from one another. The average In—O distance of 2.14 (3) Å is comparable to lengths of 2.18 (5) Å (Marezio, 1966) in In_2O_3, 2.127 (4) and 2.186 (4) Å in $Sr_3In(BO_3)_3$ (Cox, Schaffers & Keszler, 1992) and 2.17 Å calculated with crystal radii for a hexa-coordinated In atom. Each pyroborate layer is formed from one type of group with sheets of $B1B3O_5$ units and $B2B4O_5$ units stacking alternately along $(\bar{1}01)$. B—O bond lengths range from 1.33 (2) to 1.42 (1) Å and compare to 1.342 (7)–1.432 (7) Å for $Sr_2LiScB_4O_{10}$, 1.33–1.38 Å for $Mg_2B_2O_5$ (Takéuchi, 1952) and 1.353 (3)–1.438 (3) Å for $Na_4B_2O_5$ (König, Hoppe & Jansen, 1979). The angles across the bridging O atoms, B1—O7—B3, 137 (1), B2—O8—B4, 131 (1)°, are similar to those in the compound $Sr_2LiScB_4O_{10}$, 133.8 (4) and 129.2 (4)°, respectively. Terminal BO_2 groups for each pyroborate anion are twisted from coplanarity by 10.5° for the $B1B3O_5$ unit and 3.1° for the $B2B4O_5$ unit compared to 13.8 and 1.1° for the corresponding anions in the Sc analog. Similar calculations have been performed on pyroborate anions for a variety of compounds (Thompson, Huang, Smith & Keszler, 1991) and deviations from planarity have been found to range from 0 to 76.8°. The ten crystallographically distinct O atoms in the structure have coordination numbers of three or four. Corresponding environments may be discerned from examination of Table 2.

This work was supported by the US National Science Foundation, Solid State Chemistry Program (DMR-8814432). Acknowledgement is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. DAK thanks the Alfred P. Sloan Foundation for a fellowship, 1989–91, and KIS acknowledges Pacific Northwest Laboratories for a DOE graduate fellowship, 1991–92.

References

Brown, I. D. (1981). *The Bond Valence Method: an Empirical Approach to Chemical Structure and Bonding. Structure and Bonding in Crystals* II, edited by M. O'Keeffe & A. Navrotsky, pp.1–30. New York: Academic Press.

Cox, J. R., Schaffers, K. I. & Keszler, D. A. (1992). In preparation.

König, V. H., Hoppe, R. & Jansen, M. (1979). *Z. Anorg. Allg. Chem.* **449**, 91–101.

Marezio, M. (1966). *Acta Cryst.* **20**, 723–728.

Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package*. Version 5.0. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

Smith, R. W. & Keszler, D. A. (1989). *J. Solid State Chem.* **81**, 305–313.

Takéuchi, Y. (1952). *Acta Cryst.* **5**, 574–581.

Thompson, P. D., Huang, J., Smith, R. W. & Keszler, D. A. (1991). *J. Solid State Chem.* **95**, 126–135.

Thompson, P. D. & Keszler, D. A. (1989). *Solid State Ion.* **32/33**, 521–527.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1993). C**49**, 214–216

Thermal Effects in the Structure of Potassium Perrhenate

By R. Julian C. Brown

Chemistry Department, Queen's University, Kingston, Ontario K7L 3N6, Canada

Brian M. Powell

AECL Research, Chalk River Laboratories, Chalk River, Ontario K0J 1J0, Canada

and Stephen N. Stuart

Division of Materials Science and Technology, CSIRO, Clayton, Victoria 3168, Australia

(*Received* 17 *November* 1991; *accepted* 6 *October* 1992)

Abstract. The structure of $KReO_4$ has been determined by neutron powder diffraction at 298, 150 and 15 K. The structural parameters at room temperature are consistent with the results of Lock & Turner [*Acta Cryst.* (1975), B**31**, 1764–1765] and their temperature dependences are normal. The orientation of the anion changes by 1.20 (13)° over this temperature range.

Table 1. *Cell dimensions*

These data were obtained from the neutron diffraction profiles assuming a neutron wavelength of 1.49978 (9) Å. E.s.d.'s are given in parentheses and are taken from the Rietveld-program output. The space group is $I4_1/a$.

T (K)	a (Å)	c (Å)	c/a	V (Å^3)
15	5.65029 (8)	12.55557 (24)	2.22211 (5)	400.85 (1)
150	5.66115 (11)	12.61100 (32)	2.22764 (7)	404.16 (2)
298	5.68174 (15)	12.71178 (44)	2.23730 (10)	410.36 (3)

0108-2701/93/020214-03$06.00

Table 2. *R factors, fractional atomic position parameters and structural data*

Parameters are given relative to the origin at $\bar{1}$ and have been multiplied by 10^4. E.s.d.'s are given in parentheses. K is at (0,7500,3750), Re is at (0,2500,1250) and values for the O atom are given in the table. The expected R_{wp} value was 3.50%.

