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Formation of the $\{Cu_3^{II}(\mu_3\text{-OH})\}^{5+}$ core in copper(II) carboxylate chemistry via use of di-2-pyridyl ketone oxime $[(py)_2CNOH]: [Cu_3(OH)(O_2CR)_2\{(py)_2CNO\}_3]$ (R = Me, Ph)

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Abstract

Reactions of $[Cu_2(O_2CMe)_4(H_2O)_2]$ or $Cu(O_2CPh)_2 \cdot 2H_2O$ with 2 or 1, respectively, molar equivalents of di-2-pyridyl ketone oxime, $(py)_2CNOH$, in MeCN-based solvent mixtures yield complexes $[Cu_3^{II}(\mu_3\text{-OH})(O_2CR)_2\{(py)_2CNO\}_3]$ (**1**, R = Me; **2**, R = Ph). Crystal structures of these compounds show similar triangles of Cu^{II} ions, centered by a triply bridging hydroxo ligand and with three edge-bridging oximate groups from the three 2.1110 $(py)_2CNO^-$ ions. Preliminary variable-temperature magnetic susceptibility studies and EPR data at 4.2 K for **1** reveal an antiferromagnetically-coupled system showing antisymmetric exchange.
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There is currently a renewed interest in the coordination chemistry of 2-pyridyl oximes, $(py)C(R)NOH$ (Scheme 1) [1]. The anionic forms, $(py)C(R)NO^-$, of these molecules are versatile ligands for a variety of research objectives [1]. Di-2-pyridyl ketone oxime [IUPAC name: di-pyridin-2-yl-methanone oxime, $(py)_2CNOH$, Scheme 1] occupies a special position [1b–4] amongst the 2-pyridyl oximes because the R group is also a 2-pyridyl group and the compound is thus a bis(2-pyridyl) oxime. Although the published coordination chemistry of $(py)_2CNOH$ and $(py)_2CNO^-$ is rich [1b], copper(II) complexes possessing *bridging* $(py)_2CNOH$ or $(py)_2CNO^-$ ligands have not been studied in detail, and the structurally characterized compounds are confined to the dinuclear complex $[Cu_2\{(py)_2CNO\}_4]$ [5a]

and to the impressive 18-MC-6 cluster $[Cu_6(ClO_4)\{(py)_2C-NO\}_6(MeCN)_6][Cu_6(ClO_4)_3\{(py)_2CNO\}_6(MeCN)_4](ClO_4)_8$ [5b].

We have been exploring "ligand blend" reactions involving carboxylates *and* the anions of 2-pyridyl oximes (Scheme 1) as a means to high-nuclearity 3d-metal species [1b,4,7,8]. Our results with Mn [4,6] and Co [7] have been very encouraging. We have thus decided to extend the exploration of the general carboxylate/2-pyridyloximate "ligand blend" in copper(II) chemistry, and we can now report that di-2-pyridyl ketone oxime $[(py)_2CNOH,$ Scheme 1] has yielded new triangular products possessing the $\{Cu_3^{II}(\mu_3\text{-OH})\}^{5+}$ core. There is currently intense interest in the synthetic and physical studies of new triangular copper(II) clusters [8,9].

