Contribution from the Dipartimento di Chimica e Scuola Normale Superiore di Pisa, I-56100 Pisa, Italy,
ICMA, Universitē de Lausanne, CH-1005 Lausanne, Switzerland, and Istituto di Strutturistica Chimica,
Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, I-43100 Parma, Italy

Copper(I)–Benzimidazole Adducts: From Mononuclear to Polymeric Complexes

Andras Toth,[†] Carlo Floriani,*[‡] Angiola Chiesi-Villa,[§] and Carlo Guastini[§]

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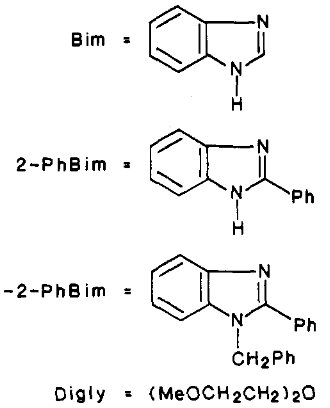
The reaction of CuI with benzimidazole (Bim) in a constant 1:2 molar ratio led to compounds having a different structure depending on the solvent used. In THF, a binuclear compound was isolated, $[Cu_2(\mu\text{-}I)_2(Bim)_4]$ (**1**). The same reaction carried out under a carbon monoxide atmosphere in the presence of $NaBPh_4$ gave $[Cu(Bim)_3(CO)](BPh_4)$ (**2**) [ν(CO) (Nujol) 2060 cm^{-1}]. When benzimidazole was allowed to react with CuI in $(MeOCH_2CH_2)_2O$ (Digly), a tetranuclear complex $[Cu_4(\mu_3\text{-}I)_4(Bim)_4]\cdot 3Digly$ (**3**) was isolated. Its X-ray analysis showed a cubane-type structure for **3** having crystallographically imposed 4-fold symmetry [Cu–I, 2.688(3)–2.720 (2) Å; Cu⋯Cu, 2.740 (3)–2.757 (3) Å]. The benzimidazole adduct isolated from MeOH, $[Cu(\mu_3\text{-}I)(Bim)]_n$ (**4**), has a stair polymeric structure containing tetracoordinate coppers [Cu–I, 2.631 (2)–2.738 (2) Å; Cu⋯Cu, 2.958 (2)–2.989 (2) Å]. Substituted benzimidazoles, 1-benzyl-2-phenylbenzimidazole (1-B-2-PhBim) and 2-phenylbenzimidazole (2-PhBim), form mononuclear and binuclear adducts with CuI in THF: $[Cu(I)(1\text{-}B\text{-}2\text{-}PhBim)_2]\cdot THF$ (**5**) [Cu–I, 2.512 (3) Å] and $[Cu_2(\mu\text{-}I)_2(2\text{-}PhBim)_2]\cdot 2THF$ (**6**) [Cu–I, 2.554 (2)–2.598 (2) Å; Cu⋯Cu, 2.546 (3) Å] containing three-coordinated coppers. Crystallographic details for X-ray structures of **3**–**6** are as follows. Complex **3**: space group $I4_1/a$ (tetragonal), $a = 22.838$ (2) Å, $c = 11.970$ (1) Å, $V = 6243.2$ (9) Å^3, $Z = 4$, $D_{calcd} = 1.742$ g cm^{-3}. The final R factor was 0.045 ($R_w = 0.044$) for 925 observed reflections. Complex **4**: space group $P2_1/c$ (monoclinic), $a = 4.337$ (1) Å, $b = 11.999$ (2) Å, $c = 16.120$ (2) Å, $\beta = 97.54$ (1)°, $V = 831.6$ (3) Å^3, $Z = 4$, $D_{calcd} = 2.465$ g cm^{-3}. The final R factor was 0.044 for 1346 observed reflections. Data for complex **5**: space group $C2/c$ (monoclinic), $a = 10.844$ (2) Å, $b = 20.778$ (4) Å, $c = 17.104$ (3) Å, $\beta = 92.23$ (2)°, $V = 3851$ (1) Å^3, $Z = 4$, $D_{calcd} = 1.434$ g cm^{-3}. The final R factor was 0.054 for 1577 observed reflections. Complex **6**: space group $P\bar{1}$ (triclinic), $a = 9.278$ (2) Å, $b = 10.947$ (2) Å, $c = 9.191$ (2) Å, $\alpha = 96.99$ (1)°, $\beta = 109.64$ (1)°, $\gamma = 89.63$ (1)°, $V = 872.1$ (4) Å^3, $Z = 1$, $D_{calcd} = 1.740$ g cm^{-3}. The final R factor was 0.042 for 2360 observed reflections.

Introduction

The addition of bases to copper(I) iodide leads to a large variety of structural forms depending mainly on steric factors existing on the ligand and on reaction conditions.[1–6] Among the ligands attracting the largest interest for their role in binding copper(I)–copper(II) in copper proteins are the imidazole derivatives.[7–9] It would be interesting to know how flexible the coordination geometry can be and to know the molecular complexity of copper(I) with benzimidazole derivatives[10,11] when the two factors mentioned above—substituents at the benzimidazole and reaction conditions—are varied. We report a synthetic and structural study on the complexes formed from the reaction of CuI with benzimidazole with a constant starting Cu/L molar ratio in different solvents and with two substituted benzimidazole ligands causing a significant steric hindrance around copper(I). Structural analogies with our results can be found in the literature for adducts forming from the reaction of CuI and a variety of Lewis bases.[1]

Chart I. Abbreviations



Experimental Section

All the reactions have been carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. [CuI],[12] 2-phenylbenzimidazole,[13] 1-benzyl-2-phenylbenzimidazole[13] have been prepared by published procedures. Infrared spectra were recorded with a Perkin-Elmer 283 spectrometer. Abbreviations are given in Chart I.

