This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Crystal Structure of the Uranyl Ion Complex of *p*-*tert*-Butylcalix[7]arene

Pierre Thuéry[a]; Martine Nierlich[a]; Mark I. Ogden[b]; Jack M. Harrowfield[c]
[a] CEA/Saclay, SCM (CNRS URA 331), Gif-sur-Yvette, France [b] School of Applied Chemistry, Curtin University of Technology, Bentley, WA, Australia [c] Special Research Centre for Advanced Minerals and Materials Processing, University of Western Australia, Nedlands, Australia

To cite this Article Thuéry, Pierre , Nierlich, Martine , Ogden, Mark I. and Harrowfield, Jack M.(1998) 'Crystal Structure of the Uranyl Ion Complex of *p*-*tert*-Butylcalix[7]arene', Supramolecular Chemistry, 9: 4, 297 — 303

To link to this Article: DOI: 10.1080/10610279808034999

URL: http://dx.doi.org/10.1080/10610279808034999

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SUPRAMOLECULAR CHEMISTRY, Vol. 9, pp. 297–303
Reprints available directly from the publisher
Photocopying permitted by license only

Crystal Structure of the Uranyl Ion Complex of *p-tert*-Butylcalix[7]arene

PIERRE THUÉRY[a,*], MARTINE NIERLICH[a], MARK I. OGDEN[b] and JACK M. HARROWFIELD[c]

[a] *CEA/Saclay, SCM (CNRS URA 331), Bât. 125, 91191 Gif-sur-Yvette, France;*
[b] *School of Applied Chemistry, Curtin University of Technology, Bentley, WA 6845, Australia;*
[c] *Special Research Centre for Advanced Minerals and Materials Processing, University of Western Australia, Nedlands, WA 6907, Australia*

(Received 27 July 1997)

The synthesis and crystal structure of the uranyl ion complex of *p-tert*-butylcalix[7]arene are reported. $(UO_2^{2+})(LH_3^{4-})(HNEt_3^{+})_2 \cdot CH_3NO_2 \cdot CH_3OH$ (1), in which LH_7 is *p-tert*-butylcalix[7]arene, crystallizes in the monoclinic space group $P2_1/c$, $a = 22.515(6)$, $b = 27.660(5)$, $c = 18.608(6)$ Å, $\beta = 113.98(2)°$, $V = 10588(10)$ Å^3, $Z = 4$. Refinement led to a final conventional R value of 0.082 for 6784 reflections. The calixarene adopts the same geometry as in its uncomplexed form, *i.e.*, it may be considered a ditopic receptor formed by the angular fusion of two cone-like cavities involving four and three phenolic units. The uranyl ion is at the centre of the base of the larger cavity and is bound to four deprotonated oxygen atoms in its equatorial plane.

Keywords: Calixarenes, uranyl ion complex, crystal structure

INTRODUCTION

Several crystal structures are known of complexes formed between the uranyl ion and *p-tert*-butylcalixarenes or bis(homo-oxa)-*p-tert*-butylcalixarenes [1–5]. Although there are gross differences associated with the ring size, conformation and degree of deprotonation of the calixarene macrocycle, the coordination environment of the uranyl ion does not vary widely. Either four or five oxygen donor atoms are found within the 'equatorial' plane of the uranyl entity and, as exemplified in the case of the complex of bis(homo-oxa)-*p-tert*-butylcalix[4]arene [1], the disposition of the donor atoms in the former case is not necessarily symmetrical nor greatly different to the disposition of four of the five atoms in the latter case. Thus, the uranium atom environment can be described as approximately pentagonal bipyramidal, although even the closest approximation to this symmetry, provided in the case of the complex of *p-tert*-butylcalix[5]arene, is considerably distorted presumably due to the presence of a proton on one of the phenol O atoms [4]. It may be that the stability of the 'cone' conformation of the smaller calixarenes is a significant influence upon the coordination geometry of their uranyl ion complexes and there is a considerable literature

---

*Corresponding author.