The reaction of $[Cu_2(O_2CMe)_4(H_2O)_4]$ with two equivalents of $(py)_2CNOH$ in MeCN under reflux for 30 min gave a dark green solution, which was evaporated to dryness under reduced pressure. The residue was dissolved
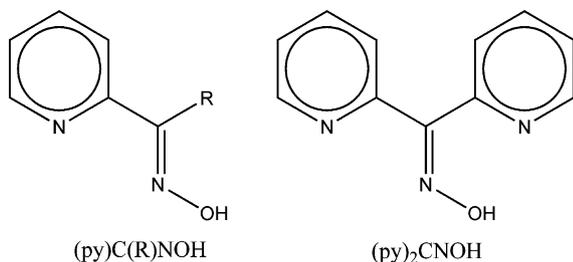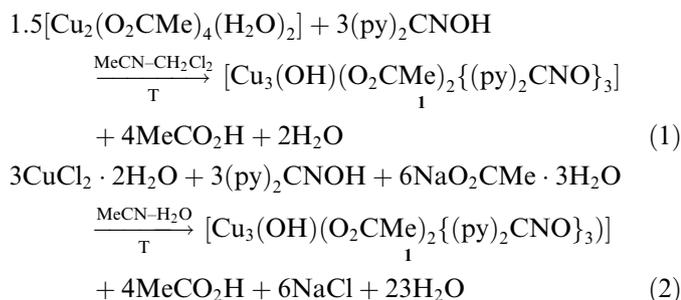
Scheme 1. Structural formulae and abbreviations of the 2-pyridyl oxime ligands discussed in the text.

in CH_2Cl_2 and layered with Et_2O. After 2 days, dark green crystals of $[Cu_3(OH)(O_2CMe)_2\{(py)_2CNO\}_3] \cdot CH_2Cl_2$ ($1 \cdot CH_2Cl_2$) [10] were isolated in 70–80% yield (Eq. (1)). Complex **1** can also be isolated in moderate yields (~40%) from the $CuCl_2 \cdot 2H_2O/(py)_2CNOH/NaO_2CMe \cdot 3H_2O$ (1:1:2) reaction mixture in $MeCN–H_2O$ (1:1, v/v) under reflux (Eq. (2)) [10]. If an excess of $(py)_2CNOH$ is present, the product is contaminated with variable amounts of the known [5a], carboxylate-free compound $[Cu_2\{(py)_2CNO\}_4]$.

$$1.5[Cu_2(O_2CMe)_4(H_2O)_2] + 3(py)_2CNOH$$
$$\xrightarrow[T]{MeCN–CH_2Cl_2} [Cu_3(OH)(O_2CMe)_2\{(py)_2CNO\}_3]$$
$$+ 4MeCO_2H + 2H_2O \qquad (1)$$

$$3CuCl_2 \cdot 2H_2O + 3(py)_2CNOH + 6NaO_2CMe \cdot 3H_2O$$
$$\xrightarrow[T]{MeCN–H_2O} [Cu_3(OH)(O_2CMe)_2\{(py)_2CNO\}_3]$$
$$+ 4MeCO_2H + 6NaCl + 23H_2O \qquad (2)$$

The molecular structure [11] of **1** consists of a near-equilateral Cu_3^{II} triangle capped by atom O(51) of the μ_3-OH^- ion. Each edge is bridged by the oximate group of an $\eta^1:\eta^1:\eta^1:\mu_2$ (or 2.1110 using Harris notation [12]) $(py)_2CNO^-$ ligand. The $Cu(2) \cdots Cu(3)$ edge is additionally bridged by an $\eta^1:\eta^1:\mu_2$ (2.11 [12]) $MeCO_2^-$ group, while a monodentate acetate completes five-coordination at Cu(1). The doubly-bridged $Cu(2) \cdots Cu(3)$ edge is the shortest [3.147(2) Å]. The μ_3-OH^- oxygen atom is 0.621 Å above the Cu_3 plane. The coordination geometry at Cu(1), Cu(2) and Cu(3) is distorted square pyramidal with the apical positions being occupied by the acetate oxygen atoms O(41), O(31) and O(32), respectively. There is a strong intramolecular hydrogen bond with the hydroxo oxygen as donor and the uncoordinated acetate oxygen as acceptor. Its dimensions are $O(51) \cdots O(42)$ 2.650 Å, $H(O51) \cdots O(42)$ 1.615 Å, $O(51)–H(O51) \cdots O(42)$ 174.9°. The intermolecular interactions in compound $1 \cdot CH_2Cl_2$ are interesting. Its crystal packing (Fig. 2) can be rationalized in terms of centrosymmetric pairs of trinuclear molecules held together by weak $Cu(3) \cdots N(23)$ [$1 - x$, $-y$, $2 - z$] and $Cu(3) \cdots N(23)$ interactions at distances of 2.832(5) Å. Atom N(23) is formally unbound to the metal ions, see Fig. 1. These interactions generate dimers of trimers [9b], no longer connected to each other.
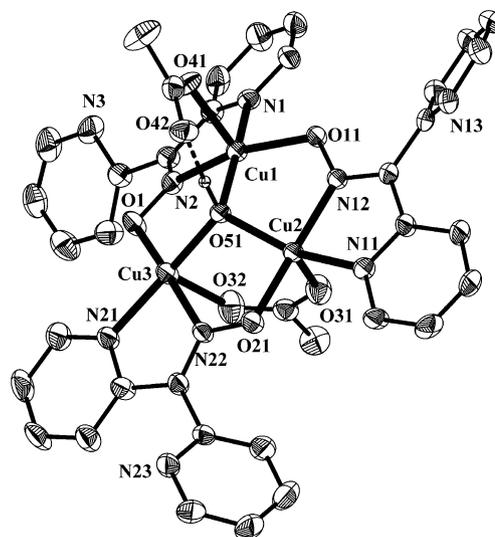

