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Syntheses, Structures, and Reactivity of Polynuclear Pyrazolato Copper(I) Complexes, Including an ab-Initio XRPD Study of $[Cu(dmnpz)]_3$ (Hdmnpz = 3,5-Dimethyl-4-nitropyrazole)

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The reaction of $[Cu(CH_3CN)_4](BF_4)$ with 3,5-dimethyl-4-nitropyrazole (Hdmnpz) in the presence of triethylamine yields the new copper(I) complexes $[Cu(dmnpz)]_3$ (**1**) and $(Et_3NH)_2[Cu_4(dmnpz)_6]$ (**2**), depending on the experimental conditions. The reactivity of **1** and **2** toward neutral ligands such as triphenylphosphine, cyclohexyl isocyanide (RNC), and carbon monoxide has been investigated. In particular, both complexes readily react with RNC, giving the dinuclear complexes $[Cu(dmnpz)(RNC)]_2$ (**4**) and $[Cu(dmnpz)(RNC)_2]_2$ (**5**), depending on the copper/RNC ratio, and with PPh_3, affording the dimeric derivative $[Cu(dmnpz)(PPh_3)]_2$ (**6**). The crystal and molecular structure of **1** has been determined ab initio using X-ray powder diffraction data from conventional laboratory equipment. Crystals of **1** are monoclinic, $C2/c$, $a = 20.057(2)$ Å, $b = 13.816(2)$ Å, $c = 7.883(1)$ Å, $\beta = 95.912(4)°$; R_F and R_{wp} 0.067 and 0.039, respectively, for Rietveld refinement on 3900 data points collected in the range $17 < 2\theta < 95°$ (Cu Kα radiation). Crystals of **1** contain planar trimers, with the copper atoms bridged by exo-bidentate ligands and short *intermolecular* Cu⋯Cu contacts (3.329(7) Å). For complexes **2** and **4**−**6**, single-crystal X-ray diffraction studies have been performed. Crystals of **2** are monoclinic, $P2_1/c$, $a = 11.026(1)$ Å, $b = 13.456(2)$ Å, $c = 18.668(5)$ Å, $\beta = 92.91(2)°$, $Z = 2$. The ionic packing of **2** contains tetranuclear complexes, with the copper atoms connected by six dmnpz ligands. Crystals of **4** are triclinic, $P\bar{1}$, $a = 7.418(1)$ Å, $b = 9.780(1)$ Å, $c = 11.177(3)$ Å, $\alpha = 109.61(2)$; $\beta = 101.34(3)°$, $\gamma = 105.82(1)°$, $Z = 2$. Crystals of **5** are triclinic, $P\bar{1}$, $a = 9.506(4)$ Å, $b = 9.957(2)$ Å, $c = 11.658(4)$ Å, $\alpha = 86.73(2)°$, $\beta = 79.54(2)°$, $\gamma = 82.47(4)°$, $Z = 1$. Crystals of **6** are triclinic, $P\bar{1}$, $a = 11.379(2)$ Å, $b = 13.592(2)$ Å, $c = 14.409(3)$ Å, $\alpha = 81.22(1)°$, $\beta = 85.21(1)°$, $\gamma = 87.55(1)°$, $Z = 2$. **4**, **5**, and **6** are binuclear complexes bearing *one* RNC, *two* RNC, and *one* triphenylphosphine ligands on each copper atom, respectively. The steric requirement of the dmnpz ligands, in the presence of RNC or PPh_3, forces the inner $[Cu_2(dmnpz)_2]$ core of the three complexes into markedly different conformations.

Introduction

The synthesis of di- and polynuclear complexes having ligands which maintain the metal centers in close proximity is an important objective in coordination metal chemistry. Interest in such systems arise mainly because of their potential role in multi-metal-centered catalysis in both biological and industrial reactions.[2] The major effort in this field is to find convenient binucleating ligands able to attain this goal. Deprotonated pyrazoles (pyrazolate anions) represents a significant class of binucleating ligands because of their capability of coordinating in an exo-bidentate fashion.[3,4]

In the recent past, we have been particularly interested in the synthesis, structural characterization and reactivity of copper(I) complexes containing exo-bidentate pyrazolate ligands, focusing our interest on the ability of these derivatives, of general formula $[Cu(pz^*)]_n$, to act as selective catalysts in the oxidation of organic substrates such as aliphatic and aromatic amines.[5]

With the aim of obtaining a deeper insight into the understanding of the steric and electronic factors that govern the nuclearity and the chemical behavior of this class of copper(I) derivatives, we began a systematic study using different pyrazoles whose donor capabilities and steric accessibility were modified by introducing substituents on the heterocyclic ring, demonstrating the structural versatility caused by the nature of the pyrazolate ligands.[6]

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In this paper we continue with our study, reporting the synthesis of two new homoleptic copper(I) pyrazolate complexes, the trinuclear $[Cu(dmnpz)]_3$ and the tetranuclear anionic $[Cu_4(dmnpz)_6]^{2-}$ species, derived from reaction of $[Cu(CH_3CN)_4](BF_4)$ with 3,5-dimethyl-4-nitropyrazole (Hdmnpz), their full structural characterization, and their reactivity with neutral ligands. The full structural characterization of the dimeric species obtained by reaction of these derivatives with cyclohexyl isocyanide and triphenylphosphine is also reported.

Results and Discussion

Synthesis of the Homoleptic Pyrazolato Complexes 1 and 2. The reaction of $[Cu(CH_3CN)_4](BF_4)$ and 3,5-dimethyl-4-nitropyrazole in acetone in the presence of triethylamine leads to the formation of two distinct products, depending on the experimental conditions.

The highly insoluble, white trinuclear derivative $[Cu(dmnpz)]_3$ (**1**) was obtained employing a 1:1 copper/dmnpz molar ratio (eq 1).

$$3[Cu(CH_3CN)_4](BF_4) + 3Hdmnpz + 3Et_3N \xrightarrow{-CH_3CN} \underset{(\mathbf{1})}{[Cu(dmnpz)]_3} + 3(Et_3NH)BF_4 \tag{1}$$

It is useful to note that the copper/dmnpz ratio required in eq 1 can be attained by carrying out the reaction either with a stoichiometric amount of Hdmnpz (and excess of Et_3N) or, alternatively, with excess Hdmnpz and stoichiometric triethylamine. In the presence of both Hdmnpz and Et_3N in excess, the orange ionic $(Et_3NH)_2[Cu_4(dmnpz)_6]$ (**2**) species was isolated instead. Indeed, the formation of **2** can be achieved by means of a true titration, adding Et_3N dropwise into an acetone solution of $[Cu(CH_3CN)_4](BF_4)$ and Hdmnpz; the formation of complex **1**, as a white suspension, was initially observed and is followed (in the presence of excess Et_3N) by its gradual dissolution to give a clear, orange solution of **2**. This observation, together with the fact that reaction of **1** with excess Hdmnpz in the presence of Et_3N quantitatively affords complex **2** (eq 2), strongly indicates that **1** is the intermediate species in the formation of **2**.

$$\underset{(\mathbf{1})}{4[Cu(dmnpz)]_3} + 6Hdmnpz \xrightarrow{Et_3N} \underset{(\mathbf{2})}{3(Et_3NH)_2[Cu_4(dmnpz)_6]} \tag{2}$$

It is well-known that group 11 metals in the +1 oxidation state form neutral binary compounds of general formula $[Cu(pz^*)]_n$ with the deprotonated form of several pyrazoles (Hpz*). The few structurally characterized systems have been found to possess a variety of molecular arrangements and oligomeric or polymeric structures, with a definite tendency of forming trimeric species.[7] Thus, on the basis of these considerations, the formation of the neutral trinuclear species $[Cu(dmnpz)]_3$ (**1**) is not unexpected.

