A trefoil knot coordinated to two lithium ions: synthesis and structure

Christiane Dietrich-Buchecker,[a]* Neri Geum Hwang[b] and Jean-Pierre Sauvage[a]*

[a] *Laboratoire de Chimie Organo-Minérale (CNRS UMR 7513), Université Louis Pasteur, Institut Le Bel, 4, rue Blaise Pascal, 67070 Strasbourg, France. Fax: +33 3 88 60 73 12;* e-mail: *sauvage@chimie.u-strasbg.fr*

[b] *Department of Chemistry, Dankook University, Cheonan 330-714, Korea*

Received (in Montpellier, France) 3rd June 1999, Accepted 29th June 1999

The very tight dicopper(I) trefoil knot that contains 1,3-phenylene spacers between the 1,10-phenanthroline subunits could be fully demetallated under drastic conditions (large excess of KCN in refluxing acetonitrile), affording thus the disentangled knotted ligand in almost quantitative yield. This free molecular knot appeared very prompt to protonate or to bind to various ions in order to regenerate the stable "entwined" conformation. Lithium in particular appeared to be ideal for occupying the tight empty coordinating sites of knot **(K-84)$_p$**. A new dilithium complex could be obtained almost quantitatively; its surprising stability allowed the determination of its molecular structure both by ^{1}H NMR and X-ray diffraction along with that also determined for its dicopper(I) precursor.

Un noeud de trèfle coordiné à deux ions lithium: synthèse et structure. La démétallation totale du noeud moléculaire très compact dont les phénanthrolines sont pontées par des groupes *m*-phénylène peut se faire dans des conditions dures (large excès de KCN dans l'acétonitrile à reflux) donnant accès, de manière quasi quantitative, au ligand libre **(K-84)$_p$**. Ce dernier se caractérise par sa forte tendance à se protoner ou à se coordiner à différents cations de manière à retrouver sa conformation la plus stable. Le lithium en particulier est apparu comme étant parfaitement adapté pour remplir les sites de coordination vaccant du noeud **(K-84)$_p$**. Cette affinité exceptionnelle a permis d'obtenir de manière quantitative un nouveau complexe dilithium. Grâce à sa surprenante stabilité il a été possible de déterminer sa structure moléculaire par RMN, spectrométrie de masse et diffraction de rayons X.

The selective complexation of Li$^+$ is still an important challenge, although the coordination chemistry of this small cation has experienced a spectacular development in the course of the three last decades.[1,2] Aromatic polyimines of the 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) families are known to form complexes with Li$^+$ since the late 30s.[3]

Macrocyclic compounds or bridged bis-chelates containing bipy or phen units have more recently been used as specific Li$^+$ chelators in relation with fluorescent lithium probes[4] or isotope separation.[5] A few examples of structurally characterized macrocyclic polypyridine complexes of Li$^+$ have been reported, which show lithium to have various coordination spheres.[6–8]

We would like to report that multiphenanthroline macroring compounds can form dinuclear Li$^+$ complexes very selectively. In particular, ligand **(K-84)$_p$**, which has the topology of a trefoil knot,[9] leads to a crystalline dilithium complex whose structure has been solved.

