Contribution from the Department of Chemistry,
University of the Witwatersrand, Johannesburg 2001, South Africa

Formation Constants of Copper(I) Chloride Complexes with *cis,cis*-1,5-Cyclooctadiene and Other Cyclic Olefins

Ilmarie Rencken and S. Walter Orchard*

Received July 16, 1985

Copper(I) chloride solutions in tetrahydrofuran develop an intense absorption band, with a peak in the 238–256-nm range, when *cis,cis*- or *cis,trans*-1,5-cyclooctadiene, *cis*- or *trans*-cyclooctene, or norbornadiene is added. The absorbances near the band maxima, as a function of olefin concentration, are consistent with the presence of a single absorbing complex, which is formulated as $(CuCl\cdot olefin)_2$. The calculated formation constants $K = [(CuCl\cdot olefin)_2]/[(CuCl)_2][olefin]^2$ strikingly illustrate the importance of a trans double bond in stabilizing the complexes. $K/L^2\ mol^{-2}$ (at 20 °C): 7800 (*cis,cis*-1,5-cyclooctadiene); 8.86×10^{12} (*cis,trans*-1,5-cyclooctadiene); 700 (*cis*-cyclooctene); 6.3×10^8 (*trans*-cyclooctene); 2800 (norbornadiene).

Introduction

The photochemical conversion of *cis,cis*-1,5-cyclooctadiene (*c,c*-COD) to tricyclo[3.3.0.0^{2,6}]octane in the presence of copper(I) chloride was discovered by Srinivasan[1] and has since been the subject of several mechanistic investigations.[2-4] It was initially proposed that photon absorption by free *c,c*-COD was the first step in the conversion,[1] but more recently we found evidence that implicated a preformed, ground-state complex of CuCl and the olefin as the primary light-absorbing species.[3] Furthermore, it appears that the isomers *cis,trans*-1,5-cyclooctadiene (*c,t*-COD) and possibly *trans,trans*-1,5-cyclooctadiene (*t,t*-COD) are intermediates in the reaction, the overall process thus involving two or more separate photochemical transformations.[2-4] In this paper we report measurements of some relevant CuCl·olefin formation constants that provide a quantitative basis on which to assess the above proposals.

Most reports of stability constants between copper(I) compounds and olefins refer to potentiometric or solubility studies in aqueous or alcoholic perchlorate media,[5] though results obtained by a gas chromatographic method have also been published.[6] The only reported stability constant involving copper(I) and any isomer of 1,5-cyclooctadiene refers to *c,c*-COD and $CuClO_4$ in acetone.[7] In connection with the photochemistry of mixtures of CuCl and *c,c*-COD, it would be more appropriate to obtain the relevant stability constants involving CuCl specifically in diethyl ether or methanol, the solvents used in previous homogeneous photolysis studies.[1,3,4] However, the solubility of free CuCl in diethyl ether is so low[8] that the use of this solvent is impractical. An ether that is better than diethyl ether as a solvent for CuCl is tetrahydrofuran (THF), and we therefore decided to employ this solvent in a UV spectroscopic study of selected CuCl–olefin complexes. The intense absorption spectra of the complexes used ensure the practicability of the spectroscopic method, even at very low concentrations of copper(I).

We report here studies involving CuCl with *c,c*-COD, *c,t*-COD, *cis*- and *trans*-cyclooctene (*c*-CO and *t*-CO), and norbornadiene (NBD). Owing to the instability of *t,t*-COD, we abandoned attempts to use it in our study; we included *c*-CO and *t*-CO because we felt that they would provide an interesting comparison with *c,c*-COD and *c,t*-COD. NBD was also studied because of the interest in Cu(I)–NBD photochemistry as a model system for the chemical storage of solar energy.[9]

The data presented here reinforce recent mechanistic proposals involving ground-state complex formation in the CuCl–*c,c*-COD photochemical system[3,4] and provide an insight into the behavior of some strongly complexing and unusual cycloolefins with CuCl.

Experimental Section

Owing to the low solubility and extreme susceptibility toward oxidation of solutions of CuCl in THF, the design of apparatus and the procedures used were aimed to prevent contact of the dissolved CuCl with air or oxidizing impurities in the solvent, while permitting rapid, simple, and accurate handling of the solutions.

Reagents. Nitrogen (African Oxygen, high purity) was further purified over BTS catalyst (BASF) at 200 °C and was used as a blanket gas in the distillation of THF and in the preparation and spectroscopic studies of all the CuCl–olefin solutions. Tetrahydrofuran and diethyl ether were purified by distillation, under purified nitrogen, from benzophenone ketyl solutions.[10] *cis,cis*-1,5-Cyclooctadiene, norbornadiene (both Merck), and *cis*-cyclooctene (Koch-Light) were slowly distilled on a spinning-band column. For *c,c*-COD, a small, late fraction of low optical density[11] was collected. These olefins were stored under nitrogen and used within 7 h.