The formation of the ionic species **2** is more surprising. The synthetic method described above (eq 1) has been verified to work well for a large series of pyrazoles.[8] In all cases, the formation of homoleptic, neutral $[Cu(pz^*)]_n$ derivatives (Hpz* = pyrazole, $n = \infty$;[9] 3,5-dimethylpyrazole, $n = 3$;[7a] 3,5-diphenylpyrazole, $n = 4$[7b]) has been observed, independent of the Cu/Hpz*/Et_3N ratios employed. The formation of $(Et_3NH)_2[Cu_4(dmnpz)_6]$ seems to be driven by the peculiar electronic properties of the 3,5-dimethyl-4-nitropyrazole rather than by steric effects. Notably, 3,5-dimethylpyrazole, possessing a steric hindrance comparable to that of Hdmnpz but deeply differing in the electronic properties,[10] gives rise to only the neutral trinuclear $[Cu(dmpz)]_3$ derivative.[7a,8]

Behavior of 2 in Solution. Complex **2** is quite stable when dissolved in deoxygenated acetone in the presence of free triethylamine. In the absence of Et_3N, fast dissociation of the dmnpz anion takes place and quantitative formation of the white trimeric $[Cu(dmnpz)]_3$ derivative is observed. The reaction is reversible, since by adding Et_3N to the reaction mixture, complex **1** easily dissolves restoring **2**. The overall process can be regarded as an equilibrium reaction between **1** and **2** (eq 3).

$$\underset{(\mathbf{2})}{3(Et_3NH)_2[Cu_4(dmnpz)_6]} \rightleftharpoons \underset{(\mathbf{1})}{4[Cu(dmnpz)]_3} + 6(Et_3NH)(dmnpz) \tag{3}$$

A further acid–base equilibrium involving proton transfer in $(Et_3NH)(dmnpz)$ accounts for the observation that free Et_3N stabilizes solutions of **2** (eq 4).

$$(Et_3NH)(dmnpz) \rightleftharpoons Hdmnpz + Et_3N \tag{4}$$

To evaluate the role of the cation in the stabilization of complex **2**, we have prepared a series of derivatives of this species with cations not possessing acidic protons, $(cat)_2[Cu_4(dmnpz)_6]$, (cat = K, **3a**; $^nBu_4N$, **3b**; $[N(PPh_3)_2]$, **3c**). These derivatives can be directly obtained employing the appropriate base (alcoholic KOH or $^nBu_4NOH$) in the synthetic procedure described for **2** or by metathetic exchange from **2** with the appropriate base or salt (KCl, KOH, $^nBu_4NOH$, $^nBu_4NCl$, $[N(PPh_3)_2]Cl$) (see Experimental Section). This latter observation, together with spectroscopic evidence (IR and ^1H NMR) and reactivity analogies, strongly suggests that, in complexes **3a–c**, the $[Cu_4(dmnpz)_6]^{2-}$ anion retains its identity, irrespective of the countercation. As expected, the new derivatives **3a–c** are quite stable in solution (in absence of oxygen), and conductivity measurements revealed the predictable behavior as 1:2 electrolytes.[11]

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(10) Differences between Hdmpz and Hdmnpz are outlined by the corresponding p*K* values, representative of the acidity and basicity of diazoles:

$$Hpz^* + H_2O \rightleftharpoons (pz^*)^- + H_3O^+$$

(pK_1): 15.00 (Hdmpz), 10.65 (Hdmnpz)

$$(H_2pz^*)^+ + H_2O \rightleftharpoons Hpz^* + H_3O^+$$

(pK_2): 4.06 (Hdmpz), − 0.45 (Hdmnpz)

See: Catalan, J.; Abboud, J. L. M.; Elguero, J. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: New York, 1987; Vol. 41, p 187.

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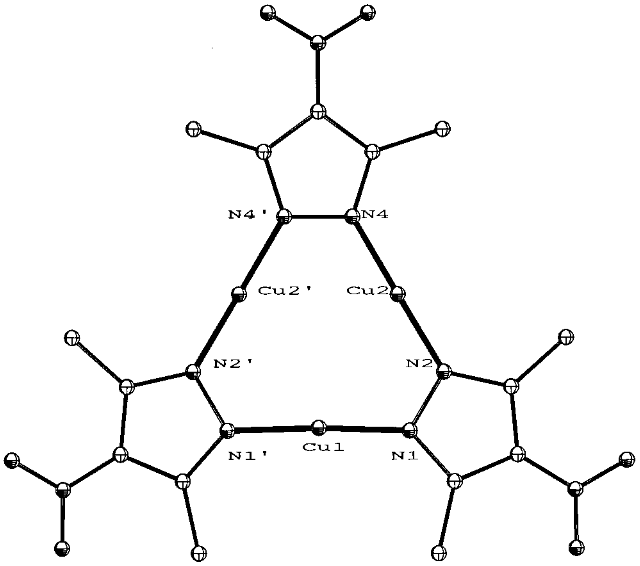

Figure 1. ORTEP plot of the $[Cu(dmnpz)]_3$ (**1**) molecule, with partial labeling scheme. Relevant bond distances (Å) and angles (deg) are Cu1−N1, 1.87(4); Cu2−N2, 1.89(5); Cu2−N4, 1.83(4); Cu1···Cu2, 3.185(11); Cu2···Cu2′, 3.255(13); N1−Cu1−N1′, 175(4); N2−Cu2−N4, 177(2); *Intermolecular* contact, Cu1···Cu2″, 3.329(7) (primed and double-primed atoms generated by the $-x, y, {}^1/_2 - z$ and $-x, -y, -z$ symmetry operations, respectively).

Complexes **1** and **2** have been fully characterized by means of X-ray diffraction. Due the marked insolubility of **1** in organic solvents, preventing the growth of crystals suitable for a single-crystal X-ray diffraction study, its structure has been solved ab initio by means of X-ray powder diffraction analysis (XRPD).[12] Complex **2**, to the best of our knowledge, is the first structurally characterized homoleptic anionic pyrazolate.[13]

Crystal and Molecular Structures of 1 and 2. The crystal structure of **1** contains neutral trimeric copper(I) molecules with idealized $\bar{6}m2$ symmetry. The molecular structure of **1** is depicted in Figure 1 together with a partial labeling scheme and selected bonding parameters. A detailed analysis of its geometry cannot be done, since it is known that XRPD studies of complex molecules need the introduction of numerous geometrical restraints and therefore cannot be compared to a single-crystal X-ray analysis; however, important chemical features such as stoichiometry, molecular shape, crystal packing, and metal−metal interatomic distances are reasonably well determined. Complex **1**, analogously to many other homoleptic pyrazolates of group 11 metals,[7,9] exhibits a triangular arrangement of metal atoms with all edges bridged by exo-bidentate dmnpz ligands with Cu(1)−Cu(2) (3.185(11) Å) and Cu(2)−Cu(2′) (3.255(13) Å) (since the molecule lies around a 2-fold axis, primed atoms were obtained by the symmetry operation $-x, y, {}^1/_2 - z$). The copper atoms are linearly coordinated by two nitrogen atoms of dmnpz ligands, which lie in the plane of the metal atoms. The coordination at the metal centers is completed by *intertriangle* contacts involving the copper atoms of a symmetry-related (−1) molecule (Cu···Cu, 3.329(7) Å), giving rise to a stepped-ribbon secondary structure of triangular complexes; a similar arrangement has also been found for all other $[M(pz^*)]_3$ (pz* = a generic pyrazolate) complexes previously cited but $[Cu(dmpz)]_3$ and $[Cu(tmpz)]_3$, for which these *aurophilic* interactions only produce dimeric supramolecular moieties. Among silver pyrazolates, it has recently been shown that also the $[Ag(pz)]_3$[9] and $[Ag(dmpz)]_3$[12a] trimers show a secondary structure which extends throughout the crystal. Interestingly, while most of the group 11 binary pyrazolates show nuclearities and packing features similar to their purely organic counterparts (obtained by formal substitution of the N−M−N fragments by N−H···N linkages),[9] this is not true for **1**, since Hdmnpz is known to form, in the solid state, helical (hydrogen bonded) polymers.[14]

