

# An unprecedented heterotrimetallic Fe/Cu/Co core for mild and highly efficient catalytic oxidation of cycloalkanes by hydrogen peroxide†

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**An unprecedented hexanuclear heterotrimetallic Fe/Cu/Co complex bearing two Cu( $\mu$ -O)<sub>2</sub>Co( $\mu$ -O)<sub>2</sub>Fe cores is easily prepared by self-assembly and acts as a remarkable catalyst for the peroxidative oxidation of cycloalkanes under mild conditions.**

Self-assembly synthesis of heteropolynuclear complexes is an expanding field in modern chemistry, stimulated by the aesthetic beauty and originality of such compounds, and also by the simplicity of this synthetic procedure and the increased significance of heterometallic materials *e.g.* in sorption, optics, conductivity, molecular magnetism and catalysis.<sup>1</sup> Although many heterometallic heterogeneous catalysts are known and even applied in various industrial-scale processes,<sup>1b,2</sup> multimetallic homogeneous catalysts, particularly heteronuclear ones, are rather scant and mainly based on polyoxometalates.<sup>3</sup> This contrasts with the developed field of bio-inspired homometallic complexes, namely with a M<sub>2</sub>( $\mu$ -O)<sub>2</sub> (M = Fe, Cu, Co) core, which mimic the functions of various enzymes.<sup>4</sup> In particular, although the synthesis of heterobimetallic Fe/Cu, Fe/Co or Cu/Co complexes has been widely reported,<sup>5</sup> there is still no example of an inorganic coordination compound bearing these three metals. Moreover, the majority of heterobi- and trimetallic species has been synthesized for magnetic investigations,<sup>6</sup> whereas their catalytic properties usually remain poorly investigated and, to our knowledge, are fully unexplored in the field of alkane functionalization.

Thus, in pursuit of our recent studies on alkane oxidation catalyzed by Fe<sup>III</sup> or Cu<sup>II</sup> systems,<sup>7</sup> the current study focuses on the search for an unprecedented heterotrimetallic Fe<sup>III</sup>/Cu<sup>II</sup>/Co<sup>III</sup> compound, preferably obtained by a simple method *e.g.* self-assembly synthesis, which could act as a catalyst for alkane

oxidation under mild conditions. A N,O-coordination environment was chosen in view of its significance in diverse biological systems<sup>4,8</sup> and in some alkane oxidation metal catalysts.<sup>9,10</sup> The choice of iron and copper was governed by their relevance in the active sites of various oxidases,<sup>8</sup> especially those which can oxidize alkanes, *e.g.* soluble<sup>11</sup> and particulate<sup>12</sup> methane monooxygenases (sMMO and pMMO, respectively). The occurrence of cobalt in oxidation type enzymes is less extended<sup>8,13</sup> but Co compounds are oxidation catalysts in several industrial processes including the oxidation of cyclohexane with Co<sup>III</sup> naphthenate.<sup>2</sup> Hopefully, the combination of three metals within each molecule of catalyst could contribute to a cooperative effect as observed *e.g.* in CO dehydrogenase with a Fe/Cu/Ni active core.<sup>14</sup> Besides, the presence of three different spin carriers could represent a model to study exchange interactions.<sup>15</sup>

Hence, we now report the new hexanuclear self-assembled [FeCuCo(L)<sub>3</sub>(NCS)<sub>2</sub>(MeOH)]<sub>2</sub>·3.2H<sub>2</sub>O (**1**, H<sub>2</sub>L = diethanolamine) complex which, to our knowledge, represents the first example of an inorganic heterotrimetallic Fe/Cu/Co coordination compound, and show that it acts as the most active catalyst or catalyst precursor, comprising any of these metals, for the peroxidative oxidation of cycloalkanes, under mild conditions, to the corresponding alcohols and ketones. Complex **1** has been prepared by one-pot reaction of Cu powder with Co(SCN)<sub>2</sub>, FeCl<sub>3</sub> and diethanolamine.† This synthesis relates to that applied by some of us<sup>6a</sup> for [Ni(H<sub>2</sub>L)<sub>2</sub>][CuCo(H<sub>2</sub>L)(L)<sub>2</sub>(NCS)]<sub>2</sub>(A)<sub>2</sub> {A = NCS (**2a**) or Br (**2b**)} but using FeCl<sub>3</sub> instead of a Ni<sup>II</sup> salt.

