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Synthesis and Reactivity of Haloacetato Derivatives of Iron(II) Including the Crystal and the Molecular Structure of $[Fe(CF_3COOH)_2(\mu\text{-}CF_3COO)_2]_n$

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The syntheses of haloacetates of iron(II) and their reactivity are described. The compound $Fe(CF_3COO)_2$, **1**, crystallizes from $CF_3COOH/(CF_3CO)_2O$ solution as the polynuclear $[Fe(CF_3COO)_2(CF_3COOH)_2]_n$, **2**, which contains bridging trifluoroacetates and monodentate trifluoroacetic acid groups. $Fe(CF_3COO)_2(DMF)_x$, as obtained from $Fe(CO)_5$ and $CF_3COOH/(CF_3CO)_2O$ in DMF, reacts with dioxygen at room temperature to give two μ_3-oxo compounds, namely, $[Fe_3(\mu_3\text{-}O)(CF_3COO)_6(DMF)_3]$, **3**, a $Fe^{(II)}–Fe^{(III)}–Fe^{(III)}$ derivative, and $[Fe_4(\mu_3\text{-}O)_2(\mu_2\text{-}CF_3COO)_6(CF_3COO)_2(DMF)_4]$, **4**, containing Fe(III) atoms only, which have been characterized by X-ray diffraction methods. Iron(II) chloro- and bromoacetates can be isolated by exchange reactions of iron(II) acetate with chloro- and bromo-substituted acetic acids in moderate to good yields. The stability of iron(II) haloacetates decreases on increasing the atomic weight and the number of halogens on the α-carbon atom. The species $Fe(CX_3COO)_2$ (X = Cl, **7**; Br, **8**), in THF solution, slowly convert into $[Fe_3(\mu_3\text{-}O)(CCl_3COO)_6(THF)_3]$, **11**, or $[Fe_3(\mu_3\text{-}O)(CBr_3COO)_6(THF)_3][FeBr_4]$, **10**, respectively. Likewise, when iron(II) acetate (or trifluoroacetate) is left for several hours in the presence of a variety of haloacetic acids in THF, selective formation of different species, depending on the nature of the starting compound and of the acid employed, is observed. The formation of these products is the result of C–X bond activation (X = Cl, Br) and haloacetato decomposition, which occurs with concomitant oxidation at the metal centers. Carboxylic acid degradation species (CH_2XCOOH, CX_4, CX_3H, CX_2H_2, X = Cl, Br) have been observed by GC-MS.

Introduction

Trifluoroacetato derivatives of transition metals are used in catalysis[1] due to the higher solubility of the precursors with respect to simple acetates and due to the fact that, being $[CF_3COO]^-$ ligands and Lewis bases weaker than hydrogen-substituted acetates, they can be easily displaced or change their coordination from bi- to monodentate, according to the electronic and steric requirements of the central metal atom.

In the framework of our research on carboxylato derivatives of transition metals, we have recently reported on the syntheses and the properties of vanadium,[2] manganese,[3] and copper[4] trihaloacetato derivatives. Copper haloacetates have been studied extensively,[4] and it has been found that the nature of the compounds depends on the haloacetate (by operating under the same experimental conditions in the presence of excess $(RCO_2)O$, anhydrous ($Cu(CH_2XCOO)_2$, X = Cl, Br) or aquo derivatives ($Cu(CHX_2COO)_2(H_2O)$, X = Cl, Br) were obtained) or on the presence of Lewis bases (according to IR spectroscopy, different coordination modes of the haloacetates—bridging monodentate, bridging bidentate, and bidentate—were observed). Moreover, the stability of copper(I) haloacetates with respect to oxidation to copper(II) decreases on increasing the number of halides on the α-carbon atom and on the atomic weight of the halogen.

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These facts, together with the recently reported synthesis of iron(II) trifluoroacetate,[3] prompted us to extend our studies to iron, and in this paper we wish to report on the preparation of halocarboxylato derivatives of iron(II), as obtained by exchange reaction, and the identification of halide transfer reactions mainly involving $[CCl_3COO]^-$ or $[CBr_3COO]^-$ anions.

Moreover, the crystal and molecular structure of the CF_3COOH adduct of iron(II) trifluoroacetate is reported, representing an addition to the rather restricted family of coordination compounds containing the carboxylate and its conjugated acid as ligands at the same time.[4a,5]

Experimental Section

All operations were carried out using standard Schlenk-tube techniques, under an atmosphere of prepurified dinitrogen. The reaction vessels were dried in an oven prior to use. Solvents were dried by conventional methods. Elemental analyses were performed by a Carlo Erba model 1106 elemental analyzer. Infrared spectra were recorded by a Perkin-Elmer model FT 1725X instrument on Nujol and polychlorotrifluoroethylene mulls under exclusion of moisture and oxygen or by a FTIR spectrometer equipped with a Perkin-Elmer UATR sampling accessory. Photochemical reactions were performed in a quartz apparatus equipped with a 150 W mercury lamp.

Commercially available $Fe(CO)_5$ (Fluka) was used without further purification. Iron(II) acetate was obtained by reaction of $Fe(CO)_5$ with $CH_3COOH/(CH_3CO)_2O$ in DMF at 140 °C.[6] Trifluoroacetic acid, CF_3COOH (Aldrich), and trifluoroacetic anhydride were used as received. The carboxylic acids, CX_3COOH, CHX_2COOH, and CH_2XCOOH, X = Cl, Br, were dried overnight in vacuo at room temperature. *N,N*-Dimethylformamide, DMF, was stirred overnight over BaO, filtered under inert atmosphere, and distilled under reduced pressure.

