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Synthesis, X-ray Structure, and Catalytic Properties of the Unprecedented Tetranuclear Copper(I) Species $[Cu(dppz)]_4$ (Hdppz = 3,5-Diphenylpyrazole)

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The reaction of $[Cu(CH_3CN)_4](BF_4)$ with 3,5-diphenylpyrazole (Hdppz) in the presence of triethylamine yields quantitatively the new copper(I) complex $[Cu(dppz)]_4$ (**1**). Reaction of **1** with stoichiometric amounts of cyclohexyl isocyanide (RNC) in diethyl ether affords the dimeric complex $[Cu(dppz)(RNC)]_2$ (**2**). For both complexes **1** and **2** an X-ray crystal structure analysis has been performed. Crystals of **1** are triclinic, space group $P\bar{1}$ (No. 2), with $a = 19.423(9)$ Å, $b = 11.627(1)$ Å, $c = 11.905(2)$ Å, $\alpha = 85.75(1)°$, $\beta = 72.92(2)°$, $\gamma = 88.92(2)°$, and $Z = 2$. The final $R = 0.047$ for 3839 reflections having $I > 3\sigma(I)$. Compound **1** consists of tetrameric $[Cu(dppz)]_4$ molecules with Cu⋯Cu interactions (average 3.12 Å) supported by dppz ligands in the *exo*-bidentate mode. Crystal of **2** are triclinic, space group $P\bar{1}$ (No. 2), with $a = 9.246(2)$ Å, $b = 9.859(4)$ Å, $c = 12.543(2)$ Å, $\alpha = 103.82(2)°$, $\beta = 102.25(2)°$, $\gamma = 110.75(2)°$, and $Z = 1$. The final $R = 0.049$ for 1545 reflections having $I > 3\sigma(I)$. Complex **2** exhibits a $Cu-[N-N]_2-Cu$ ring in a rather unusual chairlike conformation. Complex **1** is catalytically active in the oxidative coupling of primary aromatic amines leading to the corresponding azobenzenes in the presence of molecular oxygen at atmospheric pressure. The reaction proceeds with a selectivity of 100%, no other oxidation products being formed. For this reaction, spectroscopic and chemical evidence seems to indicate the intermediacy of a copper(II) imido species.

Introduction

The synthesis of multimetallic transition-metal complexes in which the metals are held at specific distances from each other is an important objective because of their potential role in multimetal-centered catalysis in both biological and industrial reactions.[2]

Among the ligands which are able to maintain the metal centers in close proximity, the pyrazolato anion, coordinated in an *exo*-bidentate fashion, appears to be a particularly appropriate candidate. Single bridged pyrazolato complexes of transition metals have been known for many years (some of these have been structurally characterized), but surprisingly, their chemistry has received little attention.

As part of a continuing study on the coordination chemistry of new and already known copper(I) systems containing a single pyrazolato bridging ligand, we recently devised a new and efficient preparative method which allows the facile synthesis of copper(I) pyrazolates of general formula $[Cu(3,5\text{-}R_2pz)]_n$.[3] We observed that the nuclearity of these systems is strongly affected by the nature of the R substituents (*i.e.* their electronic and steric properties). Our previous results confirmed that also the chemical behavior of these species is related to the donor capabilities and steric accessibility of the pyrazolato ligand.

We reported that the unprecedented octanuclear copper(II) hydroxo complex $[Cu_8(dmpz)_8(OH)_8]$ (Hdmpz = 3,5-dimethylpyrazole) is obtained by reacting the trinuclear[4] copper(I) species $[Cu(dmpz)]_3$ with O_2 at atmospheric pressure in wet pyridine.[5] The oxidation reaction carried out on $[Cu(dcmpz)]_n$ (Hdcmpz = 3,5-dicarbomethoxypyrazole) under identical experimental conditions gave the mononuclear copper(II)–pyrazolato complex $[Cu(dcmpz)_2(py)_2]$, which contains two mutually *trans* pyrazolate ligands coordinated in a unidentate fashion.[6] The catalytic properties of $[Cu(dmpz)]_3$ in the oxidation or oxygenation of organic substrates (*e.g.* primary aromatic amines, $(PhCH_2)_2NH$, PPh_3) have been investigated, confirming that $[Cu_8(dmpz)_8(OH)_8]$ is the active intermediate species in these reactions.[5] Moreover, both $[Cu(dmpz)]_3$ and $[Cu(dcmpz)]_n$ react with cyclohexyl isocyanide (RNC) giving dinuclear copper(I) complexes bearing two bridging pyrazolato groups and two terminal isocyanide ligands, $[Cu(dmpz)(RNC)]_2$[7] and $[Cu(dcmpz)(RNC)]_2$.[8] These two derivatives are topologically equivalent; however, the patterns of bond distances and angles of the $Cu-[N-N]_2-Cu$ rings, as well as their conformations, are markedly different.

In the present paper, we report on the synthesis of $[Cu(dppz)]_4$ (**1**) (Hdppz = 3,5-diphenylpyrazole), having a pyrazolato ligand bearing bulky substituents in the 3,5-positions, and its catalytic properties in the selective oxidative coupling of aromatic primary amines to the corresponding azobenzenes. The X-ray crystal structures of the tetranuclear species and of the doubly bridged pyrazolato complex $[Cu(dppz)(RNC)]_2$ (**2**) (R = cyclohexyl) derived from the reaction of **1** with cyclohexyl isocyanide are also reported.

Experimental Section

Cyclohexyl isocyanide (Aldrich Chemical Co.) and 3,5-diphenylpyrazole (Lancaster Synthesis) were used as supplied. Solvents were dried and distilled by standard methods. Aniline was vacuum-distilled prior to use; the other aromatic amines were recrystallized from *n*-hexane.

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Tetrakis(acetonitrile)copper(I) tetrafluoroborate was prepared by following a procedure analogous to that reported for the synthesis of [Cu(CH_3CN)$_4$](PF_6)[9] but employing aqueous HBF_4 instead of HPF_6. Infrared spectra were recorded on a Bio Rad FTS-7 instrument. GC-MS analyses were carried out with a HP5890 gas chromatograph fitted with a 25 m (3 μm) PS255 capillary column fitted with a HP5971A MSD. Elemental analyses were carried out at the Microanalytical Laboratory of this University (C, H, N) and at the Mikroanalytisches Labor Pascher, Remagen, Germany (Cu).

