

Les ions Cs⁺ se placent autour de l'ion U₂O₄F₈⁴⁻. Par rapport à l'atome d'uranium, les dix ions césium les plus proches se trouvent à une distance de 4,29 à 5,21 Å. Les autres distances sont supérieures à 7 Å. Les ions césium Cs(2) se trouvent dans une sorte de tunnel. Chacun d'eux a pour voisins des atomes de fluor et des molécules d'eau. A l'intérieur du tunnel, la distance entre deux atomes de césium est de 4,64 Å. Les plus proches voisins du césium ainsi que leur distance à ce dernier sont répertoriés dans le Tableau 4. Les ions césium Cs(1) se trouvent dans des cavités. Les atomes voisins sont les atomes d'oxygène et de fluor. Enfin, la molécule d'eau relie deux dimères entre eux. En effet, l'atome d'oxygène de l'eau se trouve à une distance 2,76 Å de l'atome de fluor F(4'') et à 3,03 Å de l'atome F(3'''). L'angle formé par les liaisons H₂O-F(4'') et H₂O-F(3''') est de 104 ± 10°. La molécule d'eau assure donc la liaison entre deux dimères à l'aide de ponts hydrogène de force moyenne.

Le Tableau 5 regroupe les coefficients d'agitation thermique anisotrope des atomes lourds. L'atome d'uranium s'agit de façon privilégiée suivant une direction voisine de O-U-O tandis que les atomes de césium s'agitent suivant des ellipsoïdes ne présentant pas de directions privilégiées remarquables.

Conclusion

L'étude structurale du composé Cs₂UO₂F₄-H₂O nous a permis de mettre en évidence l'existence d'un ion binucléaire formé à partir de deux ions dipyramidales UO₂F₃²⁻ par mise en commun d'une arête de base.

Tableau 5. Les ellipsoïdes d'agitation thermique des atomes d'uranium et de césium

	Déplacement quadratique moyen en Å ²	Cosinus directeurs des axes des ellipsoïdes par rapport aux axes de la maille a, b, c' avec c' perpendiculaire à (a, b).		
Uranium	0,014	-0,68	0,03	0,73
	0,004	-0,30	0,90	-0,32
	0,003	0,68	0,44	0,60
Cs(1)	0,036	-0,60	-0,11	0,79
	0,034	-0,04	0,99	0,11
	0,009	0,80	-0,04	0,60
Cs(2)	0,038	0,81	0,18	-0,56
	0,031	0,59	-0,26	0,77
	0,011	0,01	0,95	0,31

D'autres études structurales, par diffraction des rayons X sur des monocristaux et par spectroscopies infrarouge et Raman, sont actuellement en cours au laboratoire dans le but de mettre en évidence d'autres types d'ions complexes que peut former l'ion uranyle avec les halogénures.

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The Crystal Structure of Oxotuberostemonine, C₂₂H₃₁NO₅*

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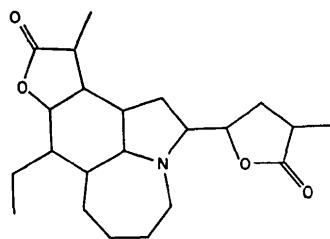
The structure of oxotuberostemonine, C₂₂H₃₁NO₅, has been determined by direct methods and refined by a least-squares procedure to an *R* index of 0.074 for 1836 observed reflexions. The space group is *P*2₁2₁2₁ and the cell dimensions are *a* = 10.30 (2), *b* = 24.50 (3), *c* = 8.34 (1) Å. The lactone ring which is fused to the cyclohexene ring has been shown to form also a *spiro* junction with the pyrrolidine ring. The molecules are held together in chains by hydrogen bonds between the hydroxyl groups and lactone oxygen atoms.

