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Thermodynamics of complexation of the uranyl(VI) ion with phenylacetate. The crystal structure of $NaUO_2L_3$ ($L=PhCH_2CO_2^-$)

A. Bismondo, U. Casellato*, L. Rizzo
Istituto di Chimica e Tecnologia dei Radioelementi, CNR, Padua (Italy)

and R. Graziani
Dipartimento di Chimica Inorganica, Università di Padova, Padua (Italy)

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Abstract

The stability constant and the enthalpy and entropy changes of formation of the 1:1 complex of uranyl(VI) with phenylacetate were determined by potentiometric and calorimetric titrations in 1.0 mol dm^{-3} aqueous solution of $NaClO_4$ at 25 °C. The values obtained for the 1:1 complex agree with the general relationship holding for aliphatic monocarboxylato uranyl(VI) complexes. The structure of $NaUO_2L_3$ ($L=PhCH_2CO_2^-$) was determined by X-ray crystallography and refined to $R=0.063$ based on 3662 observed reflections. The compound is monoclinic, space group $P2_1/n$, with $a=25.056(5)$, $b=19.210(5)$, $c=16.136(6)$ Å, and $\beta=101.69(3)$°. There are three independent $NaUO_2L_3$ complex molecules in the asymmetric unit of the cell. The $UO_2L_3^-$ anions, where three bidentate ligands are equatorially bonded to the uranyl ion, are structurally similar and are held together by a network of close contacts with the neighbouring Na^+ ions.

Introduction

Much work has been devoted to the determination of the composition and thermodynamic functions of uranyl complexes with aliphatic carboxylic acids in water solution, while less attention has been given to the complexation of this cation with aromatic carboxylic acids [1]. A number of uranyl complexes with aliphatic monocarboxylic acids has already been examined. They are complexes whose stability strongly depends on the basicity of the ligands, and a linear relationship was found between log β_1 of the 1:1 complex and pK_a of the acid. With the aim of extending the study to complexes of actinide ions with aromatic carboxylic acids as ligands, and correlating the behaviour of the compounds in solution and in the solid, we report here on the thermodynamics of the uranyl(VI)/phenylacetate system and on the crystal structure of $NaUO_2L_3$ (L = phenylacetate), the product obtained on reacting phenylacetic acid with uranyl diperchlorate in aqueous solution.

TABLE 1. Crystal and intensity data for $NaUO_2L_3$

Formula	$C_{24}H_{21}NaO_8U$
Formula weight	698
a (Å)	25.056(5)
b (Å)	19.210(5)
c (Å)	16.136(6)
β	101.69(4)°
V (Å^3)	7606(3)
D_c (g/cm^3)	1.83
Molecules/cell	12
Crystal system	monoclinic
Space group	$P2_1/n$
$F(000)$	3983
μ(Mo kα) (cm^{-1})	62
Scan method	$\theta/2\theta$
θ_{max} (°)	50
Scan speed (°/min)	2
Recorded intensities	10188
Observed intensities (Å)	3662
Wavelength (Mo Kα) (Å)	0.7107
Corrections	Lp, absorption [5]
Final R factor	0.063

Experimental

Stock solutions of $UO_2(ClO_4)_2$ containing an excess of $HClO_4$ were prepared and standardized as reported [2]. The solutions of phenylacetic acid were prepared by weight, using commercial products without further purification. They were checked by potentiometry with NaOH. The potentiometric and calorimetric measurements on the uranyl ion were carried out by adding a known amount of a buffered ligand solution to a

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*Author to whom correspondence should be addressed.

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TABLE 2. Atomic coordinates for the three independent $NaUO_2L_3$ units