Preparation of $Fe(CF_3COO)_2(DMF)$, 1·DMF. A solution of CF_3COOH (24.0 mL, 312 mmol) in DMF (200 mL) was treated with $Fe(CO)_5$ (20.0 mL, 148 mmol) and heated at ca. 140 °C. After 3 h, gas evolution had ceased and no iron carbonyl derivative was detected in solution (IR spectrum). The colorless solution was evaporated in vacuo at 110 °C, thus obtaining a colorless solid residue. After the addition of toluene (300 mL), the suspension was filtered, washed with toluene (4 × 10 mL), and dried in vacuo at room temperature. The solid residue was treated with THF (100 mL) and, after 14 h of stirring at room temperature, the resulting suspension was filtered and the solid was washed with THF (3 × 10 mL) and dried in vacuo affording **1**·DMF[7] (32.5 g, 62% yield) as a microcrystalline colorless solid. Anal. Calcd for $C_7H_7F_6FeNO_5$: C, 23.7; H, 2.0; N, 3.9. Found: C, 23.5; H, 1.8; N, 3.6. IR (Nujol and polychlorotrifluoroethylene mull): 1671vs (ν_{as}(COO)), 1649vs, 1459s (ν_s(COO)), 1210vs ($\nu_{as}(CF_3)$), 1147s ($\nu_s(CF_3)$), 846m−s, 795m−s, 725m−s, 666w cm^{-1}.

Reaction of 1·DMF with O_2 in THF: Preparation of 3 and 4. A colorless solution of **1**·DMF (1.93 g, 5.44 mmol) in THF (40 mL) was saturated with dry oxygen and stirred at room temperature for 3 h. The volume of the dark red solution was reduced to ca. 15 mL, and heptane was added (20 mL) to form two layers. After 6 days, well formed red and black crystals were filtered, dried briefly in vacuo, and separated under the microscope. No attempt was made to increase the yields of the two products.

The black crystals (0.10 g, 2%) corresponded to **3**. Anal. Calcd for $C_{21}H_{21}F_{18}Fe_3N_3O_{16}$: C, 23.3; H, 2.0; N, 3.9. Found: C, 24.3; H, 2.4; N, 3.4. IR (Nujol and polychlorotrifluoroethylene mull): 1703s, 1651vs, 1501m−w, 1462s, 1369s, 1229s, 1201, 1158s, 853m, 795m, 727s, 692m, 670m−w cm^{-1}.

The red crystals (0.060 g, 3% yield) were identified as **4**. Anal. Calcd for $C_{28}H_{28}F_{24}Fe_4N_4O_{21}$: C, 23.4; H, 2.0; N, 3.9. Found: C, 23.3; H, 2.2; N, 3.6. IR (Nujol and polychlorotrifluoroethylene mull): 1713m−w, 1691m−w, 1637vs, 1466m, 1416m−w, 1377m, 1204vs, 1166m, 1157m, 1146m, 853m−w, 797m−w, 727m, 649m cm^{-1}.

A gas-volumetric control of the reaction showed that 3.37 mmol of **1**·DMF in THF (25 mL) absorbed dioxygen at 21.7 °C up to a O_2/Fe molar ratio of 0.22 in 3 h.

1. Preparation of $Fe(CH_{3-n}X_nCOO)_2$ Complexes. 1A. $Fe(CF_3COO)_2$·THF, 1·THF. A solution of CF_3COOH (19.5 mmol) in THF (50 mL) was treated with $Fe(CH_3COO)_2$, **5** (1.69 g, 9.72 mmol). The solid slowly dissolved, and a colorless solution was obtained after ca. 2 h of stirring at room temperature. The volume of the solution was reduced to ca. 5 mL in vacuo at room temperature; addition of heptane (30 mL) caused the separation of a colorless solid which was recovered by filtration and identified (after drying in vacuo for 2 h) as **1**·THF (2.47 g, 85% yield, IR and elemental analysis).

The treatment of **1**·DMF with 2 equiv of CH_3COOH in THF under the experimental conditions described above did not produce appreciable amounts of **5**, and unreacted **1**·DMF was recovered in almost quantitative yields.

1B. $Fe(CHCl_2COO)_2(THF)$, 6. A solution of $CHCl_2COOH$ (19.4 mmol) in THF (50 mL) was treated with **5** (1.49 g, 8.57 mmol). The colorless suspension was stirred at room temperature for 3 days. The colorless solid was recovered by filtration, washed with THF (2 × 2 mL), and dried in vacuo at room temperature (2 h), affording **6** (3.16 g, 96% yield) as a microcrystalline, colorless, air-sensitive solid. Anal. Calcd for $C_8H_{10}Cl_4FeO_5$: C, 25.0; H, 2.6. Found: C, 25.2; H, 2.8. IR (Nujol and polychlorotrifluoroethylene mull): 2897w, 1631vs (ν_{as}(COO)), 1461s, 1402vs (ν_s(COO)), 1378m−s, 1367m−s, 1296mw, 1223m−s, 1042s (ν_{as}(C−O−C), THF), 921w, 882m−w (ν_{as}(C−O−C), THF), 827m−s, 771m−s, 718s, 666m−s cm^{-1}.

1C. $Fe(CCl_3COO)_2(THF)$, 7. A solution of CCl_3COOH (2.92 g, 17.8 mmol) in THF (50 mL) was treated with **5** (1.53 g, 8.79 mmol). The initially colorless suspension turned red-orange after 2 h of stirring at room temperature; the solid isolated consisted of

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(5) (a) $[TiCl_2(RCOO)(RCOOH)]_2O$, R = Et: Barrow, H.; Brown, D. A.; Alcock, N. W.; Errington, W.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1994**, 3533. R = Bu^t: Barrow, H.; Brown, D. A.; Alcock, N. W.; Clase, H. J.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1994**, 195. (b) $Ti_2Cl_7(RCOO)(RCOOH)$, R = *p*-ClC_6H_4, CH = CHMe: Alcock, N. W.; Brown, D. A.; Illson, T. F.; Roe, S. M.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* 1991, 873. (c) $MM'(C_6H_5COO)_4(C_6H_5COOH)_2$, M = M′ = Cr: Cotton, F. A.; Extine M. W.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 176. M = M′ = Ru: Spohn, M.; Strähle, J.; Hiller, W. *Z. Naturforsch.* **1986**, *B41*, 541. M = Cu, M′ = Ni: Spohn, M. Ph.D. Thesis, Universität Tübingen, 1986. (d) $[V_3(\mu_3\text{-}O)(CH_3COO)_6(CH_3COOH)_2(THF)][VCl_4(CH_3COOH)_2]$: Cotton, F., A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1982**, *21*, 3316. (e) $Ru_2(CH_3COO)_4(CH_3COOH)_2\cdot0.7H_2O$: Cotton, F. A.; Makutz, M.; Zhong, B. *Inorg. Chem.* **1988**, *27*, 4368. (f) $Cr_2(CH_3COO)_4(CH_3COOH)_2$: Cotton, F. A.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 2004. (g) $Cu_2(CH_3COO)_4(CH_3COOH)_2$: Rao, V. M.; Sathyanarayana, D. N.; Manohar, H. *J. Chem. Soc., Dalton Trans.* **1983**, 2167.

