impose une rotation de 44° par rapport à la position *syn*-éclipsée prévue par les effets électroniques (van Meurs & van Koningsveld, 1976). Une projection de Newman suivant la direction C(12)—C(14) montre que le cycle phényle et l'un des groupements hydroxyméthyle sont en position éclipsée.

Cette conformation ne peut être imposée par une interaction intramoléculaire des atomes d'hydrogène. En effet aucune distance interatomique ne peut correspondre à des liaisons hydrogène. Par contre des liaisons hydrogène intermoléculaires sont vraisemblablement à l'origine de la conformation relative des fonctions benzyliques et du groupement phényle: $O(17)—O(19)_{101} = 2{,}743\ (5)$ Å; $O(19)_{101}—HO(19)_{101} = 0{,}72\ (7)$, $HO(19)_{101}—O(17) = 2{,}03\ (8)$ Å et $O(17)—O(19)'_{100} = 2{,}762\ (5)$ Å; $O(17)—HO(17) = 0{,}73\ (8)$, $HO(17)—O(19)'_{100} = 2{,}04\ (7)$ Å.

La cohésion du cristal est due aux liaisons hydrogène intermoléculaires, cette cohésion est renforcée par des contacts de van der Waals. Il est à signaler que ce type de motif cristallin se retrouve dans des composés analogues ne comportant toutefois qu'une fonction hydroxy (Dusausoy, Lecomte, Protas & Besançon, 1973).

A l'heure actuelle, parmi une classe de composé fort nombreuse, il n'existe encore que peu d'exemples d'additions de carbanions benzyliques arène chrome tricarbonyle sur des composés électrophiles autres que les dérivés halogénés. La déprotonation de la position benzylique s'avère être une voie d'accès efficace et sélective à toute une série de composés. La nature de la base utilisée en l'occurrence le *tert*-butylate de potassium, est à l'origine de l'activation de la position benzylique. L'utilisation du butyllithium active les positions du noyau benzénique, cette dernière propriété a été largement exploitée en synthèse.

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The Barium 3,5-Dinitrobenzoate Benzo-15-crown-5 Complex,* $Ba^{2+}.2C_7H_3N_2O_6^-.C_{14}H_{20}O_5$

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Abstract. $M_r = 827{\cdot}9$, triclinic, $P\bar{1}$, $a = 13{\cdot}694\ (7)$, $b = 14{\cdot}183\ (7)$, $c = 9{\cdot}781\ (5)$ Å, $\alpha = 105{\cdot}64\ (4)$, $\beta = 100{\cdot}97\ (4)$, $\gamma = 109{\cdot}36\ (4)°$, $V = 1642{\cdot}1\ (14)$ Å^3, $Z = 2$, $D_x = 1{\cdot}674$ g cm^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0{\cdot}70926$ Å, $\mu(\text{Mo } K\alpha) = 11{\cdot}88$ cm^{-1}, $F(000) = 828$, $T = 294$ K, $R = 0{\cdot}039$ for 3835 observed unique data. The complex crystallizes as a dimer in which the two Ba^{2+} ions are linked by four carboxylate bridges; the crown ethers are also coordinated to the Ba^{2+} ions resulting in a coordination number of nine for each Ba^{2+}. The Ba^{2+} ion lies 1·877 (1) Å out of the plane of the five crown oxygens.

Introduction. For a number of years one of us (NSP) has been interested in the comparative preferences of different alkali and alkaline earth cations (M^{z+}) for neutral ligands over anionic species (Poonia & Bajaj, 1979). One of the approaches has been to study ligand/anion preferences of different cations through X-ray structural studies of M^{z+} complexes with a common neutral ligand, *e.g.* benzo-15-crown-5

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* Bis(3,5-dinitrobenzoato)(6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxabenzocyclopentadecene)barium.

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(B15C5). The counteracting anion had been either 2,4,6-trinitrophenolate (pic$^-$) (Bhagwat, Manohar & Poonia, 1980*a*,*b*, 1981; Ward, Popov & Poonia, 1984; Venkatasubramanian, Poonia, Hackert, Clinger & Ernst, 1984*a*,*b*) or 3,5-dinitrobenzoate (3,5-DNB$^-$) (Venkatasubramanian, Poonia & Chaudhuri, 1984; Cradwick & Poonia, 1977; Hackert, Clinger, Ernst & Poonia, 1984). Structures of B15C5 complexes with 3,5-DNB$^-$ salts of large divalent cations have not been investigated as yet and this led us to study the structure of the complex $Ba^{2+}(3,5\text{-}DNB^-)_2(B15C5)$.

