

Trinuclear, Tetranuclear, and Polymeric Cu^{II} Complexes from the First Use of 2-Pyridylcyanoxime in Transition Metal Chemistry: Synthetic, Structural, and Magnetic Studies

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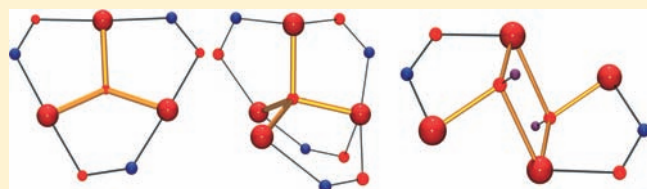
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S Supporting Information

ABSTRACT: The first use of 2-pyridylcyanoxime, (py)C(CN)NOH, in transition metal chemistry is described. Depending on the nature of the metal starting material and the reaction conditions employed, the Cu^{II}/(py)C(CN)NOH system has provided access to complexes [Cu₃O{(py)C(CN)NO}₃(NO₃)-(H₂O)₂(MeOH)] (1), [Cu₄O{(py)C(CN)NO}₄(O₂CMe)₂] (2), [Cu₄(OH)₂{(py)C(CN)NO}₂(O₂CPh)₄]_{2n} · n[Cu₄(OH)₂{(py)C(CN)NO}₂(O₂CPh)₄] (3), and [Cu{(py)C(CN)NO}₂]_n (4). The molecule of 1 consists of three Cu^{II} atoms in a strictly equilateral arrangement bridged by a central μ₃-oxide group. The molecule of 2 consists of a tetrahedron of Cu^{II} atoms held together by a central μ₄-oxide ion, four η¹:η¹:η¹:μ-(py)C(CN)NO⁻ ligands and two η¹:η¹:μ-MeCO₂⁻ groups. The crystal structure of 3 consists of [Cu₄(OH)₂{(py)C(CN)NO}₂(O₂CPh)₄]_{2n} double chains and discrete cluster [Cu₄(OH)₂{(py)C(CN)NO}₂(O₂CPh)₄] molecules. The crystal structure of 4 consists of neutral polymeric chains based on centrosymmetric mononuclear [Cu{(py)C(CN)NO}₂] units. The Cu^{II} atoms are doubly bridged by the oximate groups of two η¹:η¹:η¹:μ-(py)C(CN)NO⁻ ligands. Variable-temperature, solid-state direct current (dc) magnetic susceptibility studies were carried out for 1–4. The data indicate very strong antiferromagnetic exchange interactions for 1–3. The obtained *J* values are discussed in depth on the basis of the structural parameters of the complexes, literature reports, and existing magnetostructural correlations.



INTRODUCTION

Two classes of compounds which currently attract the intense interest of inorganic chemists are molecular clusters¹ and coordination polymers² (also known as organic–inorganic hybrid polymers in the case where the metal–organic connectivity is interrupted by “inorganic” bridges). There are many reasons for this,^{3–7} not least of which is the aesthetic beauty of their structures. For example, polynuclear three-dimensional (3d)-metal complexes often display interesting and occasionally novel magnetic properties, including high ground-state spin values,⁶ and single-molecule magnetism behavior.⁷ The 3d-metal ions have attractive features for a new generation of coordination polymers. By carefully selecting the ligand (mainly the organic one) and the metal ion, researchers aim to tune the physical properties and thus realize various applications of this class of compounds in catalysis, electrical conductivity, luminescence, magnetism, molecular electronics, nonlinear optics, sensing, zeolitic behavior, gas storage, and medicine.⁸ Coordination polymers are also significant from a structural chemistry perspective.⁹

There are now several empirically established approaches to a variety of metal clusters¹⁰ and polymers.^{2,11} One fertile route is the use of oxime ligands, since the oximate function is a good bridging group and thus fosters formation of polynuclear or

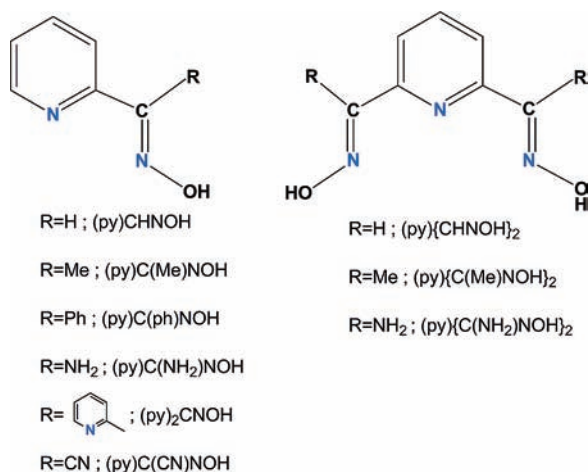
polymeric products.¹² There is currently a renewed interest in the chemistry of metal oxime systems.^{13–22} 2-pyridyl oximes²³ and 2,6-pyridyl dioximes²⁴ (Chart 1) are currently popular ligands for a variety of research objectives, including μ₂-μ₄ behaviors; the activation of 2-pyridyl oximes by 3d-metal centers toward further reaction is also becoming a fruitful area of research.²⁵ Such anionic ligands have been central “players” in several areas of single-molecule^{26,27} and single-chain²⁸ magnetism.

Efforts to date by us^{25a,b,26,27,29} and other groups^{24,28,30} have mainly concentrated on 2-pyridyl oximes bearing H, Me, Ph, NH₂, and 2-pyridyl groups as the R moiety and on 2,6-pyridyl dioxime ligands with R = H, Me, and NH₂. We have very recently extended our work to 2-pyridylcyanoxime (2-(oximino)-2-pyridylacetonitrile; (py)C(CN)NOH in Chart 1). The presence of the cyano functionality is expected to alter, because of its potential coordination capability and different electronic properties and hydrogen bonding effects, the coordination chemistry of this ligand (and hence the identity of the resultant products) in comparison with that of the (py)C(R)NOH (R = H, Me, Ph, 2-pyridyl, etc.) ligands. There are no literature reports of any

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Chart 1. Structural Formulae and Abbreviation of the Ligands Discussed in the Text



transition metal clusters or polymers of neutral or anionic (py)C(CN)NOH (only a $Tl^I/(py)C(CN)NO^-$ compound has been reported³¹), but its 2-pyridyl oxime and cyano functionalities suggested a rich potential for the isolation of such complexes. The crystal structure of the free ligand was reported³² in 1999.

In the present work, we report the first use of the (py)C(CN)OH ligand in transition metal chemistry by describing Cu^{II} clusters and polymers of the anionic form of the ligand which exhibit unusual structural features and interesting magnetic characteristics.

EXPERIMENTAL SECTION

Syntheses. All manipulations were performed under aerobic conditions using reagents (mainly from Sigma-Aldrich Inc. and Fluka AG) and solvents as received. The ligand 2-pyridylcyanoxime, (py)C(CN)NOH, was synthesized from 2-pyridylacetonitrile, KNO_2 , and glacial $MeCO_2H$ at $-50^\circ C$ following the reported method.³² $Cu(O_2CPh)_2 \cdot 2H_2O$ was prepared in high yield by the direct reaction of aqueous solutions of $CuSO_4 \cdot 5H_2O$ and NaO_2CPh in an 1:2 ratio; the compound was characterized by microanalyses and IR spectroscopy.

$[Cu_3O\{(py)C(CN)NO\}_3(NO_3)(H_2O)_2(MeOH)]$ (**1**). Solid (py)C(CN)NOH (0.029 g, 0.20 mmol) was added to a blue solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.047 g, 0.20 mmol) in MeOH (30 mL). The solid immediately dissolved, and the resulting dark green solution was stirred for 2 h, filtered, and allowed to slowly evaporate at room temperature. X-ray quality, cubic dark green crystals of the product slowly grew over a period of 10 days. The crystals were collected by filtration, washed with Et_2O (3×3 mL), and dried in air. Yield 65%. Anal. Calcd for $C_{22}H_{20}N_{10}O_{10}Cu_3$ (MW, 775.1) C, 34.09; H, 2.60; N, 18.07%. Found: C, 34.37; H, 2.47; N, 18.31%. IR (KBr, cm^{-1}): 3440mb, 1601 m, 1506 m, 1471s, 1419 m, 1383vs, 1339 m, 1306 m, 1213s, 1159w, 1110w, 1061w, 1037s, 784w, 711 m, 668vw, 553w, 422w.