(6) Calderazzo, F.; Floriani, C.; Henzi, R.; L'Eplattenier, F. *J. Chem. Soc. A* **1969**, 1378.

(7) The amount of DMF retained by the compound depends on the drying conditions: in our experiments the DMF/Fe molar ratio ranged from 1.6 to 0.5.

a mixture of iron(II) trichloroacetate and acetate (IR spectrum on a solid sample). A qualitative test (Ag^+ in aqueous acidic solution) on the surnatant liquid was positive for chloride ion. After 90 h of stirring at room temperature, the colorless solid was recovered by filtration, washed with THF (2 × 2 mL), and dried in vacuo at room temperature (2 h), affording **7** (2.66 g, 67% yield) as a microcrystalline, colorless, air-sensitive solid. Anal. Calcd for $C_8H_8Cl_6FeO_5$: C, 21.2; H, 1.8. Found: C, 21.0; H, 1.7. IR (Nujol and polychlorotrifluoroethylene mull): 2897w, 1651vs,br (ν_{as}(COO)), 1513m−w, 1462m−s (ν_s(COO)), 1377m−s, 1026m−w (ν_{as}(C−O−C), THF), 885m,w,sh (ν_s(C−O−C), THF), 837m−s 739s, 683s cm^{-1}.

1D. $Fe(CBr_3COO)_2(THF)_2$, 8. A solution of CBr_3COOH (6.01 g, 20.2 mmol) in THF (50 mL) was treated with **5** (1.530 g, 8.80 mmol). The initially colorless suspension quickly turned red-orange and a qualitative test (Ag^+ in aqueous acidic solution) on the surnatant liquid was positive for bromide ion. The colorless solid was recovered by filtration, washed with THF (2 × 2 mL), and dried in vacuo at room temperature (1 h), affording **8** (3.44 g, 49% yield) as a microcrystalline, colorless, air-sensitive solid. Anal. Calcd for $C_{12}H_{16}Br_6FeO_6$: C, 18.2; H, 2.0. Found: C, 18.1; H, 2.2. IR (solid state): 3016w, 2973w, 2879w, 1618vs (ν_{as}(COO)), 1406m, 1374 m−s (ν_s(COO)), 1193m, 1159m, 1039s (ν_{as}(C−O−C), THF), 918w, 881m (ν_s(C−O−C), THF), 700s, 691s cm^{-1}

1E. $Fe(CHBr_2COO)_2(THF)$, 9. Experimental procedures as in section 1D; reaction time 20 h. Compound was a microcrystalline, colorless, air-sensitive solid (74% yield from $CHBr_2COOH$ and **5**). Anal. Calcd for $C_8H_{10}Br_4FeO_5$: C, 17.1; H, 1.8. Found: C, 17.6; H, 2.1. IR (solid state): 3019w, 2964w, 2889w, 1616vs (ν_{as}(COO)), 1405m, 1372m−s (ν_s(COO)), 1194m, 1159m, 1036s (ν_{as}(C−O−C), THF), 918w, 877m (ν_s(C−O−C), THF), 807m, 690vs cm^{-1}.

2. Reactivity of $Fe(CH_{3-n}X_nCOO)_2$ Complexes. 2A. Preparation of $[Fe_3(\mu_3\text{-}O)(CBr_3COO)_6(THF)_3][FeBr_4]$, 10. A solution of **8** (0.80 g, 1.0 mmol) in THF (40 mL) was stirred for 48 h at room temperature. A GC-MS analysis was carried out on an aliquot of the final reaction mixture; the analysis revealed the presence of $CH_2BrCOOH$, CBr_4, CBr_3H, and CBr_2H_2. The volume of the remaining solution was reduced to ca. 5 mL in vacuo at room temperature; addition of heptane (30 mL) allowed the isolation of **10** (0.18 g, 39% yield) as an orange microcrystalline solid which could be recrystallized from CH_2Cl_2 layered with diethyl ether, at room temperature. Anal. Calcd for $C_{24}H_{24}Br_{22}Fe_4O_{16}$: C, 11.3; H, 0.9. Found: C, 11.5; H, 1.1. IR (solid state): 2420w, 1631s (ν_{as}(COO)), 1400s (ν_s(COO)), 1230m, 1226m−s, 1091m, 1023m−s (ν_{as}(C−O−C), THF), 938m, 876m (ν_s(C−O−C), THF), 841vs, 726s, 679vs cm^{-1}.

2B. Preparation of $Fe_3(\mu_3\text{-}O)(CCl_3COO)_6(THF)_3$, 11. Experimental procedures as in section 2A; reaction time 72 h. Compound was a microcrystalline red solid (40% yield from **7**). GC-MS analysis: CCl_4, CCl_3H, CH_2Cl_2. Crystals suitable for X-ray analysis were obtained at room temperature from a THF solution layered with diethyl ether. Anal. Calcd for $C_{24}H_{24}Cl_{18}Fe_3O_{16}$: C, 21.0; H, 1.8. Found: C, 20.8; H, 2.0. IR (solid state): 2394w, 2901vw, 1657s (ν_{as}(COO)), 1396vs (ν_s(COO)), 1261m, 1226m−s, 1091m, 1023m−s (ν_{as}(C−O−C), THF), 957w−m, 873m (ν_s(C−O−C), THF), 819s, 795s, 711s, 674vs cm^{-1}.

The same product was obtained by reaction of **5** with excess CCl_3COOH in THF solution.