cis,trans-1,5-Cyclooctadiene was prepared from *c,c*-COD by using a modification of the method of Deyrup and Betkouski.[12] A stirred suspension of 500 mL of THF, 100 mL of *c,c*-COD, and 45 g of CuCl in a cylindrical quartz vessel was irradiated by 10 15-W low-pressure mercury lamps for 10 days. The recovered solid was treated with a concentrated solution of ammonia, which liberated the *c,c*-COD present in the solid. The *c,c*-COD was extracted with hexane and discarded. Addition of solid NaCN to the aqueous layer liberated *c,t*-COD and *t,t*-COD, which were extracted into pentane. The *t,t*-COD was preferentially removed by shaking the pentane layer with a suitable quantity of aqueous silver nitrate. After separation of the organic solution, it was concentrated by low-pressure and, ultimately, vacuum distillation to yield a solution of 99.5% pure *c,t*-COD in pentane.[13] The concentration of this solution was accurately determined by gas–liquid chromatography on a 2-m glass column packed with 10% 1,2-bis(cyanoethoxy)ethane (Anakrom 545A). *c,c*-COD was used to calibrate the response of the flame ionization detector, which was assumed to be the same for both isomers.[14] The *c,t*-COD concentrate was stored under vacuum at −196 °C.

trans-Cyclooctene was prepared according to Deyrup and Betkouski,[12] vacuum distilled and stored under nitrogen. The product was 97.6% pure, solvent and *c*-CO being the main impurities.

Bis(μ-chloro)bis(*cis,cis*-1,5-cyclooctadiene)dicopper(I) was prepared by the method of Haight et al.[15] and was stored in a foil-wrapped Schlenk tube, under nitrogen. The corresponding complex between CuCl and *c,t*-COD was prepared in a similar fashion. Both compounds gave satisfactory elemental analyses for $C_8H_{12}CuCl$.

Specialized Apparatus and Procedures. The flasks used for collecting distilled solvent and for preparing solutions and the quartz spectrophotometer cells were all fitted with "Mininert" valves to aid in the exclusion of air. Transfer of solutions between containers was effected by using gas-tight syringes.

---

(1) Srinivasan, R. *J. Am. Chem. Soc.* **1964**, *86*, 3318.

(2) Whitesides, G. M.; Goe, G. L.; Cope, A. C. *J. Am. Chem. Soc.* **1969**, *91*, 2608.

(3) Grobbelaar, E.; Kutal, C.; Orchard, S. W. *Inorg. Chem.* **1982**, *21*, 414.

(4) Chow, Y. L.; Buono-Core, G. E.; Shen, Y. *Organometallics* **1984**, *3*, 702.

(5) Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163.

(6) Doering, C. E.; Geyer, R.; Burkhardt, G. *Z. Chem.* **1975**, *15*, 319.

(7) Manahan, S. E. *Inorg. Chem.* **1966**, *5*, 2063.

(8) An estimate, based on spectral data,[3] gave a solubility of $\sim 6 \times 10^{-6}$ mol L^{-1}.

(9) Hautala, R. R.; King, R. B.; Kutal, C. In *Solar Energy: Chemical Conversion and Storage*; Hautala, R. R., King, R. B., Kutal, C., Eds.; Humana: Clifton, NJ, 1979; p 333.

(10) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; p 439.

(11) The measured extinction coefficient of the distilled *c,c*-COD at 250 nm was typically in the range 3 ± 2 L $mol^{-1}\ cm^{-1}$.

(12) Deyrup, J. A.; Betkouski, M. *J. Org. Chem.* **1972**, *37*, 3561.

(13) Attempts to further concentrate the *c,t*-COD by low-temperature distillation led to loss of olefin, apparently by polymerization. This problem has also been noted by Chow et al.[4]

(14) Purnell, H. *Gas Chromatography*; Wiley: New York, 1962; p 304.

(15) Haight, H. L.; Doyle, J. R.; Baenziger, N. C.; Richards, G. F. *Inorg. Chem.* **1963**, *2*, 1301.

0020-1669/86/1325-1972$01.50/0

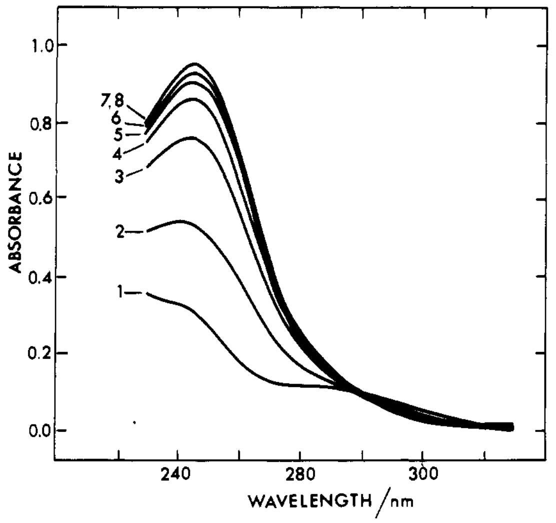

Figure 1. Ultraviolet absorption spectra of 4.0 mL of a 6.86 × 10^{-5} mol L^{-1} solution of ($CuCl\cdot$*c,c*-COD)$_2$ in THF at 20.0 °C after addition of increasing amounts of *c,c*-COD. For curves 1–8, the total volumes of *c,c*-COD added were, respectively, 0, 3, 6, 9, 12, 15, 25, and 45 μL.

