Figure 2. Ligand field spectrum of V(II) in CsCaCl₃ in the 5000–25 000-cm⁻¹ region. The inset in the upper right corner shows an expanded view of the high-energy portion of the second band at 77 K.

Table II. Spectral Data for the Ligand Field Spectrum of V(II) in CsCaCl₃

Assignment	Temp, K	Oscillator strength (f)	Energy, cm⁻¹ Obsd	Energy, cm⁻¹ Calcd^a
$^4A_{2g} \rightarrow {}^4T_{2g}$	296	3.2×10^{-5}	7 100	
	77	2.2×10^{-5}	7 200	7 200
$^4A_{2g} \rightarrow {}^4T_{1g}(F)$	296	8.4×10^{-5}	11 300	
	77	5.5×10^{-5}	11 700	11 620
$^4A_{2g} \rightarrow {}^2T_{1g}$	296			
	77		12 810	12 240
$^4A_{2g} \rightarrow {}^4T_{1g}(P)$	296	8.9×10^{-5}	18 700	
	77	4.9×10^{-5}	19 100	19 130

^{a} Calculated values were obtained from the spectral parameters $Dq = 720$, $B = 610$, and $C = 2500$ cm⁻¹.

out in order to obtain a quantitative fit of the observed transition energies. The assignments and results of the calculations are presented in Table II. The calculated energies were obtained from the crystal field matrices for a d³ system given by Tanabe and Sugano.⁷ The value of the crystal field parameter, Dq, was taken from the energy of the first absorption band ($^4A_{2g} \rightarrow {}^4T_{2g}$; $E = 10Dq$). The interelectronic repulsion parameters, B and C, were varied until a good fit between the observed and calculated energies was obtained. The fit of the spin-allowed bands is quite good while the agreement between the observed and calculated energy of the spin-forbidden, $^4A_{2g} \rightarrow {}^2T_{2g}$, transition is noticeably poorer. The values of B and C are quite similar to those obtained by Smith in an analysis of the spectrum of VCl₂.⁸ It should be pointed out that we have obtained the transition energies from the band maxima rather than from the position of the 0–0 transition. (This seems to be a reasonable procedure since the spectrum shows no resolved vibronic structure.) Thus, the actual value of Dq must be somewhat smaller than that used in our calculations.

The oscillator strengths of the three spin-allowed transitions are typical of those of d–d transitions in octahedral complexes. The intensities of all three bands decrease noticeably when the crystal is cooled from room to liquid nitrogen temperature (see Figure 2 and Table II). This decrease in intensity, especially in the low-energy portion of each of the bands, is characteristic of a vibronic intensity mechanism. The one spin-forbidden transition that is observed most likely becomes allowed by "borrowing" intensity from the nearby $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transition.

The ligand field spectrum of V(II) in CsCaCl₃ differs from those of pure V(II) salts such as VCl₂⁸,⁹ and KVCl₃¹⁰ in two notable respects. The Dq value for V(II) in CaCaCl₃ is about 200 cm⁻¹ smaller than those of the pure salts. This is consistent

with the argument presented earlier that the CsCaCl₃ lattice forces the V(II) ion into an environment which has greater than normal metal–chlorine separations. The other significant difference is that the spectra of VCl₂ and KVCl₃ contain a number of fairly intense spin-forbidden bands which do not appear in the spectrum of V(II) in CsCaCl₃. These bands are made allowed by the exchange interactions which take place between V(II) ions.⁸,¹⁰ Since the V(II) ions in the doped CsCaCl₃ crystals are present in low concentrations, there are no significant exchange interactions. Thus, the spin-forbidden bands do not appear.

In summary, it appears that the spectroscopic properties of V(II) in CsCaCl₃ are consistent with those expected of a perfectly octahedral VCl₆⁴⁻ complex which has somewhat longer than normal vanadium–chlorine distances.

Registry No. CsVCl₃, 59389-02-5; CsCaCl₃, 12323-36-3; VCl₆⁴⁻, 28659-55-4.