Fig. 1. Partially labeled ORTEP diagram of **1** at 30% thermal probability ellipsoids (the intramolecular H-bond is shown as dashed line). Selected interatomic distances (Å) and angles (°): $Cu(1) \cdots Cu(2)$ 3.210(6), $Cu(1) \cdots Cu(3)$ 3.248(3), $Cu(2) \cdots Cu(3)$ 3.147(2), Cu(1)–O(11) 1.975(5), Cu(1)–O(41) 2.175(6), Cu(1)–O(51) 1.944(5), Cu(2)–N(11) 1.978(6), Cu(2)–O(51) 1.949(5), Cu(3)–O(32) 2.309(7), Cu(3)–O(51) 1.949(5) and O(11)–Cu(1)–N(2) 160.2(3), O(51)–Cu(1)–N(1) 169.0(2), O(21)–Cu(2)–N(12) 170.8(2), O(51)–Cu(2)–N(11) 157.5(3), O(1)–Cu(3)–N(22) 171.7(3), O(51)–Cu(3)–N(21) 164.9(3), Cu(1)–O(51)–Cu(2) 110.7(2), Cu(1)–O(51)–Cu(3) 113.1(2), Cu(2)–O(51)–Cu(3) 107.3(2).

Compound **1** could alternatively be described as a rare example of an inverse 9-metallacrown-3 complex [2]. Using metallacrown nomenclature, the formula of the complex is $\{(OH)[inv9\text{-}MC_{Cu(II)N\{(py)_2CNO\}}\text{-}3](O_2CMe)_2\} \cdot CH_2Cl_2$.

In order to investigate to what extent the nature of the substituent on the carboxylate carbon might affect the identity of the products (and to what extent this might prove a route to new cluster types), we studied the $Cu(O_2C\text{-}Ph)_2 \cdot 2H_2O/(py)_2CNOH$ reaction system. The reaction of $Cu(O_2CPh)_2 \cdot 2H_2O$ with one equivalent of $(py)_2CNOH$ in $MeCN–H_2O$ (10:1, v/v) under reflux for 2 h gave a dark green slurry, which was filtered to remove a small amount of non-reacted copper(II) benzoate. The resulting filtrate was layered with Et_2O–n-hexane (1:1, v/v); slow mixing
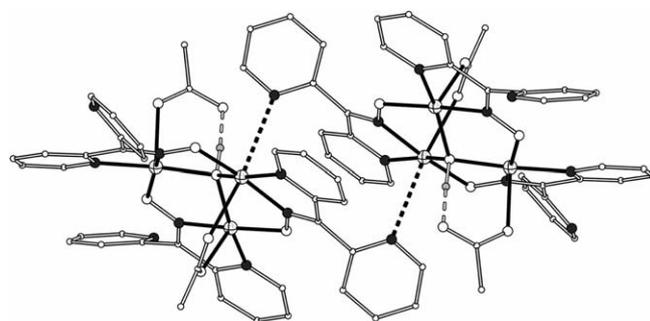

