cuprates having other geometries and to see how well these may be rationalized for the series of complexes using simple bonding models. Several attempts have been made to apply crystal field theory to the chlorocuprates, but more sophisticated calculations suggest that such a model is quite unrealistic.[1] Perhaps the best simple bonding model currently available for metal complexes is the angular overlap model (AOM) of Jorgensen and Schäffer.[9] This has recently been successfully applied to the interpretation of the spectral properties of a variety of metal complexes.[10,11] The AOM suggests that the energy e by which a metal d orbital is raised upon interaction with a ligand orbital is given by $e = S^2K$, where S is the diatomic overlap integral and K is a constant. The total energy of each orbital is obtained by summing the effects of all the ligand orbitals using the angular overlap matrix appropriate to the geometry of the complex. Both σ and π effects are included, and as the Cu (3d) and Cl (3p) overlap integrals have been reported as a function of Cu–Cl bond length[12] the AOM allows the d-orbital energies of a whole series of complexes of different geometries to be expressed as a function of just two parameters, K_σ and K_π. In its simplest form, the AOM predicts that for a spherical ligand such as Cl^- the condition $K_\sigma = K_\pi$ should be satisfied. In practice, it has been proposed that the model may need to be extended in several ways, e.g., by the inclusion of electrostatic effects or ligand–ligand interactions,[10] bonding with ligand s orbitals, or the admixture of metal s or p orbitals with the d functions.[13] The equations relating the d-orbital energies to K_σ and K_π have been given elsewhere for square-planar, tetragonal-octahedral, distorted tetrahedral, and trigonal-bipyramidal ligand coordination.[10,13] These were used to fit the electronic transition energies observed at low temperature for 7 copper(II) complexes of accurately known molecular geometry including all these stereochemistries by a least-squares technique, and the results are shown in Table I. Except for the transition ${}^2B_1(d_{x^2-y^2}) \rightarrow {}^2A_1(d_{z^2})$ in planar $CuCl_4^{2-}$ the calculated and observed energies agree quite well, the "best fit" ligand field parameters being $K_\sigma = 1.01 \times 10^6$ and $K_\pi = 1.21 \times 10^6$ cm^{-1}. Removal of this transition from the calculations gave "best fit" parameters $K_\sigma = 0.94 \times 10^6$ and $K_\pi = 0.93 \times 10^6$ cm^{-1} with the only discrepancies greater than 1000 cm^{-1} occurring for the ${}^2B_{1g}(d_{x^2-y^2}) \rightarrow {}^2A_{1g}(d_{z^2})$ transitions of the tetragonal-octahedral chromophores in $(EtNH_3)_2CuCl_4$ and $(n\text{-}PrNH_3)_2CuCl_4$. Considering the wide range of stereochemistries covered, the agreement between the calculated and observed transition energies is remarkably good. Moreover, in agreement with the simple model $K_\sigma \approx K_\pi$. Participation of ligand s orbitals in the bonding or the presence of ligand–ligand interactions should cause K_σ to differ from K_π as well as produce systematic discrepancies in the spectral fits of complexes with differing stereochemistries.[10,13] However, the ${}^2B_{1g}(d_{x^2-y^2}) \rightarrow {}^2A_{1g}(d_{z^2})$ transition energy in planar $CuCl_4^{2-}$ is underestimated by ~5000 cm^{-1}. Smith has recently proposed[13] that in this complex the $a_{1g}(d_{z^2})$ orbital is lowered in energy by configuration interaction with the a_{1g}(4s) orbital. In D_{4h} symmetry these two orbitals are mixed by an amount dependent on the difference in ligand interaction along the x and z axes. Because the 4s orbital is so diffuse, its interaction with the ligand orbitals is large even at the long axial bond lengths in the tetragonally distorted octahedral complexes,[13] and it is only in the rigorously planar $CuCl_4^{2-}$ ion that the $a_{1g}(d_{z^2})$ orbital is lowered drastically in energy. The overall spectral fit (see Table I) suggests a depression of ~5000 cm^{-1} in planar $CuCl_4^{2-}$, ~1400 cm^{-1} in $(EtNH_3)_2CuCl_4$ and $(n\text{-}PrNH_3)_2CuCl_4$ (axial bond lengths ~3 Å), and ~800 cm^{-1} in $CsCuCl_3$ (axial bond lengths 2.78 Å). Assuming an energy of ~150 000 cm^{-1} for the 4s orbital,[14] simple perturbation theory suggests a molecular orbital coefficient of ~0.2 for this orbital in the ground-state wave function of planar $CuCl_4^{2-}$. While this has not been confirmed directly for the copper(II) complex, EPR spectral measurements of the isotropic hyperfine constants of low-spin planar cobalt(II) complexes with $A_{1g}(d_{z^2})$ ground states suggest molecular orbital coefficients of 0.15–0.25 for the 4s orbital in these complexes also[15] and that the participation of this orbital in the ground state decreases on axial ligation.[15,16] It would, thus, seem that while the AOM is adequate to describe the bonding in metal complexes having significant ligand interactions along each of the cartesian molecular axes, in the case of planar compounds it is necessary to include the metal 4s orbital in the bonding scheme.

