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Giuseppe Bruno[a]; Sebastiano Campagna[a]; Antonio Mamo[b]; Francesco Nicolo[a]; Silvio Quici[c]
[a] Dipartimento di Chimica Inorganica, Analitica e Struttura Molecolare, Universitá di Messina, Messina, Italy [b] Istituto Chimico, Facoltá di Ingegneria, Universitá di Catania, Catania, Italy [c] Centro CNR, Sintesi e Stereochimica Speciale Sistemi Organici, Milano, Italy

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New polydentate building blocks

GIUSEPPE BRUNO[a], SEBASTIANO CAMPAGNA[a], ANTONIO MAMO*[b], FRANCESCO NICOLO'[a] and SILVIO QUICI[c]

[a]Dipartimento di Chimica Inorganica, Analitica e Struttura Molecolare, Universita' di Messina, Via Sperone 31, Vill. S. Agata, Messina, Italy, [b]Istituto Chimico, Facolta' di Ingegneria, Universita' di Catania, V. le A. Doria 8, 95125 Catania, Italy and [c]Centro CNR, Sintesi e Stereochimica Speciale Sistemi Organici, Via Golgi 19, 20133 Milano, Italy

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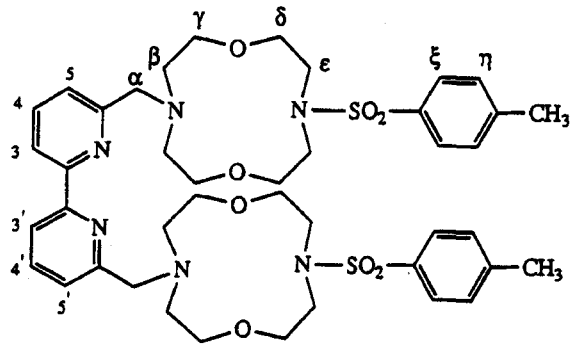
Two new ligands, 6,6'-bis[10(4-tosyl)-1,7-dioxa-4,10-diazacyclododecane]methyl-2,2'-bipyridine (BTAMB) and 2,9-bis[10-(4-tosyl)-1,7-dioxa-4,10-diazacyclododecane]methyl 1,10-phenanthroline (BTAMP) and their copper(I) complexes $[Cu(BTAMB)_2]BF_4$, 1, and $[Cu(BTAMP)_2]BF_4$, 2, have been synthesized and characterized. The reaction of these ligands with $Eu(ClO_4)_3 \cdot 6D_2O$ in CH_3CN gave invariably diprotonated species $BTAMB \cdot 2HClO_4$, 3, and $BTAMP \cdot 2HClO_4$, 4, as shown by ^1H NMR spectral studies and X-ray analysis of 3: monoclinic space group *C2/c*, *a* = 16.240(3), *b* = 17.607(4), *c* = 17.754(3) Å, β = 95.10 (1)°, *Z* = 4, *R* = 0.050. The main characteristic of the molecule is its double-spiral arrangement around the crystallographic two-fold axis.

INTRODUCTION

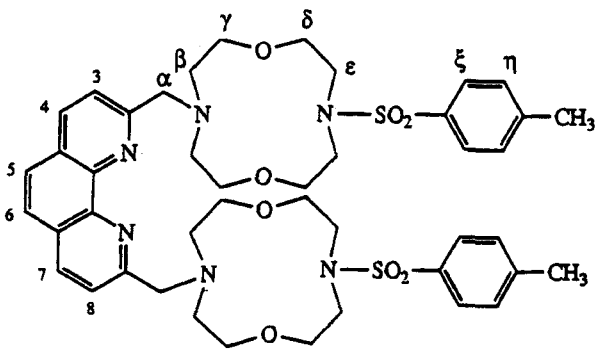
It is well known that copper(I) complexes of 2,2'-bipyridines and 1,10 phenanthrolines are unable to adopt a square-planar configuration because of steric interactions between hydrogen atoms α to the nitrogen[1] and, as a consequence, they exhibit pseudotetrahedral geometries[2]. Based on this geometric feature, polypyridine copper(I) complexes have been used to produce helicate[3], catenates[4] or to cross-link through non-covalent bonds to form bipyridyl-functionalized peptides.[5]

One of us has been interested in the synthesis of lipophilic macropolycyclic ligands[6] which are known for their complexation of predominantly alkali and alkaline earth metals. Owing to the wide interest in mono- and dinuclear complexes which can model metallo-proteins[7], we have designed new building blocks that combine "hard" and "soft" coordination sites, which can be used as starting material for the synthesis of more sophisticated macropolycyclic cage ligands or as model compounds for helicoidal polymer structures.

This paper describes the synthesis and characterization, as precursors of model compounds for polyamides, of two new ligands 6,6'-bis[10-(4-tosyl)-1,7-dioxa-4,10-diazacyclododecane]methyl-2,2'-bipyridine (**BTAMB**) [Bis-Tosyl-Azacrownether-Methyl-Bipyridine] and 2,9-bis[10-(4-tosyl)-1,7-dioxa-4,10-diazacyclododecane] methyl-1,10-phenanthroline (**BTAMP**) [Bis-Tosyl-Azacrownether-Methyl-Phenanthroline] (Scheme 1) and the study of their complexing properties with respect to copper(I) cation (for the above reasons), and



BTAMB



BTAMP

Scheme 1

*To whom correspondence should be addressed.

europium(III) cation, owing to the use as potential probes in fluoroimmunoassays of its complexes.[8]

We were able to synthesize and to characterize the complexes $[Cu(BTAMB)_2]BF_4$, **1**, and $[Cu(BTAMP)_2]BF_4$, **2**. All efforts to get the corresponding Eu(III) complexes furnished only a perchlorate salt of the diprotonated ligands BTAMB·$2HClO_4$, **3**, and BTAMP·$2HClO_4$, **4**, as confirmed by X-ray and ^{1}H-NMR data.