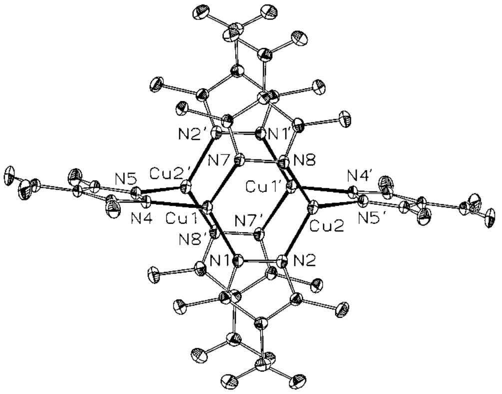

Figure 2. ORTEP plot of the $[Cu_4(dmnpz)_6]^{2-}$ anion, with partial labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

The molecular structure of anion **2** is shown in Figure 2 together with a labeling scheme. Selected bond parameters are reported in Table 1. The tetranuclear anion sits about a crystallographic inversion center, thus having a strictly planar metal core imposed by symmetry. The four copper atoms are arranged at the corners of a parallelogram with side lengths of 3.324(1) (Cu(1)···Cu(2)) and 3.019(1) (Cu(1)···Cu(2′)) Å (primed atoms were generated with the $(-x, -y, 1 - z)$ symmetry operation), well beyond the range normally accepted for a Cu−Cu covalent bond. The internal angles of the parallelogram are significantly different from 90°, Cu(2)−Cu(1)−Cu(2′) and Cu(1)−Cu(2)−Cu(1′) being 101.92(2) and 78.08(2)°, respectively. The cationic compound $[Cu_4(pydz)_6]^{2+}$ [15] is strictly akin to anion **2**, containing a tetranuclear copper framework bridged by six pyridazine ligands. However, this complex exhibits a more regular metal arrangement with Cu···Cu interactions of 3.264(1) and 3.096(1) Å and Cu−Cu−Cu angles equal to 90° within 1°. Each copper center in **2** is trigonally coordinated by nitrogen atoms belonging to the 3,5-dimethyl-4-nitropyrazolate ligands, bridging all edges of the parallelogram. Similarly to Munakata's complex,[15] the long Cu−Cu edges are doubly bridged by two dmnpz ligands placed on opposite sides with respect to the Cu_4 plane, in a nearly orthogonal orientation (with dihedral angles between the dmnpz rings (N(1)−N(2)) or (N(7)−N(8)) least-squares planes and Cu_4 of 84.65(9) and 86.97(8)°, respectively). On the contrary, the

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[13] The synthesis and characterization of a series of anionic complexes of 3,5-pyrazoledicarboxylic acid (H_3dcbpz) as a dinucleating trianionic ligand, i.e. $[M_2(cod)_2(dcbpz)]^-$, $[M_2(CO)_4(dcbpz)]^-$ (M = Rh, Ir), and $[M_2(dcbpz)]^{2-}$ (M = Pt(II), Pd(II), Ni(II), Cu(II)) have been reported. However, X-ray structure determinations evidenced that the trianionic dcbpz ligand coordinates to the two metal centers via the pyrazole N atom and the carboxylate O atoms. See: (a) Bayon, J. C.; Net, G.; Esteban, P.; Rasmussen, P. G.; Bergstrom, D. F. *Inorg. Chem.* **1991**, *30*, 4771. (b) Bayon, J. C.; Esteban, P.; Net, G.; Rasmussen, P. G.; Baker, K. N.; Hahn, C. W.; Gumz, M. M. *Inorg. Chem.* **1991**, *30*, 2572.

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Table 1. Selected Bond Distances (Å) and Angles (deg) for Compounds **2**, **4**, **5**, and **6**

compound **2**		compound **6**	
Cu(1)···Cu(2)	3.3238(8)	Cu(1)···Cu(2)	3.1813(6)
Cu(1)···Cu(2′)	3.019(1)	Cu(1)−P(1))	2.1877(7)
Cu(1)−N(1)	1.981(3)	Cu(1)−N(1)	1.986(2)
Cu(1)−N(4)	1.977(3)	Cu(1)−N(4)	1.969(2)
Cu(1)−N(7)	1.975(3)	Cu(2)−P(2)	2.1863(7)
Cu(2)−N(2)	1.980(3)	Cu(2)−N(2)	1.957(2)
Cu(2)−N(5′)	1.955(3)	Cu(2)−N(5)	2.020(2)
Cu(2)−N(8)	1.951(3)	N(1)−N(2)	1.390(3)
N(1)−N(2)	1.400(4)	N(4)−N(5)	1.394(3)
N(4)−N(5)	1.391(4)	N(1)−Cu(1)−P(1)	119.42(6)
N(7)−N(8)	1.402(4)	N(1)−Cu(1)−N(4)	109.94(8)
Cu(1)···Cu(2)···Cu(1′)	78.08(2)	N(4)−Cu(1)−P(1)	128.25(6)
Cu(2)···Cu(1)···Cu(2′)	101.92(2)	N(2)−Cu(2)−P(2)	134.62(6)
		N(2)−Cu(2)−N(5)	109.80(8)
		N(5)−Cu(2)−P(2)	113.48(6)

	compound **4**	compound **5**
Cu···Cu′	3.540(1)	3.728(2)
Cu−N(1)	1.974(3)	2.037(2)
Cu−N(2′)	1.972(3)	2.034(2)
Cu−C(6)	1.869(6)	1.930(3)
Cu−C(13)		1.937(4)
N(1)−N(2)	1.388(4)	1.389(3)
N(4)−C(6)	1.142(7)	1.141(4)
N(4)−C(7)	1.463(5)	1.459(4)
N(5)−C(13)		1.150(4)
N(5)−C(14)		1.520(4)
N(1)−Cu−N(2′)	113.78(13)	109.87(9)
C(6)−Cu−N(1)	121.5(2)	108.62(12)
C(6)−Cu−N(2′)	124.6(2)	108.84(12)
C(13)−Cu−N(1)		108.60(12)
C(13)−Cu−N(2′)		107.65(13)
C(6)−Cu−C(13)		113.24(14)
N(4)−C(6)−Cu	178.3(7)	176.3(3)
C(6)−N(4)−C(7)	176.9(7)	173.4(3)
N(5)−C(13)−Cu		176.3(3)
C(13)−N(5)−C(14)		176.5(3)

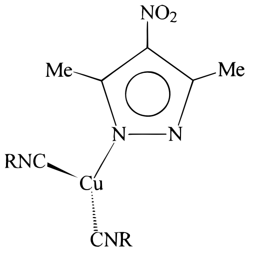
short edges of the metal parallelogram are bridged by only one dmnpz ligand nearly coplanar with the Cu_4 core (dihedral angle between the dmnpz (N(4)−N(5)) least-squares plane and Cu_4 = 8.5(2)°). Given the role of the bridging exo-bidentate dmnpz ligands and the actual values of the Cu−Cu distances, any interaction between the copper atoms is weak at best. The two crystallographically independent copper atoms, while being both trigonally coordinated, exhibit different degrees of pyramidalization. Indeed, Cu(1) is placed within experimental error in the same plane of its coordinating atoms N(1), N(4), and N(7) (deviation 0.003(2) Å), while Cu(2) is well off the plane defined by N(2), N(5′), and N(8) (deviation 0.795(3) Å), with the apex of the pyramid pointing away from the center of the molecule. The distortion of the coordination environment is also reflected by the deviation of the copper atoms from the dmnpz ligands planes (Cu(1), 0.095(6) and 0.174(6) Å out of the N(1)−N(2) and N(7)−N(8) dmnpz planes, respectively; Cu(2), 0.559(6) and 0.609(6) Å out of the N(1)−N(2) and N(7)−N(8) dmnpz planes, respectively). [For Cu(2) there is also an in plane distortion with two Cu−N interactions significantly shorter than the third one (Cu(2)−N(5′) 1.955(3), Cu(2)−N(8) 1.951(3), Cu(2)−N(2) 1.980(3) Å).] The $Cu(1)(N-N)_2Cu(2)$ six-membered metallocycle displays a sofa conformation with Cu(2) 0.586(3) Å out of the Cu(1)/N(1)/N(2)/N(7)/N(8) average plane (maximum deviation 0.038(2) Å). The dmnpz ligands bridging the long side of the tetracopper parallelogram face each other at a distance of about 3.4 Å, allowing some $\pi-\pi$ stabilizing *intramolecular* interaction. The N−N bond distances of the three ligands are markedly longer (average 1.398 Å) than those found in polymeric Hdmnpz for which a value of 1.34(1) Å has been found. This phenomenon, as already pointed out by Ehlert et al.,[7a] could be associated with a $Cu(d_\pi)$−dmnpz(π*) interaction between metal and the nitropyrazole orbitals of acidic character. None of the dmnpz rings deviate significantly from planarity, all having the nitro group almost coplanar with the ring.