supporting the notion that a cone calix[6]arene could provide an 'ideal' hexagonal-planar O_6 garland for UO_2^{2+} [7, 8]. With *p-tert*-butylcalix[6]-arene, however, we have described a complex in which the metal ions are not included in the *lower rim* cavity: two uranyl ions bridge two calixarene molecules, resulting in a dimeric species, in which each uranyl ion has four nearly symmetrically disposed equatorial donor atoms provided by being bound to two phenolic oxygen atoms from each calixarene [3]. We have also found that in a different solvent system a trinuclear species involving five equatorial donor atoms for each uranium may be isolated but that here the *p-tert*-butylcalix[6]arene is bound only in a bridging bidentate form [5]. A further significant change in the coordination chemistry occurs with *p-tert*--butylcalix[8]arene, where the size of the macrocycle is apparently sufficient for two uranyl ions to fit within the cavity, each of them bonded to four phenolic oxygen atoms and one bridging hydroxyl ion [2]. Again, a minor change in the synthetic procedure allows the isolation of a trinuclear species which is effectively a uranyl ion adduct of the dinuclear complex in which the third uranyl ion is not directly bonded to the phenolic oxygen atoms [5]. We have also reported recently the structure of the binuclear uranyl complex of an acyclic calix[6]arene analogue [6]. These several observations of significant ring size effects indicated that the calix[7]arene system should be of particular interest and so we report our observations herein. In fact, crystal structure studies of calix[7]arenes are rare: they are restricted to the determination of the structure of the *p*-ethyl derivative, [9] and of that of the pyridine adduct of the *p-tert*-butyl derivative [10]. In both cases, the calixarene conformation is similar and was analysed as if composed of two distinct parts, which were described as half a calix[6] and half a calix[8]arene [9], or as trimeric and tetrameric subunits [10]. We describe here the third structure of a calix[7]arene, which is the first one of a metal complex.

DISCUSSION

The uranyl complex of *p-tert*-butylcalix[7]arene is readily formed in organic solvents, by combining the uranyl cation and the calixarene in the presence of a base such as triethylamine. Complex formation is indicated by the rapid formation of a deep orange colour, as has been observed in other uranyl/calixarene systems [1 – 5]. The 300 MHz ^1H NMR spectrum of the isolated complex in CD_2Cl_2 is severely broadened at room temperature. This contrasts with the spectrum of the uranyl complex of bis(homooxa)-*p-tert*-butylcalix[4]arene [1], which is sharp and shows no significant changes over the range −60 to 55°C. In the present case, cooling the NMR solution allows some useful observations to be made. At −10°C, two phenolic proton signals appear at δ 8.36 and 12.28, integrating for one and two protons respectively, suggesting that the calix[7]arene has lost four phenolic protons and consistent with the indication from the structure determination that the complex molecule has an effective plane of symmetry bisecting both the tetrameric unit binding the uranyl ion and the trimeric unit. Four *tert*-butyl proton resonances in the ratio 2:2:2:1 are also indicative of the retention of the solid state structure in solution. A broad triplet and quartet are observed at δ −0.2 and 0.9 respectively, suggesting by analogy with previous observations, [1] that a triethylammonium cation is included within the cavity of the calixarene, resulting in the upfield shift of these resonances. Further deductions concerning the conformation of the calixarene were complicated by changes in the spectrum that were not fully resolved at the lowest temperature attained (−50°C), and hence an X-ray diffraction study was undertaken.

The complex crystallised readily from various solvents. Crystals suitable for X-ray crystallography were obtained from nitromethane/methanol **1**, and also acetonitrile **2**. While both gave satisfactory data, the data from **1** was better behaved upon refinement, and it is this structure that is reported here. *ORTEPII* [11] drawings of the molecular unit of **1** are represented in Figures 1 and 2 and selected bond distances and angles are given in Table I (bond lengths and angles in the calixarene moiety and the counter-ions and solvents do not deviate significantly from the usual ones).

The structure determination gives the overall formula $(UO_2^{2+})(LH_3^{4-})\cdot(HNEt_3^+)_2\cdot CH_3NO_2\cdot CH_3OH$, where L^{7-} is the heptaanion of *p-tert*-butylcalix[7]arene. The complex molecule does not possess any true symmetry element but may be considered to be bisected by a symmetry plane if the triethylammonium cations and *tert*-butyl groups are ignored. The overall calixarene conformation is close to that observed in the structure previously reported for the uncomplexed form [9, 10], and is not significantly affected by uranyl complexation. The uranyl ion is located in the calixarene *lower-rim* cavity, and is bound, in its equatorial plane, to the four oxygen atoms pertaining to the tetrameric subunit (O(1)–O(4)). The four U-O distances are equivalent, in the range 2.21(1)–2.33(1) (mean value 2.28(5)) Å. Such values, compared with those in the previously reported structures [1–4, 6], indicate that the four phenolic oxygen atoms have been deprotonated, which is confirmed by the presence of two triethylammonium ions. The four coordinated oxygen atoms define a plane within ±0.03(1) Å, the uranium atom being at 0.005(1) Å from this mean plane. The O(uranyl)-U-O(calix) angles have a mean value of 90(2)°, indicative of a nearly perfect equatorial environment for the linear uranyl ion. The O(calix)-U-O(calix) angles span a wider range, the angle involving the non-adjacent atoms O(1) and O(4) being the larger (107.9(4)°): the uranyl environment is a slightly distorted square plane, less regular than the one observed in the *p-tert*-butylcalix[6]arene dimer [3] but very similar to that found in the complex of bis(homo-