Synthesis of [Cu(dppz)]$_4$ (1). To an acetone solution (25 mL) of 3,5-diphenylpyrazole (Hdppz) (1.05 g, 4.77 mmol) was added [Cu(CH_3CN)$_4$](BF_4) (1.00 g, 3.18 mmol) under nitrogen. The colorless solution was stirred for 5 min, and triethylamine (1.50 g, 15.9 mmol) was added dropwise. A white precipitate suddenly formed. The suspension was stirred for 30 min, and then the product was filtered out, washed with acetone, and dried under vacuum: yield 98%; mp 108 °C. Anal. Calcd for $C_{60}H_{44}Cu_4N_8$: C, 63.72; H, 3.89; N, 9.91. Found: C, 63.75; H, 3.92; N, 9.88. Crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of the complex. The identity of the powder and single-crystal phases was certified by X-ray powder diffraction.

Synthesis of [Cu(dppz)(RNC)]$_2$ (2). To a diethyl ether solution (10 mL) of cyclohexyl isocyanide (92.6 mg, 0.85 mmol) was added [Cu(dppz)]$_4$ (200 mg, 0.71 mmol). A clear solution formed from which, in about 10 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*-pentane, and dried under vacuum: yield 86%; mp 142 °C. Anal. Calcd for $C_{44}H_{44}Cu_2N_6$: C, 67.43; H, 5.62; N, 10.73. Found: C, 67.48; H, 5.64; N, 10.71. Crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-pentane into a dichloromethane solution of the complex.

Catalytic Reactions. In a typical experiment, to a solution of complex **1** (100 mg, 0.086 mmol) in 1,2-dichloroethane (10 mL) thermostated at 60 °C was added the aromatic amine under a dioxygen atmosphere (ratio copper/substrate = 1/25). The conversion was monitored by sampling periodically the reaction mixture and analyzing by GC–MS. Data plotted in Figure 2 were obtained after 4 h of reaction.

Synthesis of the Species [Cu]$_R$. [Cu(dppz)]$_4$ (1.06 g, 0.938 mmol) was added to a solution of *p*-$RC_6H_4NH_2$ (ratio copper/amine = 1/6) in 100 mL of 1,2-dichloroethane. The solution was maintained under stirring at 60 °C and in an oxygen atmosphere for 18 h. The solvent was then evaporated, and the resulting brown-red residue was thoroughly washed with diethyl ether until all the unreacted amines and the formed azobenzenes were completely removed (TLC test, about 200 mL of diethyl ether). The resulting black solid was finally washed with *n*-hexane (50 mL) and dried under vacuum. Anal. Calcd for $C_{84}H_{84}Cu_4N_{12}O_{12}$ ([Cu]$_{OMe}$): C, 59.09; H, 4.92; Cu, 14.88; N, 9.85; O, 11.25. Found: C, 59.17; H, 4.84; Cu, 14.80; N, 9.86. Calcd for $C_{42}H_{42}Cu_4N_6$ ([Cu]$_{Me}$): C, 57.01; H, 4.75; Cu, 28.73; N, 9.50. Found: C, 57.23; H, 4.69; Cu, 28.31; N, 9.55. MW: calcd, 884; found, 855 (vaporimetric, CH_2Cl_2 solutions). Azobenzenes have been easily obtained in a pure form by evaporating the Et_2O solution, dissolving the residue in CH_2Cl_2 (20 mL), and extracting the unreacted amine with 2 N HCl. The CH_2Cl_2 phase was then dried over anhydrous Na_2SO_4 and filtered on a bed of Al_2O_3 which adsorbs the small amounts of complex dissolved during the previous manipulations.

Reaction of [Cu]$_R$ with 1,10-Phenanthroline. To a solution of about 300 mg of [Cu]$_R$ (R = Me, OMe, COOMe) in 1,2-dichloroethane (8 mL) was added 1,10-phenanthroline (200 mg) under nitrogen. After 1 h under stirring no traces of azobenzenes were detected by GC–MS analysis. A further amount of 1,10-phenanthroline (600 mg) was then added, and the solution was refluxed for 4 h. Also in this case no azobenzenes were detected. The same results were obtained by carrying out the reaction under an oxygen atmosphere or employing ethylenediamine in place of 1,10-phenanthroline.

X-ray Crystal Structure Determination of Compound 1 and 2. Crystal data and experimental conditions are summarized in Table 1. A colorless and a white prismatic crystal of approximate dimensions 0.15 × 0.15 × 0.05 and 0.22 × 0.20 × 0.05 mm, for **1** and **2**, respectively, were mounted on a tip of a glass fiber and placed onto a goniometer head. The intensity data were collected on an Enraf-Nonius CAD4 automated diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A least-squares fit of 25 randomly oriented intense reflections with θ ranging from 8 to 12° provided the unit cell parameters. Intensities were collected using a variable scan range with a 25% extension at each end for background determination. Three standard reflections were measured at regular intervals and showed no decay of the scattering power of the crystals over the data collection period. Both data sets were corrected for Lorentz and polarization effects. The empirical absorption correction described in ref 10 (ψ-scan; ψ = 0–360°, every 10°) was performed, using three reflections with χ near 90°.

Table 1. Summary of Crystal Data for Complexes [Cu(dppz)]$_4$ (**1**) and [Cu(dppz)(RNC)]$_2$ (**2**)

	compd	
	1	**2**
formula	$C_{60}H_{44}Cu_4N_8$	$C_{44}H_{44}Cu_2N_6$
fw	1131.23	783.96
cryst system	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	19.423(9)	9.246(2)
b, Å	11.627(1)	9.859(4)
c, Å	11.905(2)	12.543(2)
α, deg	85.75(1)	103.82(2)
β, deg	72.92(2)	102.25(2)
γ, deg	88.92(2)	110.75(2)
cell vol, Å^3	2563(1)	981(1)
Z	2	1
D_{calc}, g cm^{-3}	1.466	1.321
wavelength, Å	0.710 73	0.710 73
μ, cm^{-1}	16.9	11.2
R	0.047	0.049
R_w	0.061	0.059

The structures were solved by conventional three-dimensional Patterson and difference Fourier methods and refined by full-matrix least squares using the SHELX package[11] locally adapted on a Silicon Graphics Indigo computer. Individual weights were assigned as follows: $w = A/(\sigma^2(F) + BF_o^2)$, with optimized values of A = 2.8413, 2.1259 and B = 0.000240, 0.001056, for **1** and **2**, respectively. Scattering factors, corrected for the real and imaginary anomalous dispersion terms, were taken from ref 12. Anisotropic thermal parameters were assigned to all copper atoms and, in **2**, also to all carbon and nitrogen atoms except those of the cyclohexyl isocyanide residues.