TABLE 2. Atomic coordinates for the three independent $NaUO_2L_3$ units

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Na1	0.2509(5)	−0.0311(7)	0.5352(9)
Na2	0.1792(6)	0.3062(9)	0.5902(10)
Na3	0.2852(6)	0.2116(8)	0.2508(10)
U1	0.23798(6)	0.16349(8)	0.46133(10)
O1	0.1737(12)	0.1452(17)	0.4040(4)
O2	0.3046(11)	0.1814(16)	0.5127(14)
O3	0.2556(17)	0.0453(26)	0.4344(25)
O4	0.2688(10)	0.1228(15)	0.3373(14)
C1	0.2714(14)	0.0609(18)	0.3610(50)
C2	0.2887(16)	0.0094(20)	0.3040(29)
C4	0.2944(10)	0.0798(16)	0.1678(21)
C5	0.3236(10)	0.1190(16)	0.1194(21)
C6	0.3804(10)	0.1215(16)	0.1414(21)
C7	0.4079(10)	0.0848(16)	0.2118(21)
C8	0.3787(10)	0.0455(16)	0.2601(21)
C3	0.3219(10)	0.0430(16)	0.2382(21)
O5	0.2433(10)	0.2604(13)	0.3632(15)
O6	0.2195(12)	0.2848(18)	0.4850(17)
C9	0.2293(15)	0.3025(19)	0.4168(35)
C10	0.2318(18)	0.3783(19)	0.3795(27)
C12	0.2755(10)	0.4572(16)	0.4987(21)
C13	0.2710(10)	0.5008(16)	0.5661(21)
C14	0.2198(10)	0.5156(16)	0.5832(21)
C15	0.1731(10)	0.4868(16)	0.5330(21)
C16	0.1776(10)	0.4431(16)	0.4657(21)
C11	0.2288(10)	0.4283(16)	0.4485(21)
O7	0.2082(8)	0.1883(13)	0.5948(14)
O8	0.2327(8)	0.0833(11)	0.5774(14)
C17	0.2196(11)	0.1295(25)	0.6285(29)
C18	0.2165(13)	0.1145(23)	0.7200(23)
C20	0.1327(10)	0.0425(11)	0.7115(16)
C21	0.0782(10)	0.0351(11)	0.7171(16)
C22	0.0494(10)	0.0923(11)	0.7385(16)
C23	0.0751(10)	0.1567(11)	0.7543(16)
C24	0.1296(10)	0.1640(11)	0.7487(16)
C19	0.1585(10)	0.1069(11)	0.7273(16)
U2	0.34858(6)	0.36319(9)	0.14384(10)
O9	0.3659(12)	0.2968(12)	0.0869(23)
O10	0.3283(11)	0.4308(14)	0.1975(28)
O11	0.2678(10)	0.2866(14)	0.1421(16)
O12	0.2577(10)	0.3696(15)	0.0434(17)
C25	0.2381(13)	0.3137(28)	0.0736(30)
C26	0.1764(20)	0.2979(26)	0.0463(32)
C28	0.1552(11)	0.2148(14)	0.1623(18)
C29	0.1402(11)	0.1480(14)	0.1826(18)
C30	0.1306(11)	0.0965(14)	0.1204(18)
C31	0.1360(11)	0.1117(14)	0.0380(18)
C32	0.1511(11)	0.1785(14)	0.0178(18)
C27	0.1607(11)	0.2301(14)	0.0800(18)
O13	0.3418(9)	0.4505(12)	0.0333(14)
O14	0.4178(10)	0.4464(14)	0.1263(18)
C33	0.3904(14)	0.4740(21)	0.0626(24)
C34	0.4122(14)	0.5342(18)	0.0150(22)
C36	0.4549(8)	0.5955(12)	0.1536(14)
C37	0.4949(8)	0.6398(12)	0.1979(14)
C38	0.5359(8)	0.6652(12)	0.1591(14)
C39	0.5369(8)	0.6463(12)	0.0759(14)
C40	0.4969(8)	0.6021(12)	0.0315(14)
C35	0.4559(8)	0.5767(12)	0.0704(14)
O15	0.4287(10)	0.3463(19)	0.2534(17)
O16	0.3609(12)	0.2784(14)	0.2598(18)
C41	0.4074(20)	0.2989(26)	0.2930(30)
C42	0.4393(16)	0.2658(25)	0.3738(29)
C44	0.4746(16)	0.3720(26)	0.4587(27)
C45	0.4707(16)	0.4186(26)	0.5236(27)
C46	0.4333(16)	0.4066(26)	0.5753(27)
C47	0.3997(16)	0.3485(26)	0.5621(27)
C48	0.4035(16)	0.3015(26)	0.4972(27)
C43	0.4410(16)	0.3135(26)	0.4455(27)
U3	0.13121(5)	0.40256(8)	0.77739(9)
O17	0.1325(11)	0.3256(13)	0.8283(19)
O18	0.1323(9)	0.4803(11)	0.7264(18)
O19	0.2107(9)	0.3513(15)	0.7203(16)
O20	0.2316(9)	0.4172(14)	0.8372(17)
C49	0.2456(17)	0.3770(18)	0.7788(25)
C50	0.3070(15)	0.3669(24)	0.7779(32)
C52	0.3284(9)	0.2530(12)	0.7184(12)
C53	0.3480(9)	0.1849(12)	0.7283(12)
C54	0.3588(9)	0.1543(12)	0.8083(12)
C55	0.3499(9)	0.1917(12)	0.8784(12)
C56	0.3303(9)	0.2598(12)	0.8685(12)
C51	0.3195(9)	0.2904(12)	0.7885(12)
O21	0.1544(9)	0.4682(12)	0.9083(15)
O22	0.0671(10)	0.4630(15)	0.8506(17)
C57	0.1064(21)	0.4883(23)	0.9088(27)
C58	0.0940(13)	0.5280(22)	0.9829(24)
C60	0.0446(10)	0.6261(14)	0.8841(15)
C61	0.0074(10)	0.6810(14)	0.8711(15)
C62	−0.0265(10)	0.6926(14)	0.9284(15)
C63	−0.0232(10)	0.6494(14)	0.9987(15)
C64	0.0140(10)	0.5945(14)	1.0117(15)
C59	0.0479(10)	0.5828(14)	0.9544(15)
O23	0.0365(9)	0.3756(20)	0.6965(18)
O24	0.1039(9)	0.3346(13)	0.6449(13)
C65	0.0512(15)	0.3409(31)	0.6381(36)
C66	0.0138(15)	0.3034(35)	0.5651(29)
C68	0.0563(14)	0.2901(16)	0.4450(25)
C69	0.0694(14)	0.3099(16)	0.3683(25)
C70	0.0499(14)	0.3727(16)	0.3304(25)
C71	0.0173(14)	0.4157(16)	0.3691(25)
C72	0.0042(14)	0.3959(16)	0.4457(25)
C67	0.0237(14)	0.3331(16)	0.4837(25)