RESULTS AND DISCUSSION

The required ligands, 6,6′-bis[10-(4-tosyl)-1,7-dioxa-4,10-diazacyclododecane]methyl-2,2′-bipyridine and 2,9-bis[10-[(4-tosyl)-1,7-dioxa-4,10-diazacyclododecane]methyl-1,10-phenanthroline, were synthesized by reacting under reflux conditions for 3 days the appropriate bis(chloromethyl)-derivate with the monotosyl diazacrown ether in acetonitrile in the presence of solid Na_2CO_3 as a base. The synthesis of copper(I) complexes with these ligands using a 2:1 ligand:metal ratio was carried out following known synthetic procedures.[3,4]

^{1}H NMR, EI and/or FAB mass, IR, and UV spectral data support the formulation of the synthesized compounds. The ^{1}H NMR spectrum of **BTAMB** (Fig. 1a) shows the expected pattern for the bpy moiety. Noteworthy, the H^3 bpy protons resonating at 8.26 ppm, are considered diagnostic for the *anti* orientation of the free ligand.[17] The diazacrown ether methylene protons show up as a set of four triplets in the 3.9 - 2.9 ppm region. These signals were assigned by comparison with the ^{1}H NMR spectrum of the azacrown ether precursor.[6] The ^{1}H NMR spectra of **BTAMP** (not reported) show in the aromatic region a sequence doublet-doublet-singlet ($H^{4/7}$, $H^{3/8}$, $H^{5/6}$, respectively), characteristic for a phenanthroline moiety. The methylene region is very similar to that of **BTAMB**.

In Fig. 1b is shown the ^{1}H NMR spectrum of complex **1** that evidences great changes in most signals with respect to the ^{1}H NMR spectrum of the free ligand **BTAMB** (Fig. 1a). Upon complexation, H^4 and H^5 bipy protons experienced a down-field shift, while H^3 protons have a very poor up-field shift ($\Delta\delta = 0.02$) owing to the balance of two opposite effects: i) shielding effect of *syn* orientation of the bipy unit, and ii) deshielding effect due to the back donation of the copper(I) electrons. The aromatic and methyl tosyl protons do not present any shift effect, while all the methylene protons experienced an up-field shift with the highest $\Delta\delta$ value for the H^α ($\Delta\delta = 0.51$ ppm). The magnitude of this effect decreases progressively on moving away from the complexation site (H^ε: $\Delta\delta = 0.11$), probably due to the shielding effect of

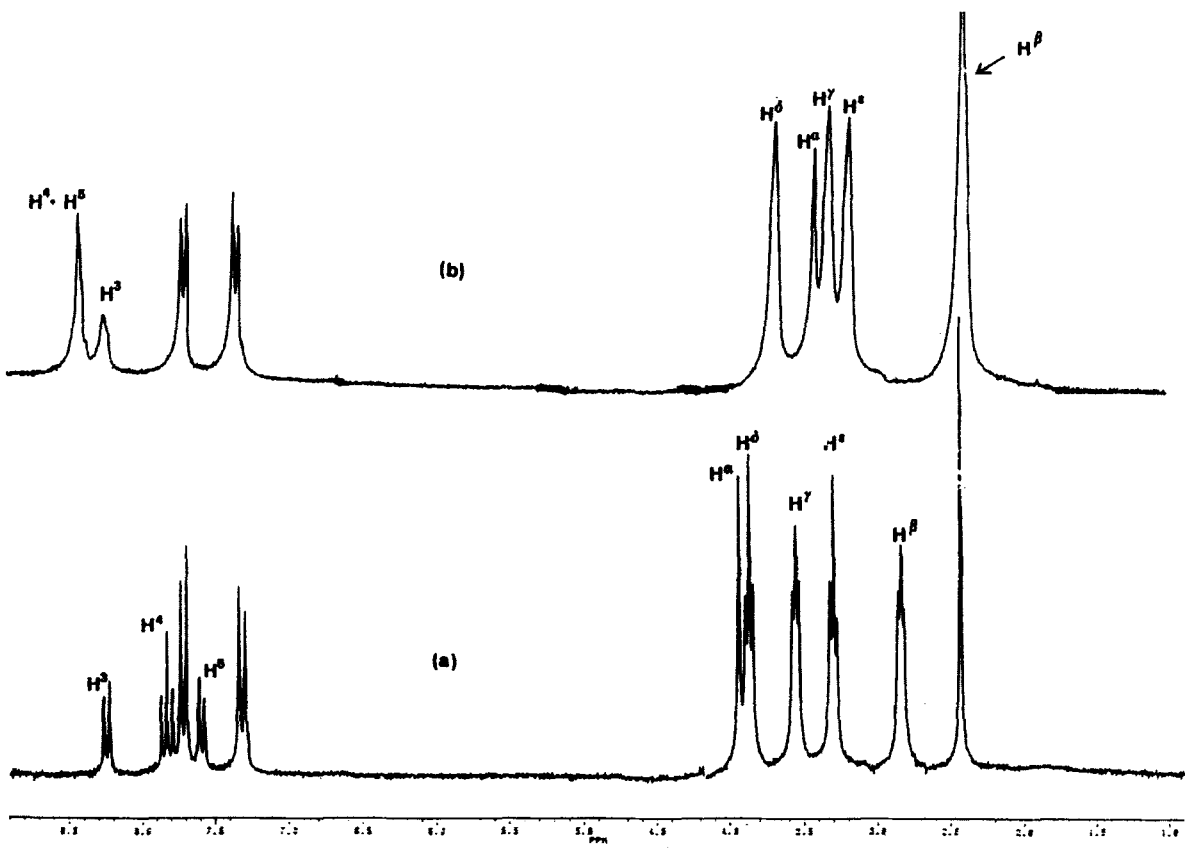


Figure 1 ^{1}H NMR spectrum of BTAMB (a) and of $[Cu(BTAMB)_2]BF_4$ (b) in $CDCl_3$.

