

Fixation of CO₂ in air: Synthesis and crystal structure of a *m*₃-CO₃-bridged tricopper(II) compound

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Abstract. A novel trinuclear copper(II) compound $[(L^3)Cu(OCIO_3)]_3(m_3-OCO_2)[ClO_4]$ has been synthesised using an N-tridentate symmetrical pyridylalkylamine ligand, N-methyl-N,N-bis(2-pyridylmethyl)amine (L^3). The structure of the complex has been determined by X-ray crystallography; it is found to crystallise in the hexagonal space group $P6_3/m$ with $a = 13.936(2)$, $b = 13.936(2)$, $c = 14.895(3)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The complex possesses a $\bar{6}$ symmetry axis passing through the carbon atom of the triply bridging carbonate ion, with the three symmetry related copper ions connected to one another through the oxygen atoms from the bridging carbonate group, giving an equilateral triangular array of copper centres. Each copper ion has distorted square pyramidal environment with the basal plane formed by three nitrogen atoms of the ligand L^3 and the oxygen atom of the bridging carbonate group. The apical position at each copper is provided by the weak oxygen coordination from the perchlorate ion.

Keywords. Copper(II) complex; triply bridging carbonate group; N-tridentate ligand; crystal structure.

1. Introduction

Studies on the reactions of Cu(I) complexes with molecular oxygen are of considerable interest because of their importance in copper-mediated stoichiometric and/or catalytic oxidative organic transformations, including O₂ processing by copper proteins.¹ In the past few years we have been investigating the reactivity of the binuclear Cu(I) complexes of tailor-made ligands with dioxygen and the dependency of the arene hydroxylation on the ligand topology^{2–4} and catalytic oxidations of sterically hindered phenols.⁵ We became interested in copper–dioxygen chemistry from the viewpoint of modelling tyrosinase-like activity^{2–5} and catechol oxidase activity⁶ and to characterize irreversibly oxidized products, from the reaction between copper(I) complexes and dioxygen.^{2,6,7}

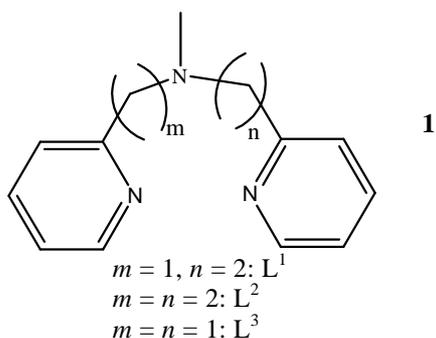
Using a tridentate ligand L^1 with chelate ring asymmetry [$L^1 = \text{methyl}[2-(2\text{-pyridyl})\text{ethyl}](2\text{-pyridylmethyl})\text{amine}$] we have been engaged^{8,9} in the synthesis, characterization and reactivity aspects of bio-inspired coordination complexes with the cores $\{M_2(m-O)(m-O_2CMe)_2\}^{z+}$ [$M = \text{Fe(III)}$,^{8b,9b} Mn(III) ,^{8d,9a}

