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A Pentanuclear Cu/Co/Ni Complex with 2-(Dimethylamino)ethanol – Observation of a Rare Molecular Structure Type and Its Place in General Structural Types: An Analysis of the Cambridge Structural Database

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Heterotrimetallic complex $[Cu^{II}_2Co^{II}Ni^{II}_2(Me_2Ea)_5Cl_5(H_2O)]\cdot CH_3CN\cdot H_2O$ has been prepared in a one-pot reaction of zero-valent copper with cobalt and nickel chlorides in an acetonitrile solution of 2-(dimethylamino)ethanol (HMe_2Ea) in the open air. The metal stoichiometry obtained by atomic absorption analysis was further confirmed by single-crystal X-ray diffraction investigations. The pentanuclear molecule is formed by a previously unknown combination of incomplete cube $M_3(\mu_3\text{-}X)(\mu\text{-}X)_3$ and triangle bipyramidal $M_3(\mu_3\text{-}X)_2(\mu\text{-}X)_2$ fragments, resulting in a zigzag arrangement of metal centers within one molecule. This type of arrangement is very uncommon for pentanuclear complexes and in particular for complexes with an odd number of metal centers. A search of the Cambridge Structural Database showed that the number of coordination compounds possessing an even number of metals is significantly greater than those containing an odd number. Possible reasons for such a distribution, as well as the synthetic and structural features of the presented compound, are discussed.

Introduction

The design and study of polynuclear metal complexes has become an active area of current research due to the potential for interesting physicochemical properties.[1] Special effort has been made to investigate complexes containing different kinds of metal atoms (heterometallic complexes) as new magnetic materials,[2] as it was shown that the combination of two (or more) different spin carriers within one molecule might lead to interesting magnetic properties. Further, although the catalytic properties of polynuclear homometallic complexes are deeply investigated,[3a,3b] the respective studies of heterobimetallic coordination compounds are scant.[3c,3d] Moreover, as far as we are aware, there is only one example of a study of the catalytic activity of a heterotrimetallic complex, which revealed the outstanding activity of the coordination compound $[Cu^{II}Co^{III}Fe^{III}(Dea)_3(NCS)_2(CH_3OH)]_2\cdot 3.2H_2O$ (H_2Dea = diethanolamine) in peroxidative oxidation of cycloalkanes.[4]

The rational design of heterometallic species (and especially heterotrimetallic species) is still one of the major challenges for inorganic chemists and exploratory synthesis. A popular multistep approach for the synthesis of these species uses a reaction between a preformed metal-containing ligand and a second type of metal ion via free coordination donors. However, this approach is hardly suitable for the construction of multinuclear heterobimetallic assemblies in which different metal atoms are linked by bridging atoms but not by 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.[5] The power of spontaneous self-assembly has long been realized, and this strategy remains the tool for generation of unprecedented and unexpected coordination compounds. Many groups attempted to make spontaneous self-assembly procedures more controllable.[6] In particular, the synthetic strategy formulated by Kessler ("Molecular structure design concept")[6a] was successfully applied to the synthesis of heterometallic complexes with simple ligands (such as methanol or 2-propanol) in dry conditions.[7] Although this concept has not been used in the present work, the idea of "molecular structure types" (MSTs) was found to be useful for comparing the structures of related compounds.

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The spontaneous self-assembly of high-nuclearity complexes is usually carried out with a simultaneous interaction of initial components (generally metal salts and ligands) in thermodynamically driven conditions (e.g. hydrothermal synthesis).[5,6] Previously, we have demonstrated that replacement of at least one of the metal salts by zero-valent metal has some advantages over the traditional synthesis, especially in the presence of protic ligands ("direct synthesis"):[8]

$$M(1)^0 + M(2)X_z + HL + Solv + O_2 \rightarrow [M(1)M(2)X_nL_m]\cdot Solv + H_2O$$

$$M^0 + nROH + n/4O_2 \rightarrow M^{n+} + nRO^- + n/2H_2O$$

This produces an alkaline medium directly, enforces a bridging coordination mode of alcohol ligands, and promotes a metal–metal bridge construction. Also, the lack of anions provides specific conditions and favors the formation of polynuclear aggregates. The reaction mixture spontaneously absorbs the dioxygen from air. The presented pathway allowed us to obtain a series of a heterobimetallic Cu/M[8] and heterotrimetallic Cu/Co/M coordination compounds.[4,9]

