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Crystal and Molecular Structure of the Trinuclear Chromium(III) and Iron(III) Complex, [Cr₂FeO(CH₃COO)₆(H₂O)₃]NO₃.CH₃COOH

By T. Głowiak, M. Kubiak, T. Szymańska-Buzar and B. Jeżowska-Trzebiatowska

Institute of Chemistry, University of Wrocław, 50-383 Wrocław, Poland

[Cr₂FeO(CH₃COO)₆(H₂O)₃]NO₃.CH₃COOH is monoclinic, space group $P2_1/c$, with $a = 11.774$ (1), $b = 14.706$ (2), $c = 15.157$ (2) Å, $\beta = 90.70$ (1)°, $Z = 4$. The structure was refined to $R = 0.061$ with 2516 counter reflexions, for which $F > 3.92\sigma(F)$. The cation possesses idealized D_{3h} symmetry with the O in the centre of an equilateral triangle.

Introduction

Trinuclear coordination compounds containing three antiferromagnetically coupled Cr or Fe ions have recently been investigated theoretically and experimentally. Neither the mechanism of unpaired electron-spin interactions nor the factors affecting the magnitudes of these interactions have been established. For an interpretation of the magnetic properties in this group of compounds studies on mixed complexes with Cr₂FeO or Fe₂CrO groups, in which the ions of different electron configurations are coupled simultaneously, are important. Such compounds have been isolated (Weinland & Gussman, 1909) but only in recent years were they subjected to detailed structural studies.

Magnetic studies (Zelentsov, Zhemchuznikova, Rakitin, Yablokov & Yakubov, 1975) and EPR spectra (Yablokov, Gaponenko, Eremin, Zelentsov & Zhemchuznikova, 1973) confirmed the appearance of pure compounds with nuclei containing two types of metal atoms and showed that exchange interactions between the Fe atoms in mixed complexes are larger than in the Fe₃O group, whereas interpretation of the Cr—Cr interactions is not so well defined.

Measurements of the electronic spectra (Zelentsov, Zhemchuznikova & Lubovskii, 1975) carried out for mixed complexes do not enable any conclusions to be drawn as to the symmetry perturbations of the $M_2M'O$ group or of the nearest environment of each metal atom. In order to determine the structural details of a complex cation containing two types of metal atoms, an

X-ray investigation of the [Cr₂FeO(CH₃COO)₆-(H₂O)₃]NO₃.CH₃COOH complex was carried out.

Experimental

The compound was prepared as described by Zelentsov *et al.* (1975). Dark-red crystals suitable for X-ray studies were obtained by slow evaporation of an acetic acid solution. Weissenberg photographs showed the crystals to be monoclinic with systematic absences 0k0, $k = 2n + 1$ and $h0l$, $l = 2n + 1$, which fix the space group uniquely as $P2_1/c$. Cell parameters were obtained by least squares from the setting angles of 15 reflexions measured on a diffractometer. The density was measured by flotation in a chloroform/bromoform mixture. Crystal data are listed in Table 1.

Intensities from a crystal $0.15 \times 0.15 \times 0.2$ mm were collected with Cu $K\alpha$ radiation on a Syntex $P2_1$ computer-controlled four-circle diffractometer with

Table 1. *Crystal data*

[Cr₂FeO(CH₃COO)₆(H₂O)₃]NO₃.CH₃COOH. FW 706.3
Monoclinic, space group $P2_1/c$

$a = 11.774$ (1)Å	$Z = 4$
$b = 14.706$ (2)	$\lambda(\text{Cu } K\alpha) = 1.5418$ Å
$c = 15.157$ (2)	$D_m = 1.78$ g cm⁻³
$\beta = 90.70$ (1)°	$D_c = 1.77$
$V = 2624$ Å³	$\mu(\text{Cu } K\alpha) = 124$ cm⁻¹

graphite monochromator. 3311 reflexions were collected by the θ–2θ scan technique. 2516 of these with $F >$ $3.92\sigma(F)$ were considered observed and used for subsequent calculations. After each group of 15 reflexions the intensity of a standard was measured and no significant change was observed. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Structure determination and refinement

