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Synthesis of $[Cu(dcmpz)]_n$ and Its Reactions with Carbon Monoxide and Cyclohexyl Isocyanide. Crystal Structures of $[Cu_2(dcmpz)_2(py)_2(CO)]$ and $[Cu(dcmpz)(RNC)]_2$ (Hdcmpz = 3,5-Dicarbomethoxypyrazole, R = Cyclohexyl)

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The reaction of $[Cu(CH_3CN)_4](BF_4)$ with 3,5-dicarbomethoxypyrazole (Hdcmpz) in the presence of triethylamine yields the new copper(I) complex $[Cu(dcmpz)]_n$ (**1**) quantitatively. This method of synthesis appears to be a particularly useful general synthetic route leading to copper(I) pyrazolates. Reaction of **1** with stoichiometric amounts of cyclohexyl isocyanide (RNC) in diethyl ether affords the dimeric complex $[Cu(dcmpz)(RNC)]_2$ (**2**). Carbonylation of **1** in pyridine leads to the isolation of the dinuclear copper(I) derivative $[Cu_2(dcmpz)_2(py)_2(CO)]$ (**3**), which represents an unprecedented dinuclear copper(I) complex containing only one *terminal* carbonyl ligand *per two* copper atoms. For both complexes **2** and **3** an X-ray crystal structure analysis has been performed. Crystals of **2** are triclinic, space group $P\bar{1}$ (No. 2), with a = 11.243 (3) Å, b = 11.188 (2) Å, c = 12.946 (3) Å, α = 90.75 (1)°, β = 100.17 (2)°, γ = 89.10 (2)°, and Z = 2. Final R = 0.030 for 4255 reflections having $I > 3\sigma(I)$. Crystals of **3** are triclinic, space group $P\bar{1}$ (No. 2), with a = 8.423 (6) Å, b = 9.462 (5) Å, c = 20.311 (8) Å, α = 77.42 (3)°, β = 88.97 (3)°, γ = 64.83 (3)°, and Z = 2. Final R = 0.043 for 2190 reflections having $I > 3\sigma(I)$.

Introduction

Univalent metal complexes containing a single pyrazolate bridging ligand have been known since 1889, when Buchner reported the formation of the insoluble silver derivative $[Ag(pz)]_n$ (Hpz = pyrazole).[2] The structure of $[Ag(pz)]_n$ has never been established, but has always been claimed to be a polymeric species. Similar polymeric or oligomeric structures probably exist in $[Cu(pz)]_n$ and in related copper(I) complexes having different substituents in the pyrazole ring.[3] Surprisingly, little attention has been devoted to the chemical behavior of these pyrazolato complexes. We recently reported that $[Cu(dmpz)]_3$ (Hdmpz = 3,5-dimethylpyrazole) quantitatively reacts with neutral ligands such as 1,10-phenanthroline (phen) and cyclohexyl isocyanide (RNC), yielding $[Cu(dmpz)(phen)]_2$ and $[Cu(dmpz)(RNC)]_2$, respectively.[4] The reactions of $[Cu(dmpz)(RNC)]_2$, which has been structurally characterized,[5] with heterocumulenes like RNCO (R = cyclohexyl), PhNCS, COS, and CS_2 have also been studied.[5] An unprecedented octanuclear copper(II) hydroxo complex, $[Cu_8(dmpz)_8(OH)_8]$, has been obtained by reacting $[Cu(dmpz)]_3$ with O_2 at atmospheric pressure in wet solvents.[6]

As part of a systematic study of the chemistry of new and already known copper(I) pyrazolate complexes, we developed a particularly useful general synthetic route which allows the facile preparation of copper(I) pyrazolate derivatives.

In this paper, we report the synthesis of $[Cu(dcmpz)]_n$ (Hdcmpz = 3,5-dicarbomethoxypyrazole), and its reaction with carbon monoxide and cyclohexyl isocyanide which led to the formation of $[Cu_2(dcmpz)_2(py)_2(CO)]$ and $[Cu(dcmpz)(RNC)]_2$ (R = cyclohexyl), respectively. The full structural characterization of these species is also reported.

Experimental Section

Cyclohexyl isocyanide and pyrazole-3,5-dicarboxylic acid were used as supplied (Aldrich Chemical Co.). Solvents were dried and distilled by standard methods. Tetrakis(acetonitrile)copper(I) tetrafluoroborate[7] and 3,5-dicarbomethoxypyrazole[8] were prepared according to literature procedures.

Table I. Crystal Data and Data Collection Parameters for Complexes **2** and **3**

compound	2	3
formula	$C_{28}H_{36}Cu_2N_6O_8$	$C_{25}H_{24}Cu_2N_6O_9$
formula weight, amu	711.71	679.58
crystal system	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	11.243 (3)	8.423 (6)
b, Å	11.188 (2)	9.462 (5)
c, Å	12.946 (3)	20.311 (8)
α, deg	90.75 (1)	77.42 (3)
β, deg	100.17 (2)	88.97 (3)
γ, deg	89.10 (2)	64.83 (3)
V, Å^3	1603 (1)	1425 (1)
Z	2	2
D_{calc}, g cm^{-3}	1.475	1.584
T, °C	22	22
radiation (graphite monochr)	Mo Kα, λ = 0.71073 Å	Mo Kα, λ = 0.71073 Å
μ(Mo Kα), cm^{-1}	13.8	15.5
min transm factor	0.87	0.81
crystal size, mm	0.15 × 0.10 × 0.08	0.20 × 0.18 × 0.05
R	0.030	0.043
R_w	0.038	0.048

Infrared spectra were recorded on a Perkin-Elmer 783 instrument; NMR spectra were obtained with a Bruker WP80 spectrometer.

Elemental analyses were carried out at the Microanalytical Laboratory of this university.

