

to lower energy than the transition to the $A_{2u}(^1A_{2u})$ state (band III), and the A term expected for this state is also positive. The transition to the predominantly singlet $E_u(^1E_u)$ likely dominates the spectrum, however. Band II also has a low sensitivity to the halogen ($2.88 \mu\text{m}^{-1}$ for Cl^- vs. $2.79 \mu\text{m}^{-1}$ for Br^-), in keeping with the metal-localized transition. The low-energy shoulder on band II (band I) for $\text{Pt}_2(\text{pop})_4\text{Cl}_2^{4-}$ and the broadness on the low-energy side of band II for $\text{Pt}_2(\text{pop})_4\text{Br}_2^{4-}$ are logically assigned as transitions to states of triplet parentage of $(e_g)^3(^1a_{2u})$. The MCD in this region is not very informative, but the $E_u(^3E_u)$ and $A_{2u}(^3E_u)$ states of $(e_g)^3(^1a_{2u})$ are certainly expected below the energy of $E_u(^1E_u)$, band II.

The high-energy band (band IV) is intense, and its position is nearly halogen independent ($4.63 \mu\text{m}^{-1}$ for Cl^- vs. $4.60 \mu\text{m}^{-1}$ for Br^-). This latter feature tends to rule out a halogen-to-metal LMCT and suggests an allowed metal-localized transition within the Pt_2P_8 cluster. Therefore, the possibilities that may be visualized from Figure 3 are transitions to $E_u(^1E_u)$ of $(e_u)^3(2a_{1g})$, $E_u(^1E_u)$ of $(e_g)^3(2a_{2u})$, and $A_{2u}(^1A_{2u})$ of $(1a_{1g})(2a_{2u})$. However, MCD does not really allow a definitive choice among these possibilities because of the difficulty of the term assignment. For example the two $E_u(^1E_u)$ states should each show a positive A term, but none are apparent. A B term would be anticipated for $A_{2u}(^1A_{2u})$ of $(1a_{1g})(2a_{2u})$, but both this state and $E_u(^1E_u)$ of $(e_g)^3(2a_{2u})$ involve the high-energy $p\sigma^*$ orbital and might be expected to occur at too high an energy to be observed. It is possible that band IV may be a combination of possibilities, with stronger B terms from several states obscuring weaker A terms. Further analysis is not possible from the present data.

Conclusions. The MCD spectra of bands I and II for $\text{Pt}_2(\text{pop})_4^{4-}$ and bands II and III for $\text{Pt}_2(\text{pop})_4\text{Cl}_2^{4-}$ or $\text{Pt}_2(\text{pop})_4\text{Br}_2^{4-}$ are quite consistent with, and tend to strengthen, the earlier assignments

of the absorption spectra.^{5-7,9,13,14} In addition, the MCD at higher energy for $\text{Pt}_2(\text{pop})_4^{4-}$ provides spectroscopic information on which to base an interpretation of the absorption spectra above $3.0 \mu\text{m}^{-1}$. The assignments suggested here differ slightly from those proposed by Azumi et al. from spin-orbit calculations.¹⁷ In particular, band V of $\text{Pt}_2(\text{pop})_4^{4-}$ is assigned here to the transition to $E_u(^1E_u)$ of $(e_u)^3(2a_{1g})$ while the calculations place the $E_u(^3E_u)$ and $A_{2u}(^3E_u)$ of $(e_u)^3(2a_{1g})$ close together (within band widths) in this region. The MCD expected for such a near degenerate situation would be a strong positive *pseudo A* term¹⁹ in contrast to the weak *A* term-strong *B* term combination observed. There is no doubt however that strong spin-orbit interaction is important in the description of any of the states from configuration involving the metal-based orbitals of the Pt_2P_8 cluster. It is interesting the way that the metal-localized spin-orbit states of Pt_2P_8 dominate the electronic structure of both $\text{Pt}_2(\text{pop})_4^{4-}$ and $\text{Pt}_2(\text{pop})_4\text{X}_2^{4-}$. This description can be compared with that of the mononuclear PtP_4 complexes where the lowest energy states originate from $d_{2u}(z)$ configurations and are also spin-orbit states with significant metal-localized character.¹⁶ This comparison leads to a picture of the Pt_2P_8 cluster as an integrated tetragonal unit that behaves like a "thick" mononuclear PtP_4 complex, and when axial ligands are added on oxidation, only a slight perturbation of the internal orbital structure occurs. The same picture emerges from both a molecular structure¹⁵ and reactivity¹¹ viewpoint for $\text{Pt}_2(\text{pop})_4^{4-}$.

