Fixing Carbon Dioxide with Copper: Crystal Structure of [LCu(μ-C_2O_4)CuL][Ph_4B]$_2$ (L = *N*,*N*′,*N*″-Triallyl-1,4,7-triazacyclononane)

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Introduction

Carbon dioxide is an abundant synthon for carbon-containing compounds.[1] There is, therefore, considerable interest in the activation[2−4] of CO_2 to form C−C bonds. The symmetric coupling of two CO_2 molecules to form the oxalate anion may be considered the simplest CO_2 coupling reaction, and though this form of coupling is readily accomplished electrochemically,[5−7] only three cases have been reported of metal complexes effecting the reductive coupling of CO_2 to give oxalate.

In two of the cases[8,9] ($Cp_2Ti^{III}(CH_2)_3NRCH_2CH_2NR(CH_2)_3$-$Ti^{III}Cp_2$ and $(Me_5Cp)_2Sm^{II}(THF)_2$) the reductant is clearly the low-valent metal ion, the resulting oxalate complexes being Cp_2-$Ti(\mu$-$C_2O_4)TiCp_2$ and $(Me_5Cp)_4Sm_2(\mu$-$C_2O_4)$, respectively. In the third case[10] the reducing agent is not obvious, the product being polymeric $\{[Ln_2(C_2O_4)_3(H_2O)_6]\cdot 3H_2O\cdot 0.5HNO_3\}_n$. In all three cases the initial activation of the CO_2 is presumably due to coordination to the relatively hard lanthanide or Ti^{III} centers. To the best of our knowledge, there is no report of reductive coupling of CO_2 caused by late-transition metal ions and in particular by “soft” Cu^I.

Results and Discussion

[LCu(μ-C_2O_4)CuL][Ph_4B]$_2$ (**1**) (L = *N*,*N*′,*N*″- triallyl-1,4,7-triazacyclononane) was originally prepared by chance as a byproduct of the synthesis of [LCu(μ-OH)CuL][BPh_4]$_2$ by aerial oxidation of CuI, L, and $NaBPh_4$. To speed up the oxidation, exhaled air was blown into the reaction vessel. Upon workup of the blue-green reaction mixture, **1** was isolated as blue prisms from $MeNO_2$ solution. The presence of $[LCu(\mu$-$C_2O_4)CuL]^{2+}$ can readily be established in reaction products by observation of a very strong band at 1660 cm^{-1} in the IR spectrum due to bridging oxalate. A series of experiments showed that both CO_2 and a trace amount of water were required for reaction.

On the assumption that the active species was the bicarbonate anion, the reaction of CuI, L, and $CsHCO_3$ in deoxygenated MeOH was investigated. In the presence of L, CuI dissolves in deoxygenated MeOH to give a pale yellow solution, which is stable for several days under dinitrogen. Upon addition of $CsHCO_3$ in deoxygenated MeOH, the solution turned pale blue over about an hour. The methanol solvent was removed and the Cu(II) complex was purified by column chromatography using a silica column and acetonitrile as the eluant. A slow moving yellow band separated from the absorbed complex and was discarded. The complex was stripped from the column using methanol/nitromethane/2 M NH_4Cl (7:1:2) and isolated as the $[BPh_4]^-$ salt. Recrystallization from nitromethane produced small blue prisms of [LCu(μ-C_2O_4)Cu][Ph_4B]$_2$ (**1**) of crystallographic quality.

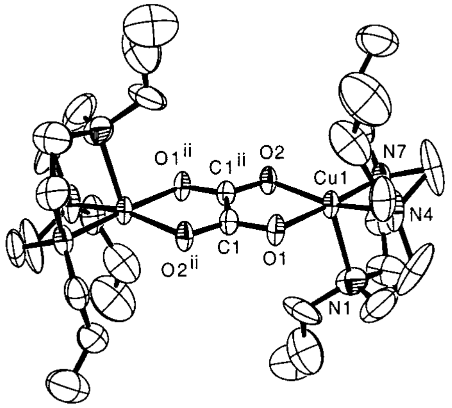

Figure 1. Ortep for Windows plot of the cation of [LCu(μ-C_2O_4)-CuL][BPh_4]$_2$ (**1**) with thermal ellipsoids at the 30% level. Important bond lengths (Å) and angles (deg) are as follows: Cu(1)−O(2), 1.982(3); Cu(1)−O(1), 1.995(3); Cu(1)−N(1), 2.162(5); Cu(1)−N(4), 2.008(4); Cu(1)−N(7), 2.016(4); C(1)−C(1)^i, 1.512(8); C(1)−O(1), 1.251(5); C(1)−O(2)^i, 1.252(5); O(1)−Cu(1)−O(2), 83.31(11); N(4)−Cu(1)−N(7), 87.19(16); N(1)−Cu(1)−N(4), 87.1(2); N(1)−Cu(1)−N(7), 85.27(17); O(1)−C(1)−O(2)^i, 126.3(4).

The structure of the cation of **1** is shown in Figure 1, along with important bond lengths and angles. The Cu atom is square pyramidal with the base being formed by two N atoms of the ligand and two O atoms of the bridging oxalate. Coordination of a sixth ligand is prevented by the proximity of the alkene arms. The Cu−Cu distance is 5.205 Å. There are a large number of structures (38 in the Cambridge database) of Cu dimers with amine ligands and a bridging oxalate ion. The Cu−Cu distance in **1** is within the range covered by these structures, and the dimensions of the oxalate anion are unexceptional.

