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Dinuclear Copper(I) Benzoato Complexes Binding Isocyanides and Azo Compounds

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The copper(I)–benzoato complex $[Cu(PhCO_2)]_4$ (**1**) is a source of the doubly bridged dimetallic unit $[Cu_2(\mu\text{-}PhCO_2)_2]$ in reaction with many substrates. Reaction with isocyanides, which parallels the reaction with carbon monoxide, leading to a very labile compound, produces two different complexes depending on the reaction solvent. In ethanol the dimeric complex $[Cu_2(\mu\text{-}PhCO_2)_2(p\text{-}MeC_6H_4NC)_2]$ (**4**) [ν(CN) (Nujol) = 2152 cm^{-1}], having the two copper(I) centers very close at 2.750 (2) Å, formed. A significant intermolecular interaction involving the copper(I) of one dimer and the carbon of the isocyanide ligand of another dimer establishes a tetrameric structure in the solid state [Cu···Cu = 2.860 (2) Å]. This intermolecular interaction does not occur in $[Cu_2(\mu\text{-}PhCO_2)_2(p\text{-}MeC_6H_4NC)_3]\cdot THF$ (**5**), which formed when the reaction between **1** and $p\text{-}MeC_6H_4NC$ was carried out in THF [Cu···Cu = 3.020 (3) Å; ν(CN) (Nujol) = 2145 and 2125 cm^{-1}]. In both complexes **4** and **5** the isocyanide has a terminal and semibridging bonding mode. The reaction of **1** with azo compounds led to polymeric structures where the $[Cu_2(\mu\text{-}PhCO_2)_2]$ dimers are bridged by the azo functionality, from the lone pairs at the nitrogen atoms. The steric hindrance of the azo compound seems to play the major role in determining the Cu:azo ratio and the structure of the complex. Benzo[*c*]cinnoline reacted with **1** to form $[Cu_2(\mu\text{-}PhCO_2)_2(\mu\text{-benzo}[c]\text{cinnoline})]_n$ (**6**), containing the almost planar eight-membered ring $[Cu_2(\mu\text{-}PhCO_2)_2]$. The Cu···Cu distances are in turn 2.788 (2) and 3.262 (2) Å along the polymeric chain. Phthalazine reacted with **1** to form $[Cu_2(\mu\text{-}PhCO_2)_2(\mu\text{-phthalazine})_2]_n$ (**7**) for which a polymeric structure analogous to that of **6** is proposed. The structures of complexes **4**–**6** have been determined. Complex **4**: space group $P\bar{1}$ (triclinic); a = 13.278 (4) Å; b = 10.690 (3) Å; c = 10.412 (2) Å; α = 104.20 (2)°; β = 95.71 (3)°; γ = 104.75 (3)°; V = 1364.7 (7) Å^3; Z = 2; D_{calcd} = 1.47 g cm^3. The final R factor was 0.044 (R_w = 0.046) for 2557 observed reflections. Complex **5**: space group $P\bar{1}$ (triclinic); a = 10.440 (2) Å; b = 19.408 (4) Å; c = 10.476 (2) Å; α = 96.77 (2)°; β = 106.20 (2)°; γ = 77.66 (2)°; V = 1987.4 (8) Å^3; Z = 2; D_{calcd} = 1.32 g cm^{-3}. The final R factor was 0.048 for 3236 observed reflections. Complex **6**: space group $Pbcn$ (orthorhombic); a = 21.679 (3) Å; b = 9.408 (1) Å; c = 10.564 (2) Å; V = 2154.6 (5) Å^3; Z = 4; D_{calcd} = 1.69 g cm^{-3}. The final R factor was 0.064 (R_w = 0.064) for 1402 observed reflections.

Introduction

There is currently a great attention paid to dinuclear copper(I) complexes.[1] Such species are extremely interesting since they can provide a two-site binding to small molecules and organic functionalities, and copper(I) has some special peculiarities. The major effort in this field is to design appropriate binucleating ligands that take care of having the two sites at the appropriate distance.[1] A much simpler approach, which can be adopted in organometallic chemistry, is to use a source of dicopper(I) unit that can survive in the presence of various ligands. Copper(I) carboxylates, which are tetrameric[2] or polymeric[3] in the solid state, react with σ and π ligands while maintaining the dimetallic unit.[4-7] A further interest in copper(I) carboxylates derives from their ability to promote catalytic hydrogenation via the heterolytic splitting of molecular hydrogen.[8] Therefore, the reaction of copper(I) carboxylates with unsaturated substrates that potentially can undergo hydrogenation seems particularly attractive. This reaction has been relatively poorly studied, except for few examples.[6,7]

The present report concerns the reactivity of copper(I) benzoate with isocyanides and azo compounds, both reactions leading to complexes containing a dicopper(I) unit doublly bridged by the benzoato group. Terminal and semibridging isocyanide and bridging azo complexes have been isolated and structurally characterized.

Experimental Section

Owing to the air sensitivity of the complexes, all reactions were carried out in a dry, oxygen-free atmosphere, with the use of standard Schlenk techniques. Solvents were purified by standard methods. Benzo[*c*]cinnoline (bzocin) and phthalazine (phz) were recrystallized before use. A modified procedure was used for the preparation of $[Cu(PhCO_2)]_4$.[7] CuI[9] and *p*-tolyl isocyanide[10] were prepared by published procedures. Infrared spectra were recorded with a Perkin-Elmer 283 spectrophotometer.