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Registry No. $[(EtNH_3)_2CuCl_4]$, 55940-27-7; $[(n\text{-}PrNH_3)_2CuCl_4]$, 55940-28-8.

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Synthesis, Properties, and X-Ray Structure of (Diethylenetriamine)copper(I) Carbonyl: a Highly Thermally Stable Copper(I) Amine Carbonyl

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Notwithstanding that copper(I) amine carbonyl chemistry is one of the oldest areas of carbonyl chemistry,[1,2] no thermally stable solution or solid-state copper(I)–amine carbonyl complexes have been isolated until recently.[3] The stabilization of the Cu–CO bond was variously ascribed to the electronic effect of the ancillary ligands around Cu(I) and/or to the charge of the metal.[4,5] Nevertheless, the isolation of very few stable Cu(I) carbonyl complexes[6] makes any prevision on the Cu–CO bond stabilization effects rather unwarranted. Very little is known about the actual coordination sphere of copper(I) involved in the activation of simple molecules, i.e., CO and O_2.[7]

One of the purposes of this work is to explore the coordination chemistry of simple ligands which (a) stabilize the +1 oxidation state of copper and (b) can impart unique chemical properties, such as the reversible binding of CO and O_2. Our results on the Cu–dien system gave us the possibility of isolating a very stable copper(I) carbonyl and of understanding the factors affecting Cu–CO stability.

Experimental Section

Reactions were carried out under an atmosphere of purified nitrogen. Methanol was dried as in the literature.[8] Infrared spectra were recorded with a Perkin-Elmer Model 282 spectrophotometer. The CO evolution was measured using previously described equipment.[9]

Preparations of the Complexes. Preparation of (Diethylenetriamine)copper(I) Carbonyl Tetraphenylborate, $[Cu(dien)CO]BPh_4$. A suspension of CuI (4.02 g, 21.0 mmol) in methanol (100 cm^3) was treated with diethylenetriamine (4 cm^3, 37.0 mmol), the CuI partially dissolving with the appearance of a slightly blue color. Carbon monoxide was then added and all of the CuI passed into the solution in 30 min, the initially slightly blue suspension becoming practically colorless. The resulting methanolic solution did not lose CO in vacuo. By addition of $NaBPh_4$ (7.22 g, 21.1 mmol), dissolved in methanol (30 cm^3), a white crystalline solid was obtained (9.37 g, 87% yield). Anal. Calcd for $[Cu(dien)CO]BPh_4$: C, 67.77; H, 6.42; N, 8.18. Found: C, 67.65; H, 6.66; N, 8.22. ν_{CO}(Nujol) 2080 cm^{-1}; ν_{CO}(THF solution) 2080 cm^{-1}.

The carbonyl is only slightly soluble in THF. It remains unchanged when heated at 100 °C in the solid state. $[Cu(dien)CO]BPh_4$, reacted with a methanolic solution of $P(OC_2H_5)_3$ (excess), yielded CO evolution in a molar ratio CO:Cu of 0.95.

Preparation of $[Cu(dien)P(OC_2H_5)_3]BPh_4$, $[Cu(dien)PPh_3]BPh_4$, and $[Cu(dien)(C_6H_{11}NC)]BPh_4$. $[Cu(dien)CO]BPh_4$ (1.3 g, 2.53 mmol) was suspended in tetrahydrofuran (50 cm^3) and reacted with $P(OC_2H_5)_3$ (0.6 cm^3, 3.45 mmol). Fast evolution of carbon monoxide was observed and at the same time all of the solid dissolved. The volume of the solution was reduced in vacuo to 20 cm^3 and, by addition of $(C_2H_5)_2O$, a white crystalline solid was obtained (1 g, 60.6% yield). Anal. Calcd for $[Cu(dien)P(OC_2H_5)_3]BPh_4$: C, 62.62; H, 7.37; N, 6.45; P, 4.76. Found: C, 62.37; H, 7.46; N, 6.44; P, 4.50. The syntheses of $[Cu(dien)(PPh_3)]BPh_4$ and $[Cu(dien)(C_6H_{11}NC)]BPh_4$, both of which are obtained as white crystalline solids stable in air, were carried out under similar conditions. Anal. Calcd for $[Cu(dien)PPh_3]BPh_4$: C, 73.84; H, 6.42; N, 5.62; P, 4.15. Found: C, 73.47; H, 6.53; N, 5.45; P, 3.95. Calcd for $[Cu(dien)(C_6H_{11}NC)]BPh_4$: C, 70.64; H, 7.4; N, 9.42. Found: C, 69.90; H, 7.84; N, 9.39. ν_{CN}(Nujol) 2150 cm^{-1}.