Ru(III) ;^{8a} $z = 2$], $\{\text{Ru}^{\text{IV}}\text{Ru}^{\text{III}}(m-O)(m-O_2CMe)_2\}^{3+}$,^{8a} $\{M_2(m-O)_2(m-O_2CMe)\}^{z+}$ [$M = \text{Mn(III)Mn(IV)}$,^{8c,8d,9a} $z = 2$; $M = \text{Mn(IV)}$,^{8c,9a,c} $z = 3$] or $\{\text{Co}^{\text{III}}_2(m-OH)_2(m-O_2CMe)\}^{3+}$.^{9b} Quite a few such cores have been structurally characterized.⁹ Recently, new insights into Cu(I)/O₂ reactivity have been provided by Karlin and co-workers from the reaction of $[(L^2)Cu^{\text{I}}(\text{MeCN})]^+$ [$L^2 = \text{bis}[2-(2\text{-pyridyl})\text{ethyl}]\text{methylamine}$] with O₂ at low-temperature.¹⁰ The product $[(L^2)Cu]_2O_2$, exists as a mixture of $m-h^2 : h^2$ -peroxodicopper(II) and some *bis-m*-oxo-dicopper(III) species. Following the observation that the reaction between $[(L^1)Cu^{\text{I}}(\text{MeCN})][ClO_4]$ and dioxygen is very fast,¹¹ we attempted to isolate and characterize the irreversibly oxidized product. It was particularly surprising for us to discover that from a reactive irreversibly oxidized ‘green species’ containing supposedly dihydroxy-bridged core, $\{[(L^1)Cu(OH)]_2\}^{2+}$, followed by workup in air, the well-formed ink-blue crystals isolated were of the tricopper(II) complex $[(L^1)Cu(OCIO_3)]_3(m_3-OCO_2)[ClO_4]$ ¹² with a triply bridging carbonate group.¹³ To understand how supporting ligand chelate ring size, as for example in going from L^1 to L^3 , critically influences the reactivity property of intermediate copper dioxygen species and the structure of irreversibly oxidized complex, we paid attention to the missing symmetrical ligand

Dedicated to the memory of the late Professor Bhaskar G Maiya

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in this series L^3 , with two methylpyridine arms *bis*[2-(2-pyridyl)ethyl]methylamine. As with for the Cu(I) complex of L^1 , with L^3 we observed similar reactivity behaviour and due to further reaction of intermediate 'green species' with CO_2 present in air, an ink-blue solid $[\{(L^3)Cu(OCIO_3)\}_3(m_3-OCO_2)][ClO_4]$ was isolated. Herein we report the synthesis, structure and properties of this new compound, **1**.



2. Experimental

2.1 Materials

All chemicals were obtained from commercial sources and used as received. Solvents were dried as reported previously.²⁻⁶ $[Cu(MeCN)_4][ClO_4]$ was synthesized following a literature method.¹⁴ The ligand N-methyl-N,N-*bis*(2-pyridylmethyl)amine (L^3) was prepared as before.^{9b,15}

2.2 Physical measurements

C, H and N elemental analyses were determined with Carlo Erba CHNSO 1110 analyser. Solution electrical conductivity measurements (298 K) were carried out with an Elico (Hyderabad, India) Type CM-82 T conductivity bridge. Electronic spectra were recorded using an Agilent 8453 diode-array spectrophotometer. EPR spectra were recorded at 298 K using Brüker EMX 1444 EPR spectrometer.

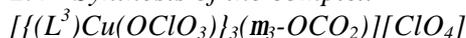
Room-temperature solid-state magnetic susceptibility measurements were done by the Faraday technique using a locally-built magnetometer. The setup^{9b} consists of an electromagnet with constant gradient pole caps (Polytronic Corporation, Mumbai), Sartorius M25-D/S balance (Göttingen, Germany), a closed cycle refrigerator, and a Lake Shore temperature controller (Cryo Industries, USA). The measurement was made at fixed main field strength of ~0.6 T. Solution-state magnetic susceptibility was

obtained by the NMR technique of Evans¹⁶ in MeCN with a PMX-60 JEOL (60 MHz) NMR spectrometer. Susceptibilities were corrected¹⁷ for diamagnetic contribution. Effective magnetic moments were calculated from $m_{\text{eff}} = 2.828 [C_M T]^{1/2}$, where C_M is the corrected molar susceptibility.