Synthesis of $Cu_2(\mu\text{-}PhCO_2)_2[(p\text{-}MeC_6H_4NC)_2]$ (4). To a ethanol suspension of $[Cu(PhCO_2)]_4$ (0.347 g, 0.47 mmol) was added $p\text{-}MeC_6H_4NC$ (0.7 mL, 5.74 mmol). A white-yellow microcrystalline solid immediately formed, which was filtered and dried. The mother liquor was partially evaporated, the solid formed was dissolved by gentle heating, and by subsequent slow cooling yellow crystals appropriate for X-ray analysis were obtained (yield ca. 20%). The two solids were identical by superimposable IR spectra. Anal. Calcd for $C_{30}H_{24}Cu_2N_2O_4$ (**4**): C, 59.70; H, 4.01; N, 4.64. Found: C, 59.50; H, 4.47; N, 4.96. ν(CN) (Nujol) = 2152 cm^{-1} (s). A single CN band was observed in solution (EtOH) at 2152 cm^{-1}.

Synthesis of $[Cu_2(\mu\text{-}PhCO_2)_2(p\text{-}MeC_6H_4NC)_3]\cdot THF$ (5). When a THF suspension (20 mL) of $[Cu(PhCO_2)]_4$ (0.39 g, 0.53 mmol) was reacted with neat *p*-tolyl isocyanide (0.52 mL, 4.26 mmol), a yellow solution formed. After partial evaporation of the solvent a white solid formed, which was filtered and dried in vacuo (yield ca. 22%). A partial evaporation of the mother liquor gave the same solid, which was dissolved by gentle heating and crystallized by slow cooling. Colorless flat hexagonal crystals suitable for X-ray analysis were obtained. The two solids

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Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	complex **4**	complex **5**	complex **6**
	$C_{30}H_{24}Cu_2N_2O_4$	$C_{42}H_{39}Cu_2N_3O_5$	$C_{26}H_{18}Cu_2N_2O_4$
cryst syst	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$ [C_i^1, No. 2]	$P\bar{1}$ [C_i^1, No. 2]	$Pbcn$ [D_{2h}^{14}, No. 60]
cell dimens at 295 K			
a, Å	13.278 (4)	10.440 (2)	21.679 (3)
b, Å	10.690 (3)	19.408 (4)	9.408 (1)
c, Å	10.412 (2)	10.476 (2)	10.564 (2)
α, deg	104.20 (2)	96.77 (2)	90
β, deg	95.71 (3)	106.20 (2)	90
γ, deg	104.75 (3)	77.66 (2)	90
V, Å^3	1364.7 (7)	1987.4 (8)	2154.6 (5)
Z	2	2	4
D_{calcd}, g cm^{-3}	1.47	1.32	1.69
mol wt	603.6	792.9	549.5
max cryst dimens, mm	0.18 × 0.32 × 0.61	0.11 × 0.29 × 0.42	0.40 × 0.19 × 0.74
linear abs, cm^{-1}	15.98	16.50	20.16
diffractometer	Siemens AED		
scan type		$\theta/2\theta$	
scan speed, deg min^{-1}		3–12	
scan width		$(\theta - 0.5°)-[\theta + (0.5 + \Delta\theta)]^a$	
radiation	Nb-filtered Mo Kα (λ = 0.7107 Å)	Ni-filtered Cu Kα (λ = 1.5418 Å)	Nb-filtered Mo Kα (λ = 0.7107 Å)
reflecns measd	$\pm h,\pm k,+l$	$\pm h,\pm k,+l$	$+h,+k,+l$
2θ range, deg	6–48	6–110	6–52
unique total data	4232	4943	2134
unique obsd data (N_o)	2557	3236	1402
criterion for observn	$I > 3\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
no. of params varied (N_v)	295	404	154
R[20]	0.044	0.048	0.064
R_w[20]	0.046		0.064
GOF[21]	1.22		0.28
N_o:N_v	8.7	8.0	9.0
A^b	1.52–1.26	1.48–1.16	1.88–1.37

[a] $\Delta\theta = (\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda \tan\theta$. [b] Maximum–minimum transmission factors.

Table II. Fractional Atomic Coordinates (×10 000) for Complex **4**

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Cu1	3192 (1)	1968 (1)	635 (1)	C12A	1551 (3)	−50 (4)	−5972 (3)
Cu2	1080 (1)	566 (1)	−91 (1)	C13A	2471 (3)	656 (4)	−6322 (3)
O1A	2977 (4)	1920 (4)	−1305 (4)	C14A	3285 (3)	1569 (4)	−5322 (3)
O2A	1291 (4)	674 (5)	−1916 (4)	C15A	3180 (3)	1777 (4)	−3972 (3)
N1A	3510 (4)	4416 (5)	2925 (5)	C1B	693 (5)	1542 (6)	1374 (6)
O1B	3403 (4)	183 (4)	484 (4)	C2B	221 (3)	2693 (4)	3573 (3)
O2B	1695 (4)	−986 (5)	−68 (5)	C3B	934 (3)	2995 (4)	4762 (3)
N1B	485 (4)	2128 (5)	2355 (5)	C4B	646 (3)	3482 (4)	5999 (3)
C1A	3393 (5)	3455 (7)	2049 (6)	C5B	−355 (3)	3665 (4)	6048 (3)
C2A	3662 (3)	5584 (3)	3944 (3)	C6B	−1067 (3)	3362 (4)	4859 (3)
C3A	3706 (3)	6797 (3)	3645 (3)	C7B	−779 (3)	2876 (4)	3622 (3)
C4A	3869 (3)	7975 (3)	4682 (3)	C8B	−700 (7)	4135 (9)	7401 (7)
C5A	3989 (3)	7940 (3)	6018 (3)	C9B	2659 (5)	−902 (7)	156 (6)
C6A	3945 (3)	6727 (3)	6317 (3)	C10B	2947 (3)	−2192 (3)	35 (4)
C7A	3782 (3)	5549 (3)	5280 (3)	C11B	2156 (3)	−3415 (3)	−258 (4)
C8A	4223 (7)	9224 (7)	7142 (7)	C12B	2427 (3)	−4615 (3)	−408 (4)
C9A	2167 (5)	1238 (6)	−2164 (6)	C13B	3488 (3)	−4592 (3)	−266 (4)
C10A	2261 (3)	1071 (4)	−3622 (3)	C14B	4278 (3)	−3369 (3)	28 (4)
C11A	1447 (3)	158 (4)	−4622 (3)	C15B	4008 (3)	−2169 (3)	178 (4)

were identical. Anal. Calcd for $C_{42}H_{39}Cu_2N_3O_5$ (**5**): C, 63.63; H, 4.96; N, 5.30. Found: C, 63.62; H, 4.79; N, 5.44. Complex **5** has two CN bands (Nujol) at 2125 (m-s) and 2145 cm^{-1} (s). In THF solution a wide intense band was observed at 2140 cm^{-1}.

