Characterization of Sodium Bromite by X-ray Crystallography and Bromine K-Edge EXAFS, IR, Raman, and NMR Spectroscopies

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Abstract: The X-ray crystal structure of sodium bromite trihydrate ($NaBrO_2{\cdot}3H_2O$) has been determined. Crystals are triclinic with space group $P\bar{1}$, $a = 5.421$ (3) Å, $b = 6.438$ (1) Å, $c = 8.999$ (1) Å, $\alpha = 72.76$ (1)°, $\beta = 87.87$ (2)°, $\gamma = 70.70$ (2)°, and $Z = 2$. Data were refined to $R = 0.0199$ (1045 reflections). The anion shows Br–O = 1.702 (2), 1.731 (2) Å and O–Br–O = 105.3 (1)°. Bromine K-edge EXAFS data are presented for $NaBrO_2{\cdot}3H_2O$ and for aqueous solutions of BrO_2^- ions, and the results are compared with the X-ray crystallographic data. Vibrational and ^{17}O NMR data for the bromite ion are also reported.

The oxoanions of bromine BrO_x^- (x = 1–4) have a long and checkered history.[1,2] Bromates (BrO_3^-) were obtained by Ballard[3] in 1826 and are familiar laboratory reagents. Solutions of hypobromous acid (HOBr) and hypobromites (BrO^-) were prepared in Ballard's early studies,[4] but isolation of the solid alkali-metal salts in a reasonably pure state is very difficult and was not achieved until 1952.[5] Perbromate (BrO_4^-) was for many years the classic "nonexistent" compound until Appelman's successful synthesis from BrO_3^- and XeF_2 or F_2.[6] The final member of the series, bromite (BrO_2^-) has been reported from time to time and its existence subsequently doubted by other workers who failed to repeat the preparations.[1,7] Solutions of "sodium bromite" have been used for many years in the textile industry,[8] and bromous acid is a postulated intermediate in the Belousov–Zhabotinskii oscillating reaction.[9] Physical data on the bromite ion are sparse and mostly contradictory, and recent editions of standard texts[2,10] are noncommittal about its existence. Very recently, sodium bromite trihydrate has become commercially available and has been introduced as a mild specific oxidant in organic chemistry, e.g., in the conversion of α,ω-diols to lactones,[11] the Hofmann degradation of amides to amines,[12] and the conversion of olefins to α-bromo ketones.[13]

As part of our studies on the oxides and oxoanions of bromine, we have determined the structure of sodium bromite both in solid and solution phases. We report a single-crystal X-ray determination of $NaBrO_2{\cdot}3H_2O$, the bromine K-edge EXAFS (extended X-ray absorption fine structure) for this material, and EXAFS, IR, Raman, and ^{17}O NMR data for aqueous solutions of bromite ions.

Table I. Crystal Data for $NaBrO_2{\cdot}3H_2O$

formula	BrH_6NaO_5
fw	188.94
unit cell	triclinic
space group	$P\bar{1}$ (no. 2)
a, b, c, Å	5.421 (3), 6.438 (1), 8.999 (1)
α, β, γ, deg	72.76 (1), 87.87 (2), 70.70 (2)
V, Å^3	282.5
Z	2
$F(000)$	184
D(calcd), g cm^{-3}	2.221
D(obsvd), g cm^{-3}	2.22 (2) (flotn)
cryst size, mm	0.4 × 0.1 × 0.1
μ(Mo Kα), cm^{-1}	71.16
θ range, deg	1.0 (min), 26.0 (max)
hkl range	$0 \le h \le 6$, $-7 \le k \le 7$, $-11 \le l \le 11$
reflctns measd	1227
unique reflctns	1102 (R_{int} = 0.006)
obsvd reflctns ($F > 2\sigma(F)$)	1045
no. of refined params	83
R	0.0199
R_w	0.0261
GOF	1.18