(*continued*)

known volume of a solution containing the metal ion ($c°_M$ = 5–30 mmol dm^{-3}) and $HClO_4$ ($c°_H$ = 15–25 mmol dm^{-3}). The buffer solutions were prepared by adding standard NaOH to the HL solutions until the required HL/L$^-$ ratios were reached. Other details on the potentiometric and calorimetric measurements are given in ref. 2. All measurements were carried out at 25 °C in 1 M $NaClO_4$ as constant ionic medium. Calculations were performed using the MINIQUAD 75 and LETAGROP KALLE programs [3, 4]. The solid compound was prepared by reacting an acidic aqueous solution of $UO_2(ClO_4)_2$ with an excess of a solution of HL (c_{HL}/c_M ratio between 3 and 5) and adding NaOH solution,

TABLE 3. Bond distances and angles for $NaUO_2L_3$

Selected bond and contact distances (Å)					
U(1)–O(1)	1.73(3)	U(2)–O(9)	1.68(3)	U(3)–O(17)	1.69(3)
U(1)–O(2)	1.76(3)	U(2)–O(10)	1.70(4)	U(3)–O(18)	1.71(2)
U(1)–O(3)	2.37(5)	U(2)–O(11)	2.50(3)	U(3)–O(19)	2.56(3)
U(1)–O(4)	2.42(2)	U(2)–O(12)	2.52(2)	U(3)–O(20)	2.52(2)
U(1)–O(5)	2.46(2)	U(2)–O(13)	2.43(2)	U(3)–O(21)	2.43(2)
U(1)–O(6)	2.42(2)	U(2)–O(14)	2.42(3)	U(3)–O(22)	2.47(3)
U(1)–O(7)	2.46(2)	U(2)–O(15)	2.41(2)	U(3)–O(23)	2.52(2)
U(1)–O(8)	2.45(2)	U(2)–O(16)	2.45(3)	U(3)–O(24)	2.48(2)
C(1)–O(3)	1.35(9)	C(25)–O(11)	1.31(5)	C(49)–O(19)	1.25(4)
C(1)–O(4)	1.25(5)	C(25)–O(12)	1.32(6)	C(49)–O(20)	1.32(5)
C(1)–C(2)	1.50(8)	C(25)–C(26)	1.55(6)	C(49)–C(50)	1.55(6)
Na(1)...O(3)	2.21(5)			Na(1)..O(8)	2.37(3)
Na(1)...O(12)^{I}	2.28(3)			Na(1)...O(13)^{I}	2.39(2)
Na(1)...O(20)^{II}	2.25(3)			Na(1)...O(21)^{II}	2.36(3)
Na(2)...O(6)	2.18(4)			Na(2)...O(7)	2.37(3)
Na(2)...O(19)	2.26(3)			Na(2)...O(24)	2.30(3)
Na(3)...O(4)	2.29(3)			Na(3)...O(5)	2.46(3)
Na(3)...O(11)	2.24(3)			Na(3)...O(16)	2.27(3)
Selected bond angles (°)					
O(1)–U(1)–O(2)	178(1)			O(3)–U(1)–O(4)	55(1)
O(9)–U(2)–O(10)	177(2)			O(5)–U(1)–O(6)	54(1)
O(17)–U(3)–O(18)	178(1)			O(7)–U(1)–O(8)	52(1)
O(11)–U(2)–O(12)	53(1)			O(19)–U(3)–O(20)	52(1)
O(13)–U(2)–O(14)	53(1)			O(21)–U(3)–O(22)	53(1)
O(15)–U(2)–O(16)	53(1)			O(23)–U(3)–O(24)	52(1)

