Inorganic Chemistry
ARTICLE
pubs.acs.org/IC

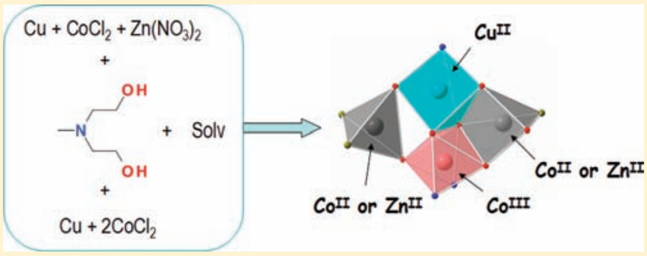
Heterometallic Cu/Co and Cu/Co/Zn Complexes Bearing Rare Asymmetric Tetranuclear Cores: Synthesis, Structures, and Magnetic and Catalytic Properties Toward the Peroxidative Oxidation of Cycloalkanes

Dmytro S. Nesterov,[†] Volodymyr N. Kokozay,[‡] Julia Jezierska,[§] Oleksiy V. Pavlyuk,[∥] Roman Boča,[⊥,#] and Armando J. L. Pombeiro*[,†]

[†]Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, TU Lisbon, Av. Rovisco Pais, 1049-001, Lisbon, Portugal
[‡]Department of Inorganic Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrs'ka st. 64, Kyiv 01601, Ukraine
[§]Faculty of Chemistry, University of Wroclaw, 14 Joliot-Curie Str., 50-383, Wroclaw, Poland
[∥]Department of Inorganic Chemistry, Franko National University, Kyrylla & Mefodiya str. 6, 79005, Lviv, Ukraine
[⊥]Institute of Inorganic Chemistry, FCHPT, Slovak University of Technology, Radlinskeho 9, 812 37 Bratislava, Slovakia
[#]Department of Chemistry, FPV, University of SS Cyril and Methodius, Trnava, Slovakia

Supporting Information

ABSTRACT: The three novel heterometallic complexes $[CuCo^{III}Co^{II}_2(MeDea)_3Cl_3(CH_3OH)_{0.55}(H_2O)_{0.45}](H_2O)_{0.45}$ (**1**), $[CuCo^{III}Zn_2(MeDea)_3Cl_3(CH_3OH)_{0.74}(H_2O)_{0.26}](H_2O)_{0.26}$ (**2**), and $[CuCo^{III}Zn_2(MeDea)_3Cl_3(DMF)]$ (**3**) have been prepared using a one-pot reaction of copper powder with cobalt chloride (**1**) and zinc nitrate (**2**, **3**) in a methanol (**1**, **2**) or dimethylformamide (**3**) solution of N-methyldiethanolamine. A search of the Cambridge Structural Database shows that the tetranuclear asymmetric cores $M_4(\mu_3\text{-}X)(\mu\text{-}X)_5$ of **1**−**3** represent an extremely rare case of M_4X_6 arrays. The magnetic investigations of **1** disclose antiferromagnetic coupling in a $Co^{II}-Cu^{II}-Co^{II}$ exchange fragment with $J_{Co-Cu}/hc = -4.76\ cm^{-1}$, $J_{Co-Co}/hc = -2.76\ cm^{-1}$, and $D_{Co}/hc = +34.3\ cm^{-1}$. Compounds **1**−**3** act as precursors for the mild peroxidative oxidation of cyclohexane to cyclohexanol and cyclohexanone with overall yields up to 23%. The synthetic and structural features as well as the thermogravimetric behavior and electrospray ionization mass spectrometry data are discussed.



INTRODUCTION

The first reports on the synthesis of heterotrimetallic coordination compounds (Cu/Ag/M; M = Mo, W) of a noncarbonyl type were published in 1992 by Xintao et al.[1] Since then, a large body of work has been devoted to related systems.[2] First, the search for heterotrimetallic complexes was stimulated by the general interest in combining three different metal centers within one assembly, since even the synthesis of heterobimetallic complexes often represents a nontrivial task. Second, it was found that such compounds are potential novel magnetic materials[2c,f,3] and "single-source precursors" for the synthesis of mixed-metal oxides.[4] However, another usual application field for coordination compounds—catalysis—is still poorly explored, not only for heterotrimetallic complexes but even for heterobimetallic ones.[5]

In particular, transition metal complexes play a crucial role in the catalytic activation of C−H bonds of hydrocarbons.[6] We have demonstrated that mono- and polynuclear copper,[7] vanadium,[7c,8] and iron[7c,9] complexes with amino alcohol or carboxylate ligands can act as remarkably active and selective catalysts or catalytic precursors for peroxidative oxidation of alkanes under mild conditions. Further, we reported the outstanding activity of the heterotrimetallic coordination compound $[Cu^{II}Co^{III}Fe^{III}(Dea)_3(NCS)_2(CH_3OH)]_2\cdot 3.2H_2O$ (H_2Dea = diethanolamine)[10] in the mild peroxidative oxidation of cyclohexane and cyclopentane (as far as we are aware of, this is the only report of a heterotrimetallic complex as a homogeneous catalyst). The combination of a few different metals within one molecule of catalyst resulted in a synergic effect,[10] and thus the investigation of catalytic systems based on heterobi- and heterotrimetallic precursors toward the mild functionalization of alkanes deserve to be further explored and represent a main objective of the present work.

The rational design of heterometallic species (and especially heterotrimetallic ones) is still one of the major challenges for inorganic chemists and exploratory synthesis. A popular multistep approach uses a reaction between a preformed metal-containing

Received: December 21, 2010
Published: April 20, 2011

ligand and a second type of metal ion via free coordination donors.[2b,c] However, this approach is hardly suitable for the construction of high-nuclearity heterobimetallic assemblies in which different metal atoms are linked by bridging atoms instead of bridging groups. The synthesis of heterotrimetallic complexes of this type by a building block or metalloligand approach becomes quite a complicated task. The solution to this problem lies in the utilization of a spontaneous self-assembly strategy, which represents a thermodynamically based self-assembly of free metal ions with mainly simple, flexible ligands that impose little or no geometrical restrictions.[3c,10,11]

We recently described a series of heterotrimetallic Cu/Co/M (where M = Ni, Zn, Cd, Fe)[10,12] complexes, which were prepared in one-pot reactions of copper powder with metal salts in the presence of an amino alcohol, according to the following systems (X = Cl, Br, NCS, OAc; HL = amino alcohol):

$$\mathrm{Cu^0 + CoX^{I}_2 + MX^{II}_2 + HL + solvent\ (in\ air)}$$

$$\mathrm{M^0} + n\mathrm{ROH} + n/4\mathrm{O_2} \rightarrow \mathrm{M}^{n+} + n\mathrm{RO^-} + n/2\mathrm{H_2O}$$

This synthetic strategy, the direct synthesis, is based on self-assembly of the building blocks, generated *in situ*, into crystalline materials.[13] Also, the lack of anions provides specific conditions and favors the formation of polynuclear aggregates.

In pursuit of the investigation of the following system:

$$\mathrm{Cu^0 + CoCl_2 + MX_2 + H_2MeDea + solvent}$$

(where M = Ni, Zn; X = Cl, NO_3, OAc; solvent = CH_3OH, CH_3CN, DMF, DMSO; H_2MeDea = N-methyldiethanolamine), we obtained a series of heterobi- (Cu/Co) and heterotrimetallic (Cu/Co/Zn) coordination compounds, $[CuCo_3(MeDea)_3Cl_3(CH_3OH)_{0.55}(H_2O)_{0.45}](H_2O)_{0.45}$ (**1**), $[CuCoZn_2(MeDea)_3Cl_3(CH_3OH)_{0.74}(H_2O)_{0.26}](H_2O)_{0.26}$ (**2**), and $[CuCoZn_2(MeDea)_3Cl_3(DMF)]$ (**3**), whose synthetic and structural features, as well as magnetic, thermogravimetric, and catalytic properties, are reported herein.

EXPERIMENTAL SECTION

All chemicals were of reagent grade and used as received. All synthetic experiments were carried out in the air. Elemental analyses for C, H, N, and metals (atomic absorption spectroscopy) were performed by the Microanalytical Service of the Instituto Superior Técnico. The analysis for metals for complexes **2** and **3** was provided by the Chemical Department of National Taras Shevchenko University. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets.

Synthesis of $[CuCo_3(MeDea)_3Cl_3(CH_3OH)_{0.55}(H_2O)_{0.45}](H_2O)_{0.45}$ (1). Copper powder (0.16 g, 2.5 mmol), $CoCl_2 \cdot 6H_2O$ (1.20 g, 5 mmol), CH_3OH (15 mL), and N-methyldiethanolamine (1.0 mL, 8.7 mmol) were heated to 50–60° and stirred magnetically until the total dissolution of copper was observed (1 h). The resulting solution was filtered. Dark green crystals suitable for X-ray analysis grew in one week after the successive addition of diethyl ether. They were filtered off, washed with CH_3OH, and finally dried in vacuo at room temperature. Yield: 0.45 g, 25% (per copper). $C_{15.55}H_{37}Cl_3Co_3CuN_3O_{7.45}$ (731.94), calcd: C, 25.52; H, 5.11; Co 24.15, Cu 8.68, N 5.74. Found: C, 25.6; H, 5.2; Co 23.0, Cu 8.6, N, 5.5.

