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Alkane Activation

Multinuclear Copper Triethanolamine Complexes as Selective Catalysts for the Peroxidative Oxidation of Alkanes under Mild Conditions**

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Copper species are widely found in nature and are present in many enzymes as di-, tri- or polynuclear Cu centers that catalyze selectively various oxidation reactions.[1] These reactions include the poorly characterized particulate methane monooxygenase (pMMO), which is present in methanotrophs, wherein a tri- or multinuclear Cu cluster catalyzes alkane hydroxylation and alkene epoxidation.[1f–i] Although increasing attention has been paid to the design of Cu complexes with polydentate ligands as models of copper oxidases[1a,b,2] and some mononuclear compounds have been

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recognized as catalysts for alkane oxidation,[3] the use of multicopper complexes for such reactions still remains an unexplored area of research. Our main aims are to find a simple synthetic method to generate multinuclear copper complexes with *N,O*-polydentate ligands and to investigate the catalytic activity of these complexes for the oxidation of alkanes under mild conditions, thus extending our interest of alkane functionalization catalyzed by biologically inspired complexes from vanadium compounds, such as synthetic amavadine and its models, to copper complexes.[4]

As a polydentate ligand, we chose an ethanolamine as it is cheap, commercially available, environmentally tolerable, is of a recognized synthetic significance,[5] and its Cu complexes have not yet been applied to alkane functionalization. Cyclohexane and methane were tested as the main substrates in view of the biological interest of the latter and the significance of the oxidized products of both starting materials, that is, cyclohexanol/cyclohexanone (manufacture of adipic acid, Nylon-6,6′ and polyamide-6) from cyclohexane[6] and methanol or other oxidized species, from methane. Attempts have been made to develop processes that have advantages (e.g., higher efficiency, selectivity, simplicity, and use of milder conditions)[7] over commercial processes.[6,7a] However, of the mononuclear Cu^I and Cu^{II} complexes tested as catalysts for cyclohexane oxidation,[3] most provide modest yields and low selectivity,[3b,e,f] require expensive[3f,i] and environmentally unfriendly[3g] reagents and various additives,[3g,i] and/or involve complicated syntheses.[3b–d,f–i] Although the catalytic oxidation of methane under relatively mild conditions is currently a matter of a high interest,[8] reported Cu catalysts are scant and have little activity. [9]

Herein we report the easy generation and characterization of copper(II) triethanolamine (H_3tea) complexes that adopt dimeric ([$Cu_2(H_2tea)_2(C_6H_5COO)_2$]·2$H_2O$; **1**), trimeric ([$Cu_3(H_2tea)_2(4\text{-}OC_6H_4COO)_2(H_2O)$]·4$H_2O$; **2**), tetrameric ([$O{\subset}Cu_4(tea)_4(BOH)_4$][$BF_4$]$_2$; **3**) and polymeric structures ([$Cu_2(H_2tea)_2\{\mu\text{-}C_6H_4(COO)_2\text{-}1,4\}$]$_n$·2*n* H_2O; **4**) and show that they are highly selective and active catalysts for the oxidation of alkanes. The addition of different types of aromatic carboxylates or Na[BF_4] to an aqueous blue solution of $Cu(NO_3)_2$, H_3tea, and NaOH provides the formation at room temperature of Cu complexes of diverse nuclearity. Hence, by adding benzoic acid, 4-hydroxybenzoic acid, Na[BF_4], or terephthalic acid one obtains compounds **1**, **2**, **3**, or **4**, respectively, which are isolated as crystalline solids in good yields (76–91%) and characterized by IR and FABMS spectroscopies, elemental analysis, and X-ray crystallography (preparation procedures and characterization details are provided as Supporting Information).[10]

The molecular structure of **1** (Figure 1a) consists of centrosymmetric binuclear fragments, [$Cu_2(H_2tea)_2$]$^{2+}$, which are stabilized by two monodentate benzoate ligands. Each Cu center has a distorted tetragonal bipyramidal geometry and each H_2tea molecule acts as a tetradentate ligand with one bridging alkoxo group. The equatorial plane is defined by the two bridging alkoxo oxygen atoms of the H_2tea ligands, one amino nitrogen atom and one carboxylate oxygen atom.