Synthesis of [$Cu_2(\mu$-$PhCO_2)_2(\mu$-bzocin)]$_n$ (6). Benzo[*c*]cinnoline (1.0 g, 5.55 mmol) was dissolved in THF (25 mL), and then [$Cu(PhCO_2)$]$_4$ was added with vigorous stirring. Sudden formation of a brown microcrystalline solid occurred (yield ca. 80%). The recrystallization of **6** was carried out as follows: When a suspension of **6** in THF was exposed to carbon monoxide [ν(CO) = 2075 cm^{-1}], the compound became slightly more soluble. The suspension was filtered under CO, and then the CO atmosphere was slowly removed from the resulting solution. Black hexagonal crystals suitable for X-ray study were obtained. The crystallization did not change the nature of the solid. Anal. Calcd for $C_{26}H_{18}Cu_2N_2O_4$ (**6**): C, 56.83; H, 3.30; N, 5.10. Found: C, 57.03; H, 3.30; N, 5.12.

Synthesis of [$Cu(\mu$-$PhCO_2)(\mu$-phz)]$_n$ (7). To a THF solution (30 mL) of phthalazine (0.73 g, 5.61 mmol) was added [$Cu(PhCO_2)$]$_4$ (1.04 g, 1.405 mmol) as a solid. The solid dissolved, giving a red solution. Evaporation of ca. one-third of the solvent resulted in the formation of a crystalline solid (yield ca. 71%). Anal. Calcd for $C_{15}H_{11}CuN_2O_2$ (**7**): C, 57.23; H, 3.52; N, 8.89. Found: C, 56.81; H, 3.52; N, 8.73.

Synthesis of [Cu_2I_2(bzocin)] (8). CuI (0.50 g, 2.62 mmol) was added to a THF solution (20 mL) of benzo[*c*]cinnoline (0.52 g, 2.88 mmol). Sudden formation of a dark brown precipitate was observed. The suspension was stirred overnight. The dark brown solid was filtered; from the yellow solution no crystalline material was recovered. Anal. Calcd for $C_{12}H_8Cu_2I_2N_2$ (**8**): C, 25.69; H, 1.44; N, 4.99. Found: C, 25.72; H, 1.41; N, 4.97.

Synthesis of [CuI(phz)]$_n$ (9). CuI (1.0 g, 5.25 mmol) was added to a THF solution (20 mL) of phthalazine (0.70 g, 5.38 mmol). Sudden formation of a largely insoluble orange solid was observed (yield ca. 60%). Attempts to recover crystalline material from the solution and recrystallization of the solid were unsuccessful. Anal. Calcd for $C_8H_6CuIn_2$ (**9**): C, 29.97; H, 1.89; N, 8.73. Found: C, 30.52; H, 2.06; N, 8.33.

X-ray Crystallography. The crystals selected for study were mounted in glass capillaries sealed under nitrogen. Extensive preliminary inves-

Table III. Fractional Atomic Coordinates (×10 000) for Complex **5**[a]

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Cu1	2320 (1)	2002 (1)	427 (1)	O1B	376 (4)	2424 (3)	626 (5)
Cu2	2566 (1)	3462 (1)	1710 (1)	O2B	663 (4)	3462 (2)	1703 (4)
N1A	4744 (6)	2007 (3)	2786 (6)	C9B	−46 (6)	3020 (4)	1114 (6)
C1A	3783 (8)	2054 (4)	1904 (7)	C10B	−1551 (3)	3236 (3)	992 (4)
C2A	5846 (5)	2062 (3)	3878 (4)	C11B	−2057 (3)	3907 (3)	1490 (4)
C3A	7090 (5)	2118 (3)	3688 (4)	C12B	−3452 (3)	4129 (3)	1325 (4)
C4A	8172 (5)	2215 (3)	4784 (4)	C13B	−4341 (3)	3680 (3)	662 (4)
C5A	8010 (5)	2257 (3)	6070 (4)	C14B	−3835 (3)	3009 (3)	164 (4)
C6A	6766 (5)	2202 (3)	6260 (4)	C15B	−2440 (3)	2787 (3)	329 (4)
C7A	5684 (5)	2104 (3)	5164 (4)	N1C	1333 (7)	676 (3)	−1074 (6)
C8A	9187 (9)	2382 (6)	7249 (9)	C1C	1813 (8)	1141 (4)	−490 (7)
O1A	2383 (5)	2517 (3)	−1160 (4)	C2C	647 (5)	156 (2)	−1796 (5)
O2A	2345 (4)	3604 (2)	−192 (4)	C3C	798 (5)	−484 (2)	−1237 (5)
C9A	2286 (6)	3168 (4)	−1175 (6)	C4C	66 (5)	−996 (2)	−1934 (5)
C10A	2074 (4)	3471 (2)	−2504 (3)	C5C	−816 (5)	−868 (2)	−3190 (5)
C11A	1997 (4)	3022 (2)	−3655 (3)	C6C	−968 (5)	−228 (2)	−3749 (5)
C12A	1714 (4)	3303 (2)	−4891 (3)	C7C	−236 (5)	284 (2)	−3052 (5)
C13A	1509 (4)	4032 (2)	−4977 (3)	C8C	−1624 (5)	−1415 (2)	−3917 (5)
C14A	1586 (4)	4481 (2)	−3826 (3)	C1	4272 (24)	1127 (12)	7472 (25)
C15A	1869 (4)	4200 (2)	−2590 (3)	C2	3694 (38)	576 (22)	6799 (35)
N1B	4689 (5)	3862 (3)	4072 (5)	C3	4296 (70)	−28 (34)	7168 (80)
C1B	3887 (6)	3704 (4)	3152 (6)	C4	6071 (57)	85 (29)	7854 (62)
C2B	5676 (4)	4043 (2)	5203 (3)	C5	6181 (52)	857 (28)	8223 (46)
C3B	6935 (4)	4115 (2)	5076 (3)	C1*	5527 (74)	617 (51)	9041 (70)
C4B	7921 (4)	4299 (2)	6196 (3)	C2*	5000 (68)	9 (33)	8295 (70)
C5B	7647 (4)	4411 (2)	7441 (3)	C3*	5296 (72)	−19 (33)	6826 (60)
C6B	6387 (4)	4339 (2)	7567 (3)	C4*	4778 (52)	781 (29)	6555 (47)
C7B	5402 (4)	4155 (2)	6448 (3)	C5*	5171 (67)	1043 (31)	8534 (71)
C8B	8708 (7)	4628 (4)	8655 (6)				

