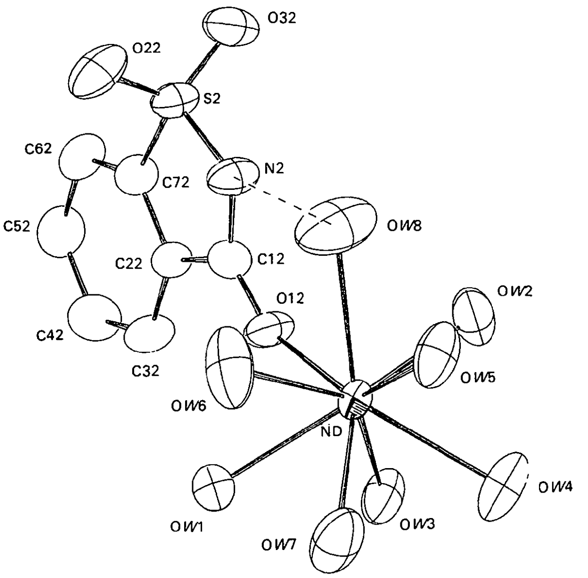

Fig. 1. Complex cation. The intramolecular hydrogen bond is marked with a dashed line. The numbering scheme for saccharinate residues 1 and 3 follows that shown here for residue 2.

vertices of the bases, and O*W*1, O*W*4 and O*W*8 as the caps. The structure is held together by a network of intermolecular hydrogen bonds, and electrostatic and van der Waals forces. The crystal packing is shown in Fig. 2.

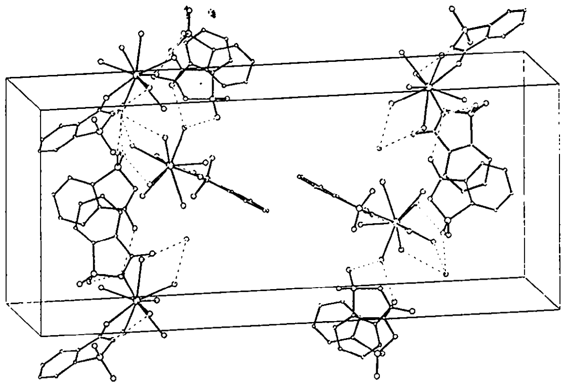

Fig. 2. View of the crystal structure. **a** is into the plane of the paper, **b** is vertical and **c** is horizontal. The dashed lines represent the hydrogen bonds.

The author thanks Professor K. Bukietyńska for helpful discussions, and Dr B. Wasylkowska and Dr J. Wasylkowski for their interest in this study. This work was supported by the Polish Academy of Sciences (project CPBP 01.12).

References

Cotton, F. A., Falvello, L. R., Llusar, R., Libby, E., Murillo, C. A. & Schwotzer, W. (1986). *Inorg. Chem.* **25**, 3423–3428.
Drew, M. G. B. (1977). *Coord. Chem. Rev.* **24**, 179–275.
Hergold-Brundić, A., Kamenar, B. & Jovanovski, G. (1989). *Acta Cryst.* C**45**, 556–558.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Jovanovski, G. & Kamenar, B. (1982). *Cryst. Struct. Commun.* **11**, 247–255.
Pople, J. A. & Beveridge, D. L. (1970). *Approximate Molecular Orbital Theory*. New York: McGraw-Hill.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Ugozzoli, F. (1987). *Comput. Chem.* **11**(2), 109–120.

Acta Cryst. (1991). C**47**, 2065–2069

Structure of Bis(dipicolinato)dioxouranium Monopicolinic Acid Hexahydrate

By A. Cousson and J. Proust

Institut Curie, Section de Physique et Chimie, UA CNRS 448, 11 *rue Pierre et Marie Curie,*
75231 *Paris CEDEX* 05, *France*

and E. N. Rizkalla

Faculty of Science, Ain Shams University, Abbassia, Cairo, Egypt

(*Received* 1 *December* 1990; *accepted* 2 *April* 1991)