Reactivity of 1 with Cyclohexyl Isocyanide (RNC) and Triphenylphosphine. The reaction of complex **1** with cyclohexyl isocyanide (RNC) in diethyl ether leads to the isolation of two different products depending on the copper/RNC molar ratio. When the reaction is carried out with a Cu/RNC ratio of 1:1 the dimeric species $[Cu(dmnpz)(RNC)]_2$ (**4**) was isolated (eq 5).

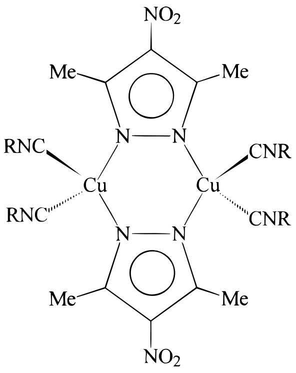
$$\underset{(\mathbf{1})}{2[Cu(dmnpz)]_3} + 6RNC \rightarrow \underset{(\mathbf{4})}{3[Cu(dmnpz)(RNC)]_2} \quad (5)$$

Analytical and spectroscopic data are in agreement with the assigned formulation. In particular, the IR spectrum of **4** shows only one absorption due to ν(NC) stretching at 2166 cm^{-1}, a value close to those found in a series of derivatives of general formula $[Cu(pz^*)(RNC)]_2$ synthesized by us in the past years (Hpz* = pyrazole, Hpz[16]; 3,5-dimethylpyrazole, Hdmpz[16]; 3,5-diphenylpyrazole, Hdppz[5a]; 3,5-dicarbomethoxypyrazole, Hdcmpz[6a]). Complex **4** was fully characterized by means of a single-crystal X-ray diffraction study (see later).

When complex **1** was reacted with excess RNC, a different derivative, analyzing as $Cu(dmnpz)(RNC)_2$ (**5**), was obtained. The IR spectra of **5** registered either in the solid state or in solution shows two absorptions attributable to ν(NC) (2165 and 2143 cm^{-1}, Nujol; 2169 and 2155 cm^{-1}, CH_2Cl_2 solution) indicating the presence of two RNC ligands coordinated to a copper center. Two possible structures can account for the assigned formulation: a mononuclear species having a dmnpz group coordinated in a rare mono-dentate fashion (**A**) or a dinuclear species having a central *core*, $Cu-[N-N-]_2-Cu$, as in derivative **4**, but possessing two tetracoordinated copper(I) centers (**B**).



A



B

The ${}^1H$ NMR of **5**, registered in CD_2Cl_2 at room temperature shows, beside the signals attributable to the cyclohexyl rings, only one signal at 2.62 ppm derived from the methyl groups of the pyrazolate ligand. The spectrum does not change significantly on lowering the temperature, as instead expected for a structure of type **A**, due the well-known scrambling of the nitrogen atoms that equalizes the 3 and 5 sites on the pyrazolate

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(16) Ardizzoia, G. A.; Angaroni, M.; La Monica, G.; Masciocchi, N.; Moret, M. *J. Chem. Soc., Dalton Trans.* **1990**, 2277.

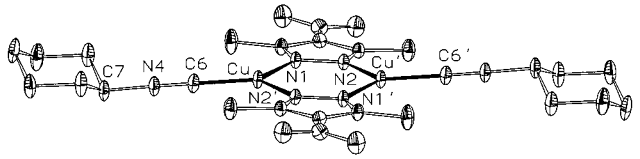

Figure 3. ORTEP plot of the $[Cu(dmnpz)(RNC)]_2$ (**4**) molecule, with partial labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

ligands coordinated in a monodentate mode.[17] Hence, a structure type **B** for complex **5** in solution seems the more plausible. The same structure was found in the solid state by means of a single-crystal X-ray diffraction study (see later).

Complex **5** can also be obtained by reacting **4** with RNC (eq 6), and despite the highly steric crowding at the copper(I) centers it is very stable in solution, not showing any dissociation of the cyclohexyl isocyanide ligands.

$$\underset{(\mathbf{1})}{2[Cu(dmnpz)]_3} \xrightarrow{RNC} \underset{(\mathbf{4})}{3[Cu(dmnpz)(RNC)]_2} \xrightarrow{RNC} \underset{(\mathbf{5})}{3[Cu(dmnpz)(RNC)_2]_2} \quad (6)$$

Also in this case the peculiar electronic properties of the dmnpz ligand play a crucial role in determining the nature of the final product. Indeed, the related $[Cu(dmpz)]_3$ derivative, possessing a molecular arrangement and steric hindrance comparable to that of complex **1**, reacts with RNC giving only the dinuclear, tricoordinated, copper(I) derivative $[Cu(dmpz)(RNC)]_2$ even in the presence of excess cyclohexyl isocyanide.[16]

The reaction of complex **1** with PPh_3 exclusively affords the dinuclear species $[Cu(dmnpz)(PPh_3)]_2$ (**6**), also in the presence of an excess of ligand (eq 7).

$$\underset{(\mathbf{1})}{2[Cu(dmnpz)]_3} + 6PPh_3 \rightarrow \underset{(\mathbf{6})}{3[Cu(dmnpz)(PPh_3)]_2} \quad (7)$$

Complex **6** is quite stable in solution (in absence of O_2), and was characterized by a single-crystal X-ray diffraction analysis.

The same derivatives obtained according to reactions 5−7 can be isolated employing the tetranuclear anionic complexes $(cat)_2[Cu_4(dmnpz)_6]$ (**2**, **3a**−**c**), instead of $[Cu(dmnpz)]_3$ (**1**). In these cases, the formation of (cat)(dmnpz) as byproduct of the reactions was evidenced.

Crystal and Molecular Structures of 4, 5 and 6. Crystals of **4**, **5**, and **6** contain discrete dimeric complexes packed with normal van der Waals interactions. Their molecular structure are reported in Figures 3, 4, and 5, respectively, with a partial labeling scheme. Selected bond parameters are reported in Table 1.

Complex **4** lies on an inversion center and contains two copper(I) atoms linked by two exo-bidentate dmnpz ligands; also connected to each metal atom there is one cyclohexyl isocyanide ligand. Therefore the copper atoms attain a planar trigonal coordination with a small deviation from the plane of atoms C(6), N(1) and N(2′) (0.032(5) Å) (primed atoms are related by the symmetry operator $1 - x, -y, -z$) and a non bonding Cu···Cu distance of 3.540(1) Å. The dimeric complex possesses an overall idealized 2/*m* symmetry with the 2-fold axis bisecting the nitro groups and the mirror plane passing through the copper atoms and NC groups.