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Complex Formation of Copper(I) Perchlorate with Ethylene or Carbon Monoxide in Water and Isolation of Related Complexes¹

Tetsuya Ogura

It is well-known that a solution containing a copper(I) salt absorbs alkenes² and carbon monoxide²,³ and that ethylene at high pressure is absorbed by solid copper(I) chloride forming an unstable complex.³⁻⁵

Recently, Kochi and his collaborators synthesized very stable olefinic complexes of copper(I) trifluoromethanesulfonate⁶⁻⁸ and they used the complexes as catalysts for some photochemical reactions of alkenes.⁹,¹⁰

Aquated copper(I) perchlorate is generated by a reduction of copper(II) perchlorate with metallic copper¹¹,¹² or a metal ion such as hexaammineruthenium(II),¹² aquated chromium(II),¹³,¹⁴ or aquated vanadium(II).¹⁴ In the absence of a suitable ligand, the copper(I) ion disproportionates to copper(II) ion and metallic copper.¹² However, copper(II) ion in an aqueous solution is reduced to a stable complex, in the presence of some olefinic ligand, by contacting it with a reducing agent¹⁵⁻¹⁹ or by electrolysis of the ion.¹⁵,²⁰,²¹

In the present work we show that a copper(I)–ethylene or –carbon monoxide complex in an aqueous solution disproportionates into copper metal and copper(II) ion when the ligand is removed by pumping. The complex is re-formed by adding the same gas to the reaction mixture. The unstable and explosive complexes which are responsible for the reaction

Table I. Determination of the Equilibrium Constants for Eq 3 at Various Temperatures[a]

	L = C_2H_4			
Temp, °C	1.8	15.8	31.3	39.6
ΔE, mmol	0.4077	0.3250	0.2362	0.1986
Press., mmHg	28.62	4.488	6.341	7.115
$10^{-5}K$, M^{-1}	16.87	7.740	3.342	2.199
	L = CO			
Temp, °C	4.0	14.9	21.9	32.6
ΔE, mmol	0.5226	0.4892	0.4625	0.4110
Press., mmHg	12.44	19.89	25.55	36.27
$10^{-8}K$, M^{-1}	25.28	7.590	4.370	1.642

[a] [Cu^{2+}] = 0.028 13 M; V = 10.00 ml.

were isolated and characterized.

Results and Discussion

Complex Formation in Solution. A suspension of copper metal in an aqueous copper(II) perchlorate solution was prepared in a vacuum system. When ethylene was introduced and the solution stirred magnetically, absorption of the gas began and the blue color of the copper(II) ion disappeared. At the end of the reaction, 1 mol of ethylene was found to combine with each copper(I) atom. On pumping out the gas phase, the ethylene was released from the solution, and copper(II) and copper metal were produced. The quantity of ethylene expelled and the amount of copper(II) re-formed are quantitatively the same as those used as starting materials. Thus, the reaction can be written as

$$Cu + Cu^{2+} + 2C_2H_4 = 2Cu(C_2H_4)^+ \qquad (1)$$
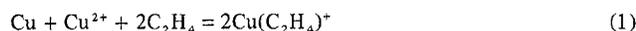
A similar reaction was observed employing carbon monoxide instead of ethylene

$$Cu + Cu^{2+} + 2CO = 2Cu(CO)^+ \qquad (2)$$

If $K(L) = [Cu(L)^+]^2/([Cu^{2+}][L]^2)$ represents the equilibrium constant for eq 1 and 2 (L = C_2H_4 or CO), then the value of $K(L)$ is given by

$$K(L) = (\Delta E/V)^2/([Cu^{2+}]_0 - \Delta E/2V)(\alpha P)^2 \qquad (3)$$

Here ΔE is the number of moles ligand absorbed in the formation of the complex, V is the volume of the solution, P is the ligand pressure, $[Cu^{2+}]_0$ is the initial molarity of copper(II), and αP is solubility of a ligand in water. The α values were selected from ref 22.

