Dirubidium(I) Cyclooctatetraenide-1-Methoxy-2-(2-methoxyethoxy)ethane

By J. H. Noordik and H. M. L. Degens

Crystallography Laboratory, University of Nijmegen, Toernooiveld, Nijmegen, The Netherlands

and J. J. Mooij

Department of Physical Chemistry, University of Nijmegen, Toernooiveld, Nijmegen, The Netherlands

Abstract. $Rb_2(C_8H_8) \cdot (CH_3OCH_2CH_2)_2O$, ($Rb_2COT$.diglyme), orthorhombic, *Pnma*, $a = 7 \cdot 705(8)$, $b = 15 \cdot 144(15)$, $c = 14 \cdot 300(10)$ Å (from diffractometer data), $Z = 4$, $D_x = 1 \cdot 65$ g cm^{-3}. The structure was refined by full-matrix least-squares methods to a final R value of $0 \cdot 067$. The crystal structure of this compound is isomorphous with that of the previously published potassium derivative (Noordik, van den Hark, Mooij & Klaassen. *Acta Cryst.* (1974). B30, 833–835).

Introduction. The preparation and mounting of the crystals were the same as for the potassium compound (Noordik *et al.*, 1974). The crystal structures of Rb_2COT.diglyme are isomorphous. An elementary analysis of Rb_2COT.diglyme resulted in Rb 41·28 (41·77), C 40·85 (41·08) and H 5·32 (5·42)% (values in parentheses are the calculated ones). Unit-cell dimensions and intensities were obtained from a badly shaped crystal of approximate dimensions $0 \cdot 8 \times 0 \cdot 6 \times 0 \cdot 4$ mm, with a computer-controlled Nonius CAD-3 diffractometer (Mo $K\alpha$ radiation, Zr-filtered, θ–2θ scan). Systematic absences were $0kl$ for $k + l$ odd and $hk0$ for h odd, and of the two choices which are consistent with these conditions (*Pnma* and $Pn2_1a$), the centrosymmetric one *Pnma* has been chosen. This choice was confirmed by the successful refinement of the structure. All intensities in four symmetry-related octants in the range $4 \cdot 5° \le \theta \le 25°$ were measured. Absorption correction did not improve the agreement between the symmetry-related sets of reflexions, because it was impossible to obtain accurate crystal

dimensions. Therefore this correction was not performed. The minimum and maximum absorption factors in the average intensities of four symmetry-related reflexions calculated for the approximate crystal dimensions given above were 6·9 and 9·1 ($\mu = 62 \cdot 26$ cm^{-1}). After averaging the symmetry-related reflexions, 1532 unique observations remained. Of this set of reflexions, five were omitted because of a very large discrepancy between the individual measurements. Of the remaining 1527 reflexions, 963 had a significant intensity $[I > 3\sigma_c(I)$, $\sigma_c(I)$ derived from counting statistics]. The intensity data were reduced to structure amplitudes by application of Lorentz and polarization factors. Values for $\sigma(F)$ were calculated according to the formula $\sigma(F) = [\sigma_c^2(F) + (0 \cdot 05 F_{obs})^2]^{1/2}$. The parameters of the isomorphous potassium compound (Noordik *et al.*, 1974) were used as the starting parameters for the refinement procedure. The structure was refined by full-matrix least-squares methods, with anisotropic thermal parameters.

Since no hydrogen atoms could be detected in a final difference map, they were not included in the refinement or in the structure factor calculation. The quantity minimized was $\sum w(|F_o| - K|F_c|)^2$ with $w = 1/\sigma^2(F)$.