Synthesis of $[Cu(dcmpz)]_n$ (1). To an acetone solution (15 mL) of 3,5-dicarbomethoxypyrazole (Hdcmpz) (585 mg, 3.18 mmol) was added $[Cu(CH_3CN)_4](BF_4)$ (500 mg, 1.59 mmol) under nitrogen. The colorless solution was stirred for 5 min, and triethylamine (482 mg, 4.77 mmol) was added dropwise. A white precipitate suddenly formed. The suspension was stirred for 30 min. The reaction vessel was then flushed with dinitrogen until the volatile components evaporated. The resulting white solid was treated with acetone (10 mL) and quickly centrifuged in a sealed tube. The residue was washed several times with acetone, centrifuged again, and then dried under vacuum. Yield: 91%. Mp: 108 °C. Anal. Calcd for $C_7H_7CuN_2O_4$: C, 34.08; H, 2.84; N, 11.36. Found: C, 34.11; H, 2.85; N, 11.35.

Synthesis of $[Cu(dcmpz)(RNC)]_2$ (2). To a diethyl ether solution (10 mL) of cyclohexyl isocyanide (170 mg, 1.56 mmol) was added $[Cu(dcmpz)]_n$ (362 mg, 1.47 mmol). A clear solution formed from which, in about 15 min, a white solid precipitated. The suspension was stirred for 30 min, and then the solid was filtered off, washed with diethyl ether and *n*-hexane, and dried under vacuum (yield 88%). Crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of the complex. Mp > 300 °C. Anal. Calcd

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Table II. Fractional Atomic Coordinates for Compound **2** (Esd's in Parentheses)

atom	*x*	*y*	*z*
Cu1	0.04051 (3)	0.11028 (3)	0.28079 (3)
Cu2	0.33268 (3)	0.03061 (3)	0.27476 (3)
O1	−0.0683 (2)	0.3375 (2)	0.2104 (2)
O2	0.0110 (2)	0.4967 (2)	0.1491 (2)
O3	0.5149 (2)	0.3885 (2)	0.1996 (2)
O4	0.5140 (2)	0.1933 (2)	0.2283 (2)
O5	−0.1690 (2)	0.0144 (2)	0.1431 (2)
O6	−0.1858 (2)	−0.1456 (2)	0.0365 (2)
O7	0.4065 (2)	−0.1597 (2)	0.1282 (2)
O8	0.2920 (2)	−0.3115 (2)	0.0568 (2)
N1	0.1603 (2)	0.2290 (2)	0.2474 (2)
N2	0.2788 (2)	0.2014 (2)	0.2529 (2)
N3	0.0799 (2)	−0.0210 (2)	0.1864 (2)
N4	0.1958 (2)	−0.0553 (2)	0.1868 (2)
N5	−0.0876 (2)	0.1348 (2)	0.4643 (2)
N6	0.5444 (2)	−0.0914 (2)	0.4079 (2)
C1	0.1416 (2)	0.3429 (2)	0.2144 (2)
C2	0.2497 (2)	0.3918 (2)	0.1997 (2)
C3	0.3337 (2)	0.2999 (2)	0.2251 (2)
C4	0.0173 (3)	0.3897 (3)	0.1928 (2)
C5	−0.1087 (3)	0.5463 (3)	0.1153 (3)
C6	0.4626 (3)	0.3010 (3)	0.2174 (2)
C7	0.6363 (3)	0.1805 (4)	0.2111 (3)
C8	0.0075 (2)	−0.0899 (2)	0.1171 (2)
C9	0.0767 (3)	−0.1734 (3)	0.0717 (2)
C10	0.1938 (2)	−0.1491 (2)	0.1183 (2)
C11	−0.1234 (3)	−0.0664 (3)	0.1017 (2)
C12	−0.3154 (3)	−0.1274 (4)	0.0148 (3)
C13	0.3088 (3)	−0.2048 (3)	0.1024 (2)
C14	0.3999 (3)	−0.3748 (3)	0.0381 (3)
C15	−0.0388 (2)	0.1215 (2)	0.3942 (2)
C16	−0.1470 (3)	0.1619 (3)	0.5531 (2)
C17	−0.0658 (3)	0.2380 (3)	0.6321 (2)
C18	−0.0484 (3)	0.3609 (3)	0.5903 (3)
C19	−0.1688 (4)	0.4230 (3)	0.5541 (3)
C20	−0.2491 (3)	0.3492 (3)	0.4729 (3)
C21	−0.2666 (3)	0.2255 (3)	0.5137 (3)
C22	0.4628 (3)	−0.0418 (3)	0.3597 (2)
C23	0.6461 (3)	−0.1632 (3)	0.4602 (3)
C24	0.7429 (3)	−0.1684 (3)	0.3930 (3)
C25	0.7037 (3)	−0.2395 (3)	0.2928 (3)
C26	0.6628 (3)	−0.3618 (3)	0.3146 (3)
C27	0.5629 (3)	−0.3561 (3)	0.3795 (3)
C28	0.6011 (3)	−0.2861 (4)	0.4802 (3)

for $C_{28}H_{36}Cu_2N_6O_8$: C, 47.26; H, 5.06; N, 11.81. Found: C, 47.19; H, 5.13; N, 11.95.

Synthesis of [Cu$_2$(dcmpz)$_2$(py)$_2$(CO)] (3). [Cu(dcmpz)]$_n$ (70 mg) was dissolved, under nitrogen, in 5 mL of pyridine. Carbon monoxide was then bubbled through the pale yellow solution. In about 30 min, a yellow solid formed. After 1 h, the solid was filtered under carbon monoxide pressure and dried under a stream of carbon monoxide (yield 46%). A second crop of **2** was obtained by adding carbon monoxide saturated diethyl ether to the mother liquors.

Crystals suitable for diffraction studies were obtained by slow diffusion of diethyl ether into a CO-saturated pyridine solution of **2** at room temperature. Anal. Calcd for $C_{25}H_{24}Cu_2N_6O_9$: C, 44.18; H, 3.54; N, 12.37. Found: C, 44.07; H, 3.35; N, 12.15.