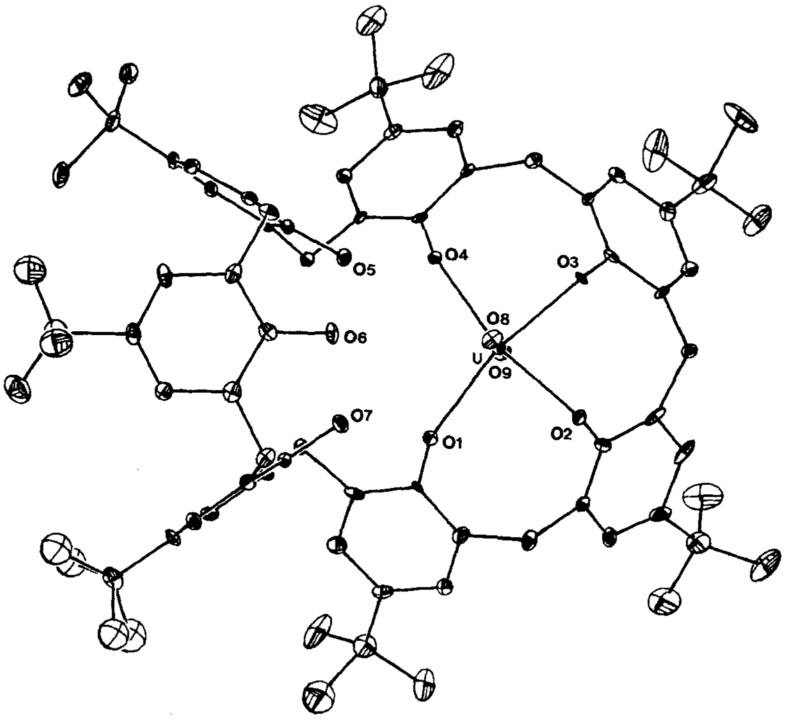

FIGURE 1 Molecular unit of 1. Counter-ions and solvent molecules omitted.

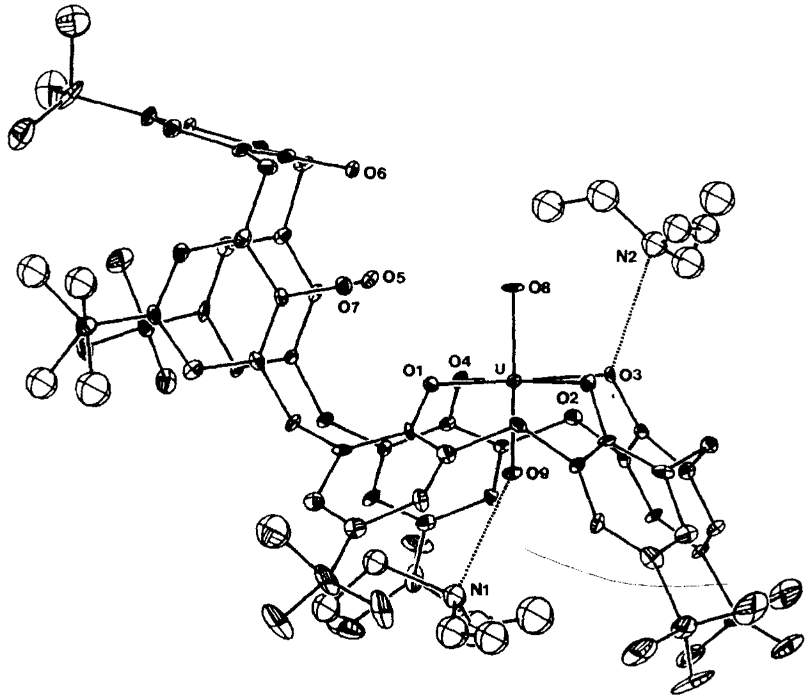

FIGURE 2 Molecular unit of 1 with counter-ions. Hydrogen bonds in dashed lines. Solvent molecules omitted.

