metal-organic compounds

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

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The title compound, $(C_{16}H_{20}N)_2[Fe_2Br_6O]$, 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 C—H···Br hydrogen bonds. Each Br^- anion forms one hydrogen bond. No C—H···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 form) and its occurrence at the active sites of proteins (Kurtz, 1990; Gorun & Lippard, 1991; Davydov et al., 1997; Scarrow et al., 1986; Stenkamp et al., 1984; Klotz & Kurtz, 1984; Nordlund et al., 1990; Reichard & Ehrenberg, 1983; Lynch et al., 1989; Gatteschi et al., 2000). The synthesis, crystal structure and magnetic properties of $(Hpy)_2[Fe_2Cl_6O]$ (Hpy is pyridinium) were reported by Drew et al. (1978). Since then, dozens of similar complexes incorporating the $[Fe_2Cl_6O]^{2-}$ unit have been synthesized and characterized by various analytical methods and by X-ray crystallography (Petridis & Terzis, 1986; Healy et al., 1983; Vasilevsky et al., 1988; Solbrig et al., 1982; Bullen et al., 1986; Armstrong & Lippard, 1985; Do et al., 1983; Adler et al., 1988; Molins et al., 1998; Senda et al., 2000; Lledós et al., 2003; Wei et al., 2004). In some cases, crystallographic problems have been associated with crystallographically imposed site symmetry C_s, C_i or C_2, which masks an orientational disorder of the anion (Haselhorst et al., 1993).

At present, approximately 50 structures containing the dinuclear $[Fe_2Cl_6O]^{2-}$ unit have been published. About one-third of them have nearly linear Fe—O—Fe cores, but the real number is difficult to estimate due to the orientational disorder. The Fe—O—Fe angle in the solid state varies from 180° to about 140°, depending on the counter-cation. The structure has been considered as bent if the Fe—O—Fe angle is between 146 and 171° (Lledós et al., 2003, and references therein); these workers analyzed the diversity of Fe—O—Fe angles varying from 140 to 180° in the X-ray crystal structures of the $[Fe_2Cl_6O]^{2-}$ dianion. Only the linear isomer was found as a minimum on the potential energy surface by theoretical calculations. Detailed studies of the crystal packing showed that the angular form occurs when attractive intermolecular interactions (C—H···O contacts) are involved. If the interactions are strong and co-operative, the O atom is displaced from its central position and the bent form is present. If no interactions are found or if they are opposed, the configuration remains linear at the potential minimum.

In the only report to date of a structure with the dinuclear $[Fe_2Br_6O]^{2-}$ entity, Evans et al. (1992) described the crystal structure of $(Fc^+)_2[(FeBr_3)_2O]^{2-}$, which was prepared from $FeBr_3$ and ferrocene (Fc). The anion consists of two corner-sharing $FeBr_3O$ tetrahedra, and the cations are ferroceniums with eclipsed cyclopentadienyl rings. A bent Fe—O—Fe angle of 159.8 (4)° was observed.

Our aim has been to synthesize different types of tetra-halometallate complexes and to investigate the structural properties of the $[MX_4]^{2-}$ anions in the solid state by varying the first-row transition metal cations (M^{II}) and the halides ($X = Br^-$ and/or Cl^-) 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.
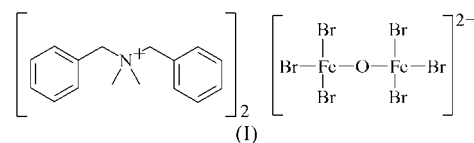
The molecular structure of (I) consists of an $[Fe_2Br_6O]^{2-}$ anion with a linear Fe—O—Fe core and two dibenzyl-dimethylammonium cations. The asymmetric unit contains one cation and one half of the μ-oxo-bis[tribromoferrate(III)] anion, which sits on an inversion centre. The structure and labelling scheme of (I) are presented in Fig. 1. Selected bond lengths and angles are presented in Table 1, which gives the geometries around the Fe^{III} cation and N atom. The linearity of the $Fe1$—$O1$—$Fe1^i$ fragment is required by the centre of symmetry [symmetry code: (i) $1 - x$, $-y$, $1 - z$]. The Fe^{III} cation is four-coordinated by three Br^- ions and the bridging oxo group. The bond angles around Fe^{III} vary between 106.82 (4) and 112.21 (4)°, which are typical values for $[Fe_2X_6O]^{2-}$ anions ($X = Br$ or 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^{III} ions in $[Fe_2X_6O]^{2-}$ anions with bent Fe—O—Fe units. During the refinement of a bent model for (I), the coordination sphere around the Fe^{III} cations is distorted away from tetrahedral geometry, giving bond angles in the range 104.3 (7)–119.5 (7)°. In addition, the work of Lledós et al. (2003) points out that the linear configuration of the $[Fe_2Br_6O]^{2-}$ 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 $[Fe_2Br_6O]^{2-}$ anion with a linear Fe—O—Fe unit to have been crystallized.

