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Remeasurement of Optically Active $NaClO_3$ and $NaBrO_3$

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Abstract. $NaClO_3$, $NaBrO_3$, both cubic, space group $P2_13$, a = 6·57584 (5) and 6·70717 (10) Å respectively, corrected to 298·2 K, for $\lambda(\mathrm{Cu}\ K\alpha_1) = 1{\cdot}540598$ Å; Z = 4, D_m = 2·49 (1), D_x = 2·486 g cm^{-3} for $NaClO_3$ and D_m = 3·34 (2), D_x = 3·321 g cm^{-3} for $NaBrO_3$. The study crystals, grown from aqueous solution by K. Nassau with 99·9% pure starting material, are shown by anomalous scattering measurements to possess the same chirality. Least-squares refinement resulted in R = 0·013 for 671 ($NaClO_3$), and R = 0·034 for 489 ($NaBrO_3$) structure factors. The Cl and Br atoms occupy distorted octahedra. Three Cl–O bonds are 1·485 (1) Å, and three others are 3·086 (1) Å. The corresponding Br–O bond lengths are 1·648 (4) and 2·974 (4) Å.

Introduction. The crystal structure of $NaClO_3$ was first determined by Zachariasen (1929) and was subsequently redetermined by Ramachandran & Chandrasekaran (1957), Aravindakshan (1959), Bower, Sparks & Trueblood (1959) and Zachariasen (1965). The crystal structure of $NaBrO_3$ was first determined by Dickinson & Goodhue (1921) and Kolkmeijer, Bijvoet & Karssen (1923) and was subsequently redetermined by Hamilton (1938) and Beurskens-Kerssen, Kroon, Endeman, Van Laar & Bijvoet (1963). Crystals of the two materials are isomorphous, in the enantiomorphous point group 23. The present interest in a complete remeasurement of the two crystal structures lies in redetermining the relationship between the chirality and the optical activity of each crystal (*cf.* Beurskens-Kerssen *et al.*, 1963; Chandrasekaran & Mohanlal, 1976). The earlier sets of atomic coordinates are collected in Table 1.

The lattice constants of $NaClO_3$ and $NaBrO_3$ were measured at 295 K, and corrected to 298·2 K, on a modified (Barns, 1967) version of Bond's (1960) precision lattice constant diffractometer, based on $\lambda(\mathrm{Cu}\ K\alpha_1) = 1{\cdot}540598$ Å. A single crystal of $NaClO_3$, ground to a sphere with diameter 0·299 (8) mm, μR = 0·190, was mounted in random orientation on a Pyrex capillary. The intensities of all reflections in a sphere with reciprocal lattice radius $(\sin\theta)/\lambda = 0{\cdot}99$ Å^{-1} and with $-12 \leq h, k, l \leq +12$ were measured on a CAD-4 diffractometer controlled by a PDP 8e computer with standard Enraf–Nonius programs. The radiation used was Nb-filtered Mo $K\alpha$. The Laue symmetry is $m3$ and the only systematic absences are $h00$ for $h = 2n + 1$, and cyclic interchange: the space group of this optically active crystal is hence $P2_13$.

7533 reflections were measured, including some duplicates and a group of four standards that followed

Table 1. *Atomic coordinates reported in the literature for* $NaClO_3$ *and for* $NaBrO_3$

x (Na)	x (Cl)	x (Br)	x (O)	y (O)	z (O)	Reference
0·064	0·417	–	0·303	0·592	0·500	Zachariasen (1929)
0·066 (1)	0·418 (1)	–	0·307 (2)	0·594 (2)	0·508 (2)	Aravindakshan (1959)
0·066 (3)	0·417 (2)	–	0·305 (2)	0·592 (2)	0·494 (2)	Bower *et al.* (1959)
0·0685 (5)	0·4186 (3)	–	0·3033 (7)	0·5938 (8)	0·5065 (9)	Zachariasen (1965)
0·09	–	0·41	0·30	0·60	0·47	Dickinson & Goodhue (1921)
0·083	–	0·417	0·306	0·50	0·417	Kolkmeijer *et al.* (1923)
0·075 (3)	–	0·405 (2)	0·258 (6)	0·614 (6)	0·480 (6)	Hamilton (1938)
0·077	–	0·4063	0·287	0·597	0·508	Beurskens-Kerssen *et al.* (1963)

every 100th reflection. No significant trends in the magnitudes of the standards were detectable, in contrast to the radiation damage observed by Zachariasen (1965) using Cu *Kα* radiation. Corrections were made for Lorentz, polarization and absorption effects, resulting in a set of F_{meas} on a relative scale. Symmetry-equivalent reflections were averaged, with reflections of type $F(hkl)$ separated from those of type $F(\bar{h}\bar{k}\bar{l})$, to give 671 independent F_{meas} and σF_{meas} [see Abrahams, Bernstein & Keve (1971) for the derivation of σF_{meas}].