In a typical procedure, the required amount of CuCl, in the form of ($CuCl\cdot$*c,c*-COD)$_2$ (up to about 2.5 mg of complex), was weighed in a foil boat on a microbalance and was transferred to a nitrogen-filled flask. A measured mass of THF was added to the flask under positive nitrogen pressure. The mixture in the sealed, foil-wrapped flask was stirred magnetically for 1 h, which was always enough time for complete dissolution of the complex. With a nitrogen-flushed syringe, 4.0 mL of solution was transferred to an air-free spectrophotometer cell. The absorption spectrum of this solution was determined against THF as a reference, between 230 and 350 nm. Small amounts of pure olefin (in the case of *c,c*-COD, NBD, and *c*-CO) or olefin solution in THF (in the case of *c,t*-COD and *t*-CO)[16] were added to the cell, and after each addition, the absorption spectrum was determined.[17]

In order to minimize errors due to loss of CuCl in solution by oxidation, its concentration was maintained at high levels, relative to its solubility, in all our experiments. The range of concentrations used, expressed in terms of $(CuCl)_2$, was between 4.6 × 10^{-5} and 10.9 × 10^{-5} mol L^{-1}.

Results

(a) Absorption Spectra. The electronic absorption spectrum of a solution of up to 10.9 × 10^{-5} mol L^{-1} ($CuCl\cdot$*c,c*-COD)$_2$ in THF, in the region 230–350 nm, is indistinguishable from the spectrum of CuCl itself at the corresponding concentration. This indicates that the complex dissociates completely into free olefin and CuCl under these conditions. The absorption spectrum of dissolved ($CuCl\cdot$*c,c*-COD)$_2$ is seen as curve 1 of Figure 1. For our studies, it was more convenient to use the complex rather than pure CuCl to prepare the solutions for spectroscopy, as the solid complex is more stable toward oxidation than CuCl and also dissolves more rapidly in THF. The small amount of *c,c*-COD introduced into solution when the complex is used as starting material is of no consequence in the study of complexation between CuCl and either *c,c*-COD or any of the other olefins used.

When small amounts of any of the olefins studied are added to a solution of the dissociated complex, a strong absorption feature develops with an absorption maximum in the region 238–256 nm. Further additions of olefin lead to growth of this absorption feature, which ultimately attains maximum development (after allowance for the absorbance due to the free olefin) once the olefin concentration reaches a certain value, specific to each olefin. The growth of the absorption feature, when *c,c*-COD is added, is shown in Figure 1. The shape and position of this absorption curve is very similar for all the olefins, and we attribute its appearance to the progressive formation of a complex or complexes between CuCl and the added olefin. When all the CuCl is complexed, further addition of olefin does not significantly alter the spectrum. In anticipation of the Discussion (vide infra) it will be assumed that the complex formed is of the general type ($CuCl\cdot$olefin)$_2$, and on this basis, from the results of many separate experiments, we have calculated average extinction coefficients for the five complexes at their absorption maxima. These, together with the corresponding values for CuCl itself, expressed in terms of $(CuCl)_2$, are given in Table I.

Table I. Extinction Coefficients and Wavelengths of Absorption Maxima for CuCl and CuCl–Olefin Complexes[a]

compd	λ_{max}/nm	ϵ_{max}/L mol^{-1} cm^{-1}
$(CuCl)_2$	238 (shoulder)	4500 ± 400 (22)
$(CuCl)_2$	280 (shoulder)	1400 ± 100 (22)
($CuCl\cdot$*c,c*-COD)$_2$	246	13100 ± 1100 (11)
($CuCl\cdot$*c,t*-COD)$_2$	244	20790 ± 50 (2)
($CuCl\cdot$NBD)$_2$	256	13200 ± 1000 (3)
($CuCl\cdot$*c*-CO)$_2$	238	15700 ± 500 (3)
($CuCl\cdot$*t*-CO)$_2$	238	21000 ± 1700 (3)

[a] Solvent = THF; temperature = 20.0 °C. Errors are 1 standard deviation; number of measurements of ϵ are shown in parentheses.

(b) Calculation of Formation Constants. The reproducibility of the λ_{max} values in Table I, independent of the nominal CuCl concentration, suggests the presence of a single absorbing complex under conditions of full complexation. Moreover, the increasing absorbance values near λ_{max} that accompany increasing olefin concentrations in the presence of CuCl are in excellent quantitative agreement with a simple complexation scheme in which only one CuCl–olefin complex, namely ($CuCl\cdot$olefin)$_2$, need be invoked. Formation constant calculations in terms of this scheme provide a valuable insight into the relative abilities of the different olefins to complex with CuCl, though the possible importance of complexes of other stoichiometries should not be overlooked (see Discussion).

