The geometry of the *dimethyl sulfide group*, bonded to B5, is entirely normal. The bond lengths B–S = 1.89 (1) Å and S–C(mean) = 1.79 (1) Å and the angle C–S–C = 101.3 (3)° are within three standard deviations of the values of 1.92 (1) Å, 1.82 Å, and 102.4 (14)° found in $B_{10}H_{12}[S(CH_3)_2]_2$.[17] The unusual feature of the dimethyl sulfide group is of course that, while it was originally attached to B6, it has "migrated" to B5 during the course of the reaction. In view of the arguments discussed in the previous paper it is likely that this "migration" occurs after the hydroboration has taken place (Scheme I, ref 4). It is clearly accompanied by a complicated rearrangement of the hydrogen atoms in the boron cage. The starting substance bis(dimethyl sulfide)-*arachno*-decaborane(12) has terminal hydrogens on each boron atom and two hydrogen bridges, viz., across B5–B10 and B7–B8.[17] One of a number of possible pathways from this starting molecule to the end product is the following: the dimethyl sulfide group at B9 leaves, and the hydrogen atoms in the bridges B7–B8 and B5–B10 move to form bridges across B8–B9 and B9–B10, thus generating the same configuration that undergoes hydroboration in $6\text{-}SB_9H_{11}$.[16] The hydroboration takes place with the cyclohexyl group attaching to B9, and a reactive intermediate now exists which has a dimethyl sulfide attached to B6. When a dimethyl sulfide molecule in the solution approaches this intermediate toward B5 (or B7), the $(CH_3)_2S$ at B6 leaves, the terminal hydrogen atom of B5 moves to B6, the hydrogen atom on B6 forms the B6–B7 bridge, and the approaching $(CH_3)_2S$ attaches at B5. It would require extended Hückel calculations of several possible intermediate molecular configurations to decide which particular pathway is the most likely one on a theoretical basis.

It is worth noting that the individual molecules in the structure presented here have a molecular asymmetry; i.e., they can occur in a Δ or in a Λ configuration.[18] In this structure the unit cell contains four Δ and four Λ molecules. It is difficult to explain why the structure prefers that arrangement to one which would contain all Δ or all Λ molecules, since this depends on intermolecular interactions in the two possible cases. A survey of hydrogen–hydrogen contacts in the present structure reveals one very short distance of 2.18 Å between H3 of one molecule and H23 of its neighbor. There are no further short contacts less than 2.45 Å, and there are fourteen neighboring H–H contacts between 2.45 and 2.67 Å.

Registry No. 9-Cyclohexyl-5(7)-(dimethyl sulfide)-*nido*-decacarborane(11), 72765-44-7.

Supplementary Material Available: Tables of the observed and calculated structure factors and of the B–B–B angles in the boron framework (13 pages). Ordering information is given on any current masthead page.

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Copper–Amine–Carbonyl Chemistry. Solution and Solid-State Studies of the Copper(I)–Ethylenediamine–Carbon Monoxide System: Synthesis and X-ray Structures of Mononuclear and Binuclear Copper(I)–Carbonyl Complexes

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Copper(I) iodide in methanol absorbs carbon monoxide at room temperature and atmospheric pressure in the presence of ethylenediamine, en, giving colorless solutions. Depending on the Cu^I/en molar ratio and the anion present, the following thermally stable copper(I) carbonyls have been isolated as white crystals: $[Cu(en)_2(CO)]I$ (I) [ν_{CO}(Nujol) 2060 cm^{-1}]; $[Cu_2(en)_3(CO)_2]I_2$ (II) [ν_{CO}(Nujol) 2062 cm^{-1}]; $[Cu_2(en)_3(CO)_2](PPh_4)_2$ (III) [ν_{CO}(Nujol) 2078 cm^{-1}]. The structure of III consists of discrete dimeric cations $[Cu_2(en)_3(CO)_2]^{2+}$ and BPh_4^- anions. The two centrosymmetric copper atoms are surrounded in a pseudotetrahedral geometry by a set of three nitrogen atoms, provided by one chelating and one bridging en, and a carbon monoxide molecule. The bond distances associated with the Cu–C–O units are Cu–C = 1.73 (1) and 1.75 (1) Å and C–O = 1.17 (2) and 1.16 (2) Å. The addition of $NaBPh_4$ to a methanolic solution of Cu(en)COCl (IV) gives at −20 °C white crystals of $[Cu(en)(CO)PhBPh_3]$ (V) [ν_{CO}(Nujol) 2117 cm^{-1}]. The ion-pair nature of V was established by an X-ray analysis. Copper(I) interacts with both a carbon monoxide molecule and one of the C=C bonds of the BPh_4^- anion, in a pseudo-trigonal-pyramidal geometry completed by an ethylenediamine molecule. The Cu–C and C–O bond distances are 1.806 (6) and 1.110 (7) Å, respectively. Crystallographic details for III are as follows: space group $P2_1/n$ (monoclinic), a = 13.769 (2) Å, b = 19.184 (3) Å, c = 9.833 (2) Å, β = 90.99 (2)°, V = 2596.9 Å^3, Z = 2. The final R factor was 4.7% for 3088 observed reflections. Crystallographic details for V are as follows: space group $P2_1/c$ (monoclinic), a = 10.301 (1) Å, b = 12.234 (1) Å, c = 18.390 (2) Å, β = 91.11 (1)°, V = 2317.1 Å^3, Z = 4. The final R factor was 4.9% for 3150 observed reflections.

Introduction

The chemistry of the copper(I)–nitrogen ligand complexes is practically restricted to the compounds containing copper(I) coordinated to unsaturated nitrogen ligands.[1] The stabilization of the (+1) oxidation state for copper should be ascribed to the nature of these nitrogens, while the amino groups stabilize the (+2) oxidation state and promote facile disproportionation of Cu(I).[2] Besides this, the extreme lability of these complexes is the reason for the paucity of structural, reactivity, and mechanistic information on copper(I)–nitrogen ligand chemistry. It must be noticed, however, that, when the (+1) oxidation state is stabilized by unsaturated nitrogen ligands, the metal center is not further available for coordinating π-acid

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molecules. The utilization of suitable saturated nitrogen ligands is much more promising in building up copper(I) compounds active in molecular activation. For the achievement of this result, the synthesis of such complexes must be carried out in the presence of both a reducing agent, i.e., I^-, and the molecule to be activated, i.e., carbon monoxide.

This paper concerns the results obtained in using ethylenediamine as a symbiotic ligand with CO in producing copper(I)–carbonyl complexes. The CuCl/en/CO system was explored a few years ago, and two unstable and elusive carbonyl complexes were described.[3] The isolation of very stable carbonyl complexes, along with their structure in the solid state, and the solid state–solution relationship will be discussed in this paper. A short account of this work was communicated.[4]

Experimental Section

Reactions were carried out under an atmosphere of purified nitrogen. Methanol and ethylenediamine were dried and distilled before use. Infrared spectra were recorded with a Perkin-Elmer 282 spectrophotometer. The CO evolution was gas volumetrically measured.