Synthesis of $[CuCoZn_2(MeDea)_3Cl_3(CH_3OH)_{0.74}(H_2O)_{0.26}](H_2O)_{0.26}$ (2). Copper powder (0.16 g, 2.5 mmol), $CoCl_2 \cdot 6H_2O$ (0.6 g, 2.5 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.74 g, 2.5 mmol), CH_3OH (20 mL), and N-methyldiethanolamine (1.0 mL, 8.7 mmol) were heated to 50–60° and stirred magnetically until the total dissolution of copper was observed (1 h). The resulting solution was filtered. Dark green crystals suitable for X-ray analysis grew in one week after the successive addition of diethyl ether. They were filtered off, washed with CH_3OH, and finally dried in vacuo at room temperature. Yield: 0.41 g, 22% (per copper). $C_{15.74}H_{37}Cl_3CoCuN_3O_{7.26}Zn_2$ (744.07), calcd: C, 25.41; H, 5.02; Co, 7.92; Cu, 8.54; N, 5.65; Zn, 17.58. Found: C, 25.4; H, 4.9; Co, 7.9; Cu, 9.1; N, 5.6; Zn 17.1.

Synthesis of $[CuCoZn_2(MeDea)_3Cl_3(DMF)]$ (3). Copper powder (0.16 g, 2.5 mmol), $CoCl_2 \cdot 6H_2O$ (0.6 g, 2.5 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.74 g, 2.5 mmol), DMF (20 mL), and N-methyldiethanolamine (1.0 mL, 8.7 mmol) were heated to 50–60° and stirred magnetically until the total dissolution of copper was observed (1 h). The resulting solution was filtered. Dark green crystals suitable for X-ray analysis grew in one week after the successive addition of diethyl ether. They were filtered off, washed with *i*PrOH, and finally dried in vacuo at room temperature. Yield: 0.81 g, 41% (per copper). $C_{18}H_{40}Cl_3CoCuN_4O_7Zn_2$ (784.10), calcd: C, 27.57; H, 5.15; Co, 7.52; Cu, 8.10; N, 7.15; Zn, 16.68. Found: C, 27.3; H, 5.0; Co 8.0; Cu, 7.8; N, 6.9; Zn, 16.5.

Crystallography. The X-ray diffraction data for **1** and **2** were collected on an Xcalibur PX kappa-geometry diffractometer with graphite-monochromated Cu Kα radiation. An analytical absorption correction was applied using the CrysAlis RED software. Data collection and reduction were made using the CrysAlis CCD and CrysAlis RED software.[14]

The diffraction data for **3** were collected using a Bruker AXS KAPPA APEX II diffractometer with graphite monochromated Mo Kα radiation. Cell parameters were retrieved using the Bruker SMART software and refined using Bruker SAINT on all of the observed reflections. Absorption corrections were applied using SADABS.[15] All of the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with the program SHELX-97.[16] In general, the non-hydrogen atoms were refined anisotropically. The C2, C4, and C5 atoms of one amino alcohol ligand in **1**–**3** were modeled as being disordered, the populations of the two conformations refined to 0.554(7), 0.741(5), and 0.822(7) and 0.446(7), 0.259(5), and 0.178(7) for **1**, **2**, and **3**, respectively. Substitutional disorder of the methanol molecule in **1** and **2** was found with an exchange of the methanol molecule with two water molecules, the site occupancies being refined to 0.554(7) and 0.446(7) (for **1**) and 0.741(5) and 0.259(5) (for **2**). All of the hydrogen atoms were placed at calculated positions and refined using a riding model with $U_{\text{iso}} = nU_{\text{eq}}$ ($n = 1.2$ for H atoms of methylene groups and the formamide group in DMF and $n = 1.5$ for other H atoms). Data collection and processing parameters for all compounds are summarized in Table 1.

Magnetic Measurements. Magnetic susceptibility data of a powdered sample of **1** were measured with a SQUID magnetometer (Quantum Design MPMSXL-5) over the temperature range 1.8–300 K at a magnetic induction of 0.5 T. Corrections for the sample holders were applied. Diamagnetic corrections for the molecules were determined from Pascal's constants.[17]

Thermogravimetric Measurements. A Perkin-Elmer STA-6000 model thermogravimetric analyzer was used for determination of the thermal stabilities of complexes **1**–**3**. Samples weighing 5–30 mg were heated under a dinitrogen flow of 30 mL min^{-1} from 30 to 1000 °C at a heating rate of 1–50 °C min^{-1}.

Electrospray-Ionization Mass Spectrometry. ESI-MS(+) spectra were run on a 500-MS LC Ion Trap instrument (Varian Inc., Alto Palo, CA, USA) equipped with an electrospray (ESI) ion source, using ca. 10^{-3} M solutions of **1**–**3** in water or methanol.

Catalytic Activity Studies. The reaction mixtures were prepared as follows: to 0.6–17 μmol (typically 10.0 μmol) of catalyst contained in the reaction flask were added 4.5 mL of MeCN, 0.0–0.6 mmol (typically 0.2 mmol) of HNO_3, 1.0 mmol of cycloalkane, and 4.00–20.0 mmol (typically 5.00 mmol) of H_2O_2 (30% in H_2O), in this order. The

Table 1. Selected Crystallographic Data for Complexes 1−3

	1	2	3
chemical formula	$C_{15.55}H_{37}Cl_3Co_3CuN_3O_{7.45}$	$C_{15.74}H_{37}Cl_3CoCuN_3O_{7.26}Zn_2$	$C_{18}H_{40}Cl_3CoCuN_4O_7Zn_2$
fw	731.94	744.07	784.10
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	16.636(6)	16.588(6)	10.2011(10)
b, Å	8.529(3)	8.499(3)	10.6830(10)
c, Å	18.603(6)	18.705(6)	13.8613(13)
α, deg	90.00	90.00	78.908(4)
β, deg	95.68(5)	95.34(4)	72.683(4)
γ, deg	90.00	90.00	84.576(3)
V, Å^3	2626.6(16)	2625.6(16)	1414.1(2)
T, K	100(2)	100(2)	150(2)
Z	4	4	2
ρ_{calcd}, g cm^{-3}	1.851	1.882	1.842
μ, cm^{-1}	18.670	11.020	3.321
F(000)	1488.0	1510	798
GoF	0.948	1.007	1.025
θ_{min}, θ_{max}, deg	4.78/76.68	4.75/76.57	1.94/27.74
reflns collected	21993	24368	28224
reflns unique	4831	5124	6596
reflns obsd [$I > 2\sigma(I)$]	2313	2843	5132
restrains/params	17/297	17/295	10/357
R_{int}	0.0958	0.0701	0.0408
R_1	0.0489	0.0417	0.0388
wR (all data)	0.0589	0.0628	0.0971
largest peak/hole, e Å^{-3}	0.81/−0.61	0.96/−0.75	1.493/−0.843

reaction mixture was stirred for 5 h at room temperature and atmospheric pressure; then 90 μL of cycloheptanone (as internal standard), 8.5 mL of diethyl ether (to extract the substrate and the products from the reaction mixture), and 1.0 g of PPh_3 (to reduce the cyclohexyl hydroperoxide, if formed, to cyclohexanol)[18] were added. The resulting mixture was stirred for 15 min, and then a sample taken from the organic phase was analyzed by GC using a FISONS Instruments GC 8000 series gas chromatograph with a DB WAX fused silica capillary column (P/N 123−7032) and the Jasco-Borwin v.1.50 software. The GC analyses of the aqueous phase showed the presence of only traces (less than 0.05%) of oxidation products. In the experiments with radical traps, the appropriate compounds, e.g., 2,6-di-*tert*-butyl-4-methylphenol (BHT), $CBrCl_3$, or Ph_2NH (2.5 mmol) were also added to the reaction mixture. Blank experiments were performed with different amounts of H_2O_2 and confirmed that no alkane oxidation products (or only traces, below 0.3%) were obtained in the absence of the metal catalyst.

RESULTS AND DISCUSSION

All of the reactions were initiated and brought to completion by heating and stirring a mixture of copper powder with the appropriate metal salts and N-methyldiethanolamine (H_2MeDea) in a CH_3OH or DMF solvent until the total dissolution of copper was observed (approximately 1 h). The compound $[CuCo_3(MeDea)_3Cl_3(CH_3OH)_{0.74}(H_2O)_{0.26}]$ (**1**) was initially synthesized during the search for heterotrimetallic Cu/Co/Ni complexes in the reaction system:

$$Cu^0 + CoX_2 + NiY_2 + H_2MeDea + \text{solvent (in air)}$$

(where X, Y = Hal, NCS, OAc, NO_3; solvent = CH_3OH, DMSO, DMF). The desired Cu/Co/Ni compound was not obtained, and the usual product was the blue powder recognized as $[Ni(H_2MeDea)_2]Cl_2$,[19] while the heterobimetallic complex **1** was the only heterometallic product to be observed. The original system for the preparation of **1** was as follows:

$$Cu^0 + CoCl_2 + NiCl_2 + 3H_2MeDea + CH_3OH \text{ (in air)}$$

Since it was found that an excess of the amino alcohol (ligand/sum of the metals = 2:1 molar ratio) leads to the formation of the above-mentioned homometallic nickel complex, the 1:1 ratio was used for all subsequent related tests. Although the elemental analysis suggested the absence of nickel in the obtained sample of **1**, the presence of some small mixing (Cu/Ni or Co/Ni) at the atomic level could not be ruled out. Thus, the next step was to reproduce complex **1** without the nickel salt in the initial system. The simple elimination of $NiCl_2$ gave a brown powder, but its composition was not identified. Then, the amount of $CoCl_2$ was increased, and finally the application of Cu/Co/H_2MeDea in a 1:2:3 ratio resulted in the desired heterobimetallic compound **1** in a satisfactory yield for this type of synthesis (ca. 25%). The formation of **1** can be described by the following reaction scheme (the replacement of some methanol positions by water in the crystal structure is not considered):

$$\begin{gathered}Cu^0 + 3CoCl_2 + 6H_2MeDea + CH_3OH + 3/4O_2 \rightarrow \\ [Cu^{II}CO^{III}CO^{II}{}_2(MeDea)_3Cl_3(CH_3OH)] \\ + 3H_2MeDea\cdot HCl + 3/2H_2O\end{gathered}$$

One should notice that the system with the 1:3 Cu/Co ratio gave complex **1** in a higher yield (*ca.* 35%). However, under these conditions, the compound starts to precipitate during the synthesis as a blue noncrystalline powder, and although the elemental analysis suggested its purity, the synthetic route with the 1:2:3 Cu/Co/H_2MeDea ratio (as described in the Experimental Section) is preferable since it leads to a crystalline solid. This avoids contaminations and reduces the possibility of metals scrambling within the sites. Although the reaction scheme for the synthesis of **1** requires a metal-to-ligand 4:6 M/H_2MeDea ratio, the increase of the ligand amount above the mentioned 4:3 M/H_2MeDea ratio did not lead to better yield and, moreover, fully prevented the formation of complex **1**. A possible explanation is that the excess of the ligand converts all the cobalt present in the reaction system to the very stable complex anion *cis*,*fac*-$[\mathrm{Co^{III}(MeDea)_2}]^-$ (see below), while the structure of **1** requires at least two cobalt equivalents to be in the Co(II) oxidation state.