2.3 X-ray crystallography

A blue block-shaped crystal of $[\{(L^3)Cu(OCIO_3)\}_3(m_3-OCO_2)][ClO_4]$ was used for data collection on a Siemens P4 diffractometer (Guru Nanak Dev University) at 293(2) K, with graphite-monochromatized Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The data were corrected for Lorentz and polarization factors. The structure was solved by direct method and refined using the programs SHELXL-97 by full matrix least squares methods based on F^2 . These programs were accessed through WINGX 1-64 crystallographic collective package.¹⁸ All non-hydrogen atoms were refined anisotropically (see below). Hydrogen atoms were fixed geometrically and were not refined. A problem was encountered with the non-coordinated perchlorate ion and hence it was fixed to refine as a rigid group, to obtain meaningful Cl–O distances. Such oxygens were refined isotropically. Crystal data, data collection, and refinement parameters are listed in table 1. Pertinent metric parameters are contained in table 2. Further details on the CIF file is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, quoting the deposition number CCDC 211680.

2.4 Synthesis of the complex



To a MeOH solution (8 ml) of $[Cu(MeCN)_4][ClO_4]$ (0.153 g, 0.47 mmol), a MeOH solution (8 ml) of L^3 (0.1 g, 0.47 mmol) was added dropwise, under N_2 atmosphere. The resulting yellow solution when exposed to O_2 , at either -40°C or 25°C , immediately turned green. Upon continued stirring of this solution for 3 h in air, the solution colour changed to greenish blue and finally to blue. After reduction of solution to half of its original volume and addition of diethyl ether (10 ml) to it afforded isolation of a blue solid (yield: 0.134 g, ~67%). Recrystallization was achieved by dissolving this solid in a mixture (2 : 1, v/v) of MeCN- H_2O (6 ml) followed by filtration and keeping in air for slow evaporation. Well-

formed ink-blue crystals thus obtained were found to be suitable for X-ray structural analysis (yield: 0.106 g, ~53%). Anal. Calcd. for C₄₀H₄₅N₉O₁₉Cl₄-Cu₃: C 37.28, H 3.50, N 9.79%. Found: C 37.51, H 3.68, N 9.82%. IR (KBr, cm⁻¹, selected peaks): 1100, 625 ν (ClO₄); 1452, 871, 771 ν (OCO₂²⁻). Conductivity (~1 mol dm⁻³ solution in MeCN at 298 K): $\Lambda_M = 200 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ [expected ranges: 120–160 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ (1 : 1); 220–300 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ (1 : 2)].¹⁹ Absorption spectrum [I_{max} , nm (e, dm³ mol⁻¹ cm⁻¹)] (in MeCN): 257 (41 400), 296 *sh* (8200), 640 (450). m_{eff}/Cu at 298 K: 1.93 m_B (solid) and 1.86 m_B (MeCN).

Table 1. Data collection and structure refinement parameters for $[\{(L^3)\text{Cu}(\text{OCIO}_3)_3\}_3(m_B\text{-OCO}_2)][\text{ClO}_4]$ **1**.

Molecular formula	C ₄₀ H ₄₅ Cl ₄ N ₉ O ₁₉ Cu ₃
M_r	1287.94
Temperature (K)	293(2)
Radiation used ($I/\text{\AA}$)	Cu-K α (1.5418)
Crystal system	Hexagonal
Space group	$P6_3/m$ (no. 176)
a (\AA)	13.936(2)
b (\AA)	13.936(2)
c (\AA)	14.895(3)
a ($^\circ$)	90.0
b ($^\circ$)	90.0
g ($^\circ$)	120.0
V (\AA^3)	2505.2(7)
Z	2
D_c (g cm ⁻³)	1.707
m/mm^{-1}	1.559
Crystal size (mm)	0.30 × 0.20 × 0.20
Reflections measured	931
Unique reflections (R_{int})	930, 1.6027
No. of reflns used ($I > 2s(I)$)	438
Restraints/refined parameters	21/112
R (F , $F^2 > 2\sigma$) (R_w)	0.0924 (0.2140)
R (F , all data) (R_w)	0.1915 (0.2959)
Goodness-of-fit on F^2	1.021
Max. (min) electron density (e \AA^{-3})	0.666, -0.653

Table 2. Selected bond distances (\AA) and bond angles (deg) in the cationic part of $[\{(L^3)\text{Cu}(\text{OCIO}_3)_3\}_3(m_B\text{-OCO}_2)][\text{ClO}_4]$, **1**.

