

Syntheses and Molecular Structures of *cis* and *trans* Monomeric Ferrocenecarboxylatocopper(II) Complexes with Imidazole Derivatives†

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The products of the reactions of 1,2-dimethylimidazole and *N*-methylimidazole with tetrakis(ferrocenecarboxylato)dicopper(II) have been isolated and characterized by single-crystal X-ray diffraction. They are the monomeric species *cis*-bis(1,2-dimethylimidazole)bis(ferrocenecarboxylato)copper(II) **1** and *trans*-bis(ferrocenecarboxylato)bis(*N*-methylimidazole)copper(II) **2**, respectively. In each complex the copper ion is in a square-planar environment consisting of two imidazole nitrogen atoms and a carboxylate oxygen atom from each ferrocenecarboxylate ligand. The second oxygen atoms of the carboxylate functionalities are involved in weak interactions with the copper ions. The η^5 -C₅H₄ and η^5 -C₅H₅ rings of the ferrocenyl moieties are nearly eclipsed with deviations from the eclipsed conformation of 9.7 and 5.5° for **1** and 4.4° for **2**.

Dimeric copper(II) carboxylates containing a variety of oxygen- and nitrogen-donor ligands have been extensively investigated and their preparations, magnetic and spectral properties have been reviewed.¹ Few monomeric copper(II) carboxylates with certain nitrogen-based ligands, including imidazoles, are known.^{2–5} These monomers can exist as *trans* or *cis* bis and tetrakis adducts which contain the CuN₂O₂ and CuN₄O₂ chromophores, respectively.

A dimeric copper(II) complex with ferrocenecarboxylate ligands has been reported;⁶ however, investigations were limited due to solubility problems. In view of the many structures found for imidazole adducts of other copper(II) carboxylates,^{2–5} it was of interest to investigate the nature of the adducts formed with the ferrocenecarboxylatocopper(II) dimeric complex. It was thought that in addition to the electronic factors that are operative, the ferrocene moiety might introduce steric restrictions which might affect the nature of the adducts. Furthermore, the multicentred adducts may present opportunities to study electronic interactions between the copper centre and the ferrocenyl groups. This article reports the synthesis, spectroscopic and X-ray structural characterization of *cis*-bis(1,2-dimethylimidazole)bis(ferrocenecarboxylato)-copper(II) **1** and *trans*-bis(ferrocenecarboxylato)bis(*N*-methylimidazole)copper(II) **2**.

Results and Discussion

Magnetic and Spectroscopic Characterization.—The magnetic and spectroscopic data for complexes **1** and **2** are summarized in Table 1. The room-temperature solid-state magnetic moments for the two bis adducts are consistent with the presence of one unpaired electron in monomeric copper(II) complexes. The assignments of IR frequencies for the antisymmetric, $\nu_{\text{asym}}(\text{CO}_2)$, and the symmetric, $\nu_{\text{sym}}(\text{CO}_2)$, stretching vibrations are given in Table 1. The $\Delta\nu$ values [$\nu_{\text{asym}}(\text{CO}_2) - \nu_{\text{sym}}(\text{CO}_2)$] of ca. 180 cm⁻¹ are in the range expected for 'unsymmetrical' bidentate co-

ordination of the carboxylate ligand.⁷ This co-ordination mode is borne out by the solid-state structures (see below).

The UV/VIS diffuse reflectance spectra of the two complexes exhibit broad low-energy electronic bands centred at about 660 nm and more intense bands at 455 nm (Table 1). The lower-energy band is due to copper d-d transitions. The λ_{max} of this transition is consistent with the assignments for other tetragonally distorted copper(II) complexes containing a CuN₂O₂...O₂ chromophore.^{16,3,8,9} The higher-energy band is the characteristic band of the ferrocenyl moiety which occurs at 460 nm for the free acid. The small shift in its position upon complexation suggests that there is very little perturbation of the molecular orbitals of the ferrocenyl moiety due to the copper(II) ion and the other ancillary ligands. This conclusion is supported by cyclic voltammetric studies.

