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μ_2-Acetato-κ^2O:O'-tris(μ_2-ferrocenecarboxylato-κ^2O:O')bis[(*N*,*N*-dimethylformamide-κO)copper(II)]. Corrigendum

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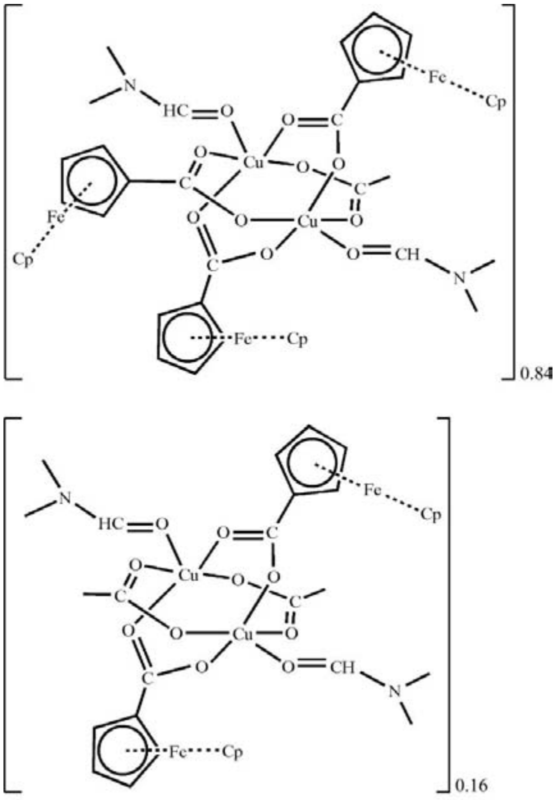
In the paper by Luo, Huang, Huang & Wang [*Acta Cryst.* (2009), C**64**, m121–m122], the structure reported as [$Cu_2Fe_3(C_5H_5)_3(C_2H_3O_2)(C_6H_4O_2)_3(C_3H_7NO)_2$] is actually a cocrystal in which one of the ferrocenecarboxylate ligands in about 16% of the molecules has been replaced with acetate. The correct structure of $[Cu_2Fe_3(C_5H_5)_3(C_2H_3O_2)(C_6H_4O_2)_3(C_3H_7NO)_2]_{0.84}$-$[Cu_2Fe_2(C_5H_5)_2(C_2H_3O_2)_2(C_6H_4O_2)_2(C_3H_7NO)_2]_{0.16}$ is now reported.

Comment

This corrigendum is to correct the report of the crystal structure of μ_2-acetato-κ^2O:O'-tris(μ_2-ferrocenecarboxylato-κ^2O:O')bis[(*N*,*N*-dimethylformamide-κO)copper(II)] (Luo *et al.*, 2008). Examination of difference electron-density maps and atomic displacement parameters suggested that the ferrocenecarboxylate ligand centred around atom Fe3 was not fully occupied. Refinement of site-occupation factors of the atoms of this ligand indicated that atom Fe3 and the C atoms of the two ferrocene rings have an occupancy of about 0.84, while the acetate part of the ligand has full occupancy. This reveals that in about 16% of the molecules, the ferrocenecarboxylate ligand centred around atom Fe3 has been replaced by acetate. Thus, the reported compound is a cocrystal of composition μ_2-acetato-κ^2O:O'-tris(μ_2-ferrocenecarboxylato-κ^2O:O')bis[(*N*,*N*-dimethylformamide-κO)copper(II)]–bis(μ_2-acetato-κ^2O:O')bis(μ_2-ferrocenecarboxylato-κ^2O:O')bis[(*N*,*N*-dimethylformamide-κO)copper(II)] (0.84/0.16), (I).

Refinement of the site-occupation factors of the other ferrocenecarboxylate ligands indicated that these sites were fully occupied. The corrected refinement results are presented here.

The presence of an additional acetate ligand in some of the molecules is understandable given that $Cu(OAc)_2{\cdot}H_2O$ was used in the synthesis and the cocrystal has apparently arisen because of inadequate purification of the product prior to crystallization.



(I)

Experimental

Crystal data

$[Cu_2Fe_3(C_5H_5)_3(C_2H_3O_2)(C_6H_4O_2)_3(C_3H_7NO)_2]_{0.84}$-$[Cu_2Fe_2(C_5H_5)_2(C_2H_3O_2)_2(C_6H_4O_2)_2(C_3H_7NO)_2]_{0.16}$
M_r = 992.40
Triclinic, $P\overline{1}$
a = 10.948 (2) Å
b = 13.548 (3) Å
c = 15.828 (3) Å
α = 108.96 (3)°
β = 94.57 (3)°
γ = 110.33 (3)°
V = 2032.3 (10) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.08 mm^{-1}
T = 298 K
0.30 × 0.26 × 0.26 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min}$ = 0.567, $T_{\max}$ = 0.607
19821 measured reflections
9106 independent reflections
6613 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.155
S = 1.06
9106 reflections
488 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.86 e Å^{-3}
$\Delta\rho_{\min}$ = −0.76 e Å^{-3}

