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A linear Fe–O–Fe unit in bis(dibenzyldimethylammonium) µ-oxo-bis[tribromoferrate(III)]

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The title compound, \((\text{C}_{16}\text{H}_{28}\text{N})_{2}[\text{Fe}_{2}\text{Br}_{6}\text{O}]\), crystallizes with one dibenzyldimethylammonium cation and one half of a µ-oxo-bis[tribromoferrate(III)] anion in the asymmetric unit. The bridging oxo group is situated on an inversion centre, resulting in a linear conformation for the Fe–O–Fe unit. The iron(III) cations have tetrahedral geometry, with bond angles in the range 106.8 (1)–112.2 (1)°. The ion pairs are held together by Coulombic forces and \(\text{C}–\text{H}–\text{Br}\) hydrogen bonds. Each \(\text{Br}–\text{O}–\text{Br}\) anion forms one hydrogen bond. No \(\text{C}–\text{H}–\text{O}\) hydrogen bonds are found between the O atom in the Fe–O–Fe unit and surrounding counter-cations, consistent with the linear configuration of the Fe–O–Fe unit.

Comment

The Fe–O–Fe unit has been of interest in inorganic chemistry because of its magnetic properties, its stability (diferric halometallate complexes) and to investigate the structural properties of the \([\text{MX}]\) anions in the solid state by varying the first-row transition metal cations (\(\text{M}^{3+}\)) and the halides (\(\text{X} = \text{Br}–\text{Cl}–\text{I}\)) in these anions. The same counter-cation, dibenzyldimethylammonium (Busi et al., 2004; Ropponen et al., 2004), was used in all experiments. A new and interesting compound, viz. the title complex, (I), was crystallized as part of these studies.

The molecular structure of (I) consists of an \([\text{Fe}_{2}\text{Br}_{6}\text{O}]^{2–}\) anion with a linear Fe–O–Fe core and two dibenzyl-dimethylammonium cations. The asymmetric unit contains one cation and one half of the µ-oxo-bis[tribromoferrate(III)] anion, which sits on an inversion centre. The structure and labelling scheme of (I) are presented in Fig. 1. Selected bond lengths and angles are presented in Table 1, which gives the geometries around the FeIII cation and N atom. The linearity of the Fe1–O1–Fe1′ fragment is required by the centre of symmetry [symmetry code: (i) \(1–x, y, 1–z\)]. The FeIII cation is four-coordinated by three \(\text{Br}–\text{O}–\text{Br}\) ions and the bridging oxo group. The bond angles around FeIII vary between 106.82 (4)° and 112.21 (4)°, which are typical values for \([\text{Fe}_{2}\text{X}_{6}\text{O}]^{2–}\) anions (\(\text{X} = \text{Br}–\text{Cl}\)). The configuration around the N atoms in the cation is also tetrahedral, with angles in the range 107.4 (4)–111.5 (4)°, typical for N atoms in quaternary ammonium cations (Busi et al., 2004, 2005, 2006).

As already mentioned, the linear shape of the Fe–O–Fe unit is obliged by the crystallographic centre of symmetry. The displacement ellipsoid of the O atom has a slightly elongated
shape, which could indicate a dynamic or static disorder between two rotational conformers. However, we note that distortions away from tetrahedral geometry are unusual for the Fe$^{II}$ ions in [Fe$_2$X$_3$O]$_2$$^{2-}$ anions with bent Fe—O—Fe units. During the refinement of a bent model for (I), the coordination sphere around the Fe$^{II}$ cations is distorted away from tetrahedral geometry, giving bond angles in the range 104.3 (7)—119.5 (7)$^\circ$. In addition, the work of Lledo et al. (2003) points out that the linear configuration of the [Fe$_2$Br$_6$O]$_2$$^{2-}$ dianion is at the potential minimum and that, generally, the bent Fe—O—Fe unit demands C—H...O hydrogen bonds from cations to bridging O atoms, which are not found in this case. Thus, two angular conformers are very unlikely. This is then the first compound including the [Fe$_2$Br$_6$O]$_2$$^{2-}$ anion with a linear Fe—O—Fe unit to have been crystallized.