Synthesis of $[Cu_2(en)_3(CO)_2]I_2$. CuI (3 g, 15.76 mmol) suspended in methanol (80 mL) containing en (2 mL, 29.9 mmol) absorbs carbon monoxide. A practically colorless solution is obtained after 30 min (ν_{CO} 2060 cm^{-1}). This solution on standing gives $[Cu_2(en)_3(CO)_2]I_2$ as a white crystalline solid (ca. 55%), which was dried in vacuo. Anal. Calcd for $[Cu_2(en)_3(CO)_2]I_2$ ($C_8H_{24}N_6O_2Cu_2I_2$): C, 15.56; H, 3.89; N, 13.61; I, 41.14. Found: C, 15.30; H, 3.91; N, 13.44; I, 40.88. The solid is very sensitive to moisture and oxygen [ν_{CO}(Nujol) 2062 cm^{-1}]. Likewise absorption of carbon monoxide occurs starting from CuCl instead of CuI, but it is reversible.

Synthesis of $[Cu(en)(CO)BPh_4]$. A suspension of CuCl (1.04 g, 10.5 mmol) in methanol (30 mL) cooled at −30 °C is exposed to an atmosphere of carbon monoxide. When the absorption stops, the so-called "CuCOCl"[5] is present as a crystalline white solid. Then a methanolic (20 mL) solution of en (0.7 mL, 10.5 mmol) is added dropwise to the suspension cooled at −20 °C.

The addition of en gives a colorless solution (ν_{CO} 2080 cm^{-1}). When $NaBPh_4$ (3.6 g, 10.5 mmol) dissolved in 20 mL of CH_3OH is added at −20 °C, a white crystalline solid is obtained (ca. 25%). It was dried with a stream of CO. Anal. Calcd for $[Cu(en)(CO)BPh_4]$ ($C_{27}H_{28}N_2OBCu$): C, 68.86; H, 5.95; N, 5.95. Found: C, 68.6; H, 5.63; N, 6.08. $[Cu(en)(CO)BPh_4]$ does not lose CO in the solid state. Reacted with $P(OEt)_3$ in methanol, it gives 0.94 mol of Co/mol of Cu [ν_{CO}(Nujol) 2117 cm^{-1}, s].

Synthesis of $[Cu_2(en)_3(CO)_2](BPh_4)_2$. CuI (1.0 g, 5.25 mmol), suspended in a methanolic (30 mL) solution of en (1.4 mL, 20.95 mmol), absorbs carbon monoxide at room temperature and atmospheric pressure for 30 min, giving a colorless or slightly green solution [$\nu_{CO}(CH_3OH)$ 2060 cm^{-1}] with a small amount of $[Cu_2(en)_3(CO)_2]I_2$. By addition of a methanolic solution (30 mL) of $NaBPh_4$ (1.8 g, 5.26 mmol), $[Cu_2(en)_3(CO)_2](BPh_4)_2$ is obtained as a white crystalline solid (ca. 40%). Dried in vacuo it does not lose CO [ν_{CO}(Nujol) 2078 cm^{-1}]. The solid, which is quite sensitive to moisture, has a high thermal stability, and it starts to decompose only when heated up to 80 °C. It reacts with a methanolic solution of $P(OEt)_3$ giving 0.96 mol of Co/mol of Cu. Anal. Calcd for $[Cu_2(en)_3(CO)_2](BPh_4)_2$ ($C_{56}H_{64}N_6O_2B_2Cu_2$): C, 67.13; H, 6.39; N, 8.89. Found: C, 67.57; H, 6.43; N, 8.34.

Synthesis of $[Cu(en)_2(CO)]I$. CuI (2.0 g, 10.5 mmol) reacts with a highly concentrated solution of en (15 mL) in methanol (15 mL) giving a white solid, which dissolves in a carbon monoxide atmosphere. This solution, which in vacuo loses CO, gives, by addition of diethyl ether (20 mL) and cooling at −70 °C, a light blue solid (ca. 52.3%). [ν_{CO}(Nujol) 2060 cm^{-1}]. Anal. Calcd for $[Cu(en)_2CO]I$ ($C_5H_{16}N_4OICu$): C, 17.73; H, 4.73; N, 16.55. Found: C, 18.04; H, 5.00; N, 16.17. The complex is quite sensitive to air.

Collection and Reduction of X-ray Intensity Data for $[Cu_2(en)_3(CO)_2](BPh_4)_2$. A prismatic crystal sealed in a thin-walled glass capillary under inert atmosphere was used for structural analysis. Cell dimensions were determined from rotation and Weissenberg photographs and refined from diffractometer measurements of 35 high-angle reflections. Crystal data are collected in Table I. Intensities were measured with a Siemens AED computer-controlled diffractometer using niobium-filtered Mo Kα radiation (λ = 0.7107 Å, takeoff angle 4°). The moving-counter–moving-crystal scan technique with a drive speed related to the number of counts on the peak (lowest speed 2.5°/min) was employed to collect 6911 reflections. No significant change in intensity was noted for a reflection periodically monitored during data collection. For intensities and background the "five-points technique"[6] was used.

Table I. Crystal Data for $[Cu_2(en)_3(CO)_2](BPh_4)_2$ and $[Cu(en)(CO)BPh_4]$

compd	$[Cu_2(en)_3(CO)_2](BPh_4)_2$	$[Cu(en)(CO)BPh_4]$
formula	$C_{56}H_{64}B_2Cu_2N_6O_2$	$C_{27}H_{28}BCuN_2O$
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, Å	13.769 (2)	10.301 (1)
b, Å	19.184 (3)	12.234 (1)
c, Å	9.833 (2)	18.390 (2)
β, deg	90.99 (2)	91.11 (1)
vol, $Å^3$	2596.9	2317.1
fw	1001.9	470.9
Z	2	4
ρ(calcd), g/cm^3	1.281	1.350
cryst size, mm^3	0.35 × 0.40 × 0.48	0.42 × 0.35 × 0.34
μ, cm^{-1}	8.65	14.48
radiation	Mo Kα	Cu Kα
2θ range, deg	5–58	6–140
no. of unique reflctns	3088 with $I > 2\sigma(I)$	3150 with $I > 2\sigma(I)$

The structure amplitudes were obtained after the usual Lorentz and polarization reduction. No correction for absorption was applied in view of the low absorbance of the sample ($\mu\bar{r}$ ca. 0.2).

Structure Solution and Refinement for $[Cu_2(en)_3(CO)_2](BPh_4)_2$. The coordinates of the copper atom were deduced from a three-dimensional Patterson map. A Fourier synthesis calculated with the contribution of the metal atom revealed the positions of all nonhydrogen atoms.