Synthesis of $[Cu(I)(Bim)_2]_2$ (1), Bis[(μ-iodo)bis(benzimidazole)copper(I)]. Benzimidazole (1.37 g, 11.55 mmol) was reacted with solid [CuI] (1.0 g, 5.25 mmol) in THF (50 mL). A bright yellow solution formed. Then Et_2O (40 mL) was added, and the solution was cooled down to 0 °C for several hours. A white microcrystalline solid formed (ca. 45%). Anal. Calcd for $C_{14}H_{12}CuIN_4$: C, 39.41; H, 2.83; N, 13.13. Found: C, 39.43; H, 2.81; N, 13.02.

Synthesis of $[Cu(Bim)_3(CO)](BPh_4)$ (2), Carbonyltris(benzimidazole)copper(I) Tetraphenylborate. Benzimidazole (1.37 g, 11.55 mmol) was added to a THF (30 mL) suspension of [CuI] (1.0 g, 5.25 mmol). A solution formed, which reacted with CO at room temperature. The addition of $NaBPh_4$ (1.98 g, 5.78 mmol) was followed by the addition of Et_2O (30 mL). The solution, cooled down to −20 °C for several hours, gave a white crystalline solid, which was filtered under carbon monoxide atmosphere (ca. 17%). ν(CO) (Nujol): 2060 cm^{-1}. Anal. Calcd for $C_{46}H_{38}BCuN_6O$: C, 70.98; H, 6.37; N, 8.56. Found: C, 70.69; H, 6.49; N, 8.51.

[†] Dipartimento di Chimica e Scuola Normale Superiore di Pisa.
[‡] Universitē de Lausanne.
[§] Università di Parma.

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Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes 3–6

	3	4	5	6
formula	$C_{28}H_{24}Cu_4I_4N_8\cdot 3C_6H_{14}O_3$	$C_7H_6CuIN_2$	$C_{40}H_{32}CuIN_4\cdot C_4H_8O$	$C_{26}H_{20}Cu_2I_2N_4\cdot 2C_4H_8O$
cryst syst	tetragonal	monoclinic	monoclinic	triclinic
space group	$I4_1/a$	$P2_1/c$	$C2/c$	$P\bar{1}$
cell params[a]				
a, Å	22.838 (2)	4.337 (1)	10.844 (2)	9.278 (2)
b, Å	22.838 (2)	11.999 (2)	20.778 (4)	10.947 (2)
c, Å	11.970 (1)	16.120 (2)	17.104 (3)	9.191 (2)
α, deg	90	90	90	96.99 (1)
β, deg	90	97.54 (1)	92.23 (2)	109.64 (1)
γ, deg	90	90	90	89.63 (1)
V, Å^3	6243.2 (9)	831.6 (3)	3851 (1)	872.1 (4)
Z	4	4	4	1
D_{calcd}, g cm^{-3}	1.742	2.465	1.434	1.740
mol wt	1636.9	308.6	831.3	913.6
cryst dimens, mm	0.15 × 0.19 × 0.47	0.25 × 0.35 × 0.65	0.18 × 0.30 × 0.54	0.27 × 0.31 × 0.55
linear abs coeff, cm^{-1}	33.6	62.4	74.4	30.1
diffractometer	*b*	*b*	Siemens AED	*b*
diffraction geometry	equatorial	equatorial	equatorial	equatorial
scan type	$\theta/2\theta$	$\theta/2\theta$	$\omega/2\theta$	$\theta/2\theta$
scan speed	0.075°/s	0.075°/s	3–12°/min	0.075°/s
scan width, deg	1.40	1.40	*c*	1.40
radiation	*d*	*d*	*e*	*d*
2θ range, deg	6–50	5–54	6–120	6–53
reflcns measd	*hkl*	$\pm h,k,l$	$\pm h,k,l$	$\pm h,\pm k,l$
tot. no. of unique data	2988	1821	3071	3619
criterion for observn	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 2\sigma(I)$	$I > 3\sigma(I)$
no. of unique obsd data	925	1346	1577	2360
no. of variables	136	100	219	199
overdetermination ratio	6.8	13.5	7.2	11.8
max Δ/σ on last cycle	0.3	0.2	0.1	0.05
$R = \sum\|\Delta F\|/\sum\|F_o\|$	0.045	0.044	0.054	0.042
$R_w = \sum w^{1/2}\|\Delta F\|/\sum w^{1/2}\|F_o\|$	0.044			
GOF = $[\sum w\|\Delta F\|^2/(\mathrm{NO} - \mathrm{NV})]$	1.40			

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 25–30 carefully centered reflections chosen from diverse regions of reciprocal space. [b] Philips PW 1100. [c] $(\theta - 0.5) - [\theta + (0.5 + \Delta\theta)]°$; $\Delta\theta = (\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda$. [d] Graphite-monochromated Mo Kα (λ = 0.7107 Å). [e] Ni-filtered Cu Kα (λ = 1.5418 Å).