We next investigated the reaction system toward the preparation of Cu/Co/Zn heterotrimetallic coordination compounds (X and Y symbols have the same meanings):

$$\mathrm{Cu^0 + CoX_2 + ZnY_2 + H_2MeDea + solvent\ (in\ air)}$$

The application of cobalt chloride with zinc nitrate or acetate in methanol or DMF resulted in the heterotrimetallic complexes $[\mathrm{CuCoZn_2(MeDea)_3Cl_3(CH_3OH)_{0.74}(H_2O)_{0.26}](H_2O)_{0.26}}$ (**2**) and $[\mathrm{CuCoZn_2(MeDea)_3Cl_3(DMF)}]$ (**3**). Although both compounds do not contain nitrate or acetate, all attempts to reproduce their formation using a chloride-only reaction system have failed. Presumably, some nitrate (or acetate) species generated in solution have a significant influence on the complex formation and crystal growth. The general reaction for the syntheses of **2** and **3** can be written as follows:

$$\mathrm{Cu^0 + CoX_2 + 2ZnCl_2 + 6H_2MeDea + solvent + 3/4O_2 \longrightarrow}$$
$$\mathrm{[Cu^{II}Co^{III}Zn_2(MeDea)_3Cl_3(Solv)] + H_2MeDea\cdot HCl}$$
$$\mathrm{+\ 2H_2MeDea\cdot HX + 3/2H_2O}$$

Although this reaction stoichiometry could suggest the 1:1:2 Cu/Co/Zn best initial ratio, the experimental results pointed to a 1:1:1 Cu/Co/Zn system as the most appropriate one (in contrast to the 1:1:2 Cu/Co/Zn ratio observed in **2** and **3**). For other ratios, a blue powder was the common product, but its composition was not clear. Probably, the use of the stoichiometry ratio could lead to immediate formation of the heterotrimetallic coordination compound with subsequent precipitation during the synthesis. A high number of components in the reaction system always result, at a first stage, in a combinatorial library with a number of components,[11d] and if the thermodynamic equilibrium is not achieved (as in the case of fast precipitation), the final compound could be contaminated or not formed at all.

The IR spectroscopic investigations of the above heterometallic compounds in the 4000−400 cm^{-1} range showed all of the characteristic ligand peaks. The presence of hydroxo groups and solvents (water, methanol) is clearly observed in the spectra in the region of 3000−3500 cm^{-1}. The broad absorption bands at 3500 cm^{-1} in the spectra of **1** and **2** can be assigned either to water or methanol molecules since these peaks are absent in the IR spectrum of **3**. The broad δ(HOH) absorptions of 1625 and 1650 cm^{-1}, assigned to water, can be identified easily for **1** and **2**, respectively, while the strong peak at 1655 cm^{-1} in the case of **3** confirms the presence of coordinated DMF.[20]

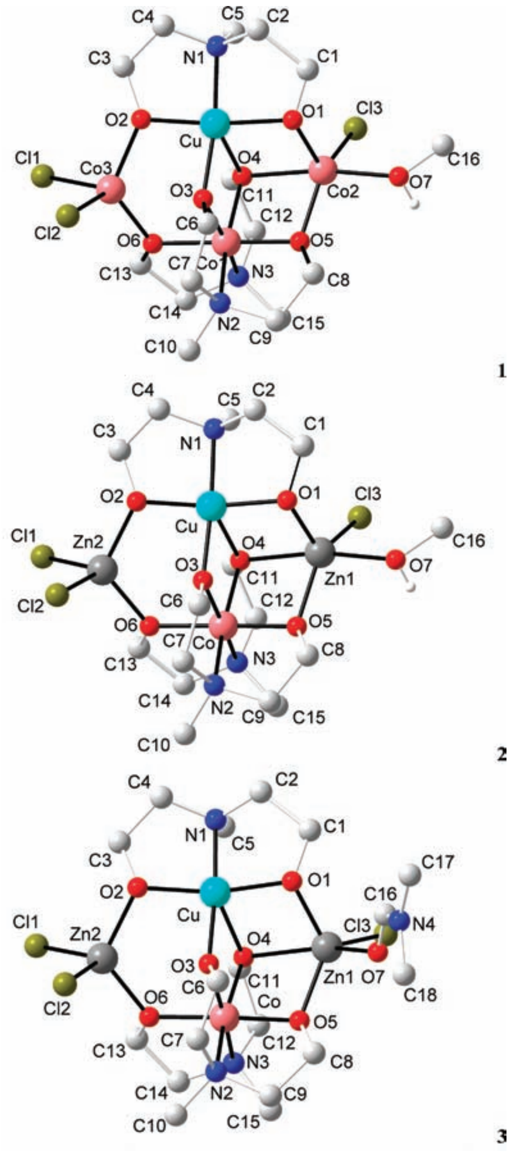


Figure 1. Molecular structures of **1**−**3** with atom numberings (hydrogen atoms from −CH, −CH_2, and −CH_3 groups were omitted for clarity).

Crystal Structures. All of the complexes feature tetranuclear metal cores comprised of four different polyhedra: an octahedron, square pyramid, trigonal bipyramid, and tetrahedron (Figures 1 and 2). The metal in the octahedral environment was easily identified as cobalt since such a *cis*,*fac*-$[\mathrm{Co^{III}(Dea)_2}]^-$ block is typical for the ligands based on the diethanolamine fragment.[10,12c−12e,21] The square pyramidal polyhedron was assigned to copper, with a typically elongated axial bond length varying from 2.307(2) to 2.339(4) Å. The other metal positions having distorted trigonal bipyramidal and almost regular tetrahedral coordination environments were assigned to cobalt (**1**) or zinc (**2** and **3**) in accordance with the elemental analysis data. The overall geometrical parameters of the molecules of **1**−**3** are very close, with the main difference arising from the coordinated solvent molecules (Table 1 and Tables S1−S3 of the Supporting Information).

Intermolecular association in the lattices of **1** and **2** (which are isostructural) occurs through hydrogen bonding of the O—H···O and O—H···Cl types involving uncoordinated water molecules (Table S4, Supporting Information). Considering only the primed component of the disordered solvents (methanol molecule coordinated to the cobalt or zinc atom for **1** or **2**, respectively), one can select 1D chains along the *c* axis (Figure S1, Supporting Information), while the water molecules (unprimed component) not only form analogous chains (Figure S2, Supporting Information) but also bridge the one-dimensional chains into the 2D ladder-type sheets lying in the *bc* plane (Figure S3, Supporting Information). The molecules of **3** do not exhibit any considerable intermolecular hydrogen bonding.

The most prominent feature of **1**−**3** is the asymmetric molecular structure type (MST) $M_4(\mu_3\text{-}X)(\mu\text{-}X)_5$ (Figure 3e). This MST belongs to the widespread general tetranuclear M_4X_6 type where the metal centers are bridged in the manner depicted in Figure 3. According to the Cambridge Structural Database (CSD),[22] the most common assembly for this tetranuclear core is of the $M_4(\mu_3\text{-}X)_2(\mu\text{-}X)_4$ type (Figure 3a), first discovered in the structure of titanium methoxide $Ti_4(OMe)_{16}$.[23] This MST can be described as a combination of two incomplete cube arrays fused via a common face. In exceptional cases, the tetranuclear MST core can have "bipyramidal" (*b*) or planar (*c*) geometrical configurations (Figure 3). The complexes of the last group (*c*) are formed preferably with uranium, but a few examples were also found for bismuth and tin. This points to the conclusion that the covalent radius of d-metals is not sufficiently large for the formation of such a structure. The MST $M_4(\mu\text{-}X)_6$ (Figure 3d), which does not contain μ_3-X bridging atoms, is less common than *a*, but nevertheless the search over the CSD revealed more than 100 hits. The association of the above MSTs into polymeric structures is uncommon. The CSD contains only 18 compounds where tetranuclear aggregates M_4X_6 (all of them belonging to type *a*, except one of type *c* and another of *d*) are bridged into a coordination framework.