Abstract. Bis[2,6-pyridinedicarboxylato(1 −)]dioxouranium–2-pyridinecarboxylic acid (1/1) hexahydrate, $[U(C_7H_4NO_4)_2O_2].C_6H_5NO_2.6H_2O$, M_r = 833·45, triclinic, $P\bar{1}$, a = 14·195 (6), b = 15·208 (8), c = 6·801 (3) Å, α = 91·63 (3), β = 93·80 (3), γ = 117·19 (4)°, V = 1300·2 Å^3, Z = 2, D_x = 2·13 Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ = 19·82 mm^{-1}, F(000) = 804, T = 290 K, R = 0·036,

0108-2701/91/102065-05$03.00

$wR = 0{\cdot}043$ for 4584 reflections with $I \geq 3\sigma(I)$. The near linear uranyl group is surrounded by a slightly distorted hexagon formed by four O and two N atoms of the two dipicolinate ligands. Bond lengths and angles are as expected for an equatorially hexacoordinated uranyl ion.

Introduction. Thermodynamic studies of the complexation of lanthanide ions with the dipicolinate (2,6-pyridinedicarboxylate) ligand showed a large degree of enhancement in the stability constant above that predicted from the electrostatic model (Gritmon, Goedken & Choppin, 1977). This extra stabilization was correlated essentially to an increase in the lanthanide–nitrogen interaction (Choppin, Goedken & Gritmon, 1977).

Similar measurements of the neptunyl system supported these conclusions (Rizkalla, Nectoux, Dabos-Seignon & Pagès, 1990*a*); however, the deviation from the 'norm' in the case of NpO_2^+ [effective central charge = 2·3 (Rizkalla, Nectoux, Dabos-Seignon & Pagès, 1990*b*)] is much less than that observed for the trivalent lanthanides. These observations as well as others based on NMR relaxation studies (Erikson, Grenthe & Puigdomenech, 1987; Ducommun, Helm, Laurenczy & Merbach, 1989) were attributed to a proportional shortening of the metal—nitrogen distance imposed by the rigid configuration of the aromatic ring.

In order to investigate this hypothesis we initiated a systematic X-ray crystallographic study of picolinate (2-pyridinecarboxylate) and dipicolinate complexes of Ca^{II}, Nd^{III}, UO_2^{2+} and Th^{IV} ions. The metal—nitrogen bond lengths of the picolinate systems are expected to represent the 'norm' whereas a comparison of the metal–nitrogen distances across the dipicolinate series would, probably, shed some light on the effect of cationic charge on the *M*—N shortening.

In connection with this work, the crystal structures of picolinic acid [monoclinic, space group C_2/c (Takusagawa & Shimada, 1973)] and dipicolinic acid monohydrate [orthorhombic, space group $P2_12_12_1$ (Takusagawa, Hirotsu & Shimada, 1973)] have also been established. Depending upon the method of preparation, the sodium salts of the tris(dipicolinato)lanthanoidate(III) were found to crystallize in the form of monoclinic, orthorhombic or hexagonal phases (Albertsson, 1970, 1972*a*,*b*). In the present paper, we report the results of the crystal structure of the uranyl–dipicolinate complex $[UO_2(C_7H_4NO_4)_2].C_6H_5NO_2.6H_2O$.

Experimental. Uranyl hydroxide was precipitated from the nitrate solution by the dropwise addition of CO_2-free sodium hydroxide solution to a pH of *ca* 8–9. The precipitate was filtered, washed thoroughly with distilled water and dried at 383 K over night. The dipicolinate complex was prepared by the intimate mixing of the solids $UO_2(OH_2).xH_2O$ and dipicolinic acid (DP) (Aldrich, > 99% purity) in a molar ratio of *ca* 1:2. The mixture was suspended in water and sealed in a Pyrex tube. The latter was heated at 453 K for 24 h and then left for slow cooling. The greenish yellow crystals obtained were in the form of regular needles and were stable to air exposure.

