Crystal Structures of the Isomorphous Prototypic Oxo-Centered Trinuclear Complexes $[Cr_3O(OOCCH_3)_6(H_2O)_3]Cl\cdot6H_2O$ and $[Fe_3O(OOCCH_3)_6(H_2O)_3]Cl\cdot6H_2O$

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Introduction

The two compounds $[Cr_3O(OOCCH_3)_6(H_2O)_3]Cl\cdot6H_2O$ and $[Fe_3O(OOCCH_3)_6(H_2O)_3]Cl\cdot6H_2O$, "CRAC" and "FEAC" **(1, 2)**, are prototypes of the general class of trinuclear "basic carboxylates" whose physical properties have been intensively studied for over 50 years.[1] They are fundamental to our understanding of magnetic interactions in exchange-coupled systems. This is partly because the triangular structure raises questions in its own right and because it can be viewed as the essential building block in larger structures, leading ultimately to extended lattices in the solid state and biological materials such as ferritins. It is firmly established that the metal ions in the oxo-centered units are antiferromagnetically coupled, but all recent measurements[2−6] indicate that the three magnetic coupling constants are not equal. Whether the inequalities are due to differences in metal−metal bond distances, metal−oxygen distances, or bond angles is a question that cannot be discussed without more accurate structural data. Attempts to rationalize vibrational spectra[7−9] and measurements of proton tunnelling[10,11] have been similarly frustrated. The crystal structure of CRAC was first reported by Figgis and Robertson,[12] and lattice parameters for FEAC were also given;[12] later the CRAC structure was reported in more detail by Chang and Jeffrey.[13] But the determination was of low accuracy, and among other anomalies, it was thought that the noncoordinated water molecules and the counteranions were extensively and mutually disordered. We now report complete structure determinations of both CRAC and FEAC. We find that the two compounds are indeed strictly isomorphous, with little disorder, and that it is possible to quantify the extent of distortion of the molecules, and particularly the central metal−oxygen clusters, from idealized trigonal geometry.

Table 1. Crystallographic Data

	1 (CRAC)	**2** (FEAC)
empirical formula	$C_{12}H_{36}ClCr_3O_{22}$	$C_{12}H_{36}ClFe_3O_{22}$
fw	723.86	735.41
space group	$P2_12_12$	$P2_12_12$
a, Å	13.700(2)	13.724(3)
b, Å	23.230(2)	23.359(5)
c, Å	9.167(2)	9.177(2)
V, Å^3	2917.4(8)	2942.0(11)
Z	4	4
ρ_{calc}, Mg m^{-3}	1.65	1.66
T, °C	25	25
diffractometer used	Rikagu	Siemens P3/V
λ(Mo Kα), Å	0.710 73	0.710 73
μ(Mo Kα), mm^{-1}	1.27	1.64
crystal size, mm	0.60 × 0.25 × 0.05	0.89 × 0.35 × 0.31
color	bottle green	orange-red
transm coeff	n.a.	0.258−0.137
final wR_2[a] (all data)	0.1296	0.1414
$\sigma(F^2)$ (all data)	1.096	1.182
final R_1 ($F_o \geq 4\sigma(F_o)$)[b]	0.0403	0.0529
Flack parameter	−0.07(3)	−0.03(3)

[a] Weighted R factors wR_2 from refinement on F^2 using *all* reflections. [b] The criterion is only used for calculation of the conventional R_1 following refinement.

Experimental Section

Preparations. The compounds $[Cr_3O(OOCCH_3)_6(OH_2)_3]Cl\cdot6H_2O$[5b] and $[Fe_3O(OOCCH_3)_6(OH_2)_3]Cl\cdot6H_2O$[8] crystallized as dark green pseudohexagonal prisms and red-brown blocks, respectively. It was also noted that when CRAC was recrystallized rapidly from dilute aqueous HCl, a varying proportion of monoclinic-appearing crystals could also be seen among the more familiar hexagonal prisms. They could also be distinguished by different IR spectra, particularly in the O−H stretching region, but were not investigated further.

Structure Analysis and Refinement. Experimental details and significant parameters are listed in Table 1. Analysis proceeded in closely similar stages for both materials. Unit cell dimensions were determined by least-squares fitting of the setting angles (25 for CRAC, 14 for FEAC). Intensity data were collected by the ω-scan method and corrected for Lorentz, polarization, and absorption effects, except that, in the case of CRAC, no absorption correction was applied; an attempted correction led to higher R factors than for the uncorrected data. Metal atoms were located from Patterson maps, and the remaining non-H atoms were located from difference Fourier maps. After isotropic refinement, it was found that some of the oxygen atoms of the water molecules of hydration (O(43), O(44), and O(45)) showed 2- or 3-fold disorder. After the atoms of the complexes had been refined anisotropically, site occupancies of the disordered oxygens were refined, with the components of each oxygen assigned a common isotropic temperature factor. These occupancies were then fixed while the water oxygens and the chloride were also refined anisotropically. Further difference Fourier maps showed the H atoms of the three aquo ligands; those on O(10) and O(20) were refined with U_{iso} set at $1.5U_{eq}$ for the respective oxygen atoms, while those on O(30) did not refine satisfactorily and their positions were fixed. Two difference peaks were observed close (i.e., *ca.* 0.9 Å) to O(40), suggesting H atoms, but no attempt was made to include these in the final refinement. The structures were shown to be the correct enantiomer from refinement of the Flack parameter. Atomic coordinates and temperature factors are listed in Tables S.1 and S.2 (Supporting Information), and selected bond distances and angles are listed in Table 2. The molecular structure is shown in Figure 1.