Fig. 2. A view of the centrosymmetric pairs of the trinuclear molecules in **1** formed through the weak $Cu \cdots N$ interactions (shown as black dashed lines). Codes: octants (copper), small open circles (carbon), large open circles (oxygen), black circles (nitrogen).
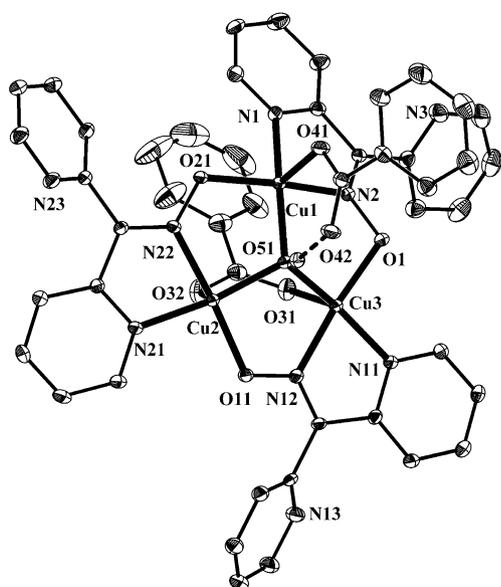
Fig. 3. Partially labeled ORTEP diagram of **2** at 30% thermal probability ellipsoids (the intramolecular H-bond is shown as dashed line). Selected interatomic distances (Å) and angles (°): Cu(1)···Cu(2) 3.229(6), Cu(1)···Cu(3) 3.242(7), Cu(2)···Cu(3) 3.132(2), Cu(1)–O(41) 2.212(3), Cu(1)–O(51) 1.949(3), Cu(2)–O(32) 2.239(4), Cu(2)–O(51) 1.936, Cu(3)–O(31) 2.252(3), Cu(3)–O(51) 1.949(3) and Cu(1)–O(51)–Cu(2) 112.5(2), Cu(1)–O(51)–Cu(3) 112.6(2), Cu(2)–O(51)–Cu(3) 107.5(2).

gave X-ray quality, olive-green crystals of [$Cu_3(OH)$-(O_2CPh)$_2${(py)$_2CNO$}$_3$] · 4H$_2$O (**2** · 4H$_2$O) in 67–70% yield [10]. Complex **2** was found to have a molecular structure (Fig. 3) [11] completely analogous to that of **1** but with PhCO$_2^-$ ligands instead of MeCO$_2^-$ groups. In contrast to **1** · CH$_2$Cl$_2$, the crystal structure of **2** · 4H$_2$O consists of *isolated* trinuclear molecules which are not further connected by weak coordination bonds to form hexamers, oligomers or polymers.