Collection and Reduction of Crystal Data. A crystal of nearly prismatic shape of $[Cu(dien)CO]BPh_4$ (I) with edges of 0.20 × 0.16 × 0.47 mm^3 was mounted, within a Lindemann capillary, under a nitrogen atmosphere. Weissenberg photographs showed $2/m$ diffraction symmetry and the systematic extinctions ($h0l$ present only for $h + l = 2n$ and $0k0$ present only for $k = 2n$) led to the space group $P2_1/n$. Approximate cell parameters were measured on photographs and exactly determined by least-squares refinement of the angular positions of 25 strong reflections ($\theta > 6°$) collected on a Philips PW 1100 single-crystal automatic diffractometer, with graphite-monochromated Mo Kα radiation. Integrated intensities of reflections were measured using an ω-scan method for $k, l > 0$ and $-16 < h < +16$, with $3° < \theta < 24°$ (scan speed 0.05° s^{-1}, scan width 1.0°, background count 10 s at the start and finish of each scan). Three equivalent reflections ($\bar{1}52$, $\bar{1}\bar{5}2$, $15\bar{2}$) were remeasured every 3 h as a check on crystal and instrument stability. No significant change in the measured intensity of these reflections was observed during data collection.

Crystal Data. $CuC_{29}H_{33}BN_3O$; mol wt 514.5; monoclinic; space group $P2_1/n$; $a = 14.832$ (1), $b = 18.737$ (3), $c = 9.599$ (1) Å; $\beta = 90.07$ (2)°; $V = 2667.7$ (9) Å^3; $Z = 4$; $D_{calcd} = 1.280$ g/cm^3; $F(000) = 1080$ electrons, Mo Kα radiation, λ 0.710 69 Å, μ(Mo Kα) = 8.8 cm^{-1}.

Structure Determination and Refinement. Intensities were corrected for Lorentz and polarization effects but not for absorption owing to the relatively small dimensions of the crystal and the low absorption factor.[10] The copper atom was located by the Patterson method, and two successive electron-density maps permitted us to locate all 35 nonhydrogen atoms. After three cycles of block-diagonal-matrix and one of full-matrix least-squares refinement, with unit weight and isotropic thermal parameters, the R factor for the 2657 observed reflections converged to 0.10.[11] A difference Fourier map revealed 24 of the 35 hydrogen atoms expected. A subsequent cycle of block-diagonal-matrix least-squares refinement was performed in which a weighting scheme $w^{1/2} = 1/(a + |F_o| + b|F_o|^2)$, where $a = 23.0$ and $b = 0.0005$, was assumed.[12] Anisotropic thermal parameters were introduced for the nonhydrogen atoms and those directly bonded to hydrogen atoms not yet located were not allowed to move. The R factor was reduced to 0.077 and a subsequent difference Fourier map revealed the next nine hydrogen atoms. The largest residual peak was 0.4 e/A$°^3$. A correction for anomalous dispersion due to copper was introduced with $\Delta f' = 0.263$ and $\Delta f'' = 1.266$,[13] and after two other block-diagonal-matrix and one full-matrix least-squares cycles the according factor dropped to 0.043.

At this time a full-matrix cycle of refinement was accomplished in which the isotropic thermal parameters of the hydrogen atoms were allowed to vary together with the thermal parameters of the heavy atoms, and in following cycle all of the positional parameters were refined.[14]

A final full-matrix cycle in which hydrogen parameters were not allowed to vary reduced the final R factor for the observed reflections to 0.03. In this last stage 316 parameters were refined by least-squares fitting of 2657 structure factors and the largest shift per error was 0.5 averaging to 0.1. The final atomic coordinates and anisotropic thermal parameters with their standard deviations are given in Table I. A table of positional and thermal parameters for the hydrogen atoms is available (Table SI of supplementary material). A listing of observed and calculated structure amplitudes is available.[15]

Results and Discussion

A methanolic suspension of CuI in presence of a slight excess of diethylenetriamine, dien, absorbs carbon monoxide irreversibly giving a colorless solution (ν_{CO} 2075 cm^{-1}). By addition of $NaBPh_4$, $[Cu(dien)CO]BPh_4$ was obtained as a white crystalline solid (I), ν_{CO}(Nujol) 2080 cm^{-1}. I, quite

$$\mathrm{CuI + dien + CO \xrightarrow[NaBPh_4]{CH_3OH} \underset{I}{[Cu(dien)CO]BPh_4}} \tag{1}$$

stable (even in air) and slightly soluble in tetrahydrofuran (THF) or acetone without decomposition or loss of carbon monoxide, ν_{CO}(THF) 2080 cm^{-1}, does not lose CO in vacuo or by heating to 100 °C in the solid state. I is highly hydrolyzable when BPh_4^- is replaced by Cl^-. I reacts with some π acids such as PPh_3, $P(OC_2H_5)_3$, or $C_6H_{11}NC$ with simultaneous evolution of carbon monoxide to give II as a white crystalline solid stable in air. The significant reduction of

$$\mathrm{[Cu(dien)CO]BPh_4 + L \xrightarrow{THF} \underset{II}{[Cu(dien)L]BPh_4} + CO} \tag{2}$$

$$\mathrm{L = PPh_3,\ P(OC_2H_5)_3,\ C_6H_{11}NC}$$

the CO stretching frequency in I[1] suggests a remarkable back-donation to CO, which is probably responsible for the increased thermal stability of I.