Two cycles of isotropic full-matrix least squares reduced the R value to 12%. After two further anisotropic least-squares cycles which brought R to 7.1%, abnormally high values of U_{33} thermal coefficients were observed for the carbonyl group. A difference Fourier map computed at this stage revealed the presence of four peaks in the neighboring carbonyl atoms: two at 0.7 and 1.0 Å from oxygen and two at distances of 0.7 Å from carbon. The atoms of the carbonyl group were therefore considered statistically distributed over two positions which were isotropically refined together with their site occupation factors. At the end of the refinement, the population parameter was 0.55 for C and 0.45 for C* and O*.

Positional parameters of 28 of the 32 hydrogen atoms were obtained from a final difference electron density map; hydrogens bonded to N(1) and C(1) were put in their geometrical positions. The refinement was continued anisotropically for heavy atoms and isotropically for hydrogens; after three cycles of "blocked" (three blocks) full-matrix least squares, the R value converged at 4.7%. Unit weights were used in the refinement. No evidence for secondary extinction was found. No unusual features were observed in the final difference Fourier synthesis. Scattering factors were those of ref 7 for Cu, those of ref 8 for O, N, C, and B, and those of ref 9 for H. All calculations were performed on a CYBER 76 computer at the Centro di Calcolo dell'Italia Nord-Orientale (Bologna) using the program SHELX-76.[10]

The final positional and thermal parameters are listed in Tables II and III. The most relevant bond distances and angles are given in Table IV, while the bond distances and angles for BPh_4^- and the equations of the planes are reported as supplementary material in

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Table II. Atomic Fractional Coordinates for $[Cu_2(en)_3(CO)_2](BPh_4)_2$ with Standard Deviations in Parentheses

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cu	0.2262 (1)	0.0874 (1)	0.1248 (1)	C(45)	0.4202 (4)	0.5510 (3)	0.8589 (5)
N(1)	0.1618 (6)	0.1051 (4)	0.3099 (6)	C(46)	0.3869 (3)	0.4831 (2)	0.8573 (4)
N(2)	0.1904 (5)	0.1893 (3)	0.0882 (3)	H1(N1)	0.201 (4)	0.097 (3)	0.378 (5)
N(3)	0.1324 (3)	0.0288 (3)	0.0095 (5)	H2(N1)	0.109 (4)	0.082 (3)	0.311 (5)
C(1)	0.1468 (10)	0.1789 (7)	0.3218 (13)	H1(N2)	0.166 (4)	0.196 (3)	0.019 (6)
C(2)	0.1316 (8)	0.2131 (5)	0.1993 (12)	H2(N2)	0.245 (4)	0.217 (3)	0.077 (5)
C(3)	0.0312 (4)	0.0224 (4)	0.0443 (7)	H1(N3)	0.152 (3)	−0.017 (3)	0.006 (5)
O	0.4256 (7)	0.0457 (5)	0.1722 (13)	H2(N3)	0.142 (3)	0.044 (2)	−0.083 (5)
C(4)	0.3440 (9)	0.0621 (6)	0.1630 (18)	H1(C1)	0.222 (4)	0.189 (3)	0.315 (6)
O*	0.4261 (8)	0.0495 (5)	0.0682 (14)	H2(C1)	0.118 (4)	0.194 (3)	0.386 (5)
C(4*)	0.3460 (10)	0.0649 (6)	0.0874 (18)	H1(C2)	0.070 (4)	0.181 (3)	0.179 (5)
B	0.2526 (3)	0.3847 (2)	0.8086 (5)	H2(C2)	0.124 (4)	0.261 (3)	0.197 (5)
C(11)	0.3250 (3)	0.3284 (2)	0.8831 (4)	H1(C3)	0.006 (3)	0.072 (3)	0.049 (5)
C(12)	0.3600 (3)	0.3397 (2)	1.0153 (4)	H2(C3)	0.043 (3)	−0.005 (3)	0.135 (5)
C(13)	0.4172 (3)	0.2925 (2)	1.0844 (5)	H(12)	0.340 (3)	0.384 (2)	1.057 (4)
C(14)	0.4422 (3)	0.2310 (2)	1.0245 (5)	H(13)	0.441 (3)	0.303 (2)	1.182 (5)
C(15)	0.4087 (3)	0.2175 (2)	0.8963 (5)	H(14)	0.485 (3)	0.198 (2)	1.071 (4)
C(16)	0.3509 (3)	0.2648 (2)	0.8276 (5)	H(15)	0.424 (3)	0.174 (2)	0.851 (4)
C(21)	0.1477 (3)	0.3735 (2)	0.8821 (4)	H(16)	0.330 (3)	0.255 (2)	0.733 (5)
C(22)	0.1125 (3)	0.4154 (3)	0.9843 (5)	H(22)	0.145 (3)	0.455 (2)	1.015 (4)
C(23)	0.0254 (4)	0.4031 (3)	1.0477 (6)	H(23)	0.009 (3)	0.437 (2)	1.122 (5)
C(24)	−0.0291 (4)	0.3470 (4)	1.0106 (6)	H(24)	−0.092 (3)	0.345 (2)	1.055 (5)
C(25)	0.0033 (4)	0.3037 (3)	0.9123 (6)	H(25)	−0.028 (3)	0.261 (3)	0.889 (5)
C(26)	0.0903 (3)	0.3164 (3)	0.8496 (5)	H(26)	0.113 (3)	0.286 (2)	0.780 (5)
C(31)	0.2439 (3)	0.3741 (2)	0.6438 (4)	H(32)	0.104 (3)	0.403 (2)	0.624 (4)
C(32)	0.1600 (3)	0.3889 (2)	0.5702 (5)	H(33)	0.090 (3)	0.400 (2)	0.383 (5)
C(33)	0.1546 (4)	0.3876 (3)	0.4293 (5)	H(34)	0.232 (3)	0.368 (2)	0.255 (5)
C(34)	0.2339 (5)	0.3711 (3)	0.3562 (6)	H(35)	0.377 (3)	0.340 (2)	0.372 (5)
C(35)	0.3192 (4)	0.3565 (3)	0.4241 (5)	H(36)	0.383 (3)	0.347 (2)	0.612 (5)
C(36)	0.3229 (3)	0.3577 (2)	0.5643 (5)	H(42)	0.164 (3)	0.511 (2)	0.767 (4)
C(41)	0.2919 (3)	0.4650 (2)	0.8259 (4)	H(43)	0.219 (3)	0.627 (2)	0.771 (5)
C(42)	0.2318 (3)	0.5213 (2)	0.7937 (5)	H(44)	0.383 (3)	0.649 (2)	0.831 (4)
C(43)	0.2639 (4)	0.5891 (3)	0.7933 (5)	H(45)	0.492 (3)	0.559 (2)	0.878 (4)
C(44)	0.3584 (4)	0.6042 (2)	0.8263 (6)	H(46)	0.433 (3)	0.446 (2)	0.884 (4)