For isomorphous $NaBrO_3$, a sphere of diameter 0·233 (4) mm, $\mu R = 1{\cdot}563$, was ground and similarly mounted. No trends with radiation exposure were found among the $NaBrO_3$ standard reflections. 3431 reflections were measured in a hemisphere of reciprocal space which, following correction and averaging, gave 489 independent F_{meas} and σF_{meas}, including $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$.

The most recent atomic coordinates for each compound given in Table 1 were used as the starting coordinates in least-squares refinement with the new data. Atomic scattering factors and anomalous dispersion corrections for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). Refinement was terminated when the largest shift in any variable was less than one-tenth the corresponding standard deviation. The thermal vibrations in both crystals can be shown, from the indicators in Table 2, to be anisotropic. A clear choice can also be made between the xyz coordinates and alternative $\bar{x}\bar{y}\bar{z}$ coordinates for the right-handed axes and Miller indices assigned, with $wR(\bar{x}\bar{y}\bar{z})/wR(xyz) = 1{\cdot}245$ for $NaClO_3$ and 1·300 for $NaBrO_3$. The corresponding Hamilton (1965) ratios, at the half-percent confidence levels, are $\mathcal{R}_{1,654,0\cdot005} = 1{\cdot}006$ and $\mathcal{R}_{1,473,0\cdot005} = 1{\cdot}009$: both study crystals hence have chirality corresponding to configuration *A* of Ramachandran & Chandrasekaran (1957). The final atomic coordinates and thermal coefficients are given in Table 3.

The extinction coefficient for $NaClO_3$, determined only for the anisotropic-vibration model, produces a maximum structure factor change of 2·5%, in $F(\bar{1}\bar{3}\bar{2})$, and less than 1% in the magnitude of wR. There is no evidence for extinction in the $NaBrO_3$ data.

The values of S in Table 2 show that σF_{meas} has been overestimated by a factor of about 2·3 for $NaClO_3$ and by about 7% for $NaBrO_3$. The quality of fit between measured and calculated structure factors* is indicated best by the normal probability plot of the ordered residuals $\delta R = (F_{\text{meas}} - F_{\text{calc}})/(\sigma F_{\text{meas}})$ *versus* the expected normal quantiles (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972). The δR plot for 95% of

Table 2. *Structural refinement indicators for* $NaClO_3$ *and* $NaBrO_3$

Definitions are given in Abrahams, Bernstein & Keve (1971).

Parameters varied	Number of variables*	$NaClO_3$			$NaBrO_3$		
		R	wR	S	R	wR	S
xyz, B, scale factor	9	0·0418	0·0682	1·390	0·0363	0·0708	1·120
$\bar{x}\bar{y}\bar{z}$, B, scale factor	9	0·0427	0·0699	1·426	0·0486	0·0842	1·332
xyz,β_{ij}, scale factor, extinction coefficient†	17	0·0130	0·0211	0·433	0·0340	0·0583	0·930
$\bar{x}\bar{y}\bar{z}$,β_{ij}, scale factor, extinction coefficient†	17	0·0160	0·0264	0·542	0·0474	0·0758	1·209

* See text for number of independent F_{meas} in each crystal.

† For $NaClO_3$: no extinction correction was necessary in $NaBrO_3$ and hence only 16 parameters were varied for this crystal; see text.