The presence of **2** of several close-lying peaks in the Fourier maps in vicinity of the isocyanide fragment has been interpreted as the result of two conformational models for the cyclohexyl isocyanide moiety, which were therefore refined using occupancy numbers of 0.5. Several refinements performed in the acentric space group $P\bar{1}$ did not converge to any ordered model and were therefore rejected.

The hydrogen atom contribution to the scattering factors (apart from those of the disordered cyclohexyl moieties) was included in the last stages of the refinement in ideal positions (C–H = 0.95 Å) with a common, refinable thermal parameter. The peaks in the final difference Fourier map were randomly located. The final values of the agreement indices are reported in Table 1. The final values of the positional parameters for compounds **1** and **2** are reported in Tables 2 and 3, respectively.

Results and Discussion

[Cu(CH_3CN)$_4$](BF_4) reacts with 3,5-diphenylpyrazole (Hdppz) in acetone in the presence of triethylamine giving quantitatively complex **1** as an insoluble white product (eq 1). The nuclearity of **1** has been ascertained by an X-ray single-crystal structure analysis (see later).

$$4[\mathrm{Cu(CH_3CN)_4}](\mathrm{BF_4}) + 4\mathrm{Hdppz} \xrightarrow[-\mathrm{CH_3CN}]{\mathrm{Et_3N}} \underset{\mathbf{1}}{[\mathrm{Cu(dppz)}]_4} + 4(\mathrm{Et_3NH})(\mathrm{BF_4}) \quad (1)$$

The method of synthesis reported in eq 1 works well not only for [Cu(dppz)]$_4$; it represents a particularly useful synthetic route also for other copper(I) pyrazolates of general formula [Cu(3,5-R_2pz)]$_n$ (*e.g.* R = H, Me, COOMe, COO*t*Bu).[3]

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Table 2. Fractional Atomic Coordinates and *B* Values for $[Cu(dppz)]_4$ (**1**) with ESD's in Parentheses

atom	*x*	*y*	*z*	*B*, Å²
Cu1	0.28868(5)	0.06531(8)	0.13522(8)	3.88(3)
Cu2	0.23326(5)	−0.17369(9)	0.09483(8)	3.96(3)
Cu3	0.21332(5)	−0.07589(9)	−0.14578(8)	3.87(3)
Cu4	0.26814(5)	0.16079(8)	−0.10582(8)	3.62(3)
N1	0.3453(3)	−0.0622(5)	0.1409(5)	3.7(1)
N2	0.3246(3)	−0.1658(5)	0.1128(5)	3.7(1)
N3	0.1425(3)	−0.1820(5)	0.0743(5)	3.8(1)
N4	0.1353(3)	−0.1422(5)	−0.0342(5)	3.8(1)
N5	0.2919(3)	−0.0114(5)	−0.2584(5)	3.5(1)
N6	0.3196(3)	0.0917(5)	−0.2418(5)	3.5(1)
N7	0.2152(3)	0.2301(5)	0.0276(5)	3.6(1)
N8	0.2318(3)	0.1916(5)	0.1295(5)	3.5(1)
C1	0.4116(4)	−0.0770(6)	0.1587(6)	3.4(2)
C2	0.4336(4)	−0.1904(7)	0.1418(7)	4.1(2)
C3	0.3779(4)	−0.2429(7)	0.1125(6)	3.8(2)
C4	0.4484(4)	0.0196(7)	0.1911(6)	3.7(2)
C5	0.4103(4)	0.1059(7)	0.2603(7)	4.3(2)
C6	0.4474(5)	0.1947(7)	0.2883(7)	5.1(2)
C7	0.5215(5)	0.1997(8)	0.2479(8)	5.6(2)
C8	0.5588(5)	0.1163(8)	0.1811(8)	5.6(2)
C9	0.5238(4)	0.0254(7)	0.1506(7)	4.5(2)
C10	0.3722(4)	−0.3629(7)	0.0842(7)	4.1(2)
C11	0.3312(5)	−0.3935(8)	0.0124(8)	5.3(2)
C12	0.3291(6)	−0.5092(9)	−0.0139(9)	6.9(3)
C13	0.3679(6)	−0.589(1)	0.0274(9)	7.3(3)
C14	0.4095(6)	−0.565(1)	0.0929(9)	7.8(3)
C15	0.4115(5)	−0.4472(9)	0.1229(9)	6.7(2)
C16	0.0766(4)	−0.2204(7)	0.1431(7)	3.9(2)
C17	0.0270(4)	−0.2049(7)	0.0803(7)	4.2(2)
C18	0.0653(4)	−0.1568(7)	−0.0309(7)	3.8(2)
C19	0.0657(4)	−0.2686(7)	0.2639(7)	4.0(2)
C20	0.1152(5)	−0.3401(8)	0.2953(8)	5.6(2)
C21	0.1013(6)	−0.3888(9)	0.4121(9)	7.2(3)
C22	0.0377(6)	−0.3660(9)	0.4913(0)	7.3(3)
C23	−0.0139(6)	−0.2990(8)	0.4623(8)	6.2(2)
C24	0.0003(5)	−0.2474(8)	0.3484(8)	5.5(2)
C25	0.0411(4)	−0.1294(7)	−0.1350(7)	4.2(2)
C26	−0.0300(5)	−0.0949(7)	−0.1181(8)	5.1(2)
C27	−0.0542(5)	−0.0693(8)	−0.2190(8)	5.9(2)
C28	−0.0097(6)	−0.0793(8)	−0.3277(9)	6.6(2)
C29	0.0605(6)	−0.1169(8)	−0.3463(9)	6.8(2)
C30	0.0864(5)	−0.1416(8)	−0.2491(8)	5.8(2)
C31	0.3315(4)	−0.0437(6)	−0.3652(6)	3.3(2)
C32	0.3851(4)	0.0373(6)	−0.4177(6)	3.6(2)
C33	0.3768(4)	0.1217(6)	−0.3373(6)	3.3(2)
C34	0.3112(4)	−0.1519(7)	−0.4062(6)	3.5(2)
C35	0.2939(4)	−0.2510(7)	−0.3333(8)	4.9(2)
C36	0.2717(5)	−0.3493(9)	−0.3740(9)	6.3(2)
C37	0.2666(5)	−0.3469(9)	−0.4860(9)	6.9(3)
C38	0.2846(5)	−0.2520(9)	−0.5599(9)	6.8(3)
C39	0.3065(5)	−0.1507(8)	−0.5213(7)	5.2(2)
C40	0.4166(4)	0.2271(6)	−0.3464(6)	3.3(2)
C41	0.3854(5)	0.3264(8)	−0.2979(8)	5.6(2)
C42	0.4276(6)	0.4265(9)	−0.3075(9)	6.5(2)
C43	0.4980(5)	0.4277(8)	−0.3699(8)	5.9(2)
C44	0.5295(5)	0.3323(8)	−0.4243(8)	6.2(2)
C45	0.4893(5)	0.2319(8)	−0.4122(7)	5.1(2)
C46	0.1731(4)	0.3240(6)	0.0513(6)	3.2(2)
C47	0.1620(4)	0.3486(6)	0.1690(6)	3.6(2)
C48	0.1996(4)	0.2652(6)	0.2137(6)	3.6(2)
C49	0.1468(4)	0.3854(7)	−0.0396(7)	3.8(2)
C50	0.1522(4)	0.3478(7)	−0.1478(7)	4.5(2)
C51	0.1270(5)	0.4082(8)	−0.2311(8)	5.5(2)
C52	0.0958(6)	0.510(1)	−0.210(1)	7.8(3)
C53	0.0871(8)	0.549(1)	−0.103(1)	12.4(4)
C54	0.1155(6)	0.491(1)	−0.018(1)	9.0(3)
C55	0.2099(4)	0.2452(7)	0.3329(7)	3.9(2)
C56	0.2400(5)	0.3317(8)	0.3765(8)	5.7(2)
C57	0.2525(5)	0.3099(9)	0.4873(9)	6.4(2)
C58	0.2318(5)	0.2076(8)	0.5495(9)	6.1(2)
C59	0.2039(5)	0.1234(8)	0.5084(8)	5.9(2)
C60	0.1923(5)	0.1417(8)	0.3967(7)	5.0(2)