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Dimerization of Cobalt(II) Tetrasulfonated Phthalocyanine in Water and Aqueous Alcoholic Solutions

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The dimerization of cobalt(II) tetrasulfonated phthalocyanine (CoTSPC) was studied in water and aqueous alcoholic solutions. The molar absorptivities, ϵ_M and ϵ_D , of the monomer and dimer species at 662 nm and the dimerization constant K_D were calculated from absorbance measurements by modifying a procedure devised by Monahan. The calculated ϵ_M agreed with the measured value of $1.21 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$; both ϵ_D and K_D values were significantly higher than previously published results, which were obtained by successive approximation methods. At a constant temperature, K_D was independent of the total CoTSPC concentration until a limiting concentration was reached. This concentration limit became lower as temperature was reduced and the extent of aggregation increased, implying that higher aggregates than the dimer were present despite the presence of an isosbestic point at 364 nm in a CoTSPC solution as concentrated as $2 \times 10^{-5} \text{ M}$. A finite and positive ΔC_p° of 0.1 kcal/(mol K) was measured over the temperature range 25–75 °C. This precluded "hydrophobic bonding" as a major factor in CoTSPC dimerization. Measurements of dimerization in aqueous methanol, ethanol, and 2-propanol solutions showed that, for a given mole fraction of alcohol, ethanol was more effective than methanol in promoting monomer formation.

Introduction

The past several years have seen increasing interest in the chemistry of the metallophthalocyanines, since these compounds are used as commercial dyes, optical and electrical materials, catalysts, and models for naturally occurring macrocycles.¹ Particular attention has focused on the water-soluble, tetrasulfonate derivative (Figure 1) since Abel and associates² discovered that the cobalt(II) complex binds oxygen reversibly. Abel's work sparked further experiments with oxygenated TSPC complexes³⁻⁷ that led to their use as oxidation catalysts in homogeneous solutions⁸⁻¹³ and on supports.¹⁴⁻²⁰

As with other water-soluble dyestuffs,²¹ transition-metal TSPC complexes aggregate in water, and the formation of the dimer has

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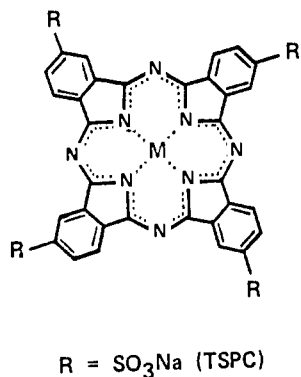


Figure 1. Structure of the phthalocyanines.

been the subject of repeated studies for a variety of transition metals.²²⁻³⁶ The dimerization constant can be obtained spectrophotometrically, since TSPC complexes absorb strongly in the visible region.²² All methods employed in the past require that the monomer spectrum be known. This spectrum is obtained either by successive dilution of the dye until the spectrum does not change with temperature or by dilution of alcohol-water mixtures to foster formation of the monomer in more concentrated solutions. In addition, further approximations on the nature of the dimer spectrum are made,³⁷ so that the concentrations of both monomer and dimer can be obtained in order to get the dimerization constant.

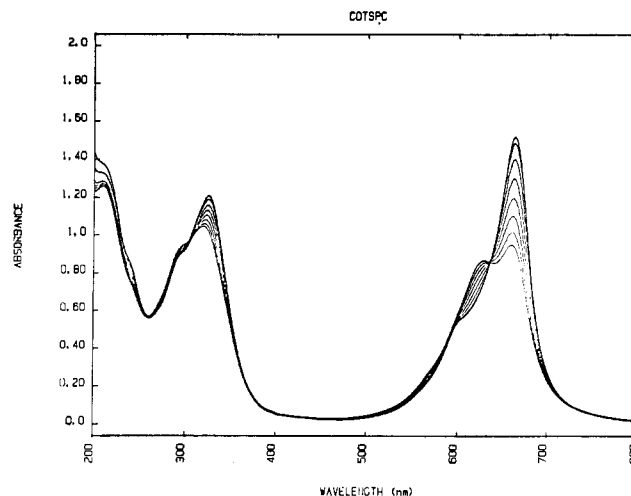


Figure 2. Spectrum of 1.97×10^{-5} M CoTSPC in water at temperatures ranging from 20 to 85 °C.