Symmetry codes: none $=x, y, z$; $^{I}=\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; $^{II}=\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$.

to give a final pH of the reaction medium of about 3.0. Yellow crystals of $NaUO_2L_3$ were obtained by slowly evaporating the solvent at room temperature. The crystals were filtered off, washed and dried *in vacuo*. *Anal.* Calc. for $C_{24}H_{21}NaO_8U$: C, 41.3; H, 3.0. Found: C, 41.4; H, 3.3%.

X-ray data

A crystal of max. dimension 0.2 mm was used for the analysis. Data collection was made with Mo Kα radiation on a Philips PW 1100 diffractometer. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings. Crystal and intensity data are reported in Table 1. The crystals are stable under irradiation. Solution of the structure was achieved by Patterson and Fourier methods, alternated with cycles of full-matrix least-squares refinement of the atomic parameters. The H atoms were located on the electron density maps but were then introduced in calculated positions with fixed C–H distances and temperature factors (C–H = 1.08 Å, $U_{iso}=0.08$ A^2). Anisotropy was introduced for the non-phenyl non-hydrogen atoms. Refinement of scale factor, positional and thermal parameters, was carried out minimizing the function $\Sigma w(\Delta F)^2$ with $w=1$. At convergence the largest shift on the refined parameters was 0.7 times the standard deviation. No significant residuals of electronic density were observed in the final electron density map. Form factors for the atoms were supplied internally by the SHELX program system [6].

Final atomic parameters are listed in Table 2, bond distances and angles are reported in Table 3.

Results and discussion

Stability constants and thermodynamic parameters for the protonation and the formation of the 1:1 complex are given in Table 4. Potentiometric and calorimetric measurements for the system were limited to small concentration of the ligand because of the low solubility of HL in water and to the limitation in using the salt of the ligand due to the high tendency of the uranyl ion to hydrolyze. In addition, the calorimetric measurements were limited by the small amounts of complexation heat evolved during the titrations. For these

TABLE 4. Thermodynamic data: stability constants and changes in enthalpy and entropy for the formation of proton and uranyl phenylacetate complexes at 25 °C in 1 M $NaClO_4$ solution

Reaction	log β	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
$H+L \rightleftharpoons HL$	4.19(1)	0.40(4)	82
$UO_2+L \rightleftharpoons UO_2L$	2.22(4)	10.80(10)	79