2C. Preparation of $[Fe_3(\mu_3\text{-}O)(CH_3COO)_5(CBr_3COO)(THF)_3][FeBr_4]$, 12. To a solution of CBr_3COOH (1.21 g, 4.07 mmol) in THF (15 mL), **5** (0.280 g, 1.61 mmol) was added. The mixture was stirred for 12 h at room temperature. A GC-MS analysis of the final solution revealed the presence of CBr_3COOH (unreacted), CBr_4, CBr_3H, CBr_2H_2, and $CH_2BrCOOH$. The solvent was removed in vacuo, and the residue was dissolved in THF (5 mL). The solution was layered with heptane, obtaining **12** (0.275 g, 50% yield) as a microcrystalline orange powder after standing at room temperature for 2 days. Anal. Calcd for $C_{24}H_{39}Br_7Fe_4O_{16}$: C, 21.1; H, 2.9. Found: C, 20.7; H, 2.7. IR (solid state): 2984w, 1588vs (ν_{as}(COO)), 1439vs (ν_s(COO)), 1411vs (ν_s(COO)), 1343m−s, 1045m, 1024m−s (ν_{as}(C−O−C), THF), 870s (ν_s(C−O−C), THF), 655ms cm^{-1}.

2D. Preparation of $Fe_3(\mu_3\text{-}O)(CCl_3COO)_6(DMF)(THF)_2$, 13. To a solution of CCl_3COOH (1.31 g, 8.02 mmol) in THF (20 mL), **1**·DMF (0.950 g, 2.68 mmol) was added. The mixture was stirred for 18 h at room temperature. A GC-MS analysis of the solution revealed the presence of CF_3COOH, CCl_3COOH (unreacted), CCl_4, CCl_3H, CCl_2H_2, and $CHCl_2COOH$. The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2 (5 mL). The solution was layered with diethyl ether and pentane, obtaining **13** (0.630 g, 51% yield) as a microcrystalline red powder after standing at ca. −20 °C for 3 days. Anal. Calcd for $C_{23}H_{23}Cl_{18}Fe_3NO_{16}$: C, 20.1; H, 1.7; N, 1.0. Found: C, 19.7; H, 2.9; N, 0.9. IR (solid state): 2982w, 2891w, 1704m, 1678s (ν_{as}(C−O), DMF), 1650vs (ν_{as}(COO)), 1488w, 1429w, 1359vs (ν_s(COO)), 1259w, 1114w, 1027m (ν_{as}(C−O−C), THF), 963w, 918w, 872m (ν_s(C−O−C), THF), 848vs, 834vs, 741s, 676vs cm^{-1}.

2E. Preparation of $[Fe_3(\mu_3\text{-}O)(CH_2BrCOO)_6(THF)_3][FeBr_4]$, 14. Experimental procedures as in section 2C; reaction time 7 days. Orange microcrystalline powder was obtained by layering the final reaction mixture with heptane, at room temperature (28% yield from **5** and excess $CH_2BrCOOH$). GC-MS analysis of the reaction mixture: CH_3COOH, $CH_2BrCOOH$ (unreacted), CBr_4, CBr_3H, CBr_2H_2. Anal. Calcd for $C_{24}H_{36}Br_{10}Fe_4O_{16}$: C, 18.0; H, 2.3. Found: C, 18.3; H, 2.0. IR (solid state): 3012w, 2962w, 1615s (ν_{as}(COO)), 1552sh,m, 1537sh,m, 1398sh,vs, 1372vs (ν_s(COO)), 1259w, 1191m−w, 1114w, 1025w (ν_{as}(C−O−C), THF), 950w, 859m (ν_s(C−O−C), THF), 796m−w, 689vs, 661s cm^{-1}.

2F. Preparation of *cis*-$[Fe(DMF)_4(THF)_2][FeBr_4]_2$, 15. Experimental procedure as in section 2C; reaction time 18 h. A microcrystalline red solid (53% yield from **1**·DMF and excess CBr_3COOH) was obtained. Crystals suitable for X-ray analysis were obtained at room temperature from a THF solution layered with diethyl ether. GC-MS analysis of the reaction mixture: CF_3COOH, CBr_3COOH (unreacted), CBr_4, CBr_3H, CBr_2H_2. Anal. Calcd for $C_{20}H_{44}Br_8Fe_3N_4O_6$: C, 19.3; H, 3.6. Found: C, 18.7; H, 3.4. IR (solid state): 2964w, 2936w, 2890w, 1672s,sh (ν_{as}(C−O), DMF), 1644vs (ν_{as}(COO)), 1493w, 1434m−w, 1362m (ν_s(COO)), 1260m, 1110m, 1028m−s (ν_{as}(C−O−C), THF), 872m−w (ν_s(C−O−C), THF), 798m−s, 685m cm^{-1}.

X-ray Crystallography. Relevant crystal parameters and details of structure solutions of $[Fe(CF_3COOH)_2(\mu\text{-}CF_3COO)_2]_n$, **2**, and *cis*-$[Fe(DMF)_4(THF)_2][FeBr_4]_2$, **15**, are listed in Table 1. The diffraction experiments were carried out on a Bruker Apex II diffractometer, equipped with a CCD detector using Mo Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[8] The structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[9] Non-hydrogen atoms were refined anisotropically, unless otherwise stated. H atoms were placed in calculated positions and refined by a riding model. Crystals of **2** show some nonmerohedral twinning. Despite different attempts to take this into account during data processing, the *R* values for

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(8) Sheldrick, G. M. *SADABS*, Program for empirical absorption correction; University of Göttingen: Göttingen, Germany, 1996.