The molecular structure of **2** (Figure 1b) consists of three metal atoms that are clustered by two oxygen bridges of two triethanolamine ligands and two carboxylate groups; the central Cu atom is an inversion center. Each lateral Cu atom is coordinated by one H_2tea ligand and the distorted square-

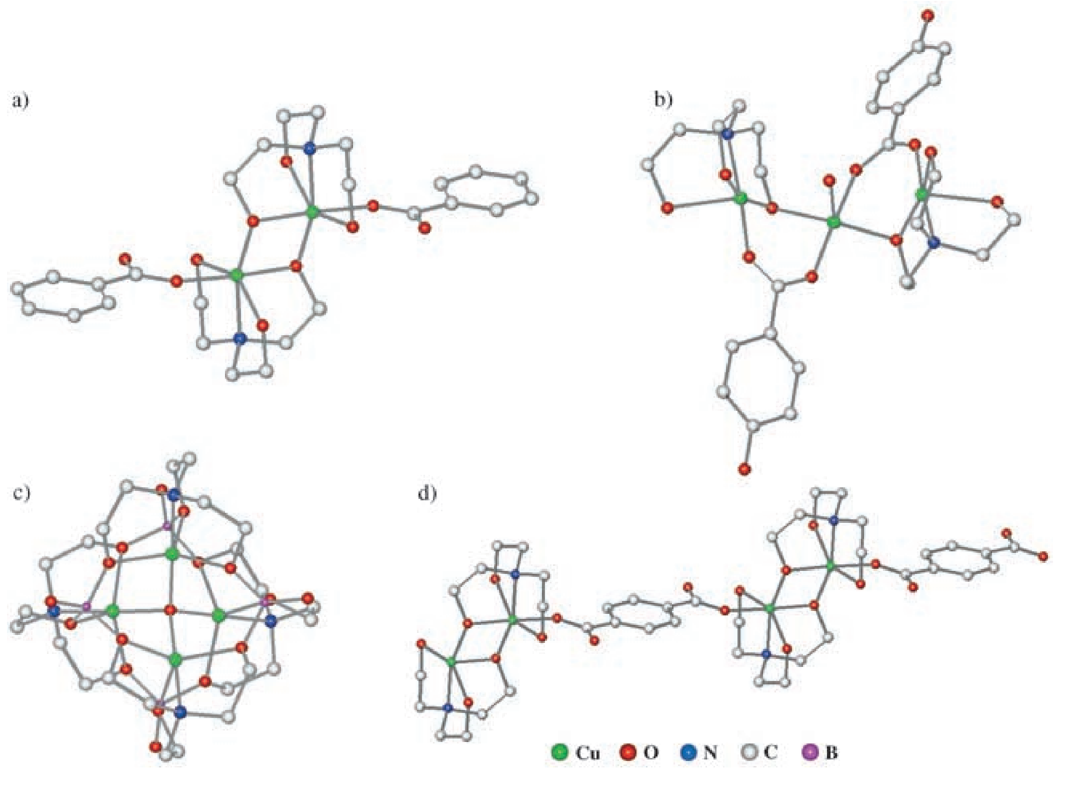


Figure 1. Ball-and-stick representation of the molecular structures of complexes **1** (a), **2** (b), **3**$^{2+}$ (c), **4** (d) (only two dinuclear repeating units are shown). Solvent molecules, counterions, and hydrogen atoms are omitted for clarity.

pyramidal geometry is completed by one carboxylate oxygen atom. The pentacoordinated central Cu atom binds with one water molecule (Cu–O 2.452(3) Å) that is involved in a hydrogen-bonding network with non-coordinated water molecules (see the Supporting Information). The overall positive charge is compensated by the deprotonation of OH groups on the substituted benzoate ligands. Although H_3tea as a tetradentate ligand has been extensively used to prepare polynuclear complexes,[5a,b] to our knowledge, compound **2** is the first example of a trinuclear complex with such a ligand.

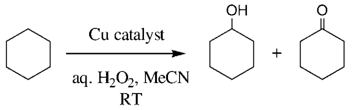
Complex **3** (Figure 1c) is composed of two metallacrown ether centrosymmetric subunits $[O\subset Cu_4(tea)_4(BOH)_4]^{2+}$ and four BF_4^- counterions per unit cell, which are linked by hydrogen bonds (see the Supporting Information). Each subunit is present in the crystal as a cyclic Cu^{II} complex, in which an oxygen atom (μ_4-O) is encapsulated in the center. Four practically equivalent copper atoms (Cu–Cu separations of 3.066(3)–3.196(3) Å) are located in the corners of an almost regular tetragon. The copper pentacoordination comprises one N and three O atoms of a deprotonated triethanolamine molecule and the μ_4-O center. Eight μ_3-O centers, two from each tea ligand, are linked to four B–OH groups (formed by an unusual conversion from $[BF_4]^-$ in alkali medium), which leads to additional tetragon stabilization.