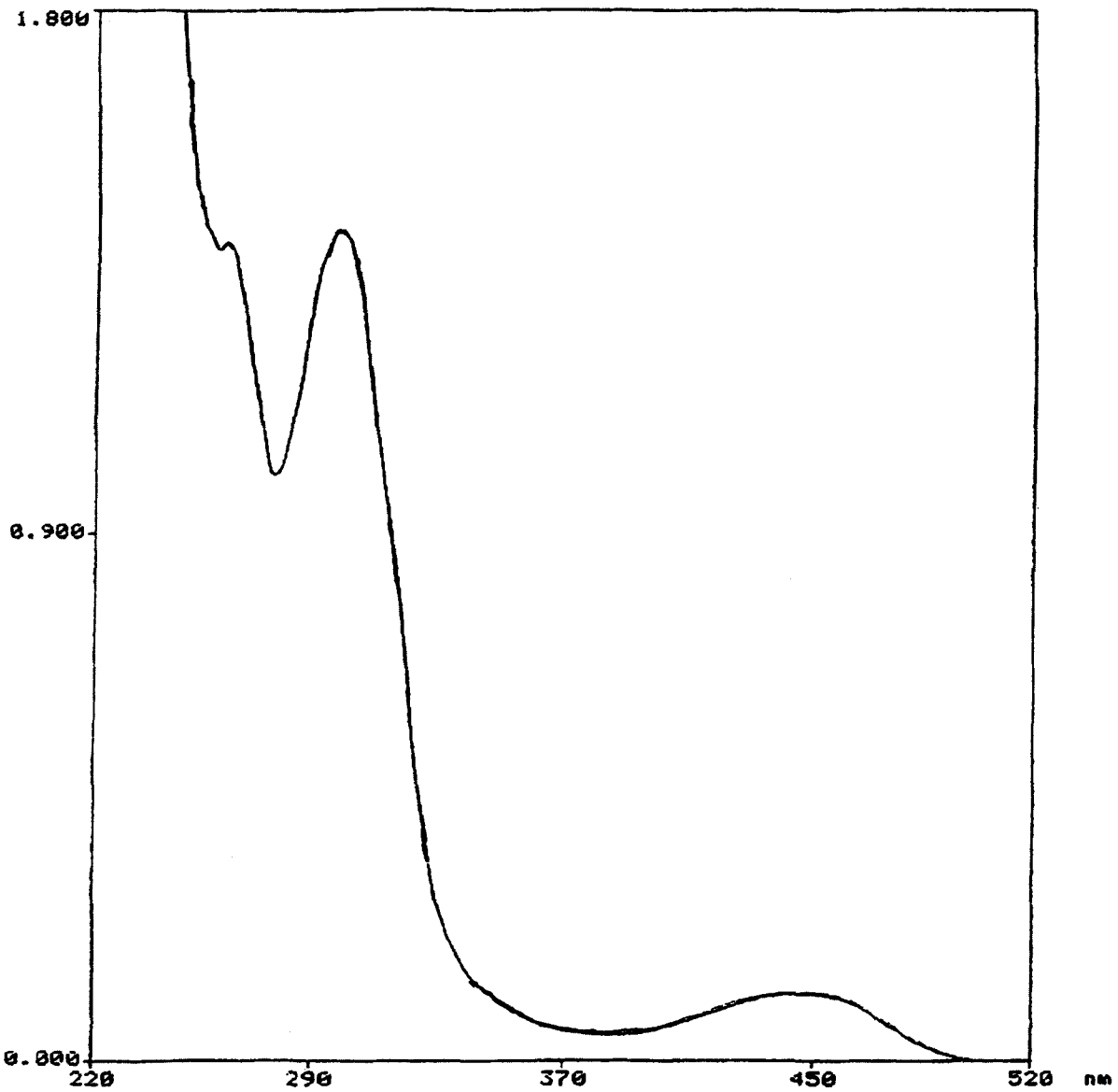


Figure 2 UV/vis spectrum of $[Cu(BTAMB)_2]BF_4$ in acetonitrile solution: c = 2.8 × 10^{-5} mol dm^{-3}.

the second bipy moiety in the pseudotetrahedral Cu(I) complex. Complex **2** shows very similar features, e.g. a down-field shift of the phenanthroline protons and an up-field shift of methylene groups.

The complexes $[Cu(BTAMB)_2]BF_4$ and $[Cu(BTAMP)_2]BF_4$ are orange and do not show luminescence properties, both at room temperature in fluid solution and at 77 °K in rigid glasses. Fig. 2 shows the UV/vis spectrum of complex **1** that is dominated by a moderately intense absorption due to a MLCT transition in the visible region (λ_{max} = 455 nm, ε = 4300 mol^{-1} cm^{-1}), and a strong absorption due a π-->π* transition centered at the bipy moiety of the ligand in the UV region (λ_{max} = 298 nm, ε = 54280 mol^{-1} cm^{-1}). The UV/vis spectrum of **2** is very similar and can be qualitatively discussed in the same way.

The complexation of **BTAMB** and **BTAMP** with $Eu(ClO_4)_3 \cdot 6D_2O$ has been attempted in CH_3CN in the presence of $CH(OC_2H_5)_3$. The ligands are not soluble in CH_3CN at r.t., but on adding dropwise a CH_3CN solution containing the Eu(III) salt (1:1 molar ratio) and refluxing for 1 h, a clear solution was obtained. Addition of ether precipitated the supposed complexes as white powders.