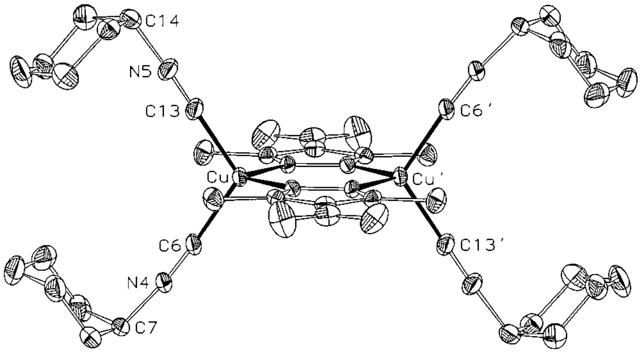

Figure 4. ORTEP plot of the $[Cu(dmnpz)(RNC)_2]_2$ (**5**) molecule, with partial labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

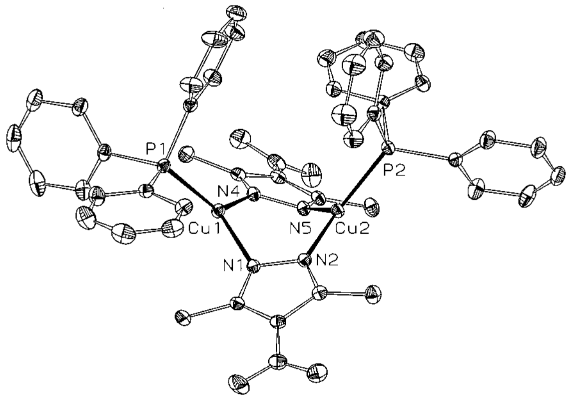

Figure 5. ORTEP plot of the $[Cu(dmnpz)(PPh_3)]_2$ (**6**) molecule, with partial labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

The C−Cu−N angles average to 123.0°, the N(1)−Cu−N(2′) angle being 113.8(1)°, similarly to that observed for complex $[Cu(3,5\text{-}dmpz)(RNC)]_2$[16] (123.46(6) and 113.0(1)°, respectively). As in the latter complex, also in the present case the six-membered $Cu-[N-N]_2-Cu$ metallocycle is nearly planar with maximum deviation from the least-squares plane of 0.024(2) Å for atoms N(1) and N(2). Also, the two independent Cu−N bond distances (average 1.973 Å) are approximately equal to those evidenced within compound $[Cu(3,5\text{-}dmpz)(RNC)]_2$[16] (1.960(2) Å).

Complex **5** lies around an inversion center but displays a much higher idealized symmetry (*mmm*) with three orthogonal mirror planes. The copper atoms are connected to two nitrogen atoms of bridging 3,5-dimethyl-4-nitropyrazolates and two cyclohexyl isocyanide ligands. The latter are on opposite sides of the central Cu_2N_4 ring, thus generating a tetrahedral coordination around the metal atoms. The increased steric crowding around the metal centers with respect to complex **4** is evidenced by the Cu−N and Cu−C bond distances which have an average value of 2.035 and 1.933 Å, respectively, significantly longer than those observed in compound $[Cu(3,5\text{-}dmpz)(RNC)]_2$[16] and in **4**. As a side effect, the intradimer Cu···Cu distance increases from 3.540(1) in **4** to 3.728(2) Å in **5** (which, to our knowledge, is the longest ever observed in μ_2-pyrazolate bridged dimers) and the N(1)−Cu−N(2′) angle drops to 109.87(9)° on changing the coordination from planar trigonal to tetrahedral. The six-membered cycle defined by the two copper and the four nitrogen atoms also in this case is planar (maximum deviation from the least-squares plane fit of 0.006(1) Å).

Compound **6** is a dimeric molecule with two copper(I) ions trigonally coordinated by two bridging dmnpz ligands and one

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[17] (a) Bandini, A. L.; Banditelli, G.; Bonati, F.; Minghetti, G.; Demartin, F.; Manassero, M. *J. Organomet. Chem.* **1984**, *269*, 91. (b) Röttger, D.; Erker, G.; Grehl, M.; Fröhlich, R. *Organometallics* **1994**, *13*, 3897.

Table 2. ν(CO) Absorptions (cm^{-1})of CO Adducts (**7a**−**d**) of (cat)$_2$[Cu$_4$(dmnpz)$_6$], **2** and **3a**−**c**

complex	cat	ν(CO)	
		solution	Nujol
7a	Et$_3$NH	2050	2045
7b	K	2050	2052
7c	Bu$_4$N	2050	2052
7d	[N(PPh$_3$)$_2$]	2050	2044

triphenylphosphine each. The presence of the methyl substituents in positions 3 and 5 on the pyrazolates and of the bulky triphenylphosphine makes the steric requirements demanding with respect to the final conformation of the whole dimeric molecule. Indeed, differently from compound **4**, in which the metal atoms, the pyrazolates and the NC groups lie in the same plane, complex **6** shows a highly puckered Cu−[N−N]$_2$−Cu six-membered ring. Adopting an almost planar disposition of the metallocycle, as observed in compound [Ag(pz)$_2$(PPh$_3$)$_2$],[18] would cause strong steric repulsion between the phenyl and methyl hydrogen atoms. The conformation presently observed guarantees the minimization of these unfavorable repulsions and at the same time allows for an efficient *intramolecular* packing of the six phenyl rings, with two of them (C(13x) and C(22x)) nearly parallel (dihedral angle 17.0(1)°). The coordination around the copper atoms significantly deviates from planarity with Cu(1) and Cu(2), 0.182(1) and 0.169(1) Å, respectively, out of the pertinent coordination plane. A strong distortion of the pyrazolate exo-bidentate bonding mode is also observed, in which the copper atoms lie out of the pyrazolate average planes with deviations ranging from a minimum of 0.163(4) Å for Cu(2) with respect to dmnpz (N(1)−N(2)) up to 0.755(4) Å for Cu(2) with respect to dmnpz (N(4)−N(5)). The resulting conformation of the six membered Cu−[N−N]$_2$−Cu ring is twist-boat; it represents an additional example of the conformational variety in this class of complexes, dictated by steric and electronic requirements, which allowed the observation of planar, boat, chair, and sofa conformations.

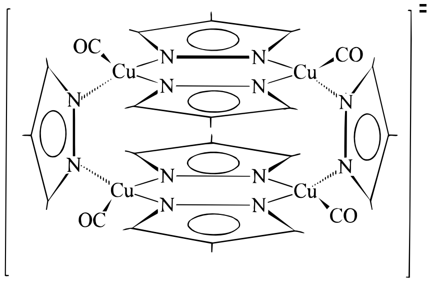
Reaction of (cat)$_2$[Cu$_4$(dmnpz)$_6$] with Carbon Monoxide. Complexes **2** (cat = Et$_3$NH) and **3** (cat = K, **3a**; Bu$_4$N, **3b**; [N(PPh$_3$)$_2$], **3c**) react with CO in acetone or CH$_2$Cl$_2$ affording the carbonyl derivatives **7a**−**d** as indicated by infrared spectroscopy (Table 2). The uptake of CO is very fast, as revealed by the fading of the color of the solutions (from orange-yellow to colorless) and it is easily reversed by bubbling N$_2$ into the solution. The carbonyl derivatives can be isolated in the solid state by evaporating the solution in a flow of carbon monoxide. Attempts to grow single crystals of the carbonyl derivatives suitable for X-ray analysis were unsuccessful, resulting in recrystallization of the starting complexes. The formulation of these derivatives is hence inferred on the basis of spectroscopic evidences. As reported in Table 2 the ν(CO) values are typical for a terminal CO group bound to a copper(I) center in a tetrahedral environment.[19] In solution, all four derivatives show the ν(CO) at 2050 cm^{-1} suggesting an identical formulation for all species (i.e., independently on the cation). Moreover, only a slight difference exists between the ν(CO) registered in solution and in Nujol mulls, suggesting that the solution structure is maintained also in the solid state.