[a] C1–C5 and C1*–C5* are the atoms of the disordered THF molecule.

Table IV. Fractional Atomic Coordinates (×10 000) for Complex **6**

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Cu	145 (1)	928 (1)	985 (1)	C6	1781 (3)	286 (6)	−2794 (5)
O1	876 (2)	984 (4)	0 (3)	C7	984 (2)	494 (5)	−1082 (5)
O2	627 (2)	−282 (4)	−1686 (3)	C8	393 (2)	4388 (5)	1517 (5)
N1	181 (2)	3124 (4)	2006 (4)	C9	219 (2)	5728 (5)	2009 (6)
C1	1598 (2)	861 (5)	−1651 (4)	C10	486 (3)	6951 (6)	1476 (6)
C2	1993 (3)	1792 (6)	−1026 (5)	C11	898 (3)	6836 (6)	497 (7)
C3	2559 (3)	2133 (7)	−1529 (6)	C12	1056 (3)	5512 (7)	−16 (6)
C4	2739 (3)	1551 (8)	−2662 (6)	C13	804 (3)	4292 (5)	493 (6)
C5	2363 (3)	618 (8)	−3290 (6)				

tigations employing rotation and Weissenberg photographs showed the crystals of complex **6** to be orthorhombic with systematic absences consistent with the space group *Pbcn*. The lack of any systematic absences indicated the crystals of **4** and **5** to be triclinic. Crystal data and details of data collection are given in Table I. Three-dimensional intensity data were collected at room temperature (295 K) on a single-crystal diffractometer. For intensities and background the profile measurement technique was used.[11] The structure amplitudes were obtained by means of standard Lorentz and polarization reduction, and the absolute scale was established by Wilson's method.[12] No absorption corrections were applied.

Solution and Refinement of the Structures.[13] The structures were solved by the heavy-atom method starting from three-dimensional Patterson syntheses and refined by full-matrix least squares anisotropically for all non-hydrogen atoms. For the three complexes all hydrogen atoms were located from different Fourier syntheses and introduced as fixed atom contributions with isotropic temperature factors fixed at 9.5 Å^2 for complexes **4** and **5** and 6.3 Å^2 for complex **6**. For complexes **4** and **5** the benzene rings were refined as rigid groups having D_{6h} symmetry (C–C = 1.39 Å). The function minimized during the least-squares refinement was $\sum w|\Delta F|^2$. The weighting scheme used was $w = k/[\sigma^2(F_o) + |g|(F_o)^2]$ based on counting statistics; k was redetermined after each structure factor calculation, and the absolute value of g was refined at the same time by fitting $(|F_o| - |F_c|)^2$ to $[\sigma^2(F_o) + |g|(F_o)^2]/k$.[13] In the final stage of refinement the values for k and g were 1.1015, 0.000616 and 0.4981, 0.0116 for complexes **4** and **6**, respectively. Unit weights were used for complex **5** since these gave a satisfactory analysis of variance.[13] During the refinement of complex **5**, the appearance in a difference density map of 10 peaks in a region far from the complex molecule indicated the presence of solvent of crystallization. This could be interpreted as one disordered THF molecule distributed over two positions with a site occupancy factor of 0.5. Final isotropic temperature factors for these "partial" atoms ranged from 12 to 22 Å^2, indicating a high thermal motion associated with disorder in this group. The effects of the anomalous dispersion were included in all structure factor calculations.[14b] Scattering factors were taken from ref 14a and Cu, from ref 15 for O, N, and C, and from Ref 16 for H.

Results and Discussion

Reaction of [Cu(PhCO$_2$)]$_4$ with Isocyanides. Copper(I) benzoate, [Cu(PhCO$_2$)]$_4$, which has the well-known tetrameric structure,[2] is a very good source of the dinuclear copper(I) unit [Cu$_2$(PhCO$_2$)$_2$] in the presence of various ligands like diphenylacetylene[6] and carbon monoxide.[7] In the latter case, for which the isolation of carbonyl species in the solid state failed

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(14) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: (a) p 99; (b) p 149.