$[Cu_4O\{(py)C(CN)NO\}_4(O_2CMe)_2] \cdot 0.25H_2O$ (**2**·**0.25H₂O**). Solid (py)C(CN)NOH (0.029 g, 0.20 mmol) was added to a green solution of $[Cu_2(O_2CMe)_4(H_2O)_2]$ (0.040 g, 0.10 mmol) in CH_2Cl_2 (25 mL). The solid soon dissolved, and the resulting dark green solution was stirred for 1 h, filtered, and layered with Et_2O (20 mL). Slow mixing gave polyhedral green crystals of the product after 2 days. The crystals were collected by filtration, washed with Et_2O (3×3 mL), and dried in air. The yield was ~80%. Anal. Calcd for $C_{32}H_{22}N_{12}O_9Cu_4 \cdot 0.25H_2O$ (MW, 977.3): C, 39.33; H, 2.32; N, 17.20%. Found: C, 38.98; H, 2.42; N, 17.02%. IR (KBr, cm^{-1}): 3447mb, 2224 m, 1602vs, 1559vs,

1491s, 1466vs, 1418sh, 1394s, 1345 m, 1305s, 1270s, 1232vs, 1154 m, 1105 m, 1061 m, 1037vs, 783vs, 734w, 709vs, 668 m.

$[Cu_4(OH)_2\{(py)C(CN)NO\}_2(O_2CPh)_4]_{2n} \cdot n[Cu_4(OH)_2\{(py)C(CN)NO\}_2(O_2CPh)_4] \cdot nMeCN$ (**3**·**MeCN**). Solid (py)C(CN)NOH (0.029 g, 0.20 mmol) was added to a pale blue solution of $Cu(O_2CPh)_2 \cdot 2H_2O$ (0.068 g, 0.20 mmol) in MeCN (30 mL). The solid immediately dissolved followed by an abrupt color change to dark green. The solution was stirred for 15 min, filtered, and layered with Et_2O/n -hexane (20 mL, 50:50 v/v). Slow mixing gave small green crystals of the product after 2 days. The crystals were collected by filtration, washed with Et_2O (3×3 mL), and dried in air. The yield was ~60%. Anal. Calcd for $C_{42}H_{30}N_6O_{12}Cu_4 \cdot (C_2H_3N)_{1/3}$ (MW, 1078.6): C 47.51; H, 2.90; N, 8.22%. Found: C, 47.65; H, 3.01; N, 8.40%. IR (KBr, cm^{-1}): 3425mb, 2215 m, 1593s, 1550vs, 1500w, 1472 m, 1439w, 1401s, 1362 m, 1307vw, 1224 m, 1110vw, 1039w, 778vw, 715 m, 678w.

$[Cu\{(py)C(CN)NO\}_2]_n$ (**4**). A pale pink solution of (py)C(CN)NOH (0.40 mmol) in MeCN (10 mL) was added dropwise to a stirred pale green solution of $Cu(BF_4)_2 \cdot 6H_2O$ (0.069 g, 0.20 mmol) in the same solvent (10 mL). The resulting dark green solution was stirred for a further 1 h and then allowed to slowly evaporate at room temperature. X-ray quality green crystals of the product grew over a period of 6–7 days. The crystals were collected by filtration, washed with Et_2O (4×2 mL), and dried in air. The yield was ~65%. Anal. Calcd for $C_{14}H_8N_6O_2Cu$ (MW, 355.8): C, 47.26; H, 2.27; N, 23.62%. Found: C, 47.50; H, 2.29; N, 23.80%. IR (KBr, cm^{-1}): 3335wb, 3087w, 2213 m, 1601s, 1486w, 1453vs, 1407vs, 1371s, 1353w, 1271w, 1235vs, 1165s, 1108w, 1064s, 1036vs, 1019w, 976w, 785vs, 744w, 708s, 652w, 499w, 415 m.

Physical Measurements. Magnetic susceptibility measurements were carried out on polycrystalline samples with a DMS5 Quantum Design susceptometer working in the range 30–300 K under magnetic fields of 0.3 T and under a field of 0.03T in the 30–2 K range to avoid saturation effects. Diamagnetic corrections were estimated from Pascal Tables. Infrared spectra (4000 – 400 cm^{-1}) were recorded from KBr pellets on a Bruker IFS-125 FT-IR spectrophotometer. Microanalyses (C, H, N) were performed by the in house facilities of the University of Barcelona.

X-ray Crystallography. The X-ray single-crystal data of compounds **1**–**4** were collected on a Bruker-AXS SMART APEX CCD diffractometer with graphite-monochromator utilizing Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), with ω -scans at 100(2) K. The crystallographic data, conditions retained for the intensity data collection, and some features of the structure refinements are listed in Table 1. Data processing, including Lorentz-polarization and absorption corrections using the SADABS³³ computer program were performed. The structures were solved by direct methods using the SHELXS-86³⁴ computer program, and refined by full-matrix least-squares methods, using the SHELXL-93 program incorporated in the SHELXTL/PC V 5.03 suite.³⁴ All non-hydrogen atoms were refined anisotropically. The H atoms attached to C were added theoretically and treated as riding on concerned parent atoms. H atoms attached to O atoms were located from difference Fourier maps, applied with isotropic U values, and included on fixed positions in the final refinement cycles. In case of **1**, occupancy of 0.6667 for H(42) and occupancy of 0.3333 for C(11), H(11A), H(11B), and H(11C), respectively, were applied. Occupancy of 0.50 was applied for atoms of disordered solvent water molecule in **2**, and for disordered atoms of MeCN solvent molecule in **3**, respectively.

Plots for publication were generated with ORTEP3 for Windows and plotted with Pov-Ray programs.³⁵

CCDC-799893–799896 (for **1**–**4**) contain the supplementary crystallographic data for this paper. See <http://www.rsc.org/> for crystallographic data in .cif or other electronic format.

RESULTS AND DISCUSSION

Syntheses and IR Spectra. Our general approach for the isolation of $Cu^{II}/(py)C(CN)NO^-$ compounds has been to treat

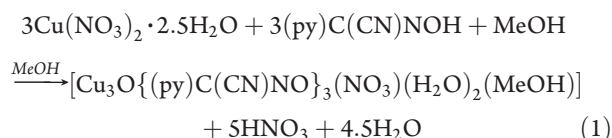
Table 1. Crystal Data and Structure Refinement for Compounds 1–4

	(1)	(2)	(3)	(4)
formula	C ₂₂ H ₂₀ Cu ₃ N ₁₀ O ₁₀	C ₃₂ H _{22.5} Cu ₄ N ₁₂ O _{9.25}	C _{42.67} H ₃₁ Cu ₄ N _{6.33} O ₁₂	C ₁₄ H ₈ CuN ₆ O ₂
mol wt	775.12	977.32	1078.61	355.81
cryst system	trigonal	monoclinic	triclinic	triclinic
space group	R $\bar{3}$	I2/a	P $\bar{1}$	P $\bar{1}$
a/Å	15.801(2)	15.875(3)	13.546(2)	4.1724(8)
b/Å	15.801(2)	25.921(5)	15.635(2)	6.963(1)
c/Å	19.599(24)	17.456(4)	16.036(3)	11.361(2)
α/deg	90	90	80.00(3)	91.37(1)
β/deg	90	94.71(3)	78.65(3)	91.03(1)
γ/deg	120	90	77.25(2)	100.72(1)
V/Å ³	4237(1)	7159(3)	3218 (1)	324.1(1)
Z	6	8	3	1
T/K	100(2)	100(2)	100(2)	100(2)
ρ _{calcd} /g m ⁻³	1.822	1.814	1.670	1.823
μ/mm ⁻¹	2.312	2.418	2.027	1.706
cryst size/mm ³	0.11 × 0.20 × 0.28	0.16 × 0.25 × 0.32	0.12 × 0.20 × 0.30	0.22 × 0.28 × 0.35
θ _{max} –θ _{min} /deg	26.3–1.8	26.0–1.4	26.4–1.3	26.4–1.8
no. reflns collected	5224	27505	25410	2513
R(int)	0.0500	0.0433	0.0814	0.029
data	1906	7031	12919	1291
params	145	521	893	106
R ^a [I > 2σ(I)]	0.0618	0.0512	0.0748	0.0543
R ^{2b} (all data)	0.1544	0.1185	0.1781	0.1309
residual/e Å ⁻³	1.242/–0.566	0.896/–0.501	1.115/–0.809	1.726/–0.522

^a $R(F_o) = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w(F_o)^2 = \{ \sum [w((F_o)^2 - (F_c)^2)^2] / \sum [w((F_o)^4)] \}^{1/2}$.