Cyclic voltammograms recorded at 100 mV s⁻¹ were obtained on CH₂Cl₂ solutions of complexes **1** and **2**. The most prominent features are quasi-reversible waves ($\Delta E = 123$ mV for **1** and 121 mV for **2**) at $E_{1/2}$ values of 0.56 V for **1** and **2**. These values and the nature of the couples are very similar to those of ferrocene and the ferrocenecarboxylate ligand in CH₂Cl₂ and are thus assigned to electron-transfer processes at the ferrocenyl moiety. The data are consistent with the conclusion that there is little perturbation of the electronic levels of the ferrocenyl moiety upon complexation through the carboxylate functions. The quasi-reversible couples exhibit i_c/i_a values of ca. 1. Both complexes exhibit weak irreversible waves between -0.20 and -0.50 V which are assumed to correspond to the Cu^{II}-Cu^I couple.

X-Band ESR spectral parameters of polycrystalline samples of complexes **1** and **2** at 298 K are in Table 1. These data are characteristic of elongated tetragonal monomeric copper(II) complexes.⁹ The ESR spectrum of **1** contains an asymmetric signal centred near 3100 G which is assigned to the perpendicular component of an axially symmetric system. A broad peak also occurs in the parallel region. The lack of copper(II) hyperfine interaction in this complex is likely due to dipole-dipole interactions between copper(II) centres of neighbouring molecules. The ESR spectrum of **2** is anisotropic and contains g_{\perp} and g_{\parallel} components. The g_{\parallel} component exhibits splitting due to hyperfine interaction involving the Cu^{II}. The spectral parameters are comparable to those of bis adducts of

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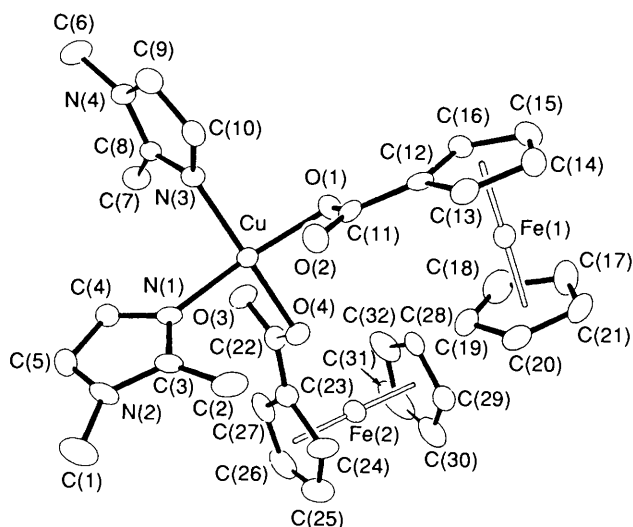
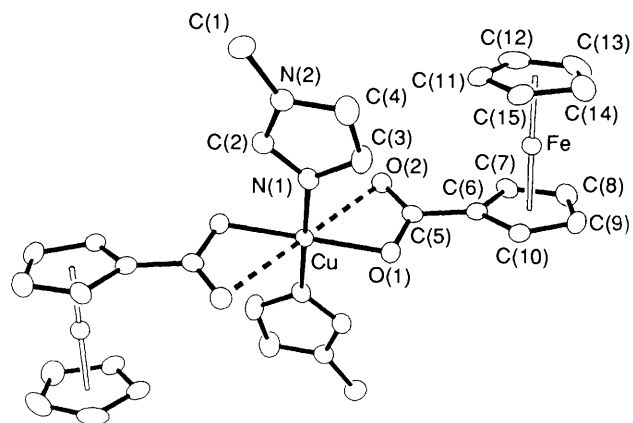
‡ Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx-xxv.

Non-SI unit employed: G = 10⁻⁴ T.

Table 1 Magnetic moments, ESR, electronic and infrared data for complexes **1** and **2**^a

Complex	μ_{eff}	g_{\perp}	g_{\parallel}	A_{\parallel}/G	$\lambda_{\text{max}}/\text{nm}$	$\nu_{\text{asym}}(\text{CO}_2)/\text{cm}^{-1}$	$\nu_{\text{sym}}(\text{CO}_2)/\text{cm}^{-1}$
1	1.85	2.069	<i>b</i>		640, 455	1568	1385
2	1.89	2.061	2.25	167	660, 455	1572	1392

^a Magnetic moments and ESR data are for polycrystalline samples. ^b A broad peak whose *g* value cannot be accurately determined appears in the parallel region of the spectrum.