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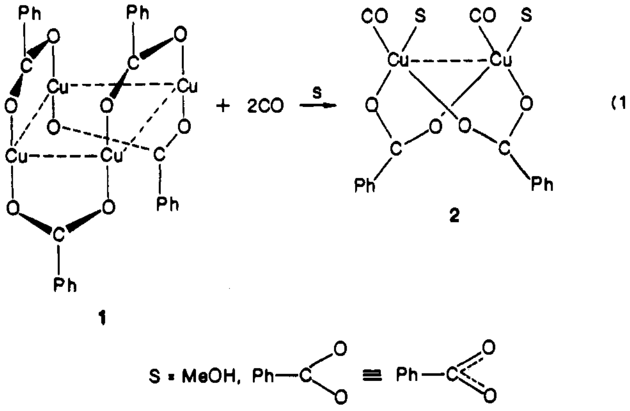
Table V. Interatomic Distances (Å) and Angles (deg) for Complexes **4** and **5**[a]

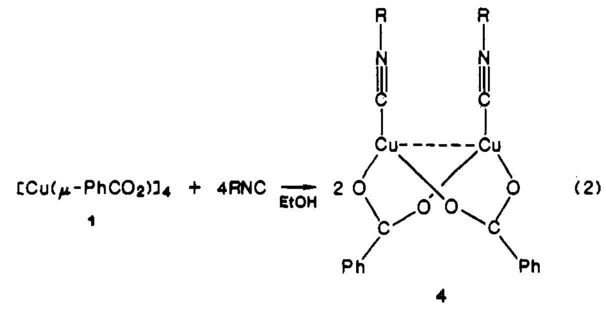
	4	**5**		**4**	**5**
Cu1–O1A	1.998 (4)	2.061 (6)	Cu2–O2A	1.975 (5)	1.986 (5)
Cu1–O1B	1.969 (5)	2.078 (5)	Cu2–O2B	2.031 (6)	1.985 (5)
Cu1–C1A	1.823 (6)	1.857 (7)	Cu2–C1B	1.824 (6)	1.831 (6)
Cu1–C1C		1.926 (8)	Cu2–C1B′	2.757 (7)	
Cu1–Cu2	2.750 (2)	3.020 (3)	Cu2–C1A		2.762 (8)
			Cu2–Cu2′	2.860 (2)	
O1A–C9A	1.256 (7)	1.247 (10)	O1B–C9B	1.262 (7)	1.250 (8)
O2A–C9A	1.250 (8)	1.250 (8)	O2B–C9B	1.254 (9)	1.248 (8)
N1A–C1A	1.159 (8)	1.154 (9)	N1B–C1B	1.159 (8)	1.146 (7)
N1A–C2A	1.380 (5)	1.390 (7)	N1B–C2B	1.384 (6)	1.402 (6)
C9A–C10A	1.506 (7)	1.516 (8)	C9B–C10B	1.502 (9)	1.510 (7)
N1C–C1C		1.154 (10)	N1C–C2C		1.389 (8)
C5A–C8A	1.508 (7)	1.518 (9)	C5B–C8B	1.531 (9)	1.520 (7)
C5C–C8C		1.501 (6)			
O1B–Cu1–C1C		93.5 (3)	O2A–Cu2–C1B	138.0 (3)	127.5 (3)
O1A–Cu1–C1C		100.0 (3)	O2A–Cu2–O2B	97.7 (2)	101.0 (2)
O1A–Cu1–O1B	100.2 (2)	102.0 (2)	C1B–Cu2–O2B	123.7 (3)	125.5 (3)
C1A–Cu1–C1C		125.3 (3)	C1A–Cu2–C1B		90.5 (3)
C1A–Cu1–O1B	133.3 (3)	118.4 (3)	C1A–Cu2–O2A		102.3 (3)
C1A–Cu1–O1A	125.4 (3)	113.5 (3)	C1A–Cu2–O2B		103.2 (3)
Cu1–C1A–N1A	178.2 (6)	172.3 (7)	C1B′–Cu2–O2A	85.5 (3)	
Cu2–C1B–N1B	175.6 (6)	178.2 (6)	C1B′–Cu2–O2B	81.4 (3)	
Cu1–C1C–N1C		170.8 (8)	C1B′–Cu2–C1B	105.9 (3)	
C1A–N1A–C2A	178.3 (6)	171.2 (7)	O1A–C9A–O2A	125.7 (6)	126.3 (6)
C1B–N1B–C2B	173.4 (6)	179.0 (7)	O1A–C9A–C10A	117.2 (6)	117.8 (6)
C1C–N1C–C2C		175.0 (8)	O2A–C9A–C10A	117.0 (6)	115.9 (6)
Cu1–O1A–C9A	125.9 (4)	125.2 (4)	O1B–C9B–O2B	125.0 (7)	126.1 (7)
Cu1–O1B–C9B	123.8 (5)	128.2 (5)	O1B–C9B–C10B	117.7 (6)	118.0 (6)
Cu2–O2A–C9A	122.5 (4)	130.3 (4)	O2B–C9B–C10B	117.4 (6)	116.0 (6)
Cu2–O2B–C9B	126.0 (5)	127.2 (4)			

[a] Atoms marked with a prime indicate a symmetry transformation by $\bar{x}$, $\bar{y}$, $\bar{z}$.

because of the lability of the Cu–CO bond,[7] a structure was proposed for the species in solution:



The structure proposed for **2** had crystallographic support from the case of the diphenylacetylene derivative $[Cu_2(\mu\text{-}PhCO_2)_2(Ph_2C_2)_2]$ (**3**).[6] A closer similarity can be found, however, in the compounds formed from the reaction of **1** with *p*-tolyl isocyanide. Reaction 2 gave different results, however, depending on the solvent used. Reaction of **1** with *p*-MeC_6H_4NC in EtOH gave a crystalline solid having a structure similar to that of **3**. A single C–N band in solution (EtOH) and in the solid state was observed for the isocyanide at rather high wavenumber (2152 cm^{-1}), as expected for an electrophilic metal like Cu(I). The solid-state analysis showed, however, that the dimeric units (Figure 1) have significant interactions with one another to form a sort of tetrameric complex, reported in Figure 2. Each copper(I) in the dimeric unit (Figure 1) has a nearly planar trigonal structure, with Cu1 and Cu2 out from their coordination planes C1A, O1A, O1B and C1B, O2A, O2B (Table SVII) by 0.116 (3) and 0.084 (2) Å, respectively. The dihedral angle between these two coordination planes is 24.6 (2)°. The $[Cu_2(PhCO_2)_2]$ fragment maintains the same structural characteristics as in the original