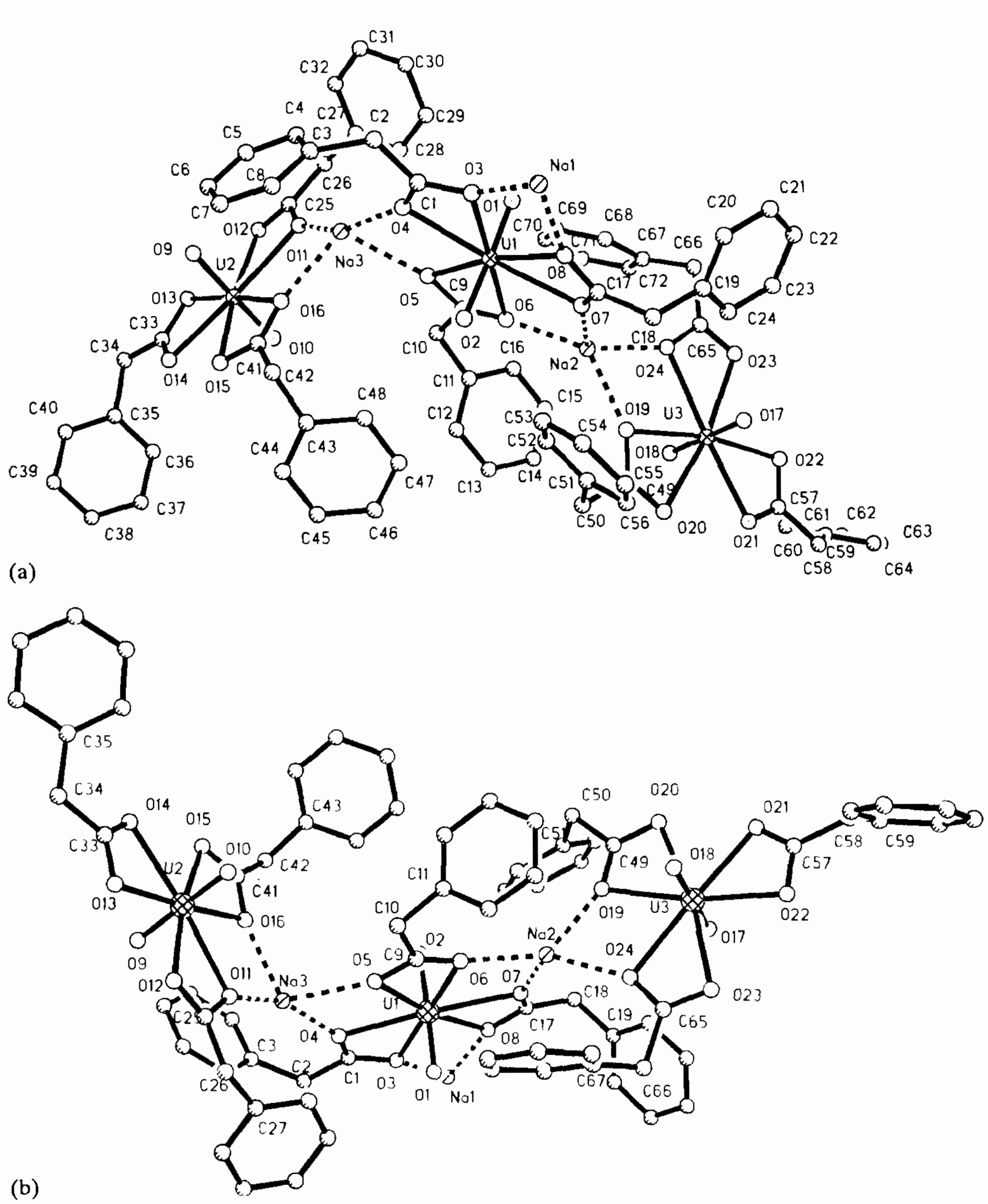

Fig. 1. (a) The crystal structure of the three independent $NaUO_2$ L_3 units with the adopted numbering scheme. (b) Another view of the ionic structure with simplified atom numbering.

reasons only calculations of the thermodynamic changes for the formation of the 1:1 complex were possible.

In previous works (ref. 7 and refs. therein) we reported the changes in the thermodynamic functions for a series of monocarboxylate ligands for which a linear relationship between the stability constants (log β values) of the 1:1 complexes and the protonation constants of the ligands was found (see ref. 7 for a complete discussion of this subject). The log β values for the formation of the uranyl(VI)–phenylacetate complex follow the same trend, and enthalpy and entropy changes for the studied system confirm it.

The fact that a compound of formula $NaUO_2L_3$ was obtained in the solid is in apparent disagreement with the presence of a 1:1 complex in solution. However, the low values of the stability constants and the relative solubilities of the species present in solution seem to indicate that the crystallized complex is probably the last soluble species and not necessarily the major solution species at equilibrium.