Table III. $[Cu_2(en)_3(CO)_2](BPh_4)_2$ Anisotropic Thermal Parameters[a] ($\times 10^4$ Å^2) and Isotropic Thermal Parameters ($\times 10^3$ Å^2)

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	atom	U
Cu	453 (3)	533 (4)	802 (5)	−63 (4)	52 (3)	−56 (3)	O	111 (4)
N(1)	1394 (55)	1074 (52)	922 (44)	−4 (38)	27 (40)	−129 (43)	C(4)	87 (4)
N(2)	758 (35)	806 (37)	1199 (55)	121 (38)	137 (37)	−91 (29)	O*	108 (5)
N(3)	575 (26)	894 (35)	899 (37)	−237 (29)	225 (24)	−131 (25)	C(4*)	69 (4)
C(1)	2431 (143)	1602 (110)	1180 (87)	−39 (83)	568 (91)	938 (104)	H1(N1)	147 (18)
C(2)	1834 (93)	722 (52)	1467 (90)	−261 (58)	177 (75)	219 (57)	H2(N1)	170 (17)
C(3)	571 (31)	979 (45)	927 (47)	−332 (37)	158 (30)	−149 (29)	H1(N2)	143 (24)
B	349 (21)	420 (23)	469 (28)	−5 (20)	27 (19)	3 (18)	H2(N2)	162 (17)
C(11)	374 (20)	413 (21)	495 (25)	18 (19)	24 (18)	−25 (16)	H1(N3)	151 (18)
C(12)	535 (24)	489 (25)	471 (26)	19 (21)	25 (20)	−7 (20)	H2(N3)	164 (17)
C(13)	573 (26)	634 (29)	483 (27)	93 (23)	−41 (22)	−26 (22)	H1(C1)	192 (21)
C(14)	542 (26)	577 (29)	743 (34)	103 (26)	−96 (24)	68 (23)	H2(C1)	130 (18)
C(15)	679 (29)	460 (26)	808 (36)	−53 (26)	−129 (26)	135 (23)	H1(C2)	196 (18)
C(16)	593 (26)	460 (24)	625 (31)	−47 (23)	−94 (23)	62 (20)	H2(C2)	119 (16)
C(21)	398 (20)	467 (23)	482 (25)	63 (19)	3 (18)	1 (17)	H1(C3)	132 (16)
C(22)	591 (25)	619 (28)	647 (30)	−30 (26)	179 (22)	7 (25)	H2(C3)	135 (16)
C(23)	718 (33)	953 (42)	750 (38)	5 (34)	298 (28)	79 (33)	H(12)	75 (15)
C(24)	604 (32)	1322 (55)	769 (40)	118 (39)	251 (30)	−144 (36)	H(13)	79 (15)
C(25)	725 (35)	1064 (47)	764 (39)	10 (35)	100 (30)	−450 (34)	H(14)	89 (15)
C(26)	616 (28)	725 (32)	582 (31)	−43 (26)	84 (24)	−205 (25)	H(15)	86 (15)
C(31)	399 (21)	391 (20)	529 (26)	25 (19)	5 (19)	−19 (16)	H(16)	71 (14)
C(32)	490 (24)	614 (27)	546 (29)	30 (22)	7 (21)	−52 (20)	H(22)	81 (15)
C(33)	737 (33)	750 (33)	555 (33)	67 (25)	−120 (26)	−125 (27)	H(23)	104 (15)
C(34)	1007 (43)	819 (38)	486 (34)	−61 (28)	41 (31)	−64 (32)	H(24)	110 (14)
C(35)	890 (39)	824 (37)	603 (35)	−93 (29)	224 (31)	110 (31)	H(25)	99 (15)
C(36)	585 (28)	666 (29)	595 (31)	−26 (24)	86 (24)	99 (24)	H(26)	74 (15)
C(41)	411 (20)	447 (22)	434 (23)	13 (24)	22 (17)	22 (18)	H(32)	90 (15)
C(42)	513 (26)	468 (25)	756 (33)	51 (23)	4 (23)	37 (20)	H(33)	98 (15)
C(43)	834 (34)	451 (25)	797 (35)	73 (27)	42 (27)	81 (28)	H(34)	95 (15)
C(44)	914 (39)	446 (29)	812 (37)	5 (25)	−45 (30)	−167 (26)	H(35)	112 (15)
C(45)	694 (31)	594 (30)	698 (33)	40 (25)	−104 (26)	−210 (25)	H(36)	72 (15)
C(46)	490 (24)	524 (26)	520 (27)	35 (21)	−57 (20)	−34 (20)	H(42)	95 (14)
							H(43)	90 (15)
							H(44)	93 (14)
							H(45)	84 (14)
							H(46)	52 (14)

[a] The anisotropic temperature factor is in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*)]$.

Table IV. Bond Distances (Å) and Angles (Deg) for $[Cu_2(en)_3(CO)_2](BPh_4)_2$

		Coordination Sphere			
Cu-N(1)	2.066 (7)	N(1)-Cu-N(2)	83.8 (3)	N(2)-Cu-C(4)	121.9 (4)
Cu-N(2)	2.046 (6)	N(1)-Cu-N(3)	107.6 (3)	N(2)-Cu-C(4*)	115.1 (5)
Cu-N(3)	2.041 (5)	N(1)-Cu-C(4)	105.7 (6)	N(3)-Cu-C(4)	123.3 (5)
Cu-C(4)	1.73 (1)	N(1)-Cu-C(4*)	130.2 (6)	N(3)-Cu-C(4*)	109.7 (5)
Cu-C(4*)	1.75 (1)	N(2)-Cu-N(3)	106.3 (3)		
		Carbonyl Ligand			
C(4)-O	1.17 (2)	Cu-C(4)-O	172 (2)		
C(4*)-O	1.16 (2)	Cu-C(4*)-O*	177 (2)		
		Ethylenediamine Ligand			
N(1)-C(1)	1.44 (2)	Cu-N(1)-C(1)	107.4 (6)	N(1)-C(1)-C(2)	114.6 (10)
N(2)-C(2)	1.45 (1)	Cu-N(2)-C(2)	107.8 (6)	C(1)-C(2)-N(2)	115.5 (9)
C(1)-C(2)	1.38 (2)				
N(3)-C(3)	1.45 (1)	Cu-N(3)-C(3)	121.2 (4)	N(3)-C(3)-C(3′)	117.4 (6)
C(3)-C(3′)	1.49 (1)				

Table V. Atomic Fractional Coordinates for $[Cu(en)(CO)BPh_4]$ with Standard Deviations in Parentheses