Table 3. *Atomic coordinates and anisotropic thermal coefficients for* $NaClO_3$ *and* $NaBrO_3$ *at* 298 K

The anisotropic thermal coefficients are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	0·06869 (13)	0·06869	0·06869	0·01042 (10)	0·01042	0·01042	−0·00172 (22)	−0·00172	−0·00172
Cl	0·41822 (5)	0·41822	0·41822	0·00679 (3)	0·00679	0·00679	−0·00088 (8)	−0·00088	−0·00088
O	0·30347 (8)	0·59239 (8)	0·50468 (8)	0·01143 (8)	0·00926 (7)	0·01477 (9)	0·00399 (13)	0·00287 (13)	−0·00522 (14)
Na	0·0775 (11)	0·0775	0·0775	0·0111 (9)	0·0111	0·0111	−0·0014 (22)	−0·0014	−0·0014
Br	0·4067 (2)	0·4067	0·0467	0·0063 (1)	0·0063	0·0063	0·0001 (3)	0·0001	0·0001
O	0·2882 (7)	0·5964 (7)	0·5085 (6)	0·0104 (6)	0·0106 (6)	0·0121 (6)	0·0092 (10)	−0·0031 (11)	−0·0123 (9)

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* A list of structure factors for both crystals has been deposited with the British Library Lending Division as Supplementary Publication SUP 32864 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Dimensions of the chlorate and bromate XO_3^- ions* (X = Cl, Br)

Compound	X–O (Å)	∠O–X–O (°)	X–O′ (Å)*	∠O′–X–O′ (°)	Reference
$NaClO_3$	1·485 (1)	106·9 (2)	3·086 (1)	63·4 (2)	Present work
$Ba(ClO_3)_2.H_2O$	1·485 (5)	106·3 (7)	3·145	102·6	Sikka, Momin, Rajagopal & Chidambaram (1968)
$RbClO_3$	1·478 (5)	105·6 (3)	3·049	75·3	Brunton (1973)
$TlClO_3.4(SCN_2H_4)$	1·45 (2)	107 (1)	†	†	Mitchell & Boeyens (1970)
$NaBrO_3$	1·648 (4)	104·1 (5)	2·974 (4)	66·0 (5)	Present work
NH_4BrO_3	1·64	105·5	2·91	76·4	Santoro & Siegel (1960)
$Hg(OH)BrO_3$	1·61 (5)	103 (3)	3·14	71	Björnlund (1971)

* O′ is at a greater distance from X than O; distances and angles given without errors are calculated from the published coordinates.

† Next nearest atoms are two N at 3·57 Å and one S at 3·74 Å.

the $NaClO_3$ terms is essentially linear, with slope of 0·331 and zero intercept: the plot for 85% of the $NaBrO_3$ terms is also linear, with slope of 0·61 and zero intercept. Apart from scaling errors in σF_{meas}, especially for small-magnitude structure factors, the bulk of the δR residuals are hence relatively free from systematic error.

Discussion. The results of measuring the rotation of the plane of polarization of 6328 Å laser light passing through crystals of $NaClO_3$ and $NaBrO_3$ will be presented in detail elsewhere. It was found that crystals of the two materials possessing identical chirality have opposite senses of optical rotation, confirming the results of Beurskens-Kerssen *et al.* (1963).

The geometry of the iodate ion has been studied much more intensively than has that of the chlorate or bromate ions. In the iodate ion, the halogen has three nearest-neighbor oxygen atoms at an average distance of about 1·809 Å and three or more others at distances ranging from about 2·65 to about 3·2 Å (*cf.* Liminga, Abrahams & Bernstein, 1977). The resulting distorted polyhedra are generally ascribed to the influence of the halogen-atom lone electron pair. Very similar atomic arrangements are found in $NaClO_3$ and $NaBrO_3$. In the chlorate, the three (identical) short halogen–oxygen distances are 1·485 (1) Å and the three long distances are 3·086 (1) Å. In the bromate, the corresponding distances are 1·648 (4) and 2·974 (4) Å. The Na atoms in both crystals occupy distorted octahedra, with two independent Na–O distances: 2·419 (1) and 2·499 (1) Å in $NaClO_3$ and 2·410 (4) and 2·522 (4) Å in $NaBrO_3$.

Dimensions reported for the chlorate and bromate ions are given in Table 4. It is noted that the difference between iodate and bromate short halogen–oxygen bond lengths (0·161 Å) is identical with that between bromate and chlorate (0·163 Å), within experimental error.

It is a pleasure to thank K. Nassau for growing the crystals used in this study.

Note added in proof:—A new redetermination of $NaClO_3$, by Burke-Laing & Trueblood [*Acta Cryst.* (1977), B**33**, 2698–2699], appeared after proofs of the present paper were corrected. A normal probability plot of the ordered statistic δp (difference between corresponding atomic parameter/pooled standard deviation) against the expected normal distribution departs only slightly from linearity, with slope of unity and zero intercept. The two new sets of atomic parameters and standard deviations are hence derived from the same statistical population, neither being biased by different systematic error.