X-Ray Crystal Structure Determination of Compounds 2 and 3. Crystal data and experimental conditions are summarized in Table I. The intensity data were collected on an Enraf-Nonius CAD4 automated diffractometer. A least-squares fit of 25 randomly oriented intense reflections with θ ranging from 8° to 12° provided the unit cell parameters. A total of 8006 and 4992 reflections (for compounds **2** and **3**) were collected using a variable scan range with a 25% extension at each end for background determination in the $6° < 2\theta < 56°$ and $6° < 2\theta < 50°$ range ($+h$, $\pm k$, $\pm l$ octants), respectively. Three standard reflections were measured at regular intervals and showed a constant decay of the scattering power of the crystal of **3** which was evaluated about 25% (on I) at the end of the data collection. The full data sets were then corrected for decay (if any) and Lorentz and polarization effects. Empirical absorption corrections were performed on the basis of ψ scans (ψ = 0–360°, every 10°) of three suitable reflections with χ values close to 90°.[9]

Table III. Fractional Atomic Coordinates for Compound **3** (Esd's in Parentheses)

atom	*x*	*y*	*z*
Cu1	0.1440 (1)	−0.04848 (9)	0.15309 (4)
Cu2	0.0951 (1)	−0.14975 (9)	0.31298 (4)
O	0.1781 (9)	0.0402 (6)	0.0076 (3)
O1	0.1405 (8)	0.2964 (5)	0.0847 (3)
O2	0.1087 (7)	0.4901 (5)	0.1360 (2)
O3	0.0936 (8)	0.0272 (5)	0.4196 (3)
O4	0.0438 (8)	0.2821 (5)	0.4054 (2)
O5	0.640 (1)	−0.5322 (7)	0.1203 (3)
O6	0.4696 (7)	−0.2780 (6)	0.0850 (3)
O7	0.3131 (7)	−0.4594 (6)	0.4130 (3)
O8	0.5484 (8)	−0.6688 (6)	0.3946 (3)
N1	0.1201 (7)	0.1072 (5)	0.2132 (3)
N2	0.1032 (7)	0.0618 (5)	0.2791 (3)
N3	0.3138 (7)	−0.2731 (6)	0.2083 (3)
N4	0.2858 (7)	−0.3104 (6)	0.2742 (3)
N5	−0.0981 (7)	−0.0511 (6)	0.1699 (3)
N6	−0.1161 (7)	−0.1666 (6)	0.3481 (3)
C	0.166 (1)	0.0073 (7)	0.0635 (4)
C1	0.1097 (8)	0.2594 (7)	0.2029 (3)
C2	0.0892 (9)	0.3078 (7)	0.2628 (3)
C3	0.0852 (9)	0.1800 (7)	0.3099 (3)
C4	0.1210 (9)	0.3456 (7)	0.1350 (4)
C5	0.117 (1)	0.5865 (8)	0.0717 (4)
C6	0.073 (1)	0.1517 (8)	0.3827 (4)
C7	0.039 (1)	0.268 (1)	0.4777 (4)
C8	0.4546 (9)	−0.4031 (7)	0.1957 (4)
C9	0.517 (1)	−0.5226 (7)	0.2544 (4)
C10	0.4081 (9)	−0.4594 (7)	0.3024 (4)
C11	0.530 (1)	−0.4146 (8)	0.1316 (4)
C12	0.546 (2)	−0.281 (1)	0.0209 (5)
C13	0.413 (1)	−0.5261 (8)	0.3754 (4)
C14	0.570 (1)	−0.745 (1)	0.4653 (5)
C15	−0.1229 (9)	−0.1860 (7)	0.1852 (4)
C16	−0.2842 (9)	−0.1812 (8)	0.1914 (5)
C17	−0.428 (1)	−0.039 (1)	0.1822 (5)
C18	−0.405 (1)	0.095 (1)	0.1679 (5)
C19	−0.241 (1)	0.0876 (8)	0.1610 (4)
C20	−0.1332 (9)	−0.3048 (8)	0.3610 (4)
C21	−0.289 (1)	−0.3149 (9)	0.3718 (4)
C22	−0.437 (1)	−0.177 (1)	0.3699 (4)
C23	−0.427 (1)	−0.0318 (9)	0.3570 (5)
C24	−0.264 (1)	−0.0332 (8)	0.3467 (4)

The structures were solved by conventional three-dimensional Patterson and Fourier difference methods, and refined by full-matrix least-squares analysis using the Enraf-Nonius Structure Determination Package (SDP)[10] and the physical constants tabulated therein on a PDP 11/73 computer. Individual weights were assigned as $w = 4|F_o|^2/\sigma^2(|F_o|^2)$ and $\sigma(|F_o|^2) = [\sigma^2(I) + (pI)^2]^{1/2}/LP$, p, the "ignorance factor", being set at 0.04. The final values of the agreement indices for 4255 and 2190 observed reflections having $I > 3\sigma(I)$ are also reported in Table I.

Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were introduced in the last stages of the refinement in ideal positions (C–H = 0.95 Å) and fixed isotropic B's (5.0 Å^2), but not refined. Anomalous scattering correction terms were taken from ref 11. The peaks in the final difference Fourier map were randomly located. The final values of the fractional atomic coordinates for **2** and **3** are reported in Tables II and III, respectively.