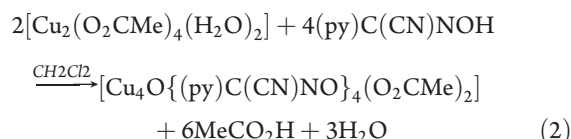
a variety of Cu^{II} sources with the ligand. Addition of external base for the deprotonation of the oxime group is not necessary because of the increased acidity of cyanoximes in comparison with other monoximes. The presence of the cyano group close to the oxime fragment makes the acidity of cyanoximes about 10³–10⁵ times greater than that of common oximes.³² A variety of reactions were explored with different solvents and under different reagent ratios, and other conditions before the following successful procedures were identified.

The 1:1 reaction between Cu(NO₃)₂·2.5H₂O and (py)C(CN)NOH in MeOH afforded a dark green solution from which was subsequently isolated [Cu₃O{(py)C(CN)NO}₃(NO₃)(H₂O)₂(MeOH)] (1) in 65% yield. Its formation is summarized in eq 1. It is remarkable that the μ₃-O²⁻ bridge is stable in an acidic reaction mixture. Small variations in the Cu^{II}/(py)C(CN)NOH ratio also gave complex 1.

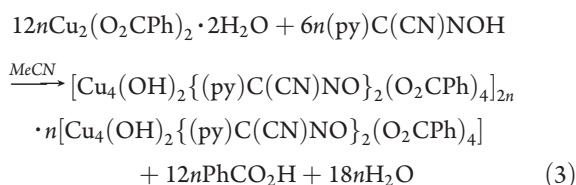


The nature of the anion present in the Cu^{II} starting material affects the product identity. The 1:2 reaction between [Cu₂(O₂CMe)₄(H₂O)₂] and (py)C(CN)NOH (Cu^{II}/ligand = 1:1) in CH₂Cl₂ afforded a dark green solution which gave [Cu₄O{(py)C(CN)NO}₄(O₂CMe)₂] (2) in high yield (~80%) upon addition of Et₂O. The preparation of the complex is summarized in eq 2. The nature of the solvent is crucial for the identity and crystallinity of the product; reaction schemes involving alcohols (MeOH, EtOH) gave non-crystalline, acetate-free materials that

we were not able to further characterize.

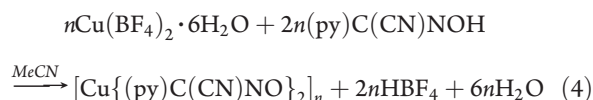


The 1:1 reaction between Cu(O₂CPh)₂·2H₂O and (py)C(CN)NOH in MeCN afforded a dark green solution from which was subsequently isolated [Cu₄(OH)₂{(py)C(CN)NO}₂(O₂CPh)₄]_{2n}·n[Cu₄(OH)₂{(py)C(CN)NO}₂(O₂CPh)₄] (3) in 60% yield, eq 3. The “wrong” Cu^{II} to (py)C(CN)NOH (4:4) reaction ratio employed for the preparation of this complex did not prove detrimental to its formation. With the identity of 3 established by single-crystal X-ray crystallography, the stoichiometric reaction ratio (4:2) was employed and led to the pure compound, albeit in lower yield.



In the above-mentioned complexes, the Cu^{II} to (py)C(CN)NOH ratio is high (1:1 in 1 and 2, and 2:1 in 3). We wondered if a compound with a lower ratio could be capable of existence. To achieve this goal we used a Cu^{II} source with a poorly coordinating anion and a low Cu^{II} to ligand reaction ratio. Thus, the 1:2 reaction between Cu(BF₄)₂·6H₂O and (py)C(CN)NOH in MeCN gave the coordination polymer [Cu{(py)C(CN)NO}₂]_n

(4) in 65% yield upon conventional workup; its formation is summarized in eq 4.



The presence of coordinated MeOH/H₂O molecules in 1 and hydroxo ligands in 3 is manifested by one broad band of medium intensity at 3440 and 3425 cm⁻¹, respectively, assigned to $\nu(\text{OH})$; their broadness and relatively low frequency are both indicative of hydrogen bonding. The in-plane deformation mode of the 2-pyridyl ring of free (py)C(CN)NOH at 633 cm⁻¹ shifts upward in the spectra of 1 (668 cm⁻¹), 2 (668 cm⁻¹), 3 (678 cm⁻¹), and 4 (652 cm⁻¹), confirming the involvement of the ring-N atom in coordination.³⁶ Several bands appear in the 1605–1365 cm⁻¹ region for the four complexes; contributions from the $\nu(\text{C}=\text{N})_{\text{oximate}}$, $\delta(\text{OH})$ [in 1 and 3 at wavenumbers higher than 1580 cm⁻¹], $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$ [in 2 and 3], and $\nu(\text{NO})_{\text{nitrate}}$ (in 1) are expected in this region, but overlap with the stretching vibrations of the aromatic (py)C(CN)NO⁻ ring renders assignments and discussion of the coordination shifts difficult. The bands at 1559 and 1418 cm⁻¹ in the spectrum of 2 are tentatively assigned to the $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$ carboxylate modes, respectively.³⁷ The parameter Δ , where $\Delta = \nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2)$, is 141 cm⁻¹, smaller than that for NaO₂CMe·3H₂O (164 cm⁻¹), as expected for the bidentate bridging mode of the acetate ligation.^{37a} The very strong band at 1383 cm⁻¹ in the spectrum of 1 is characteristic of the presence of ionic nitrates and is assigned to the $\nu_3(E')$ [$\nu_{\text{d}}(\text{NO})$] mode of the *D*_{3h} NO₃⁻ ion.³⁸ Its appearance is rather surprising because the molecule of 1 contains a coordinated nitrate group, and provides strong evidence for the replacement of the coordinated NO₃⁻ by Br⁻ ions during the preparation of the KBr pellet.³⁹ Color changes were not observed during the pellet preparation. The medium intensity band at 1055 for free (py)C(CN)NOH can be assigned to the $\nu(\text{NO})_{\text{oxime}}$ mode;^{13,29e} the wavenumber of this vibration increases to ~1100 cm⁻¹ in the spectra of the complexes. This shift to higher frequencies has been discussed^{29e,40} and is in accord with the fact that upon deprotonation and oximate-O coordination, there is a higher contribution of N=O to the electronic structure of the oximate group; consequently the $\nu(\text{NO})$ vibration shifts to a higher wavenumber relative to that for the free oxime ligand.

Description of the Structures. [Cu₃O{(py)C(CN)NO}₃(NO₃)(H₂O)₂(MeOH)] (1). A partially labeled plot of the neutral trinuclear unit present in compound 1 is shown in Figure 1 (top). Selected bond parameters are listed in Table 2. The molecule consists of three Cu^{II} atoms in a triangular arrangement bridged by central μ_3 -oxide atom O(2). Each edge of the Cu₃ triangle is bridged by an $\eta^1:\eta^1:\eta^1:\mu$ -(py)C(CN)NO⁻ ligand (I, Chart 2), with the pyridyl and oximate nitrogen atoms chelating a Cu^{II} atom and forming a five-membered chelate ring, and the oximate oxygen atom binding a neighboring metal ion. The nitrogen atom of the $\eta^1:\eta^1:\eta^1:\mu_3$ -NO₃⁻ group (II, Chart 2) and the oxide atom are located on a 3-fold symmetry axis; the triangle is thus equilateral with a Cu···Cu distance of 3.285(1) Å. The nitrate nitrogen and the oxide atoms are 2.451(4) Å above and 0.469(4) Å below the Cu₃ plane, respectively. The O(4) atom, from a disordered H₂O/MeOH ligand, completes six-coordination at each metal ion.