Fig. 3a shows the ^1H NMR spectrum of **3** [obtained by reacting **BTAMB** with $Eu(ClO_4)_3 \cdot 6D_2O$)], that evidences dramatic changes expecially in the methylene region with respect to the free ligand (see Fig. 1a), which might indicate the formation of the desired complex. However the highest mass peak observable in its FAB (+) mass spectrum was at *m/z* 937, corresponding to $BTAMB \cdot H_2ClO_4^+$, while no peaks were present showing the expected isotopic pattern for Eu. The elemental

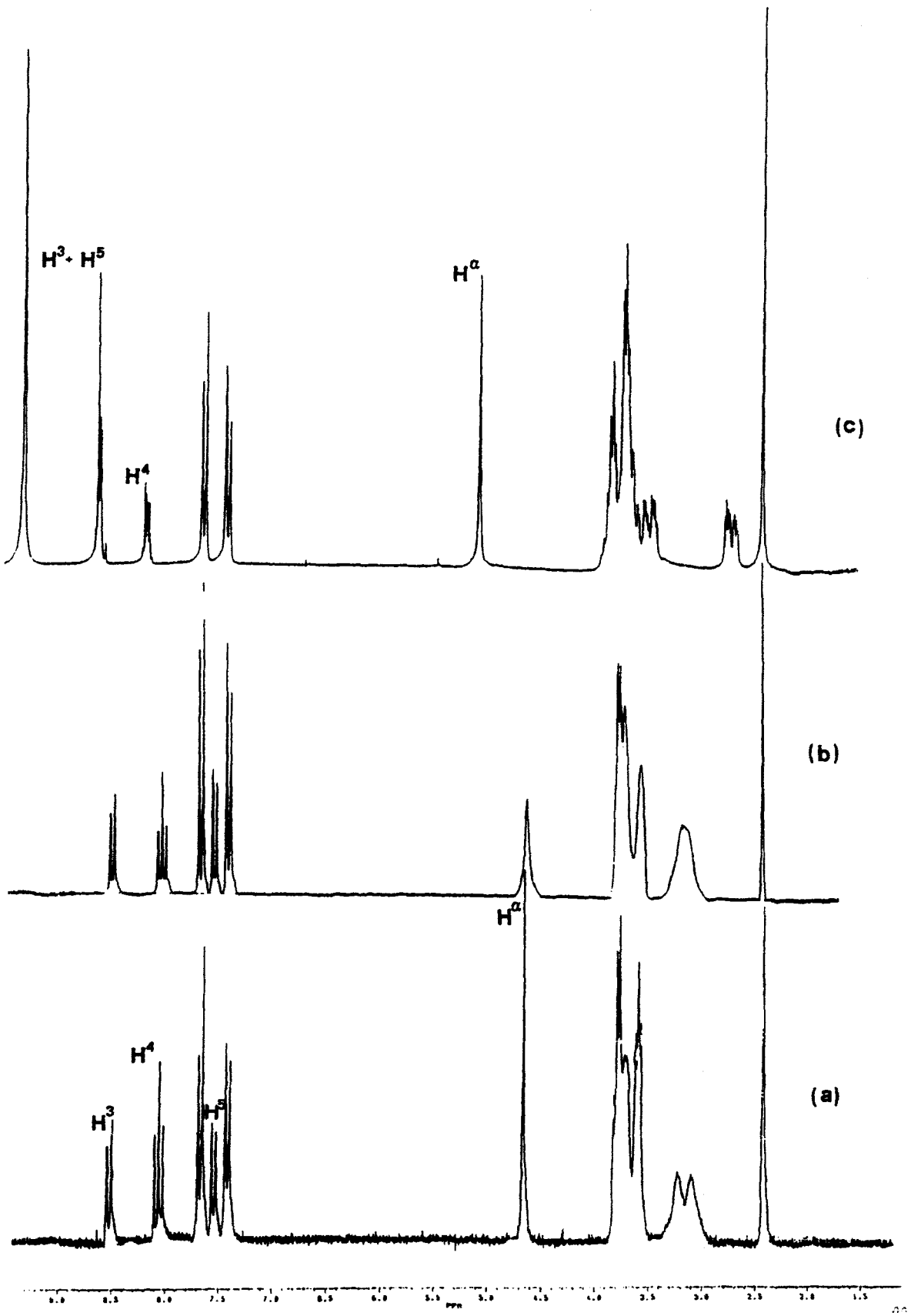


Figure 3 ^{1}H NMR spectrum of BTAMB·2$HClO_4$ (a), of BTAMB + deuterated $HClO_4$ (1 equiv.), and of BTAMB + deuterated $HClO_4$ (excess).

analysis was in agreement with the formulation BTAMB·2$HClO_4$, **3**.

To confirm that protonation (and not complexation) of the ligand had occurred, we added drop-by-drop a solution of deuterated $HClO_4$ in CD_3CN (1 equiv) to the ^1H NMR tube containing a sample of the ligand BTAMB in CD_3CN. Fig. 3b shows that the ^1H NMR spectrum obtained in this way is almost identical to the ^1H NMR spectrum in Fig. 3a, indicating that the protonation has occurred at the two more basic nitrogen atoms (bipy-CH_2-N^+-azacrown). Upon further addition of the deuterated $HClO_4$ solution, the bipy nitrogens are also protonated as indicated by the ^1H NMR spectrum in Fig. 3c, where it is easy to note a larger down-field shift of the α-bipyridyl methylene protons and an overlapping of the H^3/H^5 bipy protons (the strong signal at δ = 9.32 is due to deuterated $HClO_4$ excess).

This protonated structure was unequivocally established by a single-crystal X-ray diffraction study. Coordinates are given in Tables 1 and 2, and the molecule is illustrated in Fig. 4.

The perchlorate salt of the diprotonated ligand crystallizes in the monoclinic space group *C2/c* with four molecules in the unit cell. The molecule is located on a crystallographic two-fold axis and shows an double-spiral disposition with the mean plane perpendicular to it passing through the middle of the bipyridyl fragment. Therefore the ligand assumes a perfect *C2v* arrangement as required by the crystal symmetry. The asymmetric

Table 1 Fractional atomic coordinates (x 10^4) for the non-hydrogen atoms of (**3**)