This paper illustrates the use of a nonlinear, least-squares program to find the dimerization constant and the molar absorptivities for the monomer and dimer over a range of dye concentrations. The dyestuff is Co^{II}TSPC (C₃₂H₁₂N₈O₁₂S₄Na₄Co·2H₂O, mol wt 1016), and results are compared with published work. In addition, the dimerization is investigated over a wide temperature range (5–75 °C) in water to determine whether the enthalpy is temperature dependent. The dimerization is also measured in alcohol-water mixtures with methanol, ethanol, or 2-propanol between 25 and 45 °C.

Experimental Section

Materials. Preparation of (29H,31H-Phthalocyanine-2,9,16,23-tetrasulfonato(2-)-N²⁹,N³⁰,N³¹,N³²)cobalt. This material was prepared by the method of Weber and Busch³⁸ using the sodium salt of 4-sulphthalic acid, ammonium chloride, urea, ammonium molybdate, and cobalt sulfate heptahydrate in hot nitrobenzene. The purification procedure for this 0.05-mol scale reaction differed slightly from the published method. The crude, dark blue product was broken apart with a spatula, rinsed with 400 mL of methanol, and finely ground in a mortar. The resulting blue powder was dissolved in 1.1 L of 1 N HCl saturated with sodium chloride to give a deep blue slurry that was heated to reflux briefly and then was cooled to room temperature and filtered. The air-dried product was dissolved in 700 mL of 0.1 N sodium hydroxide, heated to 80 °C, and filtered (no residue). Sodium chloride (270 g) was added to salt out the product. This slurry was heated with stirring at 80 °C for 3 h while ammonia evolved. Upon cooling to room temperature, the product was isolated by filtration. This reprecipitation was repeated twice, and the final precipitate was washed with 1.8 L of 80% aqueous ethanol to remove occluded NaCl. A convenient final purification was achieved by washing the blue powder in the thimble of a Soxhlet apparatus with hot 95% ethanol for 18 h. The product was then dried in vacuo for 2 days to give 22.0 g (54%) of the desired CoTSPC as determined by UV-vis spectroscopy. Alcohols were HPLC grade and were used without further purification. Doubly distilled, deionized water was used in all solutions.

Measurements. All spectrophotometric measurements are made with a diode-array UV-vis spectrophotometer (HP 8450A) equipped with a temperature controller (HP 89100A). The equipment is controlled by a microcomputer to provide at least six repeated measurements of each sample at 1 min intervals starting about 5 min after the cell compartment reached the controlled temperature.

All of the sample solutions were freshly made on the same day absorbances were measured to avoid errors caused by absorption of the dye to the walls of the glass containers, and the absorbances were corrected for volume changes of the solutions at various temperatures. Conductivities were measured with a CDM83 conductivity meter (Radiometer).

Determination of Dimerization Constants. The absorbance, A , of a solution in a 1-cm cell containing only monomer and dimer is

$$A = \epsilon_M[M] + 2\epsilon_D[D] \quad (1)$$

where ϵ_M and ϵ_D are molar absorptivities (M⁻¹ cm⁻¹) of monomer and

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Table I. Absorptivity of CoTSPC in Water at 662 nm and at 65 and 75 °C

$10^7 \times$ [CoTSPC], M	$10^{-5}\epsilon,^a$ M ⁻¹ cm ⁻¹		$10^7 \times$ [CoTSPC], M	$10^{-5}\epsilon,^a$ M ⁻¹ cm ⁻¹	
	65 °C	75 °C		65 °C	75 °C
0.88	1.2	1.2	3.36	1.07	1.09
1.88	1.09	1.09	4.40	1.05	1.07
1.95	1.10	1.10	5.23	1.04	1.05
2.27	1.08	1.08	9.11	1.03	1.04
2.52	1.07	1.09	11.4	1.01	1.03

^a Absorptivity based on concentration of total cobalt(II).