The Cu^{II} atoms are near-octahedral (4 + 1 + 1 coordination) exhibiting a Jahn–Teller (JT) distortion, as expected for a d⁹ ion

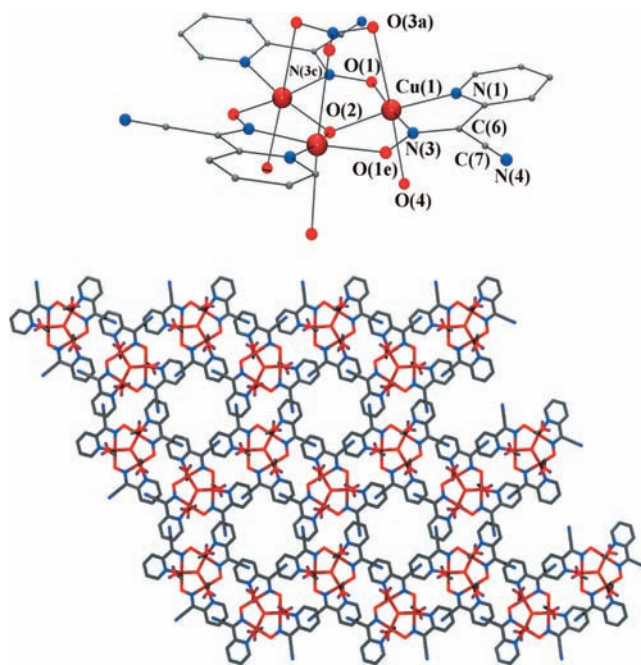
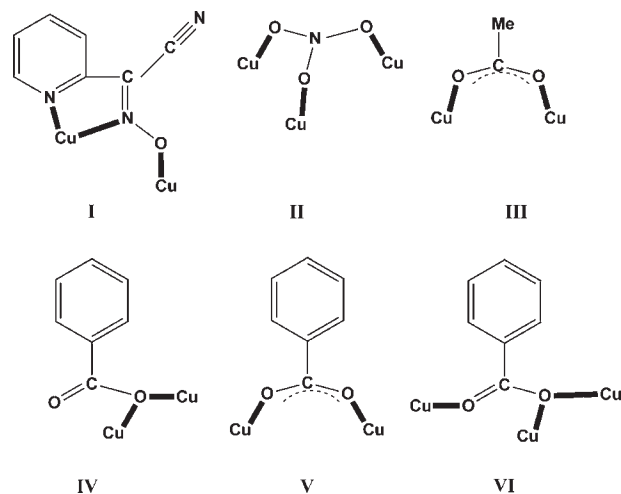


Figure 1. Partially labeled Pov-Ray plot of the trinuclear complex 1 (top) and 2D H-bonded arrangement of its triangular molecules (bottom).

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Compound 1

Cu(1)–O(1)	1.957(3)	Cu(1)–N(1)	1.981(3)
Cu(1)–O(2)	1.954(1)	Cu(1)–N(3)	2.002(3)
Cu(1)–O(3a)	2.540(3)	Cu(1)–O(4)	2.365(4)
N(3)–O(1)	1.301(5)	Cu(1)–O(1)–N(3c)	113.4(3)
C(7)–N(4)	1.141(4)	Cu(1)–N(3)–O(1e)	126.3(2)
		Cu(1)–O(2)–Cu(1c,e)	114.42(9)

Chart 2. Crystallographically Established Coordination Modes of the (py)C(CN)NO⁻, NO₃⁻, MeCO₂⁻, and PhCO₂⁻ Ligands in Complexes 1–4



in this geometry. As is most often the case for Cu^{II} atoms, the JT distortion is a pronounced axial elongation. The JT axis in 1 is the

O(nitrate)-Cu-O(H₂O/MeOH) axis, with Cu–O distances of 2.540(3) and 2.365(4) Å, respectively. The Cu–N–O–Cu torsion angles are 11.1(3)°. The angle between the mean plane of the almost planar (py)C(CN)NO[−] ligand and the Cu₃ plane is 11.08(6)°. The non-coordinated cyano groups interact by means of H bonds with the O(4) H₂O/MeOH oxygen atoms of neighboring molecules (O⋯N = 2.977(5) Å) creating a two-dimensional (2D) supramolecular arrangement of Cu₃ units placed at 120° (Figure 1, bottom). A last structural feature of **1** deserves a comment: The oximate C–N [1.309(5) Å] and N–O [1.301(5) Å] bond lengths are slightly larger and smaller than the corresponding ones [C–N = 1.287(2) Å, N–O = 1.367(2) Å] in the free ligand³² indicating that this anionic group is delocalized. Using the metallacrown terminology,^{30c,d} complex **1** is an inverse-9-MC_{CuII}{(py)C(CN)NO}₃ metallacrown.

Complex **1** is a rare example of a discrete cluster containing the {Cu₃(μ₃-O)}⁴⁺ core,⁴¹ Cu^{II}₆ clusters⁴² and coordination polymers based on Cu^{II,II,II}₃(μ₃-O) units are also known.⁴³ However, it is the first such complex with an oximate ligation. Compound **1** is structurally similar to the members of a small family^{30c,d,41e,44} of triangular Cu^{II} oximate complexes containing the {Cu₃(μ₃-X)}⁵⁺ core, where the X[−] ligand is a hydroxo or an alkoxy group. These complexes follow some general trends: (i) The Cu^{II} atoms and the oximate ligands define a plane; (ii) the central μ₃-donor is well out of this plane; (iii) axial/apical coordination sites (often 4 + 1) are occupied by anions or solvent molecules; (iv) tetrahedral anions (e.g., SO₄^{2−}, ClO₄[−]) act as tripodal bridges to one side of the molecule, whereas carboxylate or related groups are bound to opposite sides of the molecule, and (v) the central μ₃-OH[−] group (if present) participates in a strong intramolecular H bond. Except being the first oximate complex with the {Cu₃(μ₃-O)}⁴⁺ core, complex **1** is also unique because it consists of two parallel planes, one containing the three Cu^{II} atoms and the other the extremely rare η¹:η¹:η¹:μ₃ NO₃[−] group.

[Cu₄O{(py)C(CN)NO}₄(O₂CMe)₂]·0.25H₂O (**2·0.25H₂O**). A plot of the structure of complex **2·0.25H₂O** is shown in Figure 2. Selected interatomic distances and angles are listed in Table 3. The crystal structure of the complex is composed of [Cu₄O{(py)C(CN)NO}₄(O₂CMe)₂] molecules and H₂O interstitial solvent molecules; the latter do not exhibit strong H-bond interactions and will not be further discussed. The tetranuclear molecule consists of a tetrahedron of Cu^{II} atoms held together by a central O(5) μ₄-oxide ion, four η¹:η¹:η¹:μ-(py)C(CN)NO[−] ligands (I, Chart 2) and two η¹:η¹:μ-MeCO₂[−] groups (III, Chart 2). Each of the four diatomic oximate groups (O(1)/N(2), O(2)/N(5), O(3)/N(8), O(4)/N(11)) spans one edge of the tetrahedron, while each of the remaining two edges is bridged by an MeCO₂[−] group (O(6)/O(7), O(8)/O(9)). The core is {Cu₄(μ₄-O)}⁶⁺; if we consider the diatomic oximate and the triatomic carboxylate groups as parts of the core, then this is becoming {Cu₄(μ₄-O)(μ-ONR)₄(μ-O₂CMe)₂}, where RNO[−] is (py)C(CN)NO[−] (Figure 2, bottom). The Cu₄(μ₄-O) tetrahedron is moderately distorted, the Cu⋯Cu distances being between 3.045(1) and 3.258(1) Å, the Cu–O–Cu angles varying from 102.9(2) to 113.1(2)°, and the Cu–O(5) bond lengths being in the range 1.933(3)–1.957(3) Å.

