



Crystal structure and synthesis of the bis(anthracene)docuprate dianion as the dipotassium salt, $[\text{K}(\text{tetrahydrofuran})_2]_2[\{\text{Cu}(9,10\text{-}\eta^2\text{-anthracene})\}_2]$, the first anionic arene complex of copper

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Dedicated to Professors Marcetta and Donald Darensbourg on the occasion of their 80th birthdays.

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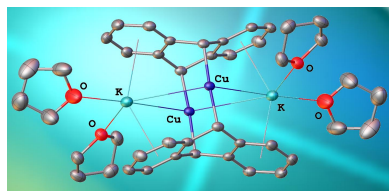
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Reactions of (tricyclohexylphosphane)copper(I) chloride with two equivalents of potassium anthracene (KAn) in tetrahydrofuran (THF) at 200 K provides air-sensitive but thermally stable (at 293 K) solutions from which yellow crystalline blocks of bis[bis(tetrahydrofuran- κO)potassium] bis(μ -anthracene- $\kappa^2 C^9:C^{10}$)-dicopper, $[\text{K}(\text{THF})_2]_2[\{\text{Cu}(9,10\text{-}\eta^2\text{-C}_{14}\text{H}_{10})\}_2]$ or $[\text{K}(\text{C}_4\text{H}_8\text{O})_2]_2[\text{Cu}_2(\text{C}_{14}\text{H}_{10})_2]$, **1**, were isolated in about 50% yield. Single-crystal X-ray crystallographic analysis of **1** confirmed the presence of the first known (arene)cuprate. Also, unlike all previously known homoleptic (anthracene)metallates of *d*-block elements, which contain metals coordinated only to terminal rings, the organocuprate unit in **1** contains copper bound to the 9,10-carbons of the central ring of anthracene. No other *d*- or *f*-block metal is known to afford an anthracene or other aromatic hydrocarbon complex having the architecture of organodicuprate **1**.

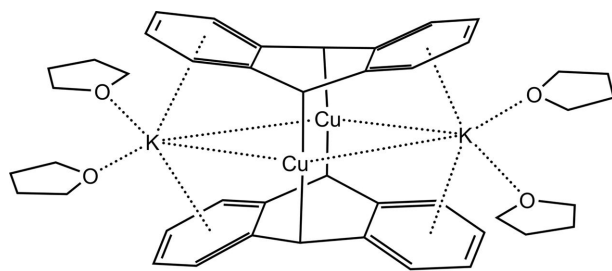
1. Introduction

Our interest in the stabilization of ‘naked’ atomic anions of *d*-block elements as homoleptic (arene)metallates (Ellis, 2019), where the arene is often a polycyclic aromatic hydrocarbon or polyarene, especially naphthalene or anthracene, led to an examination of ‘anionic copper’ (Rieke *et al.*, 1990) or ‘ Cu^{1-} ’ (Stack *et al.*, 1993), reported more than 30 years ago. In these studies, the assumed, but never isolated or characterized, cuprate species was generally prepared in tetrahydrofuran (THF) at subambient temperatures, *ca* 170 K, by addition of soluble Cu^{I} halide complexes to two equivalents of lithium naphthalene (LiNp). Although the cuprate was originally speculated to be a copper analog of the monoatomic gold anion, Au^{1-} , established to be present in cesium auride, CsAu (Knecht *et al.*, 1978), and subsequently observed in single crystals of $[\text{Me}_4\text{N}][\text{Au}]$, wherein Au^{1-} has about the same ionic radius as Br^{1-} (Dietzel & Jansen, 2001), the *bona fide* atomic copper anion has only been identified in the gas phase (Hotop *et al.*, 1973). Indeed, to our knowledge, no substance containing copper in a formal negative oxidation state is known in a condensed phase, possibly except for the cryogenic species, $[\text{Cu}(\text{CO})_n]^{1-}$ ($n = 1, 2$, or 3), which have been proposed to exist in solid neon at 4–10 K (Zhou & Andrews, 1999). Based on prior studies of compounds containing naphthalene-stabilized transition-metal anions (Ellis, 2006), we believed that these highly thermolabile solutions might contain presently unknown homoleptic (naphthalene)-cuprates (Davies, 2011). Owing to the extreme thermal



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instability of these solutions above 170 K, our attempts to isolate or characterize products from these reactions have failed to date. However, recognition of the usual greater thermal stability in solution and/or the solid state of (anthracene)metallates of *d*-block elements, compared to formally analogous (naphthalene)metallates (Kucera *et al.*, 2022), led to conducting previously unreported reactions of copper(I) halides with alkali metal anthracene radical anions, *MAn* (*M* = Li, Na, or K; An = anthracene), in THF. Also, because stoichiometrically analogous naphthalene and anthracene complexes of a given *d*-block element may possess very similar molecular structures, particularly in the solid state (Ellis, 2019), identification of an (anthracene)cuprate would be of substantial interest in shedding light on the possible nature of the previously reported ‘anionic copper’ (Rieke *et al.*, 1990) or ‘Cu^{−1}’ (Stack *et al.*, 1993).



Scheme 1

Although ‘anionic copper’ was often prepared by the reaction of the lithium naphthalene radical anion with triorganophosphane adducts of copper(I) halides, [CuX(PR₃)₃]_n (*X* = Cl, Br, or I; *R* = phenyl or *n*-butyl) (Rieke *et al.*, 1990), owing to the particularly good solubility in THF and accessibility of [CuCl(PCy₃)₃]₂ (Cy = cyclohexyl) (Churchill & Rotella, 1979), this was the only copper precursor employed in our initial study reported herein. Also, we elected not to use triphenylphosphane (PPh₃) adducts of copper(I) halides due to the ease with which coordinated or free PPh₃ and mixed tertiary aryl–alkyl phosphanes undergo reductive cleavage of P–C(aryl) bonds, unlike trialkylphosphanes (Chou *et al.*, 1986). Although reactions of [CuCl(PCy₃)₃]₂ with four equivalents of *MAn* (*M* = Li, Na, or K) in THF appear by NMR spectra to afford similar products in solution, owing to the facile isolation and crystallization of the potassium salt, only the latter will be described now. Thus, the addition of a colorless solution of [CuCl(PCy₃)₃]₂ in THF to a dark-blue solution of KAn (molar ratio: 2 KAn/Cu) in THF at 200 K, led to the formation of an air-sensitive but thermally stable (at 293 K) yellow–brown solution, from which yellow crystalline blocks of [K(THF)₂]₂[(Cu(9,10-η²-C₁₄H₁₀))₂], **1**, were isolated (Fig. 1).

Single-crystal X-ray diffraction (SCXRD) characterization of **1** confirmed the presence of an (anthracene)cuprate, the first anionic arene complex of copper. However, unlike all previously known homoleptic (anthracene)metallates of the *d*-block elements (Ellis, 2019), including the recently reported bis(anthracene)divanadate(1−) (Kucera *et al.*, 2022), which

contain metals coordinated only to terminal rings, the organocuprate unit in **1** contains Cu atoms bound to the 9,10-carbons of the central ring of anthracene. Mononuclear heteroleptic complexes of *d*- and *f*-block elements containing *M*(9,10-η²-anthracene) moieties have been structurally authenticated for the Group 3 elements scandium (Ellis *et al.*, 2018; Ghana *et al.*, 2020; Zhu *et al.*, 2023) and lutetium (Roitershtein *et al.*, 1992, 1993), and the *f*-block elements thulium (Fedushkin *et al.*, 2001) and thorium (Yu *et al.*, 2020). Unique uranium anthracene complexes containing individual metals bound to both the terminal and central rings of different anthracene ligands have been published recently (Murillo *et al.*, 2021, 2022). Dinuclear complexes of scandium (Huang *et al.*, 2011, 2014), yttrium (Fryzuk *et al.*, 2000), and iron (Hatanaka *et al.*, 2012) containing bridging anthracenes, in which one metal binds to the terminal ring and the other *anti* to the central ring of anthracene, are also known. However, none of these species are of particular relevance to **1** and will not be discussed further. Although *d*-block complexes with η⁶-coordination of the central ring of untethered specially substituted anthracenes, for example, 2,3,6,7-tetramethoxy-9,10-dimethylanthracene, have been confirmed recently (Karslyan *et al.*, 2017; Kuchuk *et al.*, 2019), no *d*- or *f*-block metal is known to afford an anthracene or other arene complex having the architecture of the organodipocuprate present in **1**.

The structure of **1** (Fig. 1) consists of a contact ion-pair complex in which two anthracene ligands, distinctly folded about the 9,10-carbons [fold angle of 36.06 (6)°, calculated from all C atoms in the anthracene ligand] are present as centrosymmetric anthracene dianions bridging two equivalent Cu atoms in a near linear fashion across the 9,10-carbons of symmetry-related rings. Equivalent [K(THF)₂]¹⁺ counter-ions interact weakly with essentially planar terminal *exo*-benzene units (mean deviations from planarity of 0.011 and 0.006 Å for rings C1–C4/C14/C13 and C5–C8/C12/C11, respectively) on **1**. Details of these interactions will be presented in Section 3.