It is very well-known that Cu(I) under various conditions absorbs carbon monoxide, reversibly, although very few well-characterized species have been isolated.[1-3] The only one for which complete, including structural, characterization is known is hydrotris(1-pyrazolyl)boratocopper(I) carbonyl, $[HB(C_3N_2H_3)_3]CuCO$.[3]

Solutions of Cu(I) in ammonia or organic bases are used in gas analysis, but CO is only loosely bonded and easily replaced.[1,2] Using ethylenediamine, en, the isolation of the less elusive, although thermally unstable and structurally not identified, carbonyls $[Cu(en)CO]Cl$ and $[Cu_2(en)_2(CO)_2]Cl_2$ was realized.[16]

Table I. Final Atomic Positional and Anisotropic Thermal Parameters ($\times 10^4$)[a, b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.26763 (2)	0.39202 (2)	0.66820 (2)	39 (1)	32 (1)	126 (1)	1 (1)	6 (1)	−8 (1)
O	0.4415 (2)	0.4421 (2)	0.7656 (5)	54 (2)	62 (2)	395 (11)	0 (2)	−33 (4)	−30 (4)
N(1)	0.2105 (2)	0.4413 (2)	0.4946 (3)	63 (2)	38 (1)	97 (5)	−2 (1)	17 (3)	1 (3)
N(2)	0.1414 (2)	0.4131 (1)	0.7637 (3)	51 (2)	23 (1)	81 (4)	7 (1)	12 (2)	−1 (2)
N(3)	0.2244 (2)	0.2869 (1)	0.6761 (4)	58 (2)	28 (1)	163 (6)	8 (1)	9 (3)	−14 (2)
C(1)	0.3740 (3)	0.4214 (2)	0.7313 (6)	49 (3)	43 (2)	202 (9)	7 (2)	−1 (4)	−20 (3)
C(2)	0.1140 (3)	0.4476 (2)	0.5199 (5)	55 (3)	50 (2)	120 (6)	0 (2)	0 (3)	20 (3)
C(3)	0.0969 (3)	0.4654 (2)	0.6722 (4)	53 (2)	38 (2)	127 (6)	14 (2)	23 (3)	19 (3)
C(4)	0.0931 (2)	0.3444 (2)	0.7749 (4)	52 (2)	27 (1)	116 (6)	0 (2)	18 (3)	1 (2)
C(5)	0.1581 (3)	0.2840 (2)	0.7906 (4)	64 (3)	25 (1)	142 (7)	2 (2)	4 (3)	−1 (2)
C(6)	0.2477 (2)	0.1228 (1)	0.1768 (3)	36 (2)	18 (1)	65 (4)	2 (1)	−2 (2)	0 (2)
C(7)	0.1686 (2)	0.1057 (2)	0.1059 (3)	40 (2)	30 (1)	73 (4)	1 (1)	−10 (2)	0 (2)
C(8)	0.1652 (2)	0.1040 (2)	−0.0401 (4)	53 (2)	37 (2)	96 (5)	3 (2)	−23 (3)	−9 (2)
C(9)	0.2396 (3)	0.1198 (2)	−0.1183 (4)	76 (3)	31 (2)	78 (5)	9 (2)	0 (3)	0 (2)
C(10)	0.3187 (3)	0.1370 (2)	−0.0521 (4)	62 (3)	33 (1)	72 (5)	−2 (2)	17 (3)	1 (2)
C(11)	0.3223 (2)	0.1385 (2)	0.0933 (3)	43 (2)	25 (1)	71 (4)	−3 (1)	4 (2)	2 (2)
C(12)	0.1583 (2)	0.1402 (1)	0.4203 (3)	29 (2)	22 (1)	67 (4)	0 (1)	−8 (2)	−4 (3)
C(13)	0.1200 (2)	0.1056 (2)	0.5348 (3)	36 (2)	30 (1)	72 (4)	0 (1)	5 (2)	1 (2)
C(14)	0.0418 (2)	0.1298 (2)	0.5997 (4)	49 (2)	41 (2)	92 (5)	0 (2)	19 (3)	2 (2)
C(15)	−0.0010 (2)	0.1913 (2)	0.5530 (4)	42 (2)	46 (2)	107 (6)	9 (2)	10 (3)	−9 (3)
C(16)	0.0349 (2)	0.2269 (2)	0.4401 (4)	45 (2)	37 (2)	107 (5)	17 (2)	−3 (3)	−5 (3)
C(17)	0.1129 (2)	0.2015 (2)	0.3757 (3)	43 (2)	28 (1)	77 (5)	3 (1)	5 (2)	1 (2)
C(18)	0.3291 (2)	0.1710 (1)	0.4151 (3)	29 (2)	20 (1)	67 (4)	3 (1)	5 (2)	−3 (2)
C(19)	0.3753 (2)	0.1555 (1)	0.5389 (3)	33 (2)	26 (1)	66 (4)	1 (1)	2 (2)	−5 (2)
C(20)	0.4349 (2)	0.2030 (2)	0.6000 (3)	40 (2)	37 (2)	70 (4)	7 (1)	−2 (2)	−10 (2)
C(21)	0.4510 (2)	0.2687 (2)	0.5409 (4)	35 (2)	40 (2)	112 (5)	−5 (1)	9 (3)	−28 (3)
C(22)	0.4051 (2)	0.2873 (2)	0.4209 (4)	57 (2)	24 (1)	116 (6)	−8 (1)	12 (3)	−3 (2)
C(23)	0.3451 (2)	0.2388 (2)	0.3601 (3)	46 (2)	23 (1)	80 (4)	−1 (1)	−1 (2)	0 (2)
C(24)	0.2803 (2)	0.0322 (1)	0.3705 (3)	37 (2)	19 (1)	52 (4)	0 (1)	2 (2)	0 (2)
C(25)	0.3700 (2)	0.0093 (1)	0.3726 (3)	39 (2)	21 (1)	83 (5)	3 (1)	8 (2)	−2 (2)
C(26)	0.3939 (2)	−0.0620 (2)	0.3722 (4)	54 (2)	30 (2)	91 (5)	14 (2)	6 (3)	−1 (2)
C(27)	0.3296 (3)	−0.1145 (2)	0.3711 (4)	79 (3)	22 (1)	97 (5)	7 (2)	9 (3)	−2 (2)
C(28)	0.2405 (3)	−0.0944 (2)	0.3695 (4)	70 (3)	21 (1)	117 (6)	−9 (2)	0 (3)	−5 (2)
C(29)	0.2165 (2)	−0.0226 (2)	0.3690 (4)	45 (2)	24 (1)	95 (5)	−1 (1)	0 (3)	−4 (2)
B	0.2537 (2)	0.1171 (2)	0.3478 (3)	31 (2)	19 (1)	62 (4)	−2 (1)	0 (2)	0 (3)