Each of the Cu^{II} atoms is in a slightly (Cu(1), Cu(2), Cu(4)) or moderately (Cu(3)) distorted square pyramidal coordination environment (N₂O₂+O donor set), with atoms O(6), O(3), O(9), and O(2) occupying the apical positions of Cu(1), Cu(2), Cu(3), and Cu(4), respectively. Thus each MeCO₂[−] group links basal-apical sites belonging to different Cu^{II} atoms. The Cu^{II}

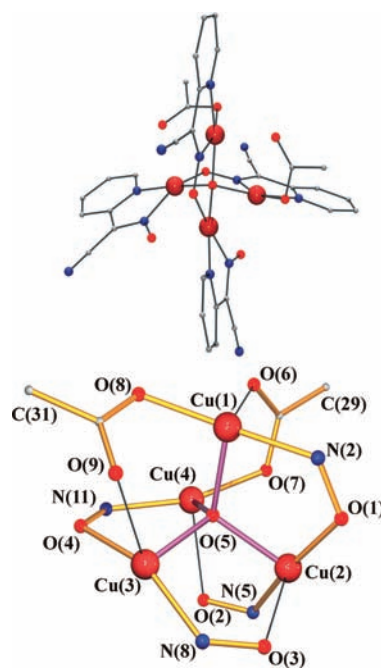


Figure 2. Structure of the tetranuclear molecule present in complex **2** (top) and labeled Pov-Ray plot of its {Cu₄(μ₄-O)(μ-ONR)₄(μ-O₂CMe)₂} core (bottom); the apical coordination bonds are shown as thin black lines.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for Compound **2**

Cu(1)–O(5)	1.947(3)	Cu(3)–O(4)	2.020(3)
Cu(1)–O(6)	2.264(3)	Cu(3)–O(5)	1.933(3)
Cu(1)–O(8)	1.954(3)	Cu(3)–O(9)	2.280(3)
Cu(1)–N(1)	2.030(4)	Cu(3)–N(7)	1.994(4)
Cu(1)–N(2)	2.015(4)	Cu(3)–N(8)	1.989(4)
Cu(2)–O(1)	1.949(3)	Cu(4)–O(2)	2.260(3)
Cu(2)–O(3)	2.204(4)	Cu(4)–O(5)	1.939(3)
Cu(2)–O(5)	1.957(3)	Cu(4)–O(7)	1.941(3)
Cu(2)–N(4)	2.004(4)	Cu(4)–N(10)	2.020(4)
Cu(2)–N(5)	1.975(4)	Cu(4)–N(11)	1.984(4)
O(1)–N(2)	1.292(5)	O(3)–N(8)	1.274(5)
O(2)–N(5)	1.292(5)	O(4)–N(11)	1.293(5)
Cu(1)–O(5)–Cu(2)	113.1(2)	Cu(2)–O(5)–Cu(3)	111.8(2)
Cu(1)–O(5)–Cu(3)	109.5(2)	Cu(2)–O(5)–Cu(4)	102.9(2)
Cu(1)–O(5)–Cu(4)	108.2(2)	Cu(3)–O(5)–Cu(4)	111.2(2)

atoms lie out of their respective basal planes toward the apical donor atoms. As expected the Cu(1)–O(6) [2.264(3) Å], Cu(2)–O(3) [2.204(4) Å], Cu(3)–O(9) [2.280(3) Å], and Cu(4)–O(2) [2.260(3) Å] bond distances are the longest. Analysis of the shape-determining bond angles using the approach of Reedijk, Addison, and co-workers⁴⁵ yields values for the trigonality index, τ , of 0.07, 0.06, 0.35, and 0.08 for Cu(1), Cu(2), Cu(3), and Cu(4), respectively ($\tau = 0$ and 1 for perfect square pyramidal and trigonal bipyramidal geometries, respectively).

No significant intra- or intermolecular H bonds are present in the crystal structure of **2·0.25H₂O**. The 2-pyridyl rings of the

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for the Three Tetranuclear Subunits of Compound 3

Isolated Subunit Cu(4)/Cu(5)			
Cu(4)–O(10)	1.911(3)	Cu(5)–O(11)	1.943(4)
Cu(4)–O(19)	1.890(3)	Cu(5)–O(17)	1.979(4)
Cu(4)–O(17)	2.495(3)	Cu(5)–O(19)	2.466(3)
Cu(4)–N(5)	1.980(5)	Cu(5)–O(19f)	1.886(3)
Cu(4)–N(9)	1.999(4)	Cu(5)–O(21)	1.985(4)
Cu(5f)–O(19)–Cu(4)	122.7(2)	Cu(5)–O(19)–Cu(5f)	95.4(1)
Cu(4)–O(19)–Cu(5)	87.1(1)		
Linked Subunits Cu(2)/Cu(1) and Cu(6)/Cu(3)			
Cu(2)–O(8)	1.963(3)	Cu(1)–O(7)	1.930(3)
Cu(2)–O(15)	1.888(3)	Cu(1)–O(13)	1.961(3)
Cu(2)–O(13)	2.621(3)	Cu(1)–O(15)	2.333(3)
Cu(2)–N(2)	1.988(4)	Cu(1)–O(15c)	1.912(3)
Cu(2)–N(7)	2.014(4)	Cu(1)–O(9)	1.987(3)
Cu(2)–O(2a)	2.546(3)		
Cu(2)–O(15)–Cu(1c)	122.7(2)	Cu(1)–O(15)–Cu(1c)	95.2(1)
Cu(2)–O(15)–Cu(1)	93.1(1)		
Cu(6)–O(6)	1.925(3)	Cu(3)–O(3)	1.952(3)
Cu(6)–O(4)	1.890(3)	Cu(3)–O(1)	1.959(3)
Cu(6)–O(1e)	2.608(4)	Cu(3)–O(4e)	2.293(3)
Cu(6)–N(1)	1.971(4)	Cu(3)–O(4)	1.899(3)
Cu(6)–N(3)	2.005(4)	Cu(3)–O(5)	1.990(3)
Cu(6)–O(14)	2.851(4)		
Cu(6)–O(4)–Cu(3)	120.7(2)	Cu(3)–O(4)–Cu(3e)	95.7(2)
Cu(6)–O(4)–Cu(3e)	94.7(1)		

four (py)C(CN)NO[−] ligands form π – π stacking interactions with symmetry-related 2-pyridyl rings of adjacent Cu₄ cluster molecules creating a 3D network.

Complex 2 is the first structurally characterized oximate complex containing the {Cu₄(μ_4 -O)}⁶⁺ core. This core is present in more than 100 tetranuclear Cu^{II} clusters, most of which have the general formula [Cu₄O_X10−*x*L_{*x*}]^{*x*−4}, where X[−] is most often Cl[−] or Br[−] and L is a monodentate ligand, and contain the {Cu₄(μ_4 -O)(μ -X)₆} core.⁴⁶

[Cu₄(OH)₂{(py)C(CN)NO}₂(O₂CPh)₄]_{2*n*} · n[Cu₄(OH)₂{(py)C(CN)NO}₂(O₂CPh)₄] · nMeCN (**3**·MeCN). The crystal structure of **3**·MeCN consists of [Cu₄(OH)₂{(py)C(CN)NO}₂(O₂CPh)₄]_{2*n*} chains, discrete [Cu₄(OH)₂{(py)C(CN)NO}₂(O₂CPh)₄] clusters, and interstitial solvent MeCN molecules. The latter do not give H-bonds and will not be further discussed. There are three independent Cu₄ subunits in the triclinic unit cell of the complex, each located on an inversion center; thus there are six crystallographically independent Cu^{II} atoms. The three Cu₄ subunits have very similar interatomic distances and angles, and thus only the subunit containing Cu(4), Cu(5) and symmetry equivalents will be discussed in some detail. The Cu(4)/Cu(5) Cu₄ subunit appears well isolated (cluster subunit) in the crystal, while the Cu(1)/Cu(2) and Cu(3)/Cu(6) tetranuclear subunits give double chains of tetramers. Selected interatomic distances are listed in Table 4.

The four Cu^{II} atoms (Cu(4), Cu(5) and symmetry equivalents) of the cluster subunit are located at four vertices of a defective dicubane⁴⁷ (two cubanes sharing one face and each missing one vertex, Figure 3) and bridged by means of oxygen

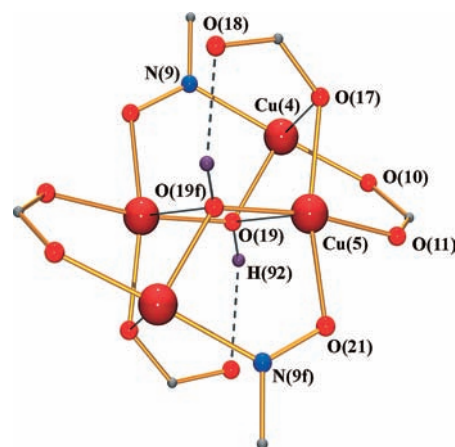


Figure 3. Partially labeled Pov-Ray plot of the {Cu₄(μ_3 -OH)₂(μ -OR)₂(μ -ONR')₂(μ -O₂CR'')₂} core that is present in the discrete Cu₄ cluster subunit of complex 3 [RO[−] and R''CO₂[−] = PhCO₂[−], R'NO[−] = (py)C(CN)NO[−]]. The symbol *f* is used for symmetry generated atoms. The dashed lines indicate H bonds.