(9) Sheldrick, G. M. *SHELX97*, Program for crystal structure determination; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Crystal Data and Details of the Structure Refinement for Compounds **2** and **15**[a]

	compound	
	2	**15**
formula	$C_8H_2F_{12}FeO_8$	$C_{20}H_{44}Br_8Fe_3N_4O_6$
mol wt	509.95	1243.42
T, K	100(2)	293(2)
radiation	Mo Kα	
cryst syst	triclinic	monoclinic
space group (no.)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a, Å	8.5335(17)	20.253(2)
b, Å	9.829(2)	12.0930(13)
c, Å	11.004(2)	35.505(4)
α, deg	114.74(3)	
β, deg	98.09(3)	91.396(2)
γ, deg	90.31(3)	
V, Å^3	827.9(3)	8693.4(17)
Z	2	8
ρ_{calc}, g cm^{-3}	2.046	1.900
μ, mm^{-1}	1.078	8.374
data/restr/params	2865/132/262	6033/482/358
$R(F_o)$ [$I > 2\sigma(I)$]	0.1123	0.0988
$R_w(F_o^2)$	0.2997	0.2675
GOF	1.051	1.029

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; GOF $= [\sum[w(F_o^2 - F_c^2)^2]/(N - P)]^{1/2}$, where N and P are the number of observations and parameters, respectively.

this structure remain quite large. The two THF and two of the four DMF ligands in **15** are disordered. Disordered atomic positions were split and refined using one occupancy parameter per disordered group.

Results and Discussion

Being interested in studying the reactivity of iron(II) halocarboxylates, we decided to use the recently described trifluoroacetate $Fe(CF_3COO)_2$, which can be prepared[3] as the trifluoroacetic acid adduct, $Fe(CF_3COO)_2(CF_3COOH)_x$, by photolysis of $Fe(CO)_5$ in $CF_3COOH/(CF_3CO)_2O$ mixtures at room temperature. Alternatively, $Fe(CF_3COO)_2(DMF)_n$ is obtained by thermal treatment of $Fe(CO)_5$ in DMF, in the presence of a slight excess of CF_3COOH.[3] The photochemical reaction was used at the beginning of the research, but later we moved to the thermal reaction due to the fact that the latter allowed the preparation of larger amounts of product: 35−40 g of $Fe(CF_3COO)_2(DMF)_n$ can generally be obtained in one run.

While preparing the iron(II) trifluoroacetate by the photochemical approach, we obtained single crystals of compound **2** directly from the mother liquor; the crystal structure has been solved and a view of the structure is reported in Figure 1. Compound **2** is polynuclear; the infinite polymer contains distorted octahedral iron atoms (Fe···Fe distance, 4.762(4) Å), each coordinated to two monodentate CF_3COOH (mean value of the Fe−O distance, 2.214 Å) and four bridging $[CF_3COO]^-$ ligands (mean value of the Fe−O distance, 2.101 Å). The two CF_3COOH groups are in relative cis-position and, as a consequence, the polymeric chain contains nearly orthogonal $Fe_2(\mu\text{-}CF_3COO)_2$ eight-membered rings connected by the iron atoms. Table 2 reports a selection of bond distance and angles.

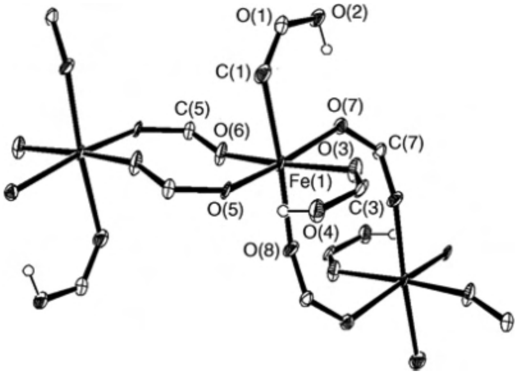

Figure 1. View of the polynuclear chain of **2**. Thermal ellipsoids are at 30% probability. The CF_3 groups have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **2**

Fe(1)−O(1)	2.219(8)	Fe(1)−O(6)	2.072(8)
Fe(1)−O(3)	2.210(8)	Fe(1)−O(7)	2.116(7)
Fe(1)−O(5)	2.123(7)	Fe(1)−O(8)	2.092(8)
O(6)−Fe(1)−O(8)	90.8(4)	O(7)−Fe(1)−O(3)	84.2(3)
O(6)−Fe(1)−O(7)	89.8(3)	O(5)−Fe(1)−O(3)	84.9(3)
O(8)−Fe(1)−O(7)	100.4(3)	O(6)−Fe(1)−O(1)	90.1(3)
O(6)−Fe(1)−O(5)	100.9(3)	O(8)−Fe(1)−O(1)	174.2(3)
O(8)−Fe(1)−O(5)	89.6(3)	O(7)−Fe(1)−O(1)	85.3(3)
O(7)−Fe(1)−O(5)	165.3(3)	O(5)−Fe(1)−O(1)	84.6(3)
O(6)−Fe(1)−O(3)	174.0(3)	O(3)−Fe(1)−O(1)	89.1(3)
O(8)−Fe(1)−O(3)	90.6(3)		

Within the coordinated CF_3COOH ligands, two different C−O bond distances are present: a shorter one (C(1)−O(1) 1.262(14) and C(3)−O(3) 1.217(14) Å) and a longer one corresponding to the C(1)−O(2) and C(3)−O(4) single bonds (1.303(14) and 1.323(14) Å, respectively). Intramolecular hydrogen bonds exist between the hydroxyl group of coordinated CF_3COOH and the oxygen atoms of the bridging $[CF_3COO]^-$ anions, the distances of O(2)···O(7) and O(4)···O(5) being 2.685(11) and 2.656(11) Å, respectively. Similar distances (2.734, 2.62, 2.642(5), 2.614, and 2.632 Å) were observed in $Cu_2(CX_3COO)_4(CX_3COOH)_2$, X = Cl,[4a] H;[5g] $M(RCOO)_4(RCOOH)_2$, M = Cr, R = CH_3;[5f] M = Ru, R = C_6H_5;[5c] M = Ru, R = C_6H_5.[5c] The elongation of the Fe(1)−O(5) and Fe(1)−O(7) bonds (2.119 Å, mean value) with respect to Fe(1)−O(6) and of the Fe(1)−O(8) bond (2.082 Å, mean value) is probably a consequence of the cited hydrogen bond.

Due to the easy loss of DMF followed by crystal breakdown, we have not been able to study the DMF adduct by X-ray crystallography. Nevertheless, on the basis of the solubility data (the compound is very soluble in DMF, slightly soluble in THF, and almost insoluble in toluene) and the molecular structure of the trifluoroacetic acid adduct, the hypothesis has been put forward that $Fe(CF_3COO)_2(DMF)_n$ is a polynuclear compound containing bridging trifluoroacetates and axial DMF groups.

