

Solubilities of Copper(II) and Chromium(III) β -Diketonates in Supercritical Carbon Dioxide

Anthony F. Lagalante, Brian N. Hansen, and Thomas J. Bruno*

Thermophysics Division, National Institute of Standards and Technology, CSTL, 325 Broadway, Boulder, Colorado 80303

Robert E. Sievers

Global Change and Environmental Quality Program, Department of Chemistry and Biochemistry, Campus Box 215, University of Colorado, Boulder, Colorado 80309

Received March 2, 1995[⊗]

The mole fraction solubilities of ten copper(II) and five chromium(III) β -diketonates were measured in supercritical carbon dioxide with a spectroscopic technique and found to vary over 4 orders of magnitude. Observed trends indicate that the solubility in supercritical carbon dioxide is strongly dictated by the character of the hydrocarbon or fluorocarbon shell surrounding the central metal atom. A group-contribution approach was used to calculate the solubility parameter of the anion of the uncomplexed β -diketone that was correlated to the experimentally measured solubility. A regular solutions approach was used for Cr(acac)₃ to quantitatively attempt to predict the solubility in supercritical carbon dioxide. Solubility data, solubility parameter trends, and limitations of regular solutions theory applied to supercritical fluids are discussed.

Introduction

The metal β -diketonates are a class of unusually volatile metal complexes. Surrounded by either a hydrocarbon or fluorocarbon shell, the central metal ion is not as susceptible to the intermolecular forces that characteristically render metal complexes nonvolatile and insoluble in nonpolar solvents but soluble in strongly polar solvents. β -Diketonate derivatives of virtually every metal and metalloid have been synthesized with a wide range of ligands. Metal β -diketonates have found use in fuel additives,^{1–4} metal–organic chemical vapor deposition (MOCVD) sources,⁵ trace metal analysis by gas chromatography,^{3,6–11} and numerous other extraction applications. Only recently has the dissolution of chelating agents in supercritical fluids been explored as a possible route to waste cleanup^{12–18} and superconducting thin film manufacturing.^{19–20}

In the present study, the mole fraction solubilities of ten copper(II) and five chromium(III) β -diketonates were measured spectroscopically in supercritical CO₂ and found to vary over 4 orders of magnitude in solubility. The trend in solubility was correlated to the hydrocarbon or fluorocarbon ligand shell utilizing a solubility parameter, δ , calculated from the group-contribution approach of Fedors.

Theory

A definition for the solubility parameter was developed by Hildebrand as the square root of the cohesive energy density.²¹ The cohesive energy is comprised of two parts; the energy of vaporization, and the energy to completely separate the molecules of the saturated vapor. In a solubility process, the molecules of the solid solute are separated from each other by the molecules of the solvent, and this is analogous to the cohesive energy term. The solubility parameter is a useful way to describe how the bulky and highly electronegative fluorine substitution around the central metal ion of a metal β -diketonate solute reduces the cohesive energy by reducing the van der Waals attraction and intermolecular hydrogen bonding of the solute. In terms of a solubility parameter, fluorine substitution for hydrogen also increases the volume contribution, resulting in an overall lower solubility parameter. Many group contributions to the solubility parameter have been devised; however, the method of Fedors^{22,23} was chosen due to the close agreement between calculated solubility parameters and solubility parameters reported from other sources and its prior use to predict qualitative trends of organic compound solubilities in supercritical fluids.²⁴ Through the use of Fedors' group contribution values for the cohesive energy density, a working solubility parameter can

* Author to whom correspondence should be addressed.

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be obtained for complex molecules that is defined by

$$\delta = \left[\frac{\sum_i \Delta U_i}{\sum_i V_i} \right]^{1/2} \quad (1)$$

where ΔU is the group contribution to the molar cohesive energy and V is the molar volume group contribution. For regular solutions, the Scatchard-Hildebrand²⁵ equation states

$$RT \ln(a_2/y_2) = V_2 \phi_1^2 (\delta_2 - \delta_1)^2 \quad (2)$$

where a is the activity, y_2 is the mole fraction, V is the molar volume, ϕ is the volume fraction, and subscripts 1 and 2 represent solvent and solute, respectively. Equation 2 provides the only predictive method for quantitating solubilities from regular solutions theory. Giddings developed the solubility parameter expression for the supercritical fluid solvent