Table II. Atomic Coordinates and Isotropic Temperature Factors (×10^3)

atom	x	y	z	U, Å^2
Br	0.11172 (5)	0.16719 (4)	0.12742 (3)	36.0 (2)[a]
Na	0.2671 (2)	0.4546 (1)	0.3975 (1)	27.6 (7)[a]
O(1)	0.1594 (3)	0.1830 (3)	0.3090 (2)	36 (2)[a]
O(2)	−0.2035 (3)	0.1600 (3)	0.1178 (2)	38 (1)[a]
O(3)	0.4848 (3)	0.5775 (3)	0.1687 (2)	33 (1)[a]
O(4)	0.7090 (3)	0.2528 (3)	0.4904 (2)	30 (1)[a]
O(5)	0.1773 (3)	0.2859 (3)	0.6752 (2)	34 (1)[a]
H(1)	0.4050 (69)	0.6543 (59)	0.0877 (41)	61 (4)[b]
H(2)	0.5674 (67)	0.4474 (62)	0.1528 (38)	61 (4)[b]
H(3)	0.7450 (62)	0.1121 (61)	0.5643 (38)	61 (4)[b]
H(4)	0.8424 (67)	0.2218 (55)	0.4227 (39)	61 (4)[b]
H(5)	0.2773 (72)	0.2923 (61)	0.7267 (41)	61 (4)[b]
H(6)	0.1717 (64)	0.1423 (62)	0.7273 (40)	61 (4)[b]

[a] Equivalent isotropic temperature factor from anisotropic atom: U_{eq} = 1/3[trace of orthogonalized U]. [b] Hydrogen atoms were given a common refined temperature factor.

Experimental Section

Spectroscopic Studies. ^{17}O NMR spectra were obtained in H_2O/D_2O (ca. 5:1 v/v) with a Bruker AM360 operating at 48.8 MHz and were referenced to external water (δ = 0); chemical shifts are reported using the high-frequency positive convention. IR spectra were obtained in nujol mulls with a Perkin-Elmer PE 983G, and Raman spectra were recorded for both solid samples and aqueous solutions with a SPEX 1401D and

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Table III. Selected Bond Lengths (Å) and Angles (deg)[a]

Br–O(1)	1.702 (2)	Br–O(2)	1.731 (2)
Na–O(1)	2.359 (2)	Na–O(5)	2.512 (2)
Na–O(3)	2.393 (2)	Na–O(4a)	2.425 (2)
Na–O(4)	2.361 (2)	Na–O(5b)	2.415 (2)
O–H	0.75 (4) min; 0.94 (4) max; 0.86 (7) mean		
O(1)–Br–O(2)	105.3 (1)	H(1)–O(3)–H(2)	104 (3)
H(3)–O(4)–H(4)	102 (3)	H(5)–O(5)–H(6)	100 (3)
O–Na–O (idealized 90)	79.4 (1) min; 101.8 (1) max		

[a] Symmetry codes: $a = 1-x, 1-y, 1-z$; $b = -x, 1-y, 1-z$.

an argon ion laser (excitation at 514.5 nm).