TABLE I Selected bond lengths (Å) and angles (°) in 1

Uranium environment			
U-O(1)	2.33(1)	U-O(2)	2.21(1)
U-O(3)	2.26(1)	U-O(4)	2.32(1)
U-O(8)	1.85(1)	U-O(9)	1.86(1)
O(1)-U-O(2)	86.5(4)	O(2)-U-O(3)	80.8(4)
O(3)-U-O(4)	84.8(4)	O(4)-U-O(1)	107.9(4)
O(1)-U-O(8)	91.5(5)	O(1)-U-O(9)	89.3(5)
O(2)-U-O(8)	91.5(5)	O(2)-U-O(9)	91.3(5)
O(3)-U-O(8)	87.1(5)	O(3)-U-O(9)	92.7(5)
O(4)-U-O(8)	89.1(5)	O(4)-U-O(9)	88.0(5)
O(8)-U-O(9)	177.1(6)		
O···O and N···O contacts			
O(1)···O(2)	3.11(2)	O(2)···O(3)	2.90(2)
O(3)···O(4)	3.09(2)	O(4)···O(1)	3.75(2)
O(4)···O(5)	2.66(2)	O(5)···O(6)	2.84(2)
O(6)···O(7)	2.85(2)	O(7)···O(1)	2.63(2)
N(2)···O(3)	2.77(3)	N(1)···O(9)	2.68(2)
Torsion angles			
Rings	ϕ	χ	
1–2	94(2)	−82(2)	
2–3	92(2)	−93(2)	
3–4	79(2)	−85(2)	
4–5	−88(2)	92(2)	
5–6	83(2)	−77(2)	
6–7	80(2)	−90(2)	
7–1	−93(2)	91(2)	

oxa)-*p*-*tert*-butylcalix[4]arene, with the respective O(calix)-U-O(calix) angles differing by no more than 1.5°. The O···O contacts between oxygen atoms pertaining to adjacent phenolic groups range from 2.63(2) to 3.11(2) Å and are indicative of slight geometric differences with the structures of neutral calix[7]arenes arising from a different intramolecular hydrogen bond pattern. In the two neutral forms described [9, 10], the O···O contacts range from 2.430(9) to 2.744(7) Å, with the exception of one contact in the pyridine complex (3.500(8) Å) [10] due to disruption of the cyclic hydrogen bond array. In the present case, the shorter contact distances are between atoms pertaining to two different subunits (O(1)···O(7) 2.63(2), O(4)···O(5) 2.66(2) Å) and are probably associated with strong hydrogen bonds between deprotonated (O(1) and O(4)) and protonated (O(5) and O(7)) oxygen atoms. The three contacts in the tetrameric subunit are larger (2.90(2) – 3.11(2) Å), in agreement with the deprotonation of the four oxygen atoms: the complexation, and not the hydrogen bonding, locks the subunit in the *cone* conformation. Within the trimeric subunit (O(5) – O(7)), the hydrogen bonds seem weaker than in the neutral form, which may be due to the involvement of O(5) and O(7) in strong hydrogen bonds with O(1) and O(4). This is consistent with the NMR studies, which showed a large difference in chemical shift between two phenolic protons (δ 12.28, presumably on O(5, 7) and the remaining phenolic proton (δ 8.36), presumably on O(6)). The dihedral angle between the oxygen mean planes corresponding to each subunit is 90.5(4)°, close to the value in the neutral form (90.8(2)°) [10]. The two triethylammonium ions are hydrogen bonded, either to a uranyl oxygen atom (N(1) ··· O(9) 2.68(2) Å, the ion being included in the hydrophobic part of the tetrameric subunit (consistent with the NMR studies), or to a deprotonated phenolic oxygen atom (N(2) ··· O(3) 2.77(3) Å). Such a situation is common in uranyl/calixarene complexes, though there are subtle variations such as in the fact that the included cation in the present case is involved in an intramolecular hydrogen bond to a uranyl oxygen while in the bis(homo-oxa)-*p-tert*-butylcalix[4]arene the included cation has an inverted configuration requiring it to form an intermolecular hydrogen bond. The calix[7]arene conformation can be described by the sequence of ϕ and χ torsion angles as defined by Ugozzoli and Andreetti [12]: comparison with the values reported for the neutral species [10] shows that, apart from slight differences in the angles values due to minor geometric changes, the sign sequence, indicative of the overall geometry, is the same in both cases. According to this sequence, both the tetrameric and the trimeric subunits are in distorted *cone* conformations. The oxygen donor atom arrays in the *cone* conformations of bis(homo-oxa)-*p-tert*-butylcalix[4]arene [1] and *p-tert*-butylcalix[5]arene [4] appear well suited for coordination of one uranyl ion, and *p-tert*-butylcalix[8]arene is able to accommodate at least two uranyl ions by adopting a conformation like that of two fused, shallow, tetrameric cones [2]. In this, it resembles the linear hexamer complex, in which a nitrate anion provides donor atoms "missing" because of the lack of the extra phenoxide donors in the macrocycle [6]. In the macrocyclic *p-tert*-butylcalix[6]arene [3], it would appear that a conformation allowing at least four donor atoms to be bound to one uranyl cation cannot be adopted, so that it functions only as a bidentate ligand. The present results for the *p-tert*-butylcalix[7]arene complex, where there is a clear preference for binding in the tetrameric rather than the trimeric subunit suggest that the bidentate case does not enable so effective an interaction with the metal. Given this and the very minor conformational changes resulting from coordination, *p-tert*-butylcalix[7]arene may be said to be "preorganised" for binding of a single uranyl ion, though a quantitative comparison with bis(homo-oxa)-*p-tert*-butylcalix[4]arene and *p-tert*-butylcalix[5]arene (at least) is necessary to further characterise selectivity in uranium binding by calixarenes: this work is currently in progress.