Table 3. Fractional Atomic Coordinates and *B* Values for $[Cu(dppz)(RNC)]_2$ (**2**) with ESD's in Parentheses

atom	*x*	*y*	*z*	*B*, Å²
Cu	0.40589(5)	0.09329(5)	0.07695(4)	4.47(2)
N1	0.5926(4)	0.2031(3)	0.0330(3)	4.13(9)
N2	0.6183(4)	0.1187(3)	−0.0608(3)	4.16(9)
C1	0.6724(4)	0.3539(4)	0.0492(3)	4.0(1)
C2	0.7510(4)	0.3690(4)	−0.0333(3)	4.3(1)
C3	0.7117(4)	0.2197(4)	−0.1010(3)	4.0(1)
C4	0.6623(3)	0.4744(3)	0.1383(2)	4.3(1)
C5	0.6617(3)	0.6058(3)	0.1156(2)	5.0(1)
C6	0.6392(3)	0.7156(3)	0.1951(2)	6.0(1)
C7	0.6172(3)	0.6941(3)	0.2971(2)	7.0(2)
C8	0.6178(3)	0.5627(3)	0.3198(2)	6.9(2)
C9	0.6404(3)	0.4529(3)	0.2404(2)	5.5(1)
C10	0.7461(3)	0.1635(3)	−0.2081(2)	4.1(1)
C11	0.8925(3)	0.2471(3)	−0.2229(2)	4.9(1)
C12	0.9211(3)	0.1960(3)	−0.3265(2)	5.8(1)
C13	0.8034(3)	0.0613(3)	−0.4152(2)	6.2(2)
C14	0.6570(3)	−0.0223(3)	−0.4004(2)	6.6(2)
C15	0.6284(3)	0.0288(3)	−0.2968(2)	5.5(1)
C16	0.237(1)	0.156(1)	0.0990(8)	3.6(2)
N3	0.140(1)	0.187(1)	0.1225(9)	4.6(2)
C17	0.053(1)	0.2442(9)	0.1864(8)	4.0(2)
C18	−0.045(1)	0.106(1)	0.223(1)	5.3(2)
C19	−0.153(1)	0.155(1)	0.2884(8)	5.7(2)
C20	−0.050(1)	0.303(1)	0.3895(8)	6.1(2)
C21	0.045(1)	0.432(1)	0.355(1)	7.7(2)
C22	0.158(1)	0.396(1)	0.295(1)	5.9(2)
C16′	0.271(1)	0.162(1)	0.130(1)	4.7(3)
N3′	0.174(1)	0.206(1)	0.147(1)	5.6(3)
C17′	0.010(1)	0.239(1)	0.147(1)	6.4(3)
C18′	−0.096(1)	0.121(1)	0.188(1)	6.6(2)
C19′	−0.020(1)	0.127(1)	0.305(1)	7.8(3)
C20′	0.046(2)	0.284(2)	0.400(1)	8.8(3)
C21′	0.189(2)	0.401(2)	0.362(1)	7.7(3)
C22′	0.110(2)	0.401(1)	0.245(1)	7.5(3)

It is to be pointed out that for the same pyrazole, Hdppz, Raptis and Fackler obtained and crystallographically characterized a trimeric species, $[Cu(dppz)]_3$, but the preparative method was in this case quite different.[13] At variance, in the case of Hdmpz, our synthetic route gave the same trimeric complex $[Cu(dmpz)]_3$ previously obtained and structurally characterized by Ehlert *et al.*,[4] as ascertained by comparing X-ray powder diffraction patterns.