Cu–N1 1.989(14)	N1–Cu–N1' 163.9(9)
Cu–N2 2.08(2)	N1–Cu–N2 82.7(4)
Cu–O1 1.940(19)	N1–Cu–O1 96.7(4)
Cu–O2 2.41(3)	N1–Cu–O2 93.9(4)
O1–C8 1.269(15)	N2–Cu–O1 170.4(7)
Cu–Cu' 4.654(14)	N2–Cu–O2 94.9(8)
	O1–Cu–O2 94.8(7)

CAUTION: Perchlorate salts of metal complexes with organic ligands and perchlorate anions are potentially explosive! Only small amounts of material should be prepared, and these should be handled with great care.

3. Results and discussion

3.1 Synthesis and properties

A very common reaction of Cu(I) complexes with dioxygen is the formation of irreversibly oxidised products, *m*-oxo/*m*-hydroxo-bridged dicopper(II) complexes.²⁰ In the framework of our current research work dealing with isolation and characterization of products due to reaction between Cu(I) complexes and dioxygen,^{2–7} during work-up in air we obtained two new tricopper(II) complexes of formula $(L^1/L^3)_3\text{Cu}_3(\text{CO}_3)(\text{ClO}_4)_4$. Careful synthetic reactions revealed that green MeOH solutions, generated by the reaction of the Cu(I) complex of L³ with dioxygen, have great affinity for atmospheric CO₂, readily (~1 h) extracting it from the air, forming triply bridging carbonate tri-copper(II) products $[\{(L^3)\text{Cu}(\text{OCIO}_3)_3\}_3(m_B\text{-OCO}_2)][\text{ClO}_4]$. The green $\{(L^3)\text{Cu}(\text{OH})\}_2^{2+}$ species is more reactive than $\{(L^1)\text{Cu}(\text{OH})\}_2^{2+}$,¹² attesting to the greater stabilizing power of L³ over L¹ towards the Cu^{II} state due to the presence of two five-membered chelate rings in L³. Thus, during reaction of reactive 'green solution', CO₂ present in air was transformed to CO₃²⁻, which was fixed on the metal centres (see below). The new complex exhibits carbonate-related IR bands^{12,13a} and MeCN solutions display absorption bands at 640 nm. Solution electrical conductivity data is considerably higher than that expected for a 1 : 1 electrolyte, implying partial dissociation in MeCN of coordinated perchlorate ions.

We have measured effective magnetic moments in the solid state as well as in the solution-state at room temperature (298 K). The m_{eff}/Cu value of this compound as a solid is 1.93 m_B and the corresponding value in MeCN solution is found to be 1.86 m_B , attesting to the fact that the solid-state structure is retained in solution. The data are in line with closely similar structurally characterized ferromagnetic complexes $[\{(L^1)\text{Cu}(\text{OCIO}_3)_3\}_3(m_B\text{-OCO}_2)][\text{ClO}_4]$,¹² for which temperature-dependent magnetic studies were performed. As for $[\{(L^1)\text{Cu}(\text{OCIO}_3)_3\}_3(m_B\text{-OCO}_2)][\text{ClO}_4]$, the EPR spectrum of this compound (powder, 298 K) exhibits a single symmetric signal at $g = 2.116$.