Variable-temperature dc magnetic susceptibility data were collected on dried **1** in the temperature range of 2.2–300 K in an applied field of 1 T (Fig. 4). At 300 K, $\chi_M T$ for **1** is 0.49 cm^3 mol^{-1} K, which is smaller than the value of 1.3 cm^3 mol^{-1} K expected for three non-interacting Cu^{II} ions with a reasonable *g* value [9c], indicating antiferromagnetic interactions. Upon cooling $\chi_M T$ decreases continuously, plateauing at 0.43–0.40 cm^3 mol^{-1} K between 175 and 100 K before decreasing further at lower temperatures; the $\chi_M T$ value is 0.27 cm^3 mol^{-1} K at 2.2 K. The "plateau" value is close to the value of $\chi_M T = 0.4$ cm^3 mol^{-1} K expected for an isolated $S = 1/2$ ground state with a reasonable *g* value for interacting Cu^{II} centers [9c]. The steady increase of the molar magnetic susceptibility χ_M upon cooling is in line with a magnetic ground state. The magnetization isotherm at 2.5 K (inset of Fig. 4), which reaches a value of 0.75 $N_A\mu_B$ at 5.5 T, is in a fairly good agreement with an $S_T = 1/2$ ground state, whereas an $S_T = 3/2$ ground state is clearly excluded. A model that takes into account isotropic exchange couplings alone failed to yield satisfactory simulation (not shown) of the temperature dependence of magnetic susceptibility. The below 100 K decline in $\chi_M T$ to a value smaller than that for one unpaired electron has been observed in other magnetically characterized trinuclear complexes containing the {$Cu_3(\mu_3$-OH)}$^{5+}$ core [9c,9e,13], and arises from intramolecular antisymmetric exchange [9c,9e,13]. This decline may also partially stem from antiferromagnetic intermolecular interactions, but since these produce the same effect on the $\chi_M T$ vs. *T* curve as the antisymmetric exchange, it is not possible to accurately evaluate these factors simultaneously. A full magnetic analysis of **1** and **2** is in progress [14].

Fig. 5 shows the X-band EPR spectrum of a powder sample of **1** recorded at 4.2 K. A strong signal is observed at ~3 kG consisting of an asymmetric derivative-like feature with $g_{eff} \sim 2.2$ and a shoulder at the lowest field part. However, the most interesting spectral observation is a relatively broad valley at $g_{eff} \sim 1.17$. This extremely low *g*-value feature cannot be due to the perpendicular component of an isolated $S = 1/2$ ground state ($g_\perp = 2.0$–2.1 would be more typical) [9c]. Such a feature was observed in few antiferromagnetically-coupled {$Cu_3(\mu_3$-OH)}$^{5+}$ complexes showing antisymmetric exchange, whose EPR
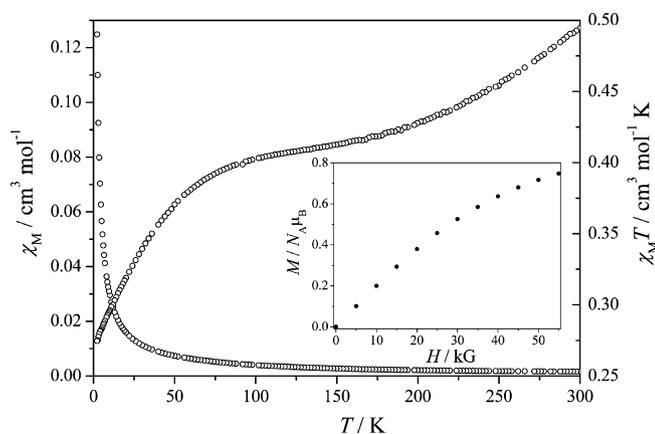

Fig. 4. Plots of $\chi_M T$ and χ_M as a function of *T* for a powder sample of **1**. The magnetization isotherm at 2.5 K is shown in the inset.
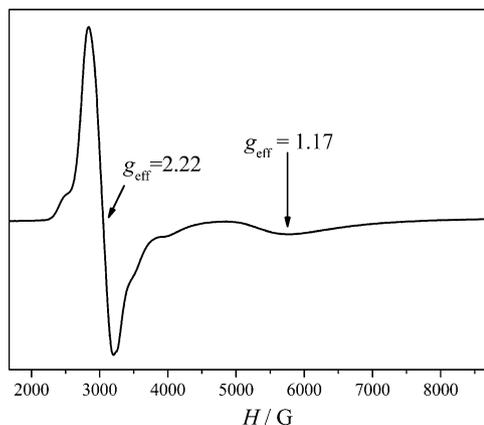