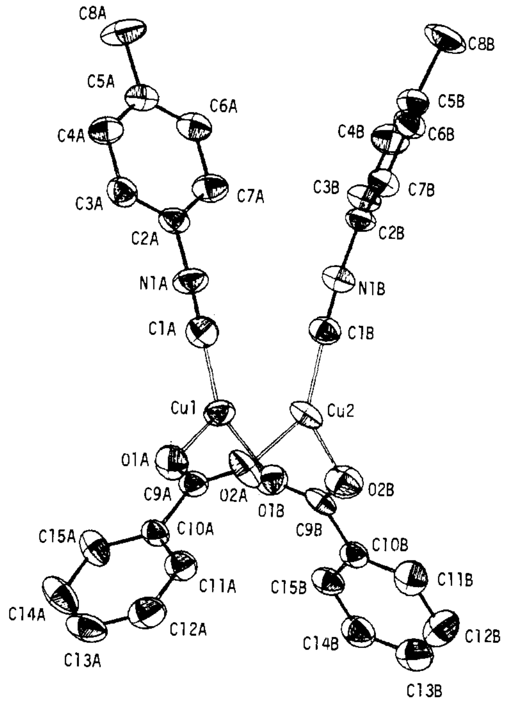


Figure 1. ORTEP drawing of complex **4** (40% probability ellipsoids).

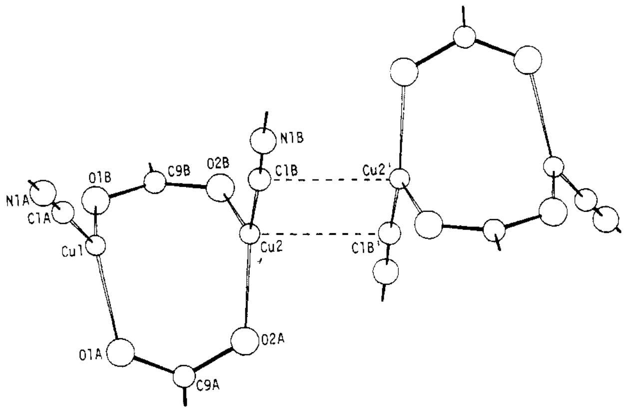
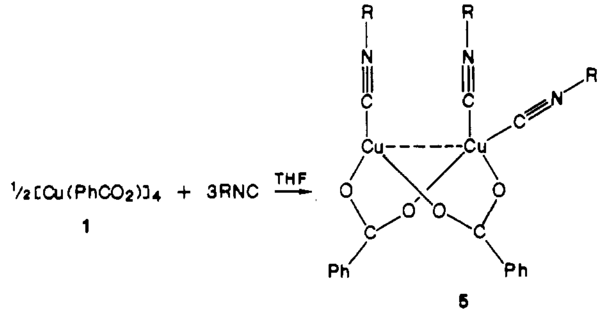


Figure 2. Projection of complex **4** showing the interactions between two dimers related by a center of symmetry. Phenyl rings are missing for clarity.

tetrameric complex[2] and in **3**,[6] such as the Cu···Cu proximity of 2.750 (2) Å. The Cu–O bond distances (Table V) are very close to those reported for **3**[6] [mean value 1.957 (10) vs. 1.953 (9) Å] and significantly shorter than those in **1**[2] [mean value 1.839 (6) Å]. The significant lengthening of Cu2–O2B [2.031 (6) Å] must be related to the different coordination number of Cu2, since this copper interacts at rather close distance [Cu2···C1B′ = 2.757 (7) Å] with the isocyanide carbon of an adjacent dimer (Figure 2). In addition, a small deviation from the linearity at the Cu–CNR unit was observed [Cu2–C1B–N1B = 175.6 (6); C1B–N1B–C2B = 173.4 (6)°]. Bond distances for the Cu–CNR fragment (Table V) are very close to those reported for the few copper(I)–isocyanide complexes structurally studied so far.[17] The incipient semibridging bonding mode of the isocyanide ligand seems likely. Such an interaction brings in a close proximity Cu2···Cu2′ [2.860 (2) Å]. This sort of close interaction between dimers to form a tetrameric unit vanished when reaction 2 was carried out in THF, since a further isocyanide molecule bonds to one of the copper(I) ions:



(3)

5

R = p-MeC$_6$H$_4$

The solvent is the factor that causes the reaction between **1** and p-MeC$_6$H$_4$ to produce **5** instead of **4**. Complex **5** has two C≡N stretching frequencies at 2125 and 2145 cm^{-1}. An ORTEP view of **5**, which crystallizes with a molecule of THF, is shown in Figure 3. The Cu–C and Cu–O bond distances of the three-coordinate copper closely resembles those found in complex **4**, while those of the tetracoordinate copper(I) are significantly longer (Table V). The two isocyanides bonded to Cu1 are significantly different [Cu1–C1A = 1.857 (7) Å vs. Cu1–C1C = 1.926 (8) Å].[17] It also must be mentioned that a sort of semibridging interaction involves Cu2 and the C1A carbon of an adjacent isocyanide [Cu2A···C1A = 2.762 (8) Å]. Furthermore, Cu2 is significantly displaced [0.269 (2) Å] from the plane defined by C1B, O2A, O2B toward C1A. The Cu1···Cu2 distance is significantly longer than in **4** [3.020 (3) Å]. Weak van der Waals interactions exist between dimers. Small but significant deviations from the linearity of the Cu–CNR fragment are observed for the isocyanide bonded to Cu1 [Cu1–C1C–N1C = 170.8 (8)°; Cu1–C1A–N1A = 172.3 (7)°]. The two aromatic rings C2A...C7A and C2B...C7B are almost parallel. Structural parameters for the Cu–CNR[17] units and PhCO$_2$[2,6,7] ligand are in the usual range.