During the large scale, thermal preparations of iron(II) trifluoroacetate, we obtained variable yields (depending on the reaction conditions) of another iron(II) derivative, probably a polynuclear compound at present under study, which can be separated from $Fe(CF_3COO)_2(DMF)_n$ by washing the raw material with THF (see Experimental Section).

Iron(II) trifluoroacetate is rather air sensitive: when a colorless solution of **1**·DMF in THF is exposed to dry O_2, red and black crystals are obtained by layering the solution with heptane. These were carefully separated under a microscope and characterized analytically, spectroscopically, and by X-ray diffraction (see Supporting Information). The black crystals consist of the trinuclear compound $Fe_3(\mu_3\text{-}O)(CF_3COO)_6(DMF)_3$, **3**, and the red crystals are the tetranuclear $Fe_4(\mu_3\text{-}O)_2(\mu_2\text{-}CF_3COO)_6(CF_3COO)_2(DMF)_4$ derivative, **4**, both of them possessing several similar structural types in the literature.[10-12] According to gas-volumetric results (a dioxygen uptake up to a O_2/Fe molar ratio of 0.22 was observed within 3 h), the oxidation of $Fe(CF_3COO)_2\cdot DMF$ is quantitative and likely to proceed according to eq 1.

$$14Fe(CF_3COO)_2\cdot DMF + 3O_2 \rightarrow \underset{\mathbf{3}}{2Fe_3(\mu_3\text{-}O)(CF_3COO)_6(DMF)_3} + \underset{\mathbf{4}}{2Fe_4(\mu_3\text{-}O)_2(\mu_2\text{-}CF_3COO)_6(CF_3COO)_2(DMF)_4} \quad (1)$$

In agreement with the existence of two types of trifluoroacetato ligands (monodentate and bidentate bridging) in **4**, the IR spectrum shows two COO asymmetric stretching vibrations at 1713 (monodentate) and 1637 cm^{-1} (bridging bidentate).[1,13] The two bands at 1466 and 1416 cm^{-1} can be attributed to the COO symmetric stretching vibrations.

Carboxylato Exchange Reactions. Due to the large availability of $Fe(CF_3COO)_2(DMF)_n$, it was decided to use this compound as starting material for the preparation of other halocarboxylates of iron(II). Unfortunately, the reaction reported in eq 2 gives only low conversion to the exchange product, which is gained if the reaction mixture is evaporated in vacuo to remove the volatile CF_3COOH eventually formed in the reaction.

$$Fe(CF_3COO)_2(DMF)_n + 2CX_3COOH \rightarrow Fe(CX_3COO)_2 + 2CF_3COOH + n\text{DMF} \quad (2)$$

$$X = H, Cl$$

As a confirmation of this observation, iron(II) trifluoroacetate is easily obtained by the reverse of the reaction reported in eq 2, i.e., the reaction of iron(II) acetate **5** with trifluoroacetic acid.

Although reactions using trifluoroacetates as starting materials have been used for the preparation of haloacetates of copper(I),[4b] the experimental observation in the case of iron(II) can be explained when considering that the driving force of the reaction is probably the O−H bond energy of the acid product and that the acid strength of the carboxylic acids in water increases on increasing the electronegativity of the halo substituents on the α-position.[14] It has to be noted that $Zn(CF_3SO_3)_2(DME)_2$ was prepared from $Zn(CF_3COO)_2(DME)_2$ and the stoichiometric amount of CF_3SO_3H.[15]

The less soluble but still largely available iron(II) acetate, $Fe(CH_3COO)_2$, **5**,[6] was then used as starting material. Due to its 3D extended structure,[16] iron(II) acetate is less soluble in THF than the trifluoroacetate, but it is still reactive to undergo full exchange (see eq 3) after some hours of stirring at room temperature in the presence of the appropriate haloacetic acid.

$$Fe(CH_3COO)_2 + 2CX_3COOH \rightarrow Fe(CX_3COO)_2 + 2CH_3COOH \quad (3)$$

$$CX_3 = CF_3, CHCl_2, CCl_3, CBr_3, CHBr_2$$

The haloacetates of iron(II) are colorless crystalline solids, sensitive to air in the solid state, and slowly decompose on standing in solution at room temperature, this decomposition being faster on increasing the number and the atomic weight of the halogen in the α-position, vide infra. IR spectra are characterized by the strong C═O stretching absorptions in the 1700−1600 cm^{-1} region, assigned to the carboxylate asymmetric vibration and the medium-to-strong C═O symmetric bands in the 1460−1370 cm^{-1} region, thus suggesting the presence of bidentate carboxylates.[13] Bands typical of the $CH_{3-n}X_n$ (X = F, Cl, Br) groups are observed in the low region of the spectrum, their positions dependent on the atomic weight of the halogen, together with the asymmetric and symmetric absorptions due to coordinated THF.

It is interesting to note that the solid haloacetates have been isolated with variable amounts of THF, as suggested by elemental analyses: generally we found a THF/Fe molar ratio of 1:1 in the microcrystalline solids after 2 h of drying in vacuo at room temperature. In one occasion, the solid compound was dried for a shorter time and the bis-THF adduct $Fe(CBr_3COO)_2(THF)_2$, **8**, was obtained. By taking into consideration that the solid structure of **2** shows two bridging acetates and two axially coordinated trifluoroacetic acid groups, we propose that the solid haloacetates have the $Fe(CX_3COO)_2(THF)_2$ composition; the axial THF can be partially lost during the drying procedure.