T (K)	R_{wp}	x_O	y_O	z_O	β (°)	Re—O (Å)	O—Re—O (°)
15	6.58%	2212 (2)	3727 (2)	461 (1)	29.02 (4)	1.739 (1)	110.54 (8)
150	7.51%	2217 (3)	3712 (3)	470 (1)	28.66 (7)	1.736 (2)	110.97 (9)
298	8.38%	2215 (4)	3669 (4)	474 (2)	27.82 (9)	1.731 (2)	110.54 (16)

Introduction. The structure of $KReO_4$ at room temperature has been reported previously by Morrow (1960) and by Lock & Turner (1975) and the thermal expansion over the temperature range 146 to 371 K has been reported by Brown, Smeltzer & Heyding (1976). However, previous studies gave no information on the temperature dependence of the orientation of the anion relative to the unit cell. This information is required for analysis of the temperature dependence of the Re NQR frequency since the electric-field gradient at the Re site is a sensitive function of the anion orientation (Brown, Shortreed, Szabo, Powell & Stuart, 1992). Powder neutron diffraction was used because of the ease of temperature control over a wide range of temperatures.

Experimental. The sample was commercial $KReO_4$ powder (Strem Chemicals Inc., Newburyport, MA, USA). It showed an NQR line at a frequency of 26.814 MHz at room temperature, consistent with previous measurements (Brown, Smeltzer & Heyding, 1976). The sample was loaded into a thin-walled vanadium can 0.75 cm in diameter and mounted in a variable-temperature closed-cycle cryostat. Measurements were taken on the E3 powder diffractometer with a 30-element detector at the NRU reactor, Chalk River. The monochromator was Si(115) and the diffractometer was calibrated by measuring the profile of a powder sample of silicon whose lattice parameter [a = 5.430940 (35) Å] was calibrated at the National Institute of Standards and Technology. The scattering angles of nine Debye–Scherrer lines observed for this Si standard were fitted to determine the neutron wavelength as 1.49978 (9) Å. Temperatures were measured by silicon diode thermometers and were held constant to 0.04 K. Data were collected between scattering angles of 8.0 and 119.95° at intervals of 0.05° and analyzed using a Rietveld program (Wiles & Young, 1981); scattering lengths were taken from Sears (1986). The background was fitted with a parabolic function and no correction for neutron absorption was applied. The results of the analysis are summarized in Tables 1 to 3.*

Table 3. *Anisotropic thermal parameters*

The anisotropic temperature factors are of the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. The parameters β_{ij} have been multiplied by 10^4 and e.s.d.'s are given in parentheses.

T (K)		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
15	K	20 (5)	20	3 (2)	0	0	0
	Re	24 (3)	24	−5 (1)	0	0	0
	O	42 (4)	46 (3)	4 (1)	2 (3)	5 (1)	0 (1)
150	K	57 (7)	57	5 (3)	0	0	0
	Re	41 (4)	41	5 (1)	0	0	0
	O	77 (5)	98 (5)	12 (1)	−7 (4)	12 (1)	−6 (2)
298	K	105 (13)	105	11 (5)	0	0	0
	Re	81 (6)	81	10 (2)	0	0	0
	O	160 (8)	223 (9)	21 (1)	−56 (7)	20 (2)	8 (3)

Discussion. The lattice parameters are consistent with those of Brown, Smeltzer & Heyding (1976) and the thermal expansion in both the **a** and **c** directions is normal. The Re—O bond length and O—Re—O bond angle do not change appreciably with temperature and are in reasonable agreement with published values: 1.723 (4) Å and 110.8 (2)° in $KReO_4$ (Lock 1975), and 1.737 (5) Å and 110.3 (2)° in NH_4ReO_4 (Kruger & Reynhardt, 1978). The anion orientation relative to the unit-cell axes [angle β defined by Kruger & Reynhardt (1978)] agrees satisfactorily with the results of Lock & Turner (1975) and changes by 1.20 (13)° between 15 and 298 K.

The anisotropic temperature parameters indicate thermal amplitudes at 298 K which are qualitatively consistent with the X-ray values obtained by Lock & Turner (1975) and decrease smoothly at the lower temperatures. The small negative value of β_{33} for Re at 15 K is probably due to neglect of a correction for absorption in the powder sample. It can be shown (Hewat, 1979) that this results in an underestimation of the thermal parameter. For the case of $KReO_4$, with values of the cross sections given by Sears (1986), we calculate the linear absorption coefficient to be approximately $\mu = 0.615\ \mathrm{cm}^{-1}$. This leads to a correction in the overall Debye–Waller factor of $\Delta B = 0.032\ \text{Å}^2$.