[a] Estimated standard deviations are in parentheses. [b] The temperature factors are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table II. Bond Distances (Å) and Angles (deg) with Their Estimated Standard Deviations

	Coordination Polyhedron		
Cu–N(1)	2.085 (4)	N(1)–Cu–N(2)	84.53 (14)
Cu–N(2)	2.123 (3)	N(1)–Cu–N(3)	108.90 (15)
Cu–N(3)	2.073 (4)	N(1)–Cu–C(1)	119.73 (21)
Cu–C(1)	1.776 (5)	N(2)–Cu–N(3)	83.54 (14)
C(1)–O	1.123 (6)	N(2)–Cu–C(1)	125.38 (21)
		N(3)–Cu–C(1)	123.82 (21)
		Cu–C(1)–O	176.57 (54)
	dien Unit		
N(1)–C(2)	1.457 (6)	Cu–N(1)–C(2)	107.51 (28)
N(2)–C(3)	1.471 (6)	Cu–N(2)–C(3)	105.14 (25)
N(2)–C(4)	1.478 (5)	Cu–N(2)–C(4)	107.25 (24)
N(3)–C(5)	1.476 (6)	C(3)–N(2)–C(4)	113.99 (33)
C(2)–C(3)	1.521 (7)	Cu–N(3)–C(5)	106.64 (26)
C(4)–C(5)	1.494 (6)	N(1)–C(2)–C(3)	110.10 (38)
		N(2)–C(3)–C(2)	110.67 (39)
		N(2)–C(4)–C(5)	110.83 (35)
		N(3)–C(5)–C(4)	109.05 (36)

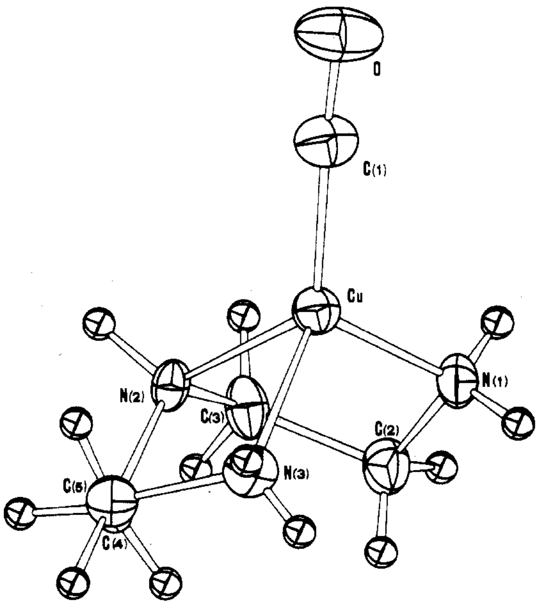

Figure 1. ORTEP view of the cation $[Cu(dien)CO]^+$ showing 20% probability ellipsoids and the atomic numbering scheme.

This is the first report describing the structure of highly thermally stable amine–copper(I) carbonyl complex.

Structure of $[Cu(dien)CO]BPh_4$. Interatomic distances and bond angles, with their estimated standard deviations for the coordination sphere of the metal and for the dien unit are given in Table II.[17] The numbering scheme together with the coordination geometry of the cation $[Cu(dien)CO]^+$ are displayed in Figure 1. The crystal consists of the discrete cation $[Cu(dien)CO]^+$ and the anion BPh_4^-. The crystal packing within the unit cell is shown in Figure 2. Bond lengths and angles in the tetraphenylborate anion are in the usual range, as well as the interplanar angles between each pair of phenyl rings.[18,19] Bond distances and angles within the dien unit do not differ significantly from values previously reported for Cu(II)–dien complexes.[20-23] No comparison is possible with Cu(I)–dien complexes, since this is the first complex of Cu(I)–dien reported structurally.