Fig. 5. X-band EPR spectrum of a powder sample of **1** at 4.2 K. Experimental conditions: microwave frequency, 9.42 GHz; microwave power, 2 mW; modulation amplitude, 2.5 G$_{pp}$.

properties have been interpreted in detail [9c]. This low g-value feature has been attributed to the perpendicular component, $g'_{\perp}$, of an axially anisotropic g' tensor from an $S' = 1/2$ system [9c]. In triangular, antiferromagnetically-coupled complexes of half-integer S centers, the axial anisotropy of the $S_T = 1/2$ ground state originates from the antisymmetric exchange interaction [13c]. The $g'_{\parallel}$ component of this system is expected to give a peak in the $g = 2.1$–2.3 region; in the spectrum shown in Fig. 5, a complex signal is observed in this region and possibly the just mentioned $g'_{\parallel}$ peak constitutes part of it.

For a coupled triangular system comprising $S = 1/2$ Cu^{II} ions there are two states with total spin $S_T = 1/2$ and one state with $S_T = 3/2$. In the case of antiferromagnetic interactions in an equilateral configuration (three equal exchange parameters), the $S_T = 1/2$ states split [15] by an amount δ. This splitting is further augmented by the antisymmetric exchange term yielding a total splitting Δ [16]. The observation of an axial effective g-tensor due to the antisymmetric term with $g'_{\perp} = 1.17 \ll \sim 2.1$ from an $S_T = 1/2$ state in the present case indicates that **1** has an isosceles or lower magnetic symmetry, i.e. $\delta \neq 0$ [17], that antisymmetric exchange is important to its magnetic structure and that $\Delta > h\nu$, where $h\nu$ is the microwave energy at X-band (~ 0.3 cm^{-1}).

In conclusion, the present preliminary work extends the body of results that emphasize the ability of anionic 2-pyridyl oximes to form interesting structural types in 3d-metal carboxylate chemistry. The initial use of di-2-pyridyl ketone oxime in reactions with copper(II) carboxylate sources has provided access to two new triangular complexes containing the $\{Cu_3(\mu_3\text{-OH})\}^{5+}$ core and possessing the extremely rare inverse 9-metallacrown-3 motif. Complex **1** exhibits interesting magnetic and EPR features and the antisymmetric exchange interaction has to be taken into account to describe the magnetic behaviour of the cluster properly. The full magnetic/EPR study of **1** and **2**, and the investigation of the dependence of various synthetic parameters on the identity of the $Cu^{II}/RCO_2^-/(py)_2CNO^-$ complexes are in progress.

Acknowledgements

Appendix A. Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, B2 1EZ, UK, on quoting the deposition numbers CCDC 297550 ($\mathbf{1} \cdot CH_2Cl_2$) and 297551 ($\mathbf{2} \cdot 4H_2O$) (fax: +44 1233 336 033; e-mail: deposit@ccdc.cam.ac.uk of http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.04.032.

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unique ($R_{\text{int}} = 0.0517$), R_1 on $F(wR_2$ on $F^2) = 0.0677$ (0.1694) for 3986 observed ($I > 2\sigma(I)$) reflections. **2**·4H$_2$O: C$_{47}$H$_{43}$N$_9$Cu$_3$O$_{12}$, $M = 1116.52$, monoclinic, P2$_1$/n, $a = 12.724(5)$ Å, $b = 14.061(6)$ Å, $c = 26.505(10)$ Å, $\beta = 92.60(1)°$, $V = 4737(3)$ Å^3, $Z = 4$, $D_c = 1.566$ g cm^{-3}, μ(Mo Kα) $= 2.184$ mm^{-1}, $T = 298$ K, 6643 reflections collected, 6484 unique ($R_{\text{int}} = 0.0236$), R_1 on $F(wR_2$ on $F^2) = 0.0432$ (0.1077) for 5234 observed ($I > 2\sigma(I)$) reflections.

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