atoms from the two μ_3 -OH[−] groups (O(19), O(19f)) and two η^2 : μ benzoate ligands (O(17), O(17f); **IV**, Chart 2). The shared face of the two cubanes is the Cu(5)O(19)Cu(5f)O(19f) one. Peripheral ligation is provided by two η^1 : η^1 : μ -(py)C(CN)NO[−] ligands (**I**, Chart 2) and two *syn-syn* η^1 : η^1 : μ -PhCO₂[−] groups (O(10)/O(11) and symmetry equivalents; **V**, Chart 2). The core is {Cu₄(μ_3 -OH)₂(μ -OR)₂}⁴⁺, where RO[−] is PhCO₂[−]. If we consider the diatomic oximate and the *syn-syn* carboxylate groups as parts of the core, then this is becoming {Cu₄(μ_3 -OH)₂(μ -OR)₂(μ -ONR')₂(μ -O₂CR'')₂}, where R'NO[−] is (py)C(CN)NO[−] and R''CO₂[−] is PhCO₂[−]; this view of the core is illustrated in Figure 3. The triply bridging hydroxo oxygen atom O(19) forms two strong bonds [1.890(3) and 1.886(3) Å] to Cu(4) and Cu(5f), and one weaker [2.466(3) Å] to Cu(5). The bridging Cu(4,5)-O(17) distances [2.495(3) and 1.979(4) Å] are fully asymmetric; this is a consequence of the basal/apical coordination of this atom. The Cu(4)–N(9)–O(21f)–Cu(5f) torsion angle is 103.5(5)°.

Atoms Cu(4) and Cu(5) adopt slightly distorted square pyramidal coordination geometries with τ values of 0.17 and 0.18, respectively. The chromophores are Cu(4)N₂O₃ and Cu(5)O₅. The apical positions for Cu(4) and Cu(5) are occupied by the doubly bridging benzoate atom O(17) and the triply bridging hydroxo atom O(19), respectively. The hydroxo atom O(19) is at basal coordination sites of Cu(4) and Cu(5f), and at the apical site of Cu(5).

There is one strong intramolecular H bond with the hydroxo oxygen (O(19), O(19f)) as the donor and the uncoordinated benzoate oxygen (O(18f), O(18)) as the acceptor; the O(19f) ··· O(18) distance is 2.604(6) Å. There is a weak π – π stacking interaction between the aromatic ring of the one of the PhCO₂[−] groups and the pyridyl ring of the (py)C(CN)NO[−] ligand; the rings are quasi parallel with a distance between centroids of 3.609(8) Å.

As mentioned above, the packing of complex 3·MeCN (Figure 4, left) reveals the formation of polymeric chains through alternation of the Cu(1)/Cu(2) and Cu(3)/Cu(6) tetranuclear subunits. The intertetramer linkage is provided by two η^1 : η^2 : μ -PhCO₂[−] groups (**VI**, Chart 2) per tetramer (Figure 4, right); these groups are η^2 : μ in the Cu(4)/Cu(5) discrete subunit. In

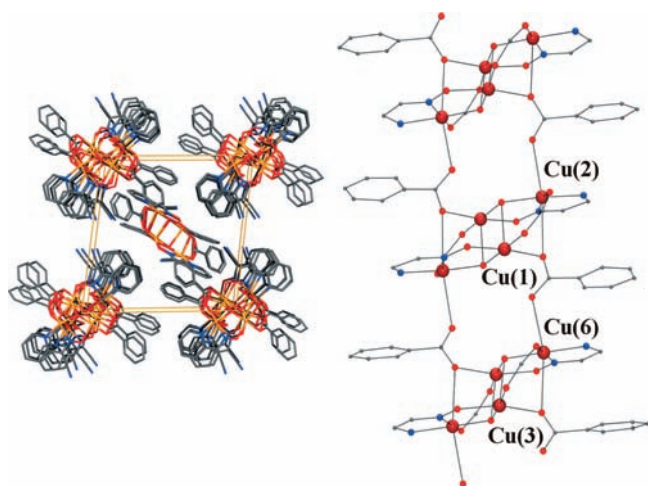


Figure 4. Packing of complex 3·MeCN showing the chains of the alternating Cu(1)/Cu(2) and Cu(3)/Cu(6) Cu_4 subunits and the discrete Cu(4)/Cu(5) tetranuclear cluster units (left), and the 1D arrangement of the Cu(1)/Cu(2) and Cu(3)/Cu(4) subunits by means of carboxylate bridges (right); in the right view the $\eta^1:\eta^1:\mu$ PhCO_2^- groups are not shown for clarity.

the chain the $\eta^1:\eta^2:\mu$ - PhCO_2^- and 2-pyridyl rings of neighboring Cu_4 subunits are parallel at 3.688(8) and 3.555(8) Å, providing significant interactions. These interactions bring the Cu_4 subunits closer allowing the free, that is, uncoordinated benzoate oxygen atoms of one subunit to axially coordinate Cu^{II} atoms of two neighboring Cu_4 subunits. In the discrete cluster subunit, Cu(4) exhibits a square pyramidal coordination, whereas the corresponding Cu(2) and Cu(6) atoms are becoming octahedral (4 + 2 coordination) in the chain. The PhCO_2^- groups have also been modified; in the discrete Cu(4)/Cu(5) Cu_4 subunit, the O(18)–O(17)–Cu(5)–O(19f) torsion angle is 3.15(3)°, and the dihedral angle between the O(17)–C(61)–O(18) carboxylate plane and the PhCO_2^- aromatic ring is 17.7(6)°; the corresponding parameters for the Cu(1)/Cu(2) and Cu(3)/Cu(6) tetranuclear subunits in the chain are 28.1(6)°/26.1(6)° and 30.7(6)°/40.2(6)°, respectively. The intertetramer interactions from the axial benzoate coordination to Cu(2) and Cu(6) also induce intracluster bonding parameter changes; the most significant change is in the Cu–N–O–Cu torsion angle, which is 10.3(5)° for the discrete Cu(4)/Cu(5) cluster subunit, and 6.9(5)° and 0.7(4)° for the Cu(1)/Cu(2) and Cu(3)/Cu(6) tetranuclear subunits, respectively, of the chain.

Complex 3 is the first defective dicubane Cu^{II} cluster with oximate ligation. Several Cu_4 clusters containing the $\{\text{Cu}_4(\mu_3\text{-OH})_2\}^{6+}$ unit, most of them with the defective dicubane motif, have been structurally characterized.^{44b,48} This unit is also a recognizable fragment of higher nuclearity Cu^{II} clusters.⁴⁹ Of some relevance to the structure of 3 is complex $[\text{Cu}_4(\mu_3\text{-OH})_2(\text{O}_2\text{CMe})_6(4\text{pds})_2]_m$ ⁵⁰ where 4pds is the twisted ligand 4,4'-dithiobis(pyridine). The compound has a 1D structure composed of an alternate linking of one rhomboid (and not defective dicubane because of the lack of doubly bridging oxygen atoms) $\{\text{Cu}_4(\mu_3\text{-OH})_2(\text{O}_2\text{CMe})_6\}$ unit and two 4pds ligands. The structural motif of 3 with the simultaneous presence of polymeric chains and isolated clusters is unprecedented in transition metal oximate chemistry.

$[\text{Cu}\{\text{(py)C(CN)NO}\}_2]_n$ (**4**). Complex 4 crystallizes in the triclinic space group $P\bar{1}$. A partially labeled plot of its asymmetric

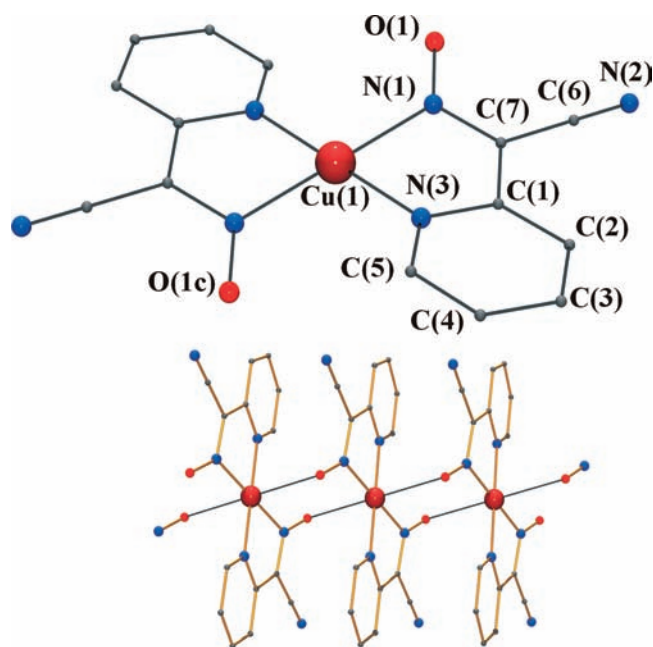


Figure 5. Partially labeled Pov-Ray plot of the asymmetric unit of complex 4 (top) and the 1D arrangement of the $\text{Cu}\{\text{(py)C(CN)NO}\}_2$ units (bottom).