Oxotuberostemonine, C₂₂H₃₁NO₅, was first isolated from the root of *Stemona tuberosa* Lour. by Kondo, Satomi & Odera (1954). It was shown by Edwards,

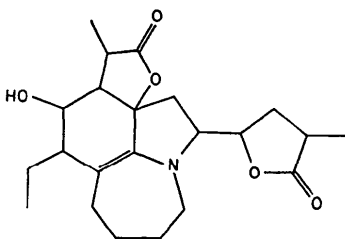
Feniak & Handa (1962) to be obtainable by mercuric acetate oxidation of tuberostemonine (I). Götz, Bögri & Gray (1961) had proposed two alternative structures for tuberostemonine, and additional nuclear magnetic resonance spectra enabled Edwards & Feniak

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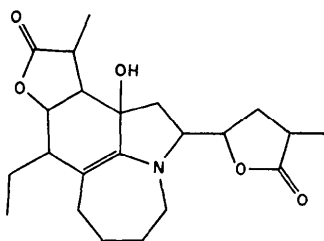
(1962) to select the correct one of these. The structure of oxotuberostemonine, however, remained undetermined although the existing chemical evidence was sufficient to eliminate a number of possibilities. An X-ray crystal structure determination was therefore undertaken and the preliminary results have been reported in an earlier communication (Huber, Hall & Maslen, 1968).



(I)



(II)



(III)

The structure revealed by this analysis (II) is very similar to the one (III) suggested by Edwards (1967) as the most likely possibility on the basis of known hydroxy enamine formation by mercuric acetate oxidation (Leonard, Miller & Thomas, 1956). The two structures differ in the position of fusion of the γ -lactone ring to the cyclohexene ring, and the position of attachment of the hydroxyl group. Both differing features can be explained as the result of a re-lactonization of (III) to give (II).

Experimental

A sample of oxotuberostemonine containing crystals suitable for X-ray study was provided by Dr O. E. Edwards. The crystals are colourless laths, elongated along the c axis.

Oxotuberostemonine, $C_{22}H_{31}NO_5$, M.W. 389.48
Orthorhombic, space group $P2_12_12_1$.

$$a = 10.297 \pm 0.015 \text{ \AA}$$

$$b = 24.50 \pm 0.03$$

$$c = 8.34 \pm 0.01$$

$$Z = 4$$

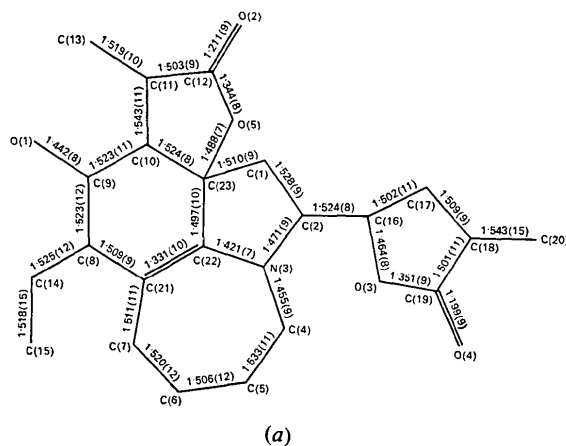
$$D_m \text{ (by flotation)} = 1.237 \text{ g.cm}^{-3}$$

$$D_x = 1.229 \text{ g.cm}^{-3}$$

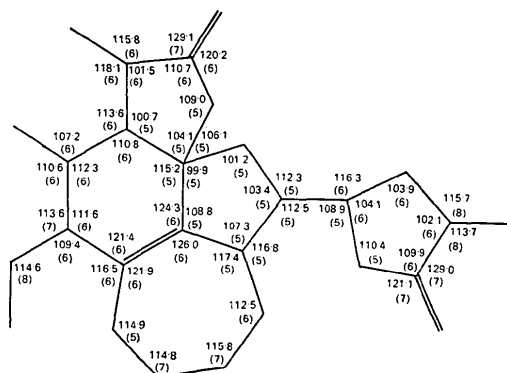
$$\mu(\text{Cu } K\alpha) = 7.15 \text{ cm}^{-1}$$

The cell dimensions were determined from precession photographs obtained with $\text{Cu } K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The space group was determined from precession and Weissenberg photographs. Systematic absences are $h00$ when h is odd, $0k0$ when k is odd, and $00l$ when l is odd.