Synthesis of $[Cu_4(\mu_3\text{-}I)_4(Bim)_4]\cdot 3Digly$ (3), Tetrakis[(μ_3-iodo)(benzimidazole)copper(I)]–Tris(diglyme). Benzimidazole (1.37 g, 11.55 mmol) and [CuI] (1.0 g, 5.25 mmol) were dissolved in $(MeOCH_2CH_2)_2O$ (20 mL). The addition of MeOH (20 mL) caused the formation of colorless crystals (ca. 36%). Anal. Calcd for $C_{46}H_{66}Cu_4I_4N_8O_9$: C, 33.75; H, 4.06; N, 6.85. Found: C, 33.74; H, 4.05; N, 6.81.

Synthesis of $[Cu(\mu_3\text{-}I)(Bim)]_n$ (4), *catena*-[(μ_3-Iodo)(benzimidazole)copper(I)]. Benzimidazole (1.24 g, 10.50 mmol) was dissolved in MeOH (30 mL) and then reacted with solid [CuI] (1.0 g, 5.25 mmol). The suspension was stirred for 5 h. The white solid formed was filtered out (ca. 81%) and then the mother liquor was partially evaporated and cooled down to 0 °C. Colorless crystals suitable for X-ray analysis were obtained after a few days. The two solids have a superimposable IR spectrum. Anal. Calcd for $C_7H_6CuIN_2$: C, 27.21; H, 1.94; N, 9.07. Found: C, 27.34; H, 1.92; N, 8.96.

Synthesis of $[Cu(I)(1\text{-}B\text{-}2\text{-}PhBim)_2]\cdot THF$ (5), Iodobis(1-benzyl-2-phenylbenzimidazole)copper(I)–Tetrahydrofuran. CuI (1.0 g, 5.25 mmol) and 1-benzyl-2-phenylbenzimidazole (3.10 g, 10.90 mmol) were suspended in THF (50 mL) and stirred for several hours. Then the suspension was warmed up and filtered when hot. The solid was collected (ca. 81%). The mother liquor gave, on cooling, slightly yellow crystals of 5. The two solids have a superimposable IR spectrum. Anal. Calcd for $C_{44}H_{40}CuIN_4O$: C, 63.58; H, 4.85; N, 6.74. Found: C, 63.68; H, 4.98; N, 6.59.

Synthesis of $[Cu_2(\mu\text{-}I)_2(2\text{-}PhBim)_2]\cdot 2THF$ (6), Bis[(μ-iodo)(2-phenylbenzimidazole)copper(I)]–Bis(tetrahydrofuran). 2-Phenylbenzimidazole (2.10 g, 10.81 mmol) was dissolved by gentle heating in THF (40 mL), and then [CuI] (1.0 g, 5.25 mmol) was added and the suspension stirred. A yellow solution formed on long stirring, and then the solvent was partially evaporated and the solution cooled down to 0 °C. A white solid precipitated (ca. 65%). The mother liquor gave by partial evaporation prismatic crystals suitable for X-ray analysis. The two solids have a superimposable IR spectrum. Anal. Calcd for $C_{34}H_{36}Cu_2I_2N_4O_2$: C, 44.69; H, 3.94; N, 6.13. Found: C, 44.69; H, 3.90; N, 6.00.

X-ray Crystallography.[14] The prismatic crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Data were collected at room temperature (295 K) on a single-crystal four-circle diffractometer. Crystal data and details of the parameters associated with data collection and structure refinement are given in Table I. The reduced cells quoted were obtained with the use of TRACER.[15] For intensities and background the "three-point" technique was used for complexes 3, 4, and 6. For complex 5 the profile measurement technique was used.[16] The structure amplitudes were obtained after the usual Lorentz and polarization corrections. The crystal quality was tested by ψ scans showing that crystal absorption effects could not be neglected. For complex 5 an absorption correction was applied by using ABSORB.[17]

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Table II. Fractional Atomic Coordinates ($\times 10^4$) for **3**

atom	*x/a*	*y/b*	*z/c*
I	9287 (1)	6825 (1)	2428 (1)
Cu	9591 (1)	7944 (1)	2946 (2)
N1	9105 (6)	8469 (6)	1941 (11)
C2	9299 (8)	8820 (9)	1156 (17)
N3	8883 (9)	9095 (7)	625 (13)
C4	7795 (11)	9016 (8)	774 (16)
C5	7352 (8)	8738 (12)	1398 (22)
C6	7506 (9)	8349 (10)	2222 (19)
C7	8080 (8)	8224 (7)	2506 (14)
C8	8495 (8)	8519 (8)	1835 (15)
C9	8361 (9)	8905 (8)	1020 (15)
C1S	−484 (38)	810 (45)	904 (79)
O1S	35 (29)	998 (29)	1573 (58)
C2SA	227 (44)	551 (46)	1977 (75)
C3SA	294 (42)	124 (44)	1673 (80)
C2SB	57 (31)	585 (34)	1056 (61)
C3SB	696 (45)	411 (43)	1695 (72)
C2S	914 (44)	70 (43)	1463 (66)
C4S	1496 (48)	−58 (41)	1503 (85)
C6S	1656 (43)	−293 (40)	440 (89)