Atom	*x*	*y*	*z*
N(1)	-441(2)	726(3)	6579(2)
C(2)	-412(3)	439(3)	7280(3)
C(3)	-1099(3)	137(4)	7571(3)
C(4)	-1834(3)	123(5)	7134(3)
C(5)	-1879(3)	429(4)	6425(3)
C(6)	-1168(3)	723(3)	6166(3)
C(7)	-1165(3)	1048(4)	5382(3)
N(8)	-479(3)	1599(3)	5333(2)
C(9)	-182(3)	1648(3)	4563(3)
C(10)	327(4)	959(4)	4416(3)
O(11)	904(2)	789(2)	5047(2)
C(12)	1616(3)	1285(4)	5130(3)
C(13)	1973(4)	1221(4)	5944(3)
N(14)	2459(3)	1902(3)	6175(3)
C(15)	2080(5)	2414(5)	6696(4)
C(16)	1402(5)	2901(4)	6323(4)
O(17)	680(3)	2450(3)	6140(2)
C(18)	27(4)	2881(4)	5768(4)
C(19)	-710(4)	2351(4)	5646(4)
S(20)	3458(1)	1820(2)	6268(1)
O(21)	3679(3)	1365(4)	5646(3)
O(22)	3785(3)	2575(4)	6363(3)
C(23)	3720(3)	1334(5)	7123(4)
C(24)	3831(3)	555(5)	7108(4)
C(25)	4027(3)	187(4)	7793(3)
C(26)	4096(3)	566(5)	8468(4)
C(27)	3976(5)	1336(5)	8462(4)
C(28)	3804(4)	1725(5)	7791(4)
C(29)	4325(5)	160(5)	9199(4)
Cl	2704(1)	1358(1)	1242(1)
O(1)	3327(4)	1467(5)	1819(3)
O(2)	2377(4)	2044(4)	956(4)
O(3)	2151(6)	835(7)	1334(5)
O(4)	3100(6)	1097(6)	596(5)

Table 2 Selected bond lengths (Å) and bond angles (°) for non-hydrogen atoms* for (**3**)

N(1)-C(2)	1.339(6)	N(1)-C(6)	1.334(6)
C(2)-C(3)	1.378(7)	C(2)-C(2)′	1.489(6)
C(3)-C(4)	1.365(7)	C(4)-C(5)	1.365(9)
C(5)-C(6)	1.381(8)	C(6)-C(7)	1.505(8)
C(7)-N(8)	1.486(7)	N(8)-C(9)	1.492(7)
N(8)-C(19)	1.497(8)	C(9)-C(10)	1.504(9)
C(10)-O(11)	1.427(6)	O(11)-C(12)	1.446(7)
C(12)-C(13)	1.513(8)	C(13)-N(14)	1.473(9)
N(14)-C(15)	1.47(1)	N(14)-S(20)	1.624(6)
C(15)-C(16)	1.50(1)	C(16)-O(17)	1.428(8)
O(17)-C(18)	1.418(8)	C(18)-C(19)	1.517(9)
S(20)-O(21)	1.436(7)	S(20)-O(22)	1.436(7)
S(20)-C(23)	1.760(7)		
C(2)-N(1)-C(6)	117.7(4)	N(1)-C(2)-C(2)′	116.4(4)
N(1)-C(2)-C(3)	122.2(4)	C(3)-C(2)-C(2)′	121.5(4)
C(2)-C(3)-C(4)	119.3(5)	C(3)-C(4)-C(5)	119.3(5)
C(4)-C(5)-C(6)	118.5(5)	N(1)-C(6)-C(5)	123.0(5)
C(5)-C(6)-C(7)	121.5(5)	N(1)-C(6)-C(7)	115.5(5)
C(6)-C(7)-N(8)	111.6(4)	C(7)-N(8)-C(19)	110.0(4)
C(7)-N(8)-C(9)	113.4(4)	C(9)-N(8)-C(19)	113.6(4)
N(8)-C(9)-C(10)	109.8(4)	C(9)-C(10)-O(11)	111.5(5)
C(10)-O(11)-C(12)	114.6(4)	O(11)-C(12)-C(13)	106.7(5)
C(12)-C(13)-N(14)	110.8(5)	C(13)-N(14)-S(20)	117.5(5)
C(13)-N(14)-C(15)	115.6(5)	C(15)-N(14)-S(20)	117.5(5)
N(14)-C(15)-C(16)	113.9(6)	C(15)-C(16)-O(17)	109.8(6)
C(16)-O(17)-C(18)	111.9(5)	O(17)-C(18)-C(19)	106.6(5)
N(8)-C(19)-C(18)	112.1(5)	N(14)-S(20)-C(23)	107.1(3)
N(14)-S(20)-O(22)	106.6(4)	N(14)-S(20)-O(21)	106.6(3)
O(22)-S(20)-C(23)	106.9(4)	O(21)-S(20)-C(23)	109.5(4)
O(21)-S(20)-O(22)	119.5(4)		

*The apex denotes an equivalent position by the symmetry operation $-x, y, 3/2-z$.

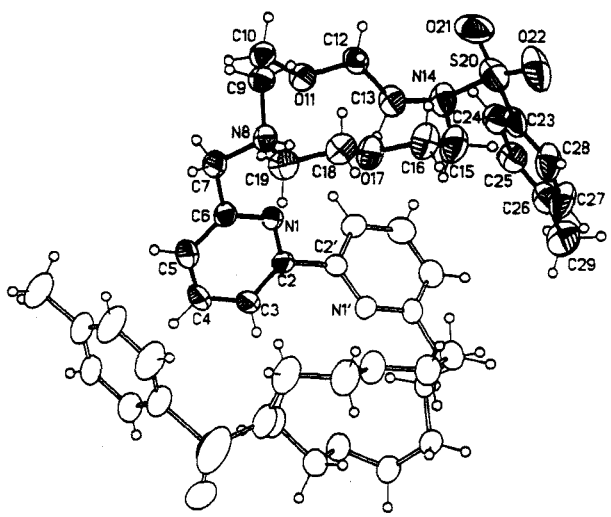


Figure 4 View of the whole ligand molecule located on a crystallographic two-fold axis. The shaded atoms represent the asymmetric unit with our numbering scheme. Thermal ellipsoids are drawn at 40% probability level while hydrogen size is arbitrary. The two perchlorate anions are omitted for clarity.

unit constitutes a half ligand and one ClO_4^- anion, resulting in a molecule-perchlorate ratio 1:2 which denotes a charge +2 on the whole ligand. Due to the difficulty in locating the hydrogen atoms on the Difference Fourier maps, the position of the unique proton was deduced by stereochemical considerations (N-H = 0.91 Å). Evaluating the different basicity of the possible sites of the molecule and comparing the geometry of the corresponding protonated examples reported in the literature, the amine nitrogen N(8) is more suitable to the protonation than the sulfoamide N(14) and pyridine N(1) atoms, even with respect to the oxygens of the sulphonyl and crown-ether moieties.