Measurement of ΔE and P at various temperatures in a constant-temperature bath enabled the value of $K(L)$ (M^{-1}) to be estimated. These values are summarized in Table I. The temperature dependences of the constants for ethylene and carbon monoxide were obtained by the least-squares treatment of the log K vs. $1/T$ data

$$\log K(C_2H_4) = 2.187 \times 10^3/T - 2.010 \pm 0.033 \qquad (4)$$

$$\log K(CO) = 3.489 \times 10^3/T - 3.177 \pm 0.039 \qquad (5)$$

where the uncertainties are standard deviations.

Isolation of the Complexes. All of the isolated complexes are explosive, but it was difficult to predict the conditions under which a sample would explode. Sometimes a complex did not explode even if it was placed on an iron plate and hit by a hammer; sometimes it exploded when merely stirred by a magnetic stirring bar covered with Teflon. On one occasion when 10 mg of a complex stored in a glass reaction vessel (10 ml) exploded, fine pieces of glass were blown farther than 10 m. This explosiveness precluded a more careful study on properties.

Two types of complexes were isolated: CuL(H$_2$O)$_2$ClO$_4$ (L = carbon monoxide, ethylene, or a half molecule of allene),

Table II. Ir Absorption Bands of the Free Ligands and Their Complexes of Copper(I) Perchlorate

	ν(C=C) or ν(CO)		ν(Cl—O)
	Free	Complex	Complex
CO	2143[a]	2130	1100 vs, 1000 sh, s
CH$_2$=CH$_2$	1623[b]	1540(?) vvw	1100 vs, 1000 sh, s
CH$_2$=C=CH$_2$	2000[c]	1658 m	1100 vs, 1000 sh, s
CH$_2$=CHCH=CH$_2$	1599[d]	1507	1100 vs, 1000 sh, s

[a] See ref 23, p 78. [b] B. L. Crawford, Jr., J. E. Dancaster, and R. G. Inskeep, *J. Chem. Phys.*, **21**, 678 (1953). [c] J. Blanc, C. Brecher, and R. S. Halford, *ibid.*, **36**, 2654 (1962). [d] R. K. Harris, *Spectrochim. Acta*, **20**, 1129 (1964).

which are colorless and transparent crystals and show a definite melting point; Cu$_2$L$_2$(H$_2$O)$_3$(ClO$_4$)$_2$ (L = carbon monoxide or a half molecule of butadiene), which are white powders and do not have a definite melting point.

The ^{1}H NMR signal of ethylenic protons shifts from 5.34 to 4.53 ppm by coordination, and that of the allenic ones, from 4.67 to 4.20. The complex multiplet in the butadiene spectrum shifts to a higher magnetic field by about 0.8 ppm on complex formation. The addition of excess ligand to a solution of complex shows no absorption band of free ligand, but the signal shifts to the free ligand side without broadening, indicating rapid ligand exchange.

Table II shows the infrared absorption bands of the free ligands and their complexes with copper(I) perchlorate. The Cu(CO)(H$_2$O)$_2$ClO$_4$ and Cu$_2$(CO)$_2$(H$_2$O)$_3$(ClO$_4$)$_2$ complexes show the same ir absorption except for a change of relative intensity attributable to the extra water molecule. Coordination of the double bond of an alkene or of carbon monoxide is also shown by the shift to lower frequency of the C=C or CO stretch.

The ir spectra of the perchlorate ion are interesting. The Cl–O stretch of the complexes in melts, as well as that of the solid complexes in Nujol, has a distinct shoulder around 1000 cm^{-1}. This observation shows that the perchlorate anion in a melt has a symmetry less than T_d; the oxygen atom of the perchlorate presumably coordinates weakly to the copper.[23]

It is well-known that acetone dimethyl ketal reacts with water[24,25]

$$(CH_3)_2C(OCH_3)_2 + H_2O = (CH_3)_2CO + CH_3OH \qquad (6)$$
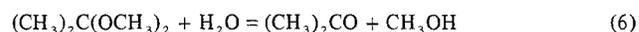
Since the equilibrium constant of the reaction in methanol at 25 °C is reported[25] as 2.5 × 10^3, the equilibrium lies to the right. Moreover, the reaction is catalyzed by a general acid–base including copper(II) ion. Therefore, any uncoordinated water molecules might be removed from a complex by preparing it in a 1:1 methanol–acetone dimethyl ketal mixture; however, the elemental analysis value of the complexes did not change by this treatment.

