Experimental

A crystal of apomorphine hydrobromide, roughly cylindrical about the *c* axis, was mounted about **c** in a Nonius Weissenberg camera. Zr-filtered Mo $K\alpha$ radiation was chosen since this wavelength gives a favourable anomalous scattering factor for bromine (*International Tables for X-ray Crystallography*, 1974). The layer *hk*1 was recorded by the integrated Weissenberg technique. The exposure time was 120 h.

Results

For the space group $P2_12_12_1$, $F(hkl) = F(\bar{h}\bar{k}\bar{l}) = F(\bar{h}kl) = F(h\bar{k}l)$ for $l > 0$, and thus the Friedel pairs are symmetrically distributed about the *h*01 and 0*k*1 axial rows. To find the pairs exhibiting the greatest anomalous dispersion effect the structure factor amplitudes of all *hk*1 with $|h| \leq 10$, $|k| \leq 10$ were calculated with the coordinates determined earlier. The members of 23 pairs differed by more than 10% in their calculated amplitudes. The reflexions of these pairs were measured on a microdensitometer, and 15 pairs were intense enough to give satisfactory readings. F_{calc} for these 30 reflexions were then calculated from the absolute configuration which is *R* at the C atom designated C(8) by Giesecke (1973), 6a in chemical literature. It was found that for all 15 pairs whenever $F^+_{\text{obs}} > F^-_{\text{obs}}$ then $F^+_{\text{calc}} > F^-_{\text{calc}}$ and *vice versa*.

The conclusion is that the correct absolute configuration of apomorphine is *R*. The arbitrarily chosen enantiomorph presented in the structure determination of apomorphine (Giesecke, 1973) is thus incorrect.

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Molecular configuration of a tridecazirconium oxide–methoxide complex.*

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Molecules of $Zr_{13}O_8(OCH_3)_{36}$ are found as a hydrolysis product in very unstable crystals [$R\bar{3}m$, $a = 17{\cdot}31$ (1), $c = 27{\cdot}75$ (2) Å]; the cubic close-packed arrangement of Zr (three above and below a plane of seven) consists of a central Zr ion bonded to eight oxide ions and 12 sevenfold-coordinate Zr ions each bonded to two oxide ions, four bridging methoxide groups and one terminal methoxide group.

Our laboratories have used the alkoxides of Ti, Nb and Zr as starting materials for the preparation of the perovskite-class of ferroelectrics and electrooptic ceramics (Dosch, 1971, 1972; Haertling & Land, 1972) and, more recently, ion-exchange materials which can be used to stabilize radioactive wastes (Lynch, Dosch, Kenna, Johnstone & Nowak, 1976). Most such precipitated materials yield amorphous diffraction patterns (Morosin & Peercy, 1976); however, crystals of a rather unstable polyzirconium oxide–methoxide intermediate were grown. The only structural study on such a metal oxide–alkoxide complex, or first hydrolysis product, which has been reported appears to be that for Ti (Watenpaugh & Caughlan, 1967), although structures of the alkoxides of Ti (Ibers, 1963; Witters & Caughlan, 1965) and Tl (Dahl, Davis, Wampler & West, 1962) are known.

Very unstable crystals containing molecules of composition $Zr_{13}O_8(OCH_3)_{36}$ plus disordered entities (possibly OH^-, Na^+ and CH_3OH) were obtained on the walls of bottles containing solutions made by mixing dilute methanol solutions of NaOH and the alkoxide of zirconium (prepared and kindly supplied by R. G. Dosch). The crystals are very sensitive to water as well as unstable in dry air. Under crossed polars in dried methyl alcohol, one can observe such crystals undergoing a spontaneous transformation (instantaneous over the entire crystal) into an amorphous material, presumably as atmospheric water diffuses through the alcohol into the crystal. Chemical analysis of small amounts of such an amorphous product showed the presence of ~3 wt% Na, with the ashed residue (ZrO_2) determined to be ~ 64%. A crudely determined density of 1·78 g cm^{-3} is consistent with $Z = 3$ molecules of $Zr_{13}O_8(OCH_3)_{36}$.