The final refinement resulted in a residual, R, of 0·067 for the 963 non-zero observed reflexions.* Final

---

Table 1. *Final atomic parameters* (*with e.s.d.'s in parentheses*)

The estimated standard deviations are those obtained from the least-squares refinement. The expression used for the anisotropic thermal parameters is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

|	X/a	Y/b	Z/c	β_{11}	β_{22}	β_{33}	β_{13}	β_{23}	β_{12}
Rb(1)	0·3000 (2)	−0·25	0·7494 (1)	0·0107 (3)	0·0097 (1)	0·0027 (1)		0·0001 (1)	
Rb(2)	0·3087 (2)	−0·25	0·3956 (1)	0·0135 (3)	0·0028 (1)	0·0026 (1)		−0·0005 (1)	
C(1)	0·521 (1)	−0·203 (1)	0·576 (1)	0·012 (2)	0·007 (1)	0·003 (1)	−0·002 (1)	−0·000 (1)	0·000 (1)
C(2)	0·390 (2)	−0·137 (1)	0·575 (1)	0·020 (3)	0·005 (1)	0·004 (1)	−0·002 (1)	0·001 (1)	−0·002 (1)
C(3)	0·210 (2)	−0·139 (1)	0·574 (1)	0·021 (3)	0·003 (1)	0·003 (1)	0·002 (1)	0·001 (1)	−0·001 (1)
C(4)	0·084 (1)	−0·204 (1)	0·572 (1)	0·010 (2)	0·007 (1)	0·003 (1)	0·001 (1)	0·000 (1)	0·000 (1)
C(5)	0·275 (2)	−0·172 (1)	0·151 (1)	0·021 (3)	0·006 (1)	0·004 (1)	−0·003 (1)	0·002 (1)	0·001 (1)
C(6)	0·190 (2)	−0·094 (1)	0·191 (1)	0·026 (3)	0·006 (1)	0·005 (1)	−0·002 (1)	−0·003 (1)	0·003 (1)
C(7)	0·183 (2)	−0·009 (1)	0·333 (1)	0·031 (4)	0·004 (1)	0·012 (1)	0·003 (1)	0·003 (2)	0·000 (1)
O(1)	0·193 (1)	−0·25	0·189 (1)	0·013 (2)	0·005 (1)	0·004 (1)		0·001 (1)	
O(2)	0·231 (1)	−0·092 (1)	0·290 (1)	0·020 (2)	0·003 (1)	0·007 (1)	0·001 (1)	−0·000 (1)	0·001 (1)
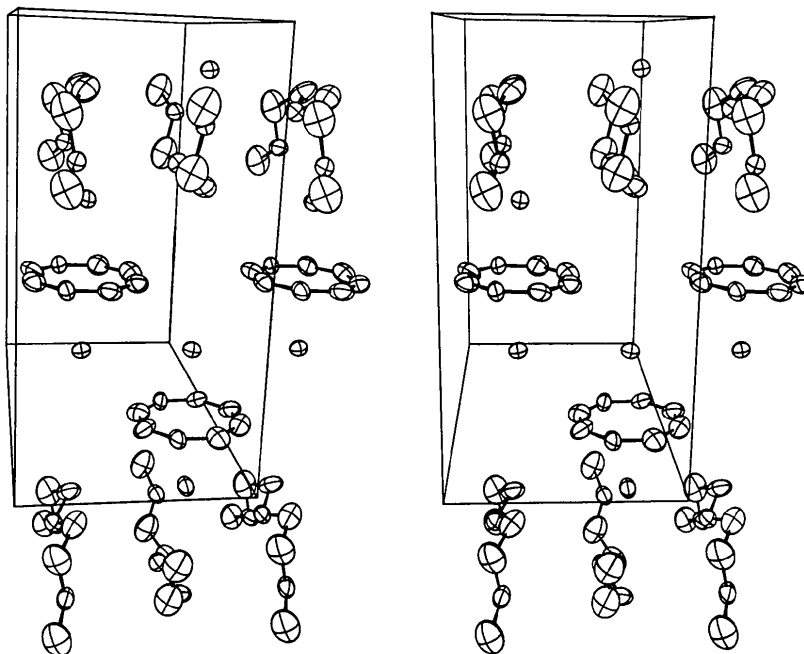
Fig. 1. Stereoscopic view of Rb$_2$COT.diglyme with the projection axis along the b axis. The vertical axis is the c axis and the horizontal the a axis.

atomic parameters are given in Table 1. The atomic scattering factors used were those for Rb$^+$ (corrected for anomalous scattering $\Delta f'$), O and C as given in *International Tables for X-ray Crystallography* (1962).