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cu	0.2156 (1)	0.0125 (1)	0.2191 (1)	C(45)	0.1095 (5)	0.6077 (4)	0.0827 (3)
C	0.2445 (5)	−0.0089 (4)	0.1236 (3)	C(46)	0.1506 (4)	0.5011 (4)	0.0970 (2)
O	0.2598 (4)	−0.0203 (3)	0.0645 (2)	H(1′)	0.0299 (45)	−0.0237 (38)	0.3015 (23)
N(1)	0.1037 (4)	−0.0668 (4)	0.2925 (2)	H(1″)	0.0830 (59)	−0.1616 (54)	0.2744 (33)
N(2)	0.3303 (4)	0.0608 (4)	0.3051 (2)	H(2′)	0.4170 (45)	0.0223 (38)	0.3077 (23)
C(1)	0.1863 (6)	−0.0667 (6)	0.3635 (4)	H(2″)	0.3565 (44)	0.1279 (39)	0.3066 (24)
C(2)	0.2516 (5)	0.0424 (5)	0.3706 (3)	H(3′)	0.1259 (42)	−0.0938 (36)	0.4120 (24)
B	0.2858 (4)	0.3488 (4)	0.1736 (2)	H(3″)	0.2485 (43)	−0.1449 (38)	0.3615 (23)
C(11)	0.4114 (3)	0.3129 (3)	0.1261 (2)	H(4′)	0.3075 (42)	0.0460 (36)	0.4153 (24)
C(12)	0.4643 (4)	0.3755 (3)	0.0707 (2)	H(4″)	0.1783 (43)	0.1158 (38)	0.3760 (23)
C(13)	0.5674 (4)	0.3376 (4)	0.0288 (2)	H(12)	0.4298 (41)	0.4504 (37)	0.0625 (23)
C(14)	0.6230 (4)	0.2373 (4)	0.0418 (2)	H(13)	0.6014 (41)	0.3858 (36)	−0.0072 (23)
C(15)	0.5728 (4)	0.1728 (4)	0.0962 (2)	H(14)	0.7015 (42)	0.2116 (36)	0.0120 (23)
C(16)	0.4689 (4)	0.2102 (3)	0.1364 (2)	H(15)	0.6009 (40)	0.0984 (37)	0.1022 (22)
C(21)	0.1689 (3)	0.2614 (3)	0.1517 (2)	H(16)	0.4339 (40)	0.1605 (36)	0.1723 (23)
C(22)	0.1389 (4)	0.2414 (3)	0.0778 (2)	H(22)	0.1939 (42)	0.2804 (36)	0.0381 (23)
C(23)	0.0334 (4)	0.1775 (4)	0.0556 (3)	H(23)	0.0211 (43)	0.1625 (35)	0.0038 (25)
C(24)	−0.0447 (4)	0.1272 (4)	0.1056 (3)	H(24)	−0.1132 (42)	0.0717 (36)	0.0882 (23)
C(25)	−0.0142 (4)	0.1397 (4)	0.1783 (3)	H(25)	−0.0497 (42)	0.0995 (36)	0.2108 (23)
C(26)	0.0903 (4)	0.2053 (3)	0.2013 (3)	H(26)	0.1023 (40)	0.2145 (36)	0.2557 (23)
C(31)	0.3183 (4)	0.3461 (3)	0.2615 (2)	H(32)	0.1320 (42)	0.3993 (36)	0.2979 (22)
C(32)	0.2225 (4)	0.3717 (4)	0.3122 (2)	H(33)	0.1715 (41)	0.3957 (35)	0.4196 (23)
C(33)	0.2452 (4)	0.3701 (4)	0.3870 (2)	H(34)	0.3838 (41)	0.3415 (36)	0.4666 (24)
C(34)	0.3662 (5)	0.3434 (4)	0.4149 (2)	H(35)	0.5570 (42)	0.2994 (36)	0.3857 (23)
C(35)	0.4645 (4)	0.3208 (4)	0.3671 (2)	H(36)	0.5108 (43)	0.3085 (35)	0.2617 (23)
C(36)	0.4406 (4)	0.3232 (3)	0.2922 (2)	H(42)	0.3556 (41)	0.5479 (35)	0.2316 (23)
C(41)	0.2386 (3)	0.4747 (3)	0.1536 (2)	H(43)	0.2849 (41)	0.7399 (47)	0.2072 (23)
C(42)	0.2853 (4)	0.5653 (3)	0.1931 (2)	H(44)	0.1269 (42)	0.7651 (38)	0.1127 (23)
C(43)	0.2446 (4)	0.6722 (4)	0.1789 (3)	H(45)	0.0505 (43)	0.6189 (37)	0.0410 (24)
C(44)	0.1560 (5)	0.6932 (4)	0.1238 (3)	H(46)	0.0381 (40)	0.4461 (36)	0.0637 (23)

Tables SI and SII. Observed and calculated structure factors are available in the supplementary material.

Collection and Reduction of X-ray Intensity Data for [Cu(en)(CO)BPh$_4$]. A prismatic crystal, suitable for X-ray measurements, was sealed in a glass capillary under an inert atmosphere. Approximate cell dimensions were obtained from rotation and Weissenberg photographs and refined by least-squares analysis of the θ values of 30 reflections ($\theta > 44°$). Crystal data are listed in Table I. The data collection and reduction were as described above. Cu Kα radiation (λ 1.541 78 Å) was used. A set of 4396 independent reflections was collected, 3150 of which, with $I > 2\sigma(I)$, were used in the analysis. No correction for extinction was made.

Structure Solution and Refinement for [Cu(en)(CO)BPh$_4$]. The structure was solved by the heavy-atom method starting from the coordinates of the copper atom deduced from the Patterson distribution. A Fourier map with the contribution of this atom revealed all nonhydrogen atoms. Full-matrix least-squares refinement with isotropic thermal parameters converged at $R = 11.7\%$. Successive cycles of "blocked" (two blocks) least squares yielded R to 7.9%. A difference electron density map revealed the positions of all hydrogen atoms which were introduced in the next calculations and refined isotropically. The final R value is 4.9%. A final difference Fourier map showed no peak greater than 0.3 e/Å^3. The function minimized in the least-squares calculations was $\sum_w|\Delta F|^2$ with unit weights. No evidence for secondary extinction was found. Atomic scattering factors and computer programs were those described above.

The final positional and thermal parameters are listed in Tables V and VI. The most relevant bond distances and angles are given in Table VII, while bond distances and angles within the BPh$_4^-$ anion and the mean planes equations are available as supplementary material in Tables SIII and SIV. A list of observed and calculated structure factors is available as supplementary material.