Results and Discussion

The two complexes are confirmed to be closely isomorphous, with four symmetry-related formula units per unit cell. Contrary

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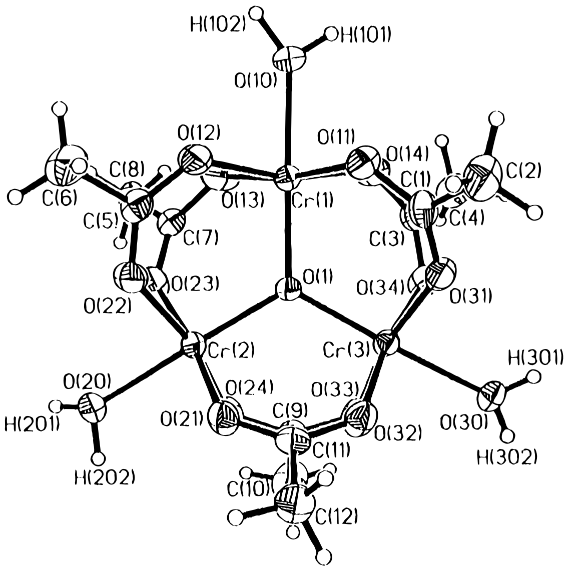

Figure 1. View of molecular structure and numbering scheme for complex cations of the salts $[M_3O(OOCCH_3)_6(OH_2)_3]Cl{\cdot}6H_2O$.

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

	1 (CRAC)	**2** (FEAC)
M(1)···M(2)	3.281(1)	3.285(1)
M(1)···M(3)	3.288(1)	3.295(1)
M(2)···M(3)	3.279(1)	3.291(1)
M(1)−O(1)	1.902(4)	1.894(3)
M(2)−O(1)	1.885(3)	1.906(4)
M(3)−O(1)	1.899(4)	1.899(3)
M(1)−O(1)−M(2)	120.05(18)	119.66(17)
M(1)−O(1)−M(3)	119.78(18)	120.61(19)
M(2)−O(1)−M(3)	120.13(18)	119.71(17)
M(1)−O(10)	2.050(4)	2.075(4)
M(2)−O(20)	2.037(4)	2.059(4)
M(3)−O(30)	2.008(4)	2.047(4)
M(1)−O(11)	1.990(4)	2.030(4)
M(1)−O(12)	1.966(4)	2.009(5)
M(1)−O(13)	1.969(4)	2.008(4)
M(1)−O(14)	1.971(4)	1.901(5)
M(2)−O(21)	1.969(4)	2.016(5)
M(2)−O(22)	1.974(4)	2.005(4)
M(2)−O(23)	1.978(4)	2.024(4)
M(2)−O(24)	1.961(4)	2.097(4)
M(3)−O(31)	1.979(4)	2.020(4)
M(3)−O(32)	1.952(4)	1.990(5)
M(3)−O(33)	1.933(4)	2.054(4)
M(3)−O(34)	1.963(4)	2.006(5)

to the earlier report on CRAC,[13] the chloride ions are well-defined, though they have anisotropic temperature factors, indicating either librational movement or unresolved static disorder between two closely spaced sites: there is no evidence that they are disordered over the same sites as the waters of crystallization. The number of such water molecules is confirmed as 6 in agreement with the earliest empirical formulas, $M_3(OH)_2(OOCCH_3)_6{\cdot}8H_2O$.[1] The molecules with atoms O(40), O(41), and O(42) do not appear to be significantly disordered. The other three (O(43), O(44), and O(45)) are disordered, but this disorder could readily be modeled. The site occupancies are very similar in the two isomorphous structures (Table 3), confirming that, although disordered, these waters are nonetheless well-defined. The earlier suggestion of a regular alternation of carboxylate C−O distances around the molecule (in effect, that the bridging ligands might better be described as acetic acid molecules rather than acetate ions) is also not confirmed. While some acetate ligands showed C−O distances that were significantly different, the majority did not, and longer C−O distances were not particularly associated with oxygens involved in hydrogen bonding.