Complex **1** has been characterized by IR and EPR spectroscopies, elemental and differential thermal analyses, magnetic susceptibility measurements† and (for the identical compound **1'** with {5MeOH·H<sub>2</sub>O} of crystallization instead of 3.2 H<sub>2</sub>O) single crystal X-ray crystallography.‡ The molecular structure (Fig. 1) is centrosymmetric with the inversion centre situated at the mid-point of the Fe<sub>2</sub>O<sub>2</sub> unit. The metal atoms are bridged by O atoms of the diethanolaminates. Although we could predict the overall geometrical relationship among the metal centers,† the presence of the heterotrimetallic core in a dimeric {CuCoFe}<sub>2</sub> form was fully unexpected. In contrast to **2**, the [Co(L)<sub>2</sub>] octahedron of **1'** connects both Cu and Fe polyhedra with intermetallic Cu(1)··Co(1) and Co(1)··Fe(1) separations of *ca.* 2.83 and 2.99 Å, respectively, that are lower than the Fe(1)··Fe(1) distance of *ca.* 3.22 Å and somewhat comparable to those found between the closest metal centers in sMMO (*ca.* 2.5 Å)<sup>4c</sup> and pMMO (*ca.* 2.6 Å),<sup>12</sup> as in many of their model complexes.<sup>4</sup> The stereochemistry of Cu(1) is square-pyramidal with an apical methanol

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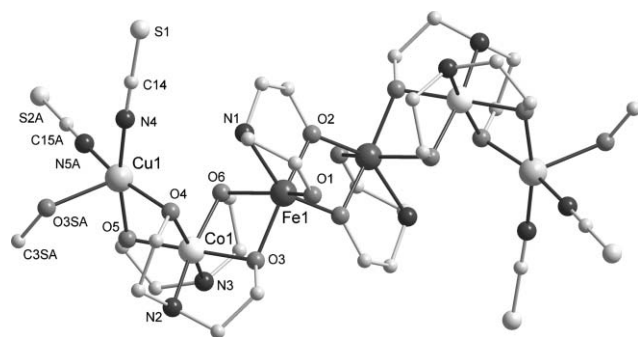
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† Electronic supplementary information (ESI) available: Synthetic procedure for **1** and full experimental details, selected bond distances and angles from single crystal diffraction data for **1'**, description of IR and TGA data, magnetic susceptibility measurements and EPR spectroscopy data. See DOI: 10.1039/b608790f



**Fig. 1** Ball-and-stick representation of the molecular structure of **1**<sup>c</sup>. The methanol and water molecules of crystallization, hydrogen atoms and disordered parts are omitted for clarity.

ligand. The geometry around Co(1) is almost octahedral, and the Co–O(N) distances are in the 1.881(2)–1.941(3) Å range. Fe(1) shows a distorted octahedral coordination to the O<sub>5</sub>N donor set. Intermolecular association in the lattice occurs through O–H...O and N–H...O H-bonding involving uncoordinated methanol molecules to form 2D sheets.<sup>‡</sup> The presence of three different coordination geometries and magnetic studies completely confirm the absence of metal scrambling in **1**, while elemental analysis is consistent with the proposed formulation.

The heterotrimetallic cluster **1** acts as a new highly active and selective catalyst or catalyst precursor for liquid biphasic (H<sub>2</sub>O/MeCN) oxidation of cycloalkanes (*i.e.* cyclopentane and cyclohexane) by H<sub>2</sub>O<sub>2</sub> in a slightly acidic medium, at room temp. and atmospheric pressure, to the corresponding cyclic alcohols (*i.e.* cyclopentanol and cyclohexanol, respectively), as the main products, and cyclic ketones (*i.e.* cyclopentanone and cyclohexanone, respectively), in lower amounts. Overall yields up to 45% based on cycloalkane and turnover numbers (TONs) up to 100 moles of products per mole of catalyst are achieved (selected results are given in Table 1). The effects on the catalytic activity of various factors such as the relative amounts of oxidant, catalyst, acetonitrile and HNO<sub>3</sub>, and reaction time have been studied in order to optimize the process. No alkane oxidation products (or only traces) are obtained in the absence of the metal catalyst.