Reactivity of Iron(II) Chloro- and Bromoacetates. Compounds **6**−**9** are not stable in THF: their colorless solutions turn deep red with kinetics dependent on the temperature (the reaction is faster at the boiling point of the

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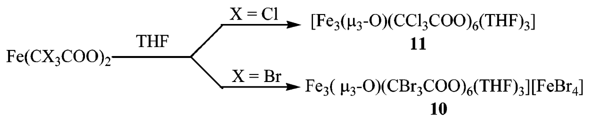
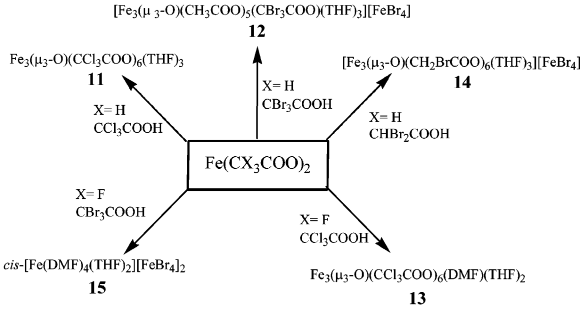
Scheme 1



Scheme 2



mixture rather than at room temperature), the nature of the halogen (compound **8** decomposes faster than **9**), the number of halogens (the rate of decomposition increases according to the sequence $CH_3 < CH_2X < CHX_2 \ll CX_3$), and the quantity of residual acid employed in the synthesis (the decomposition reaction is accelerated by the presence of excess acid). Reactions are accompanied by formation of CX_4, CX_3H, CX_2H_2 (X = Cl, Br), and of $CH_2BrCOOH$ or $CHCl_2COOH$ in the case of $CX_3 = CBr_3, CCl_3$, respectively, which have been detected by GC-MS analyses carried out on the reaction mixtures.

Dark red solid residues have been obtained upon removal of the solvent. Although complicated mixtures of products have been obtained from **6** and **9**, the compounds $Fe_3(\mu_3\text{-}O)(CCl_3COO)_6(THF)_3$, **11**, and $[Fe_3(\mu_3\text{-}O)(CBr_3COO)_6(THF)_3][FeBr_4]$, **10**, have been isolated in satisfactory yields (Scheme 1) and characterized by elemental analysis, IR spectroscopy, and X-ray diffraction[17] (the crystal structure of compound **11** is reported as Supporting Information) in the cases of **7** and **8**.

The experimental evidence described above points out that the degradation of iron(II) chloro- and bromoacetates is a complicated process which includes C−X bond activation, redox exchanges involving the metal centers (see the formation of the $[FeBr_4]^-$ anion and the presence of Fe(III) in the final products), and decomposition of the haloacetate ions (see formation of organohalides). The latter process is likely to supply the oxygen atom required for the formation of the μ-oxo-centered products.[18] It is noticeable that decomposition of CX_3COOH (X = Br, Cl) occurs at considerable rates, in solution, only at high temperatures.[19] In other words, the degradation of iron(II) chloro- and bromoacetates, in inert atmosphere, represents an alternative route to the synthesis, although in lower yields, of mixed-valence, tri-iron, oxo-centered compounds, analogous to that reported in the previous section, which is prepared by direct oxidation of iron(II) trifluoroacetate with dioxygen.

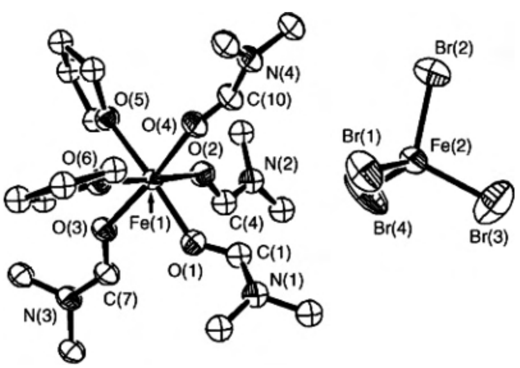


Figure 2. View of the structure of **15**. Only one [FeBr4]$^-$ anion has been reported. Thermal ellipsoids are at 20% probability.

To investigate this point further, we decided to consider the reaction of the acetate **5** or, alternatively, of the trifluoroacetate, **1**·DMF, with a slight excess of CX_3COOH ($CX_3 = CCl_3, CBr_3, CH_2Br$), in THF solution over longer periods of time.

By operating under these conditions, we have found that **5** reacts with CCl_3COOH or CBr_3COOH, yielding **11** or $[Fe_3(\mu_3\text{-}O)(CH_3COO)_5(CBr_3COO)(THF)_3][FeBr_4]$, **12**, respectively (see Scheme 2), coherent with results found for the decomposition of **7** and **8**. The presence of two types of carboxylates in **12** is proposed on the basis of the IR spectrum in the 1800−1500 cm^{-1} region, which contains bands assigned to the asymmetric and symmetric vibrations of the two $[RCOO]^-$ groups. The reactions of **1**·DMF with CCl_3COOH and of **5** with $CH_2BrCOOH$ give similar outcomes, resulting in formation of the trinuclear complexes $[Fe_3(\mu_3\text{-}O)(CCl_3COO)_6(DMF)(THF)_2]$, **13**, and $[Fe_3(\mu_3\text{-}O)(CH_2BrCOO)_6(THF)_3][FeBr_4]$, **14**, respectively, characterized by IR spectroscopy and elemental analysis.

Surprisingly, the reaction of **1**·DMF with excess CBr_3COOH affords a compound not containing carboxylates. It has been identified by X-ray diffraction as the ionic $Fe^{(II)}/Fe^{(III)}$ derivative *cis*-$[Fe(DMF)_4(THF)_2][FeBr_4]_2$, **15** (see Figure 2); a selection of bond distances and angles is reported in Table 3. The compound consists of two nearly tetrahedral $[FeBr_4]^-$ anions and one *cis*-$[Fe(DMF)_4(THF)_2]^{2+}$ dication, which possesses a slightly distorted octahedral geometry (O_{axial}−Fe−$O_{equatorial}$, 90.7°, mean value; $O_{equatorial}$−Fe−$O_{equatorial}$, 175.9°). The ligands coordinated to the dication are disordered around their Fe−O bonding vector and, in particular, both the THF ligands and two of the four DMF ligands have been split into two positions. Rotational disorder is also displayed by the two $[FeBr_4]^-$ anions for which the bromide ligands show high thermal ellipsoids. Two sets of significantly different Fe−O bond distances are observed:

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(17) Low quality crystals have been obtained for the product obtained from **10** in THF. Crystal data: rhombohedral, *R*3, $a = 15.86(2)$ Å, $c = 14.14(4)$ Å. Due to the low quality of the diffraction pattern, it has not been possible to fully solve and refine the structure. Nonetheless, there is evidence for the presence in the unit cell of three $[FeBr_4]^-$ anions and three $[Fe_3(\mu_3\text{-}O)(CX_3COO)_6L_3]^+$ cations. The nature of X and L has not been determined.