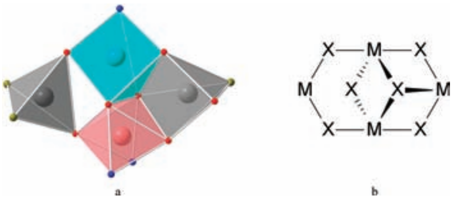


Figure 2. Polyhedral (a) and schematic (b) representations of the asymmetric $M_4(\mu_3\text{-}X)(\mu\text{-}X)_5$ core in **1**−**3**. Color codes (for **2** and **3**; in the case of **1**, the positions of zinc are occupied by cobalt): Cu, cyan; Co, pink; Zn, gray.

It is noteworthy to mention that the MST $M_4(\mu_3\text{-}X)(\mu\text{-}X)_5$ (e) of compounds **1**−**3** is the most rare among all the types (Figure 3). This is also the only asymmetric type (point group C_1), since all of the others concern C_{2h} (a, d), C_{2v} (b), or D_{2h} (c) symmetry point groups. The statistical abundance of the intermetallic torsion angles (Figure 4) within the structures of the real complexes of the *a*, *c*, and *d* types (Figure 3) confirms the high symmetry required by an ideal MST: more than 90% of the complexes reveal completely planar centrosymmetric structures. The respective angles for MST e lie in the range from 153 to 170°. We were able to find only five examples of complexes with such a structure (e), and one of them, $[CuCoZn_2(Dea)_3Cl_3(CH_3OH))]\cdot CH_3OH$ (**4**),[12d] displays a coordination core that is practically identical to those of **1**−**3**. That compound was also obtained by direct synthesis using unsubstituted diethanolamine (H_2Dea) as a ligand.

The prediction of the composition and structure of a self-assembled compound represents a nontrivial task,[24] and moreover, the reversible nature of the coordination reactions accounts for further difficulties. For example, it was noticed by Lehn[11d] that the self-assembly process in a multicomponent reaction

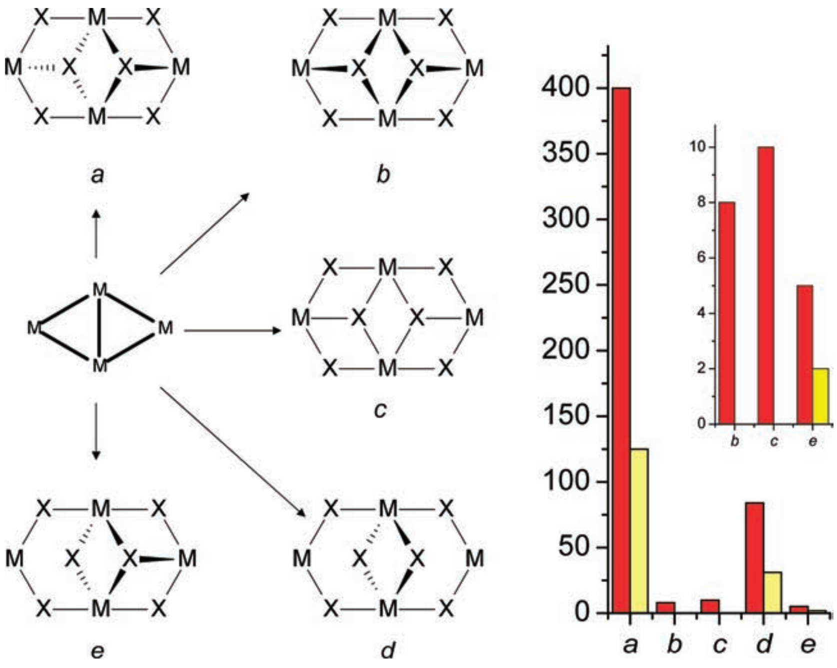


Figure 3. Typical geometries of M_4X_6 molecular structure types (MST). The histogram represents the distribution of the respective MSTs (total quantities are red, the heterometallic parts are yellow). The inset shows the distribution of *b*, *c*, and *e* types in detail. Type *e* is that of complexes **1**−**3**.

system, where a number of metal ions interact with a number of ligands (including anions, solvent, moisture, etc.), always proceeds via a Dynamic Combinatorial Library (DCL) stage. The nature of a dominant component in DCL is defined by a complicated search process directed by kinetic and thermodynamic parameters. The number of these parameters (i.e., number of intercomponents impacts) dramatically increases with the number of initial components (as in the case for **1**−**4**), making the quantitative predictability procedure hardly applicable. However, despite the complexity of the reaction processes for **1**−**4**, the following aspects can be considered.

The presence of the chloride anion is required for the formation of the coordination core of **1**−**4**. For instance, the Cu/Co/Zn reaction systems based on thiocyanates, acetates, or mixtures thereof and diethanolamine gave the heterometallic complexes $[\mathrm{CuCoZn(Dea)_2(H_2Dea)(OAc)_3}]$[12c] and $[\mathrm{Co_2Zn_2(Dea)_2(H_2Dea)_2(NCS)_4}]\cdot\mathrm{DMSO}$[12d] bearing $\mathrm{M_3}(\mu\text{-X})_4$ and centrosymmetric $\mathrm{M_4}(\mu\text{-X})_6$ (Figure 3d) MSTs, respectively. The coordination mode of the diethanolamine-based ligands to the copper and cobalt metal centers in **1**−**4** is as expected, the cobalt pertaining to the *cis,fac*-$[\mathrm{Co^{III}(Dea)_2}]^-$ block and the copper atom bearing one trihapto ligand molecule meridionally coordinated. In all of these complexes (including the above-mentioned CuCoZn, $\mathrm{Co_2Zn_2}$, and some others[13b,25]), the coordination environments of the zinc metal centers are comprised of solvent molecules or anions only, and not of diethanol amine ligands. Thus, the $\{\mathrm{CuCo^{III}(Dea)_3}\}$ moiety seems to have a predominant role in the formation of all of the mentioned Cu/Co/M coordination compounds. Such a hypothesis is confirmed by the observation of Co(II) in **1**, instead of the Zn(II) present in the other complexes (which looks unusual since the coordination chemistries of these two ions differ greatly), and also by other Cu/Co/Ni, Cu/Co/Cd, and Cu/Co/Fe complexes based on the same $\{\mathrm{CuCo^{III}(Dea)_3}\}$ fragment.[10,12c−12e,21a] The coordinated solvent molecule in **1**−**4** (instead of a fourth halide ligand, which is common for tetranuclear $\mathrm{M_4}(\mu_3\text{-X})_n(\mu\text{-X})_m$ assemblies) makes the molecule uncharged, avoiding the need for a charge compensator.

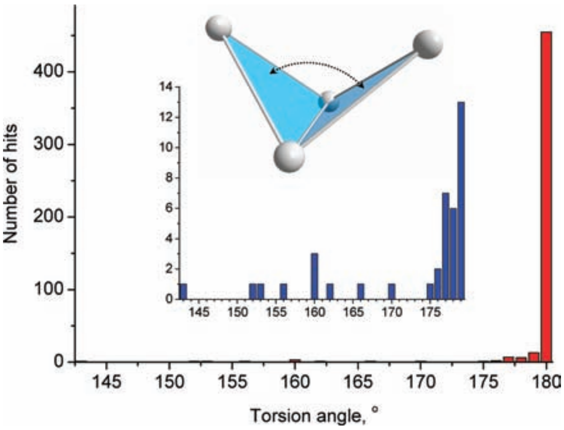


Figure 4. Statistical abundance of the torsion angles formed by the metal centers in the tetranuclear $\mathrm{M_4X_6}$ molecules, within the available CSD structures.

Magnetic Properties of 1. The measured magnetic moment of a sample has been converted to the molar magnetic susceptibility and then to the effective magnetic moment $\mu_{\mathrm{eff}} = 798(\chi'_{\mathrm{mol}}T)^{1/2}\mu_{\mathrm{B}}$ (SI units are employed) where χ'_{mol} stands for the molar magnetic susceptibility corrected to the underlying diamagnetism via Pascal constants. The thermal variation of the effective magnetic moment is displayed in Figure 5. It can be seen that the room-temperature value corresponds to $\mu_{\mathrm{eff}} = 6.5\ \mu_{\mathrm{B}}$; the theoretical value for the uncoupled $\{\mathrm{Co^{II}, Cu^{II}, Co^{II}}\}$ system, as estimated by eq 1, is $\mu_{\mathrm{eff}} = 2.87g_{\mathrm{eff}}$ when uniform g factors are used, implying a reasonable value of $g_{\mathrm{eff}} = 2.26$.

$$\mu_{\mathrm{eff}} = [2g_{\mathrm{Co}}^2 s_{\mathrm{Co}}(s_{\mathrm{Co}}+1) + g_{\mathrm{Cu}}^2 s_{\mathrm{Cu}}(s_{\mathrm{Cu}}+1)]^{1/2}\mu_{\mathrm{B}} \qquad (1)$$

On cooling, the effective magnetic moment decreases gradually, and this is a fingerprint of the dominating antiferromagnetic interaction. For a linear arrangement of the magnetic entities in the complex, the ground state is neither minimum spin ($S_{\mathrm{min}} = 1/2$) nor maximum ($S_{\mathrm{max}} = 7/2$). With a triangular spin model

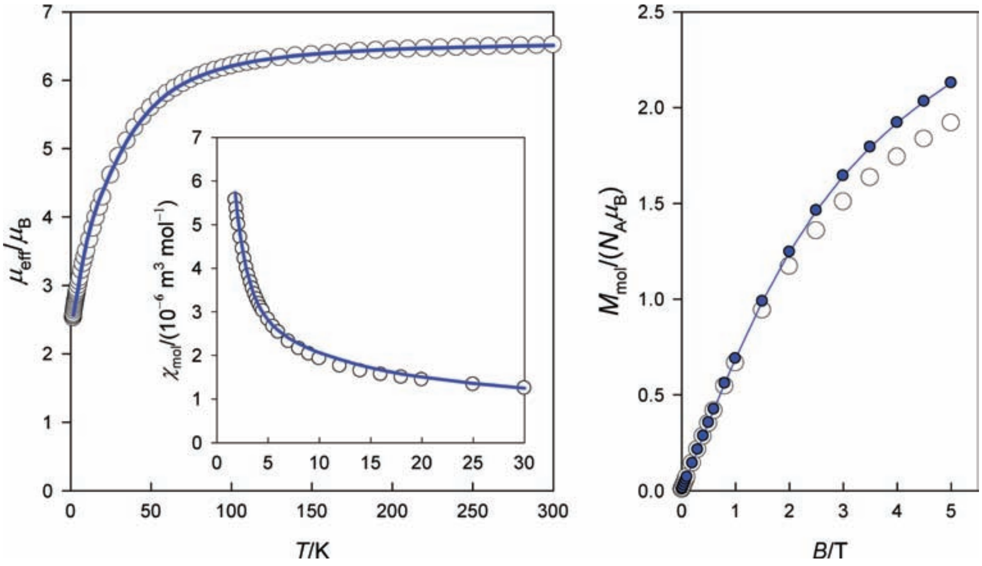


Figure 5. Magnetic functions for **1**. Left, temperature dependence of the effective magnetic moment; right, field dependence of the magnetization at 2.0 K. Open circles, experimental data; lines, fitted.