Results and Discussion

The reaction of [Cu(CH$_3$CN)$_4$](BF$_4$) with 3,5-dicarbomethoxypyrazole (Hdcmpz) in acetone in the presence of triethylamine leads to the isolation of [Cu(dcmpz)]$_n$ (**1**) (eq 1). This method

$$[\mathrm{Cu(CH_3CN)_4}](\mathrm{BF_4}) + \mathrm{Hdcmpz} \xrightarrow{\mathrm{Et_3N}} (1/n)[\mathrm{Cu(dcmpz)}]_n + (\mathrm{Et_3NH})(\mathrm{BF_4}) + 4\mathrm{CH_3CN} \quad (1)$$

of synthesis works well not only for this particular compound but also for other copper(I) pyrazolate complexes such as [Cu(pz)]$_n$ (Hpz = pyrazole) and [Cu(dmpz)]$_3$ (Hdmpz = 3,5-dimethyl-

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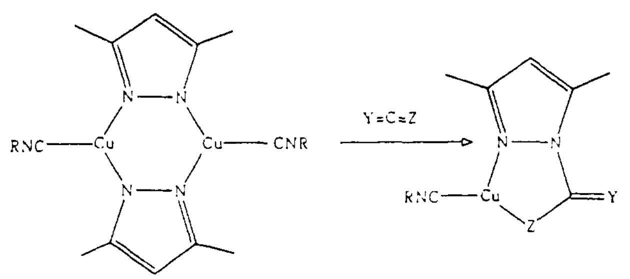
Scheme I



R = cyclohexyl

Y = S, Z = NPh
Y = O, Z = NR
Y = O, Z = S

pyrazole), quantitative yields being obtained in all cases. The very low solubility of **1** in the common organic solvents prevented solution studies and growth of crystals suitable for an X-ray investigation. The formulation of **1** as an oligomeric complex is only tentatively suggested. X-ray powder diffraction studies are in progress with the aim to verify its nuclearity. The IR spectrum of **1** exhibits only one ν(C=O) at 1723 cm^{-1} (Nujol mull), suggesting the equivalence of the carbonyl groups of the two COOMe substituents in the 3,5-positions of the pyrazole ring. This absorption lies quite at the same frequency as for the dimeric species $[Cu(dcmpz)(RNC)]_2$ (**2**) (R = cyclohexyl), whose X-ray crystal structure ruled out interactions between the C=O groups and the copper center (see later).

We have verified that the synthetic method reported above (eq 1) gives copper(I) pyrazolates whose nuclearity is related to the pyrazole employed. In fact, 3,5-diphenylpyrazole (Hdppz) led to the isolation of a tetrameric complex, $[Cu(dppz)]_4$, whose crystal structure refinement is now in progress. The preparation of this unprecedented tetranuclear copper(I) pyrazolate derivative and its reaction with small molecules will be reported elsewhere.[12] Notably, a trimeric copper(I) complex, $[Cu(dppz)]_3$, has been obtained by Raptis and Fackler,[13a] employing a different synthetic route. In contrast, the same trimeric species reported by M. K. Ehlert et al.[13b] is obtained when Hdmpz is employed.

Reaction of 1 with Cyclohexyl Isocyanide. Reaction of **1** with cyclohexyl isocyanide (RNC) in diethyl ether affords complex **2**, $[Cu(dcmpz)(RNC)]_2$. Complex **2** was isolated as a white crystalline solid. Its IR spectrum shows the ν(NC) band at 2170 cm^{-1}, a value quite close to that observed in the dinuclear copper(I) pyrazolate derivative $[Cu(dmpz)(RNC)]_2$.[4] Only one ν(C=O) band has been observed for **2** at 1717 cm^{-1}.

The ^{1}H NMR spectrum of **2** (CD_2Cl_2) shows very sharp signals arising from the dcmpz ligand at 3.82 ($COOCH_3$) and 7.13 (C(4)–H) ppm. The pattern of these signals does not change by lowering the temperature to −80 °C. In these conditions only the well-known dynamic behavior of the cyclohexyl rings is observed. The ^{13}C NMR spectrum (CD_2Cl_2) also ruled out any fluxional property of either pyrazolate groups or the Cu–(N–N)$_2$–Cu ring. In fact, only sharp signals are observed at 51.4 (COO*C*H$_3$), 110.9 (C(4)), 142.7 (C(3), C(5)), and 162.9 (*C*OOCH$_3$) ppm.

We have already reported[5] that the facile reactions take place when $[Cu(dmpz)(RNC)]_2$ is treated with heterocumulenes such as cyclohexyl isocyanate, phenyl isothiocyanate, and carbonyl sulfide (Scheme I).

The reaction products result from *formal* nucleophilic addition of 3,5-dimethylpyrazolate anion to the central carbon of the heterocumulenes, to give a new bidentate ligand. In the case of COS, spectroscopic and chemical evidences suggested the formation of the intermediate species [Cu(dmpz)(RNC)(COS)], containing a S-bonded σ-coordinated COS ligand. Complex **2** contains a pyrazolate anion whose COOMe groups should favor the σ-coordination of the heterocumulene, increasing the acidic character of the copper atom. Moreover, one should expect also a lowering of the nucleophilic character of the pyrazolate, preventing the insertion of heterocumulenes into the Cu–N bond. In spite of many different attempts, complex **2** did not show any significant reactivity toward the aforementioned heterocumulenes. The lack of reactions leading to the formation of the bidentate ligands analogous to those reported in Scheme I confirmed that the dcmpz anion is now less nucleophilic. On the other hand, the COOMe groups seem not to be electron-withdrawing enough to enhance the acidic character of the copper center.

Reaction of 1 with Carbon Monoxide. $[Cu(dcmpz)]_n$ (**1**) easily dissolves in pyridine, affording pale yellow solutions. Attempts made in order to isolate and characterize the product present in such solutions failed, the starting polymeric species **1** being in any case recovered. The ^{1}H and ^{13}C NMR spectra of such a pyridine solution were recorded with the aim to ascertain the nature of the species present in solution. In the ^{1}H NMR spectrum (pyridine-d_5) two signals were present at 3.66 ($COOCH_3$) and 7.94 (C(4)–H) ppm. The ^{1}H NMR spectrum remained unchanged by varying the temperature in the range −35 to +20 °C. In the ^{13}C NMR spectrum four signals are present at 51.2 (COO*C*H$_3$), 119.4 (C(4)), 143.2 (C(3), C(5)), and 164.1 (*C*OOCH$_3$) ppm. Also in this case, the value and the shape of the peaks did not vary by lowering the temperature.

The analogy existing between these NMR spectra and those of $[Cu(dcmpz)(RNC)]_2$ discussed above seems to suggest that pyridine solutions of $[Cu(dcmpz)]_n$ may contain a dimeric species, e.g., $[Cu(dcmpz)(py)]_2$.