The Cambridge Structural Database (CSD)[10] contains only three Cu/Co/Ni complexes,[9b,11] and they show interesting magnetic properties and solution behavior. However, all these complexes are based either on the bridging ligands[11] or cation–anion structures.[9b] Taking into account the fact that the appropriate proximity between the few different metal centers in a heterometallic complex would allow more pronounced cooperation between the metals, we aimed at the synthesis of a $Cu^{II}/Co^{II}/Ni^{II}$ coordination compound where all metal ions would be linked only by bridging atoms, but not groups. This combination of different metals resembles recently published Cu/Co/Fe,[4] Cu/Co/Pb,[9b] and Cu/Co/Cd[9b] coordination compounds whose properties suggest that the heterotrimetallic complexes have great potential to improve various catalytic processes and also provide a unique material that stimulates the elaboration of new theoretical models in order to simulate quantitatively their magnetic properties.

Thus, continuing the investigations on a direct synthesis of heterometallic complexes starting from zero-valent metal, we have studied the initial system containing copper powder, cobalt chloride, nickel chloride and 2-(dimethylamino)ethanol (HMe_2Ea). We present here the synthesis and crystal structure of the novel complex $[Cu^{II}_2Co^{II}Ni^{II}_2(Me_2Ea)_5Cl_5(H_2O)]\cdot CH_3CN\cdot H_2O$, which exhibits a rather rare combination of $M_3(\mu_3\text{-}X)(\mu\text{-}X)_3$ and $M_3(\mu_3\text{-}X)_2(\mu\text{-}X)_2$ molecular structure types fused via common edges forming a pentanuclear molecule. Also, as far as we are aware, this compound represents the first example of a $Cu^{II}/Co^{II}/Ni^{II}$ heterotrimetallic assembly, since all known Cu/Co/Ni complexes contain cobalt only in the trivalent oxidation state.

Results and Discussion

The copper powder and metal salts were used in an equimolar ratio in acetonitrile, and 2-(dimethylamino)ethanol was then added. The reaction was initiated and brought to completion by heating and stirring. Green solutions were obtained at the end of the reaction that afforded dark green microcrystals of the complex after addition of diethyl ether.

The IR spectrum of the complex shows the characteristic bands of the 2-(dimethylamino)ethanol ligand. The strong absorption band at approximately 3400 cm^{-1} was attributed to ν(OH) vibrations due to coordinated and free water molecules. The presence of an uncoordinated acetonitrile molecule is confirmed by the weak ν(CN) absorption peak at 2245 cm^{-1}, typical for uncoordinated nitriles.[12]

The single-crystal X-ray analysis revealed the molecular nature of the compound (Figure 1). The copper atoms have a distorted square pyramid geometry of the coordination polyhedra with the axial bond lengths Cu1–Cl1 and Cu2–Cl4 of 2.7714(7) and 2.8033(11) Å, respectively (Table S1). The Co5 atom has a distorted trigonal bipyramidal environment with *trans* angle of 157.31(8)° and *cis* angles within the Co5, Cl5, Cl1, O22 plane ranging from 115.02(3)° to 122.90(7)°. Both Ni3 and Ni4 metal centers have distorted octahedral coordination polyhedra, the *trans* angles varying from 161.46(8)° to 170.47(8)° and from 160.81(8)° to 168.53(6)° for Ni3 and Ni4, respectively. Intermolecular association in the lattice occurs through the hydrogen bonding of the O–H···O and O–H···Cl types involving uncoordinated water molecule to form chains along the *a* axis (Table S2, Figure S1).