Since the complexation of *c,c*-COD with CuCl is our primary concern and since the calculations in this case are in some respects simpler than for some of the other olefins studied, we will initially consider the calculation of stability constants for this system. The following equilibria are proposed as a working representation of the interaction of *c,c*-COD and CuCl in THF:

$$(\mathrm{CuCl})_2 + c,c\text{-COD} \overset{K_1}{\rightleftharpoons} (\mathrm{CuCl})_2\cdot c,c\text{-COD} \tag{1}$$

$$(\mathrm{CuCl})_2\cdot c,c\text{-COD} + c,c\text{-COD} \overset{K_2}{\rightleftharpoons} (\mathrm{CuCl}\cdot c,c\text{-COD})_2 \tag{2}$$

This scheme is similar to that which was previously proposed for diethyl ether solutions,[3] except that in the present case the solutions were not saturated with respect to CuCl and thus its solubility equilibrium is not involved. We designate the equilibrium concentrations of *c,c*-COD, $(CuCl)_2$, $(CuCl)_2\cdot$*c,c*-COD, ($CuCl\cdot$*c,c*-COD)$_2$, and total $(CuCl)_2$ species as C_0–C_4, respectively, and the extinction coefficients of the four individual species at 250 nm, near the absorption maximum of ($CuCl\cdot$*c,c*-COD)$_2$, as ϵ_0–ϵ_3. Then

$$K_1 = C_2/(C_0C_1) \tag{3}$$

$$K_2 = C_3/C_0C_2 \tag{4}$$

$$C_4 = C_1 + C_2 + C_3 \tag{5}$$

Eliminating C_2 and C_3, one obtains the relation

$$C_1 = C_4/(1 + K_1C_0 + K_1K_2C_0^2) \tag{6}$$

Through an appropriate combination of (3), (4), and (6), it is thus possible to express C_1, C_2, or C_3 in terms of C_0 (the concentration of "free" *c,c*-COD), C_4 (the total, known concentration

---

(16) In order to monitor progressive formation it was more convenient to add these olefins in the form of dilute solutions, typically 1% v/v. For example, 3.6 × 10^{-7} mol of CuCl in 4.0 mL of solution was completely complexed by the addition of only 2 μL (1.6 × 10^{-5} mol) of *t*-CO.

(17) In the case of *c,c*-COD, olefin was added to the sample cell only; correction for the absorbance of the free olefin was made later in order to determine the absorbance of the complex and free CuCl. With NBD, *c*-CO, and *c,t*-COD, equal volumes of olefin were added to both reference and sample cells, thereby automatically correcting for the olefin absorbance. The amount of *t*-CO used and its extinction coefficient were so small that no correction of the absorbance for olefin absorption was necessary.

of $(CuCl)_2$), and the two constants K_1 and K_2.

Let the experimentally measured absorbance at 250 nm be designated A_{exptl}. The absorbance contribution due to the uncomplexed olefin present is $\epsilon_0 C_0 l$ where l is the path length of the cell. We define a corrected absorbance, A_{cor}, as

$$A_{\text{cor}} = A_{\text{exptl}} - \epsilon_0 C_0 l \tag{7}$$

Ideally, the corrected absorbance should consist of the contributions of the various CuCl-containing species. If values for the various concentrations, extinction coefficients, and stability constants are available, the sum of these contributions can be calculated as A_{calcd}, where

$$\begin{aligned} A_{\text{calcd}} &= (\epsilon_1 C_1 + \epsilon_2 C_2 + \epsilon_3 C_3) l \\ &= \frac{C_4(\epsilon_1 + K_1 \epsilon_2 C_0 + K_1 K_2 \epsilon_3 C_0^2) l}{1 + K_1 C_0 + K_1 K_2 C_0^2} \end{aligned} \tag{8}$$

Of the quantities in (8), three can readily be calculated directly from experimental data; these are C_0, C_4 and ϵ_1. The fraction of the total olefin that was complexed with CuCl was always sufficiently small that C_0, the concentration of free *c,c*-COD, could be equated with the total *c,c*-COD concentration. By the use of reasonable, assumed trial values of the other quantities, A_{calcd} can be determined and compared with the corresponding A_{cor} value obtained experimentally, for each olefin concentration used. A measure of the agreement between experiment and calculation is the quantity E, where

$$E = \sum (A_{\text{cor}} - A_{\text{calcd}})^2 \tag{9}$$

and the sum is taken over the points corresponding to all values of C_0. The better the choice of parameters K_1, K_2, ϵ_2, and ϵ_3, the more closely will A_{cor} and A_{calcd} correspond over the range of olefin concentrations used and the smaller will E be.

A computer program was written in BASIC, and run on an Apple IIE+, in which E was calculated on the basis of trial values of K_1, K_2, ϵ_2, and ϵ_3 and then, in an iterative procedure, these values were systematically altered in order to find that set of values which minimized E. This routine ensured that values of the parameters being optimized would be within 0.1% of the "best fit" values. In essence, this is a form of procedure for stability constant calculations first proposed by Sillen.[18] In this way an excellent correlation between experimental and calculated absorbance benaviour could be obtained, with typical E values of about 3×10^{-4} for eight values of C_0. This corresponds to a root-mean-square difference between A_{calcd} and A_{cor} of 0.006, which is about 1% of a typical A_{cor} value.