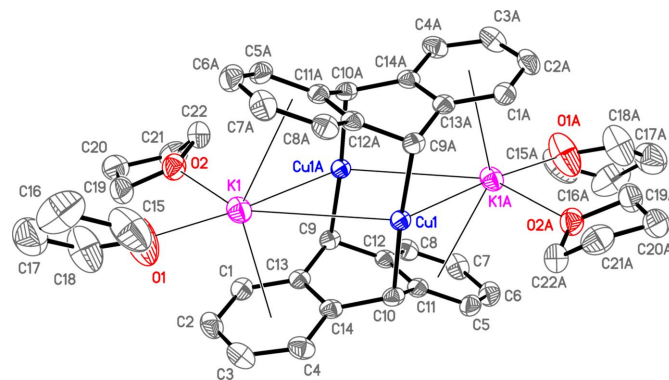


Figure 1

Anisotropic displacement ellipsoid plot of **1**, drawn at the 50% probability level with H atoms omitted. Symmetry-equivalent atoms (‘A’ label) were generated by inversion (−*x*, −*y* + 1, −*z* + 1). The K₂Cu₂ core is asymmetric (Å): Cu1...K1 = 3.6637 (15), Cu1...K1A = 3.3762 (9), and Cu1...Cu1A = 2.6172 (7).

To the best of our knowledge, only the long-known dimeric organoalunate complexes $[(\text{AlR}_2)(\text{arene})]_2^{2-}$ [R = methyl; arene = naphthalene, **2** (Brauer & Stucky, 1970), and anthracene, **3** (see Fig. 2; Brauer & Stucky, 1972)] possess molecular structures in the solid state very similar to that observed for the organocuprate dimer in **1**, *vide infra*. In particular, the coordinated anthracenes in both the cuprate, **1**, and the alunate, **3**, are effectively functioning as 9,10-dihydro-9,10-anthrylene dianionic units with about one negative charge on each of the mixed sp^2/sp^3 -hybridized 9,10 bridgehead carbons. Thus, the respective copper and aluminium anthracene complexes contain formally Cu^{1+} and Al^{3+} , both closed-shell ions. One major difference in the molecular structures of the anionic components of **1**, **2**, and **3** is the coordination environment about the metals. Whilst the four-coordinated Al atoms in **2** and **3** adopt distorted tetrahedral geometries, the dimeric structure observed for organocuprate **1** contains identical two-coordinate Cu atoms with a nearly linear C—Cu—C angle of $174.74(7)^\circ$. The substantially different steric impacts of the dimethylaluminium groups in **3** compared to the Cu atoms in **1** are responsible for some dramatic and surprising differences in the molecular structures of these two stoichiometrically similar contact ion-pair complexes (see Section 3). It should also be pointed out that dimeric neutral nonmetal or metalloid adducts of anthracene are known, which have molecular structures similar to the dimeric anion in **3**, including anthracene-based macrocyclic diphosphanes, $[(\text{PX}_2)(9,10-\eta^2\text{-An})]_2$, with $X = \text{Cl}$ (Velian *et al.*, 2014) and phenyl (Riu *et al.*, 2020). Indeed, the oldest example, now known as the photodimer of anthracene, di-*para*-anthracene, was first reported nearly 160 years ago (see Bouas-Laurent *et al.*, 2000) and forms as poorly soluble microcrystals when solutions of anthracene in benzene, toluene, *etc.*, are exposed to sunlight/UV radiation. Structural characterization by SCXRD showed that the labile dimer arises by symmetrical coupling of the 9,10-carbons on two anthracenes, where the bridgehead C—C distance [$1.624(3) \text{ \AA}$] is long (Choi & Marinkas, 1980), resulting in a low dissociation energy of the dimer, calculated to be $9 \pm 3 \text{ kcal mol}^{-1}$ (Grimme *et al.*, 2006). Interestingly, **1** may be considered formally to be a molecule in which atomic copper anions have been inserted into each of the two bridgehead C—C bonds of the anthracene dimer, thereby increasing the separation of the bridgehead C atoms from $1.624(3)$ to $3.98(1) \text{ \AA}$.

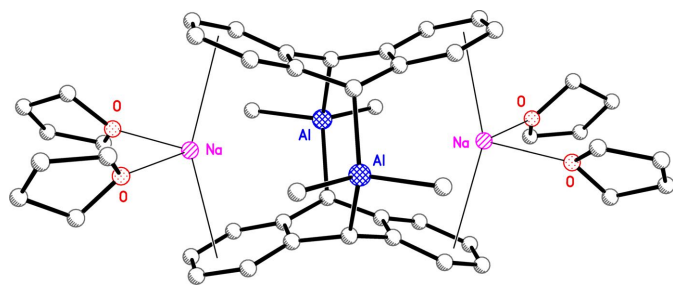


Figure 2
The molecular plot of **3**.

Unperturbed mononuclear homo-diorganocuprate complexes, $[\text{CuR}_2]^{1-}$ (R = alkyl, aryl, *etc.*), also have close to linear C—Cu—C units and are formulated to contain two carbanions bound to Cu^I by quite polar Cu—C σ bonds, where the Cu—C distance in **1** [$1.989(2) \text{ \AA}$] is well within the range of $1.83\text{--}2.05 \text{ \AA}$ observed previously for homoleptic diorganocuprates (Davies, 2011). Although Cu^I commonly adopts coordination numbers 2–4 in mononuclear complexes, organodicuprate **1** contains two quite bulky dianionic hydrocarbyl units, which appear to favor the formation of the observed structure containing two-coordinated Cu^I with essentially linear C—Cu—C units, as expected for $d^{10} \text{Cu}^I$ (Cotton *et al.*, 1999). Owing to the latter, the separation of the 9,10-carbons on individual anthracene groups in **1** effectively defines the Cu...Cu distance of $2.6172(7) \text{ \AA}$. Prior studies suggest that $d^{10}\text{Cu}$ – $d^{10}\text{Cu}$ interactions are very weak to non-existent when the Cu...Cu separation is greater than $\sim 2.50 \text{ \AA}$ in molecular entities containing Cu^I complexes (Mehrotra & Hoffmann, 1978; Cotton *et al.*, 1988; Merz & Hoffmann, 1988).

Although $d^{10}\text{Cu}$ – $d^{10}\text{Cu}$ or ‘cuprophilic’ interactions (Harisomayajula *et al.*, 2019) appear unlikely to stabilize the dimeric structure adopted by **1** in the solid state, the significant contact ion-pairing and resulting increase in its crystalline lattice stabilization may play a key role in the formation of the observed bis(anthracene)dicuprate(2–) complex, relative to unknown monomeric monoanions, *i.e.* $[\{\text{Cu}(\text{THF})_x\}(9,10-\eta^2\text{-An})]^{1-}$ ($x = 0\text{--}2$), which would likely be strained metallacycles, *vide infra*. In the case of the structurally related organoaluminium complexes **2** and **3**, it was proposed that the dimeric, rather than plausible monomeric structures, ‘are favored by smaller deviations from tetrahedral angles about the aluminum atoms in the dianions rather than about the aluminum atom in the hypothetical monoanions.’ However, surprisingly, the possible importance of contact ion-pairing in contributing to the stabilization of the dimers in the solid state, and possibly also in solution, was not considered (Brauer & Stucky, 1972). Most interestingly, the bis(naphthalene)dialanate(2–) salt, **2**, was originally prepared and proposed to be a monomer, $[\{\text{AlMe}_2\}(1,4-\eta^2\text{-Np})]^{1-}$ (Np = naphthalene), based only on a proton NMR spectrum in THF and identification of 1,4-dihydronaphthalene as a key hydrolysis product (Lehmkuhl, 1966). Later, the identical salt, as crystalline **2**, dissolved in THF, was found to afford a proton NMR spectrum in good agreement with that of the purported monomer (Brauer & Stucky, 1970). In both SCXRD studies on **2** and **3**, the possibility that they could be present as monomers in solution appears to have been implicitly rejected (Brauer & Stucky, 1970, 1972). However, the later structural authentication of an (anthracene)aluminium monomer, the neutral metallacycle $[\{\text{AlEt}(\text{THF})\}(9,10-\eta^2\text{-9,10-bis(trimethylsilyl)anthracene})]$, **4**, strongly suggests that the natures of **2** and **3** in solution merit reinvestigation. It should also be emphasized that presently we cannot rule out the possibility that monomeric forms of **1** could be present in THF or other solvents (see Section 2).

The structure of the alane monomer **4** is consistent with that expected of a strained metallacycle, *vide infra*, *i.e.* a sharp C9—Al—C10 angle of 81.5° for four-coordinated aluminium

and an average Al—C(bridgehead) distance of 2.057 (4) Å, which is significantly longer than the normal Al—C(Et) distance of 1.966 (4) Å present in **4** (Lehmkuhl *et al.*, 1985). Structurally similar (anthracene)alane and (anthracene)alanate(1[−]) monomers have been prepared recently by novel additions of anthracene to an Al^I complex (Bakewell *et al.*, 2020) and a dialkylaluminum anion (Sugita *et al.*, 2020), respectively.