Diffraction data were obtained on various specimens encapsulated in glass capillaries filled with oil. All the specimens showed some radiation degradation. A set of intensities (2037 independent reflections to $2\theta = 55°$ with Mo $K\alpha$) was obtained by normalizing against a rapidly collected (3° min^{-1}) small set, the radiation-corrected (using standards) θ–2θ scanned (1° min^{-1}, 20 s background count times) data sets. No attempt was made to correct for the absorption of the oil or glass capillary. A Patterson synthesis yielded the Zr positions, and subsequent Fourier synthesis together with least-squares refinement of positional and thermal parameters yielded the molecular structure of the tridecazirconium oxide–methoxide complex (Fig. 1). The func-

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tion minimized was $\Sigma\,\omega[|F_o| - |F_c|]^2$ with ω a function of counting statistics. With anisotropic thermal parameters for the Zr and O atoms, except O(7), and isotropic values for O(7) (see Fig. 1) and methoxide C atoms, $R = 0{\cdot}105$. Atoms O(7) and C(7) are placed on disordered positions about the symmetry mirror. It is also evident on difference Fourier syntheses that there is anisotropic thermal motion of the other C atoms and that possibly C(4) may be disordered. Rather large holes are found between the molecules located about $0,0,\frac{1}{2}$ and symmetry-equivalent points; the distance from $0,0,\frac{1}{3}$ to $0,0,\frac{1}{2}$ (the midpoint) is 4·65 Å with C(6) approaching $0,0,\frac{1}{3}$ at 4·51 Å. However, it is not clear from various attempts to refine peaks of electron density what the arrangement of the approximately four Na^+ ions per formula unit determined by chemical analysis, charge balancing OH^- or OCH_3^- ions as well as possible CH_3OH groups might be. The two largest (sharp) peaks proved to be artifacts and would not sustain refinement even when partial occupancy parameters were employed. The refined positional parameters shown in Table 1 labeled C(10) through C(18) were obtained by placing C atoms at sites of broad peaks corresponding to about 2 e with a fixed thermal parameter, $U = 0{\cdot}25$ Å^2, and allowing the population parameter to vary (initially set to 0·1). Table 1 gives the population parameter in place of the fixed value of U. Since some of these positions were connected by smeared 'tubes' of density, the author does not propose that such positions are exact; neither is any attempt made to describe a particular geometrical arrangement for the disordered entities which might be constructed from such positions. All the population parameters are small and R was reduced only to 0·101.*

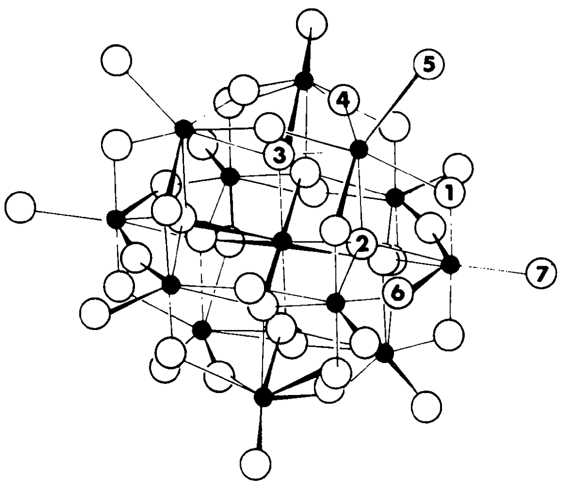

Fig. 1. The arrangement of Zr and O atoms in molecules of tridecazirconium oxide–methoxide. The molecules are located on $\bar{3}m$ symmetry sites; however, the departures from an idealized $m3m$ (O_h) symmetry are very small. Solid and open circles represent Zr and O atoms respectively; O(2) and O(3) are oxide ions while the remainder are part of methoxide groups; C atoms are not shown and are labeled consistent with the O atom to which they are attached.