In order to see whether a simpler version of this complexation scheme would also fit the experimental results, two limiting forms of (8) were also considered. First, if the situation exists where C_2 is always negligibly small ($K_2 >> K_1$), one has

$$A_{\text{calcd}} = \frac{C_4(\epsilon_1 + K_1 K_2 \epsilon_3 C_0^2) l}{1 + K_1 K_2 C_0^2} \tag{10}$$

Alternatively, if C_3 is always sufficiently small, (8) reduces to

$$A_{\text{calcd}} = \frac{C_4(\epsilon_1 + K_1 \epsilon_2 C_0) l}{1 + K_1 C_0} \tag{11}$$

Each of these equations has essentially only two values requiring optimization, these being $K = K_1 K_2$ and ϵ_3 for (10) and K_1 and ϵ_2 for (11).

Another complexation scheme, which avoids postulating the existence of uncomplexed dimeric CuCl, was also investigated. The scheme was

$$2\text{CuCl} + 2c,c\text{-COD} \overset{K_3}{\rightleftharpoons} (\text{CuCl}\cdot c,c\text{-COD})_2 \tag{12}$$

The existing program for calculating K and ϵ values was appropriately modified to represent complexation according to this scheme. Again two parameters, the stability constant and the extinction coefficient of the complex, were optimized by using the results of five runs with CuCl and either *c,c*-COD or NBD. In all cases the best fit values of K_3 and ϵ_3 yielded poorer fits with experiment (as reflected by the value of E) than when (8) or (10) was used.

Table II. Corrected Measured Absorbances (A_{cor}) at 250 nm and Calculated Absorbances (A_{calcd}) for Different Complexation Schemes[a]

amt of *c,c*-COD added/μL	$10^3 \times$ [*c,c*-COD]/ mol L^{-1}	A_{cor}	A_{calcd}[b]			
			(8)	(10)	(11)	(12)
0.0	0.13	0.218	0.218	0.218	0.224	0.218
2.0	4.20	0.305	0.302	0.301	0.373	0.347
4.0	8.27	0.453	0.454	0.453	0.480	0.500
6.0	12.3	0.580	0.581	0.581	0.561	0.599
10.0	20.5	0.719	0.722	0.723	0.675	0.707
15.0	30.6	0.803	0.793	0.794	0.767	0.777
20.0	40.7	0.821	0.823	0.823	0.827	0.813
25.0	50.8	0.835	0.837	0.837	0.870	0.833

[a] For *c,c*-COD added to 4.0 mL of a 6.41×10^{-5} mol L^{-1} solution of $(\text{CuCl}\cdot c,c\text{-COD})_2$ in THF at 20.0 °C. [b] For (8): $K_1 = 1.08$, $K_2 = 8140$, $\epsilon_1 = 3400$, $\epsilon_2 = 13\,800$, $\epsilon_3 = 13\,600$. For (10): $K = 8240$, $\epsilon_1 = 3400$, $\epsilon_3 = 13\,600$. For (11): $K_1 = 47.7$, $\epsilon_1 = 3400$, $\epsilon_2 = 17\,900$. For (12): $K_3 = 6.24 \times 10^7$, $\epsilon_1 = 3400$, $\epsilon_3 = 14\,700$. Units: K_i, $(\text{mol L}^{-1})^n$; ϵ_i: L mol^{-1} cm^{-1}.

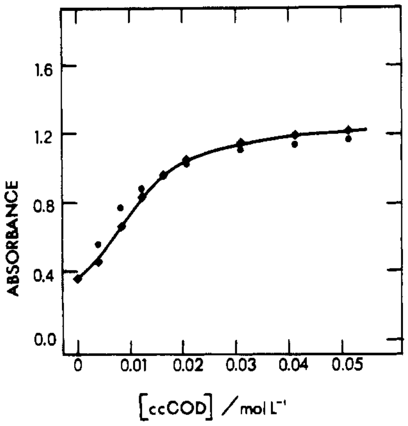

Figure 2. Comparison of corrected measured absorbances (A_{cor}) and calculated absorbances (A_{calcd}) of an initially 9.20×10^{-5} mol L^{-1} solution of $(\text{CuCl}\cdot c,c\text{-COD})_2$ in THF, as a function of *c,c*-COD concentration. T = 20.0 °C; λ = 250 nm. Key: (◆) (10); (●) (12). The line is drawn through the experimentally derived A_{cor} points, which are not shown.

The "best fit" absorbances calculated by using the four different complexation schemes mentioned above are shown in Table II, along with the corrected experimental values, A_{cor}, for a typical experiment. The corresponding E values, calculated according to (9) are as follows: 1.17×10^{-4}, (8); 1.25×10^{-4}, (10); 1.03×10^{-2}, (11); 5.18×10^{-3}, (12). Clearly (8) and (10) fit the data far better than is the case for the other two schemes. A graphical comparison of (10), (12), and experiment is shown in Figure 2.