A more well-known related complex is the monomeric (anthracene)Mg solvate in crystalline $[\{\text{Mg}(\text{THF})_3\}(9,10\text{-}\eta^2\text{-An})]$, **5**, possessing a C9—Mg—C10 angle of 71.4°. This angle is significantly sharper than the corresponding angle in **4**, likely owing in part to the higher coordination number of Mg in **5**. The latter also contains a rather long Mg—C distance of 2.30 (2) Å (Engelhardt *et al.*, 1988) compared to that present in $[(9\text{-anthracenyl})\text{Mg}(\mu\text{-Br})\text{-di-}n\text{-butyl ether}]_2$, a dimeric Grignard reagent with bridging bromides and an essentially unstrained Mg—C bond with a distance of 2.132 (2) Å (Bock *et al.*, 1996). For related reasons, **5** appears to be the first (anthracene)metal complex to be recognized as a strained metallacycle (Bogdanović *et al.*, 1987). In solution, **5** is a metastable species, which following facile loss of THF in hexane or diethyl ether, readily eliminates free anthracene and is proposed to initially form ‘quasi-atomic’ magnesium under strictly anaerobic conditions (Bönnemann *et al.*, 1983). The latter rapidly forms a mirror of magnesium metal in the absence of other reactants (Alonso *et al.*, 1987). Compound **5** has been found by the Cummins group (Velian & Cummins, 2012) and others to be a highly useful precursor to numerous new strained monomeric main group element adducts of anthracene, including the formal Ge^{IV} complex $[\{\text{GeMe}_2\}\text{-(}9,10\text{-}\eta^2\text{-An)}]$, **6**, or 2,3:5,6-dibenzo-7-dimethylgermanorbornadiene. X-ray structure characterization of **6**, Me₂GeAn, revealed a sharp C9—Ge—C10 angle of 77.72 (5)°, and Ge—C(9,10 or bridgehead) distances [average 2.030 (1) Å] which are significantly longer than the Ge—C(Me) distance [average 1.943 (4) Å] (Velian *et al.*, 2015). The latter is statistically identical to that observed for Me₄Ge [1.945 (3) Å; Hencher & Mustoe, 1975]. Compound **6** suffers thermal loss of anthracene at 373 K in toluene to produce in good yield an intriguing dimethylgermylene, Me₂Ge, adduct $[\{\text{Ge}_2\text{Me}_4\}\text{-(}9,10\text{-}\eta^2\text{-An)}]$, **7**, which may arise *via* insertion of highly reactive Me₂Ge into a strained Ge—C(bridgehead) bond of **6**. However, also possible is an initial dimerization of Me₂Ge to the digermene, Me₄Ge₂, followed by its facile [4 + 2] cycloaddition to free anthracene, which was established previously to afford **7** (Sakurai *et al.*, 1982). Also noteworthy is that the thermolysis of two equivalents of **6** to form the less strained **7** and free anthracene has been calculated to have a quite favorable free energy change (ΔG) of *ca* −37 kcal mol^{−1} of **7** (Velian *et al.*, 2015). Finally, under milder conditions, **6** has been shown to function as an Me₂Ge group transfer reagent (Geeson *et al.*, 2019).

Of particular relevance to our discussion is that neutral **6** is isoelectronic and likely of similar structure to the presently unknown alanate, $[\{\text{AlMe}_2\}(9,10\text{-}\eta^2\text{-An})]^{1-}$, the monomer of structurally characterized dimeric **3** (Brauer & Stucky, 1972).

To the best of our knowledge, none of the reported formally strained metallacyclic monomers, $[\{ML_n\}(9,10\text{-}\eta^2\text{-An})]^z$ ($z = 0$ or -1), are presently known to form dimers (or oligomers) related to **1**, **2**, or **3**. Calculations on the structures and relative stabilities of the monomeric forms of **1**, **2**, and **3**, compared to the respective dimers, would be of considerable interest. Inclusion of contact ion-pairing could be of key importance in such a study, but might prove to be a nontrivial extension.

In contrast to **1**, which contains only Cu—C σ -bonds, all prior (arene)copper compounds have been characterized as π -complexes, including the homoleptic cationic species, $[\text{Cu}(\text{arene})_2]^{1+}$ [arene = 1,2-difluorobenzene (Santiso-Quiñones *et al.*, 2009), 1,3,5-trimethylbenzene, and hexamethylbenzene (Wright *et al.*, 2010, 2015)], which exhibit the long-known copper- η^2 -arene structural motif, first observed in $[\text{Cu}(\text{benzene})][(\mu\text{-Cl})_3\text{AlCl}]$ (Turner & Amma, 1966). More recently, unprecedented copper-arene π -complexes containing unsupported η^6 -arene binding modes in the 18-electron species $[\text{Cu}(\text{C}_6\text{Me}_6)(\text{PR}_3)]\text{PF}_6$ (R = phenyl or phenoxide) were described (Wright *et al.*, 2015). Although unsupported naphthalene, anthracene, or related polyarene complexes of copper remain unknown, except in the case of **1** for anthracene, polyarenes bearing substituents which effectively bind to Cu^I can also coordinate to copper. For example, a cationic Cu- η^2 -naphthyl complex with a neutral 1-naphthyl-appended NS₂ macrocyclic ligand (Conry, 1998) and an unusual $[\text{Cu}\{\eta^6\text{-}9,10\text{-bis}(N\text{-}n\text{-propyl-}N\text{-diphenylphosphano)aminomethyl}\}\text{anthracene}\}]^{1+}$ complex, in which Cu^I is constrained *via* chelation with diphenylphosphanyl groups to lie over the central ring of nearly planar anthracene (Xu *et al.*, 2003), have been characterized by SCXRD. Whereas the Cu- η^2 -naphthyl complex has unexceptional Cu—C distances [2.129 (6) and 2.414 (6) Å] for asymmetric π -bonding of the 1-naphthyl group, the Cu—C distances in the copper- η^6 -anthracene complex are in the range 2.773–3.021 Å. These are much longer than usual in (arene)copper complexes, indicative, at best, of a very weak copper-anthracene interaction (Xu *et al.*, 2003). For example, in $[\text{Cu}(\eta^6\text{-C}_6\text{Me}_6)(\text{PR}_3)]\text{PF}_6$, the Cu—C distances are in the range 2.253–2.300 Å (Wright *et al.*, 2015).

2. Experimental

2.1. Synthesis and crystallization

All manipulations were carried out under argon in a standard glove-box and/or using Schlenk techniques to maintain strictly anaerobic conditions (Shriver, 1969; Wayda & Darensbourg, 1987). Solvents were dried by standard methods, as described previously (Brennessel & Ellis, 2012). Reagent-grade anthracene (99%) was sublimed *in vacuo* and $[\text{CuCl}(\text{PCy}_3)]_2$ (Cy = cyclohexyl) was prepared as described previously (Churchill & Rotella, 1979). NMR samples were sealed under argon into 5 mm tubes and analyzed on a Varian Unity 500 MHz or a Bruker Avance III 400 MHz spectrometer. ¹H and ¹³C chemical shifts are given with reference to residual ¹H and ¹³C solvent resonances relative to tetramethylsilane.

Table 1
Experimental details.

Crystal data	
Chemical formula	[K(C ₄ H ₈ O) ₂] ₂ [Cu(C ₁₄ H ₁₀) ₂]
<i>M</i> _r	850.13
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	173 (2)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.6864 (19), 10.484 (2), 10.658 (2)
α , β , γ (°)	66.22 (3), 89.67 (3), 82.73 (3)
<i>V</i> (Å ³)	981.2 (4)
<i>Z</i>	1
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.34
Crystal size (mm)	0.40 × 0.40 × 0.20
Data collection	
Diffractometer	Bruker SMART platform CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 1996)
<i>T</i> _{min} , <i>T</i> _{max}	0.630, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	11455, 4459, 3853
<i>R</i> _{int}	0.024
(sin θ/λ) _{max} (Å ⁻¹)	0.650
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.029, 0.073, 1.04
No. of reflections	4459
No. of parameters	275
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.34, -0.31

Computer programs: *SMART* (Bruker, 2003), *SAINT* (Bruker, 2003), *SHELXT2018* (Sheldrick, 2015a), *SHELXL2019* (Sheldrick, 2015b), and *SHELXTL* (Sheldrick, 2008).

2.1.1. [K(THF)₂]₂[Cu(C₁₄H₁₀)₂] (1). Sublimed anthracene (0.939 g, 5.27 mmol) and shiny pieces of potassium metal (0.211 g, 5.40 mmol) were transferred in an argon-filled glove-box to a round-bottomed Schlenk flask, along with a glass-enclosed magnetic stirrer bar. Subsequently, THF (100 ml) was added and the mixture was stirred vigorously in the dark for 6 h at 293 K to afford a deep-blue solution of potassium anthracene (KAn), which is susceptible to photo-oxidation by visible light. This solution/slurry was cooled to 200 K with stirring and to it was transferred *via* cannula a cold (200 K) colorless solution of [CuCl(PCy₃)₂] (1.000 g, 1.318 mmol) in THF (50 ml) and stirring continued for 12 h at 200 K. The resulting yellow-brown solution was warmed over a *ca* 6 h period to near 290 K (room temperature) and filtered (medium or P4 porosity frit) to remove KCl. After careful evaporation of all but about 20 ml of solvent *in vacuo* at 273–293 K, pentane (100 ml) was added with stirring. The resulting slurry was filtered, washed vigorously with pentane (2 × 10 ml) and dried *in vacuo* to afford 0.59 g (53% yield, based on the copper precursor) of homogeneous yellow solid [K(THF)₂]₂[Cu(C₁₄H₁₀)₂], **1**. No elemental analysis was conducted on the bulk solid **1**, so its composition is based exclusively on the SCXRD study and NMR spectra. X-ray-quality yellow blocks of **1** were grown from a pentane-layered saturated solution in THF at 240 K over a 6 d period.