Reaction of 1 with Cyclohexyl Isocyanide. By reaction of $[Cu(dppz)]_4$ (**1**) with cyclohexyl isocyanide (RNC) in diethyl ether, the dimeric complex $[Cu(dppz)(RNC)]_2$ (**2**) has been obtained. Complex **2** was isolated as a white crystalline solid. Its IR spectrum shows ν(NC) at 2168 cm^{-1}, a value quite close to those observed in the dinuclear copper(I) analogues $[Cu(dmpz)(RNC)]_2$[7] (ν(NC) = 2164 cm^{-1}) and $[Cu(dcmpz)(RNC)]_2$[8] (ν(NC) = 2170 cm^{-1}). These double-bridged copper(I)–pyrazolato complexes are topologically equivalent. However, the pattern of bond distances and angles of the Cu–[N–N]$_2$–Cu rings, as well as their conformations, show marked differences and will be discussed later.

Catalytic Properties of 1. $[Cu(dppz)]_4$ reacts with molecular oxygen giving rise to green solutions. The rate of oxidation is related to the nature of the solvent employed. In noncoordinating solvents (dichloromethane, 1,2-dichloroethane, toluene) the oxidation reaction is rather slow; on the contrary, faster reactions were observed when pyridine was used. From the solutions green copper(II) species were in all case isolated; when the reaction is carried out in pyridine, IR evidence suggests the presence of this molecule in the copper coordination sphere.

Unfortunately, attempts made in order to ascertain the nature of these oxidation products were at the moment fruitless. In any case, these copper(II) species were repeatedly tested in order to verify their eventual stoichiometric (under N_2) or catalytic (under O_2) activity in the oxidation of organic substrates such as primary and secondary amines, PPh_3, and isocyanides. These studies were performed with the aim to find analogies with the behavior of

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(13) Raptis, R. G.; Fackler, J. P., Jr. *Inorg. Chem.* **1988**, *27*, 4149.

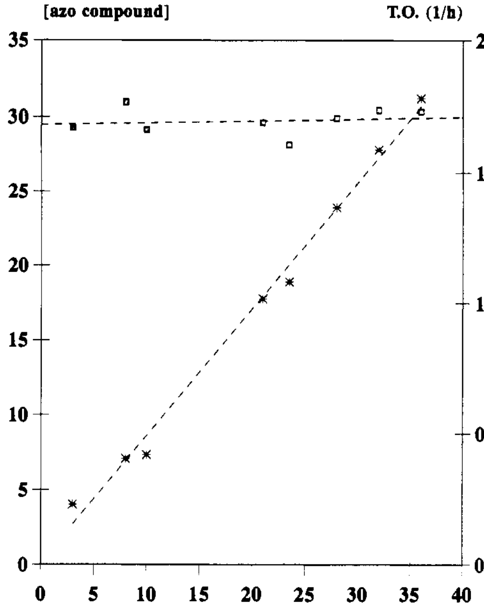

Figure 1. Turnover (□) and azotoluene yield (*) vs time for the catalytic oxidative coupling of *p*-toluidine.

[$Cu_8(dmpz)_8(OH)_8$]. In all experiments the organic substrates were recovered unchanged, no oxidation or oxygenation products being detected.

On the contrary, when [Cu(dppz)]$_4$ is reacted with molecular oxygen in the presence of primary aromatic amines at 60 °C in 1,2-dichloroethane, the catalytic selective oxidative coupling leading to the corresponding azobenzenes was observed (eq 2).

$$2p\text{-}RC_6H_4NH_2 + O_2 \xrightarrow{1} p\text{-}RC_6H_4N = NC_6H_4\text{-}p\text{-}R + 2H_2O \qquad (2)$$

A 100% selectivity has been verified for reaction 2. It is worth noticing that, although the catalyst did not show high activity, this not decrease with time (Figure 1), this behaviour markedly differing from that observed for [Cu(dmpz)]$_3$.[5]

Reaction 2 has been carried out using a series of different *para*-substituted aromatic primary amines, with the objective to study the influence of the *para*-substituent on the activity of the catalytic species. It has been found that a strict relation exists between the pK_a of the amine and the observed conversion. Figure 2 shows the significant results of this study: moving from aniline up to anisidine, we observed an increasing conversion with increasing basicity of the amine, the maximum being observed for p-$CH_3OC_6H_4NH_2$. The conversion drops down in the case of R = $N(CH_3)_2$, *i.e.* with the most basic amine used in these investigations. When reaction 2 is carried out with an equimolar mixture of two different amines, a mixture of symmetric and asymmetric azobenzenes is obtained. The composition of this mixture has been confirmed to be related to the basicity of both amines (Figure 2).

Although tentatively, we put forward the hypothesis that the oxidative coupling of the aromatic amines (eq 2) takes place *via* the preliminary coordination of the amine, followed by proton abstraction. The first step is favored by an increasing basicity of the amine. On the contrary, the presence of electron-donating groups on the *para* position makes less favorable the subsequent step. The overall process should then represent a subtle balance of these two effects. This fact could therefore justify the observed low conversion in the case of the strongly basic *N*,*N*-dimethyl-1,4-phenylenediamine.

In an attempt to gain more insight into the mechanism of the oxidative coupling, we looked at the fate of the starting [Cu(dppz)]$_4$ (**1**), in the reaction medium. After removal of the unreacted amines (p-$RC_6H_4NH_2$) and the formed azobenzenes (see Experimental Section), black copper(II) species (deep-red colored in CH_2Cl_2 solution) [Cu]$_R$, where R represent the *para*-substituent of the various amines, were in any case isolated. It has been verified that the [Cu]$_R$ species are able to promote the oxidative coupling of the aromatic amines *only* in the presence of oxygen. Under an inert atmosphere, no coupling was observed. The behavior of this intermediate species appears quite different from that of the intermediate product, [$Cu_8(dmpz)_8(OH)_8$], isolated when the oxidative coupling was catalyzed by [Cu(dmpz)]$_3$.[5] In the latter case the stoichiometric oxidation of primary aromatic amines to azobenzenes was verified even in the absence of oxygen.