A systematic deviation of (12) from the observed experimental behavior is clearly evidenced. In view of the simplicity and accuracy of (10) in reproducing the experimental absorbance behavior of all the CuCl–olefin complexes, it was used for the calculation of the stability constants reported below. The use of (10) thus implies the complexation scheme

$$(\text{CuCl})_2 + 2c,c\text{-COD} \overset{K}{\rightleftharpoons} (\text{CuCl}\cdot c,c\text{-COD})_2 \tag{13}$$

A computational procedure similar to that outlined above was employed in the treatment of data for NBD and *c*-CO in the presence of CuCl. In the case of *c,t*-COD and *t*-CO, which complex more strongly, a modified program was necessary to allow for the fact that the concentration of complexed olefin was an appreciable fraction of the total olefin concentration. The procedure used was for the program to select a trial value of C_0, and then to check that $C_0 + 2C_3$ was equal, within an arbitrary small

---

[18] Sillen, L. G. *Acta Chem. Scand.* **1962**, *16*, 158.

Table III. Calculated Formation Constants K and Extinction Coefficients of $(CuCl{\cdot}olefin)_2$ Complexes[a]

		$T = 10\ °C$			$T = 20\ °C$			$T = 30\ °C$		
olefin	λ/nm	a	$K/L^2\ mol^{-2}$	$\epsilon/L\ mol^{-1}\ cm^{-1}$	a	$K/L^2\ mol^{-2}$	$\epsilon/L\ mol^{-1}\ cm^{-1}$	a	$K/L^2\ mol^{-2}$	$\epsilon/L\ mol^{-1}\ cm^{-1}$
c,c-COD	250	4	12 100 ± 400	14 100 ± 1200	11	7800 ± 500	13 000 ± 1100	7	5100 ± 1000	12 800 ± 1000
c,t-COD	244	2	$(6.33 \pm 0.02) \times 10^{13}$	21 250 ± 90	2	$(8.86 \pm 0.03) \times 10^{12}$	20 790 ± 50	2	$(1.64 \pm 0.01) \times 10^{12}$	19 800 ± 200
NBD	260	3	4700 ± 500	13 500 ± 1700	3	2800 ± 200	13 100 ± 700	2	2000 ± 200	13 200 ± 400
c-CO	240				3	700 ± 40	15 400 ± 300			
t-CO	240	3	$(16.6 \pm 3.1) \times 10^8$	19 900 ± 300	3	$(6.3 \pm 1.2) \times 10^8$	20 600 ± 1400	2	$(3.8 \pm 0.7) \times 10^8$	18 500 ± 700

[a] $K = [(CuCl{\cdot}olefin)_2]/[(CuCl)_2][olefin]^2$; a is the number of runs used in the calculation of corresponding K and ϵ.

Table IV. Calculated Enthalpies and Entropies of Complex Formation for CuCl–Olefin Complexes[a]

compd	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
$(CuCl{\cdot}c,c\text{-}COD)_2$	−32 ± 2	−33 ± 6
$(CuCl{\cdot}c,t\text{-}COD)_2$	−130 ± 2	−196 ± 6
$(CuCl{\cdot}NBD)_2$	−30 ± 3	−37 ± 10
$(CuCl{\cdot}t\text{-}CO)_2$	−54 ± 7	−16 ± 23

[a] Based on formation constants presented in Table II; mean temperature 20.0 °C.

limit, to the total olefin concentration.

The value of C_3 was calculated through the relations

$$C_3 = K_1K_2C_0{}^2C_1 \tag{14}$$

$$C_1 = C_4/(1 + K_1K_2C_0{}^2) \tag{15}$$

where (15) is a limiting case of (6), appropriate for the situation where C_2 is always small. Self-consistent values of C_0 and C_3 were thus obtained by using a programmed procedure in which C_0 was iteratively estimated, until a value was obtained which led to $C_0 + 2C_3$ being sufficiently close to the total measured olefin concentration. When the program was run with both K and ϵ_3 as variables requiring optimization and with the iterative procedure for determining C_0, it was unduly slow. It was therefore decided to treat ϵ_3 as a fixed, known value, and to optimize only K. The extinction coefficient of the complex, ϵ_3, was readily calculated from the absorbance of a solution of fully complexed CuCl.

By the use of methods outlined above, values of K and ϵ_3 were obtained for the different complexes at temperatures in the range 10–30 °C. These results are summarized in Table III.

From the temperature dependence of the formation constants, we have calculated the corresponding enthalpy and entropy changes by using the van't Hoff equation. The results are presented in Table IV. The ΔH values for the two *trans*-olefin complexes (−130 and −54 kJ mol^{-1} for *c,t*-COD and *t*-CO, respectively) are in fact very similar when compared on a "per double bond" basis. The ΔS value for $(CuCl{\cdot}c,t\text{-}COD)_2$ is very much more negative than for the other complexes, but in view of the much greater exothermicity associated with its formation, the olefin must be very tightly bound in the complex and a very unfavorable entropy change is to be expected.