Discussion. In the sequence of structural studies on alkali-metal aromatic radical ion pairs, the crystal and molecular structure of K$_2$COT.diglyme has been published (Noordik *et al.*, 1974). In that article we mentioned the succesful preparation of Rb$_2$COT.diglyme, the structure of which is described here.

Fig. 2. Projection along **b** of the structure lying between $y=0$ and $\frac{1}{2}$. The upper half of the cell contents are related by the centres of symmetry (small circles) and have been omitted for clarity. There is a mirror plane at $y=\frac{1}{4}$.

The crystal structure of Rb$_2$COT.diglyme is isomorphous with the structure of K$_2$COT.diglyme and therefore no detailed illustrations of the structure are presented here. Instead a stereoscopic view of the unit cell of Rb$_2$COT.diglyme is given (Fig. 1).

In a Rb$_2$COT unit the average Rb–C distance is

Table 2. *Bond lengths* (Å) *and angles* (°)

Oxygen atom O(1) is on the mirror plane and C(7) is the methyl carbon atom. A single prime indicates a screw-axis-related atom ($\frac{1}{2}+x, y, \frac{1}{2}-z$). A double prime indicates a mirror-related atom ($x, \frac{1}{2}-y, z$).
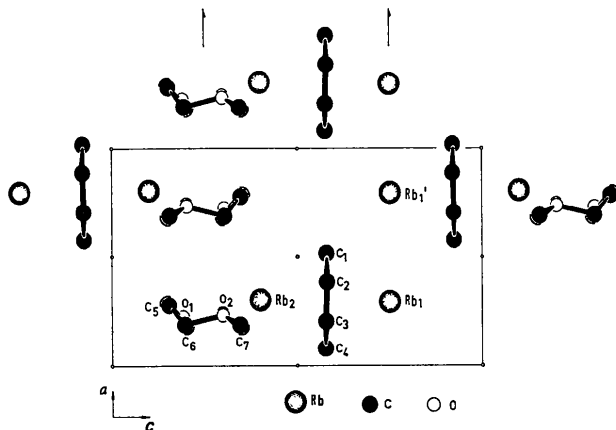
Diglyme		Diglyme	
O(1)–C(5)	1·45 (2)	C(5″)–O(1)–C(5)	109 (1)
C(5)–C(6)	1·47 (2)	O(1)—C(5)–C(6)	109 (1)
C(6)–O(2)	1·45 (2)	C(5)—C(6)–O(2)	107 (1)
O(2)–C(7)	1·44 (2)	C(6)—O(2)–C(7)	113 (1)

Rb(2)–diglyme		Rb(2)–COT	
Rb(2)–O(1)	3·08 (1)	Rb(2)–C(1)	3·14 (1)
Rb(2)–O(2)	2·90 (1)	Rb(2)–C(2)	3·15 (1)
Rb(2)–O(1′)	3·20 (1)	Rb(2)–C(3)	3·15 (1)
		Rb(2)–C(4)	3·14 (1)

COT		COT	
C(1)–C(1″)	1·42 (2)	C(1″)–C(1)–C(2)	135 (1)
C(1)–C(2)	1·43 (2)	C(1)—C(2)–C(3)	134 (1)
C(2)–C(3)	1·39 (2)	C(2)—C(3)–C(4)	136 (1)
C(3)–C(4)	1·38 (2)	C(3)—C(4)–C(4″)	135 (1)
C(4)–C(4″)	1·40 (2)		

Rb(1)–COT		Rb(1)–COT	
Rb(1)–C(1)	3·09 (1)	Rb(1)–C(4)	3·11 (1)
Rb(1)–C(2)	3·10 (1)	Rb(1′)–C(1)	3·37 (1)
Rb(1)–C(3)	3·10 (1)	Rb(1′)–C(4)	3·43 (1)

3·10(1) Å for Rb(1) and 3·15(1) Å for Rb(2). The shortest Rb–C distances of rubidium ion Rb(1) to the COT rings of two other Rb$_2$COT units are 3·37(1) Å and 3·43(1) Å for the distances Rb(1')–C(1) and Rb(1')–C(4) respectively. Bond distances and angles are summarized in Table 2. The numbering system is shown in Fig. 2. The cyclooctatetraene dianion is planar and has an average C–C bond length of 1·40 ± 0·02 Å. A weighted least-squares plane through the C atoms of the COT ring (0·0169X + 0·0Y − 1·0Z + 8·20 Å = 0) has all of the atoms of the ring within 0·01 ± 0·01 Å of the plane.