We verified that a reaction takes place if carbon monoxide is bubbled through the pyridine solutions of $[Cu(dcmpz)]_n$. The IR spectrum, registered after a few minutes, exhibits a strong, sharp absorption at 2073 cm^{-1}, which is diagnostic for the presence of a terminal carbonyl group in tetracoordinate copper(I) environments.[14] The carbonyl species present in the pyridine solution was shown to contain a labile CO. In fact, this is lost by bubbling dinitrogen. Moreover, evaporation of the solvent gave the starting $[Cu(dcmpz)]_n$ as the only product.

If carbon monoxide is bubbled for longer times (ca. 30 min), $[Cu_2(dcmpz)_2(py)_2(CO)]$ (**3**) separates as a microcrystalline pale yellow solid. The IR spectrum of **3** (Nujol mull) showed the carbonyl absorption at 2083 cm^{-1}. Three bands are found in the 1700–1750-cm^{-1} region (1730, 1716, 1705, cm^{-1}) assignable to ν(C=O) of nonequivalent $COOCH_3$ groups. When the IR spectrum of **3** is recorded in pyridine, the ν(C=O) absorption is found at 2073 cm^{-1}. An IR monitoring of such pyridine solutions shows a rapid loss of carbon monoxide. $[Cu_2(dcmpz)_2(py)_2(CO)]$ did not lose CO in vacuo at room temperature. When heated at 60 °C in vacuo, loss of carbon monoxide and pyridine was verified, the polynuclear $[Cu(dcmpz)]_n$ (**1**) being recovered.

In order to establish whether complex **3** is representative of the species present in solution or whether we are in the presence of two distinct products, we decided to register the ^{1}H and ^{13}C NMR spectra of pyridine-d_5 solutions containing $[Cu(dcmpz)]_n$ under a CO atmosphere.

The ^{1}H NMR spectrum, recorded at 20 °C, exhibits a broad peak at 3.67 ppm ($COOCH_3$) and a very broad signal at 7.92 ppm (C(4)–H). By lowering the temperature to −35 °C, the signal at higher fields splits into two well-separated peaks (3.59 and 3.70 ppm), while the signal at 7.92 sharpens. Also the ^{13}C NMR spectrum, recorded at −35 °C, shows a splitting of the signals assignable to COO*C*H$_3$ (50.6, 51.3 ppm), C(3) and C(5) (147.3 and 148.5 ppm), and the ester carbonyl (163.4 and 163.8 ppm), while the C(4) shows only one resonance at 119.3 ppm. We did not succeed in observing the signal attributable to the bound CO.

Fluxional behavior involving a unidentate ligand is thus revealed by both ^{1}H and ^{13}C NMR spectra. Such dynamic processes

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Table IV. Relevant Bond Distances (Å) and Angles (deg) in Compound **2**

Distances			
Cu1···Cu2	3.404 (1)		
Cu1–N1	2.010 (2)		
Cu1–N3	1.992 (2)		
Cu1–C15	1.849 (3)		
Cu2–N2	2.004 (2)		
Cu2–N4	1.997 (2)		
Cu2–C22	1.851 (3)		
N1–N2	1.352 (2)	N3–N4	1.353 (2)
N1–C1	1.352 (3)	N3–C8	1.344 (2)
C1–C2	1.385 (3)	C8–C9	1.395 (3)
C2–C3	1.388 (3)	C9–C10	1.378 (3)
C3–N2	1.355 (3)	C10–N4	1.362 (3)
C1–C4	1.466 (3)	C8–C11	1.469 (3)
C4–O1	1.190 (3)	C11–O5	1.199 (3)
C4–O2	1.326 (3)	C11–O6	1.335 (3)
O2–C5	1.445 (3)	O6–C12	1.447 (3)
C3–C6	1.470 (3)	C10–C13	1.472 (3)
C6–O3	1.195 (3)	C13–O7	1.206 (3)
C6–O4	1.326 (3)	C13–O8	1.325 (3)
O4–C7	1.436 (3)	O8–C14	1.451 (3)
C15–N5	1.148 (3)	C22–N6	1.153 (3)
N5–C16	1.455 (3)	N6–C23	1.457 (3)
Angles			
N1–Cu1–N3	97.32 (8)	N2–Cu2–N4	101.45 (8)
N1–Cu1–C15	124.90 (9)	N2–Cu2–C22	133.09 (10)
N3–Cu1–C15	135.51 (9)	N4–Cu2–C22	125.25 (10)
Cu1–C15–N5	176.4 (2)	Cu2–C22–N6	176.1 (2)
C15–N5–C16	175.4 (3)	C22–N6–C23	174.1 (3)

Table V. Synoptic Collection of the Geometrical Parameters of the Cu_2N_4 Metallocycles for [Cu(dmpz)(RNC)]$_2$ and Compound **2**

	[Cu(dmpz)(RNC)]$_2$	[Cu(dcmpz)(RNC)]$_2$
Cu···Cu, Å	3.558	3.404
Cu–N (av), Å	1.960	2.001
N–N (av), Å	1.396	1.352
Cu–C (av) [RNC], Å	1.853	1.850
C–N (av) [RNC], Å	1.159	1.151
Cu–N–N (av), deg	123.4	120.7
N–Cu–N (av), deg	113.0	99.4
dihedral angle between pyrazolate rings, deg	180.0	119.6

involving pyrazoles or pyrazolate groups have been already observed.[15] On the basis of the NMR spectra, we tentatively formulate the carbonyl species present in the pyridine solutions as the tetracoordinate complex [Cu(dcmpz)(py)$_2$(CO)], containing a unidentate dcmpz ligand.