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for the Asymmetric Unit of Compound 4

Cu(1)–N(1)	2.009(3)	Cu(1)–N(3)	2.007(3)
Cu(1)–(1a)	2.633(3)	O(1)–N(1)	1.292(4)
N(1)–Cu(1)–N(3)	80.9(1)	N(1)–Cu(1)–N(3c)	99.1(1)
Cu(1)···Cu(1b)	4.1724(8)	Cu(1)–N(1)–O(1)–Cu(1b)	79.1(3)

unit is shown in Figure 5 (top). Selected interatomic distances and angles are listed in Table 5. Its crystal structure consists of neutral polymeric chains based on centrosymmetric mononuclear $[\text{Cu}\{\text{(py)C(CN)NO}\}_2]$ units; a portion of one such chain is shown in Figure 5 (bottom). The Cu^{II} atoms are doubly bridged by the oximate groups of two $\eta^1:\eta^1:\eta^1:\mu$ - $(\text{py)C(CN)NO}^-$ ligands (**I**, Chart 2).

Each ligand chelates one Cu^{II} atom forming two 5-membered CuNCCN chelating rings, while its deprotonated oximate oxygen atom is terminally bound to a neighboring metal ion; the cyano group of the ligand remains uncoordinated.

The coordination geometry about the Cu^{II} center is described as elongated octahedral (4 + 2); the two symmetry-related oximate oxygen atoms define the JT axis of the metal [Cu(1)–O(1a) = 2.633(3) Å]. The equatorial bond angles deviate from the ideal 90° value because of the restriction imposed from the chelating ring, with the N(1)–Cu(1)–N(3) angle being 80.9(1)°. The metal···metal distance is 4.1724(8) Å. Significant H bonds or/and π – π stacking interactions were not located in the crystal structure. Compound 4 is the first chain polymer of any transition metal ion containing double oximate bridges.

Magnetic Measurements and Correlations. Variable-temperature direct current (dc) magnetic susceptibility studies were performed on powdered samples of compounds **1**–**4** in applied fields of 0.3 T (300–30 K) and 0.03 T (30–2.0 K). The

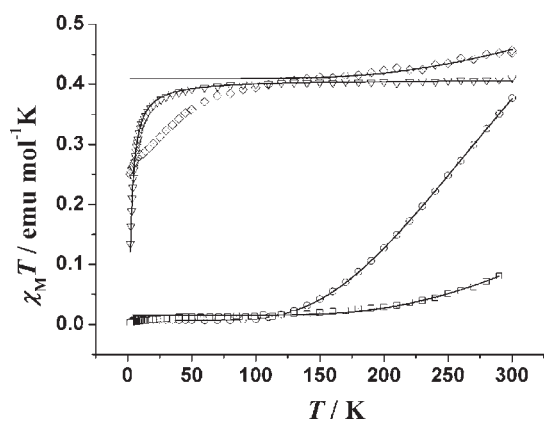
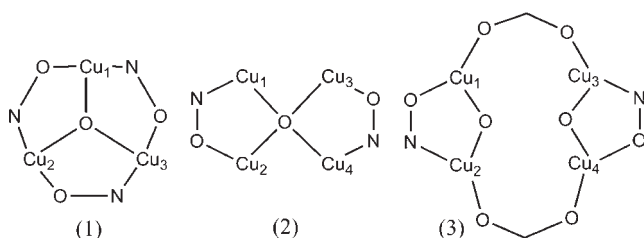


Figure 6. Plot of the $\chi_M T$ product versus T for compounds **1** (diamonds), **2** (dot centered circles), **3** (squares), and **4** (triangles). The solid lines are the fits of the data; see the text for the fit parameters.

Chart 3. Main Superexchange Pathways for Compounds **1–3**^a



^aWeak interactions as those derived from axial-equatorial interactions have been suppressed in the simplified cores.

data are plotted as $\chi_M T$ versus T in Figure 6. The room temperature $\chi_M T$ value for complex **1** is $0.46 \text{ cm}^3 \text{ K mol}^{-1}$. This value is much lower than the value of $1.125 \text{ cm}^3 \text{ K mol}^{-1}$ with $g = 2.0$ expected for a complex of three noninteracting $S = 1/2$ spins, indicating a very strong antiferromagnetic coupling even at 300 K. The $\chi_M T$ product decreases slightly with decreasing temperature in the range 300–150 K to a value of $0.41 \text{ cm}^3 \text{ K mol}^{-1}$ that agrees very well with the expected one for an $S = 1/2$ ground state. The curve shows a plateau around 150 K before a more rapid decrease of $\chi_M T$ below this temperature to a minimum value of $0.25 \text{ cm}^3 \text{ K mol}^{-1}$ at 2.0 K. The decrease below ~ 150 K is attributed to the antisymmetric exchange interaction⁵¹ which plays an important role in the magnetic behavior of triangular Cu^{II} complexes.^{44c,51} Because of the 3-fold symmetry of the complex (Chart 3, left) and to the antisymmetric exchange, the fitting of the experimental data was performed in the 300–150 K range by means of the analytical expression derived from the isotropic spin Hamiltonian given by eq 5.

$$H = -J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_3) \quad (5)$$

The best-fit parameters are $J = -485 \text{ cm}^{-1}$ and $g = 2.091$. As it is very common in oximate-bridged Cu^{II} complexes,^{12,23,41d} the superexchange interaction is strongly antiferromagnetic. Comparison with similar systems is not easy because the number of the magnetically studied Cu^{II} triangles is not large and additional axial bridging often modifies the value of the coupling constant. It should be mentioned at this point that the relationship of J values to the $\text{Cu}-\text{O}-\text{Cu}$ angle in complexes possessing the $\{\text{Cu}^{\text{II}}_3(\mu_3\text{-O})\}^{4+}$ core has been discussed and analyzed.⁵² In an excellent

theoretical study on complexes containing the $\{\text{Cu}^{\text{II}}_3(\mu_3\text{-O}/\text{OH})(\mu\text{-ONR}')_3\}^{+/2+}$ unit, Tangoulis, Tsipis, Kessissoglou, and co-workers have derived^{30c} the linear correlation $J (\text{cm}^{-1}) = 1068.4R - 937.7$, where R is the distance of the $\mu_3\text{-O}^{2-}/\text{OH}^-$ group from the centroid of the Cu_3 triangle. The R value for **1** is 0.469 \AA and the predicted J value is -436.6 cm^{-1} , in good agreement with the value derived from the fitting procedure (-485 cm^{-1}).

The $\chi_M T$ values at room temperature for **2** and **3** are 0.37 and $0.08 \text{ cm}^3 \text{ K mol}^{-1}$, respectively. These values are much lower than the expected one ($1.50 \text{ cm}^3 \text{ K mol}^{-1}$ with $g = 2.0$) for a system comprising four noninteracting Cu^{II} centers. The $\chi_M T$ products rapidly decrease with decreasing temperature, reaching a constant value very close to zero below ~ 100 K. The χ_M values show a continuous decrease upon cooling, and the curves show broad minima at ~ 85 K (**2**) and ~ 130 K (**3**), but below these temperature they slightly increase because of the presence of small amounts of paramagnetic, possibly monomeric impurities. The maxima in the χ_M versus T plots should be located above room temperature in both cases. The just described behavior is indicative of very strong antiferromagnetic interactions between the Cu^{II} centers.