3.2 Crystal structure of $\{[(L^3)Cu(OCIO_3)]_3(m_3-OCO_2)\}^+ [(ClO_4)]^-$

The molecular structure is made up of $\{[(L^3)Cu(OCIO_3)]_3(m_3-OCO_2)\}^+$ trinuclear complex cations (figure 1) and perchlorate anions. The carbonate group lies on the crystallographically required $\bar{6}$ symmetry axis. Each copper ion is five-coordinate with the basal plane formed by three nitrogen atoms of the ligand L^3 and the oxygen atom of the bridging carbonate group. The apical position is satisfied at each copper centre by the weak oxygen coordination of the perchlorate ion [2.41(3) Å]. Based on the structural index parameter of Addison *et al*²¹ the coordination geometry of the Cu(II) centre can be described as distorted square pyramid ($t = 0.108$). Thus the presence of two methylpyridine arms in L^3 renders the metal-site geometry more distorted towards trigonal bipyramidal than the closely similar complex $\{[(L^1)Cu(OCIO_3)]_3(m_3-OCO_2)\}^+ [(ClO_4)]^-$ ($t = 0.026$) with an unsymmetrical tridentate ligand (L^1), with one methylpyridine and one ethylpyridine arms.¹² The three symmetry-related Cu(II) centres are slightly [0.158(1) Å] out of the carbonate plane to-

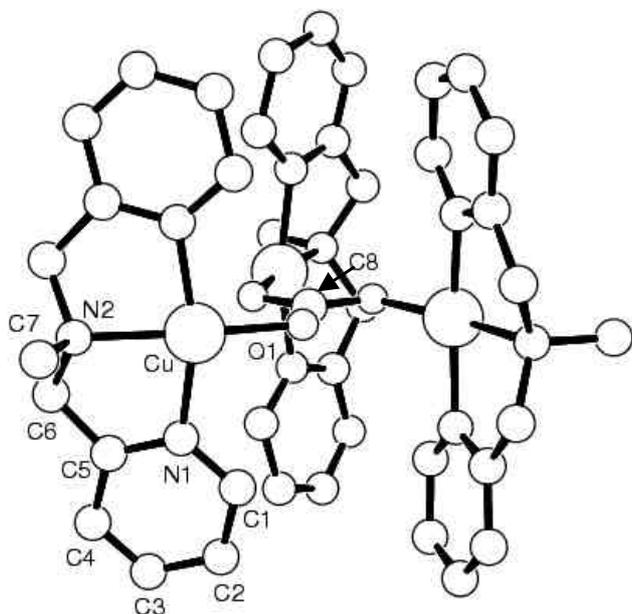


Figure 1. View of the structure of the cationic trinuclear unit $\{[(L^3)Cu(OCIO_3)]_3(m_3-CO_3)\}^+$ (perchlorate coordination is not shown for clarity) in the crystal of its perchlorate salt $\{[(L^3)Cu(OCIO_3)]_3(m_3-OCO_2)\}^+ [(ClO_4)]^-$, **1**. Hydrogen atoms are omitted for clarity. Unlabelled atoms are related to labelled atoms by the crystallographic $\bar{6}$ axis.

wards the perchlorate oxygen atom O_2 and the CuN_3O planes are tilted with respect to the practically planar CO_3Cu_3 fragment at a dihedral angle of $89.99(4)^\circ$. Each oxygen atom of the carbonate group [C–O distance: 1.269(15) Å] is bonded to a different copper atom, giving an equilateral triangular array of copper atoms, with a central m_3 -carbonate bridge. It is worth noting that in the present complex all the Cu–N/O bond distances are longer by ~ 0.05 Å than that observed in the closely similar complex with unsymmetrical tridentate ligand L^1 .¹²