Table III. Fractional Atomic Coordinates ($\times 10^4$) for **4**

atom	*x/a*	*y/b*	*z/c*
I	7469 (1)	6610 (1)	4837.0 (4)
Cu	7236 (4)	4462 (1)	4508 (1)
N1	6485 (17)	4111 (7)	3278 (4)
C2	4578 (22)	3314 (9)	2938 (6)
N3	4511 (19)	3267 (7)	2088 (5)
C4	7087 (23)	4470 (10)	1078 (6)
C5	9074 (27)	5385 (10)	1083 (7)
C6	10298 (24)	5893 (10)	1834 (7)
C7	9646 (23)	5535 (9)	2605 (6)
C8	7616 (20)	4627 (8)	2614 (5)
C9	6442 (20)	4123 (8)	1857 (6)

For complexes **3**, **4**, and **6** the absorption correction was made by following ref 18. The function minimized during the full-matrix least-squares refinement was $\sum w(\Delta F)\hat{E}^2$. Unit weights were applied for **4–6** since these gave acceptable agreement analyses. For **3** a weighting scheme based on counting statistics[14] was applied. Anomalous scattering corrections were included in all structure factor calculations.[19b] Scattering factors for neutral atoms were taken from ref 19a for non-hydrogen atoms and from ref 20 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary.

The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was first isotropic and then anisotropic for non-H atoms, except for the atoms of THF solvent molecule in complex **5** and of diglyme solvent molecule in complex **3**. In complex **5** the solvent molecule lying on a 2-fold axis is affected by high thermal motion (or disorder). In complex **3** the solvent diglyme molecule is very poorly defined, being affected by disorder probably around the center of symmetry. The best fit was found by refining nine residual peaks from a ΔF map with site occupancy factors of 0.375 [from the copper/diglyme stoichiometric molar ratio (4/3)]. No other peak was relevant enough to be considered in refinement. Solution and refinement were based on the observed reflections. All the hydrogen atoms except those associated with the disordered solvent molecules (complexes **3** and **5**) were located in difference maps and introduced in the subsequent refinement as fixed contributors ($U_{iso} = 0.08$ Å^2). The final difference maps showed no unusual features, with no significant peak above the general background. Final atomic coordinates for non-hydrogen atoms are listed in Tables II–VI.

Results and Discussion

Although the reaction conditions affect significantly the solid-state structure of the compounds forming from the reaction of CuI with benzimidazole, it would be difficult to rationalize the causes.

Table IV. Fractional Atomic Coordinates ($\times 10^4$) for **5**

atom	*x/a*	*y/b*	*z/c*
I	0	1275 (1)	2500
Cu	0	66 (1)	2500
N1	−214 (6)	−425 (3)	1508 (4)
C2	465 (8)	−896 (4)	1271 (5)
N3	153 (7)	−1090 (3)	516 (4)
C4	−1541 (10)	−673 (5)	−427 (5)
C5	−2483 (11)	−248 (6)	−460 (7)
C6	−2718 (10)	162 (6)	175 (8)
C7	−2023 (10)	157 (5)	877 (6)
C8	−1055 (9)	−299 (4)	912 (5)
C9	−853 (9)	−708 (5)	281 (6)
C1	1479 (8)	−1204 (5)	1743 (5)
C11	2308 (10)	−815 (5)	2178 (6)
C12	3183 (11)	−1099 (6)	2682 (7)
C13	3298 (11)	−1746 (7)	2728 (7)
C14	2458 (13)	−2144 (6)	2310 (7)
C15	1547 (10)	−1859 (5)	1801 (6)
C16	816 (9)	−1522 (5)	4 (6)
C17	276 (8)	−2184 (5)	−48 (5)
C18	−749 (10)	−2391 (5)	338 (6)
C19	−1159 (10)	−3020 (6)	264 (7)
C20	−558 (11)	−3449 (5)	−190 (7)
C21	460 (12)	−3247 (5)	−583 (7)
C22	883 (9)	−2630 (5)	−506 (6)
O1S	5000	1623 (20)	2500
C2S	4201 (24)	1118 (13)	2970 (16)
C3S	4412 (26)	560 (14)	2348 (20)

Table V. Fractional Atomic Coordinates ($\times 10^4$) for **6**

atom	*x/a*	*y/b*	*z/c*
I	3032 (1)	365 (1)	2905 (1)
Cu	4962 (1)	1083 (1)	5668 (1)
N1	5061 (6)	2831 (4)	6524 (6)
C2	4223 (8)	3519 (5)	7180 (8)
N3	4701 (7)	4727 (5)	7478 (7)
C4	6804 (9)	5841 (6)	6905 (9)
C5	7952 (10)	5598 (7)	6283 (10)
C6	8215 (10)	4404 (8)	5734 (10)
C7	7314 (9)	3415 (7)	5763 (9)
C8	6157 (8)	3639 (6)	6373 (8)
C9	5923 (8)	4830 (6)	6961 (8)
C10	2930 (8)	3078 (6)	7567 (8)
C11	2508 (9)	3714 (7)	8759 (9)
C12	1286 (11)	3247 (10)	9121 (10)
C13	497 (10)	2206 (9)	8306 (12)
C14	892 (10)	1578 (7)	7123 (12)
C15	2088 (9)	2012 (7)	6738 (10)
O1	6476 (7)	3187 (5)	1141 (7)
C16	5754 (12)	2019 (9)	960 (15)
C17	6941 (13)	1143 (9)	1591 (13)
C18	8402 (13)	1781 (11)	1745 (16)
C19	7961 (12)	2972 (10)	1133 (16)