Gas-volumetric measurements and spectroscopic evidences have established that the reaction of carbon monoxide with hemocyanin, the oxygen-transporting copper protein in the hemolymph of many mollusks and arthropods, affords a carbonyl adduct in which the binuclear active site binds only one molecule of CO in nonbridging fashion.[16] An analogy can be drawn between the CO–hemocyanin adduct and the dinuclear carbonyl complex **3** described in the present paper. The observed stoichiometry of carbon monoxide binding to hemocyanin has been interpreted in terms of different actual coordination of the two copper atoms.[16] In our case, the formation of **3** is a consequence of steric effects due to the two pyridine ligands, which prevent the binding of a second molecule of CO (see later).

Description of the Structure of [Cu(dcmpz)(RNC)]$_2$ (2) and [Cu$_2$(dcmpz)$_2$(py)$_2$(CO)] (3). Compound **2** consists of a discrete binuclear complex of Cu(I), bridged by two dcmpz ligands and bound to two RNC (R = cyclohexyl) groups. The ORTEP drawing

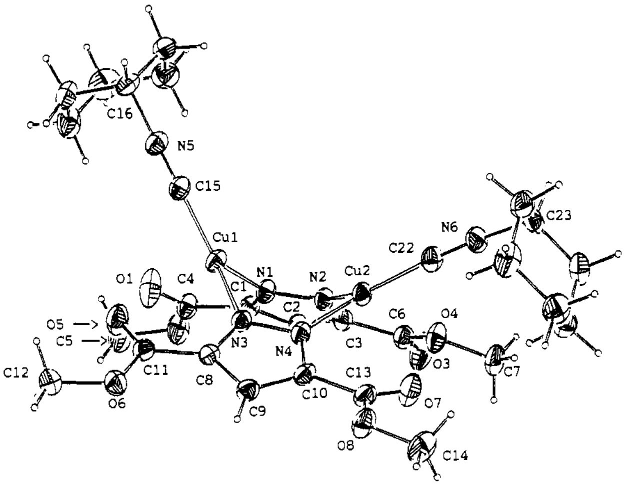

Figure 1. ORTEP drawing of complex **2** with partial labeling scheme. Thermal ellipsoids are drawn at 30% probability level.

Table VI. Relevant Bond Distances (Å) and Angles (deg) in Compound **3**

Distances			
Cu1···Cu2	3.250 (1)		
Cu1–N1	2.056 (5)		
Cu1–N3	2.062 (5)		
Cu1–N5	2.071 (5)		
Cu1–C	1.810 (8)		
Cu2–N2	2.000 (5)		
Cu2–N4	1.977 (5)		
Cu2–N6	1.961 (5)		
C–O	1.126 (8)		
N1–N2	1.337 (6)	N3–N4	1.351 (6)
N1–C1	1.374 (7)	N3–C8	1.368 (8)
C1–C2	1.374 (8)	C8–C9	1.381 (8)
C2–C3	1.382 (8)	C9–C10	1.378 (9)
C3–N2	1.351 (7)	C10–N4	1.345 (7)
C1–C4	1.466 (8)	C8–C11	1.441 (9)
C4–O1	1.193 (7)	C11–O6	1.175 (6)
C4–O2	1.332 (7)	C11–O5	1.323 (7)
O2–C5	1.441 (8)	O5–C12	1.443 (9)
C3–C6	1.454 (9)	C10–C13	1.475 (9)
C6–O3	1.194 (7)	C13–O7	1.193 (8)
C6–O4	1.334 (8)	C13–O8	1.324 (8)
O4–C7	1.447 (8)	O8–C14	1.435 (9)
N5–C15	1.325 (7)	N6–C20	1.345 (8)
C15–C16	1.345 (10)	C20–C21	1.362 (10)
C16–C17	1.350 (12)	C21–C22	1.362 (10)
C17–C18	1.327 (12)	C22–C23	1.381 (11)
C18–C19	1.357 (10)	C23–C24	1.376 (10)
C19–N5	1.328 (8)	C24–N6	1.341 (8)
Angles			
N1–Cu1–N3	105.7 (2)	N2–Cu2–N4	107.7 (2)
N1–Cu1–N5	95.8 (2)	N2–Cu2–N6	122.3 (2)
N1–Cu1–C	119.7 (2)	N4–Cu2–N6	126.4 (2)
N3–Cu1–N5	101.5 (2)		
N3–Cu1–C	119.1 (3)		
N5–Cu1–C	111.3 (3)		
Cu1–C–O	178.5 (7)		

of the molecule is reported in Figure 1; relevant bond distances and angles are collected in Table IV.

[Cu(dcmpz)(RNC)]$_2$ is topologically equivalent to the already reported[5] [Cu(dmpz)(RNC)]$_2$ analogue; however, the pattern of bond distances and angles of the $\overline{\text{Cu–N–N–Cu–N–N}}$ ring, as well as its conformation, is markedly different. Table V contains some of the geometrical parameters characterizing the two homologues; the most striking features are the differences in the Cu···Cu contacts, as well as in the dihedral angles between the pyrazolate rings; while it can be easily understood that the 2/*m* symmetry of the dmpz derivative could not be maintained in **2**, owing to the

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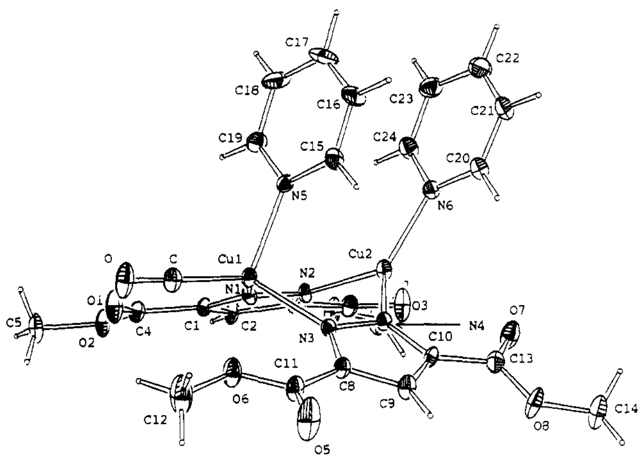

Figure 2. ORTEP drawing of complex **3** with partial labeling scheme. Thermal ellipsoids are drawn at 30% probability level.

presence of bulker, although flexible, –COOMe residues, the marked shortening of the intermetallic interaction in **2** could be in principle explained by the relaxation of a significantly sterically strained situation present in $[Cu(dmpz)(RNC)]_2$, which, among the few known pyrazolate-bridged copper compounds, has an exceptionally long Cu⋯Cu distance. Both cyclohexyl rings are in a chair conformation (see Figure 1).