Three-dimensional intensity data were obtained from multiple-film equi-inclination Weissenberg photographs recorded with $\text{Cu } K\alpha$ radiation for the 0–6 layers about c and the 0–3 layers about a . The crystals used for the c - and a -axis data collection had approximate dimensions $0.15 \times 0.05 \times 0.30 \text{ mm}$ and $0.2 \times 0.05 \times 0.2 \text{ mm}$ respectively, and were mounted with



(a)



(b)

Fig. 1. (a) Intermolecular bond lengths (\AA), corrected for rotational oscillation, and (in parentheses, $\times 10^3$) their e.s.d.'s. (b) Intramolecular angles ($^\circ$), uncorrected for rotational oscillation, and (in parentheses, $\times 10$) their e.s.d.'s.

their longest dimension parallel to the rotation axis. Intensities were estimated by visual comparison with a calibrated intensity scale, and corrected for Lorentz and polarization factors. Absorption corrections were considered to be unnecessary, but a correction for secondary extinction was applied later during the refinement. Of the 2748 independent reflexions theoretically accessible with Cu $K\alpha$ radiation, 2188 reflexions were recorded. Of these, 352 had intensities too weak to be measured, and were excluded from the refinement. They are, however, included in Table 3, where they are assigned $F_o = F_{\min}/\sqrt{3}$, F_{\min} being the minimum amplitude observable in the particular region of reciprocal space.

Data from the various layers were put on a common relative scale initially by comparing the F^2 values of reflexions common to each pair of interesting layers.

Structure determination and refinement

The structure was solved by direct methods as described previously (Huber, Hall & Maslen, 1968). Refinement was by block-diagonal least-squares calculations. All hydrogen atoms were located on a difference map. The weighting scheme used throughout was of the form

$$w = 1/\{1 + [(|F_o| - g)/f]^2\},$$

and the final values of f and g were 7.0 e and -6.0 e respectively. Scattering factor values were taken from

Table 2. *Hydrogen atom parameters*

Coordinates are $\times 10^3$. Standard deviations are given in parentheses for parameters which were refined.

	x/a	y/b	z/c	B
H(1)*	298 (7)	3 (3)	-362 (9)	4.6 (1.8)Å ²
H(1a)	461	189	25	2.5
H(1b)	546	204	-135	2.5
H(2)	277	234	-73	2.4
H(4a)	137	210	-345	3.1
H(4b)	174	274	-316	3.1
H(5a)	115	264	-585	3.8
H(5b)	271	277	-579	3.8
H(6a)	164	170	-620	4.0
H(6b)	214	209	-768	4.0
H(7a)	379	149	-725	3.8
H(7b)	428	206	-642	3.8
H(8)	402	69	-578	3.5
H(9)	491	24	-342	2.8
H(10)	573	99	-196	2.3
H(11)	496	79	61	2.7
H(13a)	416 (8)	-15 (3)	102 (9)	4.4 (1.8)
H(13b)	409 (6)	-20 (3)	-90 (8)	3.0 (1.5)
H(13c)	572 (7)	-5 (3)	17 (8)	3.4 (1.5)
H(14a)	640	114	-456	4.3
H(14b)	592	121	-641	4.3
H(15a)	573 (9)	6 (3)	-616 (10)	5.8 (2.1)
H(15b)	678 (8)	36 (3)	-489 (10)	5.6 (2.2)
H(15c)	727 (11)	46 (4)	-652 (13)	9.9 (3.0)
H(16)	476	300	-211	2.6
H(17a)	422	286	123	3.2
H(17b)	562	299	39	3.2
H(18)	514	390	6	3.4
H(20a)	413 (5)	429 (2)	207 (7)	1.7 (1.1)
H(20b)	508 (13)	372 (5)	313 (17)	14.1 (4.4)
H(20c)	334 (11)	365 (5)	264 (14)	11.7 (3.7)

* H(1) is attached to O(1), and each of the other hydrogen atoms is attached to a carbon atom bearing the same number.