Table VI. Bond Distances (Å) in the Benzimidazole Fragment

	3	**4**	**5**	**6**
N1–C2	1.31 (2)	1.33 (1)	1.30 (1)	1.316 (9)
N1–C8	1.40 (2)	1.38 (1)	1.37 (1)	1.404 (9)
N3–C2	1.30 (3)	1.37 (1)	1.38 (1)	1.363 (8)
N3–C9	1.35 (3)	1.41 (1)	1.40 (1)	1.379 (9)
C4–C5	1.41 (3)	1.40 (2)	1.35 (2)	1.38 (1)
C4–C9	1.35 (3)	1.39 (1)	1.40 (1)	1.40 (1)
C5–C6	1.37 (3)	1.40 (2)	1.41 (2)	1.39 (1)
C6–C7	1.38 (3)	1.38 (2)	1.39 (2)	1.38 (1)
C7–C8	1.41 (3)	1.40 (1)	1.41 (1)	1.38 (1)
C8–C9	1.35 (3)	1.40 (1)	1.40 (1)	1.39 (1)

Reactions in Scheme I have been carried out with a constant 1/2 Cu/L molar ratio. The solvent was the only variable of the reaction able to affect the structure of the final compound. The metal adjusts its stoichiometry independently of the starting Cu/L ratio. In fact, in the carbonylation reaction the monocarbonyl **2** has a 1/3 Cu/L molar ratio. We can only suggest that the structure of the compound may, indirectly, depend on the nature

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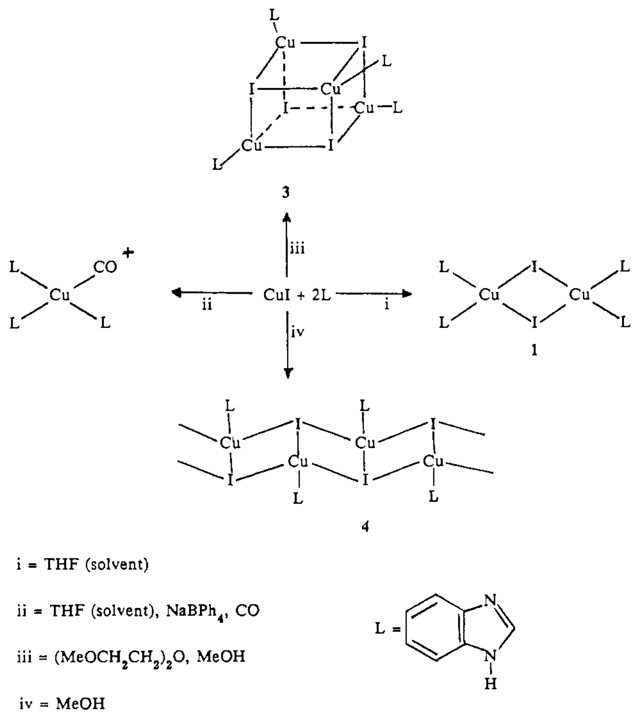
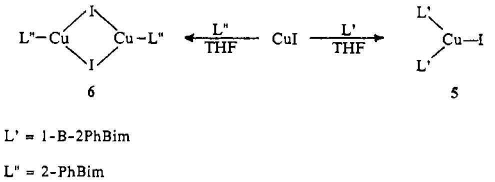
Scheme I



Scheme II



of the solvated monomeric precursor existing in the different solutions and acting as building block of the final polynuclear structure. Maintaining the same Cu/L molar ratio and carrying the reaction in THF, which seems to favor the formation of low nuclearity species, where the steric effect can be more important in terms of structural changes, we used two substituted benzimidazoles L′ and L″ (Scheme II).

The bulky ligands affect mainly the coordination number of copper(I) decreasing from 4 to 3, as expected, in complexes **5** and **6** vs complexes **1–4**. It has to be pointed out that benzimidazole acts as a Lewis base by using the nitrogen in position 3. The structural parameters of the benzimidazole fragment are very close for all the structures (**3–6**) reported (Table VI). The structure assignment for complexes **1** and **2** is mainly based on the stoichiometry and on the analogy with the structures for other CuI adducts with nitrogen-containing Lewis bases, like quinoline and substituted pyridines.[1,5] A detailed description of the structures is reported below.

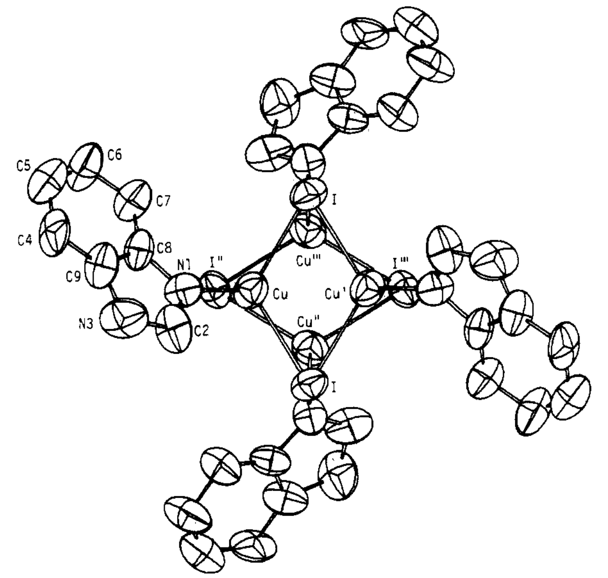


Figure 1. ORTEP drawing showing the 4 symmetry for complex **3** (55% probability ellipsoids).