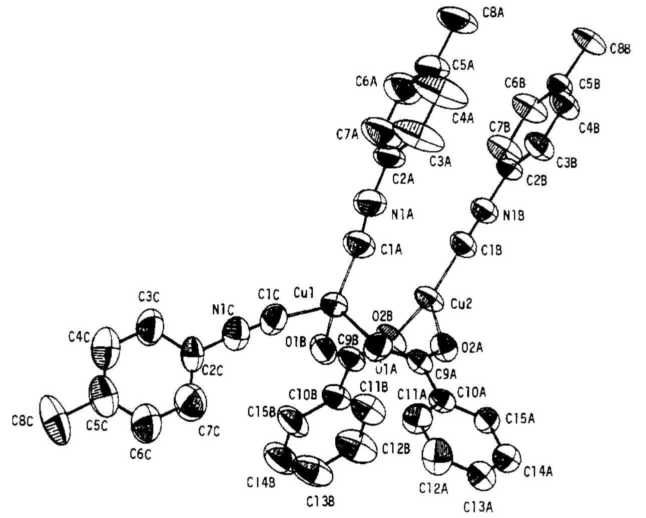
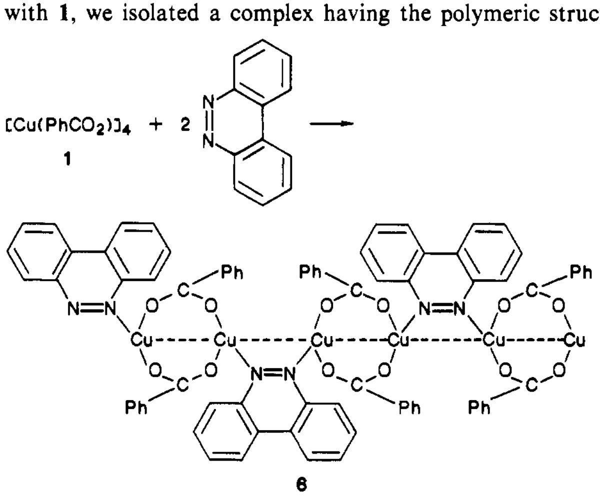


Figure 3. ORTEP drawing of complex **5** (40% probability ellipsoids).

Reaction of [Cu(PhCO$_2$)]$_4$ with Azo Compounds. A study on the reactivity of azo compounds with **1** is suggested by the close resemblance of the azo group to the C≡C bond,[18] because both are unsaturated substrates that can undergo hydrogenation. Copper(I) carbonylato species are, in fact, the first well-defined homogeneous catalysts for hydrogenation.[8]

While the reaction of **1** with azobenzene led to some labile species, which we were not able to identify analytically or spectroscopically, more successful results were obtained from the reaction of **1** with ring-fixed azo compounds, like benzo[*c*]cinnoline or phthalazine. Reacting a THF solution of benzo[*c*]cinnoline with **1**, we isolated a complex having the polymeric structure



(4)

6

An ORTEP view of the structure is reported in Figure 4. The polymer is built up by the centrosymmetric dimers [Cu(PhCO$_2$)]$_2$ bridged by the azo group from benzo[*c*]cinnoline. Steric hinderance is probably responsible for the stoichiometry of **6**, so that copper(I) can bind a single nitrogen atom and is three-coordinate (vide infra). The Cu···Cu distances along the chain are 2.788 (2) Å within the dimers and 3.262 (2) Å across the dimers. The conformation of the eight-membered ring [Cu$_2$(PhCO$_2$)$_2$] is completely different from that observed in **3**–**5**, where the ring is folded along the Cu···Cu direction by a value close to 90°; the ring is nearly planar in **6**. Copper(I) can be considered either three- or four-coordinate via weak interaction with an oxygen atom

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Table VI. Bond Distances (Å) and Angles (deg) for Complex **6**[a]

Cu–O1	1.897 (4)	O1–Cu–N	101.6 (2)	Cu′–Cu–O2′	83.9 (1)
Cu–N	2.332 (4)	O1–Cu–O2′	160.8 (2)	Cu′–Cu–O2‴	128.1 (1)
Cu–O2′	1.928 (4)	N–Cu–O2′	97.5 (2)	O2‴–Cu–O1	100.4 (2)
Cu–Cu′	2.788 (2)	Cu′–Cu–O1	78.3 (1)	O2‴–Cu–O2′	85.2 (2)
Cu–O2‴	2.741 (4)	Cu′–Cu–N	155.2 (1)	O2‴–Cu–N	76.6 (2)

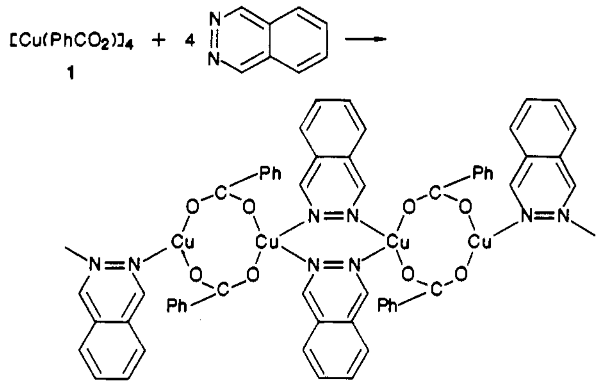
N–N″	1.306 (8)	C10–C11	1.371 (10)	O1–C7	1.255 (6)	C3–C4	1.373 (9)
N–C8	1.376 (6)	C11–C12	1.401 (9)	O2–C7	1.241 (6)	C4–C5	1.369 (10)
C8–C9	1.415 (7)	C12–C13	1.380 (8)	C7–C1	1.501 (6)	C5–C6	1.401 (9)
C9–C9″	1.406 (11)	C13–C8	1.404 (8)	C1–C2	1.391 (7)	C6–C1	1.381 (7)
C9–C10	1.406 (8)			C2–C3	1.375 (9)		