Copper(II), H_3tea, and terephthalic acid are involved in the formation of the 1D coordination polymer **4** (Figure 1d), which is constructed from unsymmetrical binuclear nodes $[Cu_2(H_2tea)_2]^{2+}$ (Cu–Cu separation of 2.905(3) Å), which has a structure similar to that of **1** and linear-type spacers. The parallel chains are arranged in neighboring layers (see the Supporting Information).

All these complexes are catalyst precursors for the oxidation of cyclohexane to cyclohexanol and cyclohexanone in acetonitrile by hydrogen peroxide in acidic medium (liquid biphasic catalysis) at room temperature (Table 1). The tri- and tetranuclear complexes **2** and **3** have evident labile sites and exhibit the highest activity with overall yields (based on cycloalkane) of up to 32% (see entries 3, 7, and 11) for a typical acid-to-catalyst molar ratio of 10:1, whereas the other complexes, **1** and **4**, required a higher amount of acid, which is conceivably to promote unsaturation of the metal centers upon ligand protonation. Turnover numbers (TONs, moles of product/mole of complex) of about 360–380 can be reached for a sufficiently high ratio of alkane to catalyst (6400).

Complexes **2** and **3** can also catalyze the peroxidative oxidation of gaseous alkanes such as methane and ethane, although less effectively than in the case of cyclohexane. For example, methanol (TON = 47, 2.2% yield) and ethanol (TON = 23, 2.1% yield) are obtained from CH_4 and C_2H_6, respectively, with catalyst **3** at 40°C at an alkane pressure of 30 atm, a H_2O_2:catalyst molar ratio of 1000, and a HNO_3:catalyst molar ratio of 20. The use of O_2 instead of H_2O_2 results in a marked decrease in the activity which, nevertheless, can still be catalytic (e.g., TON = 4 for oxidation of methane to methanol with catalyst **3** and $p(O_2) = 2$ atm, the other conditions being similar to those given above).

Table 1: Peroxidative oxidation of cyclohexane catalyzed by complexes **1**–**4**.[a]



Entry	Catalyst	$n(H_2O_2)$/ n(catalyst)	t [h]	Yield [%][b]		
				Cyclohexanol	Cyclohexanone	Total[c]
1	**1**	200	6	5.0	7.2	12.2
2	**1**	400	6	6.0	9.4	15.4
3	**2**	200	6	19.9	10.6	30.5
4	**2**	400	6	7.9	6.8	14.7
5[d]	**2**	200	72	19.3	6.3	25.6
6[d]	**2**	400	72	20.3	9.0	29.3
7[d]	**2**	800	72	16.7	14.9	31.6
8	**3**	200	6	15.4	11.8	27.2
9	**3**	400	6	14.2	8.9	23.1
10[d]	**3**	200	72	20.6	6.5	27.1
11[d]	**3**	400	72	20.8	9.8	30.6
12[d]	**3**	800	72	13.5	10.5	24.0
13	**4**	200	6	6.5	5.8	12.3
14	**4**	400	6	7.0	8.6	15.6
15	$Cu(NO_3)_2$[e]	200	6	1.1	2.1	3.2
16	$Cu(NO_3)_2$[e]	400	6	1.6	3.8	5.4

[a] Reaction conditions: catalyst (0.025 mmol), H_2O_2 (2.50–10.00 mmol), C_6H_{12} (0.63 mmol). Full experimental details are provided in the Supporting Information. [b] Moles of product/100 moles of cyclohexane. [c] Cyclohexanol + cyclohexanone. [d] Catalyst (0.0125 mmol). [e] For comparative purposes.