Features of the present crystals are similar to those of a complex described earlier, $[Rh_3O(CH_3COO)_6(H_2O)_3]$-$ClO_4.2H_2O$ (Głowiak, Kubiak & Szymańska-Buzar, 1977). Similarities were confirmed by comparing Patterson syntheses. The first distribution of electron density was obtained by introducing coordinates of the Rh, bridge O and terminal O atoms from the Rh complex. The positions of other atoms were found from

successive difference syntheses. The Cr and Fe atoms are statistically distributed. Isotropic refinement gave $R = 0.09$. Refinement with anisotropic temperature factors gave $R_1 = 0.063$ and $R_2 = 0.065$ ($R_1 = 0.086$, $R_2 = 0.066$ with unobserved reflexions). The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. All calculations were performed with the Syntex XTL System (Nova 1200 computer and additional external disk memory). The final positional parameters are given in Table 2. Tables 3 and 4 contain the interatomic distances and valence angles. The atom numbering is shown in Fig. 1.*

Description of the structure

The structure of the cation is similar to that in other trinuclear metal compounds (Figgis & Robertson, 1965; Chang & Jeffrey, 1970; Hessel & Romers, 1969; Anzenhofer & De Boer, 1969; Cotton & Norman, 1972; Lis & Jeżowska-Trzebiatowska, 1977; Głowiak, Kubiak & Szymańska-Buzar, 1977). The central O atom lies almost exactly (0.007 Å) in a plane formed by the three metal atoms at about 1.89 Å from each. The average distance between the metal atoms is 3.28 Å.

The O atoms of acetate groups and water molecules complete the octahedral environment of metal atoms.

Table 2. *Final positional parameters with e.s.d.'s in parentheses*

	x	y	z
$M(1)$	0.0962 (1)	0.3953 (1)	0.3730 (1)
$M(2)$	0.3210 (1)	0.2682 (1)	0.4092 (1)
$M(3)$	0.3303 (1)	0.4334 (1)	0.2640 (1)
O_b	0.2491 (5)	0.3658 (4)	0.3493 (4)
$O_t(1)$	−0.0744 (5)	0.4214 (5)	0.4024 (5)
$O_t(2)$	0.3958 (6)	0.1617 (5)	0.4845 (5)
$O_t(3)$	0.4144 (6)	0.5098 (5)	0.1723 (5)
O(1)	0.1230 (6)	0.4040 (6)	0.5046 (5)
O(2)	0.2544 (6)	0.2985 (5)	0.5263 (5)
O(3)	0.0443 (6)	0.2684 (5)	0.3815 (6)
O(4)	0.1960 (6)	0.1793 (5)	0.3846 (5)
O(5)	0.4576 (6)	0.3406 (5)	0.4434 (5)
O(6)	0.4663 (6)	0.4504 (5)	0.3419 (5)
O(7)	0.3996 (6)	0.2167 (5)	0.3067 (5)
O(8)	0.4044 (7)	0.3287 (5)	0.2061 (5)
O(9)	0.2729 (6)	0.5532 (5)	0.3024 (5)
O(10)	0.1116 (6)	0.5297 (5)	0.3723 (6)
O(11)	0.2081 (6)	0.4200 (6)	0.1741 (5)
O(12)	0.0491 (6)	0.3926 (6)	0.2469 (5)
C(1)	0.1838 (10)	0.3548 (8)	0.5543 (8)
C(2)	0.1705 (11)	0.3639 (8)	0.6538 (7)
C(3)	0.0899 (11)	0.1908 (8)	0.3752 (7)
C(4)	0.0131 (10)	0.1105 (8)	0.3582 (8)
C(5)	0.5038 (10)	0.4081 (8)	0.4092 (8)
C(6)	0.6133 (9)	0.4450 (8)	0.4506 (8)
C(7)	0.4289 (9)	0.2492 (9)	0.2328 (9)
C(8)	0.5055 (10)	0.6872 (8)	0.3292 (8)
C(9)	0.1873 (8)	0.5805 (8)	0.3429 (8)
C(10)	0.1708 (10)	0.6818 (8)	0.3584 (9)
C(11)	0.1050 (10)	0.3990 (8)	0.1775 (8)
C(12)	0.0449 (10)	0.3796 (9)	0.0901 (7)
N	0.7188 (11)	0.2354 (8)	0.3816 (8)
$O_N(1)$	−0.3256 (9)	0.1611 (6)	0.4060 (6)
$O_N(2)$	−0.3133 (9)	0.2761 (7)	0.3150 (7)
$O_N(3)$	−0.2075 (7)	0.2692 (6)	0.4321 (7)
$O_{ac}(1)$	0.7553 (7)	0.1002 (7)	0.5560 (6)
$O_{ac}(2)$	0.5762 (7)	0.0629 (6)	0.5697 (6)
$C_{ac}(1)$	0.6720 (11)	0.0645 (9)	0.6026 (10)
$C_{ac}(2)$	0.7037 (11)	0.0282 (9)	0.6913 (8)