Results

Copper iodide absorbs in methanol in the presence of an excess of ethylenediamine, en, at room temperature and atmospheric pressure of carbon monoxide. The utilization of a large excess of en over CuI (e.g., using a 1:1 en/CH$_3$OH mixture as solvent) allows the isolation of [Cu(en)$_2$(CO)]I (I) [ν_{CO}(Nujol) 2060 cm^{-1}], as a white crystalline solid. With a lower en/CuI molar ratio (in the range 2–4), a methanolic suspension of CuI absorbs one carbon monoxide per copper(I) giving a colorless solution, without noticeable disproportionation of Cu(I) to Cu(II).[2]

$$2CuI + 3en + 2CO \rightarrow \underset{II}{[Cu_2(en)_3(CO)_2]I_2} \qquad (1)$$

Under the conditions specified in the Experimental Section, the solution on standing gives II [ν_{CO}(Nujol) 2062 cm^{-1}] as

Table VI. [Cu(en)(CO)BPh$_4$] Anisotropic Thermal Parameters[a] (×10^4 Å^2) for Nonhydrogen Atoms and Isotropic Thermal Parameters (×10^3 Å^2) for Hydrogen Atoms

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	atom	U
Cu	672 (4)	729 (5)	603 (4)	8 (4)	83 (3)	−118 (4)	H(1′)	77 (14)
C	782 (32)	470 (27)	749 (32)	15 (25)	66 (26)	108 (24)	H(1″)	66 (23)
O	1470 (37)	833 (27)	668 (22)	−54 (21)	157 (23)	280 (26)	H(2′)	88 (15)
N(1)	580 (24)	901 (32)	678 (28)	294 (24)	−100 (22)	−140 (23)	H(2″)	103 (15)
N(2)	592 (26)	699 (29)	763 (27)	89 (23)	−57 (21)	−156 (21)	H(3′)	107 (13)
C(1)	676 (36)	880 (47)	704 (39)	312 (35)	−207 (32)	−207 (33)	H(3″)	96 (14)
C(2)	706 (33)	792 (38)	565 (30)	83 (26)	−112 (26)	−38 (29)	H(4′)	87 (14)
B	322 (20)	428 (25)	341 (21)	21 (18)	13 (16)	26 (18)	H(4″)	86 (14)
C(11)	302 (18)	454 (22)	346 (18)	−1 (16)	−17 (14)	−14 (16)	H(12)	53 (14)
C(12)	409 (21)	451 (24)	413 (20)	49 (18)	8 (16)	18 (18)	H(13)	72 (14)
C(13)	451 (23)	606 (28)	410 (21)	28 (20)	98 (17)	−53 (20)	H(14)	51 (14)
C(14)	360 (21)	641 (28)	437 (22)	−93 (20)	31 (17)	9 (19)	H(15)	76 (13)
C(15)	437 (22)	467 (25)	553 (24)	−45 (20)	37 (18)	84 (19)	H(16)	40 (14)
C(16)	406 (21)	478 (24)	486 (22)	87 (19)	75 (17)	45 (18)	H(22)	61 (14)
C(21)	319 (18)	380 (20)	425 (20)	36 (16)	32 (15)	61 (16)	H(23)	89 (13)
C(22)	432 (22)	440 (23)	446 (22)	34 (18)	−19 (18)	26 (18)	H(24)	73 (13)
C(23)	500 (24)	555 (27)	611 (28)	−41 (23)	−125 (21)	43 (21)	H(25)	63 (14)
C(24)	385 (23)	541 (28)	925 (38)	−14 (26)	−68 (23)	−51 (20)	H(26)	32 (14)
C(25)	381 (22)	518 (27)	822 (33)	115 (24)	180 (22)	1 (19)	H(32)	53 (14)
C(26)	379 (20)	476 (24)	500 (23)	61 (19)	92 (17)	61 (17)	H(33)	87 (13)
C(31)	411 (20)	419 (22)	374 (19)	35 (16)	−13 (15)	46 (17)	H(34)	62 (14)
C(32)	451 (22)	570 (26)	408 (21)	−11 (19)	12 (17)	121 (20)	H(35)	79 (14)
C(33)	651 (28)	606 (28)	395 (22)	−5 (20)	80 (20)	117 (23)	H(36)	51 (13)
C(34)	715 (30)	654 (30)	347 (22)	16 (21)	−75 (21)	55 (23)	H(42)	49 (14)
C(35)	514 (25)	723 (31)	429 (23)	26 (21)	−107 (19)	14 (23)	H(43)	82 (14)
C(36)	380 (20)	584 (25)	412 (21)	34 (19)	−22 (16)	9 (19)	H(44)	83 (14)
C(41)	330 (18)	434 (22)	370 (18)	41 (16)	46 (15)	10 (16)	H(45)	82 (14)
C(42)	375 (21)	513 (25)	522 (24)	12 (20)	16 (18)	−17 (19)	H(46)	66 (14)
C(43)	543 (26)	471 (26)	677 (29)	−14 (23)	112 (22)	−74 (21)		
C(44)	586 (27)	497 (28)	715 (30)	142 (24)	120 (23)	94 (23)		
C(45)	579 (27)	542 (29)	631 (29)	122 (24)	−94 (23)	66 (22)		
C(46)	525 (23)	496 (26)	505 (23)	53 (21)	−99 (18)	24 (20)		

[a] The anisotropic temperature factor is in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*)]$.

Table VII. Bond Distances (Å) and Angles (Deg) for [Cu(en)(CO)BPh$_4$]

		Coordination Sphere			
Cu-N(1)	2.038 (4)	N(1)-Cu-N(2)	87.2 (2)	C(25)-Cu-N(2)	119.9 (2)
Cu-N(2)	2.043 (4)	N(1)-Cu-C	132.9 (2)	C(26)-Cu-C	95.5 (2)
Cu-C	1.806 (6)	N(2)-Cu-C	133.7 (2)	C(26)-Cu-N(1)	102.7 (2)
Cu-C(25)	2.919 (5)	A-Cu-N(1)	95.0 (2)	C(26)-Cu-N(2)	96.3 (2)
Cu-C(26)	2.706 (4)	A-Cu-N(2)	108.7 (2)	C(25)-Cu-C(26)	28.5 (2)
Cu-A	2.725 (5)[a]	A-Cu-C	92.0 (2)	Cu-C(25)-C(26)	67.3 (3)
		C(25)-Cu-C	88.6 (2)	Cu-C(26)-C(25)	84.2 (3)
		C(25)-Cu-N(1)	87.6 (2)		
		Carbonyl Ligand			
C-O	1.110 (7)	Cu-C-O	178.3 (5)		
		Ethylenediamine Ligand			
N(1)-C(1)	1.545 (8)	Cu-N(1)-C(1)	104.5 (3)	N(1)-C(1)-C(2)	108.3 (5)
N(2)-C(2)	1.482 (7)	Cu-N(2)-C(2)	105.5 (3)	N(2)-C(2)-C(1)	108.4 (5)
C(1)-C(2)	1.499 (9)				

[a] A is the midpoint of C(25)-C(26).

a white microcrystalline solid. On replacement of CuI with CuCl, the absorption of CO becomes reversible. The carbonyl complex $[Cu_2(en)_3(CO)_2]^{2+}$ was isolated as tetraphenylborate derivative, $[Cu_2(en)_3(CO)_2](BPh_4)_2$ (III) [ν_{CO}(Nujol) 2078 cm^{-1}], by the addition of NaBPh$_4$ to the solution coming from reaction 1.