The dien acts as a tridentate ligand, while CO completes the (distorted) tetrahedral arrangement of the donor atoms around Cu (Figure 1). The central secondary nitrogen atom bonds at a significantly longer distance [2.123 (3) Å] to the copper atom than do the terminal nitrogens [mean value of

Table III. Comparison of the Cu-N Distances (Å) for Some Cu-dien Complexes

Atoms	Cu(dien)$_2^{2+}$ [20]	Cu(dien)$_2^{2+}$ [21]	Cu(dien)$^{2+}$ [22]	Cu(dien)$^{2+}$ [23]	Cu(dien)$^{+}$ [a]
Cu-N$_{term}$[b]	2.265 (23) 2.203 (11) 2.170 (12) 2.236 (14)	2.350 (28) 2.459 (26) 2.131 (24) 2.066 (25)	2.009 (8) 1.996 (8)	2.002 (3) 2.040 (3)	2.085 (4) 2.073 (4)
Cu-N$_{mid}$[b]	2.018 (11) 2.002 (10)	2.040 (23) 2.027 (26)	2.021 (7)	2.009 (3)	2.123 (3)

[a] This study. [b] N$_{term}$ = terminal nitrogen atoms of the dien ligand; N$_{mid}$ = middle nitrogen atom of the dien ligand.

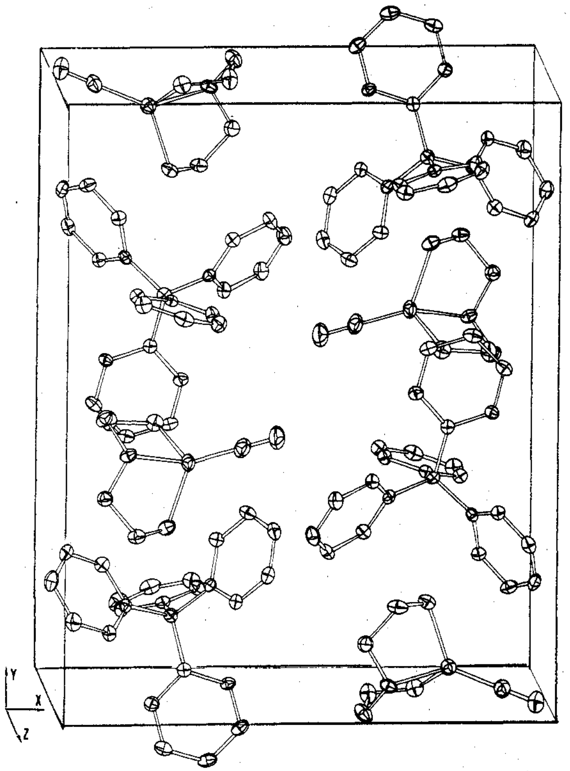

Figure 2. Molecular packing diagram for [Cu(dien)CO]$^+$BPh$_4^-$.

2.079 (4) Å], whose distances from copper are practically equivalent. This is a reverse trend from that observed for all other Cu-dien complexes shown in Table III. The methylene carbons at N(2) [C(3) and C(4)] and at the terminal nitrogen atoms [C(2) and C(5)] show the following deviations from the N(1)-N(2)-N(3) plane: -0.62, -0.97, -1.10, -0.42 Å, respectively. Two intramolecular N-Cu-N angles are significantly less than the ideal tetrahedral angle of 109.5° [N(1)-Cu-N(2) = 84.53 (14)°; N(2)-Cu-N(3) = 83.54 (14)°]. This is due to a combination of the constraints within the dien ligand and the requirements for normal copper-nitrogen bond distances. The N(1)-Cu-N(3) angle, being N(1) and N(3) independent, assumes the normal value. This necessarily affects the N-Cu-C(1) angles, all of which are considerably greater than the ideal tetrahedral angle and range from 119.7 (2) to 123.8 (2)°. The more significant values associated with the Cu-CO unit are the Cu-C(1) and C(1)-O bond lengths which are respectively 1.776 (5) and 1.123 (6) Å and which agree quite well with the values reported for hydrotris(1-pyrazolyl)boratocopper(I) carbonyl, [HB($C_3N_2H_3$)$_3$]Cu(CO), of 1.765 (14) and 1.260 (6) Å for Cu-C and C-O, respectively. The Cu-C(1)-O system is practically linear, the angle being 176.57 (54)°.

The ν_{CO} of 2080 cm^{-1} is unusually low for a copper carbonyl, and this comes from the presence of good symbiotic existence of dien and CO around copper(I).[1] The results reported together with those recently cited in the literature[24] give the possibility of ascribing the high stability of the isolated carbonyl complex (a) to the highly basic nitrogen as donor atoms, (b) to the polydentate nature of the ligand, or (c) to the nature of the counteranion, the highest stability being found for the BPh$_4^-$.