doi:10.1107/S0108270110009443

H atoms bonded to C atoms were allowed for in idealized positions using the riding-model approximation, with C—H = 0.93 [cyclopentadienyl (Cp)] or 0.96 Å (methyl) and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for the Cp rings and 1.5$U_{\rm eq}$(C) for the methyl groups. The ferrocenecarboxylate ligand centred around atom Fe3 is disordered with an acetate ligand at the same site. Refinement of a common site-occupation factor for atom Fe3 and the C atoms of the two associated Cp rings, except atom C24, which also belongs to the acetate ligand, led to a value of 0.841 (3). The site-occupation factors of the methyl H atoms of the minor-component acetate ligand were refined with a complementary value of 0.159 (3). Atoms C29, C30, C31, C32 and C33 of one Cp group were refined with the same anisotropic displacement parameters using the EADP instruction in *SHELXL97* (Sheldrick, 2008). The same type of constraint was also applied to the four methyl C atoms of the dimethylformamide ligands (C37, C38, C40 and C41).

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO* (Rigaku, 1998); data reduction: *RAPID-AUTO* (Rigaku, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL/PC* (Sheldrick, 1993); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3142). Services for accessing these data are described at the back of the journal.

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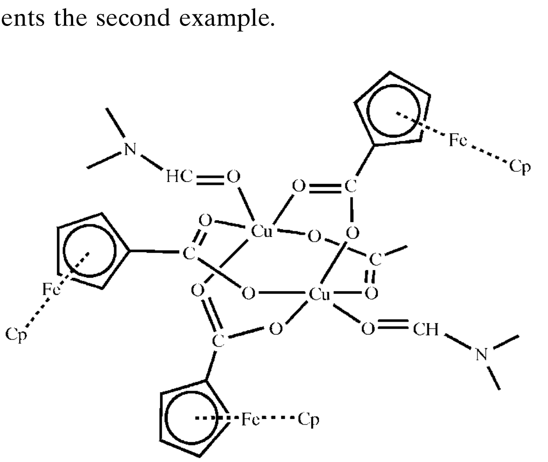
The title compound, $[Cu_2Fe_3(C_5H_5)_3(C_2H_3O_2)(C_6H_4O_2)_3(C_3H_7NO)_2]$, belongs to the classic dimeric paddle-wheel structure type. It is an unusual example in that it contains two different carboxylate groups, i.e. ferrocenecarboxylate and acetate. With three ferrocenecarboxylate groups and only one acetate group bridging the two Cu centres, a noncentrosymmetric molecular arrangement results.

Comment

Dimeric copper(II) carboxylates and their adducts, $[Cu_2(O_2CR)_2L_2]$, have played a major role in copper(II) carboxylate chemistry (Agterberg *et al.*, 1997; Moulton *et al.*, 2003). The related complexes have received much attention because of their potential use as anti-inflammatory drugs (Demertzi *et al.*, 2004; Weder *et al.*, 2004). In addition, such complexes are good models for the investigation of the exchange interaction between paramagnetic centres in discrete molecules (Costa *et al.*, 1998). The polarizability of the *R* group on the carboxylate has a vital relationship with the magnitude of the magnetic interaction (Porter & Doedens, 1984; Schlam *et al.*, 2000). While the ferrocenyl unit itself always affects electron interactions in compounds, in this case it may help to probe the influence of the substituent *R* on the magnetic behaviour. Moreover, compounds containing ferrocenyl units always show some unusual properties and have potential applications in the field of materials science, such as molecular sensors (eer, 1992), molecular magnets (Miller & Epstein, 1994) and nonlinear optical materials (Long, 1995). Dinuclear copper(II) complexes with two different kinds of carboxylate groups still remain rare, especially ones with bulky carboxylate groups like ferrocenecarboxylate (Churchill *et al.*, 1985), which may be due to the existence of evident steric hindrance. We report here the synthesis and crystal structure of the title dimeric copper(II) carboxylate, (I), with ferrocenecarboxylate and acetate groups.

Only one noncentrosymmetric dimeric copper(II) carboxylate, $Cu_2\ \mu$-$[(CO)_9Co_3(\mu_3$-$CCO_2)]_3[\mu$-$(CH_3CO_2)](OC_4H_8)_2$ (anares *et al.*, 1985), has been reported to date, according to the Cambridge Structural Database (*CONQUEST*, Version 1.3, updated May 2007; Bruno *et al.*, 2002). Thus, complex (I) represents the second example.