Table II. Absorptivity of CoTSPC at 662 nm in Ethanol-Water Solutions at 35 °C

20% EtOH ^a		40% EtOH ^a		60% EtOH ^a	
[C _T] ^b	ε ^c	[C _T] ^b	ε ^c	[C _T] ^b	ε ^c
0.202	1.14	0.204	1.22	0.201	1.21
1.01	1.11	1.02	1.19	1.01	1.23
2.02	1.07	2.04	1.18	2.01	1.24
10.1	1.07	10.2	1.14	10.1	1.22
		20.4	1.08	20.1	1.08

^a Percent by volume. ^b M × 10⁻⁶. ^c M⁻¹ cm⁻¹ × 10⁵.

dimer, respectively, with ε_D expressed in terms of the monomer, and [M] and [D] are concentrations (M) of monomer and dimer, respectively. The equilibrium between monomer and dimer is

$$K_D = [D]/[M]^2 \quad (2)$$

where K_D is the dimerization constant (M⁻¹), assuming that the activity coefficients are unity for dilute solutions. Since the total concentration of CoTSPC, [C_T], is

$$[C_T] = [M] + 2[D] \quad (3)$$

eq 1-3 can be combined to give

$$A = \epsilon_M \left[\frac{-1 + (1 + 8K_D[C_T])^{1/2}}{4K_D} \right] + \epsilon_D \left[[C_T] - \frac{-1 + (1 + 8K_D[C_T])^{1/2}}{4K_D} \right] \quad (4)$$

The absorbances of up to 18 solutions of different CoTSPC concentrations were measured at a given wavelength after temperature equilibration. A nonlinear least-squares program³⁹ based on the Gauss-Newton technique was used to fit the measured absorbances vs. [C_T] in eq 4. Following a procedure recommended by Monahan,⁴⁰ the value of ε_M determined independently was fixed and ε_D and K_D were allowed to vary. Best fit values of ε_D at each temperature were averaged to give a single value of ε_D; then, K_D was calculated for each value of [C_T]. Runs were also made with all parameters allowed to vary in order to compare the best fit ε_M with the value of ε_M measured in alcohol-water mixtures.

Results

CoTSPC Spectrum in Water. Figure 2 illustrates the spectrum of 1.97×10^{-5} M CoTSPC in water at temperatures ranging from 20 to 85 °C at approximately 10 °C intervals. The peak absorbance at 662 nm grows as temperature increases, and an isosbestic point appears at 634 nm that has been interpreted in the past as evidence that aggregates larger than the dimer were absent.

Monomer Molar Absorptivity. The monomer's molar absorptivity was measured by each of the two methods described earlier. The absorptivities were recorded in pure water for a series of solutions ranging in concentration $(11.4-0.88) \times 10^{-7}$ M at 10 °C intervals from 25 to 75 °C. This method is limited by the precision obtainable in such dilute solutions. Replicate measurements with a given solution showed that the absorbance could be measured with a standard deviation of 5×10^{-4} AU. Table I summarizes the results at 65 and 75 °C; no measureable change

Table III. Fitted Values of ε_M and ε_D from (4)^a

T, °C	10 ⁻⁵ ε _M , M ⁻¹ cm ⁻¹	10 ⁻⁵ ε _D , M ⁻¹ cm ⁻¹	T, °C	10 ⁻⁵ ε _M , M ⁻¹ cm ⁻¹	10 ⁻⁵ ε _D , M ⁻¹ cm ⁻¹
5	1.03 ± 0.20	0.34 ± 0.02	45	1.12 ± 0.08	0.40 ± 0.03
15	1.10 ± 0.39	0.34 ± 0.04	55	1.13 ± 0.07	0.46 ± 0.03
25	1.19 ± 0.36	0.36 ± 0.03	65	1.17 ± 0.08	0.59 ± 0.02
35	1.17 ± 0.23	0.38 ± 0.04	75	1.18 ± 0.09	0.66 ± 0.02

^a Errors are standard deviations of the mean as computed by the program. Absorbances at 662 nm of 18 solutions over the concentration range 9×10^{-8} to 2×10^{-5} M were used to calculate ε_M and ε_D at each temperature (see eq 4).