X-ray Structure of $NaBrO_2 \cdot 3H_2O$. Suitable crystals were present in the commercial sample. Many attempts to mount crystals in glass capillaries for X-ray examination proved unsuccessful due to rapid decomposition, and the method that proved most successful was to use an epoxy resin adhesive to mount the crystal on a glass fiber. Preliminary photographic examination established the crystal system and approximate cell dimensions. With an Enraf-Nonius CAD4 diffractometer and Mo Kα radiation monochromated with graphite (λ = 0.71069 Å), accurate cell dimensions were obtained from 25 reflections recorded from a room-temperature crystal. Table I summarizes the crystal data and refinement details. A standard reflection showed decay of 14.6% during the course of the experiment, and this was allowed for in the data reduction process along with Lorentz and polarization corrections. An empirical ψ-scan absorption correction (transmission: minimum 85.0%; maximum 99.9%) was applied. A Patterson synthesis was used to locate the Br atom and subsequent structure factor, and electron density syntheses located the remaining non-hydrogen atoms. At a later stage of refinement (R = 0.028), the difference electron density synthesis showed clear evidence for six H atoms (0.69–0.58 e Å^{-3}), and these were introduced into the model with a common refined temperature factor. Full-matrix least-squares refinement converged to $R = 0.0199$ {R_w = 0.0261; anisotropic (Br, Na, O) and isotropic (H) atoms; $w = 1/[\sigma^2(F) + 0.0003F^2]$; maximum shift/error = 0.2; residual electron density, 0.29 to −0.57 e Å^{-3}}. Atomic scattering factors for neutral atoms and anomalous dispersion corrections were taken from SHELX-76[14] (Br, O, H) and ref 15 (Na). All calculations were carried out on an IBM3090 computer using the programs SHELX-76[14] and ORTEP.[16] The atomic coordinates and thermal parameters are given in Table II, and selected bond distances and angles are listed in Table III.

Extended X-ray Absorption Fine-Structure Studies. EXAFS data at the bromine K edge were recorded in transmission mode with a double-crystal silicon 220 monochromator on beam line 9 at the Daresbury synchrotron radiation source. The operating energy was 2.0 GeV with an average current of 180 mA. The solid samples were diluted with boron nitride (ca. 10% by mass of bromine) and were run between "Sellotape" strips using 1-mm aluminum spacers. Solution spectra were recorded from saturated aqueous solutions in a PTFE cell (path length 3 mm) with Mylar windows. The data treatment utilized the programs PAXAS and EXCURVE.[17,18] The transferability of phase shifts was confirmed by comparison of data for model compounds ($NaBrO_3$ and $KBrO_4$) with X-ray crystallographic data.

Results and Discussion

The $NaBrO_2 \cdot 3H_2O$ used in this work was obtained from a commercial source (Fluka Chemicals, >95% pure), and its purity was checked by Raman spectroscopy. For the yellow solid, Raman bands were noted at 728, 680, and 330 cm^{-1}, while aqueous solutions yielded features at 710 and 320 cm^{-1}. These data are in close agreement with the work of Evans and Lo[19] and Djeda-Mariadassou et al.[20] Bands due to bromate ions[20] were absent from our solid spectra and from freshly prepared solutions.

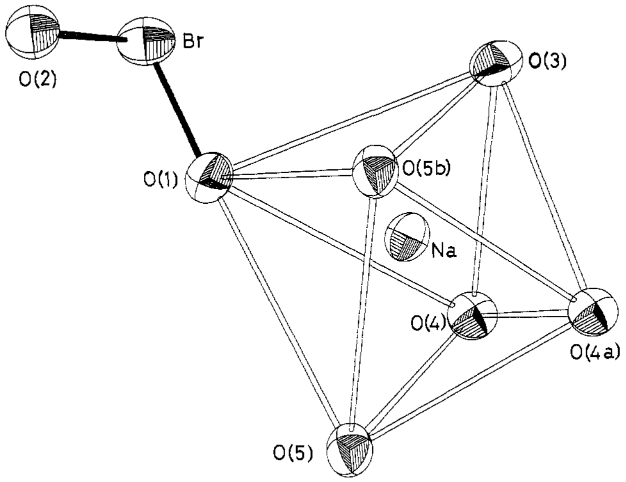

Figure 1. View of the bromite anion and the sodium coordination polyhedron showing the atom numbering scheme. Atoms have been drawn with 50% probability surface.