Single crystal of dimensions 0·052 × 0·114 × 0·42 mm. Philips PW 1100 diffractometer with graphite monochromator; 'Flying Stepscan' at 0·02° s^{-1}, lattice parameters by least-squares procedure from setting angles of 25 reflections, θ between 10 and 25°. 5021 reflections with $(\sin\theta/\lambda)_{\max} = 0{\cdot}601$ Å^{-1}, $-15 \leq h \leq 15, -18 \leq k \leq 18, 0 \leq l \leq 8$. Three standard reflexions (600, 030, 102) measured every hour, mean standard deviation less than 0·02; absorption correction using the analytical method of de Meulenaer & Tompa (1965); transmission between 0·085 and 0·433. Structure solved by Patterson method and successive Fourier maps; H atoms found from difference syntheses; complex atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). All non-H atoms were given anisotropic thermal parameters; isotropic thermal parameters for H atoms. Full-matrix least-squares refinement on *F*. Final *R* values: R_F 0·036, wR 0·043 (unit weights) for 4584 reflections ($I > 3\sigma I$). $S = 2{\cdot}1$, $(\Delta/\sigma)_{\max} = 0{\cdot}07$. Max. height in final difference Fourier synthesis 2·3 e Å^{-3} localized on U atoms (min. height −2·2 e Å^{-3}). All calculations performed using *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985); VAX 6310 computer used.

Discussion. Atomic positional and equivalent isotropic thermal parameters are reported in Table 1, intramolecular distances and angles are listed in Table 2.* The numbers shown in parentheses are the same as those associated with the structure illustrated in Fig. 1. Fig. 2 is a stereoscopic view of the packing (*ORTEP*, Johnson, 1965).

The overall geometry of the uranium coordination sphere approximates to that of a flattened hexagonal bipyramid with the uranyl O atoms O(1) and O(2) in the axial positions and the carboxylate O atoms O(3), O(5), O(7) and O(9) and the dipicolinate N atoms N(1) and N(2) occupying the corners of the

---

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54178 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic positional parameters with U_{eq} values for non-*H *atoms*

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

	x	y	z	U_{eq}(Å^2)
U(1)	0·07397 (2)	0·28413 (2)	0·23925 (4)	0·0139
C(1)	−0·1148 (6)	0·0387 (6)	0·185 (1)	0·0293
C(2)	−0·0177 (6)	0·0254 (6)	0·237 (1)	0·0256
C(3)	−0·0199 (7)	−0·0660 (6)	0·260 (1)	0·0311
C(4)	0·0756 (7)	−0·0666 (7)	0·312 (1)	0·0367
C(5)	0·1683 (7)	0·0194 (6)	0·333 (1)	0·0334
C(6)	0·1641 (6)	0·1080 (6)	0·299 (1)	0·0260
C(7)	0·2597 (6)	0·2057 (6)	0·306 (1)	0·0288
C(8)	−0·1157 (6)	0·3637 (6)	0·247 (1)	0·0286
C(9)	−0·0226 (6)	0·4613 (6)	0·249 (1)	0·0217
C(10)	−0·0265 (6)	0·5505 (6)	0·254 (1)	0·0286
C(11)	0·0659 (7)	0·6373 (6)	0·258 (1)	0·0337
C(12)	0·1621 (7)	0·6338 (6)	0·255 (1)	0·0306
C(13)	0·1596 (6)	0·5421 (6)	0·251 (1)	0·0242
C(14)	0·2573 (6)	0·5288 (6)	0·248 (1)	0·0266
C(15)	0·6334 (7)	0·7273 (7)	0·198 (1)	0·0345
C(16)	0·6100 (6)	0·6221 (6)	0·227 (1)	0·0283
C(17)	0·6855 (7)	0·5888 (7)	0·237 (1)	0·0348
C(18)	0·6539 (7)	0·4890 (7)	0·258 (1)	0·0382
C(19)	0·5471 (7)	0·4252 (7)	0·269 (1)	0·0352
C(20)	0·4741 (6)	0·4614 (6)	0·259 (1)	0·0300
N(1)	0·0725 (5)	0·1106 (5)	0·2561 (9)	0·0214
N(2)	0·0704 (5)	0·4569 (4)	0·2472 (9)	0·0205
N(3)	0·5065 (5)	0·5583 (5)	0·238 (1)	0·0276
O(1)	0·0752 (4)	0·2824 (4)	−0·0159 (9)	0·0311
O(2)	0·0736 (4)	0·2856 (4)	0·4945 (9)	0·0325
O(3)	−0·0964 (4)	0·1280 (4)	0·173 (1)	0·0370
O(4)	−0·2042 (5)	−0·0320 (5)	0·151 (1)	0·0398
O(5)	0·2404 (4)	0·2785 (4)	0·280 (1)	0·0319
O(6)	0·3501 (5)	0·2125 (5)	0·334 (1)	0·0476
O(7)	−0·0967 (4)	0·2894 (4)	0·243 (1)	0·0329
O(8)	−0·2064 (5)	0·3595 (5)	0·252 (1)	0·0399
O(9)	0·2427 (5)	0·4406 (4)	0·249 (1)	0·0360
O(10)	0·3456 (4)	0·6019 (4)	0·245 (1)	0·0359
O(11)	0·7346 (5)	0·7867 (5)	0·210 (1)	0·0431
O(12)	0·5629 (5)	0·7495 (5)	0·163 (1)	0·0488
O(101)	0·6229 (7)	0·2255 (7)	0·019 (1)	0·0740
O(102)	0·2611 (7)	0·8730 (7)	0·116 (1)	0·0719
O(103)	0·7307 (8)	0·1372 (7)	0·455 (2)	0·0847
O(104)	0·4224 (9)	0·0838 (9)	0·123 (2)	0·1100
O(105)	0·439 (1)	0·804 (1)	0·495 (2)	0·1195
O(106)	0·546 (1)	0·976 (1)	0·273 (2)	0·1289