Table 1. *Fractional coordinates and vibration tensor components (Å²)*

$$T = \exp [-2\pi^2 (U_{11}a^*2h^2 + \dots + 2U_{23}b^*c^*kl + \dots)]$$

All quantities are $\times 10^4$. The e.s.d.'s are shown in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
O(1)	3022 (4)	424 (1)	-3087 (6)	455 (19)	389 (15)	836 (34)	-346 (40)	-66 (46)	-217 (29)
O(2)	2161 (4)	636 (2)	706 (6)	467 (20)	481 (18)	820 (34)	444 (44)	369 (46)	77 (32)
O(3)	3037 (4)	3334 (1)	-1413 (5)	471 (18)	338 (15)	591 (28)	-84 (36)	-250 (40)	120 (27)
O(4)	2395 (5)	4110 (2)	-304 (8)	626 (25)	499 (21)	1102 (43)	-201 (57)	83 (60)	368 (40)
O(5)	2817 (3)	1295 (1)	-914 (4)	321 (15)	332 (12)	432 (21)	92 (31)	59 (31)	20 (24)
C(1)	4560 (5)	1939 (2)	-954 (7)	407 (22)	353 (18)	325 (28)	44 (42)	-5 (44)	-23 (35)
C(2)	3571 (5)	2372 (2)	-1435 (7)	371 (20)	328 (18)	381 (31)	-6 (41)	-43 (47)	12 (33)
N(3)	3280 (4)	2239 (1)	-3110 (6)	387 (19)	295 (15)	357 (25)	-23 (34)	-197 (39)	111 (28)
C(4)	2018 (5)	2405 (2)	-3715 (7)	421 (24)	471 (24)	507 (38)	-148 (53)	-217 (54)	175 (41)
C(5)	2014 (6)	2487 (3)	-5534 (7)	609 (32)	633 (30)	327 (36)	155 (58)	-272 (57)	197 (54)
C(6)	2278 (6)	1985 (3)	-6520 (8)	629 (36)	754 (37)	337 (32)	132 (62)	-351 (63)	239 (60)
C(7)	3634 (6)	1751 (3)	-6332 (7)	562 (30)	669 (30)	307 (30)	-114 (54)	-110 (56)	254 (52)
C(8)	4491 (6)	899 (2)	-4896 (8)	540 (27)	408 (24)	487 (38)	-206 (52)	-149 (58)	180 (44)
C(9)	4353 (5)	580 (2)	-3342 (9)	405 (23)	304 (18)	698 (42)	-96 (51)	-8 (56)	14 (33)
C(10)	4775 (4)	910 (2)	-1890 (7)	342 (20)	356 (18)	396 (32)	128 (45)	82 (46)	24 (33)
C(11)	4401 (5)	645 (2)	-280 (8)	328 (20)	392 (21)	529 (35)	351 (50)	32 (47)	23 (33)
C(12)	3022 (5)	832 (2)	-92 (8)	370 (21)	347 (21)	611 (40)	182 (48)	84 (55)	-1 (36)
C(13)	4630 (6)	37 (2)	-77 (10)	604 (34)	429 (27)	1015 (65)	501 (70)	172 (81)	303 (50)
C(14)	5891 (6)	960 (3)	-5455 (10)	545 (32)	678 (33)	636 (46)	228 (70)	298 (67)	259 (55)
C(15)	6566 (10)	427 (4)	-5857 (13)	1079 (66)	912 (52)	1067 (75)	173 (108)	510 (120)	1190 (105)
C(16)	4099 (4)	2948 (2)	-1238 (7)	343 (21)	325 (18)	537 (37)	-16 (46)	-42 (49)	61 (33)
C(17)	4675 (5)	3083 (2)	356 (8)	452 (25)	392 (21)	553 (37)	-82 (54)	-261 (55)	41 (41)
C(18)	4405 (6)	3683 (2)	551 (9)	541 (29)	359 (21)	713 (44)	-133 (58)	-66 (61)	-136 (42)
C(19)	3181 (5)	3752 (2)	-379 (8)	519 (26)	328 (18)	577 (37)	-49 (50)	61 (57)	1 (40)
C(20)	4313 (12)	3889 (3)	2290 (11)	1426 (87)	745 (46)	676 (55)	-518 (86)	-417 (121)	197 (102)
C(21)	3873 (5)	1455 (2)	-4773 (7)	439 (23)	371 (18)	321 (28)	-25 (42)	11 (48)	-4 (36)
C(22)	3659 (4)	1689 (2)	-3362 (7)	364 (20)	335 (18)	378 (31)	-62 (41)	-122 (47)	18 (32)
C(23)	4022 (4)	1443 (2)	-1788 (7)	308 (19)	286 (18)	380 (29)	85 (39)	-77 (43)	-19 (29)