Table 3. Site Occupancies for Disordered Waters of Solvation

	1 (CRAC)	**2** (FEAC)
O(43a)	0.502(11)	0.515(13)
O(43b)	0.498(14)	0.485(13)
O(44a)	0.693(20)	0.730(21)
O(44b)	0.307(20)	0.270(20)
O(45a)	0.454(11)	0.499(13)
O(45b)	0.280(17)	0.230(17)
O(45c)	0.266(14)	0.271(17)

The central $(\mu_3\text{-}O)M_3(OH_2)_3$ units deviate from planarity to a slight but significant extent. Full details are given in Table S.3 (Supporting Information). In both complexes, the central oxygen is displaced from the plane of the three metal atoms, by 0.013(4) Å in FEAC and by 0.023(3) Å in CRAC. The three aquo oxygens, on the other hand, are all displaced toward the opposite face of the M_3 triangle, resulting in a "dishlike" distortion toward C_{3v} symmetry. However the deviations are much less than that found in the pivalate-bridged iron complex $[Fe_3O(OOCMe_3)_6(MeOH)_3]Cl$, where the displacement is 0.24 Å,[14] and the thermal ellipsoids of the central oxygens in the two present compounds are not strongly elongated in directions perpendicular to the M_3O plane, confirming that the observed near-planar structures of the central cores do not result from disorder of the central oxygens above and below the M_3 planes.

Data of comparable accuracy are available for only two other complexes containing the central $[O(Cr{-}OH_2)_3]$ unit: $[Cr_3O(OOCC_2H_5)_6(OH_2)_3]NO_3{\cdot}2H_2O$[15] and $[Cr_3O(OOCCH_3)_6(OH_2)_3]Cl{\cdot}3SC(NH_2)_2{\cdot}2H_2O$.[16] In both of these, two of the three chromium sites are equivalent by crystallographic symmetry, but in the propionate complex, at least it is possible that molecular asymmetry is concealed by disorder. What the three structures can show is that the mean Cr−Cr, O−Cr, and Cr−OH_2 distances all vary from one complex to another, again by amounts which exceed experimental error. This suggests a certain degree of plasticity in the cluster framework, such that changes in the crystal environment of the complex can lead to changes in the geometry of the M_3O core. However it is clear in these systems that the M−OH_2 distances are all greater than those found in the analogous mononuclear complexes $[M(OH_2)_6]^{3+}$.[17] This confirms that M−OH_2 bonds in the oxo-centered trimer complexes are weakened, as suggested previously on the basis of vibrational spectroscopy[18] and reaction kinetics.[19]

Deviations from 3-fold symmetry are small but statistically significant. To define them, we take any set of distances which would be identical in the symmetrical case and compare the standard deviation of the set, σ, with the average of the experimental errors (esd's) for the set. From the three metal−metal distances, in CRAC we find $\sigma = 0.004$ Å, and while this is small in relation to the mean Cr−Cr distance of 3.283 Å, it is approximately 4 times the average esd. For FEAC, the ratio

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σ/esd for the Fe−Fe distances is also about 4. For the distances from metal to water, σ/esd is 4.6 for CRAC and 4.0 for FEAC. For metal to central oxygen distances, the asymmetry is less but still real, with σ/esd being ∼2 for CRAC and 1.5 for FEAC. Given the extreme sensitivity of metal−metal electronic interactions to local coordination geometry, it is not surprising that all compounds of this type examined so far have shown magnetic and thermodynamic properties significantly different from those predicted from 3-fold symmetry.[1−6]

The *difference* in symmetry between the two complex cations can be expressed most concisely by saying that the chromium complex appears very close to an "isosceles" geometry, while the iron complex has no such tendency and can best be described as "scalene". That is, in the chromium complex, the distances Cr(1)−Cr(2) and Cr(2)−Cr(3) are almost equal and significantly shorter than C(31)−Cr(3), while Cr(1)−O(1) and Cr(3)−O(1) are almost equal and significantly longer than Cr(2)−O(1). In the iron complex, all three Fe−Fe distances are different and there is no obvious pattern. The differences in metal−ligand atom distances are also revealing. The mean $M-OH_2$ distances differ by an amount which is very close to the difference between $M-OH_2$ distances in the mononuclear ions $[M(OH_2)_6]^{3+}$: 0.028 Å in the present complexes and 0.025 Å in the isomorphous salts $CsM(SeO_4)_2 \cdot 12H_2O$.[17] The difference in mean metal−carboxylate oxygen distances is considerably more than this, i.e. 0.046 Å. On the other hand mean, metal−central oxide distances are almost the same in the two compounds. Evidently, the Fe^{3+} ions, although larger than Cr^{3+}, interact more strongly twith the central oxide ion. There is much evidence that, in compounds of this type, the oxide ion provides the principal magnetic superexchange pathway,[20,21] and the difference in magnetic coupling constants is also large; typically, J(Fe−Fe) $= -35$ cm^{-1} and J(Cr−Cr) $= -9.5$ cm^{-1}.[1,5b,6] A question now arise as to whether the closer distances are the result of stronger electronic interactions between the neighboring ions or whether it is the other way round and they are driven by the constraint of the carboxylate-bridged framework. But before such questions can be dealt with, it will be necessary to obtain low-temperature data and to take into account any structural phase transitions.

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Supporting Information Available: Tables S.1 and S.2, listing atomic coordinates of CRAC and FEAC, and Table S.3, giving deviations of oxygen atoms from the M_3 planes (5 pages). Ordering information is given on any current masthead page.

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