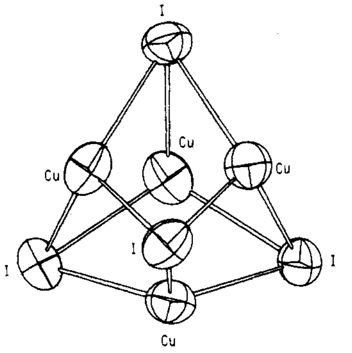


Figure 2. Complex **3**: a view of the Cu_4I_4 structure.

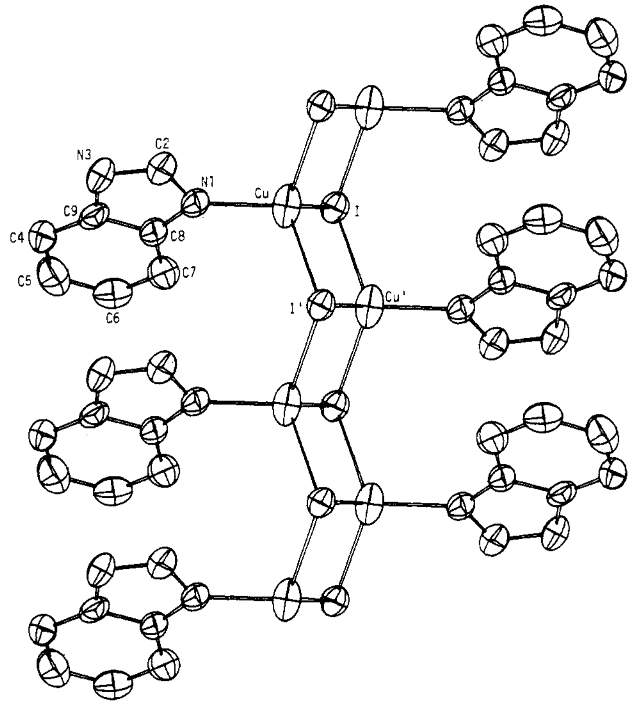


Figure 3. ORTEP drawing for complex **4** (55% probability ellipsoids).

Complex **3** consists of tetrametallic units and disordered diglyme solvent molecules in a copper/diglyme molar ratio of 4/3, separated by van der Waals contacts. The tetramers have crystallographically imposed $\bar{4}$ symmetry and a cubane-like arrangement of the Cu_4I_4 core. Figure 1 shows the labeling scheme for atoms in the molecule, and Figure 2 provides a view of the Cu_4I_4 core. Each copper exhibits a tetrahedral coordination, being linked to three μ_3-iodide ions and a terminal Bim ligand. The structural parameters are very close to those of related compounds.[1a,6a] Table VII lists bond distances and angles in the copper(I) coordination sphere for all complexes. The geometry of the Cu_4I_4 core is almost symmetric having the following separations: Cu–I, 2.688 (3)–2.720 (2) Å, Cu···Cu, 2.740 (3)–2.757 (3) Å, I···I = 4.480 (2)–4.485 (2) Å. The repulsion between the iodine atoms causes, as usually,[21] a narrowing of the Cu-I-Cu angles [60.9 (1)–61.3 (1)°] and an enlargement of the I–Cu–I angles [111.9 (1)–112.9 (1)°] with respect to the cubic angle. Copper is 0.093 (2) Å out of the plane through the benzimidazole ligand, which is planar within experimental error. All the other intramolecular bond distances and angles appear to be normal in spite of the rather

Table VII. Interatomic Distances (Å) and Angles (deg) in the Copper(I) Coordination Sphere

	3	4	5	6
Cu–I	2.720 (2)	2.631 (2)	2.512 (3)	2.598 (2)
Cu–I′	2.689 (2)	2.738 (2)		2.554 (2)
Cu–I″	2.688 (3)	2.722 (2)		
Cu–N1	2.03 (1)	2.011 (7)	1.986 (7)	1.969 (5)
Cu–Cu′	2.757 (3)	2.958 (2)		2.546 (3)
Cu–Cu″	2.740 (3)	2.989 (2)		
Cu–Cu‴	2.740 (3)			
I–I′	4.485 (2)	4.482 (2)		4.479 (2)
I–I″	4.480 (2)	4.441 (2)		
I–Cu–I′	112.0 (1)	113.2 (1)		120.8 (1)
I–Cu–I″	111.9 (1)	112.1 (1)		
I′–Cu–I″	112.9 (1)	105.2 (1)		
I–Cu–N1	106.3 (4)	113.6 (2)	120.9 (2)	118.9 (2)
I′–Cu–N1	105.6 (4)	104.4 (2)	118.2 (3)[a]	119.7 (2)
I″–Cu–N1	107.6 (4)	107.6 (2)		
Cu–I–Cu′	61.3 (1)	66.8 (1)		59.2 (1)
Cu′–I–Cu″	60.9 (1)[b]	105.2 (1)		
Cu–I–Cu″	61.3 (1)[b]	67.9 (1)		
symm operation				
single prime	$2 - x, {}^3/_2 - y, z$	$1 - x, 1 - y, 1 - z$	$-x, y, {}^1/_2 - z$	$1 - x, -y, 1 - z$
double prime	${}^1/_4 + y, {}^7/_4 - x, {}^3/_4 - z$	$2 - x, 1 - y, 1 - z$		
triple prime	${}^7/_4 - y, x - {}^1/_4, {}^3/_4 - z$			

[a] This value refers to the angle N1–Cu–N1′. [b] These values refer to Cu′–I′–Cu″ and Cu–I′–Cu″, respectively.