Experimental. An aqueous solution, 0·1*M* in $Ba^{2+}(OH^-)_2$, containing as a suspension 3,5-dinitrobenzoic acid (3,5-DNBH) (equivalent to 0·2*M*), was digested on a steam bath for about two hours to form the solid $Ba^{2+}(3,5\text{-}DNB^-)_2$. The residue was filtered, digested with ethanol to eliminate any unreacted 3,5-DNBH, refiltered, and dried at about 373 K. An ethanolic solution, 1·0 m*M* in B15C5, containing as a suspension $Ba^{2+}(3,5\text{-}DNB^-)_2$ (equivalent to 0·1 m*M*), was refluxed for one hour to obtain a yellow solution of the $Ba^{2+}(3,5\text{-}DNB^-)_2(B15C5)$ complex. The solution was decanted from any undissolved material and was allowed to evaporate slowly at room temperature. The deep-yellow diamond-shaped crystals so obtained were washed with cold benzene to eliminate any cocrystallized B15C5.

Crystal size 0·10 × 0·18 × 0·26 mm; crystal faces [*hkl*, distance (mm) to origin within crystal] $(\bar{1}11)$ 0·061, $(1\bar{1}\bar{1})$ 0·034, (010) 0·087, $(0\bar{1}0)$ 0·067, $(1\bar{1}0)$ 0·084, $(\bar{1}10)$ 0·095, (001) 0·085, $(00\bar{1})$ 0·053, $(\bar{1}01)$ 0·073, $(10\bar{1})$ 0·015; Picker FACS-I diffractometer, lattice parameters from 14 reflections with $35 < 2\theta < 37°$, absorption-correction (Templeton & Templeton, 1973) factors 1·079 to 1·235, $(\sin\theta/\lambda)_{\max} = 0·596$ Å^{-1}, $0 \le h \le 16$, $-16 \le k \le 15$, $-11 \le l \le 11$, standard reflections (and intensities) $1\bar{3}0$ (22005·3 to 19383·3), 213 (31065·7 to 28226·6), 011 (25507·5 to 23081·7); 6083 reflections measured, 5817 unique, $R_{\rm int} = 0·031$, 1982 unobserved $[I < 3\sigma(I)]$; Patterson and direct methods [*MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978)], refinement on *F*, calculated H-atom positions, anisotropic non-H atoms, H atoms fixed, $R = 0·039$, $wR = 0·038$, $S = 0·991$, $w = 1/\sigma(F)^2$, $(\Delta/\sigma)_{\max} = 0·47$, $\Delta\rho$ excursions 0·70 to $-0·85$ e Å^{-3}; no secondary extinction correction; atomic scattering factors, *f*′ and *f*″ from *International Tables for X-ray Crystallography* (1974), computations using DEC PDP 8/I, DEC PDP 11/40, and CDC Cyber 170 Model 750 computers and the programs listed in Table 7 (deposited).

Discussion. Fig. 1 shows the numbering of the atoms and Fig. 2 the structure of the $Ba^{2+}(3,5\text{-}DNB^-)_2(B15C5)$ complex. Tables 1 to 6 list atomic coordinates, anisotropic thermal parameters, interatomic distances, interatomic angles, least-squares planes, and torsion angles, respectively.*

Stoichiometrically, the complex is 1:1 while in the crystal it exists as 2:2 (dimerized) because of bridging provided by the carboxylate oxygens. The cation is involved in a ninefold coordination through all the five crown oxygens [2·888 (4) to 3·092 (5) Å] and one anionic oxygen [2·639 (5) to 2·694 (4) Å] from each of the four carboxylate groups. The overall system presents an effective encagement of the cation wherein the involvement of the anionic oxygens is extensive. In the system $Ba^{2+}(pic^-)_2(B15C5).H_2O$ (Venkatasubramanian, Poonia, Hackert, Clinger & Ernst, 1984*a*,*b*), there is a discrete 1:1 complexation with no such bridging and dimerization. Dimerization has been observed only for the crown complexes of low charge density M^+ ions (Rb^+ and Cs^+), with a crown of the 18C6 size, with bridging *via* the cation associating NCS^- (Dobler & Phizackerley, 1974; Mallinson, 1975; Hašek & Huml, 1978) and/or *via* a stereochemically juxtaposed donor function on the crown such as the NO_2 group (Hlavatá, Hašek & Huml, 1978; Hašek, Hlavatá & Huml, 1977).