Complexes **7a**−**d** are stable enough in the solid state at room temperature if maintained under a CO atmosphere or under N$_2$ at −20 °C, but rapidly lose CO if heated under vacuum (60 °C, 10^{-2} Torr), restoring the starting complexes (eq 8). This last

$$\underset{(\mathbf{2},\ \mathbf{3a-c})}{(\mathrm{cat})_2[\mathrm{Cu}_4(\mathrm{dmnpz})_6]} + 4\mathrm{CO} \underset{\mathrm{N}_2\text{ or vacuum}}{\rightleftharpoons} \underset{(\mathbf{7a-d})}{(\mathrm{cat})_2[\mathrm{Cu}_4(\mathrm{dmnpz})_6(\mathrm{CO})_4]} \quad (8)$$

observation prompts us to suggest that the uptake of CO does not cause a significant rearrangement of the molecular structure of the starting complexes and that the carbonyl derivatives maintain a tetranuclear arrangement. The thermal behavior could not be easily explained if major rearrangements leading to the tetrameric units were required.

In addition, a thermogravimetric study of the potassium derivative, **7b**, decarbonylation, revealed the presence of *one* molecule of CO *per* copper center. On these basis, the formulation of derivatives **7a**−**d** as tetranuclear species containing tetracoordinated copper(I) centers seems plausible.



A similar behavior was also found for the previously reported tetranuclear [Cu(OtBu)(CO)]$_4$ copper(I) carbonyl complex, which was shown to retain, after carbonylation, the nuclearity of the parent [Cu(O-tBu)]$_4$ complex, although with Cu$_4$O$_4$ *cores* possessing different geometries (cubane vs planar).[20]

A further substantiation of this hypothesis is found in the close similarity between the ^{1}H and ^{13}C NMR spectra of the starting complexes and those of the carbonylated species. The ^{1}H NMR spectrum of complex **3a** shows only one signal attributable to the methyl groups of the dmnpz ligands (2.31 ppm); bubbling CO causes only a slight downfield shift of the signal (2.56 ppm). This behavior is substantially unchanged on lowering the temperature. The ^{13}C NMR spectrum shows similar results, as long as the signals attributable to the dmnpz ligand are concerned. Unfortunately, the signals due to the coordinated CO molecules went undetected (probably due to the lability of the CO ligand), hiding helpful information.

The possible formation of a dinuclear species of formula [Cu(dmnpz)(CO)]$_2$, reminiscent of the structure of the RNC or PPh$_3$ derivatives (**4** and **6**), is, in our opinion, to be ruled out on the basis of two observations: (i) the frequency of the ν(CO) does not match those found in tricoordinated copper(I) centers,[19] and (ii) the uptake of CO is not depleted by the presence in the reaction medium of the (cat)(dmnpz) salts, as verified in the case of (Et$_3$NH)$_2$[Cu$_4$(dmnpz)$_6$] (**2**). In fact, in this case, the presence in solution of Et$_3$N and Hdmnpz was found to be necessary in order to prevent the precipitation of [Cu(dmnpz)]$_3$.

A dinuclear pyrazolate complex, having only one CO group coordinated in a terminal mode to a copper(I) center, [Cu$_2$(dcmpz)$_2$(py)$_2$(CO)], was indeed recently reported by us and crystallographically characterized.[6a] However, in that case, the

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(18) Ardizzoia, G. A.; La Monica, G.; Maspero, A.; Moret, M.; Masciocchi, N. *Inorg. Chem.* **1997**, *36*, 2321.

(19) (a) Sorrell, T. N.; Jameson, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 6013. (b) Pasquali, M.; Floriani, C. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: Duilderland, NY, 1983; p 311.

(20) (a) Tsuda, T.; Habu, H.; Horiguchi, S.; Saegusa, T. *J. Am. Chem. Soc.* **1974**, *96*, 5930. (b) Geerts, R. L.; Huffman, J. C.; Folting, K.; Lemmen, T. H.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 3503.

presence of pyridine was necessary to "depolymerize" the starting homoleptic (presumably trimeric) $[Cu(dcmpz)]_x$ complex, affording the dinuclear $[Cu(dcmpz)(py)]_2$ intermediate as the actual reactive species.

Conclusions

The synthesis, the structural properties and the reactivity toward neutral ligands such as cyclohexyl isocyanide and triphenylphosphine of the new homoleptic $[Cu(dmnpz)]_3$ and $(cat)_2[Cu_4(dmnpz_6]$ copper(I) pyrazolato complexes have been described. A comparison between $[Cu(dmnpz)]_3$ and the structural analogue $[Cu(dmpz)]_3$ has shown that the electronic properties of the dinucleating pyrazolate anions play a major role compared with the steric ones as long as the reactivity of the species is concerned; however, subtle steric features of the ligand seems to drive the stereochemistry of the reaction products (i.e., in particular the conformation of the $Cu-[N-N]_2-Cu$ rings). Studies are in progress in order to verify these hypotheses by employing suitable substituted pyrazoles.

In addition, the structural characterization of **1**, which only appears as fine microcrystalline powders, has shown that, if the complexity of the structural problem is not too large, ab initio XRPD methods from *conventional* laboratory equipment may afford valuable, otherwise inaccessible, structural information, such as metal atom coordination, nuclearity of the species, and its relevant crystal packing features.[12b]

Experimental Section

Solvents were dried and purified by standard methods. 3,5-Dimethylpyrazole, cyclohexyl isocyanide, and triethylamine were used as supplied (Aldrich Chemical Co.), and triphenylphosphine (Merck) was recrystallized from methanol before use. $[Cu(CH_3CN)_4](BF_4)$[21] and 3,5-dimethyl-4-nitropyrazole[22] were prepared according to literature procedures. Infrared spectra were taken on a Bio-Rad FTIR 7 instrument, thermogravimetric analyses were obtained under nitrogen atmosphere employing a Perkin-Elmer TGA 7 HIGH IE, and ^1H and ^{13}C NMR spectra were acquired on a Bruker AC-200 FT spectrometer. Elemental analyses were performed at the Microanalytical Laboratory of this University (C, H, N). All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques.

Synthesis of $[Cu(dmnpz)]_3$, 1. To an acetone solution of 3,5-dimethyl-4-nitropyrazole (400 mg, 2.84 mmol) was added $[Cu(CH_3CN)_4](BF_4)$ (850 mg, 2.70 mmol) under stirring. The colorless solution was stirred for 5 min, and triethylamine (1 mL) was added dropwise. A white precipitate suddenly formed. After 15 min stirring, complex **1** was collected by filtration, washed with acetone, and dried under vacuum (95% yield). Anal. Calcd for $C_{15}H_{18}Cu_3N_9O_6$: C, 29.48; H, 2.95; N, 20.64. Found: C, 29.31; H, 2.70; N, 20.25.

Synthesis of $(Et_3NH)_2[Cu_4(dmnpz)_6]$, 2. Triethylamine (2 mL) was added dropwise to a solution of 3,5-dimethyl-4-nitropyrazole (1.00 g, 7.09 mmol) and $[Cu(CH_3CN)_4](BF_4)$ (700 mg, 2.22 mmol) in acetone (10 mL). A white precipitate (complex **1**) initially formed, and subsequently the color of the suspension turned to orange. The suspension was stirred for an additional half hour, and then the orange solid was filtered off, washed with a small amount of acetone (5 mL), and dried under vacuum (81% yield). Crystals suitable for X-ray analysis were obtained by slow evaporation of an acetone solution of **2**. Anal. Calcd for $C_{42}H_{68}Cu_4N_{20}O_{12}$: C, 38.83; H, 5.24; N, 21.57. Found: C, 38.59; H, 5.17; N, 21.51.

Synthesis of $K_2[Cu_4(dmnpz)_6]$, 3a, and $(Bu_4N)_2[Cu_4(dmnpz)_6]$, 3b. These compounds were obtained as described for **2** but using a methanol solution of KOH or $(Bu_4N)OH$, respectively, instead of triethylamine or by treating a methanol suspension of **2** with alcoholic KOH or $(Bu_4N)OH$. Anal. Calcd for $C_{30}H_{36}Cu_4K_2N_{18}O_{12}$ (**3a**) (90% yield): C, 30.72; H, 3.07; N, 21.50. Found: C, 30.15; H, 2.94; N, 20.79. Calcd for $C_{62}H_{108}Cu_4N_{20}O_{12}$ (**3b**) (76% yield): C, 47.15; H, 6.84; N, 17.74. Found: C, 47.35; H, 6.70; N, 17.24.