Table 2. *Intramolecular bond distances* (Å) *and angles* (°)

U(1)—O(1)	1·736 (6)	U(1)—O(2)	1·736 (6)
U(1)—N(1)	2·636 (6)	U(1)—N(2)	2·650 (6)
U(1)—O(3)	2·498 (6)	U(1)—O(5)	2·401 (5)
U(1)—O(7)	2·462 (5)	U(1)—O(9)	2·482 (6)
U(1)—H(51)	2·3877 (2)	U(1)—H(71)	2·3907 (2)
C(1)—C(2)	1·50 (1)	C(1)—O(3)	1·27 (1)
C(1)—O(4)	1·23 (1)	C(2)—C(3)	1·39 (1)
C(2)—N(1)	1·34 (1)	C(3)—C(4)	1·38 (1)
C(4)—C(5)	1·36 (1)	C(5)—C(6)	1·40 (1)
C(6)—C(7)	1·48 (1)	C(6)—N(1)	1·33 (1)
C(7)—O(5)	1·27 (1)	C(7)—O(6)	1·24 (1)
C(8)—C(9)	1·47 (1)	C(8)—O(7)	1·28 (1)
C(8)—O(8)	1·26 (1)	C(9)—C(10)	1·38 (1)
C(9)—N(2)	1·353 (9)	C(10)—C(11)	1·37 (1)
C(11)—C(12)	1·39 (1)	C(12)—C(13)	1·38 (1)
C(13)—C(14)	1·49 (1)	C(13)—N(2)	1·33 (1)
C(14)—O(9)	1·26 (1)	C(14)—O(10)	1·241 (9)
C(15)—C(16)	1·50 (1)	C(15)—O(11)	1·30 (1)
C(15)—O(12)	1·21 (1)	C(16)—C(17)	1·38 (1)
C(16)—N(3)	1·35 (1)	C(17)—C(18)	1·39 (1)
C(18)—C(19)	1·39 (1)	C(19)—C(20)	1·38 (1)
C(20)—N(3)	1·34 (1)		