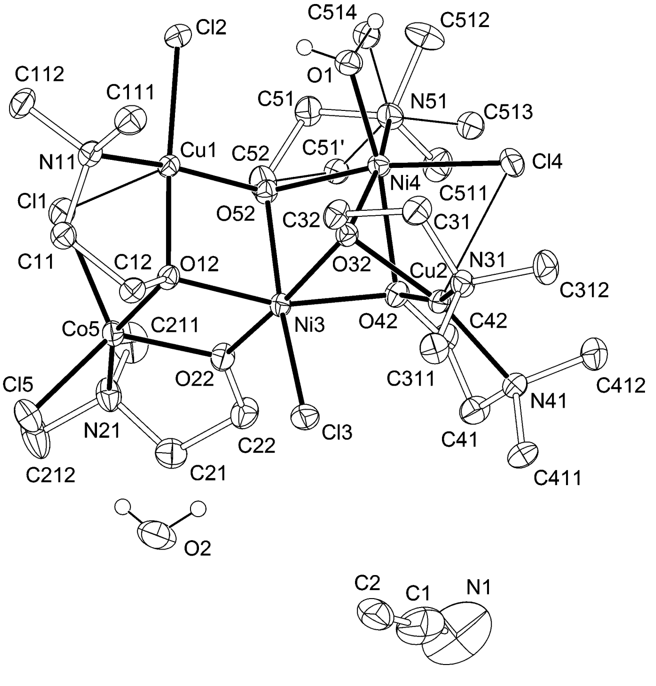

Figure 1. Molecular structure of $[Cu_2CoNi_2(Me_2Ea)_5Cl_5(H_2O)]\cdot CH_3CN\cdot H_2O$ with the numbering scheme (hydrogen atoms from amino alcohol ligands are omitted for clarity, the non-hydrogen atoms are shown as 50% ellipsoids).

The metal atoms were assigned on the basis of coordination geometry and from refinement. Although there is a possibility of scrambling of the metals in the Co and Ni metal atoms sites, refinement suggested that any such mixing is less than 2% for the Ni3 and Ni4 sites and less than 5% for the Co5 site. These data are consistent with the results of the elemental analysis. The minor Co/Ni scrambling can be explained by the similarity of the crystal chemistry of cobalt and nickel in a divalent oxidation state.[13] The CSD contains 36 crystal structures of coordination compounds containing both cobalt and nickel (the structures containing M–C bonds were excluded; the cation–anion compounds were not considered). Most of these complexes were obtained by building block or metalloligand approaches,[14] where the kinetic stability of the preformed units prevents metal scrambling. On the other hand, there are a number of pure Co^{II}/Ni^{II} complexes obtained by spontaneous self-assembly,[15] indicating the suitability of this strategy for the purpose of obtaining Co/Ni compounds. Also, it is known that some ligands stabilize the Co^{III} oxidation state, and the spontaneous oxidation of the cobalt often occurs in the respective reaction systems, thus preventing the scrambling.[16] The typical example is the diethanolamine (H_2Dea) ligand, which forms stable and easily identifiable *fac*,*mer*-$[Co^{III}(Dea)_2]^-$ block.[4,8d,9b,9c,9d,17] In contrast to this, the 2-(dimethylamino)ethanol ligand does not form specific complex fragments either with cobalt or with nickel. For instance, the search in the CSD revealed two pairs of coordination compounds $\{[M^{II}(HMe_2Ea)_2(OAc)_2]$ and $[M^{II}(HMe_2Ea)(acac)_2]$; acac = acetylacetone$\}$,[18,19] which have the same structure both for M = Co[18] and M = Ni,[19] while the heterometallic Co/Ni complexes with the HMe_2Ea ligand were not found. Both of these complexes possess almost regular octahedral coordination geometry around the metal center, which is typical for both cobalt and nickel.[13] Thus, the reaction system containing the cobalt and nickel salts and 2-(dimethylamino)ethanol most probably will result in a coordination compound with mixed Co/Ni positions. In the present investigation, we were interested in finding out how the copper ion affects the final crystal structure and the Co/Ni distribution of the final compound. The molecular structure type of $[Cu_2CoNi_2(Me_2Ea)_5Cl_5(H_2O)]\cdot CH_3CN\cdot H_2O$ contains octahedral and trigonal bipyramidal environments (apart from square-pyramidal polyhedra, typical for Cu^{II}), and probably the presence of these different coordination polyhedra allows to minimize the scrambling of the metals within the molecule.