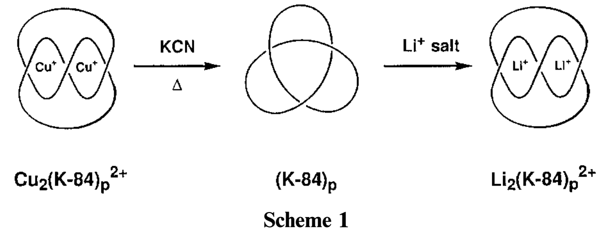
Results and discussion

Strategy

The easy access to the dicopper(I) knot **Cu$_2$(K-84)$_p$$^{2+}$** previously described by our group[9] allowed us to study its demetallation by potassium cyanide.[10] Due to its very tight knotted structure, **Cu$_2$(K-84)$_p$$^{2+}$** displays an exceedingly large kinetic inertness toward the nucleophilic attack of CN$^-$ ions, which, under usual conditions (*i.e.*, at room temperature) led exclusively to the monocopper(I) complex **Cu(K-84)$_p$$^+$**.[11] Nevertheless, with much more drastic conditions, removal of both copper(I) ions can be achieved affording thus the disentangled ligand **(K-84)$_p$** (see Scheme 1). This free molecular knot appears very prompt to protonate or to bind various metal cations in order to regenerate the thermodynamically more stable "entwined" conformation. The accidental spontaneous formation of a small amount of a **Li$_2$(K-84)$_p$$^{2+}$** complex when drying free knot **(K-84)$_p$** over potassium carbonate (commercial grade K_2CO_3 contains ~5 × 10^{-5} % lithium) led us to conclude that lithium, due to its small size, was probably an ideal candidate to be hosted by the tight empty coordinating sites of **(K-84)$_p$**. This assumption was fully confirmed by the quantitative formation of the complex **Li$_2$(K-84)$_p$$^{2+}$** upon the deliberate addition of a lithium salt to a solution of free knot **(K-84)$_p$**.

Preparation and characterization of ligand (K-84)$_p$ and its lithium complex Li$_2$(K-84)$_p$$^{2+}$

Treatment of **Cu$_2$(K-84)$_p$$^{2+}$** by a large excess of KCN in refluxing wet acetonitrile led to the metal-free knot **(K-84)$_p$**, which could be purified by column chromatography over basic alumina (54% yield). Its ^{1}H NMR spectrum showed that the demetallation process was accompanied by a profound conformational change (Fig. 1). Although this change was routinely observed during the demetallation of most of the catenates and knots[9] previously prepared in our laboratory, such a conformational changeover was surprising for an obviously very tight molecular structure. Indeed, the sharp and well resolved signals obtained here for **(K-84)$_p$** contrast strongly with the broad overlapping signals of the previously studied



Scheme 1

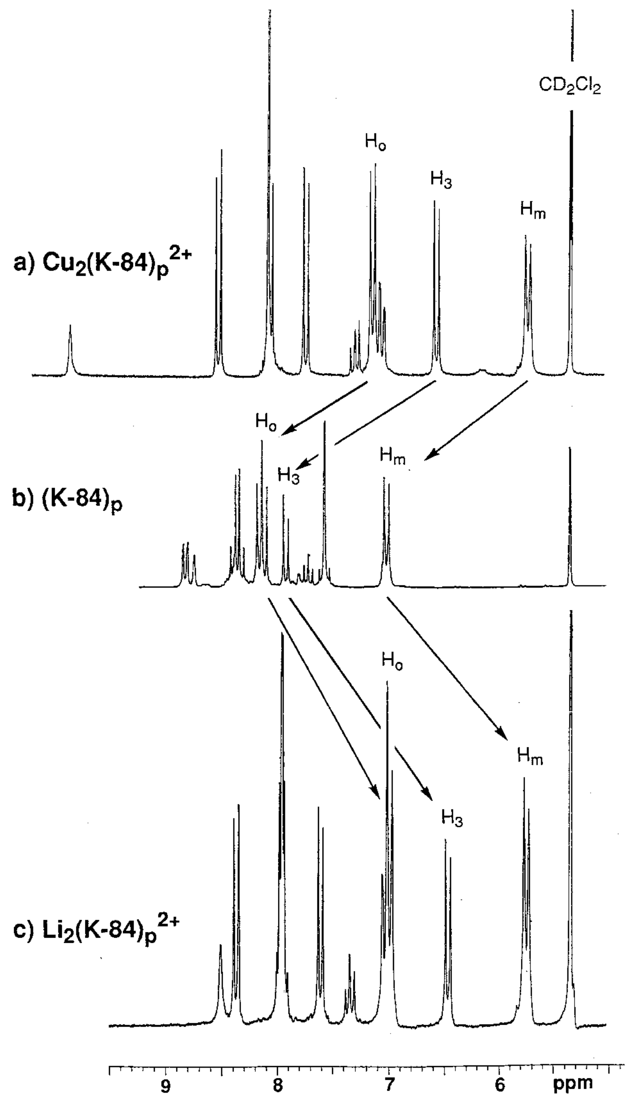


Fig. 1 ^1H NMR at 200 MHz in CD_2Cl_2 (aromatic region) of the dicopper(I) knot (*a*), the free knot (*b*) and the dilithium complex (*c*).

