

Synthesis and Characterisation of the First Oxazoline Coordination Compounds Containing the $\text{Cu}(\text{F}_6\text{acac})_2$ Unit: X-ray Diffraction Studies of $\text{Cu}(\kappa^2\text{-O, O}'\text{-F}_6\text{acac})_2(\kappa^1\text{-N-Meox})$ and $\text{Cu}(\kappa^2\text{-O, O}'\text{-F}_6\text{acac})_2(\kappa^1\text{-N-Etox})$ [$\text{F}_6\text{acac} = \text{C}_5\text{HF}_6\text{O}_2$; Meox = 2-methyl-2-oxazoline; Etox = 2-ethyl-2-oxazoline]

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Abstract

The synthesis and characterisation (elemental analysis, IR, X-ray diffraction) of the first two oxazoline coordination compounds of $\text{Cu}(\text{F}_6\text{acac})_2$ are described. Both of these complexes are five-coordinate mononuclear formally Cu(II) materials with a slightly distorted square pyramidal coordination motif around the metal centre. The structures are compared and contrasted to other N-donor complexes of $\text{Cu}(\text{F}_6\text{acac})_2$.

Keywords: oxazoline, copper, hexafluoroacetylacetonato, coordination complex, oxazole

Introduction

The chemistry of 4,5-dihydro-2-oxazoles, more commonly referred to as oxazolines, has expanded exponentially since the early seminal work of Meyers and his predecessors.¹⁻³ Oxazolines are now considered one of the "privileged" classes of ligands and are now routinely used in both regio- and enantio-selective catalysis,⁴ coordination chemistry,⁵ directed *ortho*-metallation strategies, polymer chemistry,⁶ *etc.* Our interest in oxazoline (ox) chemistry is centred on both novel ligand designs and coordination chemistry^{7,8} with a long term goal of improving the catalytic performance of such materials.⁹ In this regard, we have recently reported several novel examples of, for example, Zn-ox coordination compounds containing dithiocarbamates,¹⁰ halides,¹¹ and acetylacetonato ligands.¹² Hence, our objectives are to expand the database of knowledge where there exists a paucity of examples of ox coordination compounds and by so doing demonstrate the methods of syntheses to such materials and discern their structural aspects. We have recently begun a program to examine Group 11 ox derivatives. In this research communication, we report and describe on the first examples of such coordination compounds incorporating $\text{Cu}(\text{F}_6\text{acac})_2$ (F_6acac = hexafluoroacetylacetonato: Figure 1) from both a synthetic and structural perspective. This copper containing starting material has been extensively studied in coordination chemistry and materials science due to its ability to coordinate a variety of N-donor ligands which includes organic radicals, heterocycles, primary amines, *etc.* A wide variety of structural bonding motifs¹³⁻³⁰ have been observed in the resulting coordination compounds.

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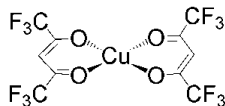


Figure 1. Schematic representation of anhydrous $\text{Cu}(\text{F}_6\text{acac})_2$.

Experimental Methods

General

A solution of 0.496 g (1.0 mmol) of hydrated $\text{Cu}(\text{F}_6\text{acac})_2$ in 100 mL of *n*-heptane was heated to reflux temperature for 40 min. and then allowed to cool to room temperature (RT). A solution of the ox (1.0 mmol; compound **1**: ox = Meox or **2**: ox = Etox) in 30 mL of Et_2O was then added and the mixture left in a freezer ($\sim -5^\circ\text{C}$) for several days. Emerald green-coloured crystals of the product separated from the mixture and were isolated by filtration. Yield: 87% (**1**) and 87% (**2**). Properties of compound **1**: mp = 80°C (decomp.); IR (KBr): strong; 1669 cm^{-1} ($\nu[\text{C}=\text{N}]$); $\mu_{\text{eff}} \approx 1.90\ \mu_{\text{B}}$ (24°C); Anal. Calc. (Found): C 29.88 (29.81), H 1.61 (1.66), N 2.49 (2.18). Properties of compound **2**: mp = 55°C (decomp.); IR (KBr): strong; 1648 cm^{-1} ($\nu[\text{C}=\text{N}]$); $\mu_{\text{eff}} \approx 1.75\ \mu_{\text{B}}$ (24°C); Anal. Calc. (Found): C 31.24 (31.28), H 1.92 (2.26), N 2.43 (2.48).