Table 3. *Interatomic distances* (Å)

$M(1)$–O_b	1.891 (6)	C(5)–C(6)	1.527 (16)
$M(1)$–O(1)	2.021 (8)	C(7)–O(7)	1.269 (15)
$M(1)$–O(3)	1.969 (8)	C(7)–O(8)	1.270 (15)
$M(1)$–O(10)	1.984 (8)	C(7)–C(8)	1.526 (17)
$M(1)$–O(12)	1.983 (8)	C(9)–O(9)	1.252 (14)
$M(1)$–$O_t(1)$	2.099 (7)	C(9)–O(10)	1.250 (14)
$M(2)$–O_b	1.892 (7)	C(9)–C(10)	1.522 (14)
$M(2)$–O(2)	1.999 (7)	C(11)–O(11)	1.254 (14)
$M(2)$–O(4)	2.000 (8)	C(11)–O(12)	1.251 (14)
$M(2)$–O(5)	1.992 (8)	C(11)–C(12)	1.522 (17)
$M(2)$–O(7)	1.971 (8)	N–$O_N(1)$	1.269 (16)
$M(2)$–$O_t(2)$	2.124 (7)	N–$O_N(2)$	1.230 (16)
$M(3)$–O_b	1.899 (7)	N–$O_N(3)$	1.253 (16)
$M(3)$–O(6)	1.994 (8)	$C_{ac}(1)$–$O_{ac}(1)$	1.324 (16)
$M(3)$–O(8)	1.979 (8)	$C_{ac}(1)$–$O_{ac}(2)$	1.228 (16)
$M(3)$–O(9)	1.977 (7)	$C_{ac}(1)$–$C_{ac}(2)$	1.490 (19)
$M(3)$–O(11)	1.980 (8)	$M(1)\cdots M(2)$	3.281 (2)
$M(3)$–$O_t(3)$	2.051 (8)	$M(1)\cdots M(3)$	3.279 (2)
C(1)–O(1)	1.261 (15)	$M(2)\cdots M(3)$	3.281 (2)
C(1)–O(2)	1.251 (14)	$O(1)\cdots O(2)$	2.213 (11)
C(1)–C(2)	1.523 (17)	$O(3)\cdots O(4)$	2.215 (14)
C(3)–O(3)	1.265 (15)	$O(5)\cdots O(6)$	2.233 (11)
C(3)–O(4)	1.267 (15)	$O(7)\cdots O(8)$	2.246 (11)
C(3)–C(4)	1.507 (17)	$O(9)\cdots O(10)$	2.213 (11)
C(5)–O(5)	1.248 (14)	$O(11)\cdots O(12)$	2.222 (11)
C(5)–O(6)	1.269 (14)	$O_{ac}(1)\cdots O_{ac}(2)$	2.191 (12)

Table 4. *Bond angles* (°)