X-ray structure of $NaUO_2L_3$

Three independent $NaUO_2L_3$ complex molecules are present in the asymmetric unit of a cell which contains altogether 12 $NaUO_2L_3$ formula units. As shown in Fig. 1, the $UO_2L_3^-$ anions are structurally similar, with three bidentate ligands equatorially bonded to the uranyl ion. Because of the relatively poor quality of the crystals,

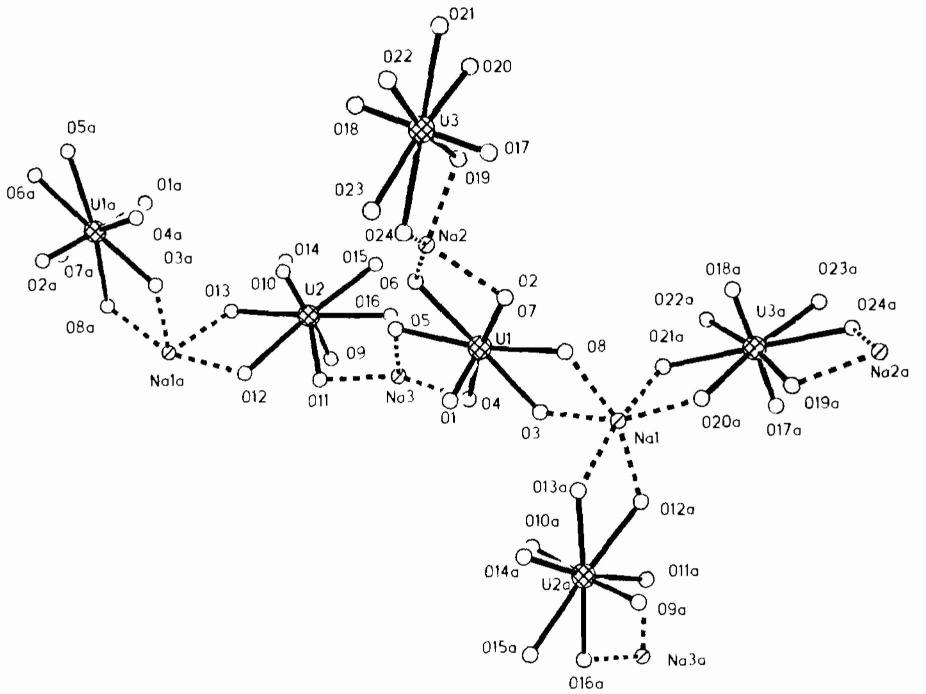

Fig. 2. Scheme of the interactions of the Na^+ cations with the neighbouring L oxygen atoms.

suggested by the very high number of reflections rejected because of their low intensity (see Table 1), and of the high absorption effects due to the presence of many heavy atoms, only in part eliminated by the applied corrections, the e.s.d.s on the final atomic coordinates are rather high, despite the rather good accordance factor. Therefore, although it is meaningless to discuss single bonds or angles with high standard deviations, the fact that there are three independent molecules with the same structure makes it possible to consider with confidence mean values calculated for a number of chemically equivalent structural details. Thus, the mean value for the 18 U–O(L) bonds is 2.45 Å, and the chelation angle, mean of the angles subtended by the nine chelating ligands, is 53°. These values agree with corresponding distances found in $Rb[UO_2(NO_3)_3]$ [8] and in $(NH_4)_4[UO_2(CO_3)_3]$ [9], that is in uranyl compounds with six equatorial donor atoms, despite the different nature of the bidentate ligands, while the same distances are significantly shorter in similar compounds with five donor oxygens. Mean plane calculations show that the six equatorial oxygen atoms are not coplanar, being alternatively displaced (by ± 0.1 to 0.2 Å) from the base plane in the usual puckered configuration. The base plane of U(1) makes an angle of 94° with that of U(2) and an angle of 89° with that of U(3). As shown in Fig. 2 the $UO_2L_3^-$ anions forming the asymmetric unit of the cell are held together by strong interactions of the ligand oxygens with the $Na^+(2)$ and $Na^+(3)$ ions, whereas $Na^+(1)$ provides linking with the neighbouring units. Both Na(2) and Na(3) make four Na...O relevant contacts while Na(1) is involved in six and can be considered as roughly octahedral. All six oxygen atoms coordinated to U(1) participate in stabilizing the structure through Na...O interactions, while only four oxygen atoms of the U(2) and four of the U(3) coordination core are involved.

Supplementary material

Observed and calculated structure factors, anisotropic thermal parameters, and H atom coordinates are available from Dr U. Casellato on request.

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