**Table 1** Peroxidative oxidation of cycloalkanes to the corresponding cyclic alcohols and ketones catalyzed by complex **1**<sup>a</sup>

Run	Alkane	<i>n</i> (H <sub>2</sub> O <sub>2</sub> )/ <i>n</i> (catalyst)	Time/h	Yield (%) <sup>b</sup> of products		
				Alcohol	Ketone	Total <sup>c</sup>
1	C <sub>6</sub> H <sub>12</sub>	300	6	34.2	3.1	37.4
2	C <sub>6</sub> H <sub>12</sub>	500	2	32.4	1.8	34.2
3	C <sub>6</sub> H <sub>12</sub>	500	4	40.2	3.0	43.2
4	C <sub>6</sub> H <sub>12</sub>	500	6	41.1	3.6	44.7
5	C <sub>6</sub> H <sub>12</sub>	500	24	34.7	4.4	39.0
6	C <sub>6</sub> H <sub>12</sub>	700	6	30.4	4.9	35.3
7	C <sub>5</sub> H <sub>10</sub>	300	6	30.6	5.1	35.7
8	C <sub>5</sub> H <sub>10</sub>	300	24	23.5	6.6	30.1
9	C <sub>5</sub> H <sub>10</sub>	500	6	25.0	7.3	32.3

<sup>a</sup> Selected data; reaction conditions: catalyst (10 μmol), aqueous 30% H<sub>2</sub>O<sub>2</sub> (3.00–7.00 mmol), cycloalkane (1.00 mmol), MeCN (4.5 mL), HNO<sub>3</sub> (0.20 mmol), see ESI for full experimental details. <sup>b</sup> Moles of product/100 moles of cycloalkane. <sup>c</sup> Alcohol + ketone; overall TON values (moles of products/moles of catalyst) are equal to the total % yield; % yields based on H<sub>2</sub>O<sub>2</sub> can be estimated as 100 × [% yield based on cycloalkane]/[*n*(H<sub>2</sub>O<sub>2</sub>)/*n*(catalyst)], *e.g.* 12.5% for run 1.

The highest overall yield of 45% or 36% for C<sub>6</sub>H<sub>12</sub> or C<sub>5</sub>H<sub>10</sub> oxidation is achieved for a H<sub>2</sub>O<sub>2</sub>/catalyst molar ratio of 500 or 300 (runs 4 or 7, respectively), and for 6 h reaction time, beyond which the yield drops due to overoxidation. However, in the C<sub>6</sub>H<sub>12</sub> oxidation shorter reaction times of 2 and 4 h already provide rather high total yields of 34 and 43%, respectively (runs 2 and 3), corresponding to TOFs of 17 and 11 mol of products/mol **1** per hour. A very high overall selectivity towards the formation of the alcohols and ketones (presumably close to 100% at peroxide/catalyst molar ratios up to 500) is achieved in both the cycloalkanes' oxidations, as supported by GC and GC-MS analyses that show no traces of any by-products. The system also exhibits a high selectivity towards the alcohols (usually *ca.* 80–95% of the total amount of products), whereas the ketones are obtained in low yields.

In contrast, complex **2a**, with a Ni centre dissociated from a Cu/Co core, exhibits a much lower catalytic activity in the peroxidative oxidation of C<sub>6</sub>H<sub>12</sub> providing the highest overall yield of 8% *vs.* 45% for catalyst **1** under similar conditions. Thus, the remarkable activity of the heterotrimetallic Fe/Cu/Co cluster **1** can be associated with the synergic effect of the three metals and the essential role of iron (in **2a** neither the Ni nor the Cu/Co core display such a high activity). Although numerous iron complexes with a N<sub>2</sub>O environment modeling sMMO have been synthesized<sup>4*c,f*,11*a*,16</sup> and applied<sup>16</sup> to oxidation of cyclohexane, their catalytic activity is usually very modest, with the exception of a hexanuclear Fe<sup>III</sup> compound derived from *p*-nitrobenzoic acid which exhibits the highest total yield of *ca.* 30%.<sup>16*a*</sup> Most of those model complexes are often unstable and very expensive, require complex ligands and multistage syntheses. This contrasts with the simple self-assembly synthesis of complex **1** based on the use of cheap and commercially available chemicals.