The activity is dependent on the molar ratio of the peroxide to catalyst (compare entries 3–7 for **2** and entries 8–12 for **3**). Typically for cyclohexane reactions of 6 h, ratios of peroxide to catalyst ranging from 200:1 to 400:1 led to the best yields. Very high selectivity towards the formation of cyclohexanol and cyclohexanone was exhibited by these systems as no traces of any by-products were detected by GC or GC–MS analyses of the final reaction mixtures. The remarkable activity of our copper complexes is even higher than those found in amavadine and related vanadium catalysts for the same reaction.[4b] Based on mass, our Cu complexes appear to exhibit an activity that is comparable to or even higher than that of pMMO (17 nmol of ethanol per min mg of catalyst **3**; 34 nmol of methanol per min mg of catalyst **3**; or 97 nmol of cyclohexanol and cyclohexanone per min mg of catalyst **2** averaged over the reaction time versus 12–17 nmol of ethanol per min mg of protein for the enzymatic hydroxylation of ethane,[1g] which is a particularly favorable substrate).

The relevance of polydentate *N*,*O*-triethanolaminate ligands is evident in view of the much lower activity of a simple copper salt such as $Cu(NO_3)_2$ under the same reaction conditions (3–5% yield, TON ≈ 1, entries 15, 16, in the case of cyclohexane oxidation; or 0.06% yield, TON = 0.6 for the methane oxidation). This is conceivably associated with the involvement of those ligands (upon decoordination of an N or O atom) in proton-transfer steps for example among H_2O_2, oxo, and/or peroxo ligands, as suggested for some vanadium catalysts that may require particular N, O additives as cocatalysts.[4,7c,11]

The above alkane reactions appear to proceed mainly by mechanisms that involve both carbon-centered and oxygencentered radicals (the former upon homolysis of an alkane C–H bond) as very pronounced decreases in product yields occur when the reactions are carried out in the presence of either a carbon-radical trap such as $CBrCl_3$ or TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) (use of the former almost completely suppresses the formation of cyclohexanol and cyclohexanone when used in excess relative to the alkane, whereas the latter leads to around 60 % suppression of activity for a stoichiometric amount in relation to the alkane)[12] or an oxygen-radical trap such as Ph_2NH (activity suppression of ca. 90 % for a stoichiometric amount relative to H_2O_2). BHT (2,6-di-*tert*-butyl-4-methylphenol) has a lower inhibition effect, commonly below 50 %.[12]

Competitive nonradical pathways can probably occur through either 1) electrophilic attack from an oxidized metal (metal-peroxo or metal-oxo) centre to an alkane C–H bond with heterolytic cleavage of this bond to give an organocopper intermediate (R^- abstraction) as proposed[6a,8c,8g] for other metals, or 2) a concerted mechanism involving a direct insertion of an activated electrophilic oxygen atom, for example, a bridging oxygen atom, into an alkane C–H bond or through a pairwise process with C–H addition to two oxygen-atoms, as suggested for biological alkane hydroxylation by pMMO.[1g]

The higher activity of catalysts **2** and **3** might be accounted for by: 1) their lower coordination number (they are five-coordinate, whereas the others are six-coordinate); 2) the presence of a labile ligand (H_2O); 3) the expected higher stability of the multinuclear structures that have relatively close copper atoms supported by various bridging ligands (in the other complexes, only μ-ethoxy-type bridges are involved in the coordination to Cu atoms at a close distance). The last feature (3) agrees with the isolation after the reaction of the tetranuclear catalyst **3**, which maintains its high activity for further catalytic assays. Moreover, it is also consistent with the proposed involvement of three or four Cu atoms in a xylyl hydroxylation reaction in which a (μ-1,1-hydroperoxide) dicopper intermediate is further activated by a second dicopper center that acts as a Lewis acid thus promoting the electrophilic character of the hydroperoxide towards the substrate.[2e,13]

In conclusion, we have found a simple and convenient route for the formation of novel di-, tri-, tetra-, and polynuclear copper triethanolamine complexes, which can be easily prepared in high yields by using cheap, commercially available, and environmentally tolerable reagents. We have also opened up the possibility of applying such copper complexes as highly selective and active catalyst precursors for single-pot alkane oxidation at room temperature with an environmentally friendly oxidant (H_2O_2 that produces only water as by-product) towards the establishment of a powerful copper-based alkane oxidation system, which mimics pMMO and has some advantages over the current industrial synthetic processes for alcohols and ketones.