International Tables for X-ray Crystallography (1962). The final R value was 0.074 for all observed reflexions.

Results

Final parameters and their standard deviations for the non-hydrogen atoms are listed in Table 1, and final hydrogen atom parameters are listed in Table 2. Final observed and calculated structure amplitudes are listed in Table 3.

The structure factors were recalculated without the

contributions of the hydrogen atoms and a three-dimensional difference synthesis was computed. Peak heights for the hydrogen atoms varied from 0.2 to 0.5 e.Å⁻³ and no other peaks higher than about 0.3 e.Å⁻³ were observed. The standard deviation of the difference density, calculated according to Cruickshank's (1959) method, is 0.088 e.Å⁻³.

Thermal motion

An analysis of the thermal motion was carried out by Cruickshank's (1956a) method. Assuming the whole

Table 3. Observed and calculated structure amplitudes (x 10) An asterisk indicates an unobserved reflection, with F_min/√3 given in place of |F_0|.

Table with multiple columns of numerical data representing observed and calculated structure amplitudes for various reflections. The table is organized into several sections, likely corresponding to different hkl planes or symmetry-equivalent reflections. Each entry includes observed values, calculated values, and sometimes a difference value. Asterisks indicate unobserved reflections.

molecule to be a rigid body vibrating about its centre of gravity resulted in physically plausible values for the elements of the translational and librational tensors, but the r.m.s. difference between the U_{ij} values calculated from these tensors and the observed U_{ij} values was unacceptably large. Agreement of the observed and calculated U_{ij} values was significantly improved when the molecule was treated in two parts, one being the lactone group which is attached at C(2), and the other being the remainder of the molecule.

For the analysis of the thermal motion of the lactone group, the origin was placed at the site of C(2), and the axes were chosen as follows: axis (2) along the C(2)–C(16) bond, axis (1) in the x – y plane and normal to axis (2), axis (3) normal to axes (1) and (2). The results indicate that the translational motion of the lactone group is approximately isotropic, with r.m.s. amplitudes of 0.16, 0.19 and 0.18 Å parallel to axes (1), (2) and (3) respectively. The r.m.s. amplitudes of rotational oscillation about these axes are 3.6, 7.5 and 3.0°, indicating significant libration of the group about the C(2)–C(16) bond.

For the analysis of the tetracyclic portion of the molecule the origin was set at the centre of gravity of the whole molecule, and molecular axes (1), (2) and (3) were defined as parallel to the unit-cell axes a , b , and c respectively. The translational vibration of this fragment is also approximately isotropic, with r.m.s. amplitudes of 0.16, 0.17 and 0.19 Å along the three axial directions, and the components of rotational oscillation about the three axes are approximately equal, being 3.2, 3.3, and 2.6° about axes (1), (2), and (3) respectively.

Bond length corrections for both portions of the molecule were calculated according to Cruickshank's (1956*b*, 1961) procedure from the ω_{ij} tensors, and are, at most, of the same order of magnitude as the e.s.d.'s. Values of the bond distances before correction are given in Table 4, and the corrected values are shown in Fig. 1(*a*). Rotational oscillation corrections to the

bond angles were too small to be significant, and therefore only the uncorrected values are given in Fig. 1(*b*). The two angles with their e.s.d.'s which were excluded from the figure for simplicity are: C(1)–C(23)–C(10), 122.1°(0.5); O(5)–C(23)–C(22), 108.8°(0.4).