EXPERIMENTAL

Synthesis

0.17 mmol of *p-tert*-butylcalix[7]arene (purchased from Acros and used without further purification) was dissolved in 20 mL of chloroform and 5 mL of triethylamine. The slow addition of a solution of 0.4 mmol of uranyl nitrate hexahydrate in 15 mL of acetonitrile resulted in a deep orange solution, that was evaporated to dryness and recrystallised several times. Final recrystallisation from nitromethane:methanol (1:1) yielded dark orange crystals of **1** suitable for X-ray crystallography.

A similar procedure, substituting acetonitrile for the chloroform solvent used above, resulted in crystals of **2** suitable for X-ray crystallography, directly from the reaction mixture. Attempts made to obtain elemental microanalyses on the dried, powdered product indicated that drying may have produced significant changes in composition relative to the crystalline material. Thus, the structure determination showed the presence of two triethylammonium cations per uranyl unit but analyses were consistent with only one (and the absorption of atmospheric water): Found C, 61.8; H, 6.8; N, 1.9%; calculated for [UO$_2$(*p-tert*-butylcalix[7]arene-3H)]. (HNEt$_3$)·CH$_3$CN·6H$_2$O, C$_{85}$H$_{126}$N$_2$O$_{13}$U, C, 61.73; H, 7.68; N, 1.69%.

Crystal Data

1 [UO$_2$(*p-tert*-butylcalix[7]arene-4H)]$^{2-}$·2HNEt$_3^+$ · CH$_3$NO$_2$ · CH$_3$OH, UO$_{12}$N$_3$C$_{91}$H$_{133}$, $M = 1699.12$; monoclinic, space group $P2_1/c$, $a = 22.515(6)$, $b = 27.660(5)$, $c = 18.608(6)$ Å, $\beta = 113.98(2)°$, $V = 10588(10)$Å^3, $Z = 4$, $D_x = 1.066$ Mg·m^{-3}, $\mu = 15.00$ cm^{-1}, $F(000) = 3552$.

2 [UO$_2$(*p-tert*-butylcalix[7]arene-4H)]$^{2-}$. 2HNEt$_3^+$ · CH$_3$CN · 2H$_2$O, UO$_{11}$N$_3$C$_{91}$H$_{133}$, $M = 1683.12$; monoclinic, space group $P2_1/c$, $a = 22.505(5)$, $b = 27.773(6)$, $c = 18.580(5)$ Å, $\beta = 113.30(2)°$, $V = 10666(10)$ Å^3, $Z = 4$, $D_x = 1.048$ Mg·m^{-3}, $\mu = 15.7$ cm^{-1}, $F(000) = 3520$.