Discussion

The absorption spectrum of CuCl in ether was first published by Srinivasan.[1] Our subsequent study, using highly purified ether, yielded a substantially different spectrum, with no absorption maximum between 220 and 340 nm.[3] Attempts to obtain a reliable spectrum of CuCl in ethanol and chloroform have been unsuccessful.[19]

The spectrum we have now obtained in THF (Figure 1) is similar in form to, but considerably more intense than, the spectrum we previously determined for a saturated solution of CuCl in ether. The quantitative reproducibility of this spectrum is fair, and we are confident that curve 1 of Figure 1 is the essentially correct UV absorption spectrum of CuCl in THF. The greater absorbance of a saturated solution of CuCl in THF as compared with ether is in the main due simply to solubility differences.[20]

The absorption bands of the complexes in Table I are so similar in appearance and position that it is reasonable to assume they arise from the same type of electronic transition. Schwendiman and Kutal have assigned the absorption feature in the case of NBD to a metal–olefin charge-transfer transition occurring in a cuprous chloride–NBD complex,[21] and have demonstrated its existence in ethanol, chloroform, and THF. Our λ_{max} and ϵ_{max} values agree reasonably well with their values in THF ($\lambda_{max} = 255$ nm, $\epsilon_{max} = 11.4 \times 10^3$ L mol^{-1} cm^{-1}), when ϵ_{max} is expressed on the basis of the same stoichiometry, namely $(CuCl{\cdot}olefin)_2$.

Our spectra of CuCl solutions in THF in the presence of *c,t*-COD show substantial quantitative differences from the spectrum of $(CuCl{\cdot}c,t\text{-}COD)_2$ reported by Chow and co-workers.[4] Thus, while our spectra yield a λ_{max} of 244 nm, their published spectrum shows a λ_{max} at about 294 nm. In view of this serious discrepancy, we prepared solutions of $(CuCl{\cdot}c,t\text{-}COD)_2$ in both ether and THF by dissolving the solid directly in the solvent. The solution gave λ_{max} values in the region 243–244 nm, fully consistent with the λ_{max} we obtained by adding *c,t*-COD to a solution of CuCl in THF. In order to establish whether oxidative processes might be responsible for the different spectrum reported by Chow, we allowed air oxidation of the ether solution of $(CuCl{\cdot}c,t\text{-}COD)_2$. Although the UV absorption spectrum was substantially altered, it still did not resemble their published one. We are thus unable to identify the cause of the discrepancy. However, in view of the stringent precautions we have taken to purify materials and exclude air and considering that all the CuCl–olefin complexes that we studied consistently showed absorption maxima in the 238–256-nm region, we are confident that the spectral details for $(CuCl{\cdot}c,t\text{-}COD)_2$ in Table I are essentially correct.

It is worthy of note that the maximum extinction coefficients of the complexes containing *c,t*-COD and *t*-CO are about 50% greater than those of the *cis*-olefins. This difference may be an artifact arising from an inappropriate choice of complex stoichiometry; indeed several different CuCl–olefin formulations have been proposed in the literature. Thus, in the solid state, *c,c*-COD forms the 1:1 dimeric complex $(CuCl{\cdot}c,c\text{-}COD)_2$,[22] NBD forms a 1:1 tetramer, $(CuCl{\cdot}NBD)_4$,[23] and *t*-CO forms a complex formulated as $(CuCl)_2(t\text{-}CO)_3$.[24] In diethyl ether solution, a complex of the general formula $(CuCl)_x(c,c\text{-}COD)_2$ (most probably $(CuCl{\cdot}c,c\text{-}COD)_2$) has been proposed,[3] while, in ethanol, NBD and CuCl apparently also form a 1:1 complex.[19] Previous measurements of copper(I)–olefin formation constants have generally been carried out in aqueous or alcoholic perchlorate media,[5] and the complexes in these cases have always been formulated as $[Cu{\cdot}olefin]^+$. In an assessment of the importance of the above findings to the present work, it should be borne in mind first that the stoichiometry of a solid obtained from a solution does not necessarily correspond to the main species present in solution, for example in the case of the silver nitrate–NBD complexes.[25] Second, relative formation constants of silver–olefin complexes are very solvent-dependent, as discussed by Harvilchuck et al.[26]

---

(19) Schwendiman, D. P.; Kutal, C. *J. Am. Chem. Soc.* **1977**, *99*, 5677.

(20) At 20 °C the solubility of free CuCl in THF appears to be at least 2.2×10^{-4} mol L^{-1}, which is ≳30 times the solubility in diethyl ether.

(21) Schwendiman, D. P.; Kutal, C. *Inorg. Chem.* **1977**, *16*, 719.

(22) van den Hende, J. H.; Baird, W. C. *J. Am. Chem. Soc.* **1963**, *85*, 1009.

(23) Baenziger, N. C.; Haight, H. L.; Doyle, J. R. *Inorg. Chem.* **1964**, *3*, 1535.

(24) Ganis, P.; Lepore, U.; Martuscelli, E. *J. Phys. Chem.* **1970**, *74*, 2439.

(25) Bennett, M. A. *Chem. Rev.* **1962**, *62*, 611.

(26) Harvilchuck, J. M.; Aikens, D. A.; Murray, R. C. *Inorg. Chem.* **1969**, *8*, 539.

Our results show evidence of further complications in the THF solution. Spectra corresponding to a small extent of complex formation between cuprous chloride and *c,c*-COD exhibit an isosbestic point in the region 285–300 nm. However, further addition of olefin leads to the breakdown of this point, and an increased absorbance is seen, even after correction for absorption by the free olefin. This behavior suggests that at low olefin concentrations, only two absorbing species, cuprous chloride and a complex, are present. However, at higher olefin concentrations the absorption near 300 nm due to other complex species cannot be ignored.