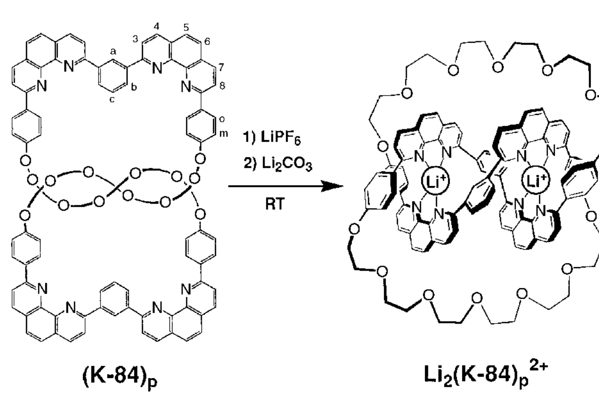


Fig. 2 A large conformational changeover occurs during the remetallation process of the free knot **(K-84)$_p$** by a lithium salt.

knot K-86[9] in which the less tight organic skeleton can undergo slow molecular rotation motions; severe mutual steric crowding between the various aromatic nuclei apparently precludes any spontaneous motion in **(K-84)$_p$**. The spectrum of Fig. 1(*b*) likely corresponds to one conformer, which does not undergo the large amplitude molecular motions observed for K-86. However, the entwined topography of the system is conformationally so favourable (aromatic stacking interactions) that the free ligand **(K-84)$_p$** will very readily complex an appropriate cationic species to regenerate this tight conformation.

The dilithium complex **Li$_2$(K-84)$_p$$^{2+}$** was prepared by a two-step procedure (Fig. 2). To an argon flushed solution of **(K-84)$_p$** in CH_2Cl_2 is added, at room temperature, a slight excess of $LiPF_6$ dissolved in methanol: the instantaneous appearance of a bright yellow colour in the solution, characteristic of protonated phenanthroline subunits, reflects the high tendency of the free knot to protonate in the presence of a trace amount of $H^+PF_6^-$. This intermediate protonated form of **(K-84)$_p$** could be converted into the target **Li$_2$(K-84)$_p$$^{2+}$** complex by the subsequent addition of a small amount of basic lithium carbonate. The progressive disappearance of the first observed yellow colouration with the simultaneous formation of a white precipitate in the solution denoted a slow competition between H^+ and Li^+. This latter conversion was brought to completion by stirring the suspension overnight. **Li$_2$(K-84)$_p$$^{2+}$** was obtained as an almost colourless solid in 90% yield after work-up and could be characterized both by NMR and mass spectroscopy. Its ^1H NMR spectrum, represented in Fig. 1(*c*), indicated clearly (high upfield chemical shift of various aromatic protons) that an entwined conformation, similar to the original one found in **Cu$_2$(K-84)$_p$$^{2+}$**, had been regenerated upon coordination of the two lithium ions by the four phenanthroline nitrogens. Interestingly, Li^+ interacts exclusively with the nitrogen atoms of **(K-84)$_p$** but not with the oxygen atoms of the hexaethyleneglycol chains.

Solid state and X-ray study

Cu$_2$(K-84)$_p$$^{2+}$·2PF$_6$$^-$. Dark red crystals suitable for X-ray analysis were obtained from a CH_2Cl_2 solution by vapour diffusion of benzene. The X-ray crystal structure of the racemic dicopper(I) knot **Cu$_2$(K-84)$_p$**$^{2+}\cdot 2PF_6^-$ is shown in Fig. 3 and selected bond distances and angles are given in Table 1.