Compound **3** consists of a discrete binuclear complex of Cu(I), bridged by two dcmpz ligands and bound to two pyridine and one carbonyl groups, as depicted in the ORTEP drawing of Figure 2. Bond distances and angles of chemical interest are reported in Table VI.

The two copper atoms are at a nonbonding distance of 3.250 Å, which is significantly shorter than the value found in **2** and $[Cu(dmpz)(RNC)]_2$[4] (see Table V), but much more similar to the Cu⋯Cu values found for polynuclear Cu(II) systems containing both pirazolate bridges and μ_2- or μ_3-OH groups (average values 3.251 Å in $[Cu_3(OH)(pz)_3(py)_2Cl_2]$,[17] 3.345 Å in $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]$,[18] and 3.238 Å in $[Cu_8(dmpz)_8(OH)_8]$,[6] Hpz = pyrazole); this suggests that some extra force, not related to the dcmpz ligands only, must be present in order to shorten the Cu⋯Cu distance, which we indicate as the intramolecular interaction between the two (axial) pyridine ligands (vide infra). Moreover, the coordination of the two copper centers is remarkably different: while Cu(2) is tricoordinated, in a fashion very similar to the geometry found for the copper atoms in $[Cu(dmpz)(RNC)]_2$, Cu(1) bears an extra ligand, the terminal CO molecule, which makes the coordination around this metal center roughly tetrahedral. As a consequence of the more crowded environment of the copper atoms (deriving also by the steric requirements imposed by the simultaneous presence of the pyridine molecules and of the dcmpz ligands, if compared to the RNC and dmpz ligands found in $[Cu(dmpz)(RNC)]_2$),[5] the coplanarity of the two pz rings observed in the latter is lost and the best planes passing through their ring atoms are at an angle of about 132.7°.

The strictly planar pyridine rings on the two different copper atoms are at an angle of 5.4°, and only 3.42 Å apart, giving rise to a strong intramolecular graphitic interaction between the two ligands; from the values reported in Table VI, one can see that the pyridine ligand bound to the Cu(2) atom is slightly inflated, if compared to the other pyridine group, and might reflect the different charge distribution determined by the different ligands' environment of the two metals.

The carbonyl ligand shows the following bonding parameters: Cu(1)–C, 1.810 (8) Å; C–O, 1.126 (8) Å; and Cu(1)–C–O 178.5 (7)°. These parameters compare well with previously reported literature data for neutral tetracoordinated copper(I) compounds, such as $[(L)Cu(O_3SCF_3)(CO)]$ (L = glyoxaldiylbis(2,4-dimethylpentan-3-imine)[19] and $[(L')Cu(CO)(I)]$ (L′ = *N,N′*-ethylenebis(benzaldimine):[20] Cu–C, 1.820 (6) and 1.800 (9) Å; C–O, 1.11 (1) and 1.12 (2) Å, respectively. An interesting feature of the CO group is that it lies almost exactly on the Cu⋯Cu direction [Cu⋯Cu–C, 178.6 (2)°]. Of the possible reasons for not observing formation of a dicarbonylcopper dimer, similar to those discussed in ref 21, the partial rigidity of the Cu_2N_4 moiety, which allows CO coordination in the pseudomirror plane relating the two dcmpz ligands and makes a double tetrahedral coordination at the copper centers highly implausible, as well as the necessity of the presence of the pyridine groups (which are depolymerizing the otherwise insoluble $[Cu(dcmpz)]_n$ white solid), seems to be of some importance.

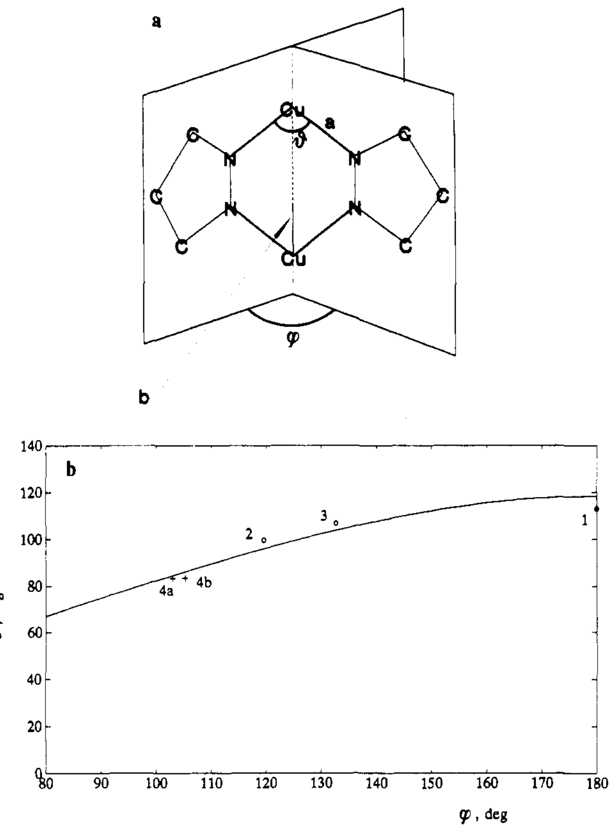

Figure 3. (a) Schematic representation of the geometrical parameters θ, φ, a, and b used in eq 2 (see text). (b) Functional dependence of $\theta(\varphi)$ for a = 2.00 Å and b = 1.02 Å (a Cu⋯Cu distance of 3.40 Å was assumed in this model). Experimental data: (1) $[Cu(dmpz)(RNC)]_2$[5], (2) complex **2**, (3) complex **3**, (4a) and (4b) $[Cu(dmpz)_2]_3$.[12]

Moreover, different from what was observed by us on Cu(II) derivatives of the very same dcmpz ligand, where some of the carbonylic oxygens of the –COOMe residues try to coordinate via long, possibly electrostatic, interactions in the apical positions of heavily elongated octahedra, in **2** and **3** no $(CH_3)O—C{=}O\cdots Cu$ interactions are observed.