Data Collection, Structure Determination and Refinement

While the results of the X-ray diffraction experiments were similar for both **1** and **2**, the refinement of the structure of **2** was badly behaved for a number of parameters, particularly those of the triethylammonium cations. Thus full details are given here only for structure **1**. The diffraction experiment was performed with an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo$K\alpha$ radiation. The crystal (0.60 × 0.50 × 0.25 mm) was introduced in a glass capillary. The lattice parameters were determined from the least-squares refinement of the setting angles of 25 reflections ($8 < \theta < 12°$). The data were collected in the range $1 < \theta < 22°$, in the ω/θ scan mode, at 243 K. The intensity decay, estimated from three standard reflections measured every 60 min, was insignificant. The data were corrected for Lorentz-polarization effects, and for absorption effects with DIFABS [13]. The structure was solved with SHELXS-86 [14] and refined by full-matrix least-squares on F. Hydrogen atoms were not included. Analytical scattering factors for neutral atoms [15] were corrected for the anomalous dispersion terms $\Delta f'$ and $\Delta f''$. 6784 observations with $I > 3\sigma(I)$, out of 12536 unique reflections measured ($R_{\text{int}} = 0.013$), were used. 829 parameters were refined (anisotropic displacement parameters for uranium and oxygen atoms and for the carbon atoms of the calixarene moiety, except those of one *tert*-butyl group, that was modeled with four isotropic terminal carbon atoms; the triethylammonium ions were refined isotropically and the solvent molecules were fixed as they appear on the Fourier map, the methanol molecule is disordered around a symmetry centre and has been modeled by two carbon atoms). The final R values were $R = 0.082$ and $R_w = 0.103$ ($w = 1/\sigma(F)^2$) and the maximum positive and negative residual densities 1.00 and -0.18 eÅ^{-3}. All calculations were performed on a Vax 4000 - 200 computer, with the Enraf-Nonius MolEN system [16].

Acknowledgments

MO acknowledges support under the Australian Research Council Postdoctoral Fellowship Scheme.

References

[1] Harrowfield, J. M., Ogden, M. I. and White, A. H. (1991). *J. Chem. Soc. Dalton. Trans.*, 979.

[2] Thuéry, P., Keller, N., Lance, M., Vigner, J. D. and Nierlich, M. (1995). *Acta Crystallogr. Sect. C*, **51**, 1570.

Thuéry, P., Keller, N., Lance, M., Vigner, J. D. and Nierlich, M. (1995). *New. J. Chem.*, **19**, 619.

[3] Thuéry, P., Lance, M. and Nierlich, M. (1996). *Supramol. Chem.*, **7**, 183.

[4] Thuéry, P. and Nierlich, M. (1997). *J. Incl. Phenom.*, **27**, 13.

[5] Delaigue, X., Harrowfield, J. M., Ogden, M. I. and White, A. H. unpublished results.

[6] Thuéry, P. and Nierlich, M. (1997). *J. Chem. Soc., Dalton Trans.*, 1481.

[7] Shinkai, S., Shiramama, Y., Satoh, H., Manabe, O., Arimura, T., Fujimoto, K. and Matsuda, T. (1989). *J. Chem. Soc., Perkin Trans.*, **2**, 1167 and references therein.

[8] Archimbaud, M., Henge-Napoli, M. H., Lilienbaum, D., Desloges, M. and Montagne, C. (1994). *Radiation Protection Dosimetry*, **53**, 327 and references therein.

[9] Perrin, M., Lecocq, S. and Asfari, Z. (1990). *C. R. Acad. Sci. Paris*, **310**, 515.

[10] Andreetti, G. D., Ugozzoli, F., Nakamoto, Y. and Ishida, S. I. (1991). *J. Incl. Phenom.*, **10**, 241.

[11] Johnson, C. K. (1976). ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee.

[12] Ugozzoli, F. and Andreetti, G. D. (1992). *J. Incl. Phenom.*, **13**, 337.

[13] Walker, N. and Stuart, D. (1983). *Acta Crystallogr. Sect. A.*, **39**, 158.

[14] Sheldrick, G. M. (1985). SHELXS-86: Program for the Solution of Crystal Structures, University of Göttingen, Germany.

[15] International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, England, 1974. Present distributor: Academic Publishers, Dordrecht, The Netherlands.

[16] MolEN: An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, The Netherlands, 1990.