X-Ray data were obtained on a Norelco unit using a 114.59-mm diameter camera. All samples were contained in sealed glass capillaries and the exposure conditions were: molybdenum tube, zirconium filter, 45 kv, and 18 ma for 4 hr. Relative intensities were estimated visually. Absorption spectra were obtained on a Beckman DU spectrophotometer using matched 1-cm quartz cells.

Discussion

The formula of the sodium salt, $Na[Cr(en)F_4]\cdot H_2O$, is consistent with that of a compound derived from the double complex, $[Cr(en)_2F_2][Cr(en)F_4]\cdot H_2O$. Since the sodium salt was isolated as a hydrate, this would indicate the complex anion is the group which contains the water of hydration in the double complex.

The formation of the red cationic species in the ion-exchange experiments, the presence of sodium fluoride in the final product, and the low equivalent weights all appear to be due to hydrolysis of the anion during the exchange reactions. Previous work in this laboratory has shown aqueous solutions of $[Cr(en)_2F_2]I$ to be sufficiently stable toward hydrolysis not to cause these effects.

The molar absorptivities of $Na[Cr(en)F_4]$ at the wavelengths of maximum absorption are roughly half that of *cis*-$[Cr(en)_2F_2]I$ at its maximum. The value at 572 mμ (34.0 M^{-1} cm^{-1}) agrees with the 32.9 M^{-1} cm^{-1} found by House and Garner for the corresponding ammonium salt; however, the values at the "blue" peak differ by 4 units with the value obtained in this investigation the larger.

The reaction of sodium tetrafluoroethylenediaminechromate(III) monohydrate with excess dry ethylenediamine at 150° produces the double complex, *cis*-difluorobis(ethylenediamine)chromium(III) tetrafluoroethylenediaminechromate(III). This reaction can be described by the equation

$$2Na[Cr(en)F_4]\cdot H_2O + en \longrightarrow [Cr(en)_2F_2][Cr(en)F_4] + 2NaF + 2H_2O$$

The double complex has a very low solubility in anhydrous ethylenediamine and this would appear to be one reason the reaction does not proceed beyond this point.

If the reaction of the sodium salt with ethylenediamine followed simple statistics the reaction product should contain 80% *cis* and 20% *trans* isomer. However, it was not possible to detect the presence of any *trans* isomer in the product. One possible explanation for the lack of the *trans* isomer is that the *trans* product isomerized during the reaction.

Another explanation is based on the fact that the fluoro groups are not equivalent in the starting material. In the complex anion two of the fluoro ligands are *trans* to each other and the other pair is *cis* to each other but *trans* to the nitrogen of the ethylenediamine. Hence, these ligands are not necessarily equally labile. If rearrangement does not occur during reaction, then the replacement of two fluoro ligands by ethylenediamine involves one fluoro group from each nonequivalent pair.

The reaction proceeds in the same fashion at steam bath temperatures so the more drastic conditions employed in the bomb reaction are not responsible for the nature of the final product. Hence, the same effect or combination of effects is operating in both cases.

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The 1,5-Cyclooctadiene Complex of Copper(I) Perchlorate

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Olefinic and acetylenic hydrocarbons are known to form complex compounds with copper(I) chloride and copper(I) bromide.[1] A great deal of interest has recently been shown in the use of cyclic olefins as ligands in copper(I) complexes.[2-5] Methods for synthesizing a number of cyclic olefin complexes of CuCl and CuBr have been reported.[4]

The cyclic olefin complexes of CuCl and CuBr are not very stable. It has been noted[4] that the "relatively stable" ones may be stored at 0° in an inert atmosphere over calcium sulfate. This instability is probably due in part to the strong complexation of copper(I) by halide ions. Even in acetonitrile, a solvent which specifically solvates copper(I),[6] the over-all formation constant[7] of $CuCl_2^-$ is 10^{10}.[8] It is apparent, therefore, that in solution in a halide medium (and presumably in the solid state as well) halide ions compete very strongly with olefins for the copper(I) ligand sites.

We have succeeded in preparing the 1,5-cyclooctadiene (cyc) complex, $Cu(cyc)_2ClO_4$, of copper(I) perchlorate by electrolysis at copper electrodes of a solution containing copper(II) perchlorate and cyc in methanol. The cyc in solution stabilizes the +1 oxidation state of copper so that the reaction at the cathode is $Cu^{2+} + 2cyc + ClO_4^- + e = Cu(cyc)_2ClO_4\downarrow$ and the anode reaction is $Cu + 2cyc + ClO_4^- = Cu(cyc)_2ClO_4\downarrow + e$.