While the thermal stability in the solid state of II and III, which do not lose CO even in vacuo, is unusually high, their reactivity toward dioxygen and moisture is considerable, and they are converted to green-blue copper(II) derivatives. By use of an en/CuI ratio lower than 1, no carbon monoxide absorption is observed. A few years ago,[3] a carbonylic species with a 1:1 en/Cu content was reported as resulting from reaction 2. The isolation and characterization of IV, which loses

$$\mathrm{CuCOCl} + \mathrm{en} \rightarrow \underset{\mathrm{IV}}{[\mathrm{Cu(en)COCl}]} \qquad (2)$$

CO in vacuo or at temperatures higher than 0 °C, are rather difficult. However, the addition of NaBPh$_4$ precipitates [Cu(en)(CO)BPh$_4$] (V) [ν_{CO}(Nujol) 2117 cm^{-1}], which is thermally stable in the solid state and, even in vacuo, does not lose CO. The molecular complexity of III and V is deduced from X-ray analyses of both complexes (vide infra). Reaction 2, carried out in the presence of an excess of en gives rise to a solution from which III is recovered by addition of NaBPh$_4$. The conversion of V by an excess of en into III further supports the following stepwise scheme for the reaction of a copper(I) source with carbon monoxide in the presence of en:

$$2\mathrm{Cu}^+ + 2\mathrm{en} + 2\mathrm{CO} \rightarrow 2[\mathrm{Cu(en)CO}]^+ \xrightarrow{+\mathrm{en}} [\mathrm{Cu_2(en)_3(CO)_2}]^{2+} \xrightarrow{+\mathrm{en}} 2[\mathrm{Cu(en)_2CO}]^+ \qquad (3)$$

All the species of the scheme have been depicted not on their real existence in solution (see Discussion) but rather on the basis of their isolation in the solid state as tetraphenylborate or iodide derivatives. Every carbonyl complex reacts with a

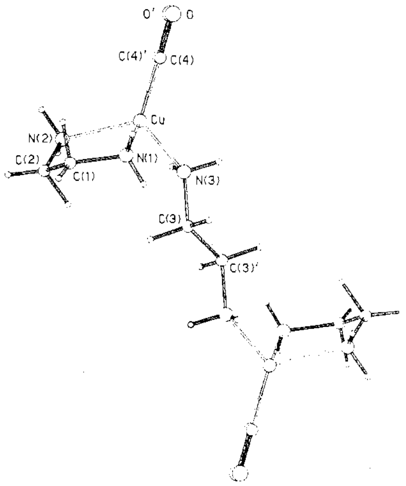

Figure 1. A perspective view of the centrosymmetric dimeric cation $[Cu(en)_3(CO)_2]^{2+}$.

methanolic solution of $P(OEt)_3$ giving 1 mol of CO/mol of copper.

Description of the Structure of $[Cu_2(en)_3(CO)_2](BPh_4)_2$ (III). The structure of III consists of discrete dimeric $[Cu_2(en)_3(CO)_2]^{2+}$ cations and BPh_4^- anions. Figure 1 shows a perspective view of the cation. The two centrosymmetric copper atoms are surrounded in a pseudotetrahedral geometry by a set of three N atoms and a carbon monoxide molecule. The nitrogens are provided by one chelating ethylenediamine, while the second one bridges the two metal atoms. The distortion of the tetrahedron mainly depends on the constraints of the chelated ethylenediamine, and this is reflected on the angle values reported in Table IV. The chelate bite distance of 2.747 (1) Å effects a distortion in the coordination polyhedron by compressing to 83.8 (3)° the N–Cu–N angle, from the expected tetrahedral value. This necessarily influences the N–Cu–carbonyl angles, some of which are considerably greater than the ideal tetrahedral value. The five-membered ring formed by the chelating en is not flat. The value of the dihedral angle between the planes defined by N(1)–C(1)–C(2) and N(2)–C(1)–C(2), which is 39.3°, has been suggested as a measure of ring pucker.[11,12] The chelate ring has the approximately *gauche* conformation found in all en complexes with C(1) and C(2) 0.27 and 0.17 Å below and above the N(2)–Cu–N(1) plane, respectively.[13] While the N–C bond lengths agree fairly well with previous results,[13] the C–C bond distance is significantly shorter as a consequence of the high thermal motion (or disorder) associated to the atoms C(1), C(2), and N(1), especially. The bridging en ligand, planar for symmetry requirements, exhibits a trans conformation about the C–C bond, as usually observed in the bridging en molecules so far studied.[14] Also the conformation around the C–N bond is trans, in agreement with the relatively high Cu⋯Cu distance [7.452 (1) Å].[14] The Cu–N–N and N–C–C bond angles in bridging en are considerably greater than the ideal tetrahedral value, probably as a result of its bridge bonding mode.

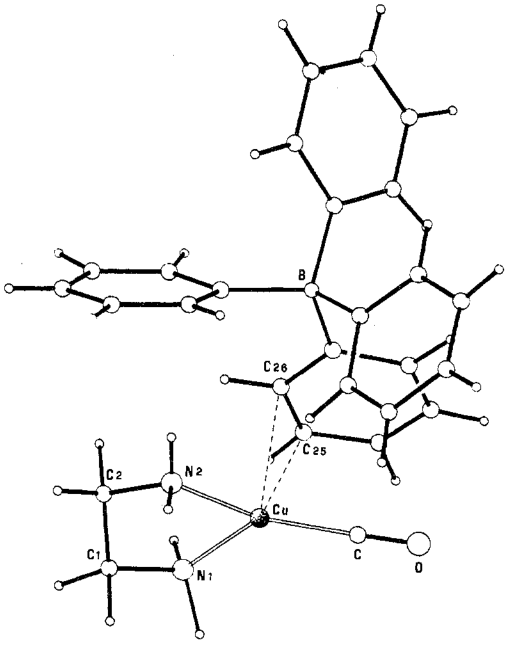

Figure 2. Molecular structure of the ion-pair $[Cu(en)(CO)BPh_4]$.