O(2)—U(1)—O(1)	179·5 (3)	N(2)—U(1)—N(1)	176·0 (2)
O(1)—U(1)—N(1)	93·0 (2)	O(1)—U(1)—N(2)	90·8 (2)
O(2)—U(1)—N(1)	86·7 (2)	O(2)—U(1)—N(2)	89·5 (2)
O(3)—U(1)—N(1)	59·7 (2)	O(3)—U(1)—N(2)	119·4 (2)
O(3)—U(1)—O(1)	84·7 (2)	O(3)—U(1)—O(2)	95·4 (2)
O(5)—U(1)—N(1)	61·1 (2)	O(5)—U(1)—N(2)	120·1 (2)
O(5)—U(1)—O(1)	92·0 (3)	O(5)—U(1)—O(2)	87·6 (3)
O(5)—U(1)—O(3)	120·4 (2)	O(7)—U(1)—N(1)	118·1 (2)
O(7)—U(1)—N(2)	60·1 (2)	O(7)—U(1)—O(1)	95·3 (2)
O(7)—U(1)—O(2)	85·2 (2)	O(7)—U(1)—O(3)	60·2 (2)
O(7)—U(1)—O(5)	172·7 (2)	O(9)—U(1)—N(1)	121·6 (2)
O(9)—U(1)—N(2)	59·9 (2)	O(9)—U(1)—O(1)	86·4 (2)
O(9)—U(1)—O(2)	93·4 (3)	O(9)—U(1)—O(3)	171·1 (2)
O(9)—U(1)—O(5)	60·6 (2)	O(9)—U(1)—O(7)	120·0 (2)
O(3)—C(1)—C(2)	114·4 (7)	O(4)—C(1)—C(2)	122·5 (7)
O(4)—C(1)—O(3)	123·0 (8)	C(3)—C(2)—C(1)	123·9 (7)
N(1)—C(2)—C(1)	113·4 (7)	N(1)—C(2)—C(3)	122·6 (7)
C(4)—C(3)—C(2)	117·6 (8)	C(5)—C(4)—C(3)	120·6 (8)
C(6)—C(5)—C(4)	118·2 (8)	C(7)—C(6)—C(5)	123·5 (7)
N(1)—C(6)—C(5)	122·0 (7)	N(1)—C(6)—C(7)	114·5 (7)
O(5)—C(7)—C(6)	114·7 (7)	O(6)—C(7)—C(6)	120·7 (7)
O(6)—C(7)—O(5)	124·6 (8)	O(7)—C(8)—C(9)	115·9 (7)
O(8)—C(8)—C(9)	118·6 (7)	O(8)—C(8)—O(7)	125·5 (8)
C(10)—C(9)—C(8)	124·7 (7)	N(2)—C(9)—C(8)	113·4 (7)
N(2)—C(9)—C(10)	121·8 (7)	C(11)—C(10)—C(9)	119·6 (7)
C(12)—C(11)—C(10)	119·1 (8)	C(13)—C(12)—C(11)	117·9 (8)
C(14)—C(13)—C(12)	122·9 (7)	N(2)—C(13)—C(12)	123·7 (7)
N(2)—C(13)—C(14)	113·4 (7)	O(9)—C(14)—C(13)	115·6 (7)
O(10)—C(14)—C(13)	120·2 (7)	O(10)—C(14)—O(9)	124·2 (7)
O(11)—C(15)—C(16)	112·2 (7)	O(12)—C(15)—C(16)	121·3 (8)
O(12)—C(15)—O(11)	126·5 (9)	C(17)—C(16)—C(15)	124·4 (7)
N(3)—C(16)—C(15)	115·2 (7)	N(3)—C(16)—C(17)	120·3 (8)
C(18)—C(17)—C(16)	119·2 (8)	C(19)—C(18)—C(17)	119·2 (8)
C(20)—C(19)—C(18)	119·9 (8)	N(3)—C(20)—C(19)	120·0 (7)
C(6)—N(1)—C(2)	118·9 (7)	C(13)—N(2)—C(9)	117·8 (7)
C(20)—N(3)—C(16)	121·4 (7)		

equatorial hexagon. The U—O bond distances within the uranyl group are identical with an average value of 1·734 (3) Å and the angle O(1)—U—O(2) = 179·4 (5)° indicating that the UO_2^{2+} group is linear within the uncertainties of the measurements. The U—O carboxylate bond lengths to both dipicolinate ligands are in the expected range (2·47–2·49 Å) except for the U—O(9) (2·39 Å) which is somewhat shorter than the average.

The U—N bond lengths (2·63 and 2·65 Å) agree well with the analogous distances in related compounds. However, the sixfold coordination around the uranyl ion results in a distorted system with only U, N(1), N(2), O(3) and O(5) in the equatorial plane. The remaining O(7) and O(9) donors lie below and above the equatorial plane, respectively. The puckered structure is observed also with most hexacoordinated uranyl complexes. Pentacoordinated compounds normally result in significantly shorter U—N distances and less strained equatorial planes (Evans, 1963).

Each of the dipicolinate ligands in the complex forms two identical five-membered rings with the uranyl ion. The bond distances and angles agree well with those reported for Ca(DP).$3H_2O$ (Strahs & Dickerson, 1968), Sr(DP).$4H_2O$ (Palmer, Wong & Lewis, 1972) and the parent dipicolinic acid (DP.H_2O) (Takusagawa, Hirotsu & Shimada, 1973). The dipicolinate (C_1–C_7) ring is coplanar with the U atom and the deviation of the ligand atoms from the least-squares plane is 0·010 Å. The plane defining the second ligand (C_8–C_{14}) has an average deviation of 0·162 Å and the dihedral angle between the two planes is 2·33°. The planes defining the individual carboxylate groups show no deviation from the least-squares planes.