The complex is moderately soluble (*ca.* 5×10^{-3} M) in acetone. The voltammetric behavior of the compound was studied in this solvent in order to determine the formula and stability of the Cu(I)–cyc complex ion in acetone solution. The rotating platinum electrode was used for the voltammetric studies because

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the dropping mercury electrode gave erratic electrode behavior in the presence of the olefin.

Experimental Section

Absolute methanol was treated with magnesium activated with iodine and fractionally distilled. Acetone, Fisher reagent grade, was allowed to stand over Drierite for 2 weeks, decanted, and fractionally distilled. K & K 1,5-cyclooctadiene was used without further purification. Copper(II) perchlorate hexahydrate (G. F. Smith Chemical Co.) was dried *in vacuo* at 70° for 48 hr. Lithium perchlorate (G. F. Smith) was dried at 180°.

The voltammetric data were taken with a Sargent Model XV polarograph. The rotating platinum electrode was pretreated before each scan by allowing it to rotate for 3 min in (1) sulfuric acid–dichromate cleaning solution and (2) acidic 1 *M* $FeSO_4$.

The infrared spectra were taken with a Beckman Model IR7 infrared spectrophotometer (Nujol mull).

Preparation of the Complex.—A 20-cm length of copper wire, No. 18 gauge, was wrapped into a spiral of 1-cm o.d. This spiral was immersed in a solution of 5.0×10^{-2} *M* copper(II) perchlorate and 0.50 *M* 1,5-cyclooctadiene. A straight copper wire was placed inside the spiral. A source of variable dc voltage was applied across the two wires. The applied voltage was adjusted (1–2 v) so that the initial current was 20 ma and the electrolysis was allowed to proceed until the current had dropped to *ca.* 1 ma. Nitrogen was bubbled through the solution during the electrolysis. The product formed as well-defined crystals on both the cathode and the anode. The product was filtered on filter paper and was washed five times with dry ether followed by drying in a nitrogen stream.

The complex is remarkably stable. It may be exposed to the atmosphere indefinitely without noticeable decomposition. It is not affected by dilute HNO_3 or $HClO_4$ but dissolves completely in concentrated NH_3 with liberation of the olefin. Dilute NaOH forms a yellow precipitate with the complex with liberation of cyc. The organic material liberated by treatment with base was identified as 1,5-cyclooctadiene from its infrared spectrum. The compound may be heated to 180° without noticeable decomposition; above 180° it chars.

The compound was analyzed for copper by EDTA titration, for Cl by fusion with sodium peroxide followed by titration of chloride with $AgNO_3$,[8] and for carbon and hydrogen with an F & M carbon–hydrogen–nitrogen analyzer, Model 185. The presence of perchlorate was confirmed by adding tetraphenylarsonium chloride to an ammoniacal solution of the complex and observing the $(C_6H_5)_4AsClO_4$ precipitated. *Anal.* Calcd for $Cu(cyc)_2ClO_4$: Cu, 16.75; C, 50.67; H, 6.38; Cl, 9.35. Found: Cu, 16.68; C, 50.85; H, 6.54; Cl, 9.32.

Results and Discussion

The compound $Cu(cyc)_2ClO_4$ differs from the cyc complexes of CuCl and CuBr,[4] Cu(cyc)Cl and Cu(cyc)Br, in that it is quite stable and has two olefin molecules per copper(I) rather than one. These two observations lend support to the idea that the halide ions compete very strongly with the olefin for the copper(I) ligand sites.

The infrared spectrum of the complex shows that the 1660-cm^{-1} C=C band of cyc has been replaced by two bands at 1638 and 1595 cm^{-1}. It has been previously reported[9] that the C=C band in Cu(cyc)Cl appears at 1612 cm^{-1}. The presence of the two bands in $Cu(cyc)_2ClO_4$ may indicate that the C=C bonds in this compound are not all equivalent.