|							
M(1)—O$_b$—M(2)	120·3 (3)	O$_b$—M(2)—O$_t$(2)	176·0 (3)	O(2)—M(2)—O(5)	88·5 (3)	M(1)—O(3)—C(3)	135·9 (8)
M(1)—O$_b$—M(3)	119·8 (3)	O$_t$(2)—M(2)—O(2)	81·5 (3)	O(2)—M(2)—O(7)	168·3 (3)	M(2)—O(4)—C(3)	131·0 (8)
M(2)—O$_b$—M(3)	119·9 (3)	O$_t$(2)—M(2)—O(4)	85·3 (3)	O(4)—M(2)—O(5)	171·0 (3)	O(6)—C(5)—C(6)	116 (1)
O$_b$—M(1)—O(1)	93·7 (3)	O$_t$(2)—M(2)—O(5)	85·8 (3)	O(4)—M(2)—O(7)	87·3 (3)	O(7)—C(7)—O(8)	124 (1)
O$_b$—M(1)—O(3)	95·2 (3)	M(2)—O(5)—C(5)	132·2 (8)	O(5)—M(2)—O(7)	91·4 (3)	O(7)—C(7)—C(8)	118 (1)
O$_b$—M(1)—O(10)	98·1 (3)	M(3)—O(6)—C(5)	133·1 (8)	O$_b$—M(3)—O(6)	94·0 (3)	O(8)—C(7)—C(8)	118 (1)
O$_b$—M(1)—O(12)	94·0 (3)	M(2)—O(7)—C(7)	133·3 (8)	O$_b$—M(3)—O(8)	97·0 (3)	O(9)—C(9)—O(10)	124 (1)
O$_b$—M(1)—O$_t$(1)	176·9 (3)	M(3)—O(8)—C(7)	132·4 (8)	O$_b$—M(3)—O(9)	95·1 (3)	O(9)—C(9)—C(10)	120 (1)
O$_t$(1)—M(1)—O(1)	85·2 (3)	M(3)—O(9)—C(9)	135·2 (7)	O$_b$—M(3)—O(11)	92·8 (3)	O(10)—C(9)—C(10)	116 (1)
O$_t$(1)—M(1)—O(3)	82·0 (3)	M(1)—O(10)—C(9)	131·5 (8)	O$_b$—M(3)—O$_t$(3)	178·2 (3)	O(11)—C(11)—O(12)	125 (1)
O$_t$(1)—M(1)—O(10)	84·7 (3)	M(3)—O(11)—C(11)	133·7 (8)	O$_t$(3)—M(3)—O(6)	86·7 (3)	O(11)—C(11)—C(12)	117 (1)
O$_t$(1)—M(1)—O(12)	87·2 (3)	M(1)—O(12)—C(11)	131·6 (8)	O$_t$(3)—M(3)—O(8)	84·6 (3)	O(12)—C(11)—C(12)	118 (1)
O(1)—M(1)—O(3)	92·3 (3)	O(1)—C(1)—O(2)	123 (1)	O$_t$(3)—M(3)—O(9)	83·2 (3)		
O(1)—M(1)—O(10)	85·9 (3)	O(1)—C(1)—C(2)	118 (1)	O$_t$(3)—M(3)—O(11)	86·6 (3)	O(1)$_{ac}$—C(1)$_{ac}$—O(2)$_{ac}$	118 (1)
O(1)—M(1)—O(12)	172·3 (3)	O(2)—C(1)—C(2)	118 (1)	O(6)—M(3)—O(8)	90·3 (3)	O(1)$_{ac}$—C(1)$_{ac}$—C(2)$_{ac}$	116 (1)
O(3)—M(1)—O(10)	166·6 (3)	O(3)—C(3)—O(4)	122 (1)	O(6)—M(3)—O(9)	89·4 (3)	O(2)$_{ac}$—C(1)$_{ac}$—C(2)$_{ac}$	125 (1)
O(3)—M(1)—O(12)	87·7 (3)	O(3)—C(3)—C(4)	118 (1)	O(6)—M(3)—O(11)	172·8 (3)		
O(1)—M(1)—O(12)	92·3 (3)	O(4)—C(3)—C(4)	120 (1)	O(8)—M(3)—O(9)	167·8 (3)	O$_N$(1)—N—O$_N$(2)	122 (1)
O$_b$—M(2)—O(2)	94·5 (3)	O(5)—C(5)—O(6)	125 (1)	O(8)—M(3)—O(11)	86·4 (3)	O$_N$(1)—N—O$_N$(3)	117 (1)
O$_b$—M(2)—O(4)	94·7 (3)	O(5)—C(5)—C(6)	119 (1)	O(9)—M(3)—O(11)	92·4 (3)	O$_N$(2)—N—O$_N$(3)	121 (1)
O$_b$—M(2)—O(5)	94·3 (3)	O$_t$(2)—M(2)—O(7)	86·8 (3)	M(1)—O(1)—C(1)	129·4 (8)		
O$_b$—M(2)—O(7)	97·2 (3)	O(2)—M(2)—O(4)	90·9 (3)	M(2)—O(2)—C(1)	135·9 (8)		
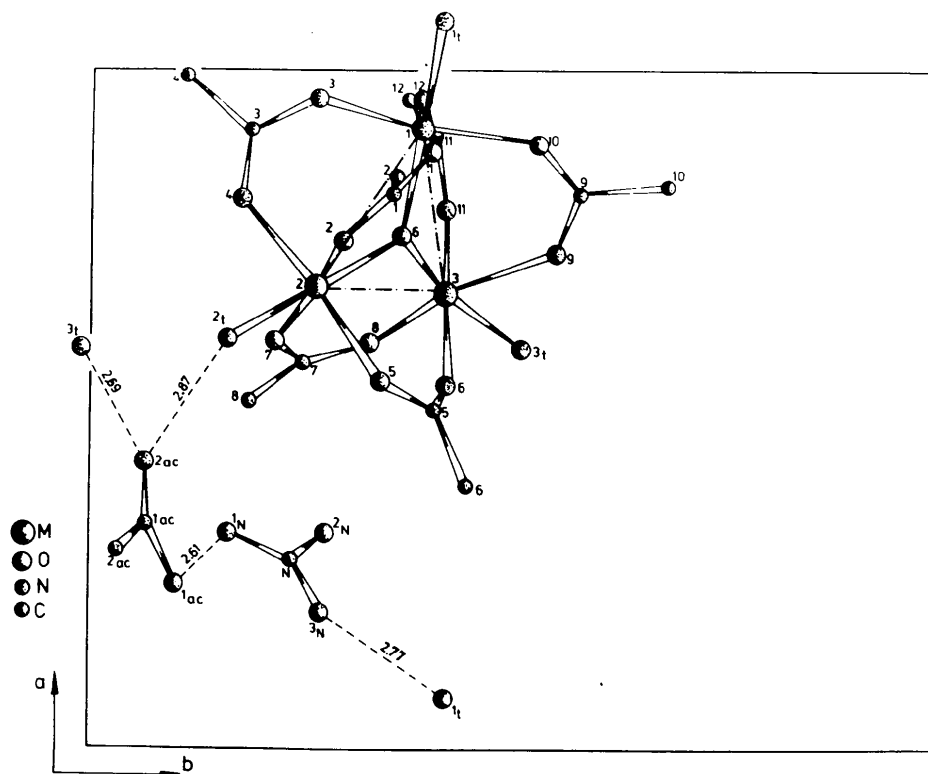
Fig. 1. Arrangement of trinuclear cation, nitrate anion and associated acetic acid molecule in the crystal of [Cr$_2$FeO(CH$_3$COO)$_6$(H$_2$O)$_3$]-NO$_3$.CH$_3$COOH. Possible OH···O hydrogen bonds are shown as broken lines.