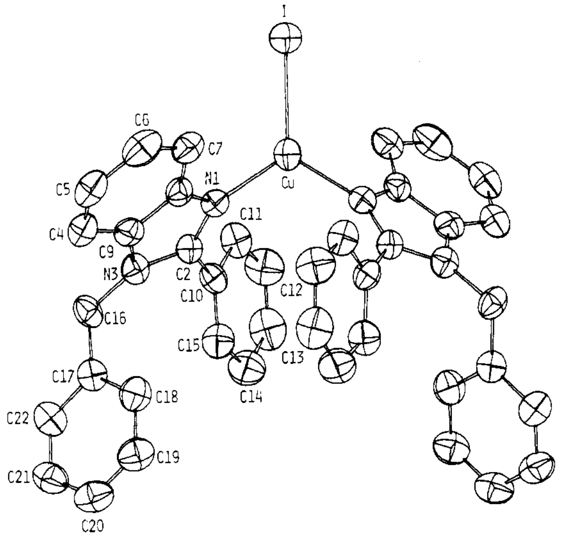


Figure 4. ORTEP drawing for complex **5** (40% probability ellipsoids).

low accuracy caused by the disorder affecting the diglyme solvent molecule.

The structure of **4** consists of an infinite "stair" polymer generated from the CuI(Bim) asymmetric unit by the center of symmetry (Figure 3). The polymer is formed by successive CuI steps in a zigzag ladder running parallel to *a*. Each Cu,I,Cu,I succession is strictly planar for symmetry requirements. The two planes intersecting at the Cu–I line form a dihedral angle of 61.2 (1)°. The copper coordination is tetrahedral, and the geometry of the stair is close to those observed for CuXL "ribbon structures"[21] with a significant asymmetry in the Cu–I distances ranging from 2.631 (2) to 2.738 (2) Å.

The crystal structure of complex **5** is shown in Figure 4, with corresponding parameters in Table VII. The copper and iodine atoms lie on special positions, the Cu–I unit being disposed on a crystallographic 2-fold axis, with the copper atom coordinated by a pair of 1-B-2-PhBim ligands. The copper atom is thus three-coordinate and together with its coordination environment is constrained by symmetry considerations to be coplanar. The Cu–N distance compares very well with those already observed,[1] as well as the Cu–I distance, which is shorter than those observed in complex **6**, where iodine exhibits a bridging coordination mode. The N–Cu–N angle [118.2 (3)°] is very close to the value expected for a trigonally coordinated system. Other bond distances and angles are normal. The complex molecules and the THF solvent molecules are separated by normal van der Waals contacts.

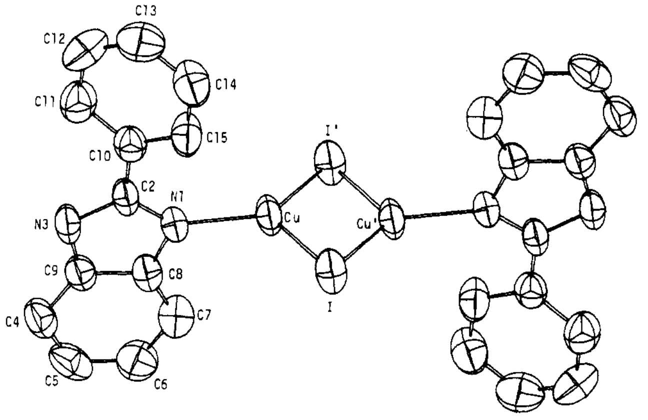


Figure 5. ORTEP drawing for complex **6** (55% probability ellipsoids).

Complex **6** is binuclear (Figure 5). The metal–halogen moiety lies close to a crystallographic inversion center, so that only one metal–iodide–base unit is crystallographically independent, the dimer being centrosymmetric. In consequence, the Cu_2I_2 group is required to be rigorously planar, while the two ligand planes must be parallel to each other. The dihedral angle between the Cu_2I_2 core and the plane through benzimidazole is 79.6 (1)°. The phenyl ring is rotated by 26.6 (2)° with respect to the last plane. Each copper atom is coordinated to two bridging iodine atoms and a terminal 2-PhBim ligand. The resulting trigonal coordination is slightly distorted, copper being 0.105 (2) Å from the plane through the coordinating atoms. The introduction of the phenyl substituent in the ligand is primarily responsible for the inability of the complex to form a pseudo-cubane or stair polymer structure, and it affects the symmetry of the complex molecule, the Cu–I bond distances being slightly but significantly different (Table VII). The geometry of the Cu_2I_2 core is close to that observed for other derivatives[1e,1g,5] with a copper–copper separation [2.546 (3) Å] in agreement with that in copper metal [2.56 Å].[22] The

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packing is mainly determined by N-H···O hydrogen bonds involving the N-H group from the base and the oxygen atom from THF [N3···O1′, 2.866 (9) Å; N3-H9···O1′, 175 (prime indicates $1 - x$, $1 - y$, $1 - z$)].