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[1] a) S. Itoh in *Comprehensive Coordination Chemistry, Vol. 8* (Eds.: J. A. McCleverty, T. J. Meyer, L. Que, W. B. Tolman), 2nd ed., Elsevier, Dordrecht, **2003**, chap. 8.15, pp. 369–393; b) D. H. Lee in *Comprehensive Coordination Chemistry, Vol. 8* (Eds.: J. A. McCleverty, T. J. Meyer, L. Que, W. B. Tolman), 2nd ed., Elsevier, Dordrecht, **2003**, chap. 8.17, pp. 437–457; c) J. J. R. Fraústo da Silva, R. J. P. Williams, *The Biological Chemistry of the Elements*, Oxford University Press, Oxford, **2001**; d) E. I. Solomon, U. M. Sundaram, T. E. Machonkin, *Chem. Rev.* **1996**, *96*, 2563; e) J. P. Klinman, *Chem. Rev.* **1996**, *96*, 2541; f) M. Ayala, E. Torres, *Appl. Catal. A* **2004**, *272*, 1; g) S. J. Elliot, M. Zhu, L. Tso, H.-H. T. Nguyen, J. H.-K. Yip, S. I. Chan, *J. Am. Chem. Soc.* **1997**, *119*, 9949; h) R. L. Lieberman, A. C. Rosenzweig, *Crit. Rev. Biochem. Mol. Biol.* **2004**, *39*, 147; i) R. L. Lieberman, A. C. Rosenzweig, *Nature* **2005**, *434*, 177.

[2] a) P. Gamez, P. G. Aubel, W. L. Driessen, J. Reedijk, *Chem. Soc. Rev.* **2001**, *30*, 376; b) K. D. Karlin, A. D. Zuberbühler in *Bioinorganic Catalysis* (Eds.: J. Reedijk, E. Bouwman), 2nd ed., Dekker, New York, **1999**, pp. 469–534; c) M. C. Mimmi, M. Gullotti, L. Santagostini, G. Battaini, E. Monzani, R. Pagliarin, G. Zoppellaro, L. Casella, *Dalton Trans.* **2004**, 2192; d) L. M. Mirica, X. Ottenwaelder, T. D. P. Stack, *Chem. Rev.* **2004**, *104*, 1013; e) E. A. Lewis, W. B. Tolman, *Chem. Rev.* **2004**, *104*, 1047.

[3] a) G. B. Shul'pin, J. Gradinaru, Y. N. Kozlov, *Org. Biomol. Chem.* **2003**, *1*, 3611; b) R. S. da Cruz, J. M. D. E. Silva, U. Arnold, M. S. Sercheli, U. Schuchardt, *J. Braz. Chem. Soc.* **2002**, *13*, 170; c) T. Ohta, T. Tachiyama, K. Yoshizawa, T. Yamabe, T. Uchida, T. Kitagawa, *Inorg. Chem.* **2000**, *39*, 4358; d) S. Velusamy, T. Punniyamurthy, *Tetrahedron Lett.* **2003**, *44*, 8955; e) U. Schuchardt, R. Pereira, M. Rufo, *J. Mol. Catal. A* **1998**, *135*, 257; f) R. Raja, P. Ratnasamy, *Catal. Lett.* **1997**, *48*, 1; g) D. H. R. Barton, S. D. Beviere, W. Chavasiri, E. Csuhai, D. Doller, *Tetrahedron* **1992**, *48*, 2895; h) T. Okuno, S. Ohba, Y. Nishida, *Polyhedron* **1997**, *16*, 3765; i) N. Komiya, T. Naota, Y. Oda, S. I. Murahashi, *J. Mol. Catal. A.* **1997**, *117*, 21.

[4] a) P. M. Reis, J. A. L. Silva, A. F. Palavra, J. J. R. F. da Silva, T. Kitamura, Y. Fujiwara, A. J. L. Pombeiro, *Angew. Chem.* **2003**, *115*, 845; *Angew. Chem. Int. Ed.* **2003**, *42*, 821; b) P. M. Reis, J. A. L. Silva, J. J. R. F. da Silva, A. J. L. Pombeiro, *Chem. Commun.* **2000**, 1845.