The M—O$_{ac}$ bonds are slightly longer (0·09 Å) than the M—O$_b$ bond and shorter (0·11 Å) than the M—O$_t$ bond. The four O atoms surrounding each metal atom, originating from four different acetate groups, form perpendicular planes to the central M_3O plane. The metal atoms are displaced from these planes towards the bridge O atom (0·18 Å on average) and hence all the O$_b$—M—O$_{ac}$ angles are larger and O$_t$—M—O$_{ac}$ smaller than 90°. A slight deviation of the O$_b$—M—O$_t$ angles from linearity results in additional deformation of the octahedral environment around the metal atom.

The complex contains two types of acetate groups

with different structural functions: bridging acetate ligands and the acetate group from the associated acetic acid molecule which stabilizes the crystal structure. The C—O bonds in the ligands have similar lengths (average 1·26 Å) which is evidence of a uniform distribution of charge around the O atoms. In the acetic acid molecule the C—O lengths are different, 1·23 Å in the carbonyl and 1·32 Å in the C—OH group.

The structure is completed by the nitrate ion which is planar with an N—O length of 1·25 Å. The stabilizing function of acetic acid in the crystal consists in the formation of hydrogen bonds between both acid O atoms and O atoms of nitrate ions and coordinated water molecules. Although the H atoms have not been located, it may be expected that $O_N(1)$ forms hydrogen bonds with hydroxyl group $O_{ac}(1)$ and $O_r(3)$, while $O_N(3)$ forms a hydrogen bond with $O_r(1)$. The $O_N(2)$ atom does not participate in hydrogen bonds and has the strongest bond to the N atom.

The structural parameters obtained for the $[Cr_2FeO-(CH_3COO)_6(H_2O)_3]^+$ cation are consistent with those determined for homonuclear Cr and Fe complexes. In spite of the absence of any conditions imposed by the point-group symmetry the cation has almost ideal D_{3h} symmetry. This fact is significant for interpretation of the low-temperature properties of trinuclear Cr and Fe acetates. Studies on the magnetic properties, and UV, IR and Mössbauer spectra, indicate that the properties of these compounds may best be described by assuming an isosceles triangle model in which interactions between one of the atom pairs are different from those between the other two pairs. The results of recent studies (Sorai, Tachiki, Suga & Seki, 1971) on the anomalous heat capacity of trinuclear Cr acetates at helium temperatures explain to a certain extent the discrepancies between the results of X-ray studies and the magnetic properties. These authors assume that at low temperatures two types of triangular groups having different exchange properties are formed. They also suggest that at low temperatures a phase transformation with a deformation of the cation may occur.

Additional information on the structure of M_3O and $M_2M'O$ groups at low temperatures may help to resolve these problems.

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