Irrespective of spectral complexities such as these, other authors have expressed caution in attempting to assign unique formulations to copper(I)–olefin complexes on the basis of UV spectral data alone.[18,27] However, our proposed complexation scheme, involving only one general type of complex, $(\mathrm{CuCl{\cdot}olefin})_2$, is in good quantitative agreement with the experimental data near the absorbance peaks. We therefore propose it as a useful practical basis for the comparison of the olefins we have studied, not as a complete representation of the complexation process.

The most notable feature of the results in Table III is the effect that the presence of a trans bond in the cycloolefin has on the stability constant. Thus our formation constants for *c*-CO, *c,c*-COD, *t*-CO, and *c,t*-COD with CuCl increase in that order and are in line with the constants for the first three olefins with silver nitrate in ethylene glycol, reported by Muhs and Weiss.[28] Our observation that *t,t*-COD can be quantitatively separated from *c,t*-COD by its preferential reaction with aqueous silver nitrate (see Experimental Section) indicates that the *trans,trans*-olefin complexes far more strongly even than its cis,trans isomer. The very large formation constant calculated for the complex of the latter compound is consistent with nearly complete (~99%) complexing of the olefin in the initial stages of olefin addition. This is borne out by a linear increase in the experimental absorbance with addition of this olefin until complexation is >80% complete. In view of the very small concentration of the free olefin in this case, the calculated formation constants for *c,t*-COD are probably subject to greater uncertainty than those for the other olefins. The instability of this olefin[13] compounds the problem, and the reported formation constants for *c,t*-COD should be treated with some caution. Measurement of the Cu(I)–*c,t*-COD formation constant by an alternative method would be of interest, but it is nevertheless clear that this olefin is quite exceptional in its ability to complex with CuCl.

Hartley[5] has argued that, for monocyclic olefins, the strain energy of the olefin is the most important factor in determining the formation constant between the olefin and silver. For open-chain pairs of *cis*- and *trans*-olefins, the strain energy of the olefin is also proposed as a factor of major importance. For the cis and trans pairs we have studied quantitatively, this observation is borne out. Thus, *c,t*-COD is more strained than *c,c*-COD[29] (a strain energy of 128 vs. 43 kJ mol^{-1}) while *t*-CO is likewise more strained than *c*-CO[30] (74 vs. 37 kJ mol^{-1}), and in both cases the trans isomer complexes far more strongly than the cis isomer. However NBD, which has a strain energy[30] (132 kJ mol^{-1}) similar to that of *c,t*-COD, complexes far less strongly, while, from our qualitative observations on the separation of *t,t*-COD from *c,t*-COD, the less strained *t,t*-COD[29] (100 kJ mol^{-1}) complexes more strongly than does *c,t*-COD with silver. It is clear then that strain energy in the olefin is not the only important factor influencing the formation constants. Steric factors are probably also very significant in the present examples, and it may be that molecular mechanics calculations could provide some useful insights. Crystal structure determinations have been reported for CuCl complexes with *c,c*-COD,[22] NBD,[23] and *t*-CO,[24] though in the cases of *c,c*-COD and *t*-CO the *R* factor exceeded 10%. Further work in this area would also be helpful.

A CuCl–NBD complex has been implicated as the photoactive species in the photolysis of solutions containing CuCl and NBD;[19] since the three 1,5-COD isomers all appear to complex more strongly than NBD, the case for proposing ground-state CuCl·COD complexes as being involved in the CuCl-sensitized photoisomerization of *c,c*-COD to tricyclooctane[3,4] is reinforced by the present results. Moreover, a calculation based on our formation constants and extinction coefficients at 20 °C shows that the $(\mathrm{CuCl{\cdot}}c,t\text{-}\mathrm{COD})_2$ complex can compete favorably with the $(\mathrm{CuCl{\cdot}}c,c\text{-}\mathrm{COD})_2$ complex for 250-nm photons even when the concentration of free *c,t*-COD is a factor of 44 000 less than that of *c,c*-COD. The low, or undectable, level of free *c,t*-COD in solution during the photolysis of CuCl–*c,c*-COD mixtures in solution,[2-4] is therefore quite understandable.

The spectroscopic method we have used is clearly of value in determining the stability constants of CuCl–olefin complexes under suitable conditions. These are that the solubility of free CuCl should be sufficiently high ($\geq 2 \times 10^{-5}$ mol L^{-1}) in the solvent used, that exceptional care is taken to exclude air and other oxidants from the solutions being studied, and that the stability constants and extinction coefficients of the complexes should be high. Most simple olefins would probably not be suited to studies of this type, as the corresponding stability constants are much smaller than those encountered in our study.

Registry No. *c,c*-COD, 1552-12-1; *c,t*-COD, 5259-71-2; NBD, 121-46-0; *c*-CO, 931-87-3; *t*-CO, 931-89-5; CuCl, 7758-89-6.

---

(27) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 1137.
(28) Muhs, M. A.; Weiss, F. T. *J. Am. Chem. Soc.* **1962**, *84*, 4697.
(29) Favini, G.; Zuccarello, F.; Buemi, G. *J. Mol. Struct.* **1969**, *3*, 385.
(30) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734.