The structure of the highly symmetric tridecazirconium oxide–methoxide complex consists of a cubic close-packed arrangement of 13 Zr ions (three above and below a plane of seven; Fig. 1 and Table 2) with an eightfold-coordinated Zr ion at the center and two other crystallographically different sevenfold-coordinated Zr ions. The central Zr ion is bonded to eight oxide ions (2·19 and 2·23 Å), arranged in a slightly trigonally distorted cube (edges of 2·52 and 2·57 Å) and each bonded to three of the other Zr atoms; each of the sevenfold Zr atoms is bonded to two oxide ions (2·15–2·19

Table 1. *Atomic positional and thermal parameters*

U_{ij} are of the form $\exp(-2\pi^2\Sigma\, U_{ij} h_i h_j a_i^* a_j^*)$ in units of 10^{-2} Å^2; for C(10)–C(18), population parameters (pp) are given since a fixed $U = 0{\cdot}25$ Å^2 was used.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr(1)	0·2048 (2)	0	0	6·6 (1)	$2U_{12}$	7·3 (2)	5·0 (1)	0·18 (9)	$2U_{13}$
Zr(2)	0	0	0	$2U_{12}$	$2U_{12}$	3·6 (3)	2·2 (1)	0	0
Zr(3)	$2y$	0·0683 (1)	0·10464 (9)	$2U_{12}$	7·7 (2)	4·9 (1)	3·7 (1)	$2U_{23}$	−0·79 (7)
O(1)	0·223 (1)	0·024 (1)	0·0784 (5)	13 (2)	17 (2)	6 (1)	12 (2)	−4 (1)	−2 (1)
O(2)	$2y$	0·0692 (6)	0·0257 (5)	$2U_{12}$	5·8 (9)	2·6 (7)	1·8 (5)	$2U_{23}$	−0·4 (4)
O(3)	0	0	0·0804 (9)	$2U_{12}$	$2U_{12}$	1 (1)	3·3 (7)	0	0
O(4)	0·0614 (9)	$2x$	0·1389 (8)	11 (1)	$2U_{12}$	9 (2)	7 (1)	−5·2 (9)	$2U_{13}$
O(5)	$2y$	0·105 (1)	0·1643 (9)	$2U_{12}$	13 (2)	7 (2)	6 (1)	$2U_{23}$	2·4 (8)
O(6)	0·1426 (8)	$2x$	0·015 (1)	10 (2)	$2U_{12}$	13 (2)	2·8 (8)	−1·5 (8)	$2U_{13}$

	x	y	z	U (or pp)		x	y	z	U (or pp)
O(7)	0·329 (3)	0·014 (5)	0·004 (3)	10 (1)	C(12)	0	0	0·38 (4)	0·1 (2)
C(1)	0·278 (4)	0·007 (4)	0·105 (2)	20 (2)	C(13)	$2y$	0·08 (2)	0·43 (2)	0·2 (2)
C(4)	0·100 (2)	$2x$	0·171 (2)	17 (2)	C(14)	0·110 (8)	$2x$	0·499 (8)	0·41 (9)
C(5)	$2y$	0·130 (2)	0·207 (2)	18 (3)	C(15)	$2y$	0·10 (3)	0·30 (3)	0·1 (1)
C(6)	0·187 (3)	$2x$	0·042 (3)	22 (3)	C(16)	$2y$	0·05 (1)	0·244 (8)	0·4 (1)
C(7)	0·416 (5)	0·039 (5)	0·013 (2)	13 (2)	C(17)	$2y$	0·05 (2)	0·34 (2)	0·2 (1)
C(10)	0	0	0·26 (6)	0·1 (3)	C(18)	0·21 (1)	0·04 (1)	0·371 (6)	0·36 (7)
C(11)	0	0	0·31 (3)	0·3 (3)					

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31967 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH 1NZ, England.