If copper(II) is not complexed appreciably by 1,5-cyclooctadiene, the following approximate equation describes the voltammetric behavior of the Cu(II)–Cu(I) and Cu(I)–Cu(0) couples in the presence of the olefin[10]

$$(E_{1/2})_c - (E_{1/2})_s = \pm 0.0591 \log \beta_p \pm (p)(0.0591) \log [\text{cyc}]$$

In the equation above $(E_{1/2})_s$ is the half-wave potential observed in the absence of ligand, β_p is the over-all formation constant of the complex species $Cu(cyc)_p{}^+$, and [cyc] is the olefin concentration. The terms on the right-hand side of the equation are positive for the Cu(II)–Cu(I) couple and negative for the Cu(I)–Cu(0) couple. The above equation provides a method of evaluating from a single plot both the ligand number and the formation constant of the complex copper(I) species. For the Cu(I)–Cu(0) couple a plot of $(E_{1/2})_c - (E_{1/2})_s$ *vs.* log [cyc] should have a slope of $-0.0591p$ and an intercept of $-0.0591 \log \beta_p$, whereas for the Cu(II)–Cu(I) couple the plot should have a slope of $+0.0591p$ and an intercept of $+0.0591 \log \beta_p$.

The half-wave potentials of the Cu(II)–Cu(I) couple were evaluated in mixtures of copper(II) and copper(I) (*ca.* 5×10^{-5} *F* in each) with concentrations adjusted such that the half-wave potentials of the composite anodic–cathodic waves occurred at zero current. The waves pass through zero current without inflection. This characteristic of the composite anodic–cathodic waves suggests that potential values near zero current are quite close to the reversible values.[7] The half-wave potentials obtained for the Cu(II)–Cu(I) couple are given in Table I.

TABLE I

HALF-WAVE POTENTIALS FOR THE Cu(II)–Cu(I) AND Cu(I)–Cu(0) COUPLES AT THE ROTATING PLATINUM ELECTRODE IN ACETONE CONTAINING 1,5-CYCLOOCTADIENE

[cyc], *M*	Log [cyc]	$(E_{1/2})_{II-I}$[a]	$(E_{1/2})_{I-0}$[b]	Log β_1
...	...	+0.509	+0.153	...
1.00×10^{-3}	−3.00	+0.593	...	4.4
1.00×10^{-3}	−3.00	...	+0.056	4.6
1.50×10^{-3}	−2.82	...	+0.045	4.6
2.50×10^{-3}	−2.60	...	+0.032	4.6
3.00×10^{-3}	−2.52	+0.621	...	4.4
4.00×10^{-3}	−2.40	...	+0.007	...
6.00×10^{-3}	−2.22	...	−0.017	...
1.05×10^{-2}	−1.98	...	−0.026	...
1.10×10^{-2}	−1.96	+0.648	...	4.3
3.10×10^{-2}	−1.51	+0.681	...	4.4
1.55×10^{-2}	−1.81	...	−0.052	...
8.10×10^{-2}	−1.09	+0.702	...	4.3

[a] Half-wave potential values for the Cu(II)–Cu(I) couple, volts *vs.* the aqueous saturated calomel electrode. [b] Half-wave potential values for the Cu(I)–Cu(0) couple, volts *vs.* the aqueous saturated calomel electrode.

A plot of $(E_{1/2})_c - (E_{1/2})_s$ *vs.* log [cyc] for the Cu(II)–Cu(I) couple is linear and has a slope of +0.059 giving a value of 1 for *p*. The value of log β_1 calculated from the Cu(II)–Cu(I) data is 4.4 ± 0.1.

Reversible waves for the reduction of copper(I) to copper(0) at the rotating platinum electrode were ob-

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tained only at ligand concentrations of 2.5×10^{-3} *F* or less and, therefore, only these current–voltage curves were used in calculating log β_1 from the Cu(I)–Cu(0) data. Over this rather limited concentration range the shift of $(E_{1/2})_c - (E_{1/2})_s$ *vs.* log [cyc] is −0.060 giving again a value of 1 for *p*. The combined behavior of the Cu(II)–Cu(I) and Cu(I)–Cu(0) couples indicates that Cu(II) is not complexed by the olefin in acetone. The value of log β_1 calculated from the Cu(I)–Cu(0) data is 4.6.

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Magnetic Studies with Copper(II) Salts. VIII. Vibrational Effects in the Singlet–Triplet Equilibrium of Copper(II) Acetate

By R. L. MARTIN

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The application of Van Vleck's equation[1] in the calculation of the temperature variation of the magnetic susceptibility of systems involving spin equilibria tacitly assumes that there is no difference between vibrational frequencies of the different spin states. The effect of neglecting this correction emerged in a recent investigation of the magnetic properties of iron(III) dithiocarbamates which lie at the $^6A_1$–$^2T_2$ crossover.[2] Although the temperature dependence of the magnetism did not conform exactly with the predictions of the Van Vleck equation, it was considered to be tractable when molecular vibrational partition functions were introduced into this equation.