¹H NMR (500 MHz, 293 K, THF-*d*₈, δ , ppm): 1.77 (*m*, 4H, THF), 3.52 (*s*, 1H, H₉), 3.63 (*m*, 4H, THF), 6.24 (*m*, 2H, H₁),

6.35 (*m*, 2H, H₂). ¹³C{¹H} NMR (125 MHz, 293 K, THF-*d*₈, δ , ppm): 24.2 (*m*, THF), 52.4 (*s*, C₉), 66.3 (*m*, THF), 117.7 (*s*, C₁), 117.9 (*s*, C₂), 145.2 (*s*, C₁₁).

It is interesting that the first structurally authenticated (by SCXRD) monomeric (anthracene)metal complex, [[Mg(THF)₃](9,10- η^2 -An)], **5** (Engelhardt *et al.*, 1988), was originally formulated to be a monomer based only on its NMR spectra in THF. Noteworthy is that the latter spectra, without THF, exhibit ¹H and ¹³C{¹H} resonances for the coordinated anthracene in **5** with quite similar values to those observed for **1**; *i.e.* ¹H NMR (400 MHz, 293 K, THF-*d*₈, δ , ppm): 3.51 (*s*, 1H, H₉), 5.95 (*m*, 2H, H₁), 6.01 (*m*, 2H, H₂); ¹³C{¹H} NMR (75.4 MHz, 293 K, THF-*d*₈, δ , ppm): 57.7 (*s*, C₉), 114.1 (*s*, C₁), 118.1 (*s*, C₂), 145.9 (*s*, C₁₁) (Bogdanović *et al.*, 1984). However, based on available data, it would now be premature to suggest that **1** may also be present as a monomer in THF. Noteworthy is that the corresponding NMR spectra for the aluminium dimer **3** in THF apparently have not been reported for comparison. Also, studies of **1** in other solvents would be of interest, as well as further NMR spectral analyses of this cuprate. Unfortunately, this latter work must be carried out independently in another laboratory because we are no longer able to examine this intriguing species.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms on anthracene C atoms were found from difference Fourier maps and refined freely. H atoms on the tetrahydrofuran ligands were placed geometrically and treated as riding atoms, with C–H = 0.99 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C).

3. Results and discussion

The asymmetric unit of **1**, which is one-half of the formula unit [K(THF)₂]₂[Cu(9,10- η^2 -An)]₂, contains one copper center and one anthracene ligand in contact with one [K(THF)₂]¹⁺ counter-ion. A crystallographic inversion center generates full well-resolved **1** (Fig. 1). The potassium cations have normal ligated THF with K–O distances [average 2.74 (7) Å] within the range 2.62 (2)–2.78 (3) Å of those observed previously in [K(THF)₂]₂[*ML*_{*n*}], where *ML*_{*n*} is [V(η^4 -Np)(η^6 -Np)]²⁻ (Np = naphthalene; Kucera *et al.*, 2022) and [U(NHDipp)₅]²⁻ (Dipp = 2,6-diisopropylphenyl; Nelson *et al.*, 1992). To help understand the molecular structure of the contact ion-pair complex, **1**, it is useful to first compare details of the metal–metal interactions in **1** with those in the only previously known (anthracene)metal dimer complex present in [Na(THF)₂]₂[[AlMe₂](9,10- η^2 -An)]₂, **3**, (Brauer & Stucky, 1972). It is important to recognize that both metal atoms, K and Cu, in **1** are appreciably larger than the corresponding atoms, Na and Al, in **3**. Thus, the sum of the covalent radii of K and Cu (3.35 Å) is greater than the corresponding sum for Na and Al (2.87 Å) (Cordero *et al.*, 2008). However, the formally nonbonded distances (Table 2) between all of the metals in **1** are considerably shorter, *i.e.* K1...Cu1 = 3.6637 (15) Å,

Table 2

Selected geometric parameters (Å, °).

Cu1—C9 ⁱ	1.9873 (19)	C8—K1 ⁱ	3.421 (2)
Cu1—C10	1.9906 (19)	C9—C13	1.480 (3)
Cu1—Cu1 ⁱ	2.6172 (7)	C9—C12	1.482 (3)
Cu1—K1 ⁱ	3.3762 (9)	C10—C14	1.478 (3)
Cu1—K1	3.6637 (15)	C10—C11	1.479 (3)
C1—K1	3.081 (2)	C11—K1 ⁱ	3.158 (2)
C2—K1	3.158 (2)	C12—K1 ⁱ	3.3324 (19)
C3—K1	3.338 (3)	C13—K1	3.170 (2)
C4—K1	3.446 (2)	C14—K1	3.364 (2)
C5—K1 ⁱ	3.100 (2)	K1—O1	2.681 (2)
C6—K1 ⁱ	3.203 (3)	K1—O2	2.8027 (16)
C7—K1 ⁱ	3.360 (2)		
C9 ⁱ —Cu1—C10	174.74 (7)	C13—C9—C12	113.07 (15)
C9 ⁱ —Cu1—Cu1 ⁱ	91.87 (6)	C14—C10—C11	113.34 (15)
C10—Cu1—Cu1 ⁱ	93.22 (6)		

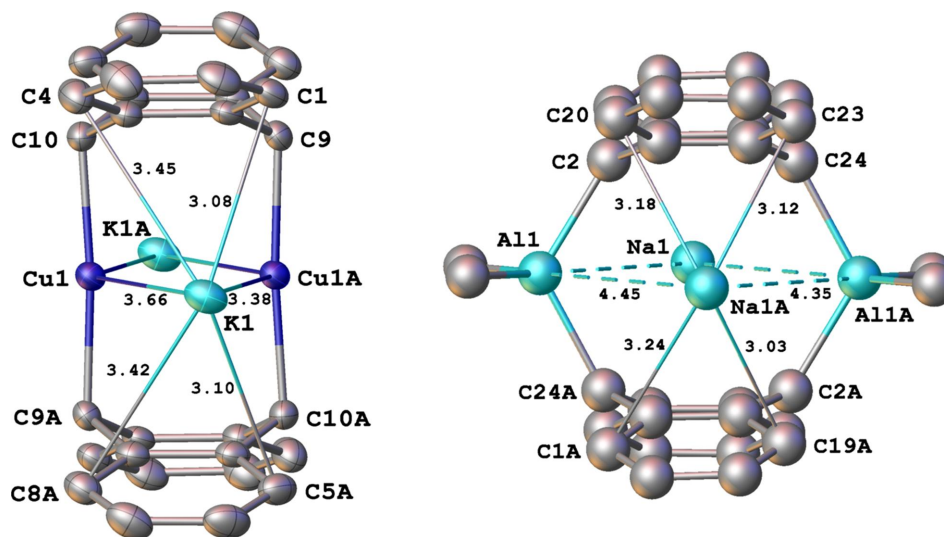
Symmetry code: (i) $-x, -y + 1, -z + 1$.

$K1 \cdots Cu1A = 3.3762$ (9) Å, $K1 \cdots K1A = 6.542$ (2) Å and $Cu1 \cdots Cu1A = 2.6171$ (7) Å [symmetry code: (A) $-x, -y + 1, -z + 1$], than the corresponding distances in **3**, *i.e.* $Na1 \cdots Al1 = 4.348$ (6) Å, $Na1 \cdots Al1A = 4.455$ (7) Å, $Na1 \cdots Na1A = 7.28$ (1) Å and $Al1 \cdots Al1A = 4.95$ Å. As described in Section 1, the rather short, but formally nonbonded, Cu $\cdots$ Cu distance in **1** arises from the essentially linear C9—Cu—C10A angle, expected for two-coordinated d^{10} Cu^I (Cotton *et al.*, 1999).

However, in **3**, the considerably smaller C9—Al—C10A angle [120.2 (4)°], resulting from the distorted tetrahedral geometry of four-coordinated Al^{III}, causes the Al $\cdots$ Al distance to be much longer (Fig. 2). Of particular interest is that the relatively uncrowded linear Cu atoms in **1** permit both solvated potassium ions to approach the cuprate centers more closely than the smaller solvated sodium ions can with the bulkier distorted tetrahedral aluminate centers in **3**. Whereas the Na $\cdots$ Al distances in **3** exhibit a small difference

[0.107 (7) Å] and, as a result, its molecular structure, without the THF groups, is fairly symmetrical and deviates only slightly from D_{2h} symmetry (Brauer & Stucky, 1972), the two K $\cdots$ Cu distances in **1** differ by 0.287 (2) Å (Fig. 1), with one potassium ion having a surprisingly short K $\cdots$ Cu distance of 3.3762 (9) Å, close to the sum of the covalent radii of K and Cu (3.35 Å) (Cordero *et al.*, 2008). As a consequence, **1** differs from **3** in having a slightly more compact but a much less symmetrical contact ion-pair structure, owing largely to the different coordination numbers of copper and aluminium, in otherwise quite similar species. Another key difference between **1** and **3** are the nonbonded bridgehead C9 $\cdots$ C10A distances [3.974 (3) and 3.57 (1) Å, respectively], which show that the two formal 9,10-coordinated anthracene dianion units are slightly further apart in **1** than they are in **3**, owing also to the different coordination numbers of copper and aluminium in these remarkable compounds, both of which are worthy of additional study.