(I)

In complex (I), the asymmetric unit contains two crystallographically independent Cu^{II} ions, three ferrocenecarboxylate groups, one acetate group and two dimethylformamide (DMF) molecules. The two Cu^{II} centres are separated by 2.618 (28) Å and each Cu^{II} centre has a square-pyramidal coordination environment, with four O atoms from three ferrocenecarboxylate groups and one acetate group in the basal plane, and an O atom from a DMF molecule in the apical position. As expected, the apical Cu—O$_{DMF}$ distances are notably longer than the basal distances between Cu and the O atoms from the carboxylate groups.

The novel character of (I) lies in its noncentrosymmetric structure type, which is still very rare in this classical kind of

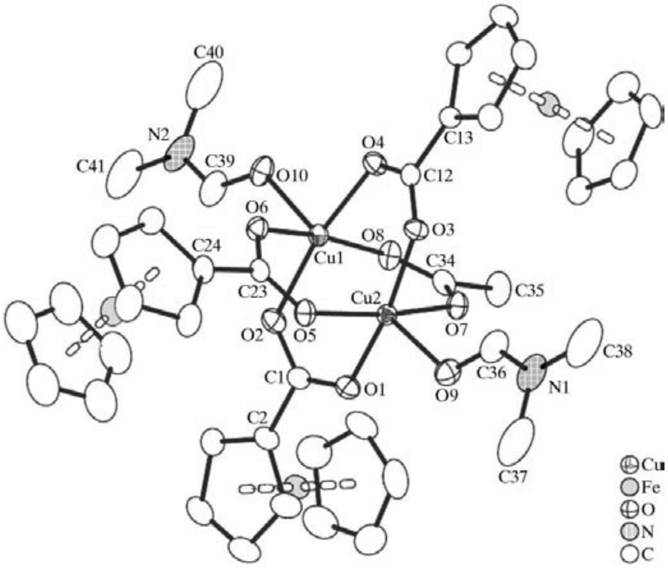


Figure 1
The structure of (I), showing the atom-labelling scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

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complex. In (I), there are three ferrocenecarboxylate groups and only one acetate group. The ferrocene substituents on the carboxylate ligands that are *trans* to each other are oriented to the same side of the Cu···Cu line, and the less bulky methyl substituent of the acetate ligand is located in the space between the two ferrocene units (Fig. 1). The arrangement of the ferrocenecarboxylate groups is therefore different from that in the centrosymmetric compound tetrakis(ferrocenecarboxylato)bis(tetrahydrofuran)copper(II) reported by Churchill *et al.* (1985), in which the four ferrocene units are arranged in a clockwise mode.

There is also a noticeable difference between the conformations of the coordination of the Cu^{II} and carboxylate O atoms of (I) and the Churchill complex. In the previously reported complex, the two Cu^{II} centres and the coordinated O atoms belonging to the same carboxylate group are nearly located in the same plane, with O—Cu—Cu—O torsion angles between them of −1.9 (3) and 0.8 (3)° for the two independent carboxylate groups. By contrast, in (I) the four corresponding torsion angles are distinctly larger: 15.0 (2), 14.4 (2), 14.0 (2) and 15.0 (2)°. The obvious variance may be due to the different steric hindrance in the complexes. Perhaps as a result of the smaller steric hindrance, the O—Cu—Cu—O torsion angles of the other noncentrosymmetric dimeric copper(II) carboxylate (anares *et al.*, 1985) are also distinctly smaller than complex (I), with values ranging from −4.0 (3) to 4.6 (3)°.

Experimental

For the preparation of (I), ferrocenecarboxylic acid (0.046 g, 0.02 mmol) and $NaHCO_3$ (0.017 g, 0.02 mmol) were dissolved in a mixture of CH_3OH (10 ml) and DMF (2 ml). The solution was stirred for 1 h at room temperature. $Cu(OAc)_2 \cdot H_2O$ (OAc is acetate; 0.020 g, 0.01 mmol) was then added and the resulting solution was stirred for 3 h. All the volatiles were removed under vacuum and the residue was dissolved in a mixture of CH_2Cl_2 and DMF (/ = 5:2). The resulting solution was allowed to stand at room temperature for about 7 d, after which rhombic crystals of (I) were collected for X-ray analysis.

Crystal data

$[Cu_2Fe_3(C_5H_5)_3(C_2H_3O_2)(C_6H_4O_2)_3(C_3H_7NO)_2]$
$M_r = 1019.41$
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$S = 1.05$
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H-atom parameters constrained
$\Delta\rho_{max} = 0.76$ e Å^{-3}
$\Delta\rho_{min} = -1.39$ e Å^{-3}

H atoms bonded to C atoms were allowed for in idealized positions using the riding-model approximation, with C—H = 0.93 [cyclopentadienyl (Cp)] and 0.96 Å (methyl), and with $U_{iso}(H) = 1.2U_{eq}(C)$. Atoms C29, C30, C31, C32 and C33 of one Cp group were refined with the same anisotropic displacement parameters using the EADP instruction in *SHELXL97* (Sheldrick, 1997). The same operation was also carried out on the methyl C atoms of the DMF molecules (C37, C38, C40 and C41).

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