The most prominent feature of the molecular structure of the presented compound is the mutual arrangement of the metals in the molecule. Such zigzag disposition of the metals is very typical for complexes with simple, flexible ligands and is very often based on the combination of incomplete cube-like arrays $M_3(\mu_3\text{-}X)(\mu\text{-}X)_3$, fused via common faces (Figure 2). In general, this results in an even number of metals, normally producing a centrosymmetrical molecule. For instance, the CSD contains 41 hexanuclear and 11 octanuclear complexes having such (or similar) structures. The number of compounds of the tetranuclear molecular structure type $\{M_4(\mu_3\text{-}X)_2(\mu\text{-}X)_4\}$ is greater than one thousand. However, we have found only a few examples of pentanuclear coordination compounds of analogous geometry: $Mo_5O_{11}(OCH_3)_4Py_4\cdot CH_3OH$ (Py = pyridine),[20] $Co_5(CO)_2(\mu_3\text{-}S)_3(PyS)$ (PyS = 2-mercapto-pyridine),[21] and $[Mn_7O_2(PhCO_2)_9(thme)_2(py)_3]$ {thme = deprotonated 1,1,1-tris(hydroxymethyl)ethane}.[22] The last complex is, in fact, a heptanuclear structure, but two terminal manganese atoms do not take part in the formation of the main body of the $\{M_3(\mu_3\text{-}X)(\mu\text{-}X)_3\}_n$ coordination core.

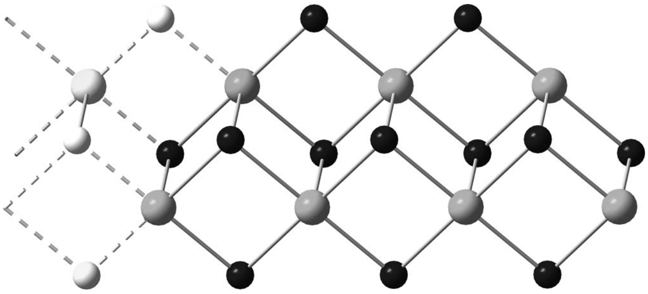

Figure 2. The illustration of a typical zigzag arrangement of metal centers formed by incomplete cube fragments joined by common faces.

It is possible to select some specific MSTs that support the formation of pentanuclear complexes, for example the $\{M_5(\mu_4\text{-}X)(\mu_3\text{-}X)_4(\mu\text{-}X)_4\}$ type possessing C_{4v} symmetry (27 hits in the CSD search), the $\{M_5(\mu_3\text{-}X)_2(\mu\text{-}X)_6\}$ type which is built up of two incomplete cube arrays joined by a common apex (7 hits), or the $\{M_5(\mu_3\text{-}X)_4(\mu\text{-}X)_6\}$ type [34 hits for a more common $\{M_5(\mu_3\text{-}X)_4\}$ type] (Figure 3). The last MST is typical for heterometallic complexes of general formula AB_4, where A is a "central" atom with a large radius that allows eight-coordinate geometry. However, pentanuclear complexes are most often formed by ligands with predefined geometry.