The present note explores the consequences of introducing vibrational partition functions into the susceptibility equation for the copper(II) acetate dimer which involves singlet and triplet states in thermal equilibrium.[3] A noteworthy difference between this compound and the mononuclear iron(III) dithiocarbamates is that the singlet and triplet spin states originate in a metal-to-metal interaction rather than in changes of metal–ligand internuclear separation with electron configuration. Accordingly, the correction is likely to be significant only if the Cu–Cu vibration frequency differs appreciably between the singlet and triplet states.

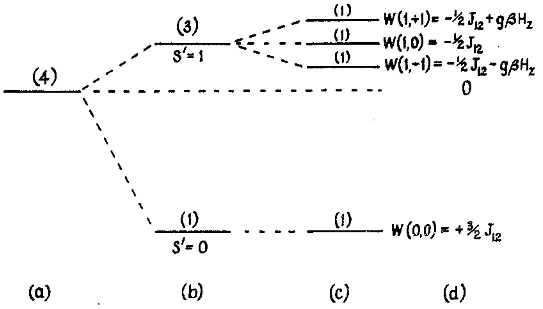

Figure 1.—(a) Lowest energy level of a system of two interacting Cu^{2+}–Cu^{2+} ions. (b) Splitting into a singlet ($S' = 0$) and a triplet ($S' = 1$) level due to spin–spin interaction, $V_{12} = -2J_{12}\hat{S}_1\cdot\hat{S}_2$. (c) Further splitting of the triplet in a magnetic field, *H*. (d) Energy levels, $W(S',M_{S'})$.

The anomalous temperature dependence of the magnetic susceptibility of the dimer is most simply described by assuming that the spin–spin interaction V_{12} between two copper atoms, 1 and 2, takes the form[1]

$$V_{12} = -2J_{12}\hat{S}_1\cdot\hat{S}_2 \tag{1}$$

where in magnetism theory J_{12} is an isotropic exchange interaction and $\hat{S}_1$ and $\hat{S}_2$ are spin operators for the two copper atoms. Ambiguities of interpretation have occasionally arisen because some authors[3–6] have preferred to write the exchange interaction in the form $V_{12} = +J_{12}\hat{S}_1\cdot\hat{S}_2$. The interaction expressed by eq 1 implies that if a pair of contiguous copper atoms have their electron spins parallel, there is an interaction energy of $-J_{12}$; if their spins are antiparallel, the interaction energy is $+J_{12}$. For copper(II) acetate, the trend of $\chi_M(T)$ data[3] confirms that J_{12} is negative so that the singlet state of the dimer lies lowest (Figure 1).

If an external homogeneous magnetic field *H* is applied along the *Z* axis, the Hamiltonian operator for the dimer is

$$\mathcal{H}_{12} = -2J_{12}\sum\hat{S}_1\cdot\hat{S}_2 - g\beta S'_Z H_Z \tag{2}$$

where $\hat{S}'_Z$ is the operator for the *Z* component of total spin. The eigenvalues of $\mathcal{H}_{12}$ are

$$W(S',M_{S'}) = -J_{12}[S'(S+1) - 2S(S+1)] - g\beta M_{S'}H_Z \tag{3}$$

For the molecule $[Cu_2(CH_3CO_2)_4(H_2O)_2]$, $S = 1/2$, $S' = 0$ or 1, and $M_{S'} = S', S' - 1$, or $-S'$, giving the manifold of spin levels shown in Figure 1; the energy difference between singlet and triplet states is $-2J_{12}$.

The variation with temperature of the magnetic susceptibility per mole of dimer is given simply by Van Vleck's formula[1]

$$\chi_M = \frac{2N\sum\limits_{S',M_{S'}}\dfrac{(W_{S'^{(1)},M_{S'}})^2}{kT}\exp(-W_{S'}{}^{(0)}/kT)}{\sum\limits_{S',M_{S'}}\exp(-W_{S'}{}^{(0)}/kT)} \tag{4}$$

where the superscripts refer to the order of the Zeeman displacements and each member of a degenerate set is counted individually. The summation (4) gives

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