Table IV. Dimer Molar Absorptivity over Various Concentration Ranges

T, °C	concn range, M × 10 ⁻¹	10 ⁻⁴ ε _D , M ⁻¹ cm ⁻¹	T, °C	concn range, M × 10 ⁻¹	10 ⁻⁴ ε _D , M ⁻¹ cm ⁻¹
25	0.9-5	7.7 ± 0.7 ^a	55	0.9-20	8.2 ± 0.2
35	0.9-10	7.3 ± 0.7	65	0.9-20	8.3 ± 0.2
45	0.9-10	8.5 ± 0.5	75	0.9-50	7.9 ± 0.1

^a Standard deviation of mean computed by the nonlinear least-squares program.

in absorbance could be detected for the lowest four concentrations from 65 to 75 °C. From these results the molar absorptivity of the monomer could only be specified as $(1.1-1.2) \times 10^5$ M⁻¹ cm⁻¹.

The molar absorptivity of monomer was also measured in alcohol solutions. The maximum absorption of the monomer in pure ethanol occurs at 662 nm, the same wavelength as in water, whereas the peak shifts to 658 nm in pure methanol. However, absorbance measurements of CoTSPC solutions in pure methanol at 658 nm showed that Beer's Law was followed and ε_M was 1.22×10^5 M⁻¹ cm⁻¹. The solubility of the dye in pure ethanol is too small to measure concentrations precisely, so experiments with ethanol were made in aqueous solution. The absorptivities of CoTSPC measured in three ethanol-water mixtures at 35 °C are listed in Table II. Beer's law is obeyed from 10⁻⁷ to 10⁻⁵ M CoTSPC in the 60% solution, while it appears that dimer was present in the 20% solution. From these results the monomer molar absorptivity was determined to be $(1.21 \pm 0.02) \times 10^5$ M⁻¹ cm⁻¹, which is consistent with values reported by Abel,² Gruen,⁴ and Sorek,⁴¹ also from measurements in aqueous alcoholic solutions.

Determination of ε_D and K_D . A total of 18 solutions ranging from 9×10^{-8} to 2×10^{-5} M were used to determine ε_M, ε_D, and K_D with the nonlinear, least-squares fit to eq 4. The absorbances were measured at 662 nm from 5 to 75 °C at 10 °C intervals. As shown in Table III, ε_D decreased steadily as temperature decreased, and the relative magnitudes of the standard deviations steadily increased as the temperature decreased. This suggested that the fit was poorer and the molar absorptivities too low at lower temperatures, possibly because higher aggregates than the dimer were present at these lower temperatures. Nonetheless, one notes that ε_M values at 65 and 75 °C agree well with the value of 1.21×10^5 M⁻¹ cm⁻¹ measured in the series of ethanol-water mixtures. Thus, the addition of cosolvent does not alter the CoTSPC monomer spectrum, an implicit assumption in most work with dye aggregates. Therefore, lower concentration ranges were progressively tried for lower temperatures, and ε_M was fixed at 1.21×10^5 M⁻¹ cm⁻¹ to try to define ε_D precisely,⁴⁰ with the results shown in Table IV. One notices that ε_D became more consistent over the temperature range 25-75 °C as data from higher concentrations were removed from the computations at lower temperatures. These results suggest that the observed isosbestic point on a dye solution of a relatively high concentration (2×10^{-5} M) does not necessarily ensure a pure monomer-dimer equilibrium. A mean value of ε_D of $(8.0 \pm 0.4) \times 10^4$ M⁻¹ cm⁻¹ was obtained from Table IV. No attempts were made in the past to determine ε_D at 662 nm. On the basis of available data of K_D , ε_M, and

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Table V. Dimerization Constants Calculated with ϵ_M and ϵ_D Fixed^a