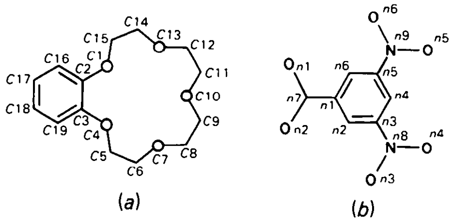

Fig. 1. The numbering of the atoms. (*a*) Benzo-15-crown-5. The numbers of *all* atoms in the crown ligand are preceded by a '*C*'. (*b*) 3,5-Dinitrobenzoate. $n = 1$ for atoms in the first 3,5-DNB$^-$ anion, $n = 2$ for atoms in the second. H atoms are numbered the same as their bonded C atoms.

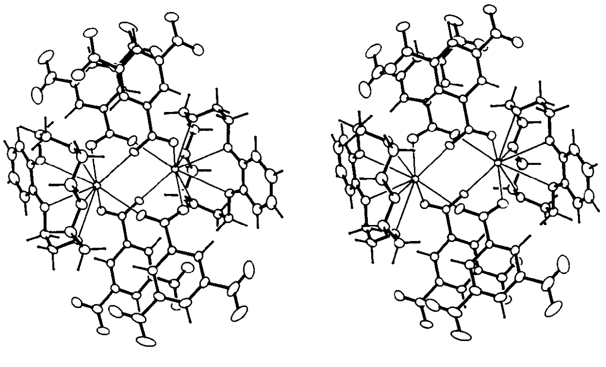

Fig. 2. The dimer of the $Ba^{2+}(3,5\text{-}DNB^-)_2(B15C5)$ complex [*ORTEP* (Johnson, 1965)].

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* Lists of structure factors and Tables 1*A* and 2 to 7 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39372 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and equivalent isotropic thermal parameters in barium* 3,5-*dinitrobenzoate benzo*-15-*crown*-5

Calculated standard deviations are indicated in parentheses.