**Fig. 1** Perspective drawing of the structure of complex **1** with the atom numbering scheme**Fig. 2** Perspective drawing of the structure of complex **2** with the atom numbering scheme

copper(II) carboxylates with *trans* square-planar CuN_2O_2 chromophores in which the copper(II) ion is bonded to two nitrogen atoms and one oxygen atom from each of two carboxylate anions. The second carboxylate oxygen atom is involved in rather weak axial interactions with the Cu.^{3-5,8-10}

Molecular Structures of Complexes 1 and 2·H₂O.—The structures of complexes **1** and **2** with the atomic labelling schemes are illustrated in Figs. 1 and 2, respectively. Atomic positional parameters are given in Tables 2 and 3, and selected bond distances and angles in Tables 4 and Table 5, respectively. The inner co-ordination sphere of the copper atom consists of two carboxylate oxygen atoms and two imidazole nitrogen atoms in a *cis* disposition for **1** and a *trans* disposition for **2**.

The deviation of the copper atom of complex **1** from the least-squares plane through N(1), N(3), O(1) and O(4) is 0.0766 Å, those of the other atoms being -0.2982 for N(1), +0.3005 for N(3), -0.3098 for O(1) and +0.3075 Å for

O(4). These deviations result in a dihedral angle between planes N(3)-Cu-N(1) and O(1)-Cu-O(4) of 25.3° compared to 0 and 90° for square-planar and tetrahedral environments, respectively. The N(3)-Cu-N(1) and O(1)-Cu-O(4) angles are 93.7(2) and 91.8(2)°, respectively. The two carboxylate oxygen atoms O(2) and O(3) are at distances of 2.666 and 2.499 Å, respectively, and thus exhibit only weak interactions with the Cu atom.

The dihedral angles between the $\eta^5\text{-C}_5\text{H}_4$ and $\eta^5\text{-C}_5\text{H}_5$ planes in the ferrocenecarboxylate ligands containing Fe(2) and Fe(1) are 2.5 and 3.2°, respectively. The $\eta^5\text{-C}_5\text{H}_4$ and $\eta^5\text{-C}_5\text{H}_5$ fragments of the ferrocenecarboxylate ligand containing Fe(2) deviate from the eclipsed conformation by 9.7° and those of the ferrocenecarboxylate ligand containing Fe(1) deviate from the eclipsed conformation by 5.5°. All Fe-C distances are in the range of those found in tetrakis(ferrocenecarboxylato)bis(tetrahydrofuran)dycopper(II).⁶

Since the Cu atom in complex **2** is located on a crystallographic inversion centre ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$) the complex has a crystallographically imposed strictly planar geometry for the four atoms nearest the Cu. The O(1)-Cu-N(1) angle is 89.0(2)°. The distance between the Cu atom and the more remote carboxylate oxygen atoms is 2.598 Å, which suggests weak interaction. The dihedral angle between the $\eta^5\text{-C}_5\text{H}_4$ and $\eta^5\text{-C}_5\text{H}_5$ planes is 2.6° and the deviation of the five-membered rings from the eclipsed conformation is 4.4°.

The two crystallographically independent ferrocenyl groups in the tetrakis(ferrocenecarboxylato)dycopper(II) complex were found to have different conformations, one eclipsed and one staggered.⁶ As discussed above for **1**, in which the two ferrocenyl groups are also crystallographically independent, both ferrocenyl groups are nearly eclipsed. Many examples of deviations of ferrocenyl groups from the staggered conformation are known.¹¹ The ferrocenyl groups of **2** are related by crystallographic symmetry.

As was found to be the case for the tetrakis(ferrocenecarboxylato)dycopper(II) complex, the $\text{O}_2\text{C-C}_5\text{H}_4$ moieties are not strictly planar. The torsional angles for these moieties in **1** are 11.6 and 5.0° about the C(11)-C(12) and C(22)-C(23) linkages, respectively. With a value of 19.8°, the torsional angle about the C(5)-C(6) linkage in **2** is somewhat larger than those found in **1**.