$10^7[C_T], M$	$10^{-6}K_D, M^{-1}$					
	$T = 25^\circ C$	$T = 35^\circ C$	$T = 45^\circ C$	$T = 55^\circ C$	$T = 65^\circ C$	$T = 75^\circ C$
0.879	7.4	3.5	2.6	1.5	0.89	0.64
1.88	7.9	3.9	2.5	1.4	0.92	0.61
1.95	8.2	3.8	2.5	1.4	0.88	0.63
2.27	8.2	3.9	2.4	1.4	0.88	0.64
2.52	8.4	4.0	2.3	1.4	0.89	0.63
3.36	8.8	4.4	2.3	1.4	0.88	0.64
4.40	8.9	4.6	2.1	1.4	0.89	0.63
5.23	9.3	5.0	2.1	1.4	0.88	0.65
9.11			1.9	1.3	0.85	0.65
11.4				1.4	0.83	0.64
20.9				1.3	0.80	0.69
52.3						0.74
mean	8.4	4.1	2.3	1.4	0.87	0.64
std dev	0.6	0.5	0.2	0.1	0.03	0.02

^a $\epsilon_M = 1.21 \times 10^5 M^{-1} cm^{-1}$; $\epsilon_D = 1.60 \times 10^5 M^{-1} cm^{-1}$.

Table VI. Dimerization Constants of CoTSPC in Alcohol-Water Solutions

X_2	$10^{-5}K_D, M^{-1}$		
	$T = 25^\circ C$	$T = 35^\circ C$	$T = 45^\circ C$
water	84	41	23
MeOH	0.10	1.4	0.88
	0.15	0.63	0.52
EtOH	0.050	22	10
	0.080	8.1 ± 1.3	5.0 ± 1.1
	0.10	1.0	0.79
	0.15	0.19 ± 0.08	0.16 ± 0.01
<i>i</i> -PrOH	0.15	0.22	

^aError represents sample standard deviations where noted. Other values are single determinations.

absorbances from two previous studies,^{4,34} ϵ_D was found to be 0.48×10^5 and $0.33 \times 10^5 M^{-1} cm^{-1}$, respectively. We believe their values were too low because they were based on low K_D values which will be discussed later.

The K_D values were calculated from the ϵ_M and ϵ_D values determined above and listed in Table V. At 5 and 15 °C, no consistent values of K_D over the concentration ranges studied could be obtained, possibly due to the presence of higher aggregates in CoTSPC solutions. A fairly constant K_D value was obtained over a range of concentrations up to a limiting concentration at each temperature from 25 to 75 °C, with higher limiting concentrations at higher temperatures. We believe that these K_D values are the true equilibrium constants because they are independent of concentrations until a high concentration is reached at each temperature and suggest this method as a routine test on the accuracies of K_D values.

Dimerization of CoTSPC in Alcohol-Water Solutions. Dimerization constants were measured in methanol, ethanol, and 2-propanol solutions. Measurements were first made with ethanol ($X_2 = 0.08$) with a series of different concentrations of CoTSPC and ϵ_D calculated in the same fashion as in water. Because of volume changes of the solution, measurements were restricted to 25, 35, and 45 °C. At these three temperatures, values of ϵ_D of 0.69, 0.79, and $0.78 \times 10^5 M^{-1} cm^{-1}$, respectively, were obtained with ϵ_M fixed at $1.21 \times 10^5 M^{-1} cm^{-1}$. This compares to the value for ϵ_D of $0.80 \times 10^5 M^{-1} cm^{-1}$ in water. For the remainder of the experiments, dimerization constants in alcohol-water were computed, assuming ϵ_M and ϵ_D to have the same values as determined in water. Table VI lists the dimerization constants in alcohol-water solutions.

Discussion

Earlier determination of CoTSPC dimerization constants in water^{25,34} were inconsistent and significantly smaller than the values reported in this study. Their K_D values were 4.03×10^5 at 20 °C³⁴ and $4.7 \times 10^5 M^{-1}$ at 48 °C²⁵ and were obtained with the approximate method of West and Pearce,³⁷ which only required

Table VII. Thermodynamic Functions of CoTSPC Dimerization in Water

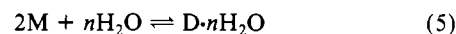
$T, ^\circ C$	$\Delta G^\circ,^a$ kcal/mol	$\Delta H^\circ,^b$ kcal/mol	$\Delta C_p^\circ,^b$ cal/(mol K)	$\Delta S^\circ,^c$ cal/(mol K)
25	-9.4	-13.34 ± 9.14	112 ± 8	-13.4
35	-9.3	-12.19 ± 0.18	111 ± 13	-9.4
45	-9.2	-11.08 ± 0.68	110 ± 9	-5.9
55	-9.2	-9.94 ± 0.14	107 ± 14	-2.4
65	-9.2	-9.25 ± 0.29	98 ± 19	1.1
75	-9.3	-7.41 ± 0.16	122 ± 8	4.5

^aCalculated from the mean values of K_D in Table V. ^bErrors are standard deviation of the mean as computed by the program using Blandamer's method (eq 6). ^cComputed from ΔH° in eq 7 and ΔG° .