$$\delta_1 = 1.25 P_c^{1/2} \left(\frac{\rho_r}{\rho_{r, \text{bp}}} \right) = 1.25 P_c^{1/2} \left(\frac{\rho_r}{2.66} \right) \quad (3)$$

where $\rho_{r, \text{bp}}$ is the reduced density at the normal boiling point of the fluid which for conventional liquid solvents is roughly 2.66.²⁶ Equation 3 has both a physical ($\rho_r/\rho_{r, \text{bp}}$) and a chemical ($P_c^{1/2}$) contribution to δ . Conventional liquid solvents depend mostly on the chemical effect of solubility, whereas compressible gases possess the additional state effect so advantageous in extraction/separation processes. As the solubility parameter difference approaches zero in eq 2, maximum solubility results, giving rise to the "like dissolves like" concept of solubility.

Although typically used as a qualitative tool, through eq 2 solubility parameters can be used in semiquantitative predictions of solubility. Rewriting eq 2 in terms of the activity coefficient, γ , gives

$$RT \ln \gamma_2 = V_2 \Phi_1^2 (\delta_2 - \delta_1)^2 \quad (4)$$

The fugacity of the solid solute, f_2^s , can be related to the fugacity of a standard state by

$$f_2^s / f_2^l = \gamma_2 \gamma_2 \quad (5)$$

where the standard state chosen is the pure, subcooled liquid state, f_2^l , of the solvent. The fugacity ratio of eq 5 can be calculated from the energy change in going from a solid to subcooled liquid and is approximated as

$$\ln \left(\frac{f_2^s}{f_2^l} \right) = \frac{-\Delta H_{\text{fus}}^m \left[\frac{T_m}{T} - 1 \right]}{RT} \quad (6)$$

where T_m is the melting point temperature and ΔH_{fus}^m is the enthalpy of fusion at the melting point.²⁷ Equation 6 can be substituted into eq 5 and solved for the activity coefficient of the solute. Equation 4 can also be solved in terms of the activity coefficient of the solute. Equating the two activity coefficients and solving for the mole fraction solubility gives

$$y_2 = \exp \left[\frac{-\Delta H_{\text{fus}}^m \left[\frac{T_m}{T} - 1 \right]}{RT} - \frac{V_2 \Phi_1^2}{RT} (\delta_2 - \delta_1)^2 \right] \quad (7)$$

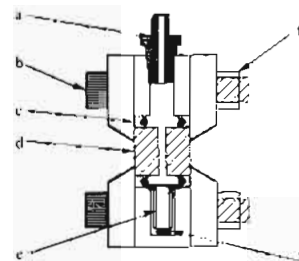


Figure 1. High-pressure equilibrium cell: (a) high-pressure fitting; (b) fastening bolt; (c) spring seal; (d) quartz window; (e) saturator; (f) backing nut; (g) poly(tetrafluoroethylene) coated stirring bar.

Using eq 7, the solubility of a given solute in a supercritical fluid can be calculated using nonideal solutions approximations.

Experimental Section

Cell Design. The cell used to measure solubilities in supercritical CO₂ is depicted in Figure 1. The use of polyurethane static spring seals to form the glass-to-metal seal offers several advantages over previously reported high-pressure cells.²⁸⁻³⁰ Since the quartz windows do not rely on a polymer seal to the window faces, no restriction is placed on the distance between the windows, allowing extremely short path lengths for high concentrations of solute or for solutes with large extinction coefficients. Furthermore, unlike compressible polymeric window face seals, the window faces are seated against 316 stainless steel (AISI designation) plates to give a constant cell path length. Stainless steel washers were easily placed behind the windows to shorten the path length further. The path length used in the following experiments was approximately 2 mm. The windows used were 12.7-mm-diameter, 6.35-mm-thickness optical grade quartz ground and polished on all surfaces. The body (1.5 cm thick, 5 cm wide, 5 cm long) and outer window plates (5-cm diameter, 0.635-cm diameter center bore for light path) were constructed from 316 stainless steel. A cavity at the bottom of the central body accommodated a saturator and a 3-mm poly(tetrafluoroethylene) coated stirring bar, coupled to external NdFeB magnets as in previous cell designs.²⁹ The saturator was a stainless steel bucket that fit loosely in the 0.635-cm central bore and rested on a 1-mm rim. The bottom of the saturator was a press fit 400 mesh stainless steel screen that allowed fluid to be centrifugally circulated through the saturator. The entire cell was heated in an aluminum block by two 50-W cartridge heaters. A platinum resistance thermometer was used to measure and control the temperature to within ± 0.2 °C using a microprocessor-based controller.