($Co^{II}-Cu^{II}-Co^{II}$ angle of 118°), the antiferromagnetic exchange yields a spin frustration.

The magnetic data were fitted by considering the spin Hamiltonian (eq 2).

$$\begin{aligned}\hat{H} = {} & -J_{\mathrm{Co-Cu}}[(\vec{S}_{\mathrm{Co2}}\cdot\vec{S}_{\mathrm{Cu}}) + (\vec{S}_{\mathrm{Co3}}\cdot\vec{S}_{\mathrm{Cu}})]\hbar^{-2} \\ & - J_{\mathrm{Co-Co}}(\vec{S}_{\mathrm{Co2}}\cdot\vec{S}_{\mathrm{Co3}})\hbar^{-2} + \mu_{\mathrm{B}}B[g_{\mathrm{Co}}(\vec{S}_{\mathrm{Co2}} + \vec{S}_{\mathrm{Co3}}) \\ & + g_{\mathrm{Cu}}\vec{S}_{\mathrm{Cu}}]\hbar^{-1} + D_{\mathrm{Co}}[(\vec{S}^{2}_{\mathrm{Co2},z} - \vec{S}^{2}_{\mathrm{Co2}}/3) \\ & + (\vec{S}^{2}_{\mathrm{Co3},z} - \vec{S}^{2}_{\mathrm{Co3}}/3)]\hbar^{-2} \qquad (2)\end{aligned}$$

The g-factor anisotropy was omitted in order to avoid an overparametrization. The fitting procedure was applied simultaneously to the susceptibility and magnetization data sets by minimizing the functional (eq 3).

$$F = [\sum_{i}^{N} |\chi_i^{\mathrm{c}} - \chi_i^{\mathrm{o}}|/\chi_i^{\mathrm{o}}] \times [\sum_{j}^{M} |M_j^{\mathrm{c}} - M_j^{\mathrm{o}}|/M_j^{\mathrm{o}}] \rightarrow \min \qquad (3)$$

The final set of magnetic parameters is as follows: $J_{\mathrm{Co-Cu}}/hc = -4.76\ \mathrm{cm}^{-1}$, $J_{\mathrm{Co-Co}}/hc = -2.76\ \mathrm{cm}^{-1}$, $g_{\mathrm{Co}} = 2.005$, $g_{\mathrm{Cu}} = 2.114$, and $D_{\mathrm{Co}}/hc = +34.3\ \mathrm{cm}^{-1}$. The discrepancy factors for the susceptibility and magnetization are $R(\chi) = 0.023$ and $R(M) = 0.094$, respectively. The negative value of the Co−Cu exchange coupling constant matches the high Co−O−Cu angle of the superexchange path. The Co−Co coupling constant on the $Co^{II}-Co^{III}-Co^{II}$ superexchange path is 2 times lower.

The ZFS parameter D has no effect on the $S = 1/2$ state. When the ground state is $S = 3/2$, the magnetization per complex should saturate to the value of $M_1 = M_{\mathrm{mol}}/(N_{\mathrm{A}}\mu_{\mathrm{B}}) = 3$ or higher. Since the observed value at $B = 5$ T is much lower, one is left with a considerable magnetic anisotropy given by the axial zero-field splitting parameter D. However, this contradicts the local electronic state of the tetrahedral Co(II) center possessing a nondegenerate ground state $^4A_2$ for which rather small g-factor anisotropy and small D values are expected.[26] There are some other hypotheses that eventually could improve the fit of the magnetization data: (i) the g-factor anisotropy at the Co(2) center can exist; (ii) the sample is contaminated by magnetically less productive centers, like mononuclear Cu^{II}; (iii) the bent architecture of the magnetic centers (C_{2v} symmetry) allows application of the antisymmetric exchange that applies in the normal plane (d_y component, when the centers are aligned in the $x-z$ plane). The involvement of the antisymmetric exchange is a complex task[27] and unmodeled so far for the present features (a bent heterometallic system).

Thermal Behavior. The thermal behaviors of complexes **1**−**3** were examined by thermogravimetric analysis, performed under an atmosphere of flowing dinitrogen gas (30 mL/min), and the thermograms, obtained with scanning rates of 10 °C/min, are shown in Figure 6. In general, the behaviors are similar with a few broad weight losses upon heating. The first, occurring at *ca.* 180−300 °C, results in a mass residue of 86, 90, and 82% for **1**, **2**, and **3**, respectively. That can be assigned to the elimination of solvents and few chlorine atoms, which corresponds to weight residues of 85.7 (solv + 2Cl), 90.8 (solv + Cl), and 81.6% (solv + 2Cl) for **1**, **2**, and **3**, respectively. Some discernible breaks at 210 and 220 °C are observed in the weight curves of **1** and **2**, corresponding to 94% mass residues for both compounds. That can be assigned to the loss of CH_3OH/H_2O solvents (96.1 and 95.6% for **1** and **2**, respectively). In contrast to this, complex **3** having DMF solvent does not exhibit such a break.

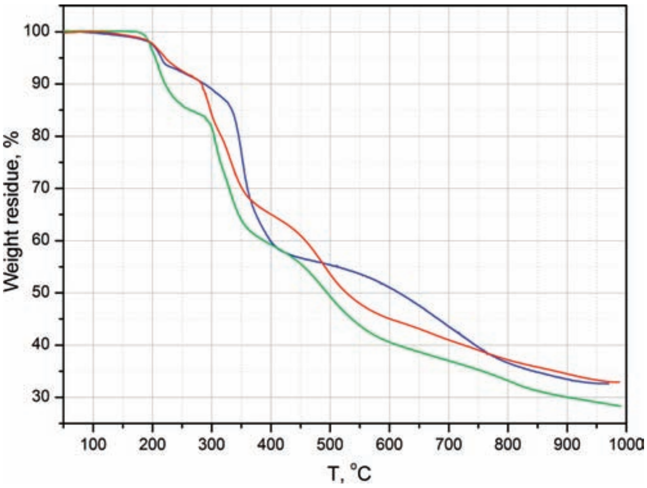


Figure 6. Thermogravimetric plot showing the loss in weight with the increase of temperature for complexes **1** (blue), **2** (red) and **3** (green) at 10°/min heating speed.

The final mass residues for **1** (33%), **2** (33%), and **3** (28%) are very close to those calculated for the $CuCoZn_2$ metal mixtures (32.8, 34.0, and 32.3%, respectively), indicating most probably the formation of some volatile compounds during the decomposition. These could be metal chlorides since some of them were recognized to be highly volatile at *ca.* 500 °C.[28] The presence of the metallic residues at the highest temperatures is rather unexpected since metal oxides are the common residues. However, an analogous behavior was observed earlier for homo- and heterometallic complexes with amino alcohols.[29] Probably, an excess of oxygen is necessary for the formation of oxide, which is not available in the case of complexes **1**−**3**. They have a M_4O_6 core composition, and the corresponding amounts of oxygen are presumably consumed in the decomposition of the amino alcohol ligand.