Besides, the activity and selectivity of **1** are higher than those reported for cyclohexane oxidations catalyzed by various Fe,<sup>3*a*,16</sup> Cu<sup>7*b*</sup> or Co<sup>3*a*,17</sup> systems. Moreover, the activity of **1** (based on mass) is comparable or even higher than those of sMMO or pMMO, although in different conditions. Hence, *e.g.* our system leads to 214 nmol of cyclohexanol + cyclohexanone per min and mg of catalyst (recalculated yield from entry 2, Table 1), averaged over the reaction time, *vs.* 84 nmol of MeOH or 17 nmol of EtOH per min and mg of sMMO or pMMO, respectively, for the enzymatic hydroxylation of methane or ethane, particularly favourable substrates for these enzymes.<sup>18</sup> Lower activities of *ca.* 40 and 73 nmol of alcohols per min and mg of protein are exhibited by sMMO in the hydroxylation of hexane and pentane, respectively.<sup>18*b*</sup> Although the oxidation of C<sub>6</sub>H<sub>12</sub> has been broadly studied<sup>3*a*,7,16,17</sup> mainly due to the use of cyclohexanone, cyclohexanol and adipic acid in nylon technology, only a few data are known for the oxidation of C<sub>5</sub>H<sub>10</sub>,<sup>7*a*,19</sup> which proceeds usually less efficiently, with the highest reported yield of *ca.* 19% achieved by using Fe<sup>III</sup> hydroxides as catalysts.<sup>7*a*</sup> In the current study, complex **1** raises the overall yield of cyclopentanol and cyclopentanone up to 35% (or *ca.* 75 nmol of products per min and mg of catalyst), corresponding to the most active catalytic system so far reported for the oxidation of C<sub>5</sub>H<sub>10</sub> under mild conditions.

The mechanism of the catalysis is still to be established, but a main radical pathway involving both C- and O-centered radicals can be proposed since the oxidations of cycloalkanes are essentially suppressed in the presence of radical trapping agents

like 2,6-di-tert-butyl-4-methylphenol, diphenylamine and  $\text{CBrCl}_3$ . This is also supported by the detection (although in low yields) in the final reaction mixtures, following a method of Shul'pin *et al.*,<sup>9</sup> of the corresponding organo-hydroperoxides which are usually formed in radical type oxidations.

In summary, the results indicate that spontaneous self-assembly can be an easy and promising pathway for the synthesis of heteropolynuclear complexes with Fe/Cu/Co assemblies. By using diethanolamine as a simple chelate-bridging ligand, we have prepared an unprecedented hexanuclear heterotrimetallic complex possessing the  $\text{Cu}(\mu\text{-O})_2\text{Co}(\mu\text{-O})_2\text{Fe}$  core and representing, to our knowledge, the first inorganic coordination compound containing these three transition metals. Their presence within each molecule conceivably accounts for the exceptionally high catalytic performance of the complex for the oxidation of cycloalkanes under mild conditions, using  $\text{H}_2\text{O}_2$  as a "green" oxidant. Further research will be focused on the mechanistic investigations and widening the family of heteropolynuclear complexes, namely towards modeling both methane monooxygenases.

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## Notes and references

† X-Ray analysis of **1**:  $\text{C}_{35}\text{H}_{84}\text{Co}_2\text{Cu}_2\text{N}_{10}\text{O}_{20}\text{S}_4\text{Fe}_2$ ,  $M = 1450.00$ , triclinic,  $P\bar{1}$ ,  $a = 8.9464(8)$ ,  $b = 10.8282(10)$ ,  $c = 16.5375(14)$  Å,  $\alpha = 97.126(7)$ ,  $\beta = 96.983(7)$ ,  $\gamma = 103.171(8)^\circ$ ,  $U = 1529.1(2)$  Å<sup>3</sup>,  $T = 100(2)$  K,  $Z = 1$ ,  $D(\text{calc}) = 1.575$  Mg m<sup>-3</sup>,  $\mu = 1.883$  mm<sup>-1</sup>,  $F(000) = 752$ ,  $\theta = 2.67\text{--}26.00^\circ$ , 13405 reflections measured, 8775 unique ( $R_{\text{int}} = 0.0232$ ) which were used in all calculations,  $R_1$  (5390 reflections with  $I > 2\sigma(I)$ ) = 0.0523,  $wR_2 = 0.1464$ . CCDC 606556. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608790f

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