Chemicals. Table 1 lists the copper(II) and chromium(III) complexes used in the study. The complexes obtained from commercial suppliers were used without further purification. For the complexes synthesized previously in our laboratory, purity was confirmed by comparison with a reported melting point. Complexes were stored in vacuum over CaSO₄ prior to measurement to prevent hydration or complexation with water. The Cu(hfa)₂ complex was initially green, indicating that water was complexed to a free site on the copper ion. Comparison to the reported melting point³¹ indicated that a single water molecule was coordinated to the complex. When the Cu(hfa)₂ complex was dried in vacuum over CaSO₄, a purple complex

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Table 1. Abbreviations Used for the Copper(II) and Chromium(III) Complexes

| abbreviation | chemical name |
|----------------------------|--|
| Cu(acac) ₂ | bis(pentane-2,4-dionato)copper(II) ^a |
| Cu(bzac) ₂ | bis(1-phenylpentane-1,3-dionato)copper(II) ^a |
| Cu(thd) ₂ | bis(2,2,6,6-tetramethylheptane-3,5-dionato)copper(II) ^a |
| Cu(tod) ₂ | bis(2,2,7-trimethyloctane-3,5-dionato)copper(II) |
| Cu(tfa) ₂ | bis(1,1,1-trifluoropentane-2,4-dionato)copper(II) ^a |
| Cu(hfa) ₂ | bis(1,1,1,6,6,6-hexafluoropentane-2,4-dionato)copper(II) ^a |
| Cu(dmhd) ₂ | bis(1,1-dimethylhexane-3,5-dionato)copper(II) |
| Cu(dibm) ₂ | bis(2,6-dimethylheptane-3,5-dionato)copper(II) |
| Cu(tfbzm) ₂ | bis(1,1,1-trifluoro-4-phenylbutane-2,4-dionato)copper(II) |
| Cr(acac) ₃ | tris(pentane-2,4-dionato)chromium(III) ^a |
| Cr(acac-Br) ₃ | tris(3-bromopentane-2,4-dionato)chromium(III) |
| Cr(thd) ₃ | tris(2,2,6,6-tetramethylheptane-3,5-dionato)chromium(III) ^a |
| trans-Cr(tfa) ₃ | trans-tris(1,1,1-trifluoropentane-2,4-dionato)chromium(III) |
| cis-Cr(tfa) ₃ | cis-tris(1,1,1-trifluoropentane-2,4-dionato)chromium(III) |

^a Compound obtained from a commercial supplier.

that matched the melting point of the dehydrated complex resulted. The *cis* and *trans* isomers of Cr(tfa)₃ were separated on an alumina column as described by Fay and Piper,³² and purity was confirmed by comparison to the reported melting point. The SFC grade CO₂ was used as received from a commercial supplier.

Solubility Measurement. The solute was loaded in the saturator and placed into the central bore above the stirring bar. The windows and spring seals were set flush to the outer surface of the central body, and the two outer window plates were bolted to the center body. After the temperature reached equilibrium at 40 °C, the cell was purged with gaseous CO₂ to remove air, and a reference spectrum was taken. The cell was pressurized with CO₂ from a syringe pump and allowed to equilibrate while being stirred for 10–15 min, after which a ultraviolet–visible (UV–vis) absorbance spectrum from 190 to 820 nm was taken on a photodiode array spectrophotometer with 2-nm resolution. The cell pressure was measured from the transducer on the syringe pump, which was calibrated within ± 0.005 MPa over the range studied, traceable to a NIST dead weight pressure balance.