Attention has been devoted to the [Cu]$_{COOMe}$ and [Cu]$_{OMe}$ species, *i.e.* to the products obtained when p-$MeO_2CC_6H_4NH_2$ and p-$MeOC_6H_4NH_2$ were employed, owing to the possibility of using the $\nu(C{=}O)$, $\nu(C_{Ar}\text{–}O)$, and $\nu(CH_3\text{–}O)$ as useful IR probes. In the free p-$MeO_2CC_6H_4NH_2$ the $\nu(C{=}O)$ is observed at 1675 cm^{-1}; the same absorption appears at 1718 cm^{-1} in p-$MeO_2CC_6H_4N{=}NC_6H_4$-p-CO_2Me and at 1720 cm^{-1} in [Cu]$_{COOMe}$. In [Cu]$_{OMe}$ the $\nu(C_{Ar}\text{–}O)$ and $\nu(CH_3\text{–}O)$ stretchings were observed at 1243 and 1031 cm^{-1}, respectively. Moreover, the absence in [Cu]$_R$ of bands attributable to ν(NH) was confirmed, and no ν(ND) were observed by treating [Cu]$_R$ with D_2O. These observations confirm the presence of the R–Ar–N groups in [Cu]$_R$ species and ruled out coordinated p-$RC_6H_4NH_2$ (amine) or p-RC_6H_4NH) (amido) ligands. Therefore, the [Cu]$_R$ species are likely to contain imido (p-RC_6H_4N) and/or *azo* ligands.

The presence in [Cu]$_R$ species of imido groups is supported by the observation that a mixture of symmetric azobenzenes (catalytic amounts) and asymmetric azobenzenes (stoichiometric amounts) is obtained when [Cu]$_R$ is treated with O_2 and p-$R'C_6H_4NH_2$ (R $\neq$ R') (eq 3). In the course of reaction 3, small amounts of symmetric $RC_6H_4N{=}NC_6H_4R$ were always found.

$$[Cu]_R \xrightarrow[O_2]{p\text{-}R'C_6H_4NH_2} \underset{\text{stoichiometric}}{RC_6H_4N{=}NC_6H_4R'} + \underset{\text{catalytic}}{R'C_6H_4N{=}NC_6H_4R'} + [Cu]_{R'} \qquad (3)$$

Elemental analyses carried out on various [Cu]$_R$ species did not allow us to draw a unique formulation irrespective of the different R substituents. On taking into account the strict similarities between the [Cu]$_R$ species (macroscopic appearance, spectroscopic properties, chemical behavior) and the analytical data (see Experimental Section), we suppose the presence of a common central "core" having a [$Cu_4(NC_6H_4R)_4$] formulation and a variable number (1–4, depending on the *para* substituent on the aromatic ring) of coordinated azo ligands. Under this hypothesis the formulations of [Cu]$_{OMe}$ and [Cu]$_{Me}$ become [$Cu_4(NArOMe)_4(MeOArN{=}NArOMe)_4$] and [$Cu_4(NArMe)_4(MeArN{=}NArMe)$], respectively.

The lack of the expected azobenzene displacement when bidentate ligands such as 1,10-phenanthroline or diamines are added (see Experimental Section) suggests that steric and/or electronic factors play a critical role in the coordination mode of the ArN=NAr moiety.

Transition-metal complexes containing coordinated imido groups are well documented in the literature, and their chemistry has been thoroughly investigated.[14] Moreover, a Ti(IV) dimer containing both a bridging phenylimido ligand and a PhNNPh fragment was already reported.[14b] To date, however, no copper-imido complexes have been characterized making it impossible

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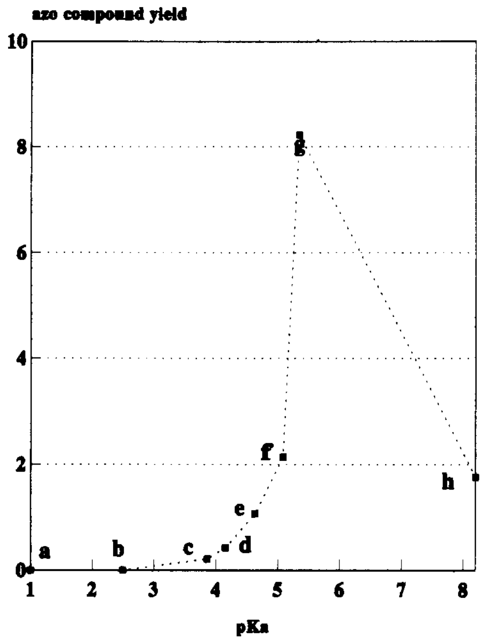

Figure 2. Azobenzenes yield vs pK_a of amine for the catalytic oxidation of *para*-substituted amines ($RC_6H_4NH_2$) to the corresponding azo compounds: R = NO_2 (a); $COOCH_3$ (b); Br (c); Cl (d); H (e); CH_3 (f); OCH_3 (g); and $N(CH_3)_2$ (h). (Yields are relative to azobenzene).

to draw complete conclusions from spectral data of $[Cu]_R$. X-ray investigations are needed in order to fully elucidate the nature of the $[Cu]_R$ species. Unfortunately, repeated attempts to grow crystals suitable for an X-ray analysis have so far proved to be unsuccessful.

Description of the Structures of Complexes 1 and 2. The crystals of **1** consist of a molecular packing of discrete tetrameric complexes, whose molecular structure, with partial labeling scheme, is depicted in Figure 3. Relevant bond distances and angles are collected in Table 4. The four copper atoms, which lie at an average nonbonding distance of 3.12 Å, are strictly coplanar, while the four bridging dppz units, each one spanning the ideal Cu···Cu edges, stem out from the two sides in an alternate fashion, giving the whole complex an idealized D_2, rather than 4-fold, symmetry. The Cu–N bond distances compare well with those found in $[Cu(dmpz)]_3$[4] but are much shorter than in the trimeric species $[Cu(dppz)]_3$],[13] which contains the same pyrazolato groups (average Cu–N = 2.08 Å). Table 5 collects the most important features relevant to the comparison of the molecular structures of $[Cu(dppz)]_4$ (**1**), $[Cu(dppz)]_3$, and $[Cu(dmpz)]_3$. From the values reported therein, it seems evident that a significant strain is present in $[Cu(dppz)]_3$, as measured for example by the molecular volume or by the N–Cu–N angles, which deviate heavily from linearity. In contrast, the N–Cu–N values for the tetramer **1** range from 179 to 180° and are in excellent agreement with the electronic requirement of linearly coordinated Cu(I) centers.