Table 2. *Bond lengths and angles*

Zr(1)–Zr(2)	3·546 (3) Å	O(1)–Zr(1)–O(7′)	92 (2)°
Zr(1)–Zr(3)	3·553 (3)	O(1)–Zr(1)–O(6)	88 (1)
Zr(2)–Zr(3)	3·552 (2)	O(1)–Zr(1)–O(6′)	92 (1)
		O(2)–Zr(1)–O(6′)	118 (1)
Zr(1)–O(2)	2·16 (1)	O(2)–Zr(1)–O(6)	70 (1)
Zr(2)–O(2)	2·19 (1)	O(2)–Zr(1)–O(7)	138 (2)
Zr(2)–O(3)	2·23 (3)	O(2)–Zr(1)–O(7′)	151 (2)
Zr(3)–O(2)	2·19 (1)	O(7)–Zr(1)–O(6)	91 (2)
Zr(3)–O(3)	2·15 (1)	O(7)–Zr(1)–O(6′)	81 (2)
		O(6)–Zr(1)–O(6′)	172 (1)
Zr(1)–O(1)	2·21 (1)		
Zr(1)–O(6)	2·19 (1)	O(2)–Zr(2)–O(2′)	70 (1)
Zr(3)–O(1)	2·12 (3)	O(2)–Zr(2)–O(2)	71 (1)
Zr(3)–O(4)	2·17 (2)		
		O(2)–Zr(3)–O(3)	72 (1)
Zr(1)–O(7)	2·03 (6)	O(1)–Zr(3)–O(4)	172 (1)
Zr(3)–O(5)	2·00 (2)	O(1)–Zr(3)–O(2)	70 (1)
		O(1)–Zr(3)–O(3)	118 (1)
O(1)–C(1)	1·38 (7)	O(1)–Zr(3)–O(5)	87 (1)
O(4)–C(4)	1·47 (4)	O(1′)–Zr(3)–O(5)	87 (1)*
O(5)–C(5)	1·39 (6)	O(1)–Zr(3)–O(4′)	87 (1)
O(6)–C(6)	1·52 (4)	O(1)–Zr(3)–O(1′)	92 (1)
O(7)–C(7)	1·34 (9)	O(2)–Zr(3)–O(4)	117 (1)
		O(3)–Zr(3)–O(4)	69 (1)
O(2)–Zr(1)–O(2′)	71 (1)°	O(5)–Zr(3)–O(3)	142 (1)
O(1)–Zr(1)–O(1)	174 (1)	O(5)–Zr(3)–O(2)	146 (1)
O(1)–Zr(1)–O(2)	69 (1)	O(5)–Zr(3)–O(4)	86 (1)
O(1)–Zr(1)–O(2′)	116 (1)	O(5)–Zr(3)–O(4)	86 (1)*
O(1)–Zr(1)–O(7)	83 (2)	O(1)–Zr(3)–O(4′)	172 (1)*

* Symmetry equivalent to a value listed; fractional parts of errors involving light atoms (<0·5) have been rounded up to (1).

Å), four bridging methoxide (2·12–2·21 Å), and one terminal methoxide group (2·00 and 2·03 Å). The coordination about these two Zr atoms is quite similar as can be seen by inspecting the angles in Table 2 (ordered for such comparison). In fact, the molecule deviates only slightly from $m3m$ (O_h) symmetry. The thermal parameters are consistent with the bonding behavior for the Zr–O skeleton, although rigid-body motion could account for part of this motion.

The disordering of C(7) appears to result from packing considerations. In the present results, the nearest-neighbor molecular contacts between closest symmetry-related positions of C(7) involve 3·66 Å separations; should C(7) not be disordered, this separation decreases below 2·80 Å, depending on the C–O separation used, with the O–C vectors pointing directly at each other. The shortest molecular contacts are between C(5) and two C(1)'s on a $\frac{2}{3},\frac{1}{3},\frac{1}{3}$-related molecule with 3·02 Å separations and O(5)–C(5)···C(1) angles of 120° as well as a symmetry-related C(5′) with a 3·13 Å separation and an O(5)–C(5)···C(5′) angle of 77°. Thus, C(5) is wedged between the three methyl groups on the adjacent molecule [and lies at a z coordinate above that for C(5′) of the molecule at $\frac{2}{3},\frac{1}{3},\frac{1}{3}$]. Hence, even though the molecules are large symmetric units, their close packing is considerably reduced from that of ideal spheres ($c/a = 3\sqrt{3}/2$) with $c/a = 1{\cdot}603$.

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New compounds with glaserite and Na_2SO_4(I) structures.

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New compounds with glaserite and Na_2SO_4(I) structures were crystallized from the melt and by solid-state reactions. The lattice parameters are reported. Superstructures and monoclinic deformations were observed.

The typical high-temperature modification of compounds A_2BX_4 with tetrahedral BX_4 complexes and medium-size to large cations A has the structure of Na_2SO_4(I) (or high-K_2SO_4) with the proposed space group $P6_3mc$ (Eysel & Hahn, 1970). Among the many low-temperature forms the glaserite structure (space group $P\bar{3}m1$) is unique since it occurs only in solid solutions with two cations of distinctly different size.

Because of their very similar powder patterns the difference between these two structures was not recognized until recently. The crystal chemistry of both structure types, in-

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