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij} a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Ba(1)	0·01752 (3)	−0·12133 (3)	0·11241 (4)	2·70
O(11)	−0·1287 (3)	−0·0355 (3)	0·1463 (5)	3·95
O(12)	−0·1555 (3)	0·0828 (3)	0·0467 (5)	3·93
O(13)	−0·5211 (4)	0·0065 (5)	−0·2464 (6)	6·70
O(14)	−0·6539 (4)	−0·1381 (5)	−0·2800 (7)	7·99
O(15)	−0·6039 (4)	−0·3675 (5)	−0·0142 (7)	7·25
O(16)	−0·4459 (4)	−0·3362 (5)	0·1167 (8)	8·45
C(11)	−0·3075 (4)	−0·0690 (5)	0·0162 (6)	2·99
C(12)	−0·3764 (5)	−0·0436 (5)	−0·0763 (7)	3·56
C(13)	−0·4859 (5)	−0·1052 (5)	−0·1282 (7)	3·95
C(14)	−0·5311 (5)	−0·1945 (5)	−0·0918 (7)	3·75
C(15)	−0·4608 (5)	−0·2177 (5)	−0·0004 (7)	3·70
C(16)	−0·3506 (5)	−0·1587 (5)	0·0524 (6)	3·28
C(17)	−0·1859 (5)	−0·0011 (5)	0·0755 (7)	3·19
N(18)	−0·5595 (5)	−0·0773 (6)	−0·2272 (7)	5·13
N(19)	−0·5071 (5)	−0·3152 (5)	0·0360 (7)	5·35
O(21)	0·1370 (4)	0·0899 (4)	0·2072 (5)	5·20
O(22)	0·1267 (4)	0·2300 (4)	0·1551 (5)	5·60
O(23)	0·3102 (8)	0·5645 (6)	0·6021 (9)	12·91
O(24)	0·4781 (6)	0·6027 (5)	0·7082 (8)	10·26
O(25)	0·6043 (5)	0·3253 (7)	0·6697 (8)	12·55
O(26)	0·5021 (6)	0·1652 (7)	0·5141 (10)	11·23
C(21)	0·2670 (4)	0·2618 (4)	0·3588 (6)	2·89
C(22)	0·2819 (5)	0·3665 (5)	0·4302 (7)	3·76
C(23)	0·3726 (6)	0·4319 (5)	0·5496 (7)	4·54
C(24)	0·4515 (6)	0·3990 (6)	0·5984 (7)	5·07
C(25)	0·4365 (5)	0·2965 (7)	0·5271 (8)	5·13
C(26)	0·3450 (5)	0·2267 (5)	0·4087 (7)	3·87
C(27)	0·1682 (5)	0·1869 (5)	0·2295 (7)	3·82
N(28)	0·3877 (8)	0·5423 (6)	0·6254 (9)	7·54
N(29)	0·5209 (6)	0·2603 (8)	0·5755 (9)	7·62
O(*C*1)	0·1149 (3)	−0·2823 (3)	0·0705 (5)	4·35
C(*C*2)	0·0573 (5)	−0·3668 (5)	−0·0637 (8)	4·01
C(*C*3)	−0·0540 (5)	−0·4135 (5)	−0·0874 (8)	4·00
O(*C*4)	−0·0854 (3)	−0·3670 (3)	0·0282 (5)	4·35
C(*C*5)	−0·1971 (5)	−0·4070 (5)	0·0192 (9)	5·01
C(*C*6)	−0·2018 (5)	−0·3580 (6)	0·1693 (9)	5·16
O(*C*7)	−0·1580 (3)	−0·2446 (3)	0·2081 (5)	4·27
C(*C*8)	−0·1405 (6)	−0·1854 (6)	0·3605 (9)	5·52
C(*C*9)	−0·0371 (7)	−0·1722 (6)	0·4627 (8)	5·82
O(*C*10)	0·0505 (4)	−0·1156 (4)	0·4166 (5)	4·78
C(*C*11)	0·1520 (6)	−0·1049 (6)	0·5021 (7)	5·17
C(*C*12)	0·2374 (6)	−0·0397 (6)	0·4492 (8)	5·35
O(*C*13)	0·2247 (3)	−0·0919 (4)	0·2969 (5)	4·31
C(*C*14)	0·2680 (5)	−0·1708 (6)	0·2732 (9)	5·19
C(*C*15)	0·2305 (5)	−0·2366 (6)	0·1132 (9)	5·06
C(*C*16)	0·1030 (6)	−0·4029 (7)	−0·1684 (10)	5·75
C(*C*17)	0·0345 (9)	−0·4885 (8)	−0·2986 (10)	7·13
C(*C*18)	−0·0743 (9)	−0·5339 (7)	−0·3225 (9)	7·01
C(*C*19)	−0·1202 (6)	−0·4971 (6)	−0·2155 (9)	5·52

The present complex is the first example known to us of a crown complex of an M^{2+} ion (and an organic anion) producing a dimeric system. For the same anion, the smaller (Na^+) and the higher charge density (Ca^{2+}) cations yield discrete 1:1 and 1:2 complexes Na^+(3,5-DNB^-)(B15C5) (Venkatasubramanian, Poonia & Chaudhuri, 1984) and Ca^{2+}(3,5-DNB^-)$_2$(B15C5)$_2$.3H_2O (Cradwick & Poonia, 1977) with the crown in question wherein 3,5-DNB^- anions act as bidentates. The Ba^{2+} ion is not involved in such a four-membered ring chelation with the carboxylate. Nevertheless, it maintains contact with the anionic oxygens and does not form a charge-separated sandwich with B15C5 which would be expected in view of the ion–cavity radius concept (Cotton & Felthouse, 1981).

Four carboxylate bridges between metal ions have been reported for several complexes such as the dimers of $Ni^{2+}[(CH_3)_3CCOO^-]_2C_{10}H_9N$ and $Cu^{2+}[(CH_3)_3CCOO^-]_2C_{13}H_9N$ (Kirillova *et al.*, 1980) and $Rh^{2+}(C_2H_5COO^-)_2L_n$ ($n = 0{\cdot}5$ or $1{\cdot}0$; L = acridine, 7-azaindole, phenazine or durenediamine) (Cotton & Felthouse, 1981). In these complexes, the geometry of the metal ions is essentially octahedral and the metal–metal distances are 2·387 (1) to 2·417 (1) Å (Rh^{2+}), 2·702 (1) Å (Cu^{2+}), and 2·754 (3) Å (Ni^{2+}). In the present complex the Ba^{2+} ion lies 1·877 (1) Å out of the plane of the five oxygen atoms of the B15C5 and has four additional coordinations to the carboxylate oxygen atoms resulting in nine-coordination and irregular geometry. Also, the Ba^{2+}–Ba^{2+} separation is quite large [4·657 (2) Å] when compared with the metal–metal separations in the Rh^{2+}, Cu^{2+}, and Ni^{2+} complexes.