Consequently, the copper atom in CuL(H$_2$O)$_2$ClO$_4$ may be surrounded tetrahedrally by one L, two oxygen atoms from water, and one oxygen from perchlorate.

Discussion

Endicott and Taube[12] measured the equilibrium constant of eq 7 as $K' = [Cu^+]^2/[Cu^{2+}] = 1 \times 10^{-6}$ M^{-1} at 25 °C.

$$Cu^{2+} + Cu = 2Cu^+ \qquad (7)$$

Combining eq 1 and 7, we derive

$$Cu^+ + C_2H_4 = Cu(C_2H_4)^+ \qquad (8)$$

Assuming $K_f = [Cu(C_2H_4)^+]/([Cu^+][C_2H_4])$ to be the equilibrium constant for eq 8, the value K_f is given by $K_f = (K/K')^{1/2}$, where K and K' are the equilibrium constants for eq 1 and 7, respectively. Since $K(C_2H_4) = 4.6 \times 10^5$ and $K(CO) = 3.3 \times 10^8$ M^{-1}, as calculated by eq 4 and 5, the

formation constants, K_f, for the copper(I) complexes with ethylene and carbon monoxide are evaluated as 7×10^5 and 2×10^7 M^{-1}, respectively.

The estimated formation constant for the copper(I)–ethylene complex at 25 °C is greater by 14 times than that of the allyl alcohol.[15] This fact indicates that the oxygen atom does not take part in a bond formation in aqueous solution; in contrast, the oxygen coordinates to the copper atom in the solid state.[16] It is noteworthy that the compositions of these complexes are almost the same: Cu(CH$_2$=CHCH$_2$OH)(H$_2$O)ClO$_4$ and Cu(CH$_2$=CH$_2$)(H$_2$O)$_2$ClO$_4$.

Experimental Section

Measurements of Equilibrium Constants. The equilibrium constants of the complex formation with ethylene or carbon monoxide were determined at various temperatures. A mixture of copper powder and an aqueous solution of copper(II) perchlorate (0.02–0.05 M) was kept in vacuo in a constant-temperature bath. The ionic strength of the solution was adjusted to 1.0 by addition of sodium perchlorate. Ethylene and carbon monoxide were stored in the other side of the system and the pressure was measured with a mercury manometer by use of a cathetometer. The stopcock was opened to introduce the ethylene or carbon monoxide to the reaction vessel containing the copper(II) solution and copper. The reaction mixture was stirred for 1 or 2 days; then most of the gas phase was expanded into a space of known volume to measure the pressure. The gas phase was then expelled from the system for the purpose of diluting any possible impurities. The equilibrium pressure was measured 1 day later, at which time no pressure change had been observed.

Synthesis of the Ethylene Complex. Ethylene gas was passed through a reaction vessel containing copper(I) perchlorate hexahydrate (0.7 g), copper powder (1 g), and a stirring bar, until all of the air was replaced by ethylene. Methanol (2 ml) was then added by use of a microsyringe through a serum cup. The reaction mixture was stirred vigorously at room temperature while the ethylene flow was continued. The blue solution turned colorless within 1 h, indicating the completion of the reaction. The solution was filtered through a sintered-glass funnel by use of ethylene pressure. The solvent was removed by a stream of ethylene at room temperature. Colorless crystals, mp 30 °C, were obtained.

The complex was weighed in an atmosphere of ethylene and was connected to a gas buret. The ligand was freed by addition of a 0.1 N NaOH solution. The evolved gas was measured and identified as ethylene by use of ir. The precipitate was filtered and used for gravimetric analysis of copper as the cupferron complex. The filtrate was analyzed for perchlorate anion as nitron perchlorate.

Anal. Calcd for Cu(C$_2$H$_4$)(H$_2$O)$_2$ClO$_4$: Cu, 28.0; C$_2$H$_4$, 12.3; ClO$_4$, 43.8. Found: Cu, 27.9; C$_2$H$_4$, 12.2; ClO$_4$, 43.9.