ϵ_M to be known. However, the values of ϵ_M used by both groups were 1.03 and $1.04 \times 10^5 M^{-1} cm^{-1}$, smaller than the value we measured or the values reported by other investigators.^{2,4,41}

Eyring and co-workers²⁴ noted a sharp increase in K_D as the total dye concentration decreased, and the reported K_D values were those extrapolated to zero total concentration. According to Eyring's group, the changes in K_D at higher concentrations were caused by an undefined activity effect, although one might have expected the dimerization constant to decrease as ionic strength decreased.³⁴ To test this further, conductivity was measured of a series of CoTSPC solutions. Little change in conductivity was observed over the range 1×10^{-5} to $1 \times 10^{-7} M$, which is the region where the sharpest change in K_D with dye concentration was reported. We believe their observation was caused by inaccurate K_D values.

Abel and co-workers³⁴ also determined the dimerization of CoTSPC in a series of methanol-water and ethanol-water solutions at 20 °C. These workers found that a plot of $\log K_D$ vs. $\log [H_2O]$ was linear and the slope was the same for ethanol or methanol aqueous solutions. Abel concluded that the dimerization of water proceeded according to



Our results contradict this interpretation, since we find that the dimerization constant decreases for a given mole fraction of alcohol as one goes from methanol to ethanol. Our results on the effect of alcohol-water on dimerization are more in line with Dewey and co-workers⁴² who found that the dimerization constant of thionine decreased markedly as ethanol content increased, and the dimerization constant was smaller for a given mole fraction of alcohol in ethanol than in methanol.

Another facet of this study was to see whether a finite heat capacity of dimerization could be detected. Since World War II many examples of temperature-dependent activation energies have been measured,⁴³ along with more rigorous methods to detect nonzero heat capacities, which have been recently reviewed by Kanerva.⁴⁴ We used the method advocated by Blandamer, Robertson, and co-workers⁴⁵ to see whether the enthalpy of dimerization of CoTSPC in water in temperature dependent.

Blandamer's expression for computing ΔC_p° is

$$K = K_0 \exp \left\{ \frac{\Delta H^\circ}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) + \frac{\Delta C_p^\circ}{R} \left(\ln \left(\frac{1}{T_0} \right) + \frac{T_0}{T} - 1 \right) \right\} \quad (6)$$

where K_0 = dimerization constant at T_0 and ΔH° = enthalpy at T_0 .

Equation 6 was obtained by integration of the van't Hoff isochore between temperatures T_0 and T , assuming ΔC_p° is constant.

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For a given set of K, T data pairs, one pair is set as K_0, T_0 and the remaining values of K, T are used in a regression of eq 6 to find a value of ΔH° at T_0 and ΔC_p° . Another pair of K, T values are selected as the new K_0, T_0 , and the process is repeated until values of ΔH° and ΔC_p° have been obtained for each temperature. The LASL nonlinear, least-squares program was also used with eq 6 to find "best fit" values of ΔH° and ΔC_p° as opposed to the linear form of eq 6 offered by Blandamer. Table VII summarizes the values of ΔH° and ΔC_p° obtained for CoTSPC dimerization in water over the temperature range 25–75 °C. These results suggest that ΔC_p° is finite and constant over the temperature range considered. To confirm this further, the values of ΔH° in Table VII were fit to a linear equation with resulting values of

$$\Delta H^\circ = -16.20 \pm 0.32 \text{ kcal/mol} + [113 \pm 6 \text{ cal/(mol K)}](T) \quad (7)$$

where T is temperature (°C). Thus, the dimerization of CoTSPC possesses a positive heat capacity of 0.1 kcal/(mol K) over the temperature range 25–75 °C.