The two aromatic rings of the 2,2′-bipyridyl moiety are staggered tending to the *transoid* arrangement, as denoted by the torsion angle N(1)-C(2)-C(2)′-N(1)′ = 130.3(5)° whose value is quite unusual[18] for this uncoordinated fragment in the known structures where it is generally observed in more flat dispositions. The C(2)-C(2)′ bond, whose length [1.489(6) Å] is in agreement with the mean value 1.49 Å reported for analogous situations, suggests no conjugation between the two pyridines, as expected by their corresponding dihedral angle 127.8(2)°.

The 1,7-dioxa-4,10-diazacyclododecane is quite flat with the atomic deviations from the planarity ranging from 0.729(6) Å (C(9)) to −0.486(6) Å (C(13)). The two oxygens and the protonated N(8) nitrogen are on the same side with respect to the mean plane of the ring, while the sulfoamide N(14) is directed in the opposite direction. Due to this arrangement the N(8) proton shows short contacts with the two O(11) and O(17) atoms of the crown [2.245(4) and 2.293(4) Å, respectively], in addition to the strong intra-molecular interaction with the nitrogen N(1) of the pyridine in the same asymmetric unit, from which the distance is 2.203(4) Å. Therefore the proton placed on the amine nitrogen of the crown seems to be stabilized by these surrounding interactions, likely in the cavity formed by the folded shape of the spiral arm, supporting the initial assumption for the choice of the best protonation site in the structure model.

The *p*-tolylsulfonyl substituent shows geometrical characteristics similar to the reported ones for analogous fragments from the literature.[19] The mean plane of the tolyl ring forms a dihedral angle of 62.8(2)° with the crown plane but is rotated in such a way as to minimize the hindrance between its *ortho*-hydrogens and the H-atoms of the crown methylenes [(C(13) and C(15) carbons)] directly bonded to the nitrogen N(14), as clearly evidenced by the solid model studies.

The ^1H NMR data of the white powder **4** obtained by reacting **BTAMP** with $Eu(ClO_4)_3 \cdot 6D_2O$ as well as the ^1H NMR data obtained on adding drop-by-drop a solution of deuterated $HClO_4$ in CD_3CN to the ^1H NMR tube containing a sample of the ligand **BTAMP** in CD_3CN, show very similar features to **3**, confirming that also in this case protonation occurs and not complexation.

It is concluded that the synthesized ligands, **BTAMB** and **BTAMP**, combining "hard" and "soft" coordination sites, form 2:1 (ligand/metal) orange air-stable Cu(I) complexes, opening the way to interesting future applications. On the other hand, the fact that the ligand **BTAMP** is not able to complex Eu(III) cation might let us to conclude that this cation is too large to fit into the hydrophilic cavity generated by the two azacrown ether moieties linked by a phenanthroline spacer. As a consequence, for the ligand **BTAMB** where the presence of a bipy group in the *anti* conformation excludes the presence of any cavity, we could expect the formation of a polymeric species with the Eu(III) cation linked as a "sandwich" between two azacrown ether moieties of two different **BTAMB** molecules. FAB studies on **3**, as reported above, exclude this hypothesis confirming that a discrete diprotonated species is formed. Therefore, as evidenced by X-ray analysis on **3**, it is postulated that each spiral arm forms a small cavity where the H^+ could attach to the diaza-dioxa-crown nitrogen opposite to the tosyl group. This protonation site is significantly stabilized by strong interactions with the two oxygens of the ring and by the nitrogen of the bipyridine fragment surrounding it. This situation, where four possible coordination sites are deactivated on each spiral arm, might be considered responsible for the crystallization of the diprotonated spiral-shaped free ligand rather than the expected Eu-complex cation.

Future work will be directed to the exploration of the binding ability of these systems toward smaller cations, to the design of better receptors for lanthanide cations, as well as to the synthesis of model compounds for polyamides by replacing the tosyl moiety with, for instance, a benzoyl group.

EXPERIMENTAL

Materials:-Bis(chloromethyl) derivative precursors,[7,9] monotosyl-diazacrown ether[6] and tetrafluoroboratetetraacetonitrile copper(I) complex[10] were prepared by the literature procedures.

All reactions were performed under an inert atmosphere of nitrogen, and the solvents dried and stored under nitrogen and over 4Å molecular sieves. Melting points are uncorrected. Elemental analyses were obtained commercially. All other reagents were reagent grade.

Physical Measurements:-Proton NMR spectra were taken on a Bruker AC 200 instrument using $SiMe_4$ as internal reference. Electron Impact (EI) and positive-ion Fast Atom Bombardment (FAB) mass spectra were taken on a Kratos MS 50 S double-focusing mass spectrom-

eter equipped with a standard FAB source, using 3-nitrobenzyl alcohol as a matrix.

Ultraviolet-visible absorption spectra were recorded on a Perkin Elmer 330 double-beam spectrophotometer using 1 cm quartz cells at room temperature.