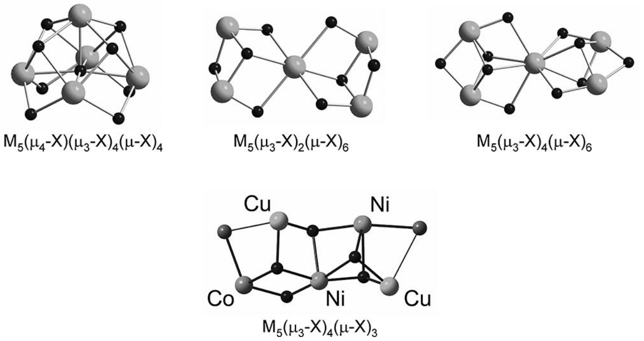

Figure 3. The geometry of M_5X_m coordination cores in typical pentanuclear molecular structure types (above) and the coordination core of the described compound (below).

Further statistical analysis of multinuclear coordination compounds of general structure M–(X–M)$_n$–X–M (where n ranges from 0 to 8; other restrictions are listed in the caption of Figure 4) in the CSD revealed that the number of complexes containing an even number of metals is significantly greater than that of complexes containing an odd number of metals (Figure 4). This interesting observation can be partially explained by the following assertions. The number of all possible molecular structure types dramatically increases with the number of interacting metals (one can name these MSTs "virtual"). However, the higher the nuclearity, the smaller the number of these MSTs are then stable enough to be formed and separated as chemical substances. This means that theoretically there is an extremely large number of potentially stable, high-nuclearity MSTs, the formation of which probably requires some special conditions. The analysis of the crystal structures of metal alkoxides, provided by Kessler[6a] and earlier by Caulton and Hubert-Pfalzgraf,[23] revealed that the size and number of metal atoms and ligands (donor atoms) have definitely more influence on the "choice" of the MSTs than their chemical nature. Moreover, the above-mentioned distribution (Figure 4) may point to the conclusion that the stability of the M_nX_m coordination core of the complex compound strongly depends on the symmetry of this core (in the absence of the ligand stabilization effect, e.g. in the case of alkoxides). The ratio of the number of μ_n-X bridging atoms to the number of metal centers is also important (the higher the better) and, as a rule, this ratio is greater for an even-nuclear, highly symmetric MST. From this point of view, the formation of asymmetric pentanuclear complexes (such as described here) is unfavorable, and stabilization by intra- and intermolecular interactions apparently plays a significant role in the formation of asymmetric pentanuclear coordination assemblies.

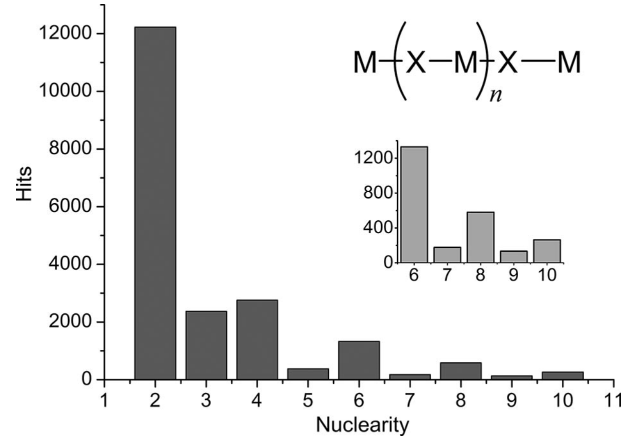

Figure 4. The dependence of the number of complexes on their nuclearity (for $0 \leq n \leq 8$). The following restrictions were applied: the search was provided only for non-polymeric transition-metal compounds where all metal centers form a molecule; the M–CO and M–CC fragments, as well as any non-transition-metal atoms, were excluded. The search over all types of metals does not essentially affect the statistical distribution but takes much more time and often causes computer problems. The inset shows the $n > 3$ region in details.