ESI Mass Spectrometry. Electrospray ionization mass spectroscopy (ESI-MS) was used as a convenient solution-based technique to examine the behavior of the heterometallic complexes in solution with the aim of screening possible transformation processes and detecting any novel species formed. The investigation of methanol solutions of **1**−**3** shows two main products of decomposition: $[CuCoM_2(MeDea)_3Cl_2]^+$ and $[CuM_2(MeDea)_3(CH_3OH)]^+$ (M = Co for **1** and Zn for **2** and **3**) which are observed for all three complexes but with different peak intensities ratios. A 100:70% ratio was observed for the heterobimetallic complex **1**, while the spectra of the heterotrimetallic complexes **2** and **3** revealed only 8% and 5% peak intensities of the $[CuZn_2(MeDea)_3(CH_3OH)]^+$ particle, respectively. The spectrum of **1** revealed numerous species within the m/z range of 260−663, most with low intensities, except the medium intensity (60%) peak at $m/z = 564$ assigned to $[Co_3(Dea)_2(HDea)Cl]^+$. This contrasts with the spectra of **2** and **3**, which show only traces of products other than $[CuCoM_2(MeDea)_3Cl_2]^+$ and $[CuM_2(MeDea)_3(CH_3OH)]^+$. No complex particle containing DMF (in the case of **3**) was found, indicating that the source of the methanol molecule in the particle $[CuM_2(MeDea)_3(CH_3OH)]^+$ was the methanol solvent. All of

Table 2. Peroxidative Oxidation of Cyclohexane to Cyclohexanol and Cyclohexanone Catalysed by Compound **1**[a]

(a) Catalyst

			yields[b] of products, %				
entry	*n*(catalyst), μmol	[catalyst], M × 10^3	ketone	alcohol	total	TON[c]	A/K[d]
1	0	0	0	0	0	–	–
2	0.6	0.11	0	0	0	0	–
3	2.3	0.46	1	2	3	13	2
4	4.5	0.90	1	6	7	16	6
5	6.0	1.20	1	9	10	17	9
6[e]	6.0	1.20	5	6	10	17	1.2
7	7.7	1.53	1	13	15	20	13
8	10.0	2.00	1	15	16	16	15
9	16.8	3.36	6	16	22	13	2.7
10[e]	16.8	3.36	6	16	22	13	2.7

(b) H_2O_2

				yields[b] of products, %			
entry	$n(H_2O_2)$, mmol	$n(H_2O_2)/n(cat)$	$[H_2O_2]$, M	ketone	alcohol	total	A/K[d]
11	0	0	0	0	0	0	–
12	4	400	0.8	1	11	12	11
13[e]	4	400	0.8	3	9	11	3
14	5	500	1	1	15	16	15
15	8	800	1.6	2	19	21	9.5
16	10	1000	2	4	19	23	4.8
17[e]	10	1000	2	8	14	22	1.8
18	20	2000	4	3	2	5	0.7

(c) HNO_3

				yields[b] of products, %			
entry	$n(HNO_3)$, μmol	$n(HNO_3)/n(cat)$	$[HNO_3]$, M	ketone	alcohol	total	A/K[d]
19	0	0	0	0	1	1	0
20	50	5	0.01	0	1	1	0
21	100	10	0.01	4	10	14	2.5
22[e]	100	10	0.02	4	8	12	2
23	200	20	0.04	1	16	17	16
24	400	40	0.08	1	14	15	14
25	600	60	0.08	1	13	14	13
26[e]	600	60	0.12	6	6	12	1

(d) Water

			yields[b] of products, %			
entry	% (H_2O)[f]	$[H_2O]$, M	ketone	alcohol	total	A/K[d]
27	7	3.8	1	16	17	15
28	13	7.1	1	17	18	17
29[e]	13	7.1	7	7	13	1
30	17	9.3	1	16	17	16
31	27	14.9	1	15	16	15
32[e]	27	14.9	8	3	11	0.4
33	47	26.0	0	5	5	–
34[e]	47	26.0	2	1	3	0.5
35	67	37.1	0	2	2	0

[a] Effects of amount of catalyst (a), H_2O_2 (b), HNO_3 (c), and water (d). Reaction conditions (unless stated otherwise): catalyst precursor (10.0 μmol), H_2O_2 (30% in H_2O; 5 mmol), C_6H_{12} (1.00 mmol), MeCN (4.5 mL), acid promoter (0.20 mmol), 5 h reaction time, ambient temperature (*ca.* 20 °C). [b] Moles of product/100 mols of cyclohexane, measured upon reduction of ROOH to the alcohol by PPh_3. [c] Overall TON values (mols of products/mol of catalyst). [d] Alcohol (cyclohexanol)/ketone (cyclohexanone) molar ratio. [e] Yields measured prior to the addition of PPh_3 (for comparative purposes). [f] Milliliters of H_2O/100 mL of MeCN.

the calculated isotropic distribution patterns match those expected for the naturally occurring isotopes of the relevant atoms.

The water ESI spectra revealed the decomposition of all complexes. The most intense peak, recognized as $[Co(HDea)_2]^+$ at *m*/*z* = 295, is observed in all spectra, while the peaks corresponding to the above-mentioned species $[CuCoM_2(MeDea)_3Cl_2]^+$ and $[CuM_2(MeDea)_3(CH_3OH)]^+$ are of low intensity for **1** and **3** (10 and 25% for **1**; 10 and 15% for **3**) and medium for **2** (60 and 85%, respectively). Interestingly, all of the spectra contain a *ca.* 25% intensity peak of the free ligand $[H_3Dea]^+$ at *m*/*z* = 120.

Thus, the coordination cores of the complexes **1**−**3** keep their integrity in methanol solution, with the elimination of some chloride anions as well as the coordinated solvent molecules, while the water media promote the complete decomposition of all of the coordination compounds.

Catalytic Properties. Compounds **1**−**3** were investigated as catalytic precursors for the oxidation, under mild conditions, of cyclohexane (CyH), by aqueous hydrogen peroxide, into cyclohexanol (CyOH) and cyclohexanone. Cyclohexane has been used as a recognized substrate model[30] in view of the importance of the products (i.e., cyclohexanol and cyclohexanone are intermediates in nylon-6,6 and polyamide-6 productions).[31] The reactions were carried out in a liquid (CH_3CN/H_2O) medium in the presence of nitric acid, at room temperature and atmospheric pressure. The presence of an acid promoter is essential for the products' formation since it can play a multiple role, by creating unsaturation at the metal upon ligand protonation, stabilizing peroxo species and hampering the decomposition of hydrogen peroxide.[7a,32] The effects on the catalytic activity of various factors, such as relative amounts of catalyst, oxidant, and nitric acid, have been studied. The obtained results are presented in Table 2 and Figure 7. No alkane oxidation products (or only traces) are obtained in the absence of any component of the catalytic system—catalyst, acid, or hydrogen peroxide.

The catalytic tests of complex **1** showed the highest overall yield of 23% (on the basis of the alkane) achieved with a H_2O_2/catalyst molar ratio of 1000:1 and a HNO_3/catalyst ratio of 20:1 (Table 2b, entry 16), for the catalyst amount of 10 μmol. However, higher yields would be expected for higher amounts of catalyst, since the former increase with the latter (Figure 7a). The highest overall TON (turnover number, moles of products per mol of catalyst precursor) of 20 was obtained for entry 7 (Table 2a), which

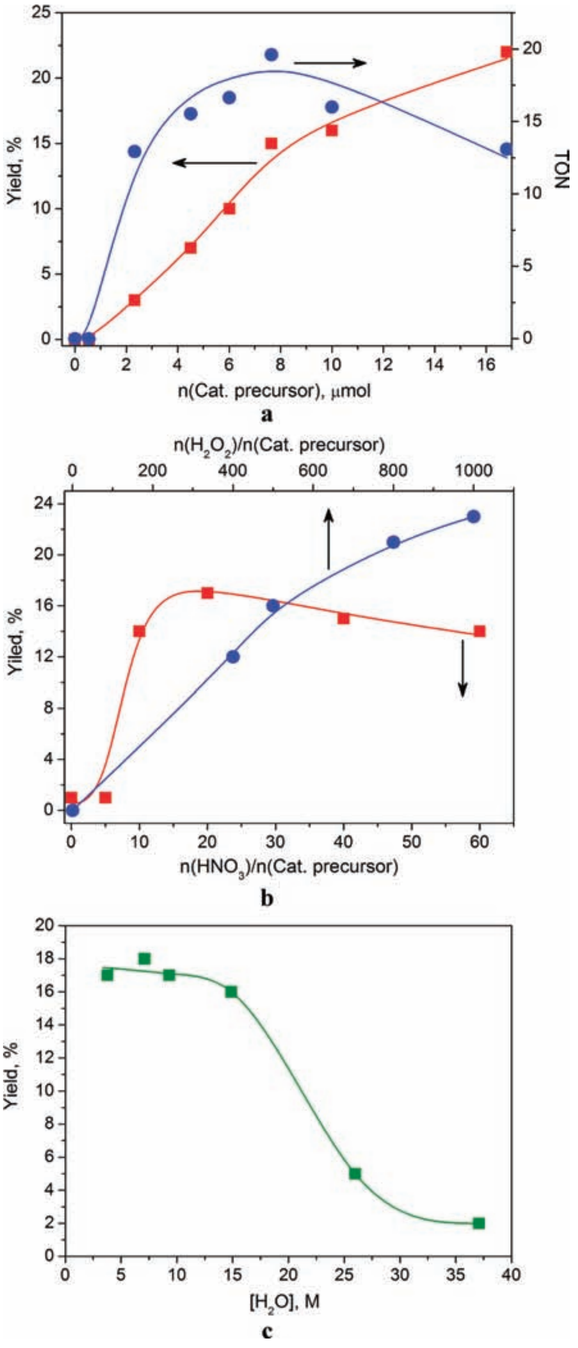
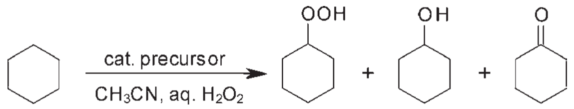


Figure 7. Effects of catalyst (a), H_2O_2 (b), HNO_3 (b), and water (c) amounts on the total yields of cyclohexanol and cyclohexanone in the peroxidative oxidation of cyclohexane with catalyst precursor **1**. Numbers and reaction conditions are those of Table 2 entries.

corresponds to the total yield of 15%. The overall TON increases with the catalyst amount until the highest value (20) is reached with 8 μmol of catalyst, beyond which a slight decrease occurs.