With its three mutually perpendicular pseudo-twofold axes, one joining the two copper ions, the second one passing through the middle of the polyoxyethylenic chains and the third one being perpendicular to the two others, knot **Cu$_2$(K-84)$_p$**$^{2+}\cdot 2PF_6^-$ presents an effective D_2 symmetry but the coordination polyhedron around each copper(I) are highly distorted with respect to the tetrahedral geometry. The chelate bite of each phenanthroline ligand imposes two narrow N–Cu–N angles (80° to 82°) but the other N–Cu–N angles appear much more "open" (111° to 140°), so that the copper(I) centres become accessible to the CN^- anions during the demetallation process, despite a globally very tight structure characterized by the short Cu···Cu distance of 4.83 Å. Very interestingly, the X-ray structure analysis revealed that the racemic mixture of the chiral dicopper(I) knot **Cu$_2$(K-84)$_p$**$^{2+}\cdot 2$ PF_6^- crystallized as a conglomerate of enantiomers: that is, a given crystal contains only one enantiomer; determination of the absolute configuration showed that the analyzed crystal corresponded to the left handed knot Λ, as was also the case

Table 1 Selected bond length (Å) and angles (°) for the knot **Cu$_2$(K-84)$_p$**$^{2+}\cdot 2PF_6^-$

Cu1 environment		Cu2 environment	
Cu1–N1	2.019	Cu2–N3	2.064
Cu1–N2	2.089	Cu2–N4	2.219
Cu1–N5	2.087	Cu2–N7	2.064
Cu1–N6	2.089	Cu2–N8	2.075
N1–Cu1–N2	82.5	N3–Cu2–N4	82.4
N1–Cu1–N5	140.4	N3–Cu2–N7	141.5
N1–Cu1–N6	111.0	N3–Cu2–N8	112.4
N2–Cu1–N5	113.4	N4–Cu2–N7	112.4
N2–Cu1–N6	140.3	N4–Cu2–N8	136.3
N5–Cu1–N6	80.5	N7–Cu2–N8	81.9

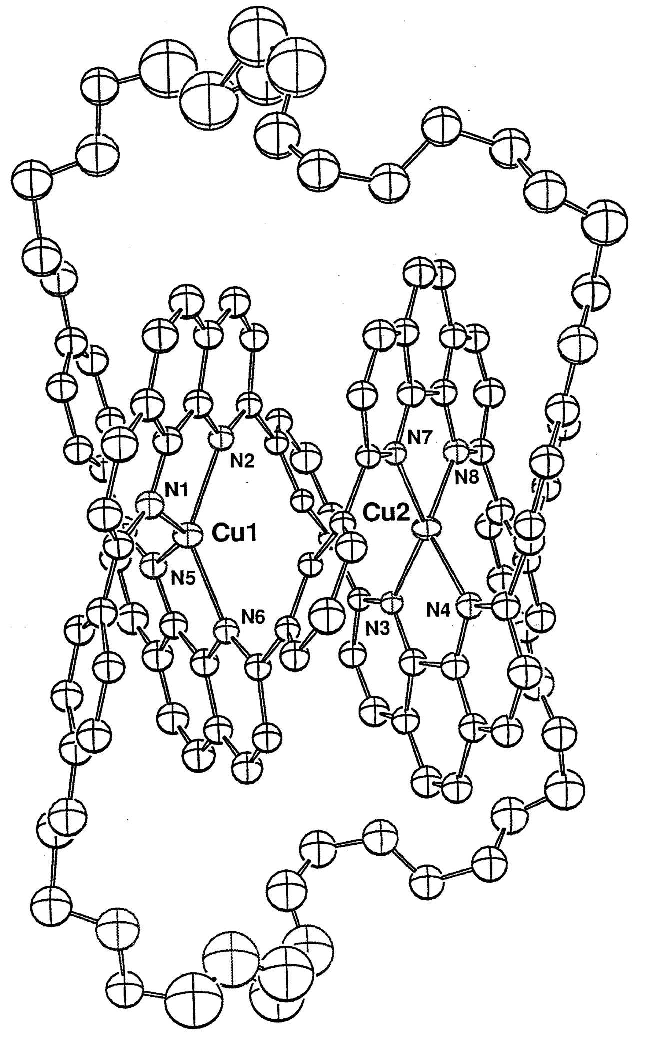


Fig. 3 Crystal structure of the dicopper(I) trefoil knot $\mathbf{Cu_2(K\text{-}84)_p}^{2+} \cdot 2PF_6^-$. The ORTEP representation shows the numbering scheme adopted for the copper and nitrogen atoms. Hydrogen atoms are omitted. Ellipsoids are at 30% electron density.