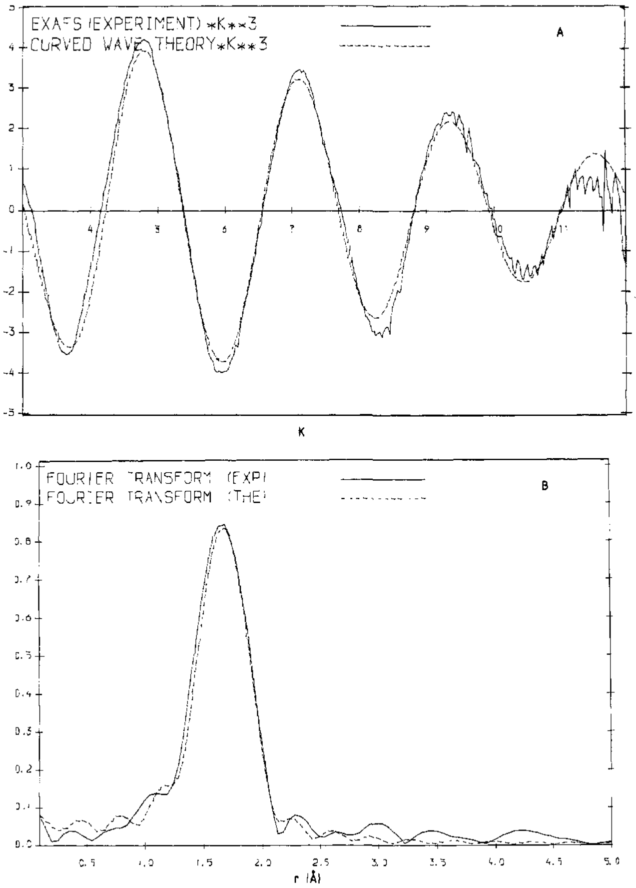

Figure 2. (A) Background subtracted EXAFS of $NaBrO_2 \cdot 3H_2O$. (B) Fourier transform of A (full line, experimental data; broken line, calculated). No smoothing or Fourier filtering has been applied to the data.

However, the presence of this decomposition product is evident in earlier Raman studies[7f] on related materials. In the IR spectrum, bands were observed at 721, 680, and 328 cm^{-1}. The ^{17}O NMR spectrum of BrO_2^- in aqueous solution shows a strong signal with δ = 145 ($w_{1/2}$ = 570 Hz), together with a second weak feature at δ = 296.5 which increased in relative intensity over the long accumulation period (ca. 17 h), and which is characteristic of BrO_3^-.[21]

The structure of $NaBrO_2 \cdot 3H_2O$ as determined by X-ray diffraction contains discrete $[BrO_2]^-$ anions and sodium cations, with

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the latter surrounded by six oxygen atoms arranged at the vertices of a distorted octahedron. One of the six O atoms is an atom from the bromite anion (see Figure 1), and the remainder are water molecules. The stoichiometry requires that some of the water molecules be associated with more than one octahedron, and zigzag chains of edge-linked octahedra are present in the solid. The compound is isomorphous with the corresponding chlorine compound,[22] and Br–O distances of 1.731 (2) and 1.702 (2) Å may be compared with Cl–O distances of 1.564 (1) and 1.557 (1) Å. The anion, as expected, is a bent species with a bond angle (O–Br–O = 105.3 (1)°) comparable with the O–Cl–O angle (108.23 (6)°) in $NaClO_2·3H_2O$.[22] The Br–O distances in the oxoanions decrease with increasing bromine oxidation state, and the present values can be compared with the Br–O distances in $NaBrO_3$[23] (1.648 (4) Å) and $KBrO_4$[24] (1.59 (1)–1.62 (1) Å).

Bromine K-edge EXAFS data were obtained for solid $NaBrO_2·3H_2O$ diluted with boron nitride and for saturated aqueous solutions. The k^3 weighted data obtained after background subtraction were used for curve fitting without smoothing or Fourier filtering, and the background-subtracted data and the corresponding Fourier transform for solid $NaBrO_2·3H_2O$ are shown in Figure 2. The fitting employed the single scattering curved wave theory as contained in the EXCURVE program and utilized ab initio phase shifts calculated in the usual manner.[18] Analysis of the data from solid-state samples gave an average Br–O distance of 1.75 Å,[25] and no further shells arising from other neighboring atoms are statistically significant. In solution, a Br–O bond length of 1.72 Å[25] was obtained. Both values compare well with the bond lengths obtained from the X-ray study and suggest that EXAFS results for related compounds of uncertain structure may be viewed with confidence.