While the planes defined by the pyrazole rings in $[Cu(dppz)]_3$ were more or less bound to lie in plane with all copper atoms (although a significant twist is present, with the maximum N···Cu_3 plane distance of 0.74 Å), the tetramer shows Cu_4/pyrazole dihedral angles in the range 52.5–58.7°.

The phenyl group orientations, with respect to the pyrazole rings to which they are attached, range 9.7 to 57.5° (average 33.7°); these values reflect the tendency of the phenyl and pyrazole rings for increasing the π delocalization over the whole ligand, as long as short H···H (diphenyl-like) interactions are avoided.

In addition, it is interesting to notice that 3,5-diphenylpyrazole[15a] and 3-methyl-5-phenylpyrazole[15b] crystallize as tetrameric molecules, held together by strong hydrogen bonding; different from most other pyrazoles, where statistically disordered or asymmetrically ordered N–H···N interactions were found, neutron diffraction studies[16] of 3-methyl-5-phenylpyrazole showed four

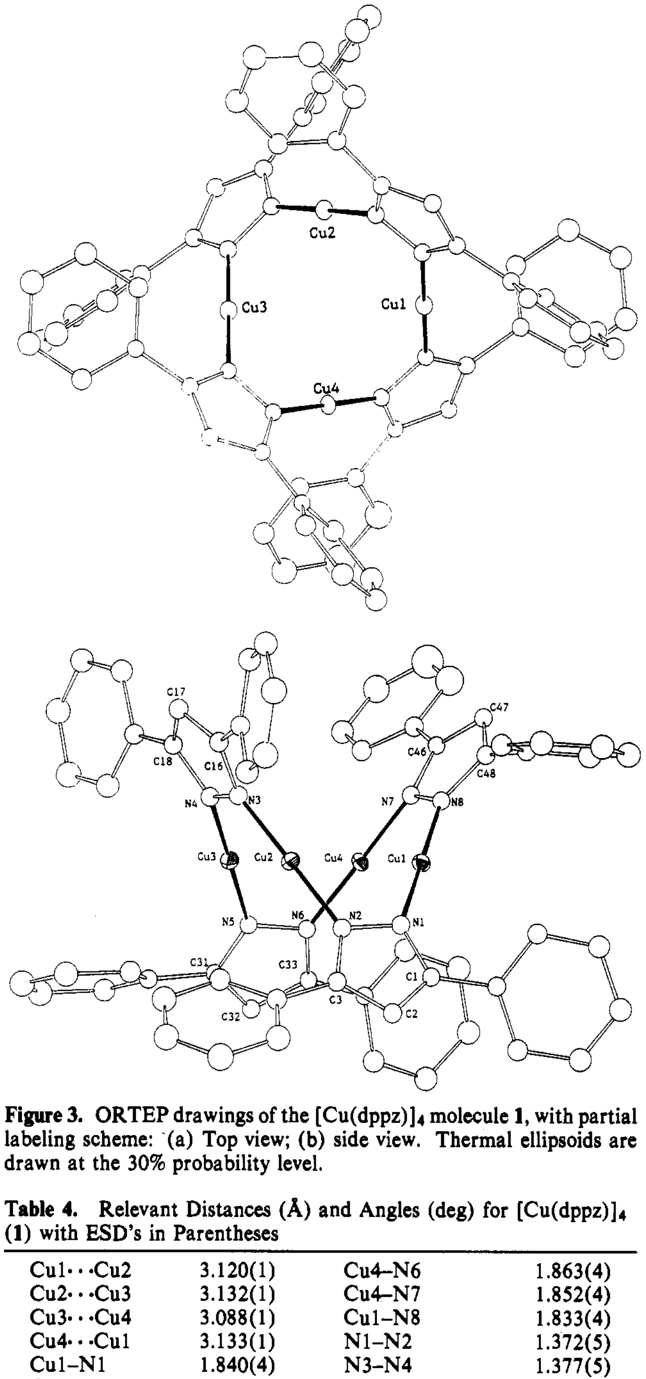

Figure 3. ORTEP drawings of the $[Cu(dppz)]_4$ molecule **1**, with partial labeling scheme: (a) Top view; (b) side view. Thermal ellipsoids are drawn at the 30% probability level.

Table 4. Relevant Distances (Å) and Angles (deg) for $[Cu(dppz)]_4$ (**1**) with ESD's in Parentheses

Cu1···Cu2	3.120(1)	Cu4–N6	1.863(4)
Cu2···Cu3	3.132(1)	Cu4–N7	1.852(4)
Cu3···Cu4	3.088(1)	Cu1–N8	1.833(4)
Cu4···Cu1	3.133(1)	N1–N2	1.372(5)
Cu1–N1	1.840(4)	N3–N4	1.377(5)
Cu2–N2	1.856(4)	N5–N6	1.368(5)
Cu2–N3	1.855(4)	N7–N8	1.384(5)
Cu3–N4	1.834(4)	C═C(Ph, av)	1.376
Cu3–N5	1.839(4)		
N1–Cu1–N8	179.6(2)	Cu2–N3–N4	117.6(3)
N2–Cu2–N3	178.9(2)	Cu3–N4–N3	119.2(3)
N4–Cu3–N5	179.2(2)	Cu3–N5–N6	130.0(3)
N6–Cu4–N7	178.6(2)	Cu4–N6–N5	115.3(3)
Cu1–N1–N2	118.8(3)	Cu4–N7–N8	114.4(3)
Cu2–N2–N1	117.2(3)	Cu1–N8–N7	121.8(3)

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Table 5. Synopsis of Relevant Geometrical Parameters of $[Cu(dmpz)]_3$, $[Cu(dppz)]_3$, and $[Cu(dppz)_4$ (**1**) (Average Distances (and Ranges) in Å; Angles (Ranges) in deg)