The magnetic moment of **1** has been obtained over the temperature range 4.2−325 K. As expected, it is antiferromagnetic ($J = -274$ cm^{-1}). This value is in the range expected[11] for a square pyramidal Cu(II) center in which the four atoms making up the square plane have the strongest interaction with the Cu ion. The antiferromagnetic coupling is slightly smaller than that found in the $[tmen(H_2O)Cu(\mu$-$C_2O_4)Cu(H_2O)tmen]^{2+}$ cation ($J = -384.5$ cm^{-1}).[11]

The mechanism of the reaction must remain speculative. It seems reasonable, however, to postulate a mechanism in which the bicarbonate anion reacts with $[LCu^I]^+$, giving $[LCu^I(HCO_3)]$. This complex then undergoes internal electron transfer to give the intermediate $[LCu^{II}(HCO_3^{\bullet -})]^+$, which can then lose an

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$[OH]^-$ ion and dimerize to give **1**. The liberated hydroxide will form water (if the reactants are CO_2 and H_2O) or CsOH (if $CsHCO_3$).

Experimental Section

Synthesis of [LCu(μ-C_4O_4)CuL][Ph_4B]$_2$ (1). (a) From CO_2. A Schlenk tube equipped with a magnetic stirring bar was charged with CuI (330 mg, 1.32 mmol) suspended in methanol (30 mL). Tetraphenylboron sodium (453 mg, 1.32 mmol) was added to the suspension followed by *N*,*N*′,*N*″-triallyl-1,4,7-triazacyclononane (253 mg, 1.32 mmol) in methanol (10 mL) and the mixture was stirred under nitrogen for 0.5 h. Carbon dioxide was passed through the solution, which gradually changed from pale yellow to blue-green over a period of 2 h. The CO_2 was bubbled through overnight to ensure complete reaction. The solvent was removed under reduced pressure and the resulting solid recrystallized from $MeNO_2$ to give blue crystals of **1**. Yield: 199 mg (21%).

(b) From $CsHCO_3$. The same weights of CuI, BPh_4, and L were used but instead of passing CO_2 gas, a solution of $CsHCO_3$ (270 mg, 1.39 mmol) in MeOH was added. The yellow solution turned blue over 1−2 h. After removal of the solvent, the complex was purified by chromatography on silica using methanol/nitromethane/2 M NH_4Cl (7:1:2) as the eluant and isolated as the $[BPh_4]^-$ salt. Recrystallization from $MeNO_2$ yielded 473 mg (53%) of **1**. Anal. Calcd for $C_{80}H_{94}Cu_2B_2N_6O_4$: C, 71.05; H, 7.01; N, 6.21. Found: C, 70.85; H, 6.96; N, 6.27.

Crystallography. Details of the data collection procedures are given in Table 1. Data were collected in bisecting mode on an Enraf-Nonius TurboCAD4, running under CAD4-Express software, using graphite monochromated X-radiation (λ = 0.71073 Å). Precise unit cell dimensions were determined by refinement of the setting angles of 25 high-angle reflections, which were flagged during data collection. Standard reflections were measured every 2 h during data collection, and no significant variation in intensities was noted. Lorentz-polarization corrections were then applied to the reflection data. Psi scans indicated that no absorption corrections were necessary. The structure was solved by direct methods (SIR97).[12] All non-H atoms were allowed anisotropic thermal motion. Aliphatic CH hydrogen atoms were included at calculated positions, with C−H = 0.96 Å, and were refined with a riding model and with U_{iso} set to 1.2 times that of the attached C atom.

Table 1. Crystallographic Data for **1**

empirical formula	$C_{80}H_{94}Cu_2B_2N_6O_4$
formula weight	1352.31
cryst. syst.	triclinic
space group	$P\bar{1}$
a/Å	11.3469(10)
b/Å	11.7724(13)
c/Å	15.516(3)
α/deg	105.789(12)
β/deg	99.798(11)
γ/deg	110.295(7)
V/Å^3	1788.5(4)
Z	1
T/K	292(2)
D_c/g cm^{-3}	1.256
μ(Mo Kα)/mm^{-1}	0.649
$R^a(I > 2\sigma I)$	0.0625
$R_w{}^b(I > 2\sigma I)$	0.1564

^{a} $R = \sum(|F_o| - |F_c|)/\sum(F_o)$. ^{b} $R_w = \{\sum(w(F_o{}^2 - F_c{}^2)^2)/\sum(w(F_o{}^2)^2\}^{1/2}$.

Refinement (SHELXL97)[13] was by full-matrix least-squares on F^2. The weighting scheme $w = [\sigma^2(F_o)^2 + (AP)^2]^{-1}$ where $P = [F_o{}^2/3 + 2F_c{}^2/3]$ was used, with $A = 0.089$. Counting statistics were used to estimate $\sigma(F_o)^2$. Neutral atom scattering factors, coefficients of anomalous dispersion, and absorption coefficients were obtained from ref 14. All calculations were carried out using the WinGX package[15] of crystallographic programs. The structural diagram was drawn using Ortep for Windows.[16]

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of [LCu(μ-C_2O_4)CuL]-[Ph_4B]$_2$ (**1**). This material is available free of charge via the Internet at http://pubs.acs.org.

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