This work was supported by the Natural Sciences and Engineering Research Council of Canada.

References

Brown, R. J. C., Shortreed, M. E., Szabo, A. J., Powell, B. M. & Stuart, S. N. (1992). *Z. Naturforsch. Teil A*, **47**, 308–312.

---

* The numbered intensity of each measured point on the profile has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55584 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR0017]

Brown, R. J. C., Smeltzer, J. G. & Heyding, R. D. (1976). *J. Magn. Reson.* **24**, 269–274.
Hewat, A. W. (1979). *Acta Cryst.* **A35**, 248.
Kruger, G. J. & Reynhardt, E. C. (1978). *Acta Cryst.* **B34**, 259–261.
Lock, C. J. L. & Turner, G. (1975). *Acta Cryst.* **B31**, 1764–1765.
Morrow, J. C. (1960). *Acta Cryst.* **13**, 443–445.
Sears, V. F. (1986). *Methods of Experimental Physics*, Vol. 23A, edited by K. Sköld & D. L. Price, pp. 521–550. San Diego: Academic Press.
Wiles, D. B. & Young, R. A. (1981). *J. Appl. Cryst.* **14**, 149–151.

Acta Cryst. (1993). C**49**, 216–219

Structure of Triphenyltin 2-[2-Bromo-4-(dimethylamino)phenylazo]benzoate

By Bankim C. Das and Goutam Biswas
Biophysics Department, Bose Institute, Calcutta-54, India

B. B. Maji
Chemistry Department, Presidency College, Calcutta-73, India

K. L. Ghatak
Chemistry Department, Durgapur Government College, India

S. N. Ganguly
Botany Department, Bose Institute, Calcutta-9, India

Y. Iitaka
Faculty of Pharmaceutical Sciences, Tokyo University, Japan

and Asok Banerjee*
Biophysics Department, Bose Institute, Calcutta-54, India

(*Received* 25 *March* 1991; *accepted* 29 *May* 1992)

Abstract. [2′-Bromo-4′-(dimethylamino)azobenzene-2-carboxylato]triphenyltin, $[\mathrm{Sn}(C_{15}H_{13}BrN_3O_2)(C_6H_5)_3]$, $M_r = 697.2$, triclinic, $P\bar{1}$, $a = 10.044\ (4)$, $b = 19.707\ (6)$, $c = 7.899\ (3)$ Å, $\alpha = 96.1\ (5)$, $\beta = 107.7\ (7)$, $\gamma = 90.3\ (5)^\circ$, $V = 1480$ Å^3, $Z = 2$, $D_x = 1.56$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1.5418$ Å, $\mu = 84$ cm^{-1}, $F(000) = 690$, $T = 288$ K, final $R = 0.049$ for 2257 observed reflections. The structure is stabilized by a network of hydrophobic and π–π interactions between C29···C24 (3.37 Å) and N1···C32 (3.38 Å), respectively. The compound forms a distorted *cis* SnC_3O_2 five-coordinated geometry at Sn owing to the formation of a four-membered chelate with the carboxylate group. The configuration at the Sn atom is a distorted trigonal bipyramid.

Introduction. Organotin carboxylates constitute an interesting class of organometallics with diverse chemical and biological properties. Various substituted organotin carboxylates are known to exhibit significant biological activities (Maji, Ghatak, Ganguly & Ray, 1989; Blunden, Cusack & Hill, 1985; Evans & Hill, 1983; Srivastava, Srivastava & Bhatia, 1977; Evans & Smith, 1975; Polster & Halacka, 1972; Kochkin, Verenikina & Chekmareva, 1961; Kochkin & Verenikina, 1961; Kochkin & Golysheva, 1961; Koopmans, 1961).

The title compound (Maji, Ghatak, Ganguly & Ray, 1989) is an organotin ester. Characterization of this compound was made on the basis of IR and UV spectral data and elemental analysis. The IR spectral data revealed the presence of a carboxylate carbonyl (C=O) group and an Sn—O bond in the organotin ester, and the UV spectrum in non-nucleophilic solvent showed a large bathochromic shift owing to a $\pi\rightarrow\pi^*$ transition in the azo chromophore of the molecule (Majee & Banerjee, 1977) indicating N→Sn coordination.

---

* To whom correspondence should be addressed.

0108-2701/93/020216-04$06.00