	$[Cu(dmpz)]_3$	$[Cu(dppz)]_3$	$[Cu(dppz)]_4$
Cu···Cu	3.22 (3.20–3.26)	3.34 (3.28–3.41)	3.12 (3.09–3.13)
Cu-N	1.85 (1.84–1.86)	2.08 (2.04–2.10)	1.85 (1.83–1.86)
N-Cu-N	173–175	169–179	179–180
N-N	1.38 (1.37–1.39)	1.40 (1.39–1.41)	1.38 (1.37–1.38)
Cu-N-N	118–121	114–120	114–122
vol of Cu(dppz), Å^3		338	320

Table 6. Relevant Distances (Å) and Angles (deg) for $[Cu(dppz)(RNC)]_2$ (**2**) with ESD's in Parentheses[a]

Cu···Cu′	3.488(1)	C2–C3	1.387(8)
Cu–N1	1.964(4)	C3–N2	1.348(7)
Cu–N2′	1.982(5)	C16–N3	1.135(7)
Cu–C16	1.841(7)	N3–C17	1.460(9)
N1–N2	1.373(6)	C1–C4	1.473(8)
N1–C1	1.343(6)	C3–C10	1.473(8)
C1–C2	1.372(7)	C=C(Ph, av)	1.373
N1–Cu–N2′	110.2(2)	Cu–N1–N2	116.8(3)
N1–Cu–C16	127.3(2)	Cu–N2′–N1′	120.4(4)
N2′–Cu–C16	122.1(2)	Cu–C16–N3	178.1(6)

[a] Primed atoms are generated by the –*x*, –*y*, –*z* symmetry operator.

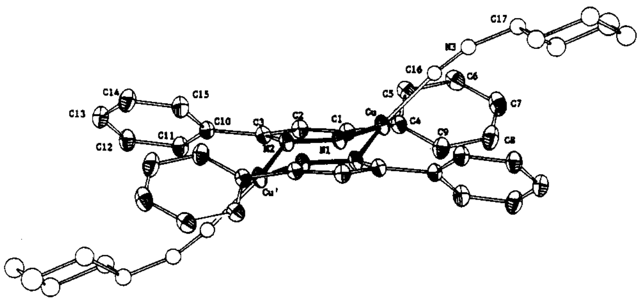

Figure 4. ORTEP drawing of the $[Cu(dppz)(RNC)]_2$ molecule **2**, with partial labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Only one conformation of the disordered cyclohexyl residue is drawn here.

shared hydrogen atoms located in the middle of the N···N vectors. Thus, formal substitution of H^+ with the (Lewis) acidic center Cu(I) would lead to the same molecular arrangement found in **1**. This analogy holds also for trimeric 3,5-dimethylpyrazole[17] and $[Cu(dmpz)]_3$,[4] as well as for pyrazole (Hpz) itself,[18] which in the solid state forms infinite chains of hydrogen-bonded molecules, and the polymeric $[Cu(pz)]_n$ phase.[15]

The crystal structure of **2** consists of a molecular packing of discrete dimeric molecules located about a crystallographic inversion center. Relevant bond distances and angles are reported in Table 6; Figure 4 contains an ORTEP drawing of the molecule, with partial labeling scheme.

Compound **2** is a dinuclear Cu(I) complex (Cu···Cu = 3.488(1) Å) bearing two bridging pyrazolato groups and two terminal isocyanide ligands, making the coordination geometry around each copper atom roughly trigonal. Thus, compound **2** is topologically equivalent to the already reported $[Cu(dmpz)(RNC)]_2$ and $[Cu(dcmpz)(RNC)]_2$ complexes, whose structural parameters and conformational analysis have been discussed in refs 7 and 8.

Surprisingly enough, complex **2** possesses a $Cu–[N–N]_2–Cu$ ring in a chairlike conformation which was not foreseen on the basis of the model proposed in ref 8, for it assumed a continuous change between the planar and the boat conformers, both possessing the copper atoms *in plane* with the pyrazolato rings. The location of the Cu atoms in **2**, well off from the plane defined by the four pyrazolato nitrogen atoms (0.62 Å), is somewhat unexpected, for it demands Cu–N vectors bent off the heterocyclic rings, in a *trans* mode.

A similar feature was however already observed in the $[Ag(dppz)]_3$ compound,[20] where, out of the three dppz units, one presents a M–N–N–M dihedral angle of 43.6°, which compares well with the value found in complex **2** (41.7°). We tentatively suggest that such a rare conformational feature is dictated by the presence of steric interactions between the phenyl groups in 3,5-positions and the cyclohexyl isocyanide groups attached to the copper atoms. Interestingly, only two other cases of chair conformations for $M–[N–N]_2–M$ rings have been found in the literature, both referring to complexes possessing a highly crowded environment about the metal atoms.[21]

Although the observed disorder (see Experimental Section) of the cyclohexyl isocyanide residues makes any detailed comparison of bond distances and angles of these moieties meaningless, nevertheless a chair conformation for both disordered fragments can be clearly recognized.

Conclusions

The catalytic system described here allowed the synthesis of azobenzenes under mild experimental conditions with high selectivities. Moreover, we have confirmed that this system does not require pyridine as the reaction medium; the latter was shown to be essential in previous related catalytic reactions studied by us[5] and by other authors.[22] Interestingly, preliminary results indicate that $[Cu(dppz)]_4$ is able to polymerize aromatic *para*-diamines leading to the corresponding polyazobenzenes. Also in this case mild conditions are required. Studies are in progress in order to ascertain the extent of the repeating unit of $(–ArN=N–)_n$ polymers. The catalytic oxidation of organic substrates other than amines (*e.g.* phenols) is also currently under investigation.

Acknowledgment. We thank the Italian Consiglio Nazionale delle Ricerche (CNR), Progetto Finalizzato Chimica Fine II, for financial support.

Supplementary Material Available: A detailed list of crystallographic parameters (Table S1) and lists of hydrogen atom positional parameters, anisotropic thermal parameters, bond distances and angles, and least-squares planes (Tables S2–S6 for **1** and Tables S7–S11 for **2**) (13 pages). Ordering information is given on any current masthead page.

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