X-ray diffraction

X-ray diffraction data of **1**.³¹ CCDC #: 873400; formula: $\text{C}_{14}\text{H}_9\text{F}_{12}\text{NO}_5\text{Cu}$; $M_r = 562.76\text{ g/mol}$; colour: green; crystal size: $0.22 \times 0.26 \times 0.49\text{ mm}^3$; space group: $P2_1/c$; $a = 8.2988(16)$, $b = 15.067(3)$, $c = 16.538(3)\text{ \AA}$; $\beta = 102.562(3)^\circ$; $V = 2018.4(7)\text{ \AA}^3$; $T = 293\text{ K}$; $Z = 4$; $\rho_{\text{calc}} = 1.85\text{ g/mL}$; $\text{MoK}\alpha = 0.71073\text{ \AA}$; $F(000) = 1108$; 2θ range: $4\text{--}50^\circ$; hkl range: ± 9 , -12 , $+17$; ± 19 ; refl. unique = 3545; refl. in refinement $I > 2\sigma(I) = 2555$; $R1$, $wR2 = 0.033$, 0.078 ; $R1$ for $I > 2\sigma(I) = 0.053$; parameters refined = 410; GoF: 1.02; Absorp. corr.: SADABS; $\Delta\rho_{\text{fin}}$ (max. / min.) = $-0.18 / +0.24\text{ e\AA}^{-3}$.

X-ray diffraction data of **2**.³¹ CCDC #: 873399; formula: $\text{C}_{15}\text{H}_{11}\text{F}_{12}\text{NO}_5\text{Cu}$; $M_r = 576.79\text{ g/mol}$; colour: green; crystal size: $0.11 \times 0.26 \times 0.44\text{ mm}^3$; space group: $Pccn$; $a = 19.352(3)$, $b = 26.662(4)$, $c = 8.2278(13)\text{ \AA}$; $V = 4245.2(12)\text{ \AA}^3$; $T = 293\text{ K}$; $Z = 8$; $\rho_{\text{calc}} = 1.80\text{ g/mL}$; $\text{MoK}\alpha = 0.71073\text{ \AA}$; $F(000) = 2280$; 2θ range: $4\text{--}50^\circ$; hkl range: -23 , $+21$; -31 , $+29$; ± 9 ; refl. unique = 3736; refl. in refinement $I > 2\sigma(I) = 2154$; $R1$, $wR2 = 0.067$, 0.175 ; $R1$ for $I > 2\sigma(I) = 0.120$; parameters refined = 307; GoF: 1.01; Absorp. corr.: SADABS; $\Delta\rho_{\text{fin}}$ (max. / min.) = $-0.42 / +0.86\text{ e\AA}^{-3}$.

Results and Discussion

The ox compounds presented herein were obtained *via* treatment of heptane solutions of hydrated $\text{Cu}(\text{F}_6\text{acac})_2$ with Et_2O solutions of either 2-methyl-2-oxazoline (Meox) or 2-ethyl-2-oxazoline (Etox). This procedure results in the isolation of emerald green complexes (**1** and **2**, respectively) upon cooling the resulting mixtures for several days below room temperature. These two compounds represent the first ox complexes of the $\text{Cu}(\text{F}_6\text{acac})_2$ unit to be isolated and structurally elucidated. Interestingly, more bulkier oxazolines, such as 2-phenyl-2-oxazoline or 4,4-dimethyl-2-phenyl-2-oxazoline, did not form isolable complexes with $\text{Cu}(\text{F}_6\text{acac})_2$ under the conditions examined. Only 1:1 (*i.e.*, mono) adducts of both of the oxazolines (Meox and Etox) with $\text{Cu}(\text{F}_6\text{acac})_2$ could be obtained even in the presence of excess ligand and/or heating. Elemental analysis measurements clearly identified the 1:1 ox:Cu ratio. The paramagnetic nature of the formal d^9 Cu(II) metal centre obviously precludes the investigation of these materials in detail by NMR spectroscopy. Hence, single crystal X-ray diffraction studies³¹ on both **1** and **2** were carried out to determine the structural motifs present in these two complexes. A list of selected bond

lengths and angles for both materials appears in Table 1; an ORTEP³² representation of a unit cell component of each of the complexes appears in Figures 2 and 3.

Table 1: Selected Bond Lengths (Å) and Angles (°) for Compounds 1 and 2†.

