Acta Cryst. (1981). B**37**, 938–939

Sodium Oxalate Structure Refinement

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(*Received* 12 *September* 1980; *accepted* 10 *November* 1980)

Abstract. $Na_2C_2O_4$, monoclinic, $P2_1/c$, $a = 3{\cdot}449\ (2)$, $b = 5{\cdot}243\ (3)$, $c = 10{\cdot}375\ (4)$ Å, $\beta = 92{\cdot}66\ (4)°$, $Z = 2$, $U = 187{\cdot}4$ Å^3, $D_x = 4{\cdot}75$ Mg m^{-3}. A low-temperature (140 K) structure refinement was performed to a final R of 0·030 for 270 reflections. The molecular structure is compared to an earlier study by Jeffrey & Parry [*J. Am. Chem. Soc.* (1954), **76**, 5283–5286].

Introduction. As part of a study of the electronic, vibrational, and magnetic-resonance spectra of various ionic oxalates, it was necessary to obtain well refined atomic positional parameters for sodium oxalate. An early structural determination by Jeffrey & Parry (1954), which used visual estimation of room-temperature photographic data, is largely confirmed although some significant differences are found.

Sodium oxalate crystals were obtained from aqueous solution by slow evaporation. The crystals grew predominantly as prisms elongated along the a axis and having well developed (011), $(01\bar{1})$, $(0\bar{1}1)$ and $(0\bar{1}\bar{1})$ faces, and poorly developed (100) basal faces. This habit repeatedly yielded doubled diffraction spots on oscillation photographs and split-peaks with background imbalances during an ω scan. A much rarer crystal habit with well developed (010) faces was also obtained. These latter crystals exhibited sharp diffraction maxima with no background imbalances during an ω scan. Cleavage of the predominant habit along (010), the only apparent cleavage plane, also eliminated the doubled diffraction spots, implying that fracturing along (010) occurred due to the low temperature of this study (140 K, as determined by thermoelectric measurement). The crystal chosen for data collection was an elongated trapezoidal prism with well developed (010), (011) and (011) faces having dimensions 0·13 × 0·23 × 0·24 mm.

Data were collected at 140 K on a Syntex $P2_1$ diffractometer using Mo $K\alpha$ radiation and a graphite monochromator. The orientation matrix and unit-cell dimensions were obtained from a least-squares fit of 24 well centered reflections having $30° < 2\theta < 40°$. The intensity data were collected using a variable-speed ω scan (2–60° min^{-1}) of a 1·0° range in ω and a 1·0° offset for stationary background counts. A total of 287 reflections with $2\theta < 45°$ were measured. Two independent check reflections, monitored at intervals throughout the data-collection period, showed a random fluctuation of <1%. The usual Lorentz and polarization corrections, but no absorption corrections, were applied. The form-factor tables of Cromer & Waber (1974) were used with corrections applied for the anomalous dispersion of the Na^+ ion. Of the original 287 reflections, only 270 with $I > 3\sigma(I)$ were used in the full-matrix least-squares refinement, which converged to $R = 0{\cdot}030$ starting from initial values for the positional parameters taken from Jeffrey & Parry (1954). The final atomic fractional coordinates and anisotropic thermal parameters are given in Table 1.*

The atomic labels, bond lengths, and angles are given in the view normal to the plane of the oxalate anion shown in Fig. 1. Thermal ellipsoids are drawn at the 50% probability level.

Discussion. The general structure is as found in the earlier study (Jeffrey & Parry, 1954), although following current convention the a and c axes have been

Table 1. *Fractional atomic coordinates, thermal parameters, and standard deviations* (*in parentheses*)