N″–N–C8	120.1 (4)	C9–C10–C11	120.4 (5)	O1–C7–O2	124.6 (5)	C2–C1–C6	119.0 (5)
N–C8–C13	116.5 (4)	C10–C11–C12	121.4 (6)	O1–C7–C1	116.5 (4)	C1–C2–C3	120.8 (5)
N–C8–C9	122.9 (4)	C11–C12–C13	119.5 (6)	O2–C7–C1	118.9 (4)	C2–C3–C4	119.8 (6)
C8–C9–C9″	116.8 (4)	C12–C13–C8	119.9 (5)	C7–C1–C2	120.0 (4)	C3–C4–C5	120.6 (6)
C8–C9–C10	118.2 (5)	C13–C8–C9	120.6 (4)	C7–C1–C6	121.0 (4)	C4–C5–C6	119.9 (6)
C10–C9–C9″	125.0 (5)					C5–C6–C1	119.9 (5)

[a] Symmetry transformations: single prime, $-x, -y, -z$; double prime, $-x, y, \frac{1}{2} - z$; triple prime, $x, -y, \frac{1}{2} + z$.

of an adjacent molecule [Cu···O2‴ = 2.741 (4) Å], Cu being 0.018 Å out of the coordination plane (O1, O2′, N) toward O2‴. The Cu–O bond distances are significantly shorter (Table VI) than those in complexes **3**–**5**. The very short N–N bond distance [N–N″ = 1.306 (8) Å], which has to be compared with that in $\{[Fe(CO)_3]_2[bzocin]\}$[19] [N–N = 1.399 (8) Å], agrees with the interaction occurring through the nitrogen lone pairs rather than through the N=N multiple bond. The bridging rather than the chelating bonding mode is expected because of the geometrical orientation of the lone pairs. On the other hand, the rather long Cu–N bond distance [2.332 (4) Å] is related to the low basicity of the heterocyclic nitrogens and has to be compared with those significantly shorter involving amino groups.[17]

Less sterically demanding azo derivatives, like phthalazines, reacted with **1** in a 1:1 Cu:phthalazine molar ratio:



(5)

7

We do not have any structural evidence for **7**, for which we did not get any suitale crystals for X-ray analysis. The structure we propose, however, has significant support from the structure of **6**. The steric hindrance that determines the difference between the structures of **6** and **7** seems to be more associated that the azo compound than the copper(I) moiety. As a matter of fact, in reacting benzo[*c*]cinnoline with copper iodide, we obtained a compound with a 2:1 Cu:benzo[*c*]cinnoline molar ratio, $[Cu_2I_2(bzocin)]_n$ (**8**), for which we can propose the same structure we found for **6**, except that the dicopper unit is Cu_2I_2. The reaction of CuI with phthalazine gave a compound with a 1:1 Cu/phthalazine molar ratio, $[Cu(I)(phz)]_n$ (**9**), for which we can likely assume a structure similar to that of **7**. Solution studies of the compounds reported in this paper are largely prevented by their insolubility in the most common innocent solvents. On the other hand, the use of highly coordinating solvents, which can achieve the solubilization of the complexes reported, may affect too much the nature of these compounds, which are normally labile with weak but significant interactions in the solid state.

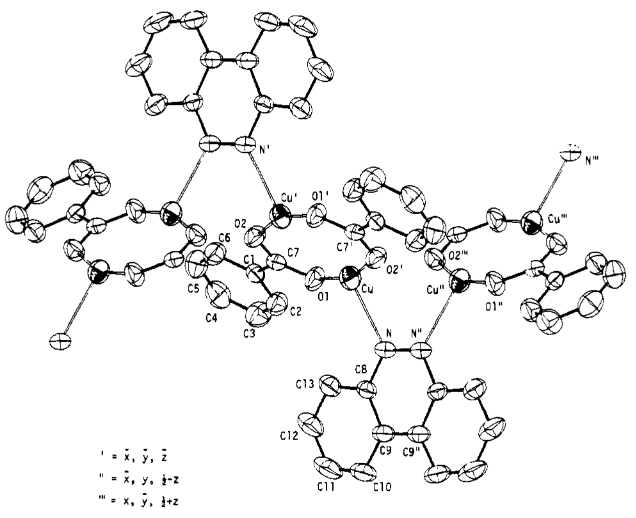


Figure 4. ORTEP drawing of the polymeric structure of complex **6** (40% probability ellipsoids).

Acknowledgment. We thank the CNR and MPI (Rome).

Registry No. **1**, 62914-01-6; **4**, 105900-32-1; **5**, 105900-31-0; **6**, 105900-33-2; **7**, 105900-29-6; **8**, 105900-34-3; **9**, 105930-62-9; azobenzene, 103-33-3.

Supplementary Material Available: Listings of hydrogen coordinates (Tables SI–SIII), thermal parameters (Tables SIV–SVI), and least-squares planes (Table SVII) for compounds **4**–**6** (7 pages); listings of observed and calculated structure factors for the three compounds (33 pages). Ordering information is given on any current masthead page.

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[19] Doedens, R. J. *Inorg. Chem.* **1970**, *9*, 429–436.

[20] $R = \sum|\Delta F|/\sum|F_o|$; $R_w = \sum w^{1/2}|\Delta F|/\sum w^{1/2}|F_o|$.

[21] Defined as $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]$, where N_o is the number of observations and N_v is the number of refined parameters.