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Supplementary Material Available: Tables of anisotropic thermal parameters, bond lengths, and bond angles (2 pages); table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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(25) Systematic errors in data collection and analysis give rise to errors of ca. ±0.02–0.03 Å in the first shell distances. $NaBrO_2·3H_2O$: $2\sigma^2 = 0.013$ Å, FI = 0.04, $R = 11.9$. $NaBrO_2$ (aqueous solution): $2\sigma^2 = 0.009$ Å, FI = 0.20, $R = 11.4$. $\mathrm{FI} = \sum_i (\chi_i^{\mathrm{T}} - \chi_i^{\mathrm{E}})k_i^3$. $R = [\int|\chi^{\mathrm{T}} - \chi^{\mathrm{E}}|k^3\,\mathrm{d}k / \int|\chi^{\mathrm{E}}|\,\mathrm{d}k] \times 100$.

Application of Molecular Dynamics and Free Energy Perturbation Methods to Metalloporphyrin–Ligand Systems. 1. CO and Dioxygen Binding to Four Heme Systems

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Abstract: We present the application of molecular mechanics/dynamics and free energy perturbation computational techniques to simulation of iron(II) porphyrin systems. Force field parameters were developed by modeling the geometry of four systems whose crystal structure is known. This force field was then used in molecular dynamics/free energy perturbation calculations, at 300 K in vacuo, on a separate set of four iron(II) porphyrin systems including models of 5,5-pyridine cyclophane heme(1,5-DCI) (I), picket fence heme(2-MeIm) (II), monochelated heme (III), and 7,7-durene cyclophane heme(1,5-DCI) (IV). The perturbation calculations reproduced reasonably well the trend in the partition coefficient, *M* value, of this set. Our simplified model indicates that the electrostatic component of both I and II favors the binding of O_2 over CO, whereas the electrostatic component of III and IV favors CO over O_2. The preference of O_2 over CO binding from the nonbonded steric component was I > II > III > IV. Molecular dynamics simulations showed that the Fe atom of the O_2 and CO complexes of I oscillated 0.06 and 0.16 Å, respectively, *lower* than those of II, even though the crystal structure and the simulation of the O_2 complex of II shows the Fe atom 0.087 Å *below* the porphyrin plane: this result suggests that the ratios of "R state" to "T state" CO/O_2 binding affinities will be extremely low for system I. The simulations also showed that even with a 7,7-strap as in IV, there is still more interaction with a bound CO than with a bound O_2.

Understanding the interaction of metalloproteins with substrates continues to be of interest.[1] The binding of small ligands to heme proteins has been extensively investigated with a variety of model systems.[2-6,9-13] These studies indicate that polarity and distal steric effects appear to dominate the discrimination between the binding of dioxygen and carbon monoxide to simple iron porphyrins. The relative binding of these two ligands to hemes and heme proteins is characterized in terms of the formal equilibrium shown in eq 1, where the $P^{i}_{1/2}$ is defined as the pressure of gas i needed to saturate one-half of all hemes in solution and is the inverse of the binding constant of gas i.

$$\mathrm{HmO_2 + CO \overset{\mathit{M}}{\rightleftharpoons} HmCO + O_2} \qquad (1)$$

$$M = \frac{[\mathrm{HMCO}][\mathrm{O_2}]}{[\mathrm{HmO_2}][\mathrm{CO}]} = \frac{P^{\mathrm{O_2}}{}_{1/2}}{P^{\mathrm{CO}}{}_{1/2}}$$

The partition coefficient,

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