It should be emphasized that these corrections are based on the rigid-body assumption, and may be greatly underestimated for some bonds, especially C(14)–C(15), C(19)–O(4), and C(18)–C(20), which are probably involved in non-rigid vibrations. In fact the lower limit for the correction to the C(14)–C(15) bond, calculated according to the Busing & Levy (1964) method, is 0.007 Å; by the rigid-body procedure this correction is only 0.0009 Å.

The average C–H bond length is 1.08 Å, while the average H–C–H angle is 110.5°. None of the values differ significantly from those expected.

Discussion

The C_{sp^3} – C_{sp^3} bond distances vary from 1.502 to 1.543 Å, and none differ from the average value of 1.522 by as much as 2σ . For the C_{sp^2} – C_{sp^3} bonds the average is 1.504 Å, and the only C–C double bond is 1.331 Å. These values agree well with standard bond lengths 1.526 ± 0.002, 1.501 ± 0.004, and 1.335 ± 0.010 Å quoted by Lide (1962) for these types of bonds respectively. The two N_{sp^2} – C_{sp^3} bonds have an average of 1.463 Å, to be compared with 1.472 ± 0.005 (Sutton, 1965) or 1.462 Å (Hall & Ahmed, 1968), while C(22)–N(3) is shortened, to 1.421 Å, because of the adjacent C(22)–C(21) double bond.

The various C–O bond distances are also quite normal. The C(9)–O(1) hydroxyl bond length is 1.442 Å, and the C–O double-bond lengths vary from 1.199 to 1.211 Å. The lower value is probably affected by an insufficient thermal motion correction. The customary difference between the two types of formally single C–O bonds in a lactone ring is observed here also. The C–O bonds adjacent to the ketone groups have an average value of 1.348, while the other C–O bonds of the ether linkage have an average value of 1.476 Å. This difference corresponds to about 16 σ , and is therefore highly significant. The effect has also been observed in such structures as jacobine bromodilactone (Mathieson & Taylor, 1961) and β -D-glucuronolactone (Kim, Jeffrey, Rosenstein & Corfield, 1967) and can be ascribed to a small but significant contribu-

tion of the valence-bond resonance form $R-C \begin{matrix} + \\ \parallel \\ O-R \end{matrix}$.

The partial double-bond character of C(12)–O(5) and C(19)–O(3) imposes approximate planarity in this structure on the groups O(2), O(5), C(11), C(12), C(23) and O(3), O(4), C(16), C(18), C(19). C(16) and C(23) deviate by only about 0.04 Å from the planes through the other four atoms of each group. C(10) and C(17) deviate by 0.6 and 0.5 Å respectively from the planes to

Table 4. *Uncorrected bond lengths and their e.s.d.'s (in parentheses, $\times 10^3$)*

Bond	Uncorrected length	Bond	Uncorrected length
O(1)–C(9)	1.439 (8) Å	C(7)–C(21)	1.509 (11) Å
O(2)–C(12)	1.209 (9)	C(8)–C(9)	1.520 (12)
O(3)–C(16)	1.454 (8)	C(8)–C(14)	1.522 (12)
O(3)–C(19)	1.347 (9)	C(8)–C(21)	1.507 (9)
O(4)–C(19)	1.194 (9)	C(9)–C(10)	1.519 (11)
O(5)–C(12)	1.342 (8)	C(10)–C(11)	1.540 (11)
O(5)–C(23)	1.484 (7)	C(10)–C(23)	1.522 (8)
C(1)–C(2)	1.525 (9)	C(11)–C(12)	1.500 (9)
C(1)–C(23)	1.505 (9)	C(11)–C(13)	1.517 (10)
C(2)–N(3)	1.466 (9)	C(14)–C(15)	1.518 (15)
C(2)–C(16)	1.520 (8)	C(16)–C(17)	1.493 (11)
N(3)–C(4)	1.452 (9)	C(17)–C(18)	1.506 (9)
N(3)–C(22)	1.418 (7)	C(18)–C(19)	1.490 (11)
C(4)–C(5)	1.530 (11)	C(18)–C(20)	1.538 (15)
C(5)–C(6)	1.503 (12)	C(21)–C(22)	1.328 (10)
C(6)–C(7)	1.518 (12)	C(22)–C(23)	1.493 (10)

which they are adjacent, giving both lactone rings the envelope conformation.