Experimental

Preparations.—The compound tetrakis(ferrocenecarboxylato)bis(tetrahydrofuran)dycopper(II), $[\text{Cu}_2(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)_4(\text{thf})_2]\cdot\text{thf}$, was synthesised by the method described previously.⁶

Bis(1,2-dimethylimidazole)bis(ferrocenecarboxylato)copper(II) 1. A solution of 1,2-dimethylimidazole (12 cm³) in methanol (10 cm³) was added to $[\text{Cu}(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)_4(\text{thf})_2]\cdot\text{thf}$ (0.50 g). The mixture was stirred for 1 h at 60 °C. The green solution was filtered into anhydrous diethyl ether and stirred until a green precipitate formed. The green complex was filtered off under reduced pressure and washed several times with anhydrous diethyl ether. Recrystallization from hot methanol containing a few drops of the neat ligand produced green crystals (Found: C, 53.45; H, 4.80; N, 7.95. Calc. for $\text{C}_{32}\text{H}_{34}\text{CuFe}_2\text{N}_4\text{O}_4$: C, 53.65; H, 4.75; N, 7.80%).

Table 2 Atomic coordinates ($\times 10^4$) for complex 1

Atom	x	y	z	Atom	x	y	z
Cu	2388(1)	3130(1)	1184(1)	C(12)	-636(6)	1513(6)	2532(3)
Fe(1)	-332(1)	1941(1)	3769(1)	C(13)	-784(6)	302(6)	3009(4)
Fe(2)	4930(1)	6917(1)	3507(1)	C(14)	-1889(6)	505(6)	3533(4)
N(1)	4168(5)	2479(5)	727(3)	C(15)	-2448(6)	1827(7)	3382(4)
N(2)	6045(5)	1269(5)	556(3)	C(16)	-1676(6)	2446(6)	2769(4)
N(3)	1252(5)	2985(5)	83(3)	C(17)	-77(8)	3198(7)	4780(4)
N(4)	285(5)	3184(5)	-1200(3)	C(18)	719(8)	3667(7)	4132(4)
O(1)	639(4)	3030(4)	1758(2)	C(19)	1680(7)	2663(8)	3952(4)
O(2)	1318(4)	872(4)	1800(3)	C(20)	1494(7)	1562(7)	4499(4)
O(3)	3400(4)	5476(4)	1363(3)	C(21)	393(7)	1897(7)	5006(4)
O(4)	3506(4)	3727(4)	2228(2)	C(22)	3910(6)	4901(6)	2014(4)
C(1)	7144(7)	249(7)	680(5)	C(23)	5084(6)	5570(6)	2545(4)
C(2)	4728(7)	680(7)	1798(4)	C(24)	5780(7)	5061(7)	3303(4)
C(3)	4958(6)	1478(6)	1042(4)	C(25)	6873(7)	6011(8)	3575(5)
C(4)	4770(6)	2941(6)	40(4)	C(26)	6828(7)	7078(8)	3015(5)
C(5)	5947(6)	2195(6)	-71(4)	C(27)	5750(7)	6824(7)	2374(4)
C(6)	-111(7)	3753(7)	-2031(4)	C(28)	2854(7)	7018(8)	3756(4)
C(7)	1875(6)	5111(6)	-656(4)	C(29)	3724(7)	6673(10)	4477(5)
C(8)	1150(6)	3771(6)	-588(3)	C(30)	4700(9)	7752(13)	4653(6)
C(9)	-191(6)	1976(6)	-906(4)	C(31)	4453(9)	8723(10)	4034(7)
C(10)	407(6)	1851(6)	-118(4)	C(32)	3308(8)	8283(7)	3476(5)
C(11)	530(6)	1792(6)	1992(3)				