The absorbance in supercritical CO₂ was calculated by subtracting an absorbance value at a nonabsorbing region of the spectrum (e.g., 820 nm) from an absorbance value at a peak maximum (approximately 670 nm for the copper(II) complexes or 560 nm for the chromium(III) complexes). Following measurement of a solubility isotherm, the cell was depressurized and rinsed with a liquid solvent, such as acetone, delivered through a syringe to remove any undissolved copper complex in the cell. When a clean blank absorbance spectrum was obtained, standards of the metal β -diketonate in either hexane or benzene that bracketed the measured absorbances in supercritical CO₂ were introduced through a syringe and an absorbance spectrum was measured. Extinction coefficients were calculated from the linear calibration curve obtained.

Results

The concentration of a given copper complex in supercritical CO₂ was determined using the Beer–Lambert law from a calibration plot of standard solutions in hexane or benzene. Hexane is taken to have approximately the same polarity as CO₂, producing negligible solvchromatic shifts and exhibiting similar extinction coefficients,^{33,34} however, the standard solutions of Cu(acac)₂, Cu(tfbzm)₂, and Cu(bzac)₂ were prepared

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Table 2. Visible Spectra Peak Maxima and Molar Extinction Coefficients, ϵ , of the Cu(tod)₂ Complex in Various Solvents

| solvent | peak maxima (nm) | ϵ (L·mol ⁻¹ ·cm ⁻¹) |
|-----------------|------------------|---|
| hexane | 668, 538 | 44.18, 39.46 |
| benzene | 664, 538 | 44.17, 39.51 |
| chloroform | 660, 538 | 46.07, 40.84 |
| CO ₂ | 666, 538 | 44.10, 39.48 |

Table 3. Illustrative Example of Fedors' Solubility Parameter Calculation for the Anion of Pentane-2,4-dione^a

| group (quantity) | $-\Delta U$ (cal mol ⁻¹) | V (mL·mol ⁻¹) |
|----------------------|--------------------------------------|---------------------------|
| –CH ₃ (2) | 2(1125) | 2(33.5) |
| –CH= (1) | 1030 | 13.5 |
| C=O (2) | 2(4150) | 2(10.8) |
| total | 11580 | 102.1 |

$$^a \delta = (11580/102.1)^{1/2} = 10.85 \text{ cal}^{1/2} \cdot \text{cm}^{-3/2}.$$

in benzene, where small wavelength shifts (2–6 nm) relative to spectra in CO₂ were evident. Molar extinction coefficients in the visible spectrum of the Cu(tod)₂ complex were determined in various solvents and CO₂ and are summarized in Table 2. From the data in Table 2, it is evident that benzene is a suitable solvent for standard solutions in cases where a complex exhibits a limited solubility in hexane. Table 4 summarizes the measured solubility at 40 °C expressed as a function of the density of CO₂ calculated using the Jacobsen–Stuart modification of the Benedict–Webb–Rubin (BWR) equation of state.³⁵ Solubility data are expressed with an average relative standard deviation of 5.0% (with a coverage factor $K = 2$)³⁶ based on nine replicate measurements at a single temperature and pressure for the Cu(dmhd)₂ complex.

The group contribution method of Fedors was used to calculate a solubility parameter to relate the experimentally measured solubilities of the copper(II) and chromium(III) β -diketonates to a calculated solubility parameter of the ligand moiety. Fedors' δ was calculated from the enolate form of the deprotonated β -diketone ligand, as this structure best represents the state of the ligand when coordinated to the central metal ion. Table 3 presents an example of Fedors' method for the pentane-2,4-dione molecule. Although the internationally recognized SI unit of energy is a joule, cohesive energies were expressed in calories (1 calorie = 4.184 Joules) due to widespread use of the calorie in the Hildebrand expression. A solubility data point at a CO₂ density of 19.867 mol L⁻¹ was chosen to relate the experimental solubility of the copper(II) and chromium(III) β -diketonates to the calculated solubility parameter of the free ligand in Figure 2.

Equation 7 was used to attempt prediction of the solubility of Cr(acac)₃ in supercritical CO₂. Using the BWR equation of state for the pure CO₂ solvent, δ_1 can be calculated from eq 3. The ΔH_{fus}^m of Cr(acac)₃ was reported to be 28.40 kJ mol⁻¹, and the melting point was reported as 216 °C.³⁷ These values along with the crystal structure volume, 257.66 mL mol⁻¹,³⁸ allowed predictive solubility calculations for the complex using eq 7. Ideal solubility ($\gamma = 1$) was calculated using eqs 5 and 6.