In the paper on K$_2$COT.diglyme (Noordik et al., 1974), we mentioned that we were unable to create paramagnetic centres in the alkali COT single crystals by ultraviolet irradiation at low temperatures. However, with X-ray irradiation produced by a W-tube at

50 kV paramagnetic centres were created, which were identified as COT monoanions by e.p.r. From the e.p.r. spectra of the K$_2$COT.diglyme single crystal (Mooij, Degens, Klaassen & de Boer, 1974) it could be concluded that the COT molecules rapidly rotate around an axis perpendicular to the aromatic plane. Results of these experiments will be published elsewhere.

References

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
MOOIJ, J. J., DEGENS, H. M. L., KLAASSEN, A. A. K. & DE BOER, E. (1974). International symposium on Organic Free Radicals, Sirmione, Italy.
NOORDIK, J. H., VAN DEN HARK, T. E. M., MOOIJ, J. J. & KLAASSEN, A. A. K. (1974). *Acta Cryst.* B30, 833–835.

Sodium Chlorite Trihydrate

BY ÇELIK TARIMCI AND ELLORY SCHEMPP

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, *U.S.A.*

AND S. C. CHANG

Physics Department, Duquesne University, Pittsburgh, Pennsylvania 15219, *U.S.A.*

Abstract. NaClO$_2$.3H$_2$O, triclinic, $P\bar{1}$, a = 5·492(1), b = 6·412(1), c = 8·832(1) Å, α = 72·06(5), β = 87·73(5), γ = 70·88(5)°, and Z = 2. The bond distances and angles of the ClO$_2^-$ group are Cl–O(1) = 1·564(1), Cl–O(2) = 1·557(1) Å, and O–Cl–O = 108·23(6)°. One of the oxygens belonging to the ClO$_2^-$ ion together with the oxygen atoms of the waters of hydration form a distorted octahedron around the sodium. These octahedra form zigzag columns by sharing edges along the a axis, and the columns are connected by hydrogen bonds. Nuclear quadrupole resonance studies have shown that the largest component of the diagonalized electric field gradient tensor is normal to the ClO$_2^-$ plane.

Introduction. The electronic structure of the chlorite ion, ClO$_2^-$, is of interest for comparison with neutral chlorine dioxide and other oxychloride anions. Although the single nuclear quadrupole resonance (n.q.r.) frequency in NaClO$_2$.xH$_2$O was observed by Ragle (1960), a complete interpretation of n.q.r. data requires knowledge of the orientation of the electric field gradient (e.f.g.) principal axes as well as the quadrupole coupling constant and asymmetry parameter. In order to determine the orientation of the e.f.g. tensor with respect to the chemical bonds

(Tarimci & Schempp, 1975), it was necessary to obtain the crystal structure. NaClO$_2$.3H$_2$O was chosen from among other chlorites because it was relatively easy to grow a large single crystal for the n.q.r. study.

In some early crystallographic studies of sodium and other chlorites, Levi & Scherillo (1930) described the morphology and reported the space group of NaClO$_2$. More recently, Curti, Rigante & Locchi (1960) attempted to solve the structure, but could not give a full description of it. Two other chlorite structures have been studied; ammonium chlorite at −35°C (the compound is unstable at room temperature) by Gillespie, Sparks & Trueblood (1959), and silver chlorite (which is explosive in the dry state) by Cooper & Marsh (1961). The crystal structure of anhydrous NaClO$_2$ has also been determined recently and will be reported later (Tarimci & Schempp, 1975).

Experimental. Sodium chlorite is commercially available as NaClO$_2$.xH$_2$O. Crystals of the trihydrate in the form of needles or thin distorted hexagonal plates are formed from aqueous solution (to which a small amount of NaOH is added to retard decomposition). Crystallization of the trihydrate takes place below the phase transition temperature of 38°C (Cunningham & Oey, 1955); above this temperature, only anhydrous