Despite the aforementioned differences, the geometries of the central anthracene ring of **1** and **3** are similar. Thus, for **1**, the bridgehead angles C11—C10—C14 [113.3 (2)°] and C12—C9—C13 [113.1 (2)°] (Table 2) do not differ significantly from the corresponding angles reported for **3** [114.1 (9) and 112 (1)°; Brauer & Stucky, 1972]. Similarly, the bridgehead C—C distances for **1** [C9—C12 = 1.482 (3) Å, C9—C13 = 1.480 (3) Å, C10—C11 = 1.479 (3) Å, and C10—C14 = 1.478 (3) Å, with average C—C = 1.480 (3) Å; Table 2], are statistically identical to corresponding C—C distances reported for **3** [average 1.49 (2) Å], which are both close to the value of 1.51 (5) Å observed previously for C(sp^2)—C(sp^3) distances (Jolly, 1976). Perhaps surprisingly, the geometry of the coordinated central ring of anthracene in the first reported structurally characterized anionic metallacyclic monomer of this type, $[Lu(\eta^5-Cp)_2](9,10-\eta^2-An)^{1-}$, is structurally nearly identical, without the metal, to those observed in the dianions

**Figure 3**

End views of **1** (left) and **3** (right) that highlight the much greater asymmetry of the dicuprate. Representative atom–atom distances are shown (Å). In **1**, the six closest C atoms to the shorter Cu $\cdots$ K contact have an average K $\cdots$ C distance of 3.14 (13) Å, while those closest to the longer Cu $\cdots$ K contact have an average K $\cdots$ C distance of 3.38 (5) Å.

of **1** and **3**, with an average bridgehead C—C distance of 1.485 (9) Å. The lutetium anion also has an average bridgehead C—C—C angle of 111.8 (5) Å, which is very close to the corresponding angles of **1** and **3**. A key structural difference in the lutetium anion is the sharp C9—Lu—C10 angle of 67.1 (2)°, owing to the metallacyclopropane character of the complex and, likely also the large bulk of the bis(cyclopentadienyl)lutetium moiety, which may well be responsible for its stability towards dimerization or oligomerization in solution (THF) and in the solid state as a crystalline [Na(diglyme)₂]¹⁺ salt (diglyme = diethylene glycol dimethyl ether) at ca 293 K (Roitershtein *et al.*, 1993).

Interactions of the alkali metal cations with the *exo*-benzene C atoms are consistent with the overall molecular structures of **1** and **3**. In the less symmetrical cuprate **1**, the K...C distances fall into a distinct 1:1 pattern, with the six C atom closest to the short K...Cu contact ion pairing (C1, C2, C5, C6, C11, and C13) having the shortest distances [average 3.14 (13) Å], whereas the K...C distances for the six C atoms closest to the long K...Cu contact (C3, C4, C7, C8, C12, and C14) are longer [average 3.38 (5) Å] (see Figs. 1 and 3). In contrast, for the aluminate **3**, the Na—C distances for the eight outer C atoms are rather similar and range from 2.94 (1) to 3.24 (1) Å, but the Na—C distances of the four more crowded ring-junction C atoms are mostly longer [average 3.28 (4) Å; Brauer & Stucky, 1972]. Finally, in **1**, the essentially planar *exo*-benzene units possess C—C distances [average 1.396 (3) Å] and C—C—C angles [average 119.9 (2)°] that are quite similar to those found in uncharged free benzene (Mitchell & Cross, 1965), indicating that the contact ion pairing is sufficiently weak to have no significant influence on the structure of the *exo*-benzene groups and that the negative charge on each anthracene ligand is essentially localized on the central ring and the appended metal center. Similar features were found for the *exo*-benzene groups in **3** (Brauer & Stucky, 1972). However, in both **1** and **3**, the interactions of the counter-ions in these contact ion-paired complexes may play an important role in defining the structures of the anionic components and perhaps their existence in the solid state. In this respect, the isolation of the bis(anthracene)docuprate(2−) with relatively weakly interacting cations, such as [K([2.2.2.]cryptand)]¹⁺, tetraalkylammonium(1+), *etc.*, would be of considerable interest. As our laboratory will be irreversibly shuttered in 2023, others are encouraged to examine these possibilities and related issues, *vide infra*.

Since our initial report on tris(1,2,3,4- η^4 -naphthalene)zirconate(2−), the first confirmed homoleptic (polyarene) metallate of a *d*-block metal (Jang & Ellis, 1994), which was remarkably labile and functioned formally as a ‘masked’ naked source of low-spin atomic Zr²⁺ in its facile reaction with carbon monoxide to afford [Zr(CO)₆]^{2−}, our research group has been interested in discovering what other *d*-block elements, throughout the periodic table, would afford related and hopefully labile complexes. Thus began our exploration in a systematic fashion of the synthesis and reactivity patterns of transition-metal compounds containing metals in formal negative oxidation states (Ellis, 2006). Early on we wondered

whether *f*-block elements would also ‘succumb’ to this strategy, but unfortunately never examined these elements (Ellis, 2019). In this regard, we would like to point to the exciting recent results of Skye Fortier and co-workers in highly challenging uranium chemistry (Murillo *et al.*, 2021, 2022). As mentioned in Section 1, we were also intrigued by early reports of ‘anionic copper’ (Rieke *et al.*, 1990) and this led to our synthesis and structural characterization of the totally unexpected dicuprate salt, **1**, described herein. Owing to the early departure of a group member, extension of this study was not possible. For example, we had hoped to examine the reactivity of **1** with good acceptor ligands, such as CO, PF₃, and P(OR)₃, and particularly organic isocyanides, to determine whether the anthracenes would be displaced to produce new formal Cu(0,1−) complexes. Noteworthy is that although isolable Cu^{1−} complexes remain unknown, very recently, the first unambiguous Cu⁰ complex was isolated, thoroughly characterized, and structurally authenticated (Graziano *et al.*, 2022). Also, examination of Rieke’s thermally unstable alleged cuprates, derived from naphthalene radical anion reductions remain of great interest because the possible ‘naphthalene stabilized cuprate’ may be a more labile source of ‘naked Cu(1−)’ than one derived from the anthracene radical anion. Extension of these studies to silver and gold promise to uncover exciting results. For example, could a *bona fide* gold anion (Jansen, 2008) be ‘tamed’ by naphthalene or anthracene to provide labile complexes, enabling the study of new aurate chemistry? We mention these possible extensions because none of this research will be carried out by us at the University of Minnesota.

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supporting information

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Crystal structure and synthesis of the bis(anthracene)docuprate dianion as the dipotassium salt, $[\text{K}(\text{tetrahydrofuran})_2]_2[\{\text{Cu}(\text{9,10-}\eta^2\text{-anthracene})\}_2]$, the first anionic arene complex of copper

Victor G. Young, William W. Brennessel and John E. Ellis

Computing details

Bis(μ -anthracene- $\kappa^2\text{C}^9\text{:C}^{10}$)dicopper bis[bis(tetrahydrofuran- κO)potassium]

Crystal data

$[\text{K}(\text{C}_4\text{H}_8\text{O})_2]_2[\text{Cu}(\text{C}_{14}\text{H}_{10})_2]$

$M_r = 850.13$

Triclinic, $P\bar{1}$

$a = 9.6864(19) \text{ \AA}$

$b = 10.484(2) \text{ \AA}$

$c = 10.658(2) \text{ \AA}$

$\alpha = 66.22(3)^\circ$

$\beta = 89.67(3)^\circ$

$\gamma = 82.73(3)^\circ$

$V = 981.2(4) \text{ \AA}^3$

$Z = 1$

$F(000) = 444$

$D_x = 1.439 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 6461 reflections

$\theta = 2.3\text{--}27.5^\circ$

$\mu = 1.34 \text{ mm}^{-1}$

$T = 173 \text{ K}$

Block, yellow

$0.40 \times 0.40 \times 0.20 \text{ mm}$

Data collection

Bruker SMART platform CCD
diffractometer

Radiation source: normal-focus sealed tube

ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.630$, $T_{\max} = 0.746$

11455 measured reflections

4459 independent reflections

3853 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.1^\circ$

$h = -12 \rightarrow 12$

$k = -13 \rightarrow 13$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.073$

