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LETTER

A New Polyhalogen Network for Bromine – Br_{10}^{2-}

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Polyhalide anions have been studied for many years, and for polyiodide anions there is a rich and varied group of poly-anions which have been structurally characterised. For polybromides, however, only the tribromide and tetrabromide anions have been characterised by X-ray analysis and, to date, no penta- or decabromide anions have been isolated and structurally characterised. Evans and Yo [1], in a vibrational study, presumed the existence of Br_5^- to account for the spectral features which they observed for the salts of the oxy-anions of bromine. Hecquet and Landais [2] concluded that similar spectral features observed in the Raman spectra of brominated acetic acid could also be ascribed to penta- and heptabromide anions.

A survey [3] of the numerous structural determinations of polyhalide anions and cations has summarised the major characteristics of the structures observed. The angles within the halogen networks are almost entirely either 90° or 180° (approximately) and the bond lengths are usually greater than those in the corresponding interhalogen. In many salts the structure of the anion is dependent upon the size and symmetry of the counter-ion.

In the present study, the reaction of 1,5-diphenylformazan and bromine has resulted in a tetrazolium compound and has yielded a unique anion, the structure of which has been unequivocally determined and its Raman spectrum observed. The polybromide anion represents a new type of polyhalogen network for bromine.

Experimental

Red crystals, suitable for X-ray analysis, were formed from the reaction mixture. Crystal data were collected with a Nicolet R3m four-circle diffractometer.

Crystal Data

$C_{13}H_{10.6}N_4Br_{5.3}$: red crystals $0.38 \times 0.26 \times 0.14$ mm; triclinic, $a = 8.572(1)$, $b = 9.711(1)$, $c = 14.166(3)$ Å; $\alpha = 75.18(1)$, $\beta = 89.84(1)$, $\gamma = 70.42(1)°$; $U = 1092.2(3)$ Å^3; space group $P\bar{1}$, $Z = 2$, $F(000) = 606.64$. Using Mo Kα radiation ($\lambda = 0.71069$ Å) and 1.4° ω-scans at a scan rate of 7.3° min^{-1}, 2863 unique reflections were collected in the range ($4 < 2\theta < 45°$) at 170 K. Of these, 2540 which had ($I > 3\sigma(I)$) were used in the structure refinement.

A Patterson synthesis revealed the positions of three bromine atoms and the remaining non-hydrogen atoms were located from difference Fourier maps. Anisotropic thermal parameters were assigned to all non-hydrogen atoms and the refinement, on 121 least-squares parameters, converged with $R = 0.0467$, $R_w = 0.0796$ and a maximum shift/error ratio of 0.05. The final difference map showed no significant features.

Results and Discussion

Only partial bromination of the formazan has occurred, so that the resulting tetrazolium salt is disordered in the 3-position. No evidence for the bromination of either of the two phenyl rings has been observed. There are boxes of Br_{10}^{2-} anions interleaved between layers of pairs of cations. Atomic nomenclature and numbering of the Br_{10}^{2-} assembly are shown in Fig. 1, together with bond lengths and bond angles.

It is a feature of all polyiodide anions that some or all of the I---I distances are intermediate between the covalent I–I and the shortest intermolecular separation. The Br–Br distances in this anion follow this trend of intermediacy.

In Table 1 all of the Br–Br bond lengths found for the Br_{10}^{2-} anion are compared with those observed in crystalline bromine and in tribromide and tetrabromide anions [3–6]. Although the best description of the new Br_{10}^{2-} anion is that it consists of two bromine molecules associated with two Br_3^- anions, it is clear that the Br5–Br6 bond length

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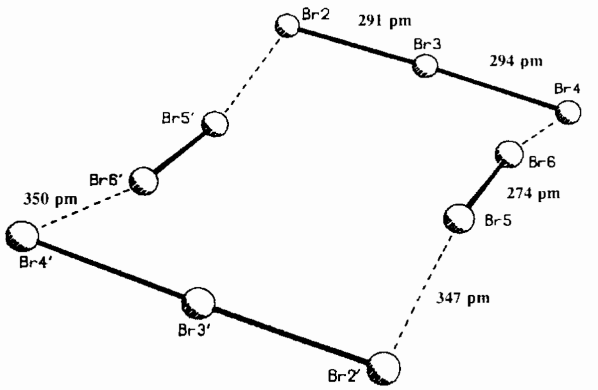

Fig. 1. The Br_{10} assembly is shown in projection. The bond lengths are indicated in pm.

in the dibromide unit differs markedly from the value found for crystalline bromine and Br_4^{2-}. There is also a significant difference between the bond lengths found for the symmetric Br_3^- anions present in this Br_{10}^{2-} anion and the much shorter bond lengths established for other symmetric Br_3^- anions. However, the Br2–Br3 and Br3–Br4 bond lengths are comparable with those observed for a network polybromide consisting of Br^- and Br_3^- units [6]. The structure of the Br_{10}^{2-} anion also closely resembles that observed for the polyiodide anion I_{16}^{4-} [7].

Our observed Raman spectrum is in agreement with our determined structure, which indicates an assemblage of ten bromine atoms as two tribromide ions and two dibromine molecules. There is no significant coupling between these sub-units resulting in Raman bands for penta- or decabromide, rather the loose arrangement found would be expected to give the weak, but reproducible, spectrum with Raman-active phonons between 50 and 200 cm^{-1}. Band centre wavenumbers attributed to the Br_{10}^{2-} anion are observed at 54, 67, 94, 144, 175 and 193 cm^{-1}.

The dibromide unit is considerably elongated at 274 pm when compared with molecular dibromine (227 pm) and a concomitant band shift is seen from *c.* 310 cm^{-1} in Br_2 [8] to 193 cm^{-1} in this structure. The Br_3^- unit is effectively symmetric with bond lengths of 291 and 294 pm and gives rise to the bands observed at 197 and 144 cm^{-1} respectively for the ν_3 asymmetric and ν_1 symmetric stretching vibrations of tribromide. The band centred at 94 cm^{-1} is attributed to the bond deformation mode, ν_2, of the Br_3^- unit. We have also recorded the Raman spectrum for I_{16}^{4-}. Band centre wavenumbers are observed at 107, 153, 171 and 205 cm^{-1} and this shows remarkable agreement with the spectrum recorded for the Br_{10}^{2-} anion.

The decabromide anion further exemplifies the remarkable catenating ability of the halogens and the structural diversity found for polyhalogen anions.

Supplementary Material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgement

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TABLE 1. Br–Br distances for Br_2 and Br_3 and Br_4 anions

Example	Br–Br (pm)	Br····Br (pm)	Reference
$Br_{2(s)}$	227	331, 379, 399	4
$((CH_3)_3NH)_2Br\cdot Br_3$	254, 253		3
$(CS_3N_2Br)Br_3$	272, 242		5
$CsBr_3$	244, 270	373, 380	3
PBr_7	239, 291	366	4
(Paraquat)$Br\cdot Br_3$	289, 297	304	6
$(W_6Br_8)Br_4(Br_4)_{2/2}$	289, 243		3
$(C_7H_{13}NH)_4(SbBr_6)_2\,2Br$	302, 228		3
$[(CH_3)_4N]_3Sb_2Br_9\cdot Br_2$	289, 231		3
Br_{10}	274, 291, 294, 347, 350		this work

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