for the resolved dextrorotatory knot (+)-$\mathbf{Cu_2(K\text{-}84)_p}^{2+} \cdot 2$ PF_6^-.[12]

$\mathbf{Li_2(K\text{-}84)_p^{2+} \cdot 2PF_6^-}$. Pale, slightly pinkish monocrystals of $\mathbf{Li_2(K\text{-}84)_p}^{2+} \cdot 2PF_6^-$ could be grown from CH_2Cl_2–C_6H_6 by vapour diffusion of benzene, thus allowing determination of its molecular structure in the solid state. The molecule is made of one single molecular ribbon knotted around the two lithium ions. Although the general molecular shape (a large hydrophobic rectangular feature) of the dilithium complex appears very similar to that found for its dicopper(I) precursor, it is nevertheless characterized by an even tighter double helical central core with a Li···Li distance of 4.29 Å. In addition, this X-ray crystallographic analysis showed that the knot $\mathbf{Li_2(K\text{-}84)_p}^{2+} \cdot 2PF_6^-$ had also crystallized as a conglomerate of enantiomers, which meant that we could hope for spontaneous resolution if the crystals containing a single enantiomer could be separated manually. Unfortunately, due to weakly diffracting crystals and statistical disorder, the number of data collected (number of data with $I > 3\sigma(I) = 1973$) was not large enough to give a highly precise solid state molecular structure as well as the absolute configuration.

In conclusion, we could prepare and crystallize the dilithium complex of a molecular trefoil knot used as ligand. The X-ray structures of the dicopper(I) and the dilithium complexes are strikingly similar. The present ligand contains both $-OCH_2CH_2O-$ and phenanthroline fragments as potentially coordinating units. Formation of the observed structure demonstrates the high affinity of Li^+ for aromatic imines.

Experimental

All solvents (CH_2Cl_2, MeOH, CH_3CN) and chemicals (KCN, $LiPF_6$, Li_2CO_3) were of the best commercially available grade and were used without further purification. ^1H NMR spectra were recorded with a Bruker WP200SY spectrometer (200 MHz). Mass spectra were obtained on a ZAB-HF spectrometer (FAB) and a VG BIOQ triple quadrupole (ES-MS). Electronic spectra were performed with a Kontron Uvikon 860 spectrometer (for absorption) and with a Shimadzu spectrofluorimeter (for emission).

Preparation of $\mathbf{(K\text{-}84)_p}$

KCN (1.00 g, 15.38 mmol) dissolved in water (5 mL) was added to $\mathbf{Cu_2(K\text{-}84)_p}^{2+}$ (0.293 g, 0.136 mmol) in CH_3CN (60 mL). The resulting solution was refluxed for 4 h after which the characteristic dark red colour of the magnetically stirred solution had disappeared. After cooling of the pale yellow solution, 50 mL of water were added in order to precipitate the free $\mathbf{(K\text{-}84)_p}$ as a white amorphous solid. The resulting suspension was subsequently filtered over a sintered glass (porosity 4) and the white solid $\mathbf{(K\text{-}84)_p}$ successively washed with H_2O basified by a few drops of NH_4OH, with EtOH and finally with diethyl ether. After these washings, we obtained 0.223 g (0.129 mmol, 95% yield) of crude $\mathbf{(K\text{-}84)_p}$ as a pale yellow solid. Further purification was achieved by column chromatography over basic alumina (eluent, 1 : 1 CH_2Cl_2–hexane) yielding 0.119 g of $\mathbf{(K\text{-}84)_p}$ (54% yield, eluent: CH_2Cl_2 containing 1–5% MeOH).