$S = 1.04$

4459 reflections

275 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2 + 0.3478P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.34 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.30 \text{ e \AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The H atoms on the metal-coordinating C atoms were found from the difference Fourier map and refined freely.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	−0.05999 (2)	0.40243 (2)	0.48345 (2)	0.02155 (7)
C1	0.38363 (19)	0.4873 (2)	0.3784 (2)	0.0276 (4)
H1	0.430 (2)	0.559 (2)	0.390 (2)	0.026 (5)*
C2	0.4151 (2)	0.4501 (2)	0.2690 (2)	0.0343 (5)
H2	0.481 (2)	0.495 (2)	0.212 (2)	0.037 (6)*
C3	0.3490 (2)	0.3475 (2)	0.2528 (2)	0.0368 (5)
H3	0.371 (2)	0.321 (2)	0.184 (2)	0.042 (6)*
C4	0.2530 (2)	0.2823 (2)	0.3460 (2)	0.0320 (4)
H4	0.206 (2)	0.208 (2)	0.338 (2)	0.029 (5)*
C5	0.1116 (2)	0.1311 (2)	0.8108 (2)	0.0308 (4)
H5	0.068 (2)	0.058 (2)	0.797 (2)	0.033 (6)*
C6	0.1389 (2)	0.1233 (2)	0.9416 (2)	0.0366 (5)
H6	0.123 (2)	0.045 (2)	1.020 (2)	0.037 (6)*
C7	0.2012 (2)	0.2276 (2)	0.9571 (2)	0.0367 (5)
H7	0.222 (2)	0.223 (2)	1.046 (2)	0.042 (6)*
C8	0.2362 (2)	0.3400 (2)	0.8413 (2)	0.0306 (4)
H8	0.282 (2)	0.416 (2)	0.8515 (19)	0.024 (5)*
C9	0.23864 (18)	0.46989 (19)	0.58254 (19)	0.0236 (4)
H9	0.301 (2)	0.524 (2)	0.602 (2)	0.026 (5)*
C10	0.10924 (18)	0.26005 (19)	0.55160 (19)	0.0244 (4)
H10	0.086 (2)	0.175 (2)	0.5485 (19)	0.023 (5)*
C11	0.14273 (18)	0.24371 (19)	0.69295 (19)	0.0247 (4)
C12	0.20785 (17)	0.35061 (19)	0.70886 (19)	0.0241 (4)
C13	0.28346 (17)	0.42684 (18)	0.47075 (18)	0.0235 (4)
C14	0.21665 (18)	0.32051 (19)	0.45431 (19)	0.0245 (4)
K1	0.11852 (4)	0.63331 (5)	0.19219 (4)	0.03269 (11)
O1	0.1757 (2)	0.6849 (3)	−0.06891 (18)	0.0786 (7)
C15	0.0817 (3)	0.7024 (4)	−0.1778 (3)	0.0731 (9)
H15A	−0.014627	0.729703	−0.157488	0.088*
H15B	0.085162	0.613167	−0.189734	0.088*
C16	0.1226 (4)	0.8113 (3)	−0.3012 (3)	0.0745 (10)
H16A	0.063451	0.902048	−0.320983	0.089*
H16B	0.114022	0.786168	−0.380697	0.089*
C17	0.2715 (3)	0.8212 (4)	−0.2734 (3)	0.0713 (9)
H17A	0.334983	0.776688	−0.321839	0.086*
H17B	0.286732	0.920583	−0.303253	0.086*
C18	0.2948 (3)	0.7440 (4)	−0.1217 (3)	0.0709 (9)

H18A	0.375707	0.669418	−0.099890	0.085*
H18B	0.314465	0.809604	−0.080451	0.085*
O2	0.27673 (15)	0.82963 (15)	0.21520 (15)	0.0367 (3)
C19	0.4093 (2)	0.8595 (2)	0.1558 (2)	0.0414 (5)
H19A	0.395866	0.919108	0.056271	0.050*
H19B	0.469354	0.770940	0.168634	0.050*
C20	0.4758 (2)	0.9354 (3)	0.2282 (3)	0.0457 (6)
H20A	0.456244	1.038622	0.176450	0.055*
H20B	0.577920	0.906881	0.241359	0.055*
C21	0.4066 (3)	0.8884 (3)	0.3651 (2)	0.0464 (6)
H21A	0.453925	0.796853	0.431901	0.056*
H21B	0.404851	0.959285	0.404746	0.056*
C22	0.2617 (2)	0.8765 (2)	0.3231 (2)	0.0423 (5)
H22A	0.218169	0.808373	0.401707	0.051*
H22B	0.202466	0.968997	0.291007	0.051*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01789 (11)	0.02101 (12)	0.02501 (12)	−0.00262 (8)	−0.00129 (8)	−0.00855 (9)
C1	0.0194 (9)	0.0277 (10)	0.0314 (10)	−0.0023 (7)	−0.0045 (7)	−0.0078 (8)
C2	0.0196 (9)	0.0443 (12)	0.0353 (11)	−0.0031 (9)	0.0026 (8)	−0.0128 (10)
C3	0.0284 (10)	0.0504 (13)	0.0385 (12)	−0.0019 (9)	0.0025 (9)	−0.0262 (11)
C4	0.0241 (9)	0.0358 (11)	0.0411 (11)	−0.0015 (8)	−0.0012 (8)	−0.0216 (9)
C5	0.0244 (9)	0.0240 (9)	0.0371 (11)	−0.0012 (8)	−0.0003 (8)	−0.0059 (8)
C6	0.0298 (10)	0.0339 (11)	0.0322 (11)	−0.0004 (9)	−0.0006 (9)	−0.0004 (9)
C7	0.0279 (10)	0.0486 (13)	0.0285 (11)	−0.0023 (9)	−0.0033 (8)	−0.0111 (10)
C8	0.0222 (9)	0.0360 (11)	0.0341 (11)	−0.0015 (8)	−0.0030 (8)	−0.0153 (9)
C9	0.0184 (8)	0.0223 (9)	0.0305 (9)	−0.0039 (7)	−0.0034 (7)	−0.0108 (8)
C10	0.0201 (8)	0.0200 (9)	0.0336 (10)	−0.0019 (7)	−0.0028 (7)	−0.0116 (8)
C11	0.0166 (8)	0.0229 (9)	0.0308 (10)	0.0009 (7)	−0.0023 (7)	−0.0078 (8)
C12	0.0164 (8)	0.0239 (9)	0.0295 (9)	0.0018 (7)	−0.0026 (7)	−0.0095 (8)
C13	0.0157 (8)	0.0225 (9)	0.0281 (9)	0.0014 (7)	−0.0054 (7)	−0.0072 (7)
C14	0.0176 (8)	0.0229 (9)	0.0319 (10)	0.0012 (7)	−0.0038 (7)	−0.0109 (8)
K1	0.0250 (2)	0.0396 (2)	0.0293 (2)	−0.00027 (18)	−0.00188 (17)	−0.01078 (19)
O1	0.0480 (11)	0.143 (2)	0.0373 (10)	−0.0145 (12)	0.0005 (8)	−0.0284 (12)
C15	0.0418 (15)	0.124 (3)	0.0574 (18)	0.0036 (16)	−0.0050 (13)	−0.0446 (19)
C16	0.114 (3)	0.0579 (18)	0.0592 (18)	−0.0113 (18)	−0.0295 (18)	−0.0309 (15)
C17	0.073 (2)	0.078 (2)	0.0529 (17)	0.0029 (17)	0.0111 (15)	−0.0209 (16)
C18	0.0525 (16)	0.119 (3)	0.0513 (16)	−0.0217 (17)	0.0036 (13)	−0.0419 (18)
O2	0.0299 (7)	0.0369 (8)	0.0394 (8)	−0.0077 (6)	0.0017 (6)	−0.0106 (7)
C19	0.0334 (11)	0.0436 (13)	0.0431 (13)	−0.0076 (10)	0.0080 (10)	−0.0129 (10)
C20	0.0276 (11)	0.0421 (13)	0.0650 (16)	−0.0074 (9)	0.0034 (10)	−0.0186 (12)
C21	0.0505 (14)	0.0396 (13)	0.0445 (13)	−0.0012 (11)	−0.0089 (11)	−0.0136 (11)
C22	0.0404 (12)	0.0394 (12)	0.0450 (13)	−0.0106 (10)	0.0119 (10)	−0.0134 (10)

Geometric parameters (Å, °)

Cu1—C9 ⁱ	1.9873 (19)	C10—H10	0.96 (2)
Cu1—C10	1.9906 (19)	C11—C12	1.420 (3)
Cu1—Cu1 ⁱ	2.6172 (7)	C11—K1 ⁱ	3.158 (2)
Cu1—K1 ⁱ	3.3762 (9)	C12—K1 ⁱ	3.3324 (19)
Cu1—K1	3.6637 (15)	C13—C14	1.426 (3)
C1—C2	1.391 (3)	C13—K1	3.170 (2)
C1—C13	1.398 (3)	C14—K1	3.364 (2)
C1—K1	3.081 (2)	K1—O1	2.681 (2)
C1—H1	0.97 (2)	K1—O2	2.8027 (16)
C2—C3	1.387 (3)	O1—C18	1.388 (3)
C2—K1	3.158 (2)	O1—C15	1.416 (3)
C2—H2	0.91 (2)	C15—C16	1.445 (4)
C3—C4	1.386 (3)	C15—H15A	0.9900
C3—K1	3.338 (3)	C15—H15B	0.9900
C3—H3	0.90 (2)	C16—C17	1.498 (4)
C4—C14	1.396 (3)	C16—H16A	0.9900
C4—K1	3.446 (2)	C16—H16B	0.9900
C4—H4	0.98 (2)	C17—C18	1.491 (4)
C5—C6	1.388 (3)	C17—H17A	0.9900
C5—C11	1.397 (3)	C17—H17B	0.9900
C5—K1 ⁱ	3.100 (2)	C18—H18A	0.9900
C5—H5	0.98 (2)	C18—H18B	0.9900
C6—C7	1.379 (3)	O2—C22	1.422 (3)
C6—K1 ⁱ	3.203 (3)	O2—C19	1.442 (2)
C6—H6	0.93 (2)	C19—C20	1.508 (3)
C7—C8	1.397 (3)	C19—H19A	0.9900
C7—K1 ⁱ	3.360 (2)	C19—H19B	0.9900
C7—H7	0.95 (2)	C20—C21	1.521 (3)
C8—C12	1.397 (3)	C20—H20A	0.9900
C8—K1 ⁱ	3.421 (2)	C20—H20B	0.9900
C8—H8	1.00 (2)	C21—C22	1.510 (3)
C9—C13	1.480 (3)	C21—H21A	0.9900
C9—C12	1.482 (3)	C21—H21B	0.9900
C9—H9	0.96 (2)	C22—H22A	0.9900
C10—C14	1.478 (3)	C22—H22B	0.9900
C10—C11	1.479 (3)		
C9 ⁱ —Cu1—C10	174.74 (7)	C2—K1—C3	24.46 (6)
C9 ⁱ —Cu1—Cu1 ⁱ	91.87 (6)	C11 ⁱ —K1—C3	144.06 (6)
C10—Cu1—Cu1 ⁱ	93.22 (6)	C13—K1—C3	51.09 (6)
C9 ⁱ —Cu1—K1 ⁱ	90.22 (6)	C6 ⁱ —K1—C3	160.97 (6)
C10—Cu1—K1 ⁱ	89.91 (6)	C12 ⁱ —K1—C3	128.10 (6)
Cu1 ⁱ —Cu1—K1 ⁱ	74.15 (3)	O1—K1—C7 ⁱ	80.71 (6)
C9 ⁱ —Cu1—K1	91.13 (6)	O2—K1—C7 ⁱ	114.16 (6)
C10—Cu1—K1	92.38 (6)	C1—K1—C7 ⁱ	169.51 (5)
Cu1 ⁱ —Cu1—K1	62.44 (2)	C5 ⁱ —K1—C7 ⁱ	43.22 (6)