The choice of dien was dictated by its stability to form the required copper(I) derivative without the necessity for other ligands. The utilization of complexes like the diethylenetriaminecopper(I) cation, Cu(dien)$^+$, as a source of d^{10} 16-electron species can be very useful in coordinative additions or, generally, in molecular activation processes.[25] It is very well-known that copper(I) activates carbon monoxide in many catalytic processes, such as insertion, oxidation, and generally nucleophilic attack.[26] Ligands like dien may be, moreover, a facsimile of the copper chelation site in hemocyanins, one of their properties being carbon monoxide binding ability.

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Registry No. [Cu(dien)CO]BPh$_4$, 65832-81-7; [Cu(dien)P(OC$_2$H$_5$)$_3$]BPh$_4$, 65832-79-3; [Cu(dien)PPh$_3$]BPh$_4$, 65832-77-1; [Cu(dien)(C$_6$H$_{11}$NC)]BPh$_4$, 65832-75-9.

Supplementary Material Available: Tables listing positional and thermal parameters for hydrogen atoms, C-H and N-H bond distances within the dien unit, distances and angles in BPh$_4^-$, dihedral angles between phenyl planes, and final structure factors (15 pages). Ordering information is given on any current masthead page.

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Evaluation of the Intrinsic Parameters of Octacyanomolybdate(IV) and -(V) and Hexacyanoferrate(II) and -(III) from a Kinetic Study of the Oxidation of Benzenediols

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The experimental rates of many outer-sphere electron-transfer reactions

$$\mathrm{Ox_1 + Red_2 \xrightarrow{k_{12}} Ox_2 + Red_1} \qquad (1)$$

agree with the Marcus free-energy relationship

$$\Delta G^*_{12} = w_{12} + \lambda_{12}(1 + \Delta G^\circ{}_{12}'/\lambda_{12})^2/4 \qquad (2)$$

where

$$k_{12} = Z \exp(-\Delta G^*_{12}/RT) \qquad (3)$$

$$\lambda_{12} = 2(\Delta G^*_{11} - w_{11} + \Delta G^*_{22} - w_{22}) \qquad (4)$$

$$\Delta G^\circ{}_{12}' = \Delta G^\circ{}_{12} + w_{21} - w_{12} \qquad (5)$$

Z is the collision number in solution, taken to be 10^{11} M^{-1} s^{-1}; ΔG^*_{11} and ΔG^*_{22} are the activation free energies for self-exchange reactions and w_{11} and w_{22} are the related work terms; w_{12} and w_{21} are the corresponding work terms involved in bringing reactants and products together, respectively.[1]

A knowledge of ΔG^{**} (where $\Delta G^{**} = \Delta G^* - w$) for the self-exchange reactions is of obvious importance in tests of the Marcus theory; the work terms can be evaluated according to

$$w = \frac{z_1 z_2 e^2}{D r^*} \exp(-\kappa r^*) \qquad (6)$$

where z_1 and z_2 are the formal charges of the reactants, D is the static dielectric constant, and r^* is the distance between the centers of reactants; the exponential coefficient is the Debye–Hückel term with κ as the reciprocal Debye radius.[2]

It is well-known that the exponential coefficient overcorrects for ionic strength outside of the Debye–Hückel region and, in turn, the zero ionic strength extrapolation undercorrects.[3] Recently, Haim and Sutin proposed an "averaged" method for estimating the work terms and in this way obtained satisfactory agreement with experimental data.[4]

In previous work we have investigated the kinetics of electron-transfer reactions between benzenediols (H_2Q) and hexachloroiridate(IV),[5] tris(1,10-phenanthroline)iron(III) and its derivatives (FeL_3^{3+}),[6] and aquopentachloro-, diaquo-, tetrachloro-, and hexabromoiridate(IV).[7] The rate-determining step of these reactions can be represented as in eq 7,

$$\mathrm{Ox + H_2Q \rightarrow Red + H_2Q^{+\cdot}} \qquad (7)$$

and a model for calculating the free-energy changes involved was proposed.[5a] Different λ_{12}'s were found to hold for different oxidant complexes.[5-7] Since benzenediols are uncharged molecules, the term w_{12} can be set equal to zero, and w_{21} (which involves an interaction of charged metal complexes with a monopositive cation radical at ionic strength 1.0 M) can also be tentatively neglected.[8] Thus, to a good approximation, $\Delta G^\circ{}_{12}' = \Delta G^\circ{}_{12}$ for all the oxidants. Moreover, since $\lambda_{12} = 2(\Delta G^{**}_{11} + \Delta G^{**}_{22})$, with ΔG^{**}_{22} (referred to benzenediols) kept constant,[9] $\Delta\Delta G^{**}_{11} = {}^1/_2\Delta\lambda_{12}$. Thus, a relative "scale" of ΔG^{**}_{11} can be derived. A problem arises in the selection of a reference for ΔG^{**}_{11}. In a previous paper,[12] we have chosen the $IrCl_6^{2-/3-}$ system, whose self-exchange rate was determined at $\mu = 0.1$ M[13] ($\Delta G^*_{11} = 7.7$ kcal mol^{-1}; $w_{11} = 1.2$ ($r = 4.3$ Å) and thus $\Delta G^{**}_{11} = 6.5$).[14] Consequently, for $FeL_3^{3+/2+}$ ΔG^{**} should be 1.5 kcal mol^{-1},[6] for $Ir(H_2O)Cl_5^{-/2-}$ and $Ir(H_2O)_2Cl_4^{0/-}$, $\Delta G^{**} = 6.5$ kcal mol^{-1},[7] and for $IrBr_6^{2-/3-}$, $\Delta G^{**} = 4.0$ kcal mol^{-1}.[7] With these values a satisfactory agreement was found between calculated and experimental data.[7,12]