Anisotropic thermal parameters are in the form: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Na	0·3020 (3)	0·0565 (2)	0·3552 (1)	1·15 (8)	0·61 (8)	0·51 (8)	0·19 (3)	−0·07 (5)	−0·10 (3)
O(1)	0·1657 (5)	−0·1222 (4)	0·1511 (1)	1·31 (9)	0·86 (9)	0·54 (11)	−0·05 (7)	−0·04 (7)	0·16 (5)
O(2)	0·2274 (6)	0·2704 (3)	0·0691 (2)	1·44 (9)	0·59 (9)	0·74 (9)	−0·13 (7)	−0·04 (7)	−0·06 (4)
C	0·1135 (8)	0·0435 (4)	0·0634 (3)	0·63 (13)	0·69 (14)	0·95 (11)	0·16 (8)	0·50 (10)	−0·04 (7)

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* A list of structure factors, and Tables 2 and 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35807 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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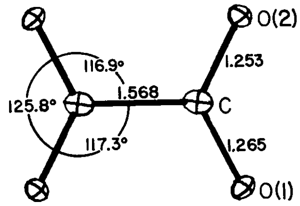

Fig. 1. Bond distances (Å) and angles (°) in the oxalate fragment. The standard deviations are 0·2° for all angles, 0·003 Å for both C—O bonds, and 0·004 Å for the C—C bond. Thermal ellipsoids are scaled to enclose 50% probability.

interchanged. The oxalate ion is planar within the experimental limits. The equation of the least-squares plane through the six atoms is given by: $-x + 0{\cdot}4649y + 1{\cdot}4720z = 0{\cdot}0000$. Displacements of the individual atoms from this plane are (in Å): C, 0·0005; O(1), −0·0001; O(2), −0·0001; with a standard deviation of 0·0004 Å.

The dimensions of the oxalate moiety are in excellent agreement with those proposed by Hahn (1957) for a completely ionized structure. The abnormally long C—C bond length found for $Na_2C_2O_4$ parallels a similar result in other oxalates (Beagley & Small, 1964; Hodgson & Ibers, 1969; Robertson, 1965), binoxalates (Küppers, 1973), and oxalic acids (Delaplane & Ibers, 1969). The 1·568 Å bond length found in the present work agrees with the average for other ionic oxalates and is longer than the average for binoxalates or oxalic acid (Küppers, 1973). A theoretical explanation by Brown & Harcourt (1963) based on delocalization of the oxygen non-bonding electrons into the C—C bond seems to account for the observations (Küppers, 1973).

The O atoms form a distorted octahedron around the Na^+ ion. The Na···O distances are listed in Table 2.* Comparison of these distances indicates that O(1) is slightly closer to the Na^+ ions than O(2), in contrast to the results of Jeffrey & Parry (1954). Also, the difference in length to the nearest Na^+ ion from O(1) and O(2) is smaller. The minor differences in the bond lengths and angles between C—O bonds probably reflect the small difference in the electrostatic perturbation of the surrounding Na^+ ions.

The principal axes of the thermal ellipsoids and orthonormal reference vectors are listed in Table 3.* Calculations of bond lengths and bond angles using isotropic thermal parameters for all atoms showed no differences outside of the standard deviations from those using anisotropic thermal parameters. No corrections to the bond lengths and angles for thermal motion were applied.

One of the authors (DAR) thanks Professor D. S. Tinti for suggesting this work and for his aid in the preparation of the manuscript. This research was supported by the National Science Foundation under Grant CHE-77-11839.

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* See deposition footnote.

* See deposition footnote.

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Acta Cryst. (1981). B**37**, 939–942

Nitrosyltris(triphenylphosphine)iridium Cyclopropane Solvate

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(*Received* 31 *October* 1980; *accepted* 29 *December* 1980)

Abstract. $[Ir(NO)(PPh_3)_3].C_3H_6$, hexagonal, $P6_3$, $a = 12{\cdot}625\ (5)$, $c = 17{\cdot}382\ (5)$ Å, $D_m = 1{\cdot}49\ (5)$, $D_c = 1{\cdot}45$ Mg m^{-3} for $Z = 2$; $R = 0{\cdot}036$, $R_w = 0{\cdot}028$ for 2797 observed reflexions. $[Ir(NO)(PPh_3)_3]$ molecules with C_3 symmetry pack along the threefold axes, surrounding channels of cyclopropane molecules which

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