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Bis(*N*,*N*-diethyldithiocarbamato)gold(III) 3,3′-Bis(1,2-dicarbollyl)aurate, $[3,3'\text{-}Au(1,2\text{-}C_2B_9H_{11})_2]^-[(Et_2NCS_2)_2Au]^+$

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Abstract. $C_4H_{22}AuB_{18}^-.C_{10}H_{20}AuN_2S_4^+$; monoclinic, $P2_1/c$; a = 8·3786 (9), b = 20·6068 (22), c = 10·0656 (11) Å, β = 105·346 (8)°, Z = 2, D_m = 1·89 (1), D_x = 1·891 (2) g cm^{-3}, μ(Mo $K\alpha$) = 89·7 cm^{-1}. R was refined to 0·022 on 1486 observed reflections. While the distances of the metal ion from the C_2B_3 facial cage atoms conform to the conventional 'slipped sandwich' description, the novel distortions of the cage itself are shown to be of importance in the description of both this and related structures.

Introduction. Single-crystal X-ray studies of the electron-rich bis(dicarbollyl) complexes containing $[3,3'\text{-}Cu(1,2\text{-}C_2B_9H_{11})_2]^{n-}$ [Cu^{II} (d^9), n = 2; Cu^{III} (d^8), n = 1] have revealed the 'slipped sandwich' structure, the Au^{III} derivative having been shown to be isomorphous with that of Cu^{III} (Wing, 1967, 1968). The structure determination of $[(C_6H_5)_3PCH_3]^+[3,3'\text{-}Cu(1,2\text{-}C_2B_9H_{11})_2]^-$ (R = 0·125 for 1559 independent reflections estimated from Weissenberg films) by Wing (1968) did not allow the bis(dicarbollyl)Cu^{III} anion to be recognized as being significantly different from the Cu^{II} analogue [R = 0·091, 2039 observed reflections, film data (Wing, 1967)], while the cage H atoms were placed in calculated positions, radially directed with B–H = 1·2 Å and C–H = 1·1 Å.

In view of the necessity to acquire accurate descriptions of both the distortions in the open C_2B_3 face and the H positions, to facilitate, for example, MO calculations as reported recently for related systems (Mingos, 1977), we have undertaken the single-crystal structure analysis of the Au^{III} complex $[3,3'\text{-}Au(1,2\text{-}C_2B_9H_{11})_2]^-[(Et_2NCS_2)_2Au]^+$. The synthesis, crystal data and some average bond lengths and angles for the C_2B_3 face and the metal–cage interactions have been given by Colquhoun, Greenhough & Wallbridge (1976).

Crystals suitable for examination were obtained by recrystallization from THF/diethyl ether. The Laue symmetry $2/m$, the systematic absences $h0l$, $l = 2n$; $0k0$, $k = 2n$ and an initial unit cell were obtained from a series of precession photographs. Accurate lattice parameters were calculated by least-squares calculations from the 2θ values of 26 reflections (2θ = 28–35°) measured at 20°C on a Syntex $P2_1$ computer-controlled diffractometer using Mo $K\alpha$ radiation (λ = 0·70926 Å). Intensities were measured on a crystal of approximate axial dimensions 0·18 × 0·12 × 0·22 mm using the θ–2θ scan technique out to 2θ = 51°. 1621 observations included 1486 independent intensities with $I > 3\sigma(I)$ (variances based on counting statistics) which were classified as observed. Three standard reflections measured periodically during the data collection showed no significant change in intensity. Lorentz and polarization corrections were carried out. Morphological examination of the crystal revealed the bounding planes to be {100} and {111}, accurate measurements of the interplanar distances being used in a local version of *ABSCOR* (Alcock, 1970) where the analytical absorption correction gave maximum and minimum transmission factors for the correction of $|F_o|$ of 0·786 (10,0,0) and 0·718 (020).

A very marked tendency for reflections with h, k and l all odd or even to be of high intensity led to the two independent Au atoms being placed on centres of symmetry at 0,0,0 and $\frac{1}{2}$,0,$\frac{1}{2}$. Chemically satisfactory positions for the S atoms were found from a Fourier synthesis phased on the Au atoms. The expected

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