The C(2)—N(1)—C(6) and C(9)—N(2)—C(13) angles are 117·2 and 118°, respectively, which rules out the possibility of having protonated N atom sites

(Takusagawa, Hirotsu & Shimada, 1973). The two protons required to maintain electrical neutrality of the molecule have been located on two of the coordinated carboxylate groups. Their positions support these conclusions, the observed differences in the distances of the C—O bonds are as expected; the C═O distances are shorter than those of the C—O(H) bond lengths.

The unit cell shows the presence of a picolinic acid molecule associated with each $UO_2(C_7H_4NO_4)_2$ unit. The presence of a picolinate ligand in the crystal lattice could arise from a partial photolytic oxidative decarboxylation of the dipicolinate ligand (Battiston, Sprignadello, Bandoli, Clemente & Tomat, 1979) during the hydrothermal synthesis of the complex.

The bond angles and distances are closely similar to those reported for the free acid (Takusagawa & Shimada, 1973) except for the C(19)–N(3) segment. These differences are probably related to the status of the nitrogen site where it is inferred from structural data (Takusagawa & Shimada, 1973) as being semi protonated. The dihedral angle between the planes of the pyridine ring and the carboxyl group is 9·0° as compared to 4·8° in the free acid structure (Takusagawa & Shimada, 1973).

In the following we will attempt to correlate structural data with observations in the solution chemistry of the dipicolinate complexes. It is well known that 'hard' acids such as actinide and lanthanide cations tend to form stable complexes with 'hard' or 'borderline' bases and, in most cases, the stability constants (log β_{101}) show a linear correlation with the sum of the ligand basicity. This correlation is valid, provided that perturbations due to steric strain in the ligands are absent, and reflects the ionic nature of the metal–ligand interaction.

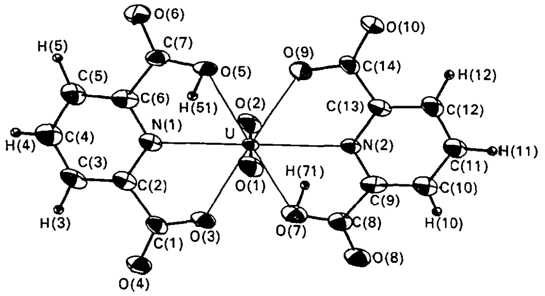

Fig. 1. Molecular structure of bis(dipicolinato)dioxouranium.

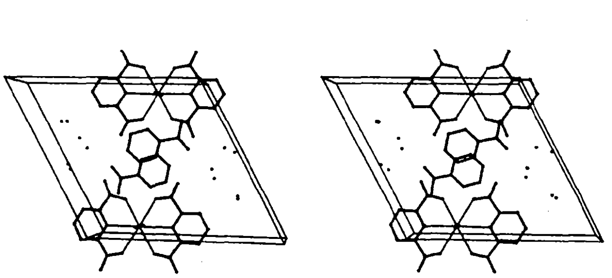

Fig. 2. Stereoscopic view of [$UO_2(C_7H_4NO_4)_2$]$C_6H_5NO_2$.6H_2O.

Within the polyaminocarboxylate series, complexation by dipicolinate anions showed an enhanced stabilization above the 'norm' (Gritmon *et al.*, 1977; Choppin *et al.*, 1977; Rizkalla, Nectoux, Dabos-Seignon & Pagès, 1990*a*). The explanation offered attributed the unusual thermodynamic stability to the rigid structure imposed by the aromatic ring which results in strong *M*—N interactions in addition to the *M*—O bonds ($M = Ln^{3+}$ or NpO_2^+). In the case of lanthanide dipicolinates, the ions $Ln(C_7H_3NO_4)_3^{3-}$ were found to exhibit D_3 symmetry, both in solution (Donato & Martin, 1972), as determined by ^{1}H NMR, and in the solid state, as revealed from the X-ray structural analysis (Albertsson, 1970, 1972*a*,*b*).