Synthesis of $\{[N(PPh_3)_2]\}_2[Cu_4(dmnpz)_6]$, 3c. To a CH_2Cl_2 (5 mL) suspension of complex **3a** (150 mg, 0.128 mmol) was added $[N(PPh_3)_2]Cl$ (147 mg, 0.256 mmol) under stirring. A white precipitate of KCl rapidly formed. The precipitate was filtered off under nitrogen, and the clear solution was evaporated to dryness, giving a yellow residue that was washed with methanol and dried under vacuum (80% yield). Anal. Calcd for $C_{102}H_{96}Cu_4N_{20}O_{12}P_2$ (**3c**): C, 58.06; H, 4.55; N, 23.28. Found: C, 58.16; H, 4.38; N, 23.01.

Synthesis of $[Cu(dmnpz)(RNC)]_2$, 4. To a suspension of complex **1** (100 mg, 0.164 mmol) in diethyl ether (10 mL) was added cyclohexyl isocyanide (RNC) (61.0 μL, 0.46 mmol, Cu/RNC molar ratio 1/1) under stirring. The white suspension was stirred for 2 h at room temperature. Complex **4** was then collected by filtration, washed with diethyl ether, and dried under vacuum (95% yield). Complex **4** can also be obtained from the ionic complexes **2** and **3a**−**d**; in this case, the presence of free neutral pyrazole in the mother liquors was confirmed. Crystals suitable for X-ray structure analysis were obtained by slow diffusion of *n*-hexane into dichloromethane solution of **4**. Anal. Calcd for $C_{24}H_{34}Cu_2N_8O_4$: C, 46.08; H, 5.44; N, 17.92. Found: C, 45.83; H, 5.47; N, 17.44.

Synthesis of $[Cu(dmnpz)(RNC)_2]_2$, 5. Complex **5** was obtained as described for **4** but using excess cyclohexyl isocyanide (Cu/RNC molar ratio 1/4) (92% yield). Crystals suitable for X-ray structure analysis were obtained by slow diffusion of *n*-heptane into 1,2-dichloroethane solution of **5**. Anal. Calcd for $C_{38}H_{56}Cu_2N_{10}O_4$: C, 54.09; H, 6.64; N, 16.61. Found: C, 53.80; H, 6.64; N, 16.20.

Synthesis of $[Cu(dmnpz)(PPh_3)]_2$, 6. Complex **1** (150 mg, 0.246 mmol) was suspended in acetone (10 mL) under nitrogen atmosphere, and triphenylphosphine (579 mg, 2.21 mmol) was added under stirring. The clear solution formed was then evaporated to dryness, yielding a yellow solid. It was washed with ethanol and diethyl ether and dried under vacuum (85% yield). Complex **6** can be alternatively obtained from the ionic derivatives **2** and **3a**−**c**. Crystals suitable for X-ray structure analysis were obtained by slow diffusion of diethyl ether into an acetone solution of **6**. Anal. Calcd for $C_{46}H_{42}Cu_2N_6O_4P_2$: C, 59.29; H, 4.51; N, 9.02. Found: C, 59.54; H, 4.53; N, 9.19.

Synthesis of Carbonyl Adducts. $(Et_3NH)_2[Cu_4(dmnpz)_6(CO)_4]$, 7a. Complex **2** (200 mg, 0.154 mmol) was dissolved under nitrogen in the minimum volume of acetone (ca. 5 mL) in the presence of 0.5 mL of triethylamine. Carbon monoxide was then bubbled through the solution. The orange solution rapidly turned colorless, and IR monitoring showed the presence of a strong absorption at 2050 cm^{-1} attributable to the carbonyl species. A pale-yellow solid was obtained removing the solvent in a flow of CO.

$(cat)_2[Cu_4(dmnpz)_6(CO)_4]$ (cat = K, 7b; Bu_4N, 7c; $[N(PPh_3)_2]$, 7d). These derivatives were obtained as described for **7a** from acetone solutions of complexes **3a**−**c** (the presence of Et_3N was in this case unnecessary). The thermal lability of derivatives **7a**−**d** precluded elemental analysis based on combustion methods. The formulation of these derivatives is given on the basis of spectroscopic and thermogravimetric data (see text).

Thermogravimetry. Several TGA measurements carried out on derivative **7b** showed an average loss of weight of about 8% (required for CO/Cu = 1:8.7%). In a preparative experiment, 275.2 mg of **7b** was weighed in a glass bulb and then heated at 60 °C under vacuum (10^{-2} Torr) for 4 h, obtaining 254.1 mg of **3a** ($\Delta m = -7.7\%$, CO/Cu = 0.87).

Crystallography: XRPD Analysis. X-ray powder diffraction data were obtained with Cu Kα radiation ($\lambda = 1.5418$ Å) on a Rigaku D-III MAX horizontal-scan powder diffractometer equipped with parallel (Soller) slits, a graphite monochromator in the diffracted beam a Na(Tl)I scintillation counter, and a pulse height amplifier discrimination. The generator was operated at 40 kV and 40 mA. Slits used: DS (1.0°); AS (1.0°); RS (0.05°). The white powder (complex **1**) was gently ground in an agate mortar to ensure homogeneity in particle size and then cautiously deposited on a quartz monocrystal (zero background holder) with the aid of a binder (5% collodion in amyl acetate). Data were collected at room temperature in the 5−95° range, in the $\theta-2\theta$

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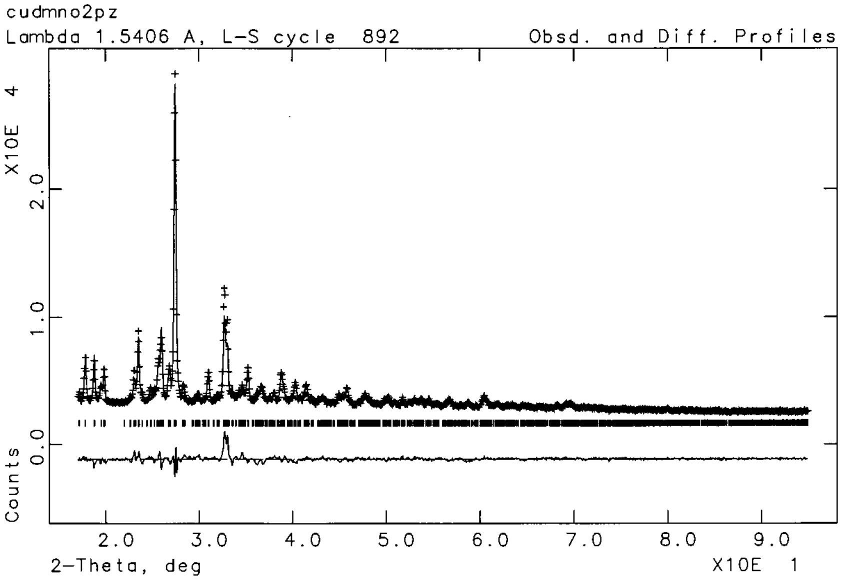

Figure 6. Final Rietveld refinement plot for [Cu(dmnpz)]$_3$ (**1**), with peak markers and difference plot at the bottom.

