)	115.6(7)
C(16)–N(5)–C(19)	119.5(6)	C(19)–N(6)–C(20)	125.2(7)
C(19)–N(6)–N(7)	113.9(6)	C(20)–N(6)–N(7)	120.9(6)
N(6)–N(7)–C(21)	124.5(7)	C(1)–C(21)–N(7)	115.4(7)
C(1)–C(2)–C(3)	118.4(7)		

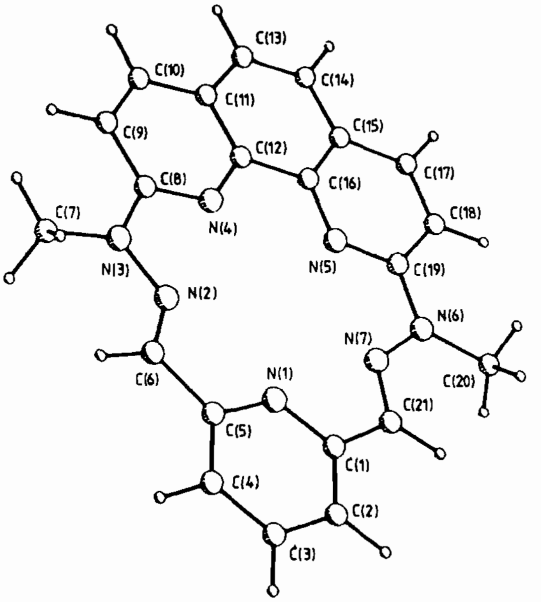

Fig. 1. The macrocyclic cation.

planes being 0.02 and 0.04 Å, respectively). These two heterocyclic subunits each subtend an angle of 1.2° to the least-squares plane through N(1), N(2), N(4), N(5) and N(7) and are inclined at an angle of 0.1° with respect to each other.

Bond lengths and bond angles within the macrocyclic cation are generally unremarkable. The two atoms N(3) and N(6) are planar and sp^2 hybridised; the sum of the bond angles around each nitrogen atom is 360.0°. This reflects π-bonding overlap of each with the directly bonded nitrogen atoms; and is also seen in the bond lengths N(2)–N(3) (1.349(7) Å) and N(6)–N(7) (1.354(9) Å). There are short non-bonded contacts between the imine methine protons and the adjacent methyl groups (H(6)–H(7b), 2.162 Å, H(6)–H(7c), 2.355 Å and H(20c)–H(21), 2.199 Å).

The lattice contains two $[MCl_4]^-$ anions. Although the original transient template reaction was performed in the presence of chromium(III) chloride, it seems most unlikely that a $[CrCl_4]^-$ salt would be obtained in the aqueous protic conditions. No compound containing the tetrahedral $[CrCl_4]^-$ anion has been structurally characterised. The M–Cl distances within the anion (2.174–2.207 Å) are in close agreement with those which are accepted within tetrachloroferrate(III) anions, and the structure refined satisfactorily when they were treated as such. The bulk of the material obtained from the transient template reaction did not contain any iron (as detected by atomic absorption analysis), and the partial microanalysis was consistent with the material simply being a chloride salt. The single crystal which was used for the X-ray structural analysis differed in morphology from the bulk of the material, and we believe that we adventitiously selected a well-formed crystal which did not parallel the bulk of the material. The origin of the iron is uncertain, but the crystal that was finally selected was from a sample which had been repeatedly recrystallised in attempts to obtain X-ray quality material, and only one single crystal suitable for crystallographic analysis was obtained. We have been unable to obtain further crystalline samples of this material, nor have we been able to obtain X-ray quality crystals of the chloride salt. The direct reaction of the salt $[H_2L]Cl_2$ with $FeCl_3$ resulted predominantly in the formation of iron(III) complexes of the macrocyclic ligand, but in acidic conditions, orange–red microcrystalline tetrachloroferrate salts could be obtained. Unfortunately, we have been unable to obtain X-ray quality crystals of these salts, and powder diffraction patterns indicate significant differences from the structurally characterised material.

Supplementary material

Tables of anisotropic displacement parameters, hydrogen atom coordinates, hydrogen atom bond angles and least-squares planes are available from the authors.

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