In the extended structure of (I), the $[Fe_2Br_6O]^{2-}$ 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. In addition to 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 $[Fe_2Br_6O]^{2-}$ 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.
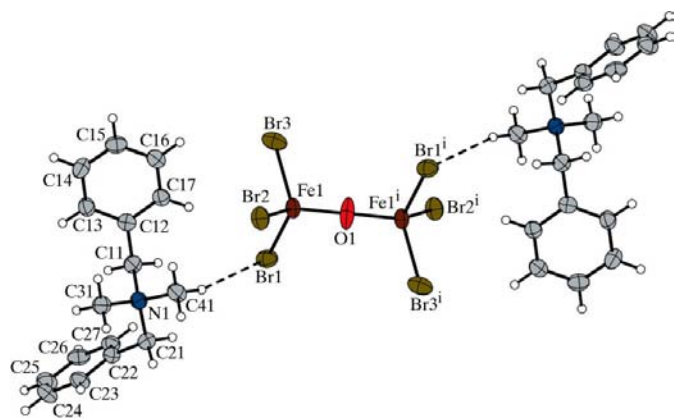

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Two of six hydrogen bonds (Br···H—C < 3.0 Å) around the anion are shown as dashed lines. [Symmetry code: (i) $1 - x$, $-y$, $1 - z$.]
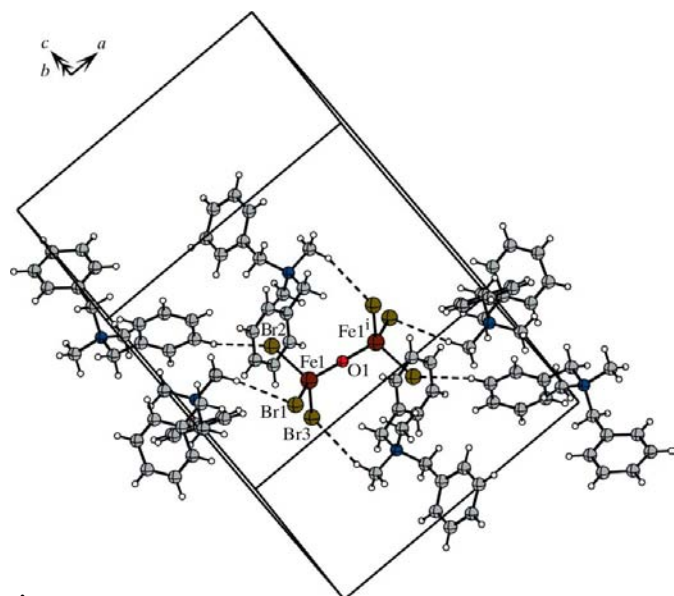
Figure 2
The packing in (I), showing C—H···Br hydrogen bonding around the $[Fe_2Br_6O]^{2-}$ anion. [Symmetry code: (i) $1 - x$, $-y$, $1 - z$.]

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

$(C_{16}H_{20}N)_2[Fe_2Br_6O]$	$Z = 4$
$M_r = 1059.82$	$D_x = 1.862$ Mg m^{-3}
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 13.800$ (3) Å	$\mu = 7.14$ mm^{-1}
$b = 14.984$ (3) Å	$T = 173$ (2) K
$c = 18.283$ (4) Å	Block, orange
$V = 3780.5$ (13) Å^3	$0.25 \times 0.15 \times 0.05$ mm

Data collection

Bruker–Nonius Kappa-APEX-II CCD area-detector diffractometer	8735 measured reflections
	4618 independent reflections
ω and φ scans	3215 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)	$R_{int} = 0.056$
	$\theta_{max} = 28.1°$
$T_{min} = 0.269$, $T_{max} = 0.717$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 14.2938P]$
$R[F^2 > 2\sigma(F^2)] = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.110$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.96$ e Å^{-3}
4618 reflections	$\Delta\rho_{min} = -0.73$ e Å^{-3}
199 parameters	Extinction correction: *SHELXL97*
H-atom parameters constrained	Extinction coefficient: 0.00036 (8)

Table 1
Selected geometric parameters (Å, °).

C11—N1	1.528 (6)	Fe1—O1	1.7523 (7)
C21—N1	1.535 (6)	Fe1—Br2	2.3601 (10)
C31—N1	1.492 (6)	Fe1—Br1	2.3622 (10)
C41—N1	1.506 (6)	Fe1—Br3	2.3808 (11)
C31—N1—C41	107.9 (4)	O1—Fe1—Br2	108.16 (4)
C31—N1—C11	111.5 (4)	O1—Fe1—Br1	110.98 (4)
C41—N1—C11	110.0 (4)	Br2—Fe1—Br1	108.73 (4)
C31—N1—C21	111.0 (4)	O1—Fe1—Br3	112.21 (4)
C41—N1—C21	107.4 (4)	Br2—Fe1—Br3	109.91 (4)
C11—N1—C21	109.0 (4)	Br1—Fe1—Br3	106.82 (4)

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C41—H41$B\cdots$Br1	0.98	2.87	3.827 (6)	165
C24—H24$A\cdots$Br2[i]	0.95	2.98	3.648 (6)	128
C41—H41$C\cdots$Br3[ii]	0.98	2.96	3.895 (6)	159

Symmetry codes: (i) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+\frac{1}{2}, -y, z+\frac{1}{2}$.

H atoms were positioned geometrically and treated as riding, with C—H = 0.95–0.99 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$ for methylene and aromatic H atoms, or $1.5U_{eq}(C)$ 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).

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.

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