K1 ⁱ —Cu1—K1	136.592 (18)	C2—K1—C7 ⁱ	161.18 (6)
C2—C1—C13	121.71 (18)	C11 ⁱ —K1—C7 ⁱ	50.92 (5)
C2—C1—K1	80.26 (12)	C13—K1—C7 ⁱ	144.00 (6)
C13—C1—K1	80.68 (11)	C6 ⁱ —K1—C7 ⁱ	24.11 (6)
C2—C1—H1	119.5 (12)	C12 ⁱ —K1—C7 ⁱ	42.69 (5)
C13—C1—H1	118.7 (12)	C3—K1—C7 ⁱ	138.90 (6)
K1—C1—H1	108.3 (12)	O1—K1—C14	122.94 (7)
C3—C2—C1	119.6 (2)	O2—K1—C14	108.40 (5)
C3—C2—K1	85.05 (13)	C1—K1—C14	43.96 (5)
C1—C2—K1	74.02 (11)	C5 ⁱ —K1—C14	127.14 (6)
C3—C2—H2	123.3 (14)	C2—K1—C14	50.92 (6)
C1—C2—H2	117.1 (14)	C11 ⁱ —K1—C14	102.00 (6)
K1—C2—H2	111.5 (14)	C13—K1—C14	24.99 (5)
C4—C3—C2	119.8 (2)	C6 ⁱ —K1—C14	143.58 (6)
C4—C3—K1	82.63 (13)	C12 ⁱ —K1—C14	92.71 (6)
C2—C3—K1	70.49 (12)	C3—K1—C14	42.52 (5)
C4—C3—H3	120.5 (16)	C7 ⁱ —K1—C14	128.40 (6)
C2—C3—H3	119.7 (16)	O1—K1—Cu1 ⁱ	174.34 (6)
K1—C3—H3	119.6 (15)	O2—K1—Cu1 ⁱ	78.73 (4)
C3—C4—C14	121.72 (19)	C1—K1—Cu1 ⁱ	69.88 (5)
C3—C4—K1	73.87 (13)	C5 ⁱ —K1—Cu1 ⁱ	70.12 (5)
C14—C4—K1	74.88 (11)	C2—K1—Cu1 ⁱ	94.42 (5)
C3—C4—H4	121.4 (12)	C11 ⁱ —K1—Cu1 ⁱ	50.60 (4)
C14—C4—H4	116.9 (12)	C13—K1—Cu1 ⁱ	50.52 (4)
K1—C4—H4	122.9 (12)	C6 ⁱ —K1—Cu1 ⁱ	94.30 (5)
C6—C5—C11	121.94 (19)	C12 ⁱ —K1—Cu1 ⁱ	60.61 (4)
C6—C5—K1 ⁱ	81.44 (13)	C3—K1—Cu1 ⁱ	100.40 (5)
C11—C5—K1 ⁱ	79.43 (11)	C7 ⁱ —K1—Cu1 ⁱ	100.32 (5)
C6—C5—H5	120.9 (13)	C14—K1—Cu1 ⁱ	60.72 (4)
C11—C5—H5	117.2 (13)	O1—K1—C8 ⁱ	98.21 (6)
K1 ⁱ —C5—H5	109.0 (12)	O2—K1—C8 ⁱ	127.95 (5)
C7—C6—C5	119.6 (2)	C1—K1—C8 ⁱ	146.66 (5)
C7—C6—K1 ⁱ	84.35 (13)	C5 ⁱ —K1—C8 ⁱ	49.76 (6)
C5—C6—K1 ⁱ	73.18 (12)	C2—K1—C8 ⁱ	150.65 (6)
C7—C6—H6	118.5 (14)	C11 ⁱ —K1—C8 ⁱ	43.01 (5)
C5—C6—H6	121.7 (14)	C13—K1—C8 ⁱ	120.92 (6)
K1 ⁱ —C6—H6	117.5 (14)	C6 ⁱ —K1—C8 ⁱ	42.36 (6)
C6—C7—C8	119.8 (2)	C12 ⁱ —K1—C8 ⁱ	23.83 (5)
C6—C7—K1 ⁱ	71.54 (12)	C3—K1—C8 ⁱ	126.98 (6)
C8—C7—K1 ⁱ	80.58 (12)	C7 ⁱ —K1—C8 ⁱ	23.75 (5)
C6—C7—H7	120.4 (14)	C14—K1—C8 ⁱ	105.06 (6)
C8—C7—H7	119.8 (14)	Cu1 ⁱ —K1—C8 ⁱ	84.40 (5)
K1 ⁱ —C7—H7	119.4 (14)	O1—K1—C4	99.52 (7)
C7—C8—C12	121.38 (19)	O2—K1—C4	118.02 (5)
C7—C8—K1 ⁱ	75.67 (12)	C1—K1—C4	49.69 (6)
C12—C8—K1 ⁱ	74.52 (11)	C5 ⁱ —K1—C4	146.82 (5)
C7—C8—H8	120.4 (11)	C2—K1—C4	42.32 (6)
C12—C8—H8	118.2 (11)	C11 ⁱ —K1—C4	121.11 (6)

K1 ⁱ —C8—H8	121.2 (11)	C13—K1—C4	42.80 (5)
C13—C9—C12	113.07 (15)	C6 ⁱ —K1—C4	150.73 (6)
C13—C9—Cu1 ⁱ	106.80 (12)	C12 ⁱ —K1—C4	105.07 (6)
C12—C9—Cu1 ⁱ	106.01 (12)	C3—K1—C4	23.51 (5)
C13—C9—H9	113.5 (12)	C7 ⁱ —K1—C4	127.46 (6)
C12—C9—H9	111.5 (12)	C14—K1—C4	23.63 (5)
Cu1 ⁱ —C9—H9	105.3 (12)	Cu1 ⁱ —K1—C4	84.31 (5)
C14—C10—C11	113.34 (15)	C8 ⁱ —K1—C4	108.62 (6)
C14—C10—Cu1	104.68 (12)	O1—K1—Cu1	142.20 (6)
C11—C10—Cu1	106.65 (12)	O2—K1—Cu1	121.92 (4)
C14—C10—H10	112.3 (12)	C1—K1—Cu1	84.17 (5)
C11—C10—H10	112.5 (12)	C5 ⁱ —K1—Cu1	84.94 (5)
Cu1—C10—H10	106.7 (12)	C2—K1—Cu1	96.93 (5)
C5—C11—C12	118.49 (17)	C11 ⁱ —K1—Cu1	59.29 (4)
C5—C11—C10	123.83 (17)	C13—K1—Cu1	58.50 (4)
C12—C11—C10	117.67 (16)	C6 ⁱ —K1—Cu1	97.51 (5)
C5—C11—K1 ⁱ	74.79 (11)	C12 ⁱ —K1—Cu1	46.67 (4)
C12—C11—K1 ⁱ	84.33 (11)	C3—K1—Cu1	85.20 (5)
C10—C11—K1 ⁱ	109.88 (11)	C7 ⁱ —K1—Cu1	86.02 (5)
C8—C12—C11	118.77 (17)	C14—K1—Cu1	46.07 (4)
C8—C12—C9	123.59 (17)	Cu1 ⁱ —K1—Cu1	43.409 (19)
C11—C12—C9	117.63 (16)	C8 ⁱ —K1—Cu1	62.49 (5)
C8—C12—K1 ⁱ	81.65 (11)	C4—K1—Cu1	61.88 (4)
C11—C12—K1 ⁱ	70.58 (10)	C18—O1—C15	109.8 (2)
C9—C12—K1 ⁱ	116.17 (11)	C18—O1—K1	119.35 (16)
C1—C13—C14	118.47 (17)	C15—O1—K1	127.81 (16)
C1—C13—C9	123.89 (17)	O1—C15—C16	107.8 (3)
C14—C13—C9	117.61 (16)	O1—C15—H15A	110.1
C1—C13—K1	73.53 (10)	C16—C15—H15A	110.1
C14—C13—K1	85.14 (11)	O1—C15—H15B	110.1
C9—C13—K1	109.69 (11)	C16—C15—H15B	110.1
C4—C14—C13	118.67 (17)	H15A—C15—H15B	108.5
C4—C14—C10	123.81 (17)	C15—C16—C17	105.7 (2)
C13—C14—C10	117.49 (16)	C15—C16—H16A	110.6
C4—C14—K1	81.49 (12)	C17—C16—H16A	110.6
C13—C14—K1	69.88 (10)	C15—C16—H16B	110.6
C10—C14—K1	116.86 (11)	C17—C16—H16B	110.6
O1—K1—O2	95.74 (7)	H16A—C16—H16B	108.7
O1—K1—C1	109.41 (6)	C18—C17—C16	104.6 (2)
O2—K1—C1	68.53 (5)	C18—C17—H17A	110.8
O1—K1—C5 ⁱ	107.73 (7)	C16—C17—H17A	110.8
O2—K1—C5 ⁱ	78.23 (5)	C18—C17—H17B	110.8
C1—K1—C5 ⁱ	131.78 (6)	C16—C17—H17B	110.8
O1—K1—C2	85.77 (7)	H17A—C17—H17B	108.9
O2—K1—C2	80.06 (5)	O1—C18—C17	108.4 (2)
C1—K1—C2	25.72 (5)	O1—C18—H18A	110.0
C5 ⁱ —K1—C2	155.40 (6)	C17—C18—H18A	110.0
O1—K1—C11 ⁱ	128.99 (6)	O1—C18—H18B	110.0