Table 3 Atomic coordinates ($\times 10^4$) for complex 2

Atom	x	y	z
Cu	5 000	5 000	5 000
N(1)	4 912(2)	7 274(6)	4 517(3)
N(2)	4 455(3)	9 635(6)	3 879(3)
C(1)	3 945(3)	10 967(8)	3 478(3)
C(2)	4 349(3)	8 219(7)	4 212(3)
C(3)	5 413(3)	8 145(7)	4 357(3)
C(4)	5 132(3)	9 604(8)	3 965(4)
Fe	6 842(1)	5 556(1)	3 576(1)
O(1)	5 976(2)	4 900(5)	5 115(2)
O(2)	5 363(2)	3 744(5)	3 934(2)
C(5)	5 931(3)	4 252(6)	4 461(3)
C(6)	6 582(3)	4 154(7)	4 348(3)
C(7)	6 709(3)	3 073(7)	3 803(3)
C(8)	7 399(3)	3 358(7)	3 905(3)
C(9)	7 705(3)	4 616(8)	4 504(3)
C(10)	7 196(3)	5 115(7)	4 771(3)
C(11)	6 008(3)	7 023(8)	2 899(3)
C(12)	6 183(3)	5 940(8)	2 410(3)
C(13)	6 894(4)	6 320(9)	2 553(4)
C(14)	7 138(3)	7 645(8)	3 124(4)
C(15)	6 586(3)	8 065(8)	3 342(3)
O(1W)	5 000	2 500	2 500

Table 4 Bond distances (\AA) and angles ($^\circ$) for complex 1

Cu-N(1)	2.001(5)	Cu-N(3)	1.990(5)
Cu-O(1)	1.962(4)	Cu-O(4)	1.983(4)
O(1)-C(11)	1.284(7)	O(2)-C(11)	1.233(7)
O(3)-C(22)	1.252(7)	O(4)-C(22)	1.274(7)
N(1)-Cu-N(3)	93.7(2)	N(1)-Cu-O(1)	157.8(2)
N(3)-Cu-O(1)	89.9(2)	N(1)-Cu-O(4)	89.7(2)
N(3)-Cu-O(4)	166.8(2)	O(1)-Cu-O(4)	91.8(2)
Cu-O(1)-C(11)	105.8(4)	Cu-O(4)-C(22)	100.6(3)
O(1)-C(11)-O(2)	124.4(5)	O(1)-C(11)-C(12)	115.3(5)
O(2)-C(11)-C(12)	120.4(5)	O(3)-C(22)-O(4)	122.6(5)
O(3)-C(22)-C(23)	119.6(5)	O(4)-C(22)-C(23)	117.7(5)

Bis(ferrocenecarboxylato)bis(N-methylimidazole)copper(II) 2. A solution of anhydrous *N*-methylimidazole (8 cm³) in methanol (50 cm³) was added to [Cu₂(O₂CC₅H₄FeC₅H₅)₄(thf)₂]-thf (0.50 g). The mixture was stirred for 1.5 h at 60 °C. The dark brownish green solution was filtered under reduced pressure and the filtrate concentrated by slow evaporation to ca. 20 cm³ then filtered. Slow evaporation of the filtrate

Table 5 Bond distances (\AA) and angles ($^\circ$) for complex 2

Cu-N(1)	1.973(4)	Cu-O(1)	1.985(4)
O(1)-C(5)	1.285(7)	O(2)-C(5)	1.258(5)
N(1)-Cu-O(1)	89.0(2)	Cu-O(1)-C(5)	104.5(3)
O(1)-C(5)-O(2)	122.1(6)	O(1)-C(5)-C(6)	116.7(4)
O(2)-C(5)-C(6)	121.2(5)		

produced dark brown crystals which were washed with anhydrous diethyl ether (Found: C, 52.40; H, 4.60; N, 8.40. Calc. for C₃₀H₃₀CuFe₂N₄O₄: C, 52.35; H, 4.35; N, 8.15%).

Physical Measurements.—Elemental C, H and N analyses were performed by Desert Analytic, Tucson, AZ. Room-temperature (298 K) magnetic susceptibility measurements on powdered samples were by the Gouy method as described previously.³ Solid-state (diffuse reflectance, 700–300 nm) UV/VIS spectra were recorded on a Cary 14 spectrophotometer equipped with a diffuse reflectance accessory that was designed locally. The accessory consists of two focusing mirrors in which one mirror directs and focuses the incident radiation onto the sample while the other mirror collects the diffuse reflected radiation and directs it to the detector. Infrared spectra were recorded as Nujol mulls and KBr discs in the 4000–450 cm⁻¹ region with an FTS-7 Bio-Rad SPC 3200 Fourier-transform spectrometer. The ESR spectra of powdered samples were taken with a JEOL Jes-PE-IX spectrometer. Electrochemical studies (cyclic voltammetry) of the complexes in CH₂Cl₂ were made by methods described previously.^{1,2}