[5] a) A. Singh, R. C. Mehrotra, *Coord. Chem. Rev.* **2004**, *248*, 101; b) J. G. Verkade, *Acc. Chem. Res.* **1993**, *26*, 483; c) R. W. Saalfrank, I. Bernt, F. Hampel, *Angew. Chem.* **2001**, *113*, 1745; *Angew. Chem. Int. Ed.* **2001**, *40*, 1700; d) W. Plass, A. Pohlmann, J. Rautengarten, *Angew. Chem.* **2001**, *113*, 4333; *Angew. Chem. Int. Ed.* **2001**, *40*, 4207; e) F. T. Chen, D. F. Li, S. Gao, X. Y. Wang, Y. Z. Li, L. M. Zheng, W. X. Tang, *Dalton Trans.* **2003**, 3283; f) R. W. Saalfrank, I. Bernt, F. Hampel, A. Scheurer, T. Nakajima, S. H. Z. Huma, F. W. Heinemann, M. Schmidtmann, A. Müller, *Polyhedron* **2003**, *22*, 2985; g) V. Tudor, G. Marin, V. Kravtsov, Yu. A. Simonov, J. Lipkowski, M. Brezeanu, M. Andruh, *Inorg. Chim. Acta* **2003**, *353*, 35; h) V. G. Makhankova, O. Yu. Vassilyeva, V. N. Kokozay, B. W. Skelton, J. Reedijk, G. A. Van Albada, L. Sorace, D. Gatteschi, *New J. Chem.* **2001**, *25*, 685; i) K. H. Whitmire, J. C. Hutchison, A. Gardberg, C. Edwards, *Inorg. Chim. Acta* **1999**, *294*, 153; j) H. Oshio, Y. Saito, T. Ito, *Angew. Chem.* **1997**, *109*, 2689; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2673.

[6] a) A. E. Shilov, G. B. Shul'pin, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluwer, Dordrecht, **2000**; b) R. Whyman, *Applied Organometallic Chemistry and Catalysis*, Oxford University Press, Oxford, **2001**.

[7] For reviews see: a) U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R. S. da Cruz, M. C. Guerreiro, D. Mandelli, E. V. Spinace, E. L. Pires, *Appl. Catal. A* **2001**, *211*, 1; b) J. M. Bregeault, *Dalton Trans.* **2003**, 3289; c) G. B. Shul'pin, *J. Mol. Catal. A* **2002**, *189*, 39; d) G. B. Shul'pin, G. V. Nizova, Y. N. Kozlov, I. G. Pechenkina, *New J. Chem.* **2002**, *26*, 1238; e) U. Schuchardt, W. A. Carvalho, E. V. Spinace, *Synlett* **1993**, *10*, 713.

[8] a) G. B. Shul'pin, G. V. Nizova, Y. N. Kozlov, L. G. Cuervo, G. Süss-Fink, *Adv. Synth. Catal.* **2004**, *346*, 317; b) I. Bar-Nahum, A. M. Khenkin, R. Neumann, *J. Am. Chem. Soc.* **2004**, *126*, 10236; c) R. A. Periana, G. Bhalla, W. J. Tenn, K. J. H. Young, X. Y. Liu, O. Mironov, C. J. Jones, V. R. Ziatdinov, *J. Mol. Catal. A* **2004**, *220*, 7; d) Q. Zhang, D. He, Q. Zhu, *J. Nat. Gas Chem.* **2003**, *12*, 81; e) M. Muehlhofer, T. Strassner, W. H. Herrmann, *Angew. Chem.* **2002**, *114*, 1817; *Angew. Chem. Int. Ed.* **2002**, *41*, 1745; f) D. Wolf, *Angew. Chem.* **1998**, *110*, 3545; *Angew. Chem. Int. Ed.* **1998**, *37*, 3351; g) C. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* **2001**, *34*, 633.

[9] a) A. O. Kuzmin, G. L. Elizarova, L. G. Matvienko, E. R. Salivanova, V. N. Parmon, *Mendeleev Commun.* **1998**, 210; b) E. D. Park, Y.-S. Hwang, C. W. Lee, J. S. Lee, *Appl. Catal. A* **2003**, *247*, 269.