O2—K1—C11 ⁱ	91.18 (5)	C17—C18—H18B	110.0
C1—K1—C11 ⁱ	120.03 (5)	H18A—C18—H18B	108.4
C5 ⁱ —K1—C11 ⁱ	25.78 (5)	C22—O2—C19	108.69 (16)
C2—K1—C11 ⁱ	145.02 (5)	C22—O2—K1	122.52 (12)
O1—K1—C13	130.60 (6)	C19—O2—K1	125.62 (13)
O2—K1—C13	83.56 (5)	O2—C19—C20	107.12 (18)
C1—K1—C13	25.79 (5)	O2—C19—H19A	110.3
C5 ⁱ —K1—C13	120.22 (6)	C20—C19—H19A	110.3
C2—K1—C13	45.27 (6)	O2—C19—H19B	110.3
C11 ⁱ —K1—C13	100.38 (6)	C20—C19—H19B	110.3
O1—K1—C6 ⁱ	84.40 (7)	H19A—C19—H19B	108.5
O2—K1—C6 ⁱ	90.13 (6)	C19—C20—C21	102.91 (18)
C1—K1—C6 ⁱ	155.17 (6)	C19—C20—H20A	111.2
C5 ⁱ —K1—C6 ⁱ	25.38 (6)	C21—C20—H20A	111.2
C2—K1—C6 ⁱ	165.33 (6)	C19—C20—H20B	111.2
C11 ⁱ —K1—C6 ⁱ	45.02 (5)	C21—C20—H20B	111.2
C13—K1—C6 ⁱ	144.82 (6)	H20A—C20—H20B	109.1
O1—K1—C12 ⁱ	121.76 (6)	C22—C21—C20	101.36 (19)
O2—K1—C12 ⁱ	116.27 (5)	C22—C21—H21A	111.5
C1—K1—C12 ⁱ	126.83 (5)	C20—C21—H21A	111.5
C5 ⁱ —K1—C12 ⁱ	44.03 (5)	C22—C21—H21B	111.5
C2—K1—C12 ⁱ	143.60 (5)	C20—C21—H21B	111.5
C11 ⁱ —K1—C12 ⁱ	25.09 (5)	H21A—C21—H21B	109.3
C13—K1—C12 ⁱ	101.73 (6)	O2—C22—C21	106.58 (18)
C6 ⁱ —K1—C12 ⁱ	50.89 (6)	O2—C22—H22A	110.4
O1—K1—C3	82.10 (7)	C21—C22—H22A	110.4
O2—K1—C3	104.48 (5)	O2—C22—H22B	110.4
C1—K1—C3	43.70 (6)	C21—C22—H22B	110.4
C5 ⁱ —K1—C3	169.66 (6)	H22A—C22—H22B	108.6
C13—C1—C2—C3	−2.0 (3)	C13—C9—C12—K1 ⁱ	−118.00 (13)
K1—C1—C2—C3	−74.58 (19)	Cu1 ⁱ —C9—C12—K1 ⁱ	−1.31 (14)
C13—C1—C2—K1	72.59 (17)	C2—C1—C13—C14	2.5 (3)
C1—C2—C3—C4	−0.5 (3)	K1—C1—C13—C14	74.88 (15)
K1—C2—C3—C4	−68.9 (2)	C2—C1—C13—C9	−175.35 (17)
C1—C2—C3—K1	68.47 (17)	K1—C1—C13—C9	−102.99 (16)
C2—C3—C4—C14	2.4 (3)	C2—C1—C13—K1	−72.36 (17)
K1—C3—C4—C14	−60.13 (18)	C12—C9—C13—C1	−144.12 (17)
C2—C3—C4—K1	62.48 (19)	Cu1 ⁱ —C9—C13—C1	99.66 (17)
C11—C5—C6—C7	−1.4 (3)	C12—C9—C13—C14	38.0 (2)
K1 ⁱ —C5—C6—C7	−73.16 (19)	Cu1 ⁱ —C9—C13—C14	−78.22 (17)
C11—C5—C6—K1 ⁱ	71.80 (17)	C12—C9—C13—K1	132.91 (12)
C5—C6—C7—C8	0.0 (3)	Cu1 ⁱ —C9—C13—K1	16.69 (13)
K1 ⁱ —C6—C7—C8	−67.02 (19)	C3—C4—C14—C13	−1.8 (3)
C5—C6—C7—K1 ⁱ	67.02 (18)	K1—C4—C14—C13	−61.43 (15)
C6—C7—C8—C12	0.9 (3)	C3—C4—C14—C10	176.36 (18)
K1 ⁱ —C7—C8—C12	−61.42 (17)	K1—C4—C14—C10	116.72 (17)
C6—C7—C8—K1 ⁱ	62.28 (18)	C3—C4—C14—K1	59.64 (19)

C6—C5—C11—C12	1.8 (3)	C1—C13—C14—C4	−0.6 (3)
K1 ⁱ —C5—C11—C12	74.68 (15)	C9—C13—C14—C4	177.38 (16)
C6—C5—C11—C10	−176.87 (18)	K1—C13—C14—C4	67.67 (16)
K1 ⁱ —C5—C11—C10	−104.01 (16)	C1—C13—C14—C10	−178.89 (16)
C6—C5—C11—K1 ⁱ	−72.86 (18)	C9—C13—C14—C10	−0.9 (2)
C14—C10—C11—C5	−143.44 (18)	K1—C13—C14—C10	−110.59 (14)
Cu1—C10—C11—C5	101.91 (18)	C1—C13—C14—K1	−68.29 (15)
C14—C10—C11—C12	37.9 (2)	C9—C13—C14—K1	109.70 (15)
Cu1—C10—C11—C12	−76.79 (17)	C11—C10—C14—C4	144.80 (18)
C14—C10—C11—K1 ⁱ	131.93 (13)	Cu1—C10—C14—C4	−99.38 (18)
Cu1—C10—C11—K1 ⁱ	17.28 (13)	C11—C10—C14—C13	−37.0 (2)
C7—C8—C12—C11	−0.4 (3)	Cu1—C10—C14—C13	78.79 (17)
K1 ⁱ —C8—C12—C11	−62.36 (15)	C11—C10—C14—K1	−117.18 (14)
C7—C8—C12—C9	177.95 (17)	Cu1—C10—C14—K1	−1.36 (14)
K1 ⁱ —C8—C12—C9	115.96 (17)	C18—O1—C15—C16	−17.6 (4)
C7—C8—C12—K1 ⁱ	61.99 (18)	K1—O1—C15—C16	142.1 (2)
C5—C11—C12—C8	−0.9 (2)	O1—C15—C16—C17	20.0 (4)
C10—C11—C12—C8	177.84 (16)	C15—C16—C17—C18	−15.0 (4)
K1 ⁱ —C11—C12—C8	68.34 (16)	C15—O1—C18—C17	7.6 (4)
C5—C11—C12—C9	−179.36 (16)	K1—O1—C18—C17	−154.1 (2)
C10—C11—C12—C9	−0.6 (2)	C16—C17—C18—O1	4.8 (4)
K1 ⁱ —C11—C12—C9	−110.09 (14)	C22—O2—C19—C20	−2.7 (2)
C5—C11—C12—K1 ⁱ	−69.27 (15)	K1—O2—C19—C20	−162.90 (13)
C10—C11—C12—K1 ⁱ	109.50 (15)	O2—C19—C20—C21	24.1 (2)
C13—C9—C12—C8	144.41 (17)	C19—C20—C21—C22	−34.7 (2)
Cu1 ⁱ —C9—C12—C8	−98.91 (17)	C19—O2—C22—C21	−20.2 (2)
C13—C9—C12—C11	−37.3 (2)	K1—O2—C22—C21	140.69 (14)
Cu1 ⁱ —C9—C12—C11	79.44 (17)	C20—C21—C22—O2	34.4 (2)

Symmetry code: (i) $-x, -y+1, -z+1$.