Table I. Kinetic Data for Benzenediol Oxidation by $Mo(CN)_8^{3-}$ [a]

Benzenediol	k, M^{-1} s^{-1} [b]	ΔG°, kcal mol^{-1} [c]	k_{calcd}, M^{-1} s^{-1} [d]
2-Methylbenzene-1,4-diol	7.6×10^4	6.1	3.0×10^4
Benzene-1,4-diol	1.1×10^4	7.8	4.3×10^3
2-Chlorobenzene-1,4-diol	3.7×10^3	8.2	2.7×10^3
4-Methylbenzene-1,2-diol	4.7×10^3	8.7	1.5×10^3
4-*tert*-Butylbenzene-1,2-diol	5.2×10^2	9.3	7.0×10^2
Benzene-1,2-diol	9.5×10^1	10.5	1.5×10^2

[a] At 20.0 °C, $[HClO_4] = 1.00$ M, $\mu = 1.0$ M; $[Mo(CN)_8^{3-}] = 5 \times 10^{-5}$ M; the concentration range for benzenediols was $(1-6) \times 10^{-4}$ M, except for 2-methylbenzene-1,4-diol ($(0.5-2) \times 10^{-4}$ M) and benzene-1,2-diol ($(5-20) \times 10^{-3}$ M). [b] The standard deviations are 4–6%. [c] Referred to the rate-determining step; calculated as described in ref 3; $E^\circ(Mo(CN)_8^{3-/4-}) = 0.80$ V.[9] [d] Calculated with eq 2; $\lambda_{12} = 21$ kcal mol^{-1}.

Table II. Kinetic Data for Benzenediol Oxidation by $Fe(CN)_6^{3-}$ [a]

Benzenediol	k, M^{-1} s^{-1} [b]	G°, kcal mol^{-1} [c]	k_{calcd}, M^{-1} s^{-1} [d]
2-Methylbenzene-1,4-diol	72	8.2	84
Benzene-1,4-diol	10	9.9	12

[a] At 20.0 °C, $[HClO_4] = 1.00$ M, $\mu = 1.0$ M; $[Fe(CN)_6^{3-}] = 1 \times 10^{-4}$ M; the concentration range of 2-methylbenzene-1,4-diol was $(1-5) \times 10^{-3}$ M and 0.10–0.20 M for benzene-1,4-diol. [b] The rate constants were estimated preferably in the early part of reaction; the standard deviation is 5–7%. [c] Referred to the rate-determining step; calculated as described in ref 3; $E^\circ(Fe(CN)_6^{3-/4-}) = 0.71$ V. [d] Calculated with eq 2; $\lambda_{12} = 30$ kcal mol^{-1}.

In order to evaluate the importance of the correct estimation of ΔG^{**} and of the work terms, we decided to investigate reaction 8 at $\mu = 0.010$ M and 25.0 °C. This reaction was

$$\mathrm{Mo(CN)_8^{3-} + Fe(CN)_6^{4-} \rightarrow Mo(CN)_8^{4-} + Fe(CN)_6^{3-}} \qquad (8)$$

previously investigated at 0.50 M H_2SO_4,[15] whereas in the present study a lower ionic strength was chosen. Moreover, with $w_{21} = w_{12}$, then $\Delta G^\circ{}_{12}' = \Delta G^\circ{}_{12}$. In order to estimate ΔG^{**} for the two reactants, their reactions with benzenediols were also investigated.

Experimental Section

Reagents. Octacyanomolybdate(IV) was prepared according to the described procedure[16] and the corresponding Mo(V) derivative was obtained by electrooxidation. All the other chemicals were of high quality and were used without further purification. Doubly distilled water was used.

Procedure. The oxidation of benzenediols was followed at 390 nm for $Mo(CN)_8^{3-}$ (ϵ 1.3×10^3 M^{-1} cm^{-1}) and at 420 nm for $Fe(CN)_6^{3-}$ (ϵ 1.0×10^3 M^{-1} cm^{-1}) with a Durrum-Gibson stopped-flow spectrophotometer. The experimental conditions are given in Tables I and II. The reaction rate of eq 8 was followed at 245 nm under second-order conditions. Plots of $\ln\{(b_0 - x)/(a_0 - x)\}$ vs. time, where a_0 and b_0 are $[Mo(CN)_8^{3-}]_0$ and $[Fe(CN)_6^{4-}]_0$, respectively, were linear

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