Close inspection of the molecular structure of **2** reveals that the main exchange interactions should be through the central $\mu_4\text{-O}^{2-}$ group and the oximate groups (N(2)/O(1) and N(11)/O(4) in Figure 2) that connect basal coordination sites of the Cu^{II} atoms. The weak basal-apical interactions can be neglected in the fitting procedure. On this basis, the fitting of the experimental data was performed by using the analytical equation derived from the spin Hamiltonian of eq 6. J_1 corresponds to the four exchange interactions mediated by the $\mu_4\text{-O}^{2-}$ group, and J_2 to the two interactions mediated by the central oxide group and one oximate bridge (Chart 3, middle). Best fit parameters are $J_1 = -81 \text{ cm}^{-1}$, $J_2 = -484 \text{ cm}^{-1}$, and $g = 2.154$.

$$H = -J_1(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_4) - J_2(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_3 \cdot \hat{S}_4) \quad (6)$$

Comparison with similar systems is not possible because there have been no reports for oximate complexes containing the $\{\text{Cu}_4(\mu_4\text{-O})\}^{6+}$ core. The J_1 value can be compared with the value of -120 cm^{-1} obtained for complex $[\text{Cu}_4(\mu_4\text{-O})(\text{bahped})_2](\text{ClO}_4)_2$,⁵³ where bahped²⁻ is the dianion of 1,3-bis-[3'-aza-4'-(3-methyl-2'-hydroxyphenyl)prop-4-en-1'-yl]-ethane-1,2-diamine; this complex is the first of this family not having any additional oligoatomic bridge between Cu^{II} atoms other than the $\mu_4\text{-O}^{2-}$ ion. The J_2 value is not unexpected in view of the remarkable ability of the oximate bridges to mediate strong antiferromagnetic exchange between Cu^{II} centers.^{12,23,30c,d,54}

The three Cu_4 subunits that are present in the crystal structure of **3** have very similar interatomic distances and angles, and we thus assume that they are magnetically similar. According to the interaction picture shown in Chart 3 (right), the analysis of the experimental data was based on the spin Hamiltonian of eq 7. J_1 is the coupling constant that corresponds to the double hydroxo/oximate bridge, and J_2 describes the exchange interaction through the single *syn-syn* carboxylato bridge.

$$H = -J_1(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_3 \cdot \hat{S}_4) - J_2(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_4) \quad (7)$$

Best fit parameters are $J_1 = -854 \text{ cm}^{-1}$ and $g = 2.101$, with J_2 undetermined. With a so large value for J_1 , it is mathematically not reliable to try to calculate J_2 . We performed fits fixing J_2 in the

–100 to 0 cm⁻¹ range (the $J_2 = 0$ value corresponds to the dinuclear model) checking that J_2 did not modify the excellent quality (Figure 6) of the fits. On the basis of the linear correlation between $-J/n$ and a (n is the number of carboxylato bridges and a the Cu–O–Cu angle), established by Chaudhuri's/Wieghardt's group for Cu^{II}₂ complexes bridged by *syn, syn* carboxylates,⁵⁵ we would expect a value close to ~50 cm⁻¹ for J_2 .

The room temperature $\chi_M T$ value for complex 4 is 0.41 cm³ K mol⁻¹. This value is close to the expected value of 0.375 cm³ K mol⁻¹ with $g = 2.0$ for one $S = 1/2$ spin. The $\chi_M T$ product shows a constant value down to 50 K, and for lower temperatures it decreases to a value of 0.13 cm³ K mol⁻¹ at 2 K, indicating a very weak antiferromagnetic coupling. Experimental data were fitted to the analytical expression derived from the Hamiltonian:⁵⁶

$$H = -\sum J(\hat{S}_i \cdot \hat{S}_{i+1}) \quad (8)$$

Best fit parameters were $J = -1.33(1)$ cm⁻¹ and $g = 2.086(2)$. This weak interaction is in good agreement with the structural data which only show axial–equatorial interactions between neighbor Cu^{II} atoms along the chain.

The great difference between the J_2 value for 2 (–484 cm⁻¹) and the J_1 value for 3 (–854 cm⁻¹) seems, at a first glance, surprising. Both refer to exchange interactions through the O²⁻ or OH⁻/oximate bridging system. However, in the light of recent density functional theory (DFT) calculations on triangular {Cu^{II}₃(μ -O/OH)(μ -ONR')₃}^{+2/+} systems,^{30c} which have correlated J with the degree of the pyramidal distortion of the Cu₃O(H) fragment (this distortion is expressed by the R parameter mentioned above or the equivalent Cu–O(H)–Cu bond angles), we may extrapolate the conclusion to isolated Cu–O(H)/oximate–Cu fragments that are present in higher nuclearity Cu^{II} clusters; thus, the strong antiferromagnetic coupling may be tuned by the Cu–O(H)–Cu bond angle. The only known compound containing dinuclear Cu–OH⁻/oximate–Cu units is the centrosymmetric trinuclear complex [Cu₃(OH)₂(L)₂(H₂O)₂](NO₃)₂,⁵⁷ where L⁻ is the monoanion of 2-[2-(α -pyridyl)ethyl]imino-3-butanone oxime. The Cu–O–Cu bond angle is 118.6(1)° and the J value is ~–900 cm⁻¹. This value compares well with the –854 cm⁻¹ value (J_1) obtained for 3 exhibiting an average Cu–O–Cu bond angle of ~122°. On the contrary, the average Cu–O–Cu bond angle within the Cu–O²⁻/oximate–Cu fragments of complex 2 (the Cu1–O5–Cu2 and Cu3–O5–Cu4 angles in the real structure, see Figure 2) is 112.2°, significantly smaller than the corresponding bond angles in 3 and [Cu₃(OH)₂(L)₂(H₂O)₂](NO₃)₂.⁵⁷ It seems that, the tetrahedral O²⁻ coordination, which gives smaller Cu–O–Cu angles, is responsible for the much weaker antiferromagnetic J_2 interaction in the oxo-bridged cluster 2 compared with the J_1 interaction in the hydroxo-bridged compound 3 (–484 cm⁻¹ vs –854 cm⁻¹). A great pyramidal distortion at the oxygen bridge (approaching sp³) leads to a situation where less efficient magnetic orbital overlap with the oxygen bridge occurs, thus significantly reducing antiferromagnetic coupling.^{48h}

CONCLUSIONS

We began this work asking whether the first use of 2-pyridylcyanoxime in transition metal chemistry would provide a route to Cu^{II} oximate cluster and polymer types not available until now, and the answer is clearly “yes”. The use of the NO₃⁻ / (py)C(CN)NO⁻, RCO₂⁻ / (py)C(CN)NO⁻ (R = Me, Ph) and BF₄⁻ / (py)C(CN)NO⁻ combinations in Cu^{II} chemistry has

provided access to two new clusters (1, 2), one 1D coordination polymer (4) and to one compound containing both chains and isolated cluster molecules (3). The obtained products are structurally interesting in multiple ways, as described in detail, and their structural motifs have not been seen before in the coordination chemistry of 2-pyridyl oximes. Compounds 1–3 also provide additional examples of Cu^{II} complexes with extremely strong (but also variable) antiferromagnetic coupling between the metal ions.

Our initial results described in this work suggest that reactions of (py)C(CN)NOH with Cu^{II} in the presence of coligands with a strong coordination ability other than nitrates and carboxylates (e.g., Cl⁻, Br⁻, N₃⁻, OCN⁻, SCN⁻, SO₄²⁻, β -diketonates, etc.) and with other paramagnetic 3D-metal ions (Mn^{II}, Mn^{III}, Fe^{II}, Fe^{III}, Co^{II}, and Ni^{II}) promise to deliver many new clusters and coordination polymers with interesting properties. We are also pursuing the employment of (py)C(CN)NO⁻ for the synthesis of mixed 3d/4f-metal clusters to study their magnetic and optical properties. A final goal of our future work will be to give a bioinorganic chemistry flavor in our efforts. Since (i) (py)C(CN)NOH has the propensity toward formation of Cu^{II}₃(μ ₃-O) species, and (ii) redox-active triangular Cu^{II} complexes are found at the active sites of important metallobiomolecules,^{5,41a,42} the road is open for the synthesis and study of bioinorganic models based on the 2-pyridylcyanoximate ligand, as successfully carried out by Raptis' group with the use of pyrazolates.^{41a,d}

ASSOCIATED CONTENT

S Supporting Information. Crystallographic data for complexes 1, 2·0.25H₂O, 3·MeCN, and 4 in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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