The distribution of ring angles in the two lactone groups is very similar to that found in D-galactono- γ -lactone (Jeffrey, Rosenstein & Vlasse, 1967) and β -D-glucurono- γ -lactone (Kim *et al.*, 1967). In the present analysis the average ring angles at O, $>C=O$, and C are 109.7, 110.3, and 102.7° respectively. The averages of the corresponding angles in the other two structures are 110, 110.5 and 103.5°.

The cyclohexene ring is in 'half-chair' form, and its fusion with the lactone ring is *cis*. The azacycloheptene ring is in chair form, and the pyrrolidine ring is puckered, with C(1) deviating most (about 0.8 Å) from the plane through N(3), C(22), C(23).

Despite the presence of a double bond at C(21)–C(22) the four adjoining atoms are significantly non-planar. The plane through N(3)–C(22)–C(23) is at an angle of 13.5° to the plane through C(7)–C(21)–C(8).

The absolute configuration of oxotuberostemonine has not been directly determined in this analysis. However, the absolute configuration of tuberostemonine methobromide dihydrate has been experimentally determined by Harada, Irie, Masaki, Osaki & Uyeo (1967), and on this basis the absolute configuration

of oxotuberostemonine must be as indicated in Fig. 2.

The packing arrangement, viewed down the *a* axis, is illustrated in Fig. 2. The molecules are held together by hydrogen bonds which involve the hydroxyl groups and lactone oxygens. The O(1)···O(2) distance is 2.79 Å, H(1)···O(2) is 1.74 Å, the angle O(1)–H(1)···O(2) is 173.7° ($\sigma=6.3^\circ$), and the angle C(12)–O(2)···H(1) is 128.1° ($\sigma=2.4^\circ$). O(1) and H(1) are respectively 0.66 and 0.48 Å out of the plane through O(2), O(5), C(11), C(12) of the adjacent molecule. The hydrogen bonds are between successive molecules along screw axes which are parallel to *c*, so that endless zigzag chains are formed.

Other intermolecular contact distances correspond to normal van der Waals interaction. The shortest contact distances for the different types of atoms found in this structure (apart from those involved in the O(1)···O(2) hydrogen bond), with corresponding distances calculated from van der Waals radii (Nyburg, 1961) given in parentheses, are H···H, 2.03 (2.0); H···C, 2.83 (2.7); H···O, 2.46 (2.4); H···N, 3.09 (2.5); C···O, 3.18 (3.1). Two methyl groups, C(19) and C(20), have a C···C distance of 3.81 Å, which is significantly less than the 4.0 Å usually suggested for such contacts. However, their hydrogen atoms are