Crystal Structure Determinations of [Cu(O₂CC₅H₄FeC₅H₅)₂(dmim)₂] 1 and [Cu(O₂CC₅H₄FeC₅H₅)₂(mim)₂]-H₂O 2·H₂O (dmim = 1,2-dimethylimidazole, mim = N-methylimidazole).—*Crystal data.* C₃₂H₃₄CuFe₂N₄O₄ 1, *M* = 713.9, triclinic, space group *P* $\bar{1}$, *a* = 9.468(2), *b* = 9.849(2), *c* = 16.011(4) \AA , α = 90.44(2), β = 94.85(2), γ = 90.47(2)°, *U* = 1487.5(6) \AA^3 , *Z* = 2, *D*_c = 1.59 g cm⁻³, *F*(000) = 734, Mo-K α X-radiation, graphite monochromator, λ = 0.710 73 \AA , μ (Mo-K α) = 17.16 cm⁻¹, *T* = 155 K. Green parallelepipeds, 0.40 \times 0.20 \times 0.10 mm.

C₃₀H₃₀CuFe₂N₄O₄·H₂O 2·H₂O, *M* = 703.8, monoclinic, space group *C*2/*c*, *a* = 21.145(3), *b* = 7.858(1), *c* = 18.573(3) \AA , β = 114.61(1)°, *U* = 2805.9(7) \AA^3 , *Z* = 4, *D*_c = 1.66 g cm⁻³, *F*(000) = 1444, Mo-K α X-radiation, graphite monochromator,

$\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 18.21 \text{ cm}^{-1}$, $T = 155 \text{ K}$. Golden-brown parallelepipeds, $0.20 \times 0.55 \times 0.70 \text{ mm}$.

Data collection and refinement. Intensity data in the 2θ range $3.5\text{--}45^\circ$ for **1** and $3.5\text{--}50^\circ$ for **2** were collected on a Siemens R3mV diffractometer equipped with a LT-2 low-temperature accessory. Three check reflections were measured every 97 reflections and showed no significant variation during data collection. Scan speeds were constant at $3.00^\circ \text{ min}^{-1}$ in ω . Intensities were measured by the $2\theta\text{--}\theta$ scan method for **1** and the ω scan method for **2**. The intensity data were corrected for Lorentz and polarization effects. Absorption corrections were made with the XABS program¹³ supplied with the SHELXTL PLUS structure-solution package which was used for structure solution and refinement.¹⁴ The unique reflections collected for **1** and **2** numbered 3918 and 2482, respectively. Those reflections with $F > 4.0\sigma(F)$ were considered observed and used in structure solution and refinement, 2803 and 2218 for **1** and **2**, respectively.

The structures were solved by Patterson and successive Fourier methods. Refinement was by full-matrix least squares with all non-hydrogen atoms being assigned anisotropic thermal parameters in the latter stages of refinement. The quantity minimized during refinement was $\sum w(F_o - F_c)^2$ and the weighting scheme used was $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ with $g = 0.0011$ for **1** and 0.0053 for **2**. During the early stages of refinement for **2** a large independent peak appeared in the difference maps and was assigned to a lattice water molecule. Hydrogen atoms (except for H_2O) were located at their calculated geometric positions [$d(\text{C-H}) = 0.96 \text{ \AA}$] and assigned isotropic thermal parameters but were not refined. Refinement converged to residuals of $R = 0.0394$ and $R' = 0.0476$ for **1** and $R = 0.0427$ and $R' = 0.067$ for **2**. The largest peaks in the final Fourier difference maps were 0.76 and 0.51 e \AA^{-3} for **1** and **2**, respectively. In complex **2** the Cu atom is located on a crystallographic inversion centre at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and the oxygen atom of the water molecule is located on a crystallographic inversion centre at $\frac{1}{2}, \frac{1}{4}, \frac{1}{4}$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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