Using the unsymmetrical (2-pyridyl)alkylamine ligand L^1 we reported/determined the X-ray structures of $[(L^1)_2Mn^{III}Mn^{IV}(m-O)_2(m-O_2CMe)][BF_4]_2 \cdot 2MeCN$,^{9c} $[(L^1)_2Fe^{III}_2(m-O)(m-O_2CMe)_2][ClO_4] \cdot 2H_2O$,^{9b} $[(L^1)_2Co^{III}_2(m-OH)_2(m-O_2CMe)][ClO_4]_3 \cdot MeCN$,^{9b} $[(L^1)Fe^{III}Cl_3]$,^{22a} $[(L^1)_2Mn^{III}_2(m-O)(m-O_2CMe)_2][ClO_4]_2$,^{9a} and $[(L^1)_2Mn^{IV}_2(m-O)_2(m-O_2CMe)][ClO_4]_3 \cdot MeCN$.^{9a} In all these compounds, the unsymmetrical ligand L^1 is coordinated uniformly in the facial mode. However, in the complexes $[(L^1)ZnCl_2]$,^{22b} $[(L^1)CuCl_2] \cdot 0.5H_2O$ ^{22c} and $\{[(L^1)Cu(OCIO_3)]_3(m_3-OCO_2)\}^+ [(ClO_4)]^-$,¹² this unsymmetrical ligand L^1 is coordinated in a meridional mode. Interestingly, the X-ray structure of $[(L^3)_2Fe^{III}_2(m-O)(m-O_2CMe)_2][ClO_4] \cdot 2H_2O$ revealed the facial mode of coordination of the symmetrical ligand L^3 .¹⁵ Thus, like unsymmetrical ligand L^1 the present symmetrical ligand L^3 also has the potential to bind in both facial as well as in meridional mode, attesting to its inherent flexibility. The Cu–N (pyridine), Cu–N (amine), Cu– OCO_2 , and Cu–Cu' distances are comparable to closely related systems.^{12,13}

3.3 Rationale for CO_2 fixation

The formation of tricopper(II) compounds with triply bridging carbonate groups is interesting owing to the efficiency of the reaction between the supposedly dihydroxy-bridged green Cu(II) species, generated by reaction of Cu(I) complexes with O_2 and CO_2 in air. This solution-generated green Cu(II) species is, in turn, responsible for fixing the very low concentration of CO_2 found in the atmosphere, and the observed coordination mode of the carbonate group. To our knowledge, in the copper(I) complexes of L^1 and L^3 , the CO_2 present in air can be fixed by the highly reactive di-*m*-hydroxo-bridged dicopper(II) species, generating tricopper(II) complexes with m_3 -carbonate bridges. It should be noted here that the *bis*-hydroxo Cu(II) complexes of Kitajima *et al*^{23a} and Sorrell *et al*^{23b} provide a more

common mode of bridging carbonate ligands between *two* copper atoms. The mechanism of CO₂ fixation by the dihydroxo complex of Cu(II) can be explained in terms of the nucleophilic attack of the hydroxo group on the electrophilic carbon of CO₂, followed by water dissociation.^{13h,24} While fixation of CO₂ by transition metal complexes is common,²⁴ only a few examples of spontaneous CO₂ uptake from air by authentic peroxy/oxo/hydroxo complexes of copper(II) to form dinuclear carbonate bridged dicopper(II) complexes are reported.^{23,25}

4. Conclusions

In the case of L², reaction between Cu(I) complex and dioxygen leads to formation of the (*m*-h²:h²-peroxy)dicopper(II) complex with coexistence of a small percentage of the *bis*(*m*-oxo)dicopper(III) complex;¹⁰ in sharp contrast to this, reactions of Cu(I) complexes of L¹ and L³ with O₂, at low-temperature (−40°C) as well as at room temperature (25°C), do not produce any copper/oxygen species. Instead, in these cases ‘green solutions’ of supposedly dihydroxo-bridged dicopper(II) species are formed. This research further demonstrates how the introduction of a small change in the chain length of the alkyl linker supporting ligand (effect of chelate ring size) drastically alters the reactivity of Cu(I) complexes with dioxygen. This insight may allow for the rational design of new pyridylalkylamine ligands for stabilization of copper–dioxygen species. The structural analysis of trinuclear Cu(II) *m*₃-carbonate complexes has shed light on the nature of the species present in ‘green solutions’ (nucleophilic character of Cu(II)-coordinated hydroxo groups) which instantaneously attack atmospheric CO₂, in line with the mechanistic view of CO₂ → CO₃^{2−} transformation in the enzyme carbonic anhydrase.²⁶

Acknowledgements

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