mode, step scan with $\Delta 2\theta = 0.02°$ and fixed time 15 s. The lowest 2θ 13 peak positions (located by standard peak-search methods) were fed to the trial and error indexing routines of TREOR.[23] The program found a reasonable agreement within the monoclinic system, with the following parameters and figures of merit: $a = 20.07$ Å; $b = 13.81$ Å; $c = 7.89$ Å; $\beta = 95.9°$; M(13) = 45; F(13) = 72 (0.004; 33). No rational transformations of this unit cell into higher symmetries could be found. Systematic absences indicated *C*2/*c* as the probable space group, which was subsequently confirmed by successful refinement. ALLHKL[24] was used to extract intensities in the 5−65° (2θ) range. SIRPOW[25] provided the initial atomic coordinates of two independent copper atoms, one of which on the 2-fold axis. Remaining atoms were located by difference Fourier techniques and geometrical model building. The final refinements were performed using GSAS,[26] which allows bond parameters (Cu−N, N−N, C−N, N−O, and C−C) to be restrained to known values; the relative contribution of the soft restraints (listed in the Supporting Information) to the total χ^2 was about 11%. An unconstrained refinement was also performed but resulted, after convergence, in a significant spread of chemically equivalent distances and was therefore rejected. However, its associated esd's are probably more reasonable; therefore, all values reported in the text and in the tables have been computed on the basis of these esd's, obtained after removal of the constraints. Low angle data ($2\theta < 17°$, six reflections only), being those most affected by instrumental aberrations (such as for fixed-slit Bragg−Brentano geometry, loss of primary beam intensity, and axial divergence effects), were discarded. Two isotropic thermal parameters were refined, one for the metal atoms (0.058(2) Å^2) and one for the lighter ones (0.106(4) Å^2). The contribution of the hydrogen atoms to the scattering factors was neglected. Atomic scattering factors were taken from the internal library of GSAS.[26] The background was refined using a six-term cosine Fourier series; a pseudo-Voigt function was found to best fit the peak shapes. The angular dependence of the peak-widths was modeled using the Caglioti *et al.*[27] dependence, with the *V* and *Z* (tan θ dependent) parameters set to zero. Final R_p, R_{wp}, and R_F values were 0.028, 0.041, and 0.067, respectively. Figure 6 shows the final Rietveld refinement plot. Table 3 contains a summary of crystal data and refinement parameters.

Table 3. Summary of Crystal Data for **1** and X-ray Powder Diffraction Structural Analysis Parameters

empirical formula	$C_{15}H_{18}Cu_3N_9O_6$
fw	610.95
crystal system	monoclinic
space group	*C*2/*c*
a, Å	20.051(2)
b, Å	13.814(2)
c, Å	7.8829(8)
β, deg	95.905(5)
V, Å^3	2171.9(6)
Z	4
F(000)	1224
D(calc), g cm^{-3}	1.868
temperature, K	293(2)
diffractometer	RigakuD-III/max
step, deg	0.02
time per step, s	15
2θ range, deg	17.0−95.0
no. of data points collected	3900
no. of independent reflections	1047
no. of data/restraints/parameters	3900/45/62
R_F[a]	0.067
R_p, R_{wp}[b]	0.028, 0.041

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$, where the sum runs over all space-group permitted reflections. [b] $R_p = \sum|y_{i,o} - y_{i,c}|/\sum y_{i,o}$; $R_{wp} = \sum w_i(y_{i,o} - y_{i,c})^2/\sum w_i y_{i,o}{}^2$, where the sum runs over all measured data points. $y_{i,o}$ and $y_{i,c}$ are the observed and calculated intensities at each *i*th point, respectively, and w_i is a statistical weight, taken as $1/y_{i,o}$.

Crystallography: Single-Crystal Analysis of 2, 4, 5 and 6. (a) Collection and Reduction of Single-Crystal X-ray Data. Suitable crystals of **2**, **4**, **5**, and **6** were mounted in air on a glass fiber tip and then onto a goniometer head. Table 4 contains details of the crystal data, data collection, and refinement procedures. Single-crystal X-ray diffraction data were collected at room temperature (i) for **5** on a Siemens SMART CCD three-circle area detector and (ii) for **2**, **4**, and **6** on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo Ka radiation ($\lambda = 0.710$ 73 Å). Unit cell parameters and an orientation matrix were obtained from least-squares refinement on 44 reflections measured in three different sets of 15 frames each in the range $2 < \theta < 23°$ for **5**, while for the other compounds the setting angles of 25 randomly distributed intense reflections with $10 < \theta < 14°$ were processed by least-squares fitting.

For **5** the intensity data were collected using the ω scan technique within the limits $4 < 2\theta < 55°$. Approximately a full sphere of data was collected with frame width set to 0.3°, the sample−detector distance fixed at 5.5 cm, and a beam exposure of 20 s per frame. The first 100 frames were recollected at the end of data collection to monitor crystal decay, which was not observed. The collected frames were then

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Table 4. Summary of X-ray Single-Crystal Data and Structure Refinement Parameters

	2	**4**	**5**	**6**
empirical formula	$C_{42}H_{36}Cu_4N_{20}O_{12}$	$C_{24}H_{34}Cu_2N_8O_4$	$C_{38}H_{56}Cu_2N_{10}O_4$	$C_{46}H_{42}Cu_2N_6O_4P_2$
fw	1267.06	625.68	844.00	931.88
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	11.026(1)	7.418(1)	9.506(4)	11.379(2)
b, Å	13.456(2)	9.780(1)	9.957(2)	13.592(2)
c, Å	18.668(5)	11.177(3)	11.658(4)	14.409(3)
α, deg		109.61(2)	86.73(2)	81.22(1)
β, deg	92.91(2)	101.34(3)	79.54(2)	85.21(1)
γ, deg		105.82(1)	82.47(4)	87.55(1)
V, Å^3	2766.1(9)	696.8(2)	1075.1(6)	2193.7(7)
Z	2	1	1	2
μ, mm^{-1}	1.59	1.57	1.04	1.09
ρ(calc), g cm^{-3}	1.521	1.491	1.304	1.411
temperature, K	293(2)	293(2)	293(2)	293(2)
R1, wR2[a]	0.0412, 0.1184	0.0477, 0.1295	0.0330, 0.0905	0.0284, 0.0719

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

processed by software SAINT for integration; an absorption correction was applied together with decay/merging (SADABS) on the 12 334 ($R_\sigma = \sum[\sigma(F_o^2)]/\sum F_o^2) = 0.0353$) collected reflections, 4809 of which are unique, with $R_{int} = \sum|F_o^2 - F_{mean}^2|/\sum F_o^2 = 0.0198$. For the crystals examined using the CAD4 diffractometer the data collections were performed by the ω scan method with variable scan speed and variable scan range. The crystal stability under diffraction was checked by monitoring three standard reflections every 180 min. In all cases, crystal decay was not observed. An empirical absorption correction was applied using ψ scans of three suitable reflections having χ values close to 90°.[28] The measured intensities were corrected for Lorentz, polarization, background, and decay effects and reduced to F_o^2.

(b) Solution and Structure Refinement. The structures were solved by direct methods (SIR92[29]) and difference Fourier methods and were subsequently refined by full-matrix least-squares against F_o^2 using reflections with $F_o^2 \geq 3\sigma(F_o^2)$ and the program SHELXL93[30] on a Silicon Graphics Indigo computer. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from ref 31. All nonhydrogen atoms were given anisotropic displacement parameters, with exception of the cation carbon atoms in **2** (which belonged to two different disordered models having 70 and 30% occupancy factors, respectively) and the minor component (14%) of the disordered cyclohexyl isocyanide ligand in **4**. To stabilize the refinements, the disordered fragments required contraints on the C−C bond distances and angles. Hydrogen atoms were included in calculated positions and refined riding on their parent carbon atoms with isotropic displacement parameters which were 1.5 (methyls, with two equally occupied disordered models) or 1.2 (phenyls or cyclohexyl isocyanides) times that of the pertinent carbon atom. No hydrogen atoms were added to the disordered triethylammonium cation in **2** and the disordered cyclohexyl isocyanide in **4**. The final conventional agreement indexes are listed in Table 4, together with other experimental details.

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Supporting Information Available: Fractional atomic coordinates, bond distances and angles, anisotropic displacement parameters, list of geometrical restraints, and a full table of crystal data and structural refinement parameters are supplied (29 pages). Ordering information is given on any current masthead page.

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