[10] X-ray crystal-structure analyses: **1**: $C_{13}H_{21}CuNO_6$, $M_r = 350.85$, monoclinic, $P21/n{:}b2$, crystal size $0.66 \times 0.43 \times 0.25$ mm^3, $a = 7.556(5)$, $b = 26.922(5)$, $c = 8.014(5)$ Å, $\alpha = 90.046(5)$, $\beta = 111.070(5)$, $\gamma = 89.980(5)°$, $V = 1521.2(14)$ Å^3, $T = 293(2)$ K, $Z = 4$, $\rho_{calcd} = 1.523$ Mg m^{-3}, $\mu = 1.461$ mm^{-1}, $F(000) = 724$, max/min transm. = 0.7115/0.4456, $\Theta = 1.51$–$25.08°$; 5318 reflections observed, 2680 unique ($R_{int} = 0.1244$); $R1 = 0.0583$, $wR2 = 0.1467$ ($I > 2\sigma(I)$), $R1 = 0.0908$, $wR2 = 0.1663$ (all data), largest difference peak and hole: 1.137/−0.803 e Å^{-3}. **2**: $C_{52}H_{90}Cu_6N_4O_{34}$, $M_r = 1696.52$, monoclinic, $C2/c$, crystal size $0.14 \times 0.09 \times 0.05$ mm^3, $a = 20.1793(4)$, $b = 11.2602(2)$, $c = 16.1429(2)$ Å, $\alpha = \gamma = 90$, $\beta = 116.5880(10)°$, $V = 3280.13(10)$ Å^3, $T = 100(2)$ K, $Z = 2$, $\rho_{calcd} = 1.718$ Mg m^{-3}, $\mu = 2.007$ mm^{-1}, $F(000) = 1752$, max/min transm. = 0.34702/0.30557, $\Theta = 3.11$–$26.36°$, 20924 reflections observed, 3341 unique ($R_{int} = 0.0383$); $R1 = 0.0338$, $wR2 = 0.0895$ ($I > 2\sigma(I)$), $R1 = 0.0380$, $wR2 = 0.0927$ (all data), largest difference peak and hole: 2.021/−0.869 e Å^{-3}. **3**: $C_{24}H_{52}B_6Cu_4F_8N_4O_{17}$, $M_r = 1139.72$, triclinic, $\bar{P}1$, crystal size $0.32 \times 0.27 \times 0.25$ mm^3, $a = 12.1081(3)$, $b = 18.4078(4)$, $c = 18.6603(5)$ Å, $\alpha = 98.928(2)$, $\beta = 100.5170(10)$, $\gamma = 101.041(2)°$, $V = 3934.82(17)$ Å^3, $T = 100(2)$ K, $Z = 4$, $\rho_{calcd} = 1.924$ Mg m^{-3}, $\mu = 2.248$ mm^{-1}, $F(000) = 2312$, max/min transm. = 0.6001/0.5305, $\Theta = 3.06$–$26.00°$; 47993 reflections observed, 15132 unique ($R_{int} = 0.0384$); $R1 = 0.0495$, $wR2 = 0.1203$ ($I > 2\sigma(I)$), $R1 = 0.0726$, $wR2 = 0.1376$ (all data), largest difference peak and hole: 1.929/−0.761 e Å^{-3}. **4**: $C_{10}H_{18}CuNO_6$ $M_r = 311.79$, triclinic, $\bar{P}1$, crystal size $0.26 \times 0.18 \times 0.11$ mm^3, $a = 7.4983(8)$, $b = 7.9730(6)$, $c = 10.8652(13)$ Å, $\alpha = 84.071(8)$, $\beta = 89.669(8)$, $\gamma = 70.382(6)°$, $V = 608.30(11)$ Å^3, $T = 100(2)$ K, $Z = 2$, $\rho_{calcd} = 1.702$ Mg m^{-3}, $\mu = 1.815$ mm^{-1}, $F(000) = 324$, max/min transm. = 0.8212/0.6448, $\Theta = 2.73$–$27.50°$; 6244 reflections observed, 2748 unique ($R_{int} = 0.0174$); $R1 = 0.0251$, $wR2 = 0.0576$ [$I > 2\sigma(I)$], $R1 = 0.0315$, $wR2 = 0.0601$ (all data), largest difference peak and hole: 0.468/−0.354 e Å^{-3}. CCDC 259925 (**1**), 259926 (**2**), 259927 (**3**), and 259928 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] G. B. Shul'pin, Y. N. Kozlov, G. V. Nizova, G. Süss-Fink, S. Stanislas, A. Kitaygorodskiy, V. S. Kulikova, *J. Chem. Soc. Perkin Trans. 2* **2001**, 1351.

[12] L. M. Slaughter, J. P. Collman, T. A. Eberspacher, J. I. Brauman, *Inorg. Chem.* **2004**, *43*, 5198.

[13] R. W. Cruse, S. Kaderli, C. J. Meyer, A. D. Zuberbühler, K. D. Karlin, *J. Am. Chem. Soc.* **1988**, *110*, 5020.