It is worth noting that an ideally planar L–Cu–(N–N)$_2$–Cu–L moiety with pseudotrigonal coordination around the metal centers can easily be deformed into a boat sytem maintaining the pattern of bond distances and only slightly decreasing the endo N–Cu–N angles. If this deformation is accompanied by a limited energetic loss or can be favored by a coordination sphere of at least one of

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the copper atoms, intrinsically possessing smaller N–Cu–N angles (i.e., tetrahedral vs trigonal), the stability of the boat conformer can be increased. A sample geometrical model in which all bond distances are kept constant and only the dihedral angle φ defined by the two pyrazolate rings is independently varied gives, for the N–Cu–N angle θ, the following expression:

$$\theta = \frac{180}{\pi}\cos^{-1}\left[\frac{b^2 + (a^2 - b^2)\cos(\phi\pi/180)}{a^2}\right] \qquad (2)$$

where a and b are defined as the average observed Cu–N bond distance and the average projection of the Cu–N vectors onto the Cu···Cu hinge, respectively. Figure 3 shows the geometrical interpretation of this model and a plot of the θ vs φ function, from which it can be observed that small deviations from 120°, down to the observed θ values of 97.3 (1)°, 101.4 (1)° (compound **2**), 105.7 (2)°, and 107.7 (2)° (compound **3**) (see Tables IV and VI), can be obtained with much larger deviations from ideal coplanarity of the pyrazolate rings.

However, despite the geometric constraints imposed by the presence of stiff rings and of bond directionality in the donor nitrogen atoms of the pyrazolate ligands, a twisted (at first sight, unplausible) conformer in a highly sterically crowded coordination sphere of titanium atoms has been found in the $[(\mathrm{Cp})_2\mathrm{Ti(pz)}]_2$ dimer.[22]

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Registry No. **1**, 141344-55-0; **2**, 141344-56-1; **3**, 141344-57-2; [Cu(CH$_3$CN)$_4$](BF$_4$), 15418-29-8.

Supplementary Material Available: A detailed list of crystallographic parameters (Table S1), full lists of bond distances and angles (Tables S2 and S3), lists of anisotropic thermal factors (Tables S4 and S5), and lists of hydrogen atom coordinates (Tables S6 and S7) (16 pages); lists of observed and calculated structure factor moduli (Tables S8 and S9) (44 pages). Ordering information is given on any current masthead page.

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Contribution from the Discipline of Coordination Chemistry and Homogeneous Catalysis,
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Synthesis of the Monooxoruthenium(V) Complexes Containing the Amino Polycarboxylic Acid Ligands EDTA and PDTA and Their Reactivities in the Oxidation of Organic Substrates. X-ray Crystal Structures of $\mathrm{K[Ru^{III}(EDTA\text{-}H)Cl]\cdot 2H_2O}$ and $\mathrm{K[Ru^{III}(PDTA\text{-}H)Cl]\cdot 0.5H_2O}$

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The syntheses and characterization of $\mathrm{K[Ru^{V}{=}O(EDTA)]}$ (**3**) and $\mathrm{K[Ru^{V}{=}O(PDTA)]}$ (**4**) are described. The kinetics of the formation of **3** and **4** by the interaction of the corresponding chloro complexes $\mathrm{K[Ru^{III}(EDTA\text{-}H)Cl]}$ (**1**) and $\mathrm{K[Ru^{III}(PDTA\text{-}H)Cl]}$ (**2**) with the oxygen atom donor NaOCl was investigated in the temperature range 30–50 °C. The activation parameters of the oxygenation reaction of **1** and **2** to **3** and **4**, respectively, are consistent with an associatively activated process. The O atom transfer reaction from **3** and **4** to the unsaturated and saturated hydrocarbons were studied spectrophotometrically in the temperature range 30–50 °C by following the disappearance of the characteristic oxo peak of the complexes at 393 nm and by product analysis. The activation parameters for the oxidation of the substrates corresponding to the rate-determining oxygen atom transfer step were determined, and a suitable mechanism was proposed. The crystal and molecular structures of the precursor complexes **1** and **2** were determined using single-crystal X-ray diffraction technique.

Introduction

Recently there has been an upsurge of interest in the ruthenium–oxo chemistry.[1-5] Many complexes containing Ru(IV)–oxo[1] and Ru(VI)–dioxo[2] moieties were reported and used as catalysts for the oxidation of a variety of organic compounds, including triphenylphosphine,[1a,b,2a] dimethyl sulfoxide,[1c] alcohols,[2a,b] phenols,[1d,e] olefins,[1a,b,2a,b] and alkanes.[2b,c,d,5] Ru(V)–oxo complexes were however comparatively less studied. The Ru(V)–oxo complex[3] $\mathrm{Ru^{V}{=}O(EDTA\text{-}H)}$ catalyzes the oxidation of PPh$_3$ by molecular O$_2$. We have earlier studied[5,6] the formation of (μ-peroxo)ruthenium(IV) complexes with amino polycarboxylic acids and the catalysis of **1** in the oxidation of several organic substrates by molecular oxygen.[7,8]

The present investigation stems from our interest of developing new routes for the oxidation of saturated and unsaturated substrates catalyzed by $\mathrm{K[Ru^{III}(EDTA\text{-}H)Cl]}$ (**1**) (EDTA-H = protonated ethylenediaminetetraacetate) and $\mathrm{K[Ru^{III}(PDTA\text{-}H)Cl]}$ (**2**) (PDTA-H = protonated propylenediaminetetraacetate) in the presence of NaOCl as a cheap oxidant, which has successfully been used as an oxidant for the epoxidation of olefins by manganese porphyrins.[9,10] We report in this paper the kinetics

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