Preparations:-6,6'-Bis[10-(4-tosyl)-1,7-dioxa-4,10-diazacyclododecane]methyl-2,2'-bipyridine(**BTAMB**). A mixture of 6,6'-bischloromethyl-2,2'bipyridine (0.253 g, 1 mmol), 4-(tosyl)-1,7-dioxa-4,10-diazacyclododecane (0.656 g, 2 mmol), and Na_2CO_3 (1.06 g, 10 mmol) in CH_3CN (100 mL) was stirred at reflux for 3 days, to afford, after cooling, filtration, and CH_2Cl_2 washing, 0.880 g of an off white powder. The product was purified by column chromatography (SiO_2; CH_2Cl_2-MeOH 9:1) followed by recrystallization from EtOH-CH_3CN to give 0.526 g (63%) of **BTAMB** as white powder. m.p. 203-205 °C. ^{1}H NMR [$CDCl_3$]: δ 8.26 (d, 2H, J = 7.69, H^3 of bipyridine), 7.82 (t, 2H, J = 7.69, H^4 of bipyridine), 7.73 (d, 4H, J = 8.25, Hη of tosyl), 7.60 (d, 2H, J = 7.69, H^5 of bipyridine), 7.33 (d, 4H, J = 8.21, Hξ of tosyl), 3.93 (s, 4H, α-bipy-CH_2), 3.86 (t, 8H, J = 4.98, δ-azacrown-CH_2), 3.55 (t, 8H, J = 4.35, γ-azacrown-CH_2), 3.30 (t, 8H, J = 4.98, ε-azacrown- CH_2), 2.83 (t, 8H, J = 4.35, β-azacrown-CH_2), 2.43 (s, 6H, -CH_3 of tosyl). EI mass spectrum: *m/z* 836 ($M^{+\cdot}$, 86%). (Found: C, 60.20; H, 6.69; N, 9.94. Calc. for $C_{42}H_{56}N_6O_8S_2$: C, 60.26; H, 6.74; N, 10.04%).

2,9-Bis[10-(4-tosyl)-1,7-dioxa-4,10-diazacyclododecane]methyl-1,10-phenanthroline(**BTAMP**). It was prepared analogously to **BTAMB**, the only difference being the different starting bis(chloromethyl) derivative. Recrystallization from CH_2Cl_2-cyclohexane afforded **BTAMP** as off white powder (70%). m.p. 90-92 °C. ^{1}H NMR [$CDCl_3$]: δ 8.34 (d, 2H, J = 8.30, $H^{4/7}$ of phenanthroline), 8.23 (d, 2H, J = 8.32, $H^{3/8}$ of phenanthroline), 7.74 (s, 2H, $H^{5/6}$ of phenanthroline), 7.72 (d, 4H, J = 7.83, Hη of tosyl), 7.32 (d, 4H, J = 7.49, Hξ of tosyl), 4.27 (s, 4H, α-phen-CH_2), 3.85 (t, 8H, J = 4.58, δ-azacrown-CH_2), 3.57 (t, 8H, J = 4.58, γ-azacrown-CH_2), 3.30 (t, 8H, J = 4.58, ε-azacrown-CH_2), 2.85 (t, 8H, J = 4.58, β-azacrown-CH_2), 2.43 (s, 6H, -CH_3 of tosyl). EI mass spectrum: *m/z* 860 ($M^{+\cdot}$, 100%). (Found: C, 61.41; H, 6.50; N, 9.78. Cal. for $C_{44}H_{56}N_6O_8S_2$: C, 61.37; H, 6.55; N, 9.81%).

[Cu(BTAMB)$_2$]BF$_4$ **1**. To a stirred solution of **BTAMB** (0.08369 g, 0.1 mmol) in acetonitrile (5 mL) was added dropwise a solution of [$Cu(CH_3CN)_4$]BF_4 (0.01573 g, 0.05 mmol) in CH_3CN (5 mL) and the mixture was allowed to reflux for 1 h. After cooling at room temperature and elimination of the solvent, CH_2Cl_2 (10 mL) was added to get a limpid orange solution. The product was purified by column chromatography (SiO_2; CH_2Cl_2-MeOH 9:1) followed by recrystallization from CH_2Cl_2-cyclohexane, to give 0.090 g of **1** (99%) as red-orange powder. ^{1}H NMR [$CDCl_3$]: δ 8.43 (bm, 8H, H^4 + H^5 of bipyridine), 8.24 (bm, 4H, H^3 of bipyridine), 7.72 (d, 8H, J = 7.85, Hη of tosyl), 7.33 (d, 8H, J = 8.06, Hξ of tosyl), 3.69 (bt, 16H, δ-azacrown-CH_2), 3.42 (bs, 8H, α-bipy-CH_2), 3.33 (bt, 16H, γ-azacrown-CH_2), 3.19 (bm, 16H, ε-azacrown-CH_2), 2.44 (s, 12h, -CH_3 of tosyl), 2.41 (bt, 16H, β-azacrown-CH_2). FAB mass spectrum *m/z* 1735 corresponding to [$Cu(BTAMB)_2$]$^+$. (Found: C, 55.50; H, 6.60; N, 8.93. Calc. for $C_{84}H_{112}BCuF_4N_{12}O_{16}S_4$: C, 55.29; H, 6.18; N, 9.21).

[Cu(BTAMP)$_2$]BF$_4$ **2**. It was prepared analogously to **1**, the only difference being the different chromatographic conditions (Al_2O_3; ethyl acetate) for the purification. Recrystallization from CH_2Cl_2-cyclohexane afforded **2** as red-orange powder (98%). ^{1}H NMR [$CDCl_3$]: δ 8.85 (m, 8H, $H^{4/7}$ + $H^{3/8}$ of phenanthroline), 8.05 (s, 4H, $H^{5/6}$ of phenanthroline), 7.73 (d, 8H, J = 7.86, Hη of tosyl), 7.36 (d, 8H, J = 7.63, Hξ of tosyl), 3.71 (bt, 16H, δ-azacrown-CH_2), 3.64 (bs, 8H, α-azacrown-CH_2), 3.31 (bt, 16H, γ-azacrown-CH_2), 3.21 (bt, 16H, ε-azacrown-CH_2), 2.46 (s, 12H, -CH_3 of tosyl), 2.35 (bt, 16H, β-azacrown-CH_2). FAB mass spectrum *m/z* 1787 corresponding to [$Cu(BTAMP)_2$]$^+$. (Found: C, 56.83; H, 5.89; N,8.92. Calc. for $C_{88}H_{112}BCuF_4N_{12}O_{16}S_4$: C, 56.44; H,6.03; N,8.97%).