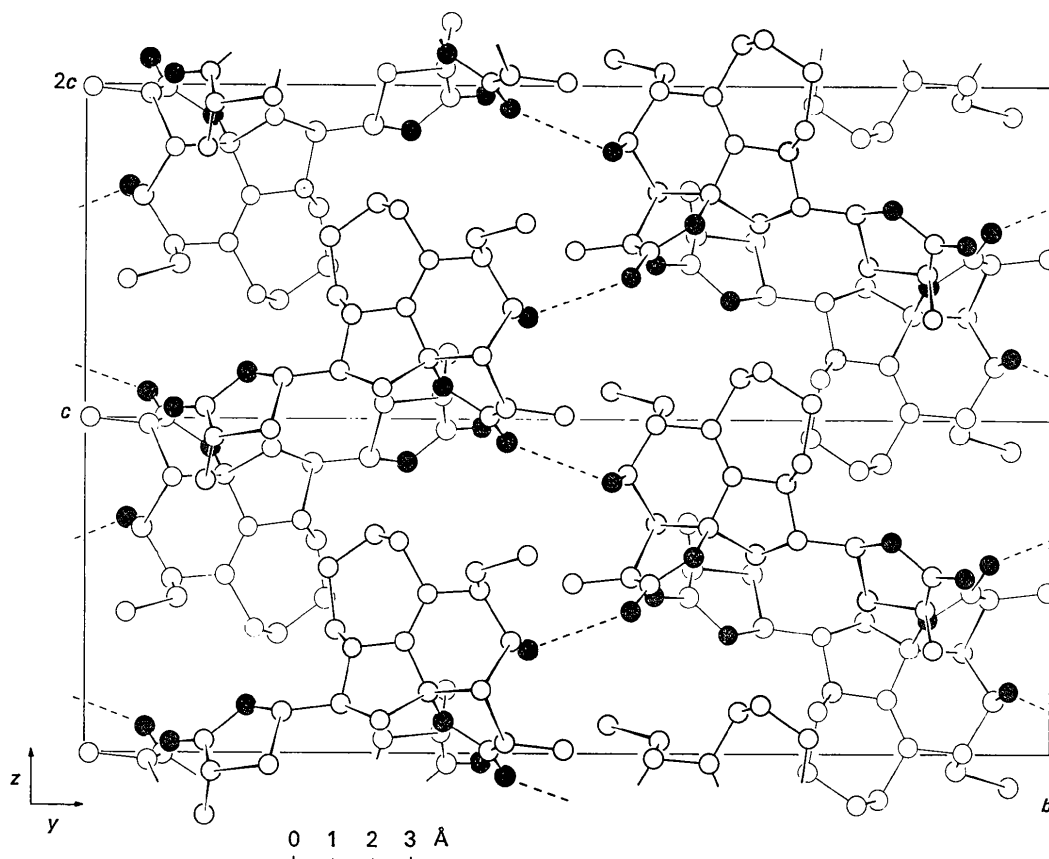


Fig. 2. A view of the structure illustrating the molecular packing. The positive direction of *a* is toward the viewer. Open, hatched, and filled circles represent carbon, nitrogen, and oxygen atoms respectively.

evidently in mutually staggered configurations because the shortest H...H contact between these groups is 2.75 Å.

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The Crystal and Molecular Structure of (I): μ -(α,ω -Octadi- π -enyl)bisbromotriisopropylphosphenickel(II) and (II): μ -(α,ω -Octadi- π -enyl)bisbromodiphenylphosphinoethanenickel(II)

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The crystal and molecular structure of the two title named binuclear complexes (I) and (II), isolated from the reaction of bromobistriisopropylphosphenickel(II) with butadiene, have been determined by X-ray methods from four-circle diffractometer data. Complex (I): triclinic, $a=13.72$, $b=7.93$, $c=7.89$ Å, $\alpha=103.1$, $\beta=83.8$, $\gamma=103.3^\circ$; space group $P\bar{1}$, 1921 reflexions, $R=0.089$. Complex (II): monoclinic, $a=18.08$, $b=22.18$, $c=17.02$ Å, $\gamma=102.2^\circ$; space group $A2/a$, 1248 reflexions, $R=0.093$. Both complexes are centrosymmetric dimers. In complex (I) the nickel atoms are four-coordinate square planar; Ni(1)-Br(1), Ni(1)-P(1), Ni(1)-C(1), Ni(1)-C(3), 2.313, 2.209, 1.99 and 2.12 Å respectively. In complex (II) the nickel atoms are five-coordinate square pyramidal; Ni-P (mean) 2.19, Ni-C (mean) 2.09 and Ni-Br 2.66 Å.

Introduction

Studies of the homogeneous dimerization and oligomerization of butadiene by nickel complexes show that

when bromobistriisopropylphosphenickel(II) reacts with butadiene, an intermediate green paramagnetic solution containing a radical nickel species is formed. This reacts further to give an orange solution from which crystals of the complex (I) are isolated. The orange solution on treatment with bisdiphenylphosphinoethane yields the red crystalline complex (II).

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