In the extended structure of (I), the [Fe$_2$Br$_6$O]$_2$$^{2-}$ anions are located at the corners of the cell and in the middle of each cell face. Each anion is surrounded by six cations. The cations are not in the ‘W’ conformation, as was the case for dibenzyldimethylammonium bromide (Busi et al., 2004). In (I), the cations have a somewhat twisted conformation. However, we note that Coulombic forces between the cations and anions, the packing in (I) is influenced by C—H...Br hydrogen bonds (Table 2) [H...Br < 3.0 Å; a mean value for H...Br of 2.96 (1) Å was given by Desiraju & Steiner (1999)], which are shown in Fig. 2. One [Fe$_2$Br$_6$O]$_2$$^{2-}$ anion acts as acceptor for six hydrogen bonds (<3.0 Å) from the dibenzyldimethylammonium cations, related in pairs by the centre of symmetry in the middle of the anion.

**Experimental**

Single crystals of the title compound were obtained from an acetonitrile solution containing stoichiometric amounts (2:1) of the dibenzyldimethylammonium halide salt (Busi et al., 2004) and anhydrous FeBr$_2$ salt. The crystals were obtained at room temperature by slow evaporation of the solvent.

**Crystal data**

(C$_{16}$H$_{20}$N)$_2$[Fe$_2$Br$_6$O]  
$M_r = 1059.82$  
Orthorhombic, Pbca  
$a = 13.800$ (3) Å  
$b = 14.984$ (3) Å  
$c = 18.283$ (4) Å  
$V = 3780.5$ (13) Å$^3$  
$\rho_{\text{calc}} = 1.862$ Mg m$^{-3}$  
$T = 173$ (2) K  
$\bar{n} = 0.73$ e Å$^{-3}$  
$\text{Block, orange}$

**Data collection**

Bruker-Nonius Kappa-APEX-II  
CCD area-detector diffractometer  
$\omega$ and $\varphi$ scans  
$8735$ measured reflections  
$4618$ independent reflections  
$3215$ reflections with $I > 2\sigma(I)$  
$R_{\text{int}} = 0.056$  
$\theta_{\text{max}} = 28.1^\circ$

**Refinement**

Refinement on $F^2$  
$R[F^2 > 2\sigma(F^2)] = 0.049$  
$wR(F^2) = 0.110$  
$S = 1.06$  
$4618$ reflections  
$199$ parameters  
H-atom parameters constrained

**Table 1**

Selected geometric parameters (Å, $^\circ$).

| C11—N1 | 1.528 (6) | Fe1—O1 | 1.7523 (7) |
| C21—N1 | 1.535 (6) | Fe1—Br1 | 2.3602 (10) |
| C31—N1 | 1.492 (6) | Fe1—Br2 | 2.3610 (10) |
| C41—N1 | 1.506 (6) | Fe1—Br3 | 2.3808 (11) |
| C31—N1—C41 | 107.9 (4) | O1—Fe1—Br2 | 108.16 (4) |
| C41—N1—C21 | 110.4 (4) | O1—Fe1—Br3 | 110.98 (4) |
| C31—N1—C21 | 111.0 (4) | Br2—Fe1—Br3 | 108.73 (4) |
| C41—N1—C21 | 107.4 (4) | Br1—Fe1—Br3 | 112.21 (4) |
| C11—N1—C21 | 109.0 (4) | Br1—Fe1—Br4 | 106.82 (4) |

**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Two of six hydrogen bonds (Br...H—C < 3.0 Å) around the anion are shown as dashed lines. [Symmetry code: (i) 1 — x, — y, 1 + z.]

**Figure 2**

The packing in (I), showing C—H...Br hydrogen bonding around the [Fe$_2$Br$_6$O]$_2$$^{2-}$ anion. [Symmetry code: (i) 1 — x, — y, 1 + z.]
H atoms were positioned geometrically and treated as riding, with C—H = 0.95–0.99 Å and with Ueq(H) = 1.2Ueq(C) for methylene and aromatic H atoms, or 1.5Ueq(C) for methyl H atoms.

Data collection: COLLECT (Nonius, 1998); cell refinement: COLLECT; data reduction: DENZO—SMN (Otwinowski & Minor, 1997); program(s) used to solve structure: SIR97 (Altomare et al., 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg, 2001); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3029). Services for accessing these data are described at the back of the journal.

References