A few structural conclusions can be drawn from the structural data reported above which are in agreement with those from the literature:[1] moving from tricoordinate copper(I) (complexes **5** and **6**) to tetracoordinate copper(I) (complexes **3** and **4**) the Cu-I and, by a lesser extent, Cu-N bond lengths increase as a consequence of the increasing coordination number, independently of the structural form (Table VII). The Cu···Cu separation seems to be strictly related to the structural form, the lower value being observed for the tricoordinate dimer, **6**. In addition moving from the $(CuIL)_2$ dimer (**6**) to the $CuIL_2$ monomer (**5**) a significant decrease in the Cu-I distances is observed, as expected. There is no significant difference in the Cu-N distances for **5** and **6**. The range of the I···I separations is rather narrow (Table VII).

Supplementary Material Available: Listings of hydrogen coordinates (Tables SI-SIV), thermal parameters (Tables SV-SVIII), and bond distances (Table SIX) (6 pages); listings of observed and calculated structure factor amplitudes (36 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Florence, Florence, I-50144 Italy, and University of Siena, Siena, Italy, ISSECC (CNR), Florence, Italy, and Facultad de Ciencias Quimicas, University of Valencia, Valencia, Spain

Anion Coordination Chemistry. 2.[1] Electrochemical, Thermodynamic, and Structural Studies on Supercomplex Formation between Large Polyammonium Cycloalkanes and the Two Complex Anions Hexacyanoferrate(II) and Hexacyanocobaltate(III)

Andrea Bencini,[2a] Antonio Bianchi,[2b] Enrique Garcia-España,[2c] Mauro Giusti,[2a] Stefano Mangani,[2d] Mauro Micheloni,*[2a] Pierluigi Orioli,[2a] and Piero Paoletti*[2a]

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The stability constants of 1:1 "supercomplexes" formed between the three large, variously protonated, polyazacycloalkanes 1,4,7,10,13,16,19,22,25-nonaazacycloheptacosane (L1), 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane (L2), and 1,4,7,10,13,16,19,22,25,28,31-undecaazacyclotritriacontane (L3) and the anions $[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$ have been determined by potentiometry at 25 °C in 0.15 $NaClO_4$. Many species are formed, and the anion $[Fe(CN)_6]^{4-}$ forms "supercomplexes" that are more stable than the corresponding species involving the less charged anion $[Co(CN)_6]^{3-}$. In the case of "supercomplexes" involving $[Fe(CN)_6]^{4-}$, the CV technique was applied to confirm potentiometric studies. Results are discussed assuming that Coulombic forces are the most important factor which governs the formation of these "supercomplexes". The molecular structure of the "supercomplex" $[H_8L2][Co(CN)_6]_2Cl_2 \cdot 10H_2O$ has been determined by single-crystal X-ray analysis. The compound crystallizes in the $P\bar{1}$ space group with a = 14.818 (3) Å, b = 10.414 (2) Å, c = 8.974 (2) Å, α = 78.68(1)°, β = 85.99 (1)°, γ = 89.67 (2)°, and Z = 1. Refinement of the atomic parameters by least squares gave a final R factor of 0.075 (R_w = 0.074) for 3178 unique reflections having $I > 3\sigma(I)$. The structure consists of discrete $(H_8L2)^{8+}$ cations, $[Co(CN)_6]^{3-}$ anions outside the macrocyclic cavity, chloride anions, and water molecules. The macrocycle displays an elongated elliptical shape, and its conformation appears essentially imposed by the strong Coulombic repulsions between the positively charged nitrogen atoms, which form two stiff parallel chains. There are two unprotonated nitrogen atoms on opposite sides of the cycle. Several hydrogen bonds are formed between the cyanide groups of one of the hexacyanocobaltate(III) anions and the macrocyclic nitrogen atoms. The hydrogen-bonding scheme is completed by several other bonds involving chloride anions and water molecules.

Introduction

Anion coordination chemistry is a rapidly growing research field.[3-5] This type of investigation has been shown important in many biological processes and synthetic chemistry.[6,7] Since most anions exist only in a limited pH range, the cationic counterparts should exist in the same interval. It has been assumed that polyazamacrocycles are especially suitable for selective binding of inorganic and organic anions, and some evidences have been reported in the last few years.[1,8,9] The cyclic molecular topology and the ability to bind many hydrogen ions enable large polyazacycloalkanes to concentrate positive charge in their polyprotonated form and strongly interact with anionic species. When the anionic species are metal complexes like $[M^{n+}(CN)_6]^{(6-n)-}$ (M = Fe(II), Fe(III), Co(III), Ru(III), etc.) the expression "supercomplexes" has been used[10,11] to describe the second-sphere coordination between the above anions and polyammonium macrocyclic receptors.

In the present work we wish to elucidate the influence of the size of the macrocyclic cavity as well as of the electrostatic charges on the complexation reactions between the series of large polyazacycloalkanes 1,4,7,10,13,16,19,22,25-nonaazacycloheptacosane ([27]aneN_9), 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane ([30]aneN_{10}), and 1,4,7,10,13,16,19,22,25,28,31-undecaazacy-

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