Compound 1		Compound 2	
Cu(1)-O(2)	1.9424(18)	Cu(1)-O(1)	1.940(5)
Cu(1)-O(4)	1.9569(17)	Cu(1)-O(4)	1.958(4)
Cu(1)-O(1)	1.9640(17)	Cu(1)-O(2)	1.958(5)
Cu(1)-N(1)	1.969(2)	Cu(1)-N(1)	1.970(6)
Cu(1)-O(3)	2.176(2)	Cu(1)-O(3)	2.200(5)
N(1)-C(13)	1.269(3)	N(1)-C(13)	1.272(9)
O(2)-Cu(1)-O(4)	175.85(8)	O(1)-Cu(1)-O(4)	172.8(2)
O(2)-Cu(1)-O(1)	90.88(8)	O(1)-Cu(1)-O(2)	90.7(2)
O(4)-Cu(1)-O(1)	89.63(7)	O(4)-Cu(1)-O(2)	87.84(19)
O(2)-Cu(1)-N(1)	88.41(8)	O(1)-Cu(1)-N(1)	90.2(2)
O(4)-Cu(1)-N(1)	89.96(8)	O(4)-Cu(1)-N(1)	89.4(2)
O(1)-Cu(1)-N(1)	163.95(8)	O(2)-Cu(1)-N(1)	165.8(2)
O(2)-Cu(1)-O(3)	94.88(8)	O(1)-Cu(1)-O(3)	98.5(2)
O(4)-Cu(1)-O(3)	89.22(7)	O(4)-Cu(1)-O(3)	88.58(19)
O(1)-Cu(1)-O(3)	92.14(8)	O(2)-Cu(1)-O(3)	93.6(2)
N(1)-Cu(1)-O(3)	103.89(8)	N(1)-Cu(1)-O(3)	100.2(2)
N(1)-C(13)-O(5)	116.9(2)	N(1)-C(13)-O(5)	116.4(7)

† Estimated standard deviations are given in parentheses.

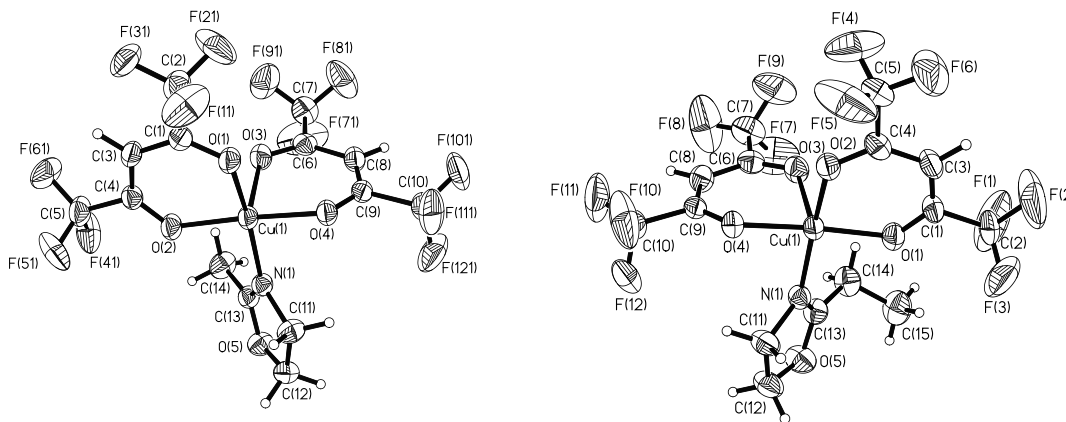


Figure 2 (left): ortep³² representation (30% probability level) of a unit cell molecule of complex 1.
Figure 3 (right): ortep³² representation (30% probability level) of a unit cell molecule of complex 2.

As is evident from Figures 2 and 3, both examples are characterised as mononuclear formally Cu(II) species with a coordination number of five. The general structural parameters for both 1 and 2 are similar to one another in terms of general bond lengths and angles (Table 1) and to the variety of known metal-ox

complexes and/or related five-coordinate $\text{Cu}(\text{F}_6\text{acac})_2(\text{N-donor})$ complexes found in the literature.^{13-30, 33-35} As expected, the complexes reported herein contain chelating $\kappa^2\text{-O,O'}$ -bonded F_6acac formally anionic groups with Cu–O bond lengths which are of the typical range (1.9–2.2 Å). The oxazoline ligand, predictably *N*-bonded,^{4, 5, 7-12, 31} occupies a basal position with one of the F_6acac *O*-atoms occupying the formal equatorial position of an idealised square pyramidal ligand arrangement. The τ_5 values, as described by Addison *et al.*,³⁶ are 0.198 for **1** and 0.117 for **2** and hence the geometry is more accurately described as slightly distorted square pyramidal in nature for both species. The position of the ox ligand is similar to that found¹⁴ in the structure of $\text{Cu}(\kappa^2\text{-O,O'-F}_6\text{acac})_2(\kappa^1\text{-N-}^i\text{BuNH}_2)$ but in contrast to other examples in which the *N*-donor ligand occupies an axial site such as in the complex $\text{Cu}(\kappa^2\text{-O,O'-F}_6\text{acac})_2(\kappa^1\text{-N-NH}_3)$.³³ The situation as noted here invariably leads one of the *O*-donor atoms to occupy a basal position and hence this Cu–O bond is notably longer (**1**: 2.176(3) Å; **2**: 2.200(5) Å) than the other three for reasons described previously.¹⁴

Conclusions

In conclusion, the synthesis and complete characterisation of the first oxazoline coordination complexes containing the $\text{Cu}(\text{F}_6\text{acac})_2$ unit have been reported. These five-coordinate mononuclear materials have a similar structure to related *N*-donor complexes containing this acetylacetonato fragment.

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