Comparison of log β_{101} values for $NpO_2(DP)^-$ and $Ln(DP)^+$ shows that the latter has much greater enhancement than that expected from the difference in the central charges of the metal ions (Rizkalla, Nectoux, Dabos-Seignon & Pagès, 1990*b*). This was attributed to the potential barrier introduced by the axial neptunyl O atoms which limits the strength of the Np^V—N bond. This is supported by the difference in Yb^{3+}—N and U^{VI}—N bond distances. Though the ionic radius of Yb^{3+} [*ca* 1·04 Å, 9-coordinate (Shannon & Prewitt, 1969)] is similar to that of U^{VI} [1·01 Å, 8-coordinate (Shannon & Prewitt, 1969)], the Yb—N bond length can be as short as 2·33 Å (Albertsson, 1970) with a minimum intramolecular O···O 'contact' distance of 2·80 (3) Å. By contrast, for the uranyl complex having the longer U—N distances (2·63 and 2·65 Å), the axial O atoms O(1) and O(2) were found to possess O···O 'contact' distances with the coordinated carboxylate groups significantly less than 3·2 Å [*e.g.* O(1)···O(7) = 2·896 and O(2)···O(3) = 2·875 Å].

References

Albertsson, J. (1970). *Acta Chem. Scand.* **24**, 1213–1229.

Albertsson, J. (1972*a*). *Acta Chem. Scand.* **26**, 985–1004.

Albertsson, J. (1972*b*). *Acta Chem. Scand.* **26**, 1005–1017.

Battiston, G. A., Sprignadello, G., Bandoli, G., Clemente, D. A. & Tomat, G. (1979). *J. Chem. Soc. Dalton Trans.* pp. 1965–1971.

Choppin, G. R., Goedken, M. P. & Gritmon, T. F. (1977). *J. Inorg. Nucl. Chem.* **39**, 2025–2030.

Donato, H. Jr & Martin, R. B. (1972). *J. Am. Chem. Soc.* **94**, 4129–4131.

Ducommun, Y., Helm, L., Laurenczy, G. & Merbach, A. E. (1989). *Inorg. Chim. Acta*, **158**, 3–4.

Erikson, T. E., Grenthe, I. & Puigdomenech, I. (1987). *Inorg. Chim. Acta*, **126**, 131–135.

Evans, H. T. Jr. (1963). *Science*, **141**, 154.

Gritmon, T. F., Goedken, M. P. & Choppin, G. R. (1977). *J. Inorg. Nucl. Chem.* **39**, 2021–2023.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.

PALMER, K. J., WONG, R. Y. & LEWIS, J. C. (1972). *Acta Cryst.* **B28**, 223–228.

RIZKALLA, E. N., NECTOUX, F., DABOS-SEIGNON, S. & PAGÈS, M. (1990*a*). *Radiochim. Acta*, **51**, 113–117.

RIZKALLA, E. N., NECTOUX, F., DABOS-SEIGNON, S. & PAGÈS, M. (1990*b*). *Radiochim. Acta*, **51**, 151–155.

SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–946.

STRAHS, G. & DICKERSON, R. E. (1968). *Acta Cryst.* **B24**, 571–578.

TAKUSAGAWA, F., HIROTSU, K. & SHIMADA, A. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2020–2027.

TAKUSAGAWA, F. & SHIMADA, A. (1973). *Chem. Lett.* pp. 1089–1090.

WATKIN, D. J., CARRUTHERS, J. R. & BETTERIDGE, P. W. (1985). *CRYSTALS*. Chemical Crystallography Laboratory, Univ. of Oxford, England.

Acta Cryst. (1991). C**47**, 2069–2073

Complexes of Manganese and Zinc Di-*tert*-butylnaphthalenesulfonate with Cyclohexano-15-crown-5 Ether Toluene Solvate

BY JOHN H. BURNS AND GREGG J. LUMETTA

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, *USA*

(*Received* 19 *October* 1990; *accepted* 26 *March* 1991)