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Table 3. Selected Bond Distances (Å) and Angles (deg) for **15**

Fe(1)−O(1)	2.101(13)	Fe(1)−O(4)	2.061(13)
Fe(1)−O(2)	2.105(13)	Fe(1)−O(5)	2.177(12)
Fe(1)−O(3)	2.076(12)	Fe(1)−O(6)	2.146(12)
Fe(2)−Br(1)	2.307(4)	Fe(2)−Br(3)	2.285(6)
Fe(2)−Br(2)	2.319(5)	Fe(2)−Br(4)	2.292(5)
Fe(3)−Br(5)	2.306(4)	Fe(3)−Br(7)	2.327(4)
Fe(3)−Br(6)	2.314(4)	Fe(3)−Br(8)	2.309(4)
O(4)−Fe(1)−O(3)	173.9(6)	O(6)−Fe(1)−O(5)	89.8(5)
O(4)−Fe(1)−O(1)	92.8(6)	Br(3)−Fe(2)−Br(4)	109.5(3)
O(3)−Fe(1)−O(1)	91.2(5)	Br(3)−Fe(2)−Br(1)	111.9(2)
O(4)−Fe(1)−O(2)	91.4(6)	Br(4)−Fe(2)−Br(1)	108.86(19)
O(3)−Fe(1)−O(2)	92.8(6)	Br(3)−Fe(2)−Br(2)	106.1(2)
O(1)−Fe(1)−O(2)	93.4(5)	Br(4)−Fe(2)−Br(2)	110.8(2)
O(4)−Fe(1)−O(6)	86.8(5)	Br(1)−Fe(2)−Br(2)	109.62(19)
O(3)−Fe(1)−O(6)	88.8(5)	Br(5)−Fe(3)−Br(8)	109.56(19)
O(1)−Fe(1)−O(6)	88.3(5)	Br(5)−Fe(3)−Br(6)	108.20(17)
O(2)−Fe(1)−O(6)	177.6(5)	Br(8)−Fe(3)−Br(6)	110.33(18)
O(4)−Fe(1)−O(5)	89.5(6)	Br(5)−Fe(3)−Br(7)	111.35(17)
O(3)−Fe(1)−O(5)	86.3(5)	Br(8)−Fe(3)−Br(7)	109.37(18)
O(1)−Fe(1)−O(5)	176.9(5)	Br(6)−Fe(3)−Br(7)	108.02(17)
O(2)−Fe(1)−O(5)	88.6(5)		

the Fe−O$_{THF}$ distance is 2.161 Å (mean value) compared with the Fe−O$_{DMF}$ distance of 2.085 Å (mean value). The overall geometry of the $[Fe(DMF)_4(THF)_2]^{2+}$ cation resembles that reported in the literature for iron(II) cations of general formula $[FeL_6]^{2+}$, which are well-known for L = DMF[20] and L = THF.[21]

As far as the $[FeBr_4]^-$ anion is concerned, the mean value of the Fe−Br distances (2.307 Å) is in the same range observed for $[p\text{-}EtC_5H_5NH][FeBr_4]$,[22] $[(N,N'\text{-}CH_3)_2C_4H_8]][FeBr_4]_2$,[23] $[Fe(\eta^5\text{-}C_5H_5)_2][FeBr_4]$,[24] $[(Ph_3PO)_2H][FeBr_4]$,[25] and $[Mo(\eta^5\text{-}C_6H_6)_2][FeBr_4]$.[26]

A GC-MS control, performed on solutions at the end of each reaction, indicated the presence of CX_3COOH (X = H, F). This fact suggests that acetate (or trifluoroacetate) exchange has probably occurred, followed by degradation of the formed iron(II) haloacetate. GC-MS detection of the organohalides CX_4, CX_3H, and CX_2H_2 (X = Br, Cl), oxidation of the iron atoms, and C−X bond activation are in agreement with this hypothesis.

Conclusions

By crystallization from $CF_3COOH/(CF_3CO)_2O$, the polymer $[Fe(CF_3COO)_2(CF_3COOH)_2]_n$ has been isolated and characterized by X-ray diffraction: it contains bridging trifluoroacetates and monodentate trifluoroacetic acid groups and adds to the restricted family of structurally characterized compounds containing both a coordinated carboxylic acid and its conjugate base.[4,5]

Iron(II) acetates are good starting material for the preparation of different halocarboxylates by exchange reactions. The resulting species are not stable in THF solution and decompose affording, inter alia, mononuclear and trinuclear μ_3-oxo complexes. Although the differences in the product types, i.e., mononuclear or trinuclear, cationic or neutral, are not easy to rationalize, the experimental results evidence the low tendency of the tribromoacetate anion to act as a ligand and the fact that extensive oxidation of the metal centers is favored by those haloacetates containing the heavier halide.

Analogous results can be achieved by reacting iron(II) acetate (or trifluoroacetate) with haloacetic acids. All of these reactions are accelerated upon increasing the following parameters of (i) temperature, (ii) atomic weight of the halogen on the α-carbon atom, (iii) number of halogens ($CH_3 < CH_2X < CHX_2 \ll CX_3$), and (iv) quantity of acid employed. The nature of the isolated compounds strongly suggests that the decompositions occur via C−X bond activation and haloacetato degradation and that these processes are accompanied by concomitant oxidation at the metal centers. This hypothesis is confirmed by the detection of various organohalide species in the final solutions. Similar arguments were invoked to explain the instability of some copper(I) haloacetates.[4]

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Supporting Information Available: Crystallographic information files (CIF) for the crystal structures of compounds **2**, **3**, **4**, **11**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data of compounds **2** (CCDC 634719), **3** (CCDC 634718), **4** (CCDC 634717), **11** (CCDC 634716), and **15** (CCDC 634715) have been deposited with the Cambridge Crystallographic Data Centre. Copies can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax, 441223336033; e-mail, deposit@ccdc.cam.ac.uk; or WWW, http://www.ccdc.cam.ac.uk).

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