$\mathbf{(K\text{-}84)_p}$: colourless glass. ^1H-NMR (CD_2Cl_2): 8.77 (dd, 4H, H_b, $J \sim 7.7$ and 1.4 Hz); 8.71 (br s, 2H, H_a); 8.37 (d, 4H, H_7, $J \sim 8.4$ Hz); 8.28 (d, 4H, H_8, $J \sim 8.4$ Hz); 8.13 (d, 8H, H_o, $J \sim 8.6$ Hz); 8.09 (d, 4H, H_4, $J \sim 8.3$ Hz); 7.90 (d, 4H, H_3, $J \sim 8.4$ Hz); 7.68 (t, 2H, H_c, $J \sim 7.7$ Hz); 7.55 (AB, 8H, $H_{5,6}$, $J \sim 8.8$ Hz); 6.98 (d, 8H, H_m, $J \sim 8.8$ Hz); 4.25 (t, 8H, H_α, $J \sim 5.5$ Hz); 3.82–3.60 (m, 40H, $H_{\beta\gamma\delta\epsilon\phi}$). MS (ES-MS): calcd for $\mathbf{(K\text{-}84)_p} \cdot H^+$: 1731.00; found: 1731.14. Calcd M/2 for $\mathbf{(K\text{-}84)_p} \cdot 2H^+$: 866.00; found: 865.85.

Preparation of $\mathbf{Li_2(K\text{-}84)_p}^{2+}$

To a degassed solution of $\mathbf{(K\text{-}84)_p}$ (0.119 g, 0.069 mmol in 50 mL CH_2Cl_2) was added at room temperature and while stirring 0.083 g (0.55 mmol) of $LiPF_6$ dissolved in 20 mL MeOH. The bright yellow acidic solution (pH ~ 3) was thereafter made basic (pH ~ 8–9) by the progressive addition of solid Li_2CO_3 and then stirred under argon at room temperature for a further 12 h after which we obtained a white precipitate in a discoloured solution. This mixture was evaporated to dryness affording a pale yellow residue, which was suspended in water before being filtered on a sintered glass (porosity 4). Additional washing of the solid remaining on the sintered glass allowed the excess of salts to be removed from $\mathbf{Li_2(K\text{-}84)_p}^{2+}$, which was recovered by dissolving it in CH_3CN. Evaporation of CH_3CN afforded 0.125 g (0.062 mmol, 89% yield) of pure $\mathbf{Li_2(K\text{-}84)_p}^{2+}$ as its PF_6^- salt.

$\mathbf{Li_2(K\text{-}84)_p}^{2+} \cdot 2PF_6^-$: very pale yellow solid (mp >280 °C). ^1H-NMR (CD_2Cl_2): 8.48 (br s, 2H, H_a); 8.34 (d, 4H, H_7, $J \sim 8.4$ Hz); 7.93 (AB, 8H, $H_{5,6}$, $J \sim 8.8$ Hz); 7.93 (d, 4H, H_4, $J \sim 8.4$ Hz); 7.58 (d, 4H, H_8, $J \sim 8.4$ Hz); 7.31 (t, 2H, H_c, $J \sim 7.7$ Hz); 7.00 (dd, 4H, H_b, $J \sim 8.0$ and 1.2 Hz); 6.97 (d, 8H, H_c, $J \sim 8.8$ Hz); 6.43 (d, 4H, H_3, $J \sim 8.4$ Hz); 5.71 (d, 8H, H_m, $J \sim 8.6$ Hz); 4.16–3.13 (m, 48H, OCH_2). MS (FAB): calcd for $\mathbf{Li_2(K\text{-}84)_p}^{2+} \cdot PF_6^-$: 1888.84; found: 1888.7. Calcd for M/2: 871.93; found: 871.4. Absorption (CH_2Cl_2) λ_{max} nm, [ε]: 320 [59300]. Emission (CH_2Cl_2, RT, λ_{max} nm): 405.

Table 2 X-ray experimental data for **$Cu_2(K\text{-}84)_p{}^{2+} \cdot 2PF_6{}^-$**

Formula	$C_{108}H_{96}N_8O_{14}Cu_2 \cdot 2PF_6 \cdot C_6H_6$
Molecular weight	2225.14
Crystal system	Orthorhombic
Space group	$P2_12_12$
a/Å	29.084(9)
b/Å	14.692(4)
c/Å	11.795(1)
U/Å^3	5040(3)
Z	2
μ/mm^{-1}	1.612
T/°C	−100
Number of data collected	3424
Number of data $[I > 3\sigma(I)]$	2776
$R(F)$	0.064
$Rw(F)$	0.088