Synthesis of the Allene Complex. In a vacuum system, allene was transferred to a reaction vessel containing a methanol solution of copper(II) perchlorate and copper powder. The mixture was stirred vigorously for 1 h. Excess copper was filtered off and the filtrate was evaporated in vacuo. The white powder remaining was analyzed as described above.

Anal. Calcd for Cu$_2$(C$_3$H$_4$)(H$_2$O)$_3$(ClO$_4$)$_2$: Cu, 30.0; C$_3$H$_4$, 9.53; ClO$_4$, 47.4. Found: Cu, 30.0; C$_3$H$_4$, 9.73; ClO$_4$, 47.3. The mole ratio of water to allene, as evaluated from the ^{1}H NMR spectra of the complex, was consistent with the calculated composition.

The Butadiene Complex. The copper(I) perchlorate complex of butadiene (mp 74 °C) was synthesized similarly to the allene complex.

Anal. Calcd for Cu$_2$(C$_4$H$_6$)(H$_2$O)$_4$(ClO$_4$)$_2$: Cu, 28.1; C$_4$H$_6$, 12.0; ClO$_4$, 44.0. Found: Cu, 28.0; C$_4$H$_6$, 11.9; ClO$_4$, 44.4. The ^{1}H NMR spectra showed that the mole ratio of water to butadiene was 4:1.

The Carbon Monoxide Complexes. The colorless crystalline complex (mp 10 °C) was synthesized similarly to the ethylene complex.

Anal. Calcd for Cu(CO)(H$_2$O)$_2$ClO$_4$: Cu, 28.0; CO, 12.3; ClO$_4$, 43.8. Found: Cu, 27.5; CO, 12.5; ClO$_4$, 43.6.

The white powdery complex was obtained by keeping Cu(CO)(H$_2$O)$_2$ClO$_4$ at 70 °C for 10 h under a nitrogen flow.

Anal. Calcd for Cu$_2$(CO)$_2$(H$_2$O)$_3$(ClO$_4$)$_2$: Cu, 29.2; CO, 12.9; ClO$_4$, 45.6. Found: Cu, 29.4; CO, 12.8; ClO$_4$, 45.9.

NMR Measurements. The samples for ^{1}H NMR measurements were prepared in the vacuum system. The NMR spectra were recorded with a 60-MHz spectrometer, Model JNM 3H60, of the Japan Electron Optics Laboratory, Ltd.

Ir Spectra. The ir spectra were obtained with a Hitachi EPI-G31. The spectrum taken in an NaCl cell was compared with that taken in a polyethylene film, since some of the complexes easily exchanged the anion. All of the samples were prepared in a nitrogen atmosphere.

Registry No. Cu(C$_2$H$_4$)(H$_2$O)$_2$ClO$_4$, 59738-25-9; Cu$_2$(C$_3$-H$_4$)(H$_2$O)$_3$(ClO$_4$)$_2$, 59811-73-3; Cu$_2$(C$_4$H$_6$)(H$_2$O)$_4$(ClO$_4$)$_2$, 59738-26-0; Cu(CO)(H$_2$O)$_2$ClO$_4$, 59729-20-3; Cu$_2$(CO)$_2$(H$_2$-O)$_3$(ClO$_4$)$_2$, 59811-74-4.

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Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Equilibria of Ethylenediamine-N,N,N',N'-tetrakis(methylenephosphonic) Acid with Cu(II), Ni(II), Co(II), Zn(II), Mg(II), Ca(II), and Fe(III) Ions in Aqueous Solution

Ramunas J. Motekaitis, Ichiro Murase, and Arthur E. Martell*

In a preliminary reinvestigation[1] of the complexing properties of ethylenediamine-N,N,N',N'-tetrakis(methylene-phosphonic) acid (EDTPO, H$_8$L), it has been shown that previous methods of preparation[2-6] were not entirely satisfactory and therefore the results reported in earlier work contain varying degrees of inaccuracy, depending on the purity of this interesting and important ligand. The analytically pure sample of EDTPO used in this investigation was obtained unambiguously through the quantitative mercuric chloride oxidation of the previously described well-characterized intermediate, ethylenediamine-N,N,N',N'-tetrakis(methylene-