BTAMB·2HClO$_4$ **3** *and BTAMP·2HClO$_4$* **4**, *attempted synthesis of Eu(III) complexes*. To a stirred solution of **BTAMB** (0.04184 g, 0.05 mmol) in acetonitrile (2 mL) was added dropwise trimethyl orthoformate (0.5 mL), and a solution of $Eu(ClO_4)_3 \cdot 6D_2O$ (0.05852 g 0.05 mmol) in CH_3CN (2 mL) and the mixture was allowed to reflux for 1h. After cooling at room temperature Et_2O (3mL) was added to get an off white powder that was recrystallized from CH_3CH-MeOH to give 0.087 g of **3** (87%) as white crystalls. ^{1}H NMR [CD_3CN]: δ 8.52 (d, 2H, J = 8.03, H^3 of bipyridine), 8.06 (t, 2H, J = 7.78, H^4 of bipyridine), 7.68 (d, 4H, J = 7.98, Hη of tosyl), 7.55 (d, 2H, J = 7.69, H^5 of bipyridine), 7.42 (d, 4H, J = 7.95, Hξ of tosyl), 4.68 (s, 4H, α-bipy-CH_2), 3.83-3.58 (m, 24H, δ+γ+ε-azacrown-CH_2), 3.17 (bm, 8H, β-azacrown-CH_2), 2.45 (s, 6H, -CH_3 of tosyl). FAB mass spectrum: *m/z* 937 corresponding to BTAMB·$H_2ClO_4^+$. (Found: C, 48.22; H, 5.66; N, 8.23; S, 6.07. Calc. for $C_{42}H_{58}N_6O_8S_2 \cdot 2ClO_4$: C, 48.59; H, 5.63; N, 8.09; S, 6.17%).

The compound **4** was obtained, starting from **BTAMP**, as off white powder analogously to **3**; its analytical data are: ^{1}H NMR [$CDCl_3$]: δ 8.80 (m, 4H, $H^{4/7}$ + $H^{3/8}$ of phenanthroline), 8.04 (s, 2H, $H^{5/6}$ of phenanthroline), 7.71 (d, 4H, J = 8.48, Hη of tosyl), 7.34 (d, 4H, J = 7.38, Hξ of tosyl), 4.44 (s, 4H, α-phenan- CH_2), 3.80-3.05 (bm, 32H, δ+γ+ε+β-azacrown-CH_2), 2.42 (s, 6H, -CH_3 of tosyl). FAB mass spectrum: *m/z* 963 corresponding to BTAMP·$H_2ClO_4^+$. (Found: C, 49.32; H, 5.70; N, 8.02; S, 5.98. Calc. for $C_{44}H_{60}N_6O_8S_2 \cdot 2ClO_4$: C, 49.66; H, 5.68; N, 7.89; S, 6.02%).

Crystal Structure Determination of BTAMB·2HClO$_4$-*Crystal Data.* $C_{42}H_{58}N_6O_8S_2 \cdot 2ClO_4$, M = 1038.0, monoclinic, space group *C2/c* (ITCno.15), *a* = 16.240(3), *b* = 17.607(4), *c* = 17.754(3)Å, β = 95.10(1)°, U = 5056(2) Å^3, Z = 4, D_c = 1.36 g cm^{-3}, $F_{(000)}$ = 2184, μ(Mo-Kα) = 2.83 cm^{-1}, λ(Mo-Kα) = 0.71073 Å.

A suitable prismatic single crystal of size 0.35 × 0.25 × 0.20 was mounted on a glass fibre and the diffraction measurements were performed at room temperature with a Siemens R3m/V automated four-circle diffractometer, using graphite-monochromated Mo-Kα radiation. Cell parameters were obtained and refined by the automatic indexing and least-squares routines applied to the setting angles of 25 accurately centered reflections in the 2θ range 15-30°. The variable-speed ω-2θ scan method was used to collect 5689 reflections (4474 unique, R_{int} = 1.2%) up to 2θ = 50° into the index ranges $-1 \le h \le 20, -1 \le k \le 21, 22 \le l \le 22$. No significant change was observed on the intensities of three standard reflections, monitored after every 100 reflections. The diffraction data were processed with the learnt-profile procedure[11] and then corrected for Lorentz-polarization effects. Absorption correction was applied by fitting a pseudo-ellipsoid to the azimutal scan data of 25 suitable reflections with high χ angles.[12]

The structures were solved by standard direct methods with SHELXTL PLUS program[13] and subsequently completed by a combination of least squares technique and Fourier syntheses. Then the model was continued to be refined with the last release of SHELXL-93.[14] All non-hydrogen atoms were refined anisotropically. The presence of the perchlorate anion (ratio 2:1) denoted the charge of +2 on the compound: considerations on the geometry and basicity of the possible basic sites suggested the protonation of the amine nitrogen in each crown-ether fragment. All hydrogen atoms were generated in calculated positions by stereochemistry considerations, with an unique fixed isotropic thermal parameter (U_{iso} = 0.080 Å^2), and during the refinement they were allowed to ride on their respective parent carbon atoms. The structure model was refined by full-matrix least squares technique using 1747 observed reflections ($F_o \ge 6*\sigma(F_o)$), minimizing the function $\Sigma\omega(F_o^2-F_c^2)^2$, converging to $R = \Sigma|F_o-F_c|/\Sigma F_o$ = 0.050 and $R' = [\Sigma\omega(F_o^2-F_c^2)^2/\Sigma\omega-(F_o^2)^2]^{1/2}$ = 0.177 with the final weighting scheme $\omega^{-1} = \exp[5.0^* (\sin\theta/\lambda)^2]/\{\sigma^2(F_o^2) + [0.0964*(\max(0.33333*Fo^2) + 0.66667*Fc^2)]^2\}$. An empirical extinction parameter was included in the refinement. The last difference map showed the largest electron density residuals (max/min = 0.58/−0.27 eÅ^{-3}) around the perchlorate due to the significant rotational disorder of the anion, as suggested by the large thermal ellipsoids of its four O-atoms. Each attempt to interpretate these peaks as further staggered ClO_4^- dispositions was unsuccessfull.

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