Whereas the larger alkali cations (K^+ to Cs^+) can be discriminated from the smaller congeners (Li^+ and Na^+) on the grounds of their low charge density (polarizability) (Poonia, 1979), the larger M^{2+} (Ba^{2+}) appears to be discriminated from Mg^{2+}, Ca^{2+}, and perhaps Sr^{2+} on the grounds of its large size coupled with its anionophilicity. Consequently, unlike Ca^{2+} in the Ca^{2+}(3,5-DNB^-)$_2$(B15C5)$_2$.3H_2O complex (Cradwick & Poonia, 1977), the Ba^{2+} ion in the present case is not contained in the four-membered ring of the chelating carboxylate function (because of large size). It is linked with as many as four anionic oxygens (because of anionophilicity), unlike the similar-sized K^+ which yields the charge-separated sandwich K^+(B15C5)$_2$(3,5-DNB^-)(3,5-DNBH)$_2$ (Hackert *et al.*, 1984). Compared to the bonding modes of Ba^{2+} towards B15C5 in the presence of pic^- (Venkatasubramanian, Poonia, Hackert, Clinger & Ernst, 1984*a*,*b*), the results in the presence of 3,5-DNB^- show yet another example of the influence of the nucleophilic properties of an anion on the coordinating properties of the countercation.

It should be noted, of course, that the above generalizations apply to the formation of crystalline complexes and cannot be safely extrapolated to their stoichiometry and structures in solutions where solvent–solute interactions are often of great importance. A combination of spectroscopic measurements on the solids and their solutions (*e.g.* NMR or IR), coupled with the knowledge of their crystalline structures, offers an interesting possibility of determining the influence of solvents on the stoichiometry and structure of macrocyclic complexes in solutions. Such studies are currently in progress in our laboratory.

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The Structure of Tetrakis(acetonitrile)tetrachlorouranium(IV), [$UCl_4(C_2H_3N)_4$]

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Abstract. $M_r = 544{\cdot}05$, monoclinic, $C2/c$, $a = 14{\cdot}709\,(4)$, $b = 8{\cdot}459\,(3)$, $c = 13{\cdot}938\,(4)$ Å, $\beta = 91{\cdot}79\,(2)^\circ$, $V = 1733{\cdot}2\,(9)$ Å^3, $Z = 4$, $D_x = 2{\cdot}085$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 94{\cdot}919$ cm^{-1}, $F(000) = 992{\cdot}0$, $T = 278$ K, $R = 0{\cdot}040$ for 1051 ($I \geq 3\sigma$) reflections. The molecules are discrete monomeric units with eight ligands coordinated in an almost ideal dodecahedral arrangement. The four nitrogen atoms form an elongated tetrahedron and the four chlorine atoms a flattened tetrahedron. Important bond distances are: U–Cl(1) 2·627 (4); U–Cl(2) 2·620 (4); U–N(1) 2·601 (13); U–N(2) 2·577 (14) Å.

Introduction. Because of their large radii, actinide-metal ions have been observed in complexes in which the coordination number has been as large as 14. Of the many possible geometries for an eight-coordinate species, the dodecahedron and the square antiprism are the most common forms (Hoard & Silverton, 1963; Blight & Kepert, 1968; Kepert, 1965). Four less frequently encountered geometries are the hexagonal bipyramid, the puckered hexagonal bipyramid, the bicapped trigonal prism and the cube.

The configurations of most of the eight-coordinate compounds of uranium are based on the dodecahedron or the square antiprism, but there are very few compounds in which the geometry is precisely either of the ideal models. Rather, intermediate forms between the two models are commonly encountered. We report here that $UCl_4(CH_3CN)_4$ very closely approximates the idealized geometry of a dodecahedron.

Experimental. In an effort to form a metal–metal-bonded uranium trimer of the type $[M_3(C_6Me_6)Cl_6]^{n+}$, analogous to those of niobium and zirconium (Goldberg, Spivack, Stanley, Eisenberg, Braitsch, Miller & Abkowitz, 1977; Stollmaier & Thewalt, 1981), a mixture of UCl_4 (760 mg), Al (42 mg), $AlCl_3$ (194 mg) and C_6Me_6 (1 g) was heated in a sealed glass tube for 4 h at 413 K. The reaction product was first extracted

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