An increase in the peroxide-to-catalyst molar ratio up to *ca.* 1000:1 results in an increase of the yield with a nearly linear dependence (Figure 7b), but a further rise of the oxidant amount leads to a yield decrease (5% for the H_2O_2/catalyst molar ratio of 2000 (Table 2b, entry 18)). Such a decay can be caused by the considerable water amount in the catalytic system (a 30% water solution of the hydrogen peroxide was used) since water was recognized as an inhibitory agent for various systems, although in some cases a promoting effect is observed for lower H_2O amounts.[7a,33] The current results are consistent with the dependence of the total yield on the water amount in the catalytic system. For a concentration below 15 M (*ca.* 30%; Table 2d, entries 27−31), the water has no considerable influence on the yield, while a further increase of the water amount leads to a pronounced decrease of the yield (entries 33−35, Figure 7c). The catalyst activity also depends on the acid promoter quantity. It undergoes a high enhancement in the HNO_3/catalyst molar ratio range of 5−20 (Figure 7b).

Scheme 1



A high overall selectivity toward the formation of the alcohol and ketone is achieved in all tests, as supported by GC analyses that show no traces of any byproduct. Moreover, the GC analyses were typically performed upon the addition of PPh_3 to the final solution, and cyclohexanol is then detected in a much higher amount than cyclohexanone, the systems thus showing an unusually high selectivity for the alcohol. In contrast, prior to the addition of PPh_3, the alcohol and ketone amounts are comparable. Such behavior is typical for catalytic systems with cyclohexyl hydroperoxide (CyOOH) present in a substantial amount at the end of the reaction (Scheme 1)

In fact, reduction of CyOOH by PPh_3 gives cyclohexanol (CyOH) as the primary product (alcohol/ketone ratio up to 16), while in the absence of PPh_3 the alcohol/ketone ratio is much lower (entries with footnote *e* in Table 2). The application of the method developed by Shul'pin[18] allowed for the estimate of the amount of CyOOH at the end of reaction as *ca.* 80% of the total of all products, for the conditions indicated for entries 6, 13, 17, 26, 28, 32, and 34 (Table 2). However, in a few cases, CyOOH was detected in low amounts (Table 2, entries 10, 22), indicating its decomposition along the reaction.

The formation of CyOOH (conceivably via reaction of Cy$\cdot$ with H_2O_2 to give CyOO$\cdot$)[7−10,18,32] suggests a main radical pathway for the catalytic reactions. In accord, the oxidation of cyclohexane is essentially suppressed in the presence of radical trapping agents (total product yields below 2% vs 16% in the presence or absence, respectively, of a radical trap for entry 8, Table 2a), such as bromotrichloromethane, diphenylamine, and 2,6-di-*tert*-butyl-4-methylphenol (BHT), thus revealing the involvement of both C- and O-centered radicals, as reported, e.g., for various copper,[7] iron,[9,10] and vanadium[8,35] catalysts.

In contrast to **1**, compounds **2** and **3** exhibit much lower activities in the peroxidative oxidation of cyclohexane, providing the highest yield of 4% under similar conditions. Thus, the activity of the $CuCo_3$ core in **1** is much greater than those of the $CuCoZn_2$ ones. This eventually can be associated either with a synergic effect of the various metal atoms in the former system or an inhibitory effect of zinc in the latter. A related situation was observed for the catalytic activity of the heterotrimetallic Cu/Co/Fe and Cu/Co/Ni complexes with diethanolamine: although the first compound showed an exceptionally high activity (45% products yield), the second one led only to an 8% yield.[10] Moreover, zinc(II), by itself, is not expected to provide a promising metal catalytic site in this field, in view of its inability to participate in oxidation chemistry. However, a better comparative analysis is prevented by the lack of comparable literature data on the peroxidative activation of alkanes by cobalt complexes, since attention is usually mainly paid to more active copper, iron, and vanadium coordination compounds.[7−10,32,35]

CONCLUSIONS

A simple and effective route has been developed for the preparation of a family of heterometallic complexes, $[CuCo_3(MeDea)_3Cl_3(CH_3OH)_{0.55}(H_2O)_{0.45}](H_2O)_{0.45}$ (**1**), $[CuCoZn_2(MeDea)_3Cl_3(CH_3OH)_{0.74}(H_2O)_{0.26}](H_2O)_{0.26}$ (**2**), and $[CuCoZn_2(MeDea)_3Cl_3(DMF)]$ (**3**), which can be readily synthesized in nonaqueous solvents through the reaction of zerovalent copper with different metal salts (Co and Zn) and N-methyldiethanolamine in the open air. All of these complexes possess the rare asymmetric $M_4(\mu_3\text{-}X)(\mu\text{-}X)_5$ molecular structure type. A statistical analysis in the CSD revealed that the MST of **1**−**3** represents the most rare type among all of the M_4X_6 MSTs with related mutual arrangements of the metal centers. It is also shown that there are five geometrically and/or topologically different MSTs, and the most widespread ones correspond to centrosymmetrical structures, which is confirmed by the analysis of the torsion M···M···M···M angles.

The thermogravimetric analysis of **1**−**3** indicates that they decompose to metals. The magnetic investigations of **1** disclose an antiferromagnetic coupling between paramagnetic centers in a $Co^{II}-Cu^{II}-Co^{II}$ exchange fragment. The heterometallic complexes **1**−**3** are shown to act as catalytic precursors for the peroxidative oxidation of cyclohexane under mild conditions. A marked activity (up to 23% products yield) and a good selectivity toward the formation of cyclohexanol are displayed by **1**, which is much more effective than **2** and **3**. The different nature of the metals at the terminal positions (Co or Zn) is the main difference between these complexes, and thus the presence of zinc can be a reason for hampering the catalytic activity of **2** and **3**, in contrast to **1**.

The work has extended the direct self-assembly approach to the synthesis of heterometallic complexes bearing a very rare type of asymmetric tetranuclear core, demonstrating the power of this approach in the field of synthesis of polynuclear heterobi- and heterotrimetallic coordination compounds. It also expanded the catalytic applications of heterometallic assemblies, in particular showing that they are promising catalyst precursors in the field of alkane functionalization under mild conditions.

The studies deserve to be extended to other heterometallic complexes, with different metals or metal combinations, and other amino alcohol ligands, eventually leading to the expansion of the rare asymmetric MST obtained herein and/or to different novel types of metal core structures.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Metal−metal distances and selected bond lengths for **1**−**3**, hydrogen bonding distances for **1** and **2**, plots of the hydrogen-bonded schemes for **1**, and CIF files of crystallography data for the structures in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Fax: +351 218464455. E-mail: pombeiro@ist.utl.pt.

ACKNOWLEDGMENT

This work has been partially supported by the Foundation for Science and Technology (FCT), Portugal, its PPCDT (FEDER funded) program, and in part by Fundamental Research fund of Ukraine (Project 28.3/017). Grant Agencies (Slovakia: VEGA 1/0052/11, APVV 0202-10, VVCE 0004-07) are also acknowledged for the financial support. Thanks are also due to Dr. M. Cândida Vaz (IST) and Dr. M. Conceição Oliveira (IST) for the elemental and ESI-MS analyses, respectively.

REFERENCES

(1) (a) Shaowu, D.; Nianyoung, Z.; Pengcheng, C.; Xintao, W.; Jiaxi, L. *Polyhedron* **1992**, *11*, 109. (b) Nianyong, Z.; Shaowu, D.; Pengcheng, C.; Xintao, W.; Jiaxi, L. *J. Coord. Chem.* **1992**, *26*, 35. (c) Shaowu, D.; Nianyong, Z.; Pengcheng, C.; Xintao, W.; Jiaxi, L. *J. Chem. Soc., Dalton Trans.* **1992**, 339.

(2) (a) Tanase, S.; Reedijk, J. *Coord. Chem. Rev.* **2006**, *250*, 2501. (b) Verani, C. N.; Rentschler, E.; Weyhermüller, T.; Bill, E.; Chaudhuri, P. *J. Chem. Soc., Dalton Trans.* **2000**, 251 and references therein. (c) Gheorghe, R.; Madalan, A. M.; Costes, J.-P.; Wernsdorfer, W.; Andruh, M. *Dalton Trans.* **2010**, *39*, 4734 and references therein. (d) Chikamoto, Y.; Kawamoto, T.; Igashira-Kamiyama, A.; Konno, T. *Inorg. Chem.* **2005**, *44*, 1601 and references therein. (e) Koutmos, M.; Coucouvanis, D. *Inorg. Chem.* **2006**, *45*, 1421 and references therein. (f) Long, J.; Chamoreau, L.-M.; Marvaud, V. *Dalton Trans.* **2010**, *39*, 2188 and references therein.

(3) See, for example: (a) Visinescu, D.; Madalan, A. M.; Andruh, M.; Duhayon, C.; Sutter, J.-P.; Ungur, L.; Van den Heuvel, W.; Chibotaru, L. F. *Chem.—Eur. J.* **2009**, *15*, 11808. (b) Amiri, H.; Mariani, M.; Lascialfari, A.; Borsa, F.; Timco, G. A.; Tuna, F.; Winpenny, R. E. P. *Phys. Rev. B* **2010**, *81*, 104408. (c) Timco, G. A.; McInnes, E. K. L.; Pritchard, R. G.; Tuna, F.; Winpenny, R. E. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 9681.

(4) See, for example: (a) Zhang, H.; Yang, J.-H.; Shpanchenko, R. V.; Abakumov, A. M.; Hadermann, J.; Clerac, R.; Dikarev, E. V. *Inorg. Chem.* **2009**, *48*, 8480. (b) Bykov, M.; Emelina, A.; Kiskin, M.; Sidorov, A.; Aleksandrov, G.; Bogomyakov, A.; Dobrokhotova, Z.; Novotortsev, V.; Eremenko, I. *Polyhedron* **2009**, *28*, 3628. (c) Seisenbaeva, G. A.; Kessler, V. G.; Pazik, R.; Strek, W. *Dalton Trans.* **2008**, 3412.