X-ray crystallography

Crystal data for **$Cu_2(K\text{-}84)_p{}^{2+}$**$\cdot 2PF_6{}^- \cdot C_6H_6$, red crystals, were collected on a Philips PW1100/16 diffractometer using CuK_α graphite monochromated radiation ($\lambda = 1.5418$ Å) at −100 °C (crystal dimensions $0.28 \times 0.25 \times 0.18$ mm^3), $\theta/2\theta$ flying step-scan mode. Absorption corrections were calculated by empirical corrections; transmission factors were 0.74/1.00. The structure was solved using direct methods and refined against $|F|$. Hydrogen atoms were introduced as fixed contributors in idealized positions ($d_{CH} = 0.95$ Å, $B_H = 1.3$ B_{equiv} for the carbon to which it was attached). Because of some disorder on atoms C50, C51, O6 and C52, these atoms were ridden on atom O5 with isotropic temperature factors; all other non-hydrogen atoms were refined anisotropically. The absolute structure was determined by refining Flack's x parameter. Final results: $R(F) = 0.064$, $Rw(F) = 0.088$, GOF = 1.466, maximum residual electronic density = 0.79 e Å^{-3}. For all computations the Nonius OpenMoleN package[13] was used. Table 2 lists the crystallographic parameters.

Data were also collected for **$Li_2(K\text{-}84)_p{}^{2+}$**$\cdot 2PF_6{}^- \cdot 2\ CH_2Cl_2$ using the same conditions as for **$Cu_2(K\text{-}84)_p{}^{2+}$**$\cdot 2\ PF_6{}^- \cdot C_6H_6$ but the number of significant data was too small to refine the structure with anisotropic temperature factors. Crystals are colourless, orthorhombic system, space group $P2_12_12$, $a = 15.452(3)$, $b = 29.627(6)$, $c = 11.740(2)$. The overall structure is similar to that of **$Cu_2(K\text{-}84)_p{}^{2+}$**$\cdot 2\ PF_6{}^-$.

CCDC reference number 440/129. See http://www.rsc.org/suppdata/nj/1999/911/ for crystallographic file in .cif format.

Acknowledgements

Financial support from the Dankook University to NGH is gratefully acknowledged. We also gratefully acknowledge the X-ray facility of the Chemistry Department, which allowed the molecular structure determinations (Laboratoire de Cristallochimie et de Chimie Structurale, UMR 7513 ULP/CNRS, Institut de Chimie, Université Louis Pasteur de Strasbourg).

References

1 U. Olsher, R. M. Izatt, J. S. Bradshaw and N. K. Dalley, *Chem. Rev.*, 1991, **91**, 137.

2 B. Dietrich, in *Comprehensive Supramolecular Chemistry*, Pergamon, Oxford, 1996, vol. 1, p. 153.

3 P. Pfeiffer and W. Christeleit, *Z. Anorg. Allg. Chem.*, 1938, **239**, 133.

4 S. Ogawa and S. Tsuchiya, *Chem. Lett.*, 1996, 709.

5 K. Ooi, H. Kanoh, H. Sugihara and K. Hiratani, *Chem. Lett.*, 1997, 615.

6 E. C. Constable, L.-Y. Chung, J. Lewis and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1986, 1719.

7 E. C. Constable, M. J. Doyle, J. Healey and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1988, 1262.

8 T. W. Bell, P. J. Cragg, M. G. B. Drew, A. Firestone and D.-I. Kwok, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 348.

9 C. O. Dietrich-Buchecker, J.-P. Sauvage, J.-P. Kintzinger, P. Maltèse, C. Pascard and J. Guilhem, *New J. Chem.*, 1992, **16**, 931. C. O. Dietrich-Buchecker, J.-P. Sauvage, A. De Cian and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1994, 2231.

10 M. Meyer, A.-M. Albrecht-Gary, C. O. Dietrich-Buchecker and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1997, **119**, 4599.

11 C. O. Dietrich-Buchecker, J.-P. Sauvage, N. Armaroli, P. Ceroni and V. Balzani, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1119.

12 C. O. Dietrich-Buchecker, G. Rapenne, J.-P. Sauvage, A. De Cian and J. Fischer, *Chem. Eur. J.*, 1999, **5**, 1432.

13 *OpenMoleN, Interactive Structure Solution*, Nonius B.V., Delft, 1997.

Paper 9/04476K