Table VIII. Cu–C and C–O Bond Distances (Å) and ν(C–O) of the Copper(I) Carbonyls So Far Structurally Identified

compd	distance		ν_{CO}, (Nujol), cm^{-1}	ref
	Cu–C	C–O		
$[HB(C_3N_2H_3)_3CuCO]$	1.765 (14)	1.120 (6)	2083	20
$[Cu(LBF_2)CO]$	1.780 (3)	1.112 (4)	2068	21
$[Cu(dien)CO](BPh_4)$	1.776 (5)	1.123 (6)	2080	19
$[Cu(en)CO(BPh_4)]$	1.806 (6)	1.110 (7)	2117	this work
$[Cu_2(en)_3(CO)_2](BPh_4)_2$	1.73 (1), 1.75 (1)	1.17 (2), 1.16 (2)	2078	this work

Description of the Structure of $[Cu(en)(CO)BPh_4]$. The molecular structure of the complex is given in Figure 2. N(1), N(2), and C donor atoms are arranged in a distorted trigonal geometry around copper(I), which interacts with two adjacent carbon atoms C(25)–C(26) of one phenyl group of the BPh_4^- anion at rather long distance [Cu–C(25) = 2.919 (5) and Cu–C(26) = 2.706 (4) Å].[15] Copper is displaced by 0.26 Å from the plane defined by N(1), N(2), C toward the C(25)–C(26) bond, which completes the distorted trigonal-pyramidal coordination around the metal. Cu–C(26) direction is tilted by 84.3° with respect to the coordination plane. The phenyl ring C(21)–C(26) makes a dihedral angle of 6.4° with respect to the plane through N(1), N(2), and C. Even in this case the chelate ring has nearly gauche conformation: the dihedral angle between the planes through N(1)–C(1)–C(2) and N(2)–C(1)–C(2) is 57.5°; C(1) and C(2) atoms lie 0.33 and 0.40 Å respectively below and above the N–Cu–N plane. The structural data associated with the CuCO units are given in Tables IV, VII, and VIII.

The Tetraphenylborate Groups. The general features of the tetraphenylborate groups are those expected.[16] In both compounds, the ring angles at the site of boron binding are small, while those adjacent to this are large; the C(3)–C(4) bond in each phenyl ring is shorter than the adjacent C(2)–C(3) bond. These values are in agreement with small deformation induced by substitution in the skeletal geometry of the benzene ring.[17] The boron atoms deviate from the planes of the phenyl rings by anywhere from 0.059 to 0.177 Å and from 0.014 to 0.157 Å respectively in $[Cu_2(en)_3(CO)_2](BPh_4)_2$

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and $[Cu(en)(CO)(BPh_4)]$. The dihedral angles between the rings usually show a wide range of values. Bond distances and angles in the tetraphenylborate group interacting with Cu seem to be not influenced by this interaction (Table SIII). In both complexes, packing is mainly determined by van der Waals contacts between methylene or amine and phenyl carbon centers.

Discussion

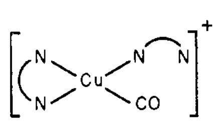
It seems to be not advisable to use ethylenediamine as a ligand for copper(I), since this ligand induces the disproportionation reaction (4) in aqueous solution.[2] In other solvents,

$$2Cu^+ + 2en \rightarrow Cu(en)_2{}^{2+} + Cu^0 \qquad (4)$$

particularly those that are able to solvate copper(I) ions more effectively than water, copper metal can be used to reduce copper(II) to copper(I) complexes. This function is fulfilled in our case by carbon monoxide and iodide anion. Therefore, starting from CuCl and en in methanol, we observed the fast formation of metallic copper along with a blue solution, while the introduction of carbon monoxide produces a practically colorless solution containing copper(I).[18] Replacing CuCl with CuI causes the following related effects: (i) disproportionation is not observed and (ii) absorption of carbon monoxide is not reversible. The reversible absorption of CO, when CuCl is used, is probably related to the fact that Cl^-, contrary to I^-, does not prevent the disproportionation of copper(I). Since copper(I) is rather labile, we expect that carbonylated solutions contain various copper–en complexes in equilibrium, including monomers and dimers. This is somewhat supported by the isolation of I–III and V in the solid state and by the conversion of V in III.

We cannot exclude the possibility that the dinuclear complex III is mainly an artificial product of the isolation in the solid state, even if present in small amount at the equilibrium in solution.

As concerns the coordination sphere of copper(I) in solution, we suppose that in all species copper(I) achieves the tetracoordination by means either of en in excess or of a solvent molecule. This is supported by the low CO stretching frequency in solution and, bona fide, in the solid-state structures. We are referring to the very few copper(I) carbonyls, the structures of which have been so far reported, $[Cu(dien)CO]BPh_4$,[19] $[HB(C_3N_2H_3)_3CuCO]$,[20] and III, while the five coordination of $[Cu(LBF_2)CO]$[21] might be an artificial feature imposed by the rigidity of the macrocyclic ligand. Notwithstanding that structural data are not available on $[Cu(en)_2CO]I$, we feel, considering the bridging bonding mode displayed by en in some complexes, that the coordination number of copper(I) is probably four even in this cases.



proposed structure for $[Cu(en)_2(CO)]^+$

The ion-pair nature of V is further proof that copper(I) has a high tendency in these complexes to be tetracoordinated. The supposed three coordination in [Cu(en)COCl] was deduced from conductivity measurements carried out in nitromethane solutions, where the role of the solvent is completely disregarded.[3] Moreover, the structural relationship between III and V suggests that the lowest amino groups/copper ratio would produce metal centers suitable for a simultaneous coordination of carbon monoxide and unsaturated CO-accepting groups. In fact, V may be considered a structural model for copper-promoting CO transfer to organic unsaturated substrates and it would imitate the labile situation often occurring in solution. The long Cu–phenyl distances, indeed, indicate only a weak binding of the aromatic unit.[15]

The carbon monoxide affinity of copper(I) strongly depends on the nature of the nitrogen donor atoms, being very high in the case of saturated unsubstituted amino groups. A significant lowering of the C–O stretching frequency, as diagnostic of the Cu–CO bond stabilization, occurs when three amino groups complete the pseudotetrahedral geometry around Cu^+.

The results here presented, compared with those using dien as a ligand for Cu^+,[19] show that the polydentate nature of the ancillary ligand is not a prerequisite to isolate stable copper–carbonyl complexes. The main difference between Cu(I)–dien and Cu(I)–en complexes stays on the possibility for Cu(I)–en complexes to have in solution a potential open coordination site on the metal. The isolation of complexes like I, III, and V represents a significant contribution not only in copper(I)–carbonyl chemistry[22,23] but even in the saturated nitrogen–copper(I) chemistry.[1,23]

The very relevant spectroscopic property of these complexes is the C–O stretching frequency,[22] which is always attractive to relate to the corresponding structural parameters. This comparison is summarized in Table VIII, which mainly indicates that there is no evident relationship between the two sets of parameters so far reported for copper(I) carbonyls. This is even depending on the expected high C–O bond order in cationic carbonyl complexes. The IR spectrum shows band patterns for chelating and bridging en which have been expected as reported in the literature.[24]

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Registry No. I, 72853-20-4; II, 69683-73-4; III, 69683-75-6; IV, 72853-21-5; V, 72853-22-6.

Supplementary Material Available: Tables SI and SIII listing distances and angles in BPh_4^- for complexes III and V, Tables SII and SIV for least-squares planes for complexes III and V, and final structure factors (27 pages). Ordering information is given on any current masthead page.

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