(5) Lassahn, P.-G.; Lozan, V.; Timco, G. A.; Christian, P.; Janiak, C.; Winpenny, R. E. P. *J. Catal.* **2004**, *222*, 260.

(6) (a) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (b) Diaz-Requejo, M. M.; Perez, P. J. *Chem. Rev.* **2008**, *108*, 3379. (c) Shul'pin, G. B. *Org. Biomol. Chem.* **2010**, *8*, 4217. (d) Shul'pin, G. B. *Mini-Rev. Org. Chem.* **2009**, *6*, 95.

(7) (a) Kirillova, M. V.; Kozlov, Y. N.; Shul'pina, L. S.; Lyakin, O. Y.; Kirillov, A. M.; Talsi, E. P.; Pombeiro, A. J. L.; Shul'pin, G. B. *J. Catal.* **2009**, *268*, 26. (b) Kirillov, A. M.; Kopylovich, M. N.; Kirillova, M. V.; Haukka, M.; da Silva, M. F. C. G.; Pombeiro, A. J. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4345. (c) Silva, T. F. S.; Alegria, E. C. B. A.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. *Adv. Synth. Catal.* **2008**, *350*, 706. (d) Contaldi, S.; Di Nicola, C.; Garau, F.; Karabach, Y. Y.; Martins, L. M. D. R. S.; Monari, M.; Pandolfo, L.; Pettinari, C.; Pombeiro, A. J. L. *Dalton Trans.* **2009**, 4928.

(8) (a) Silva, T. F. S.; Luzyanin, K. V.; Kirillova, M. V.; da Silva, M. F. C. G.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. *Adv. Synth. Catal.* **2010**, *352*, 171. (b) Pombeiro, A. J. L. *ACS Symp. Ser.* **2007**, *974*, 51.

(9) Fernandes, R. R.; Kirillova, M. V.; da Silva, J. A. L.; da Silva, J. J. R. F.; Pombeiro, A. J. L. *Appl. Catal., A* **2009**, *353*, 107.

(10) Nesterov, D. S.; Kokozay, V. N.; Dyakonenko, V. V.; Shishkin, O. V.; Jezierska, J.; Ozarowski, A.; Kirillov, A. M.; Kopylovich, M. N.; Pombeiro, A. J. L. *Chem. Commun.* **2006**, 4605.Pombeiro, A. J. L.; Kirillov, A. M.; Kopylovich, M. N.; Kokozay, V. N.; Nesterov, D. S. Patent PT 103526, 2007.

(11) (a) Winpenny, R. E. P. *Comp. Coord. Chem. II* **2004**, *7*, 125. (b) Wang, W.-G.; Zhou, A.-J.; Zhang, W.-X.; Tong, M.-L.; Chen, X.-M.; Nakano, M.; Beedle, C. C.; Hendrickson, D. N. *J. Am. Chem. Soc.* **2007**,

129, 1014. (c) Zhang, J.-J.; Hu, S.-M.; Xiang, S.-C.; Sheng, T.; Wu, X.-T.; Li, Y.-M. *Inorg. Chem.* **2006**, *45*, 7173. (d) Lehn, J.-M. *Chem.—Eur. J.* **1999**, *5*, 2455.

(12) (a) Nesterov, D. S.; Kokozay, V. N.; Skelton, B. W. *Eur. J. Inorg. Chem.* **2009**, 5469. (b) Nesterov, D. S.; Kokozay, V. N.; Skelton, B. W.; Jezierska, J.; Ozarowski, A. *Dalton Trans.* **2007**, 558. (c) Nesterov, D. S.; Kokozay, V. N.; Skelton, B. W. *Acta Crystallogr, Sect. C* **2006**, *62*, m246. (d) Nesterov, D. S.; Makhankova, V. G.; Kokozay, V. N.; Skelton, B. W. *Inorg. Chim. Acta* **2005**, *358*, 4519. (e) Nesterov, D. S.; Makhankova, V. G.; Vassilyeva, O. Y.; Kovbasyuk, L. A.; Skelton, B. W.; Jezierska, J. *Inorg. Chem.* **2004**, *43*, 7868.

(13) (a) Vreshch, O. V.; Nesterova, O. V.; Kokozay, V. N.; Skelton, W. W.; Gómez-García, C. J.; Jezierska, J. *Inorg. Chem. Commun.* **2009**, *12*, 890. (b) Semenaka, V. V.; Nesterova, O. V.; Kokozay, V. N.; Dyakonenko, V. V.; Zubatyuk, R. I.; Shishkin, O. V.; Boča, R.; Jezierska, J.; Ozarowski, A. *Inorg. Chem.* **2010**, *49*, 5460 and references therein. (c) Nesterova, O. V.; Petrusenko, S. R.; Kokozay, V. N.; Skelton, B. W.; Jezierska, J.; Linert, W.; Ozarowski, A. *Dalton Trans.* **2008**, 1431 and references therein.

(14) *CrysAlis CCD*; *CrysAlis RED*, version 1.171; Oxford Diffraction Ltd.: Abingdon, U.K., 2006.

(15) *APEX2*; *SAINT*; Bruker AXS, Inc.: Madison, WI, 2004.

(16) (a) Sheldrick, G. M. *SHELXS-97*; *SHELXL-97*; University of Gottingen: Gottingen, Germany, 1997. (b) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

(17) König, E. *Magnetic Properties of Coordination and Organometallic Transition Metal Complexes*; Springer-Verlag: Berlin, 1966.

(18) (a) Shul'pin, G. B. *J. Mol. Catal. A: Chem.* **2002**, *189*, 39. (b) Shul'pin, G. B. *C. R. Chimie* **2003**, *6*, 163. (c) Shul'pin, G. B.; Kozlov, Y. N.; Shul'pina, L. S.; Petrovskiy, P. V. *Appl. Organomet. Chem.* **2010**, *24*, 464.

(19) Wilson, S.; Hendrickson, D.; Rheingold, A. L. *Private Communication* 2005.

(20) Hill, C. L.; Williamson, M. M. *Inorg. Chem.* **1985**, *24*, 2836.

(21) (a) Makhankova, V. G.; Vassilyeva, O. Y.; Kokozay, V. N.; Reedijk, J.; Van Albada, G. A.; Jezierska, J.; Skelton, B. W. *Eur. J. Inorg. Chem.* **2002**, 2163. (b) Tudor, V.; Marin, G.; Lloret, F.; Kravtsov, V. C.; Simonov, Y. A.; Julve, M.; Andruh, M. *Inorg. Chim. Acta* **2008**, *361*, 3446. (c) Bertrand, J. A.; Fujita, E.; Van Derveer, D. G. *Inorg. Chem.* **1979**, *18*, 230.

(22) CSD (version 5.31; May 2010): Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380.

(23) Ibers, J. A. *Nature* **1963**, *197*, 686.

(24) (a) Dunitz, J. D.; Gavezzotti, A. *Chem. Soc. Rev.* **2009**, *38*, 2622. (b) Gavezzotti, A. *Acc. Chem. Res.* **1994**, *27*, 309. (c) Ball, P. *Nature* **1996**, *381*, 648.

(25) Semenaka, V. V.; Nesterova, O. V.; Kokozay, V. N.; Zybatyuk, R. I.; Shishkin, O. V.; Boča, R.; Gómez-García, C. G.; Clemente-Juan, J. M.; Jezierska, J. *Polyhedron* **2010**, *29*, 1326.

(26) Boča, R. *Struct. Bonding (Berlin)* **2006**, *117*, 1.

(27) Boča, R.; Herchel, R. *Coord. Chem. Rev.* **2010**, *254*, 2973.

(28) (a) García-Martínez, O.; Millán, P.; Rojas, R. M.; Torralvo, M. J. *J. Mat. Chem.* **1988**, *23*, 1334. (b) Lumme, P; Junkkarinen, K. *Suomen Kemistilehti* **1968**, *B41*, 114.

(29) Hamid, M.; Tahir, A. A.; Mazhar, M.; Zeller, M.; Molloy, K. C.; Hunter, A. D. *Inorg. Chem.* **2006**, *45*, 10457.

(30) Schuchardt, U.; Cardoso, D.; Sercheli, R.; Pereira, R.; da Cruz, R. S.; Guerreiro, M. C.; Mandelli, D.; Spinace, E. V.; Pires, E. L. *Appl. Catal., A* **2001**, *211*, 1.

(31) *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: Weinheim, Germany, 2002.

(32) (a) Gruenwald, K. R.; Kirillov, A. M.; Haukka, M.; Sanchiz, J.; Pombeiro, A. J. L. *Dalton Trans.* **2009**, 2109. (b) Kirillov, A. M.; Kopylovich, M. N.; Kirillova, M. V.; Karabach, E. Y.; Haukka, M.; da Silva, M. F. C. G.; Pombeiro, A. J. L. *Adv. Synth. Catal.* **2006**, *348*, 159.

(33) Kuznetsov, M. L.; Pombeiro, A. J. L. *Inorg. Chem.* **2009**, *48*, 307.

(34) Shul'pin, G. B.; Kozlov, Y. N.; Shul'pina, L. S.; Kudinov, A. R.; Mandelli, D. *Inorg. Chem.* **2009**, *48*, 10480.

(35) (a) Kirillova, M. V.; Kirillov, A. M.; Pombeiro, A. J. L. *Chem.—Eur. J.* **2010**, *16*, 9585. (b) Kirillova, M. V.; Kuznetsov, M. L.; Reis, P. M.; da Silva, J. A. L.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Am. Chem. Soc.* **2007**, *129*, 10531.