Abstract. (1) Bis(3,7-di-*tert*-butylnaphthalenesulfonato)(2,5,8,11,14-pentaoxabicyclo[13.4.0]nonadecane)manganese monohydrate toluene (1/1), $Mn(C_{18}H_{23}O_3S)_2(C_{14}H_{26}O_5).H_2O.C_7H_8$, $M_r = 1078{\cdot}33$, monoclinic, $P2_1/c$, $a = 12{\cdot}737$ (1), $b = 39{\cdot}460$ (4), $c = 12{\cdot}765$ (1) Å, $\beta = 116{\cdot}40$ (1)°, $V = 5747$ (2) $Å^3$, $Z = 4$, $D_m = 1{\cdot}24$, $D_x = 1{\cdot}25\ g\ cm^{-3}$, $\lambda(Mo\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 3{\cdot}47\ cm^{-1}$, $F(000) = 2308$, $T = 297$ K, $R(F) = 0{\cdot}069$ for 3060 reflections $[I > 2\sigma(I)]$. (2) Bis(3,7-di-*tert*-butylnaphthalenesulfonato)(2,5,8,11,14-pentaoxabicyclo[13.4.0]nonadecane)zinc monohydrate toluene (1/1), $Zn(C_{18}H_{23}O_3S)_2(C_{14}H_{26}O_5).H_2O.C_7H_8$, $M_r = 1088{\cdot}77$, monoclinic, $P2_1/c$, $a = 12{\cdot}766$ (2), $b = 39{\cdot}083$ (5), $c = 12{\cdot}771$ (2) Å, $\beta = 116{\cdot}44$ (1)°, $V = 5705$ (2) $Å^3$, $Z = 4$, $D_m = 1{\cdot}28$, $D_x = 1{\cdot}27\ g\ cm^{-3}$, $\lambda(Mo\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 5{\cdot}69\ cm^{-1}$, $F(000) = 2328$, $T = 297$ K, $R(F) = 0{\cdot}067$ for 2240 reflections $[I > 2\sigma(I)]$. Complexes are isostructural. The cation is inside the crown and bonded to its five O atoms and to one O atom of a sulfonate and to one water molecule, forming a pentagonal bipyramid coordination. The second sulfonate ion is hydrogen bonded to the water. There is disorder affecting a *tert*-butyl group and possibly the toluene solvate.

Introduction. The ligands used in this work, cyclohexano-15-crown-5 (CH15C5) and di-*tert*-butylnaphthalenesulfonic acid (HDtBNS) are models for the more extensively alkylated ligands used in solvent extraction studies, *tert*-butylcyclohexano-15-crown-5 and didodecylnaphthalenesulfonic acid. When a mixture of the latter two compounds was used to extract the divalent transition metals Mn, Fe, Co, Ni, Cu and Zn, macrocycle-induced enhancement in the extraction by the sulfonic acid occurred only for Mn and Zn (McDowell, Moyer, Case & Case, 1986; Lumetta, Moyer & Johnson, 1990). The fact that these d^5 and d^{10} ions behave differently suggests that ligand-field effects may be important here; thus a structure determination is needed to ascertain the distribution of O atoms about the cation. Specifically, octahedral or pentagonal bipyramidal coordination would be expected, depending on whether the cation resides within the macro-ring and on whether the sulfonate ions are directly attached to it. IR spectral studies of the extraction system above indicate that the crown ether and water compete in forming inner-sphere complexes with these ions (Lumetta & Moyer, 1991).

No previous structures of Mn^{2+} complexed by 15-crown-5 are known, and those with 18-crown-6 do not have the Mn^{2+} ion attached to the ring (Knöchel, Kopf, Oehler & Rudolph, 1978). Several zinc chloride complexes have been crystallized with the Zn atom in the 15-crown-5 cavity, including $[ZnCl(15\text{-crown-}5)H_2O]_2Zn_2Cl_6$ (Ivakina, Bel'sky, Strel'tsova, Storozhenko & Bulychev, 1989), $[ZnCl(15\text{-crown-}5)(C_3H_6O_2)]_2Zn_2Cl_6$ and $[Zn(15\text{-crown-}5)(CH_3CN)_2]Zn_2Cl_6(CH_3CN)$ (Bel'sky, Strel'tsova, Bulychev, Storozhenko, Ivakina & Gorbunov, 1989). Yet in $ZnCl_2(H_2O)_2(15\text{-crown-}5)$ the Zn atom is not bonded to the crown (Dejehet, Debuyst & Declercq, 1986). No structures involving CH15C5 are yet reported.

Experimental.

Synthesis of (1). 3,7-Di-*tert*-butylnaphthalenesulfonic acid (HDtBNS) was prepared using a published

0108-2701/91/102069-05$03.00