A number of factors have been proposed to account for forces contributing to dimerization of dye molecules such as van der Waals forces, charge-charge interactions, hydrophobic interactions, or the role of the water. The presence of a positive heat capacity rules out hydrophobic interaction as a major contributor, since hydrophobic interactions display a negative heat capacity as discussed recently by Evans and Lumry⁴⁶ with regard to critical micelle formation.

Another piece of evidence to support our contention that hydrophobic bonding does not contribute to dimerization is the rapid dissolution of CoTSPC in water as opposed to alcohol, which is characteristic of an electrolyte as opposed to a hydrophobic solute. The crucial aspect of dimerization of CoTSPC appears to be electrostatic interactions from the charged sulfonate groups, so that CoTSPC can be considered as a typical polyelectrolyte in solution.

Evans and Lumry also point out that it is dangerous to use ΔH° and ΔS° values near room temperature to interpret the thermodynamics of association, since the unique structure of water imposes contributions to ΔH° and ΔS° that compensate. Evans suggests that one use hydrazine in place of water as a solvent or examine ΔH° and ΔS° at high temperatures where the unique water structure disappears. Using values of ΔH° and ΔS° at 75 °C (Table VII), one sees that CoTSPC dimerization has a positive entropy. In the view of the fact that formation of a dimer should produce a negative entropy, a sizable contribution to entropy may come from release of water molecules on dimer formation. This is further substantiated by a recent article by Ohling⁴⁷ who measured the pressure dependence of dimerization of methylene blue and pyronine G dyes. He found that the volume change on dimerization was negative, which he attributed to release of water on dimer formation. Thus, we agree with Abel et al.³⁴ that water participates in dimer formation, but we find that water is released into the bulk solvent when the dimer forms as opposed to their contention that water is incorporated into the dimer.

Registry No. CoTSPC, 14586-48-2.

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Copper(I) Complexes of Olefins Produced by Olefin Chemical Ionization of Copper(II) β -Diketonates

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Olefins serve as effective chemical ionization reagents for copper(II) complexes of β -diketonates. Reactions induced by the proton transfer from ions in the high-pressure olefins include fragmentation of the complex, reduction of the copper(II) to copper(I), and subsequent reaction of the copper(I) species with the reagent olefin. This reaction sequence is most pronounced when the ligand is hexafluoroacetylacetonate, but is observed for trifluoroacetylacetonates and acetylacetonates as well. In addition, condensation reactions of the metal complexes occur to form cluster ions. Comparable reactions are noted between reagent ions and metal complexes. When cluster ions contain Cu(I), these ions are seen to react with neutral reagent molecules to form olefin complexes comparable to those observed for fragment ions.

Introduction

There has been continued interest in the olefin complexes of Cu(I). Among other properties, they have been implicated as intermediates in the copper-catalyzed photoreactions of many olefins.¹ Considerable attention has been paid to the role of Cu(I) in the photoisomerization of norbornadiene to quadacyclane because of the potential usefulness of these systems for storage of solar energy.²

More generally there has been growing interest in the use of metal atoms as potential chemical ionization agents. Metal ions generated by a laser focused on a copper foil have induced reactions in organic molecules.³ Mass spectrometric investigations of the electron-impact-induced reactions in the vapor phase of volatile neutral copper(II) complexes have been interpreted as exhibiting intramolecular redox steps that yield a variety of Cu(I)

species including Cu(I) as a free metal ion.⁴ The latter method of generating Cu(I) ions may be more gentle than the former.

The combination of the interest in Cu(I) as a catalyst in photoreactions of olefins and the possibility of directly demonstrating the reactions of the Cu(I) oxidation state and comparing those reactions to reactions of Cu(II) complexes has motivated us to investigate the olefin chemical ionization (CI) of several Cu(II) β -diketonates.

Experimental Section

A Varian-MAT 112 mass spectrometer equipped with a CI source was used to obtain mass spectra. The typical charge-transfer agent, isobutane, was replaced by various unsaturated hydrocarbons. The unsaturated hydrocarbons used included ethene, propene, allene, propyne, methylpropene (isobutene), 1-butene, *cis*-2-butene, and 1,3-butadiene. These gases were obtained commercially (instrument grade or better) and were used without further purification. Typical pressures in the source were estimated by measuring the ratio of CH_5^+ intensity to total ion intensity in the mass spectra of methane, following the work of Field,

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