Conclusions

The systematic search for new heterotrimetallic complexes has now resulted in a coordination compound whose molecular structure represents the first combination of incomplete cube $M_3(\mu_3\text{-}X)(\mu\text{-}X)_3$ and triangle bipyramidal $M_3(\mu_3\text{-}X)_2(\mu\text{-}X)_2$ fragments, resulting in an asymmetric pentanuclear molecule. The formation of such a structure is unexpected, as pentanuclear complexes are usually realized in symmetric molecular structure types. The subsequent statistical analysis in the CSD revealed that, in general, complexes containing an even number of metals are more common. The origin of this observation is not clear, and although we were able to make suppositions that the symmetry of the coordination core as well as the ratio of the number of μ_n-X bridging atoms to the number of metal centers plays a crucial role, the detailed understanding of this fact requires further theoretical investigations.

Experimental Section

All chemicals were of reagent grade and used as received. All experiments were carried out in air. Elemental analyses for metals were performed by atomic absorption spectroscopy by the Department of Chemistry, National Taras Shevchenko University of Kiev. Infrared spectra were recorded as KBr discs with a Spectrum BX-FT IR "Perkin–Elmer" spectrophotometer in the 4000–400 cm^{-1} region.

Synthesis of $[Cu_2CoNi_2(Me_2Ea)_5Cl_5(H_2O)]\cdot CH_3CN\cdot H_2O$: Copper powder (0.16 g, 2.5 mmol), $CoCl_2\cdot 6H_2O$ (0.6 g, 2.5 mmol), $NiCl_2\cdot 6H_2O$ (0.59 g, 2.5 mmol), CH_3CN (20 mL), and 2-(dimethylamino)ethanol (1.5 mL, 15 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 successive addition of diethyl ether. They were filtered off, washed with CH_3CN and finally dried in vacuo at room temperature. Yield: 0.27 g, 22% (per copper). $C_{22}H_{57}Cl_5CoCu_2N_6Ni_2O_7$ (998.42): calcd. C 26.47, H 5.75, Co 5.90, Cu 12.73, N 8.42, Ni 11.76; found C 26.5, H 5.60, Co 5.70, Cu 12.80, N 8.50, Ni 11.5.

Crystal Structure Determination: Diffraction data were collected with a Bruker SMART CCD area-detector diffractometer (ω scans) equipped with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The data were corrected for the effects of absorption by using the multiscan method of SADABS.[24] The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with the program SHELXL-97.[25] Water molecule H atoms were refined with geometrical restraints. All remaining H atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the isotropic displacement parameter of the parent atom. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms. The C51, C511 and C512 atoms of one amino alcohol ligand were modeled as being disordered, the populations of the two components refining to 0.818(6) and 1–0.818(6). All bond lengths and angles within the amino alcohol, chloride, and water ligands are as expected.

Details of X-ray Analysis: $C_{22}H_{57}Cl_5CoCu_2N_6Ni_2O_7$, M = 998.42, Triclinic $P\bar{1}$, a = 11.4714(12) Å, b = 11.5610(12) Å, c = 16.446(2) Å, α = 84.177(3)°, β = 72.976(3)°, γ = 71.435(2)°, V = 1976.9(4) Å^3, T = 150(2) K, Z = 2, D(calc) = 1.677 g cm^{-3}, μ = 2.786 mm^{-1}, F(000) = 1026, $\theta_{\max}$ = 38.42°, 40059 reflections collected, 20371 reflections unique (R_{int} = 0.047) 13455 reflections with $I > 2\sigma(I)$; R_1, wR_2 [$I > 2\sigma(I)$] = 0.048, 0.117; R_1, wR_2 (all data) = 0.085, 0.128. GoF = 1.092, largest difference peak, hole: 1.43, –0.89 e Å^{-3}.

CCDC-738810 contains 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.

Supporting Information (see footnote on the first page of this article): Metal–metal distances, selected bond lengths and angles (Table S1), hydrogen-bonding distances and angles (Table S2), and hydrogen-bonding scheme (Figure S1) for $[Cu_2CoNi_2(Me_2Ea)_5Cl_5(H_2O)]\cdot CH_3CN\cdot H_2O$.

Acknowledgments

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