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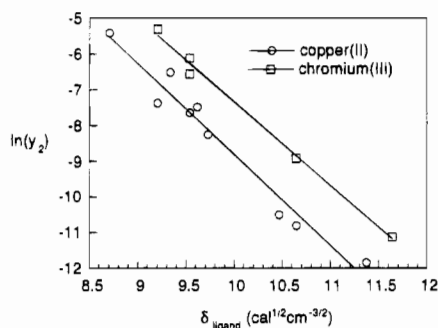
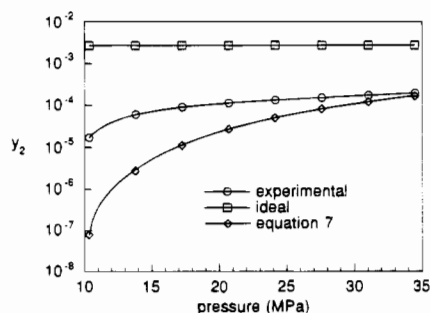
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Table 4. Experimental Mole Fraction Solubilities in Supercritical CO₂ at 40 °C and δ (cal^{1/2}·cm^{-3/2}) of the Ligand

| complex | δ | mole fraction solubility ($\times 10^5$) for given pressure (MPa) (density g·mL ⁻¹) | | | | | | | |
|--|----------|---|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| | | 10.34 (0.652) | 13.79 (0.760) | 17.24 (0.811) | 20.68 (0.847) | 24.13 (0.874) | 27.58 (0.897) | 31.03 (0.916) | 34.47 (0.933) |
| Cu(acac) ₂ | 10.65 | 0.750 | 1.300 | 1.612 | 1.845 | 2.006 | 2.120 | 2.229 | 2.307 |
| Cu(bzac) ₂ | 11.37 | 0.179 | 0.324 | 0.462 | 0.599 | 0.721 | 0.838 | 0.944 | 1.047 |
| Cu(thd) ₂ | 9.21 | 6.173 | 30.35 | 44.69 | 58.24 | 62.74 | 67.97 | 71.64 | 74.15 |
| Cu(tod) ₂ | 9.34 | 26.03 | 49.00 | 77.51 | 114.1 | 148.8 | 181.0 | 212.8 | 269.7 |
| Cu(tfa) ₂ | 9.54 | 29.60 | 31.33 | 35.27 | 42.08 | 48.18 | 54.62 | 57.38 | 59.38 |
| Cu(hfa) ₂ ·H ₂ O | | 152.0 | 174.1 | 206.3 | 241.7 | 261.0 | 291.3 | 332.0 | 414.0 |
| Cu(hfa) ₂ | 8.71 | 225.1 | 321.1 | 353.5 | 382.0 | 449.7 | 502.7 | 569.9 | |
| Cu(dmhd) ₂ | 9.73 | | 3.696 | 15.40 | 20.51 | 26.04 | 32.11 | 34.01 | 36.21 |
| Cu(dibm) ₂ | 9.62 | 9.170 | 27.26 | 38.60 | 46.19 | 56.13 | 73.05 | 79.42 | 88.41 |
| Cu(tfbzm) ₂ | 10.47 | | 0.702 | 1.424 | 2.113 | 2.740 | 3.313 | 3.843 | 4.269 |
| Cu(acac) ₃ | 10.65 | 1.716 | 6.068 | 9.094 | 11.27 | 13.25 | 15.03 | 17.04 | 19.09 |
| Cr(acac-Br) ₃ | 11.64 | 0.496 | 0.745 | 1.030 | 1.276 | 1.467 | | | |
| Cr(thd) ₃ | 9.21 | 400.0 | 372.2 | 420.8 | 449.4 | 496.6 | 574.0 | 604.9 | |
| <i>trans</i> -Cr(tfa) ₃ | 9.54 | 147.9 | 169.1 | 177.3 | 197.4 | 222.4 | 250.6 | 263.8 | 272.1 |
| <i>cis</i> -Cr(tfa) ₃ | 9.54 | 67.30 | 87.81 | 113.9 | 135.6 | 142.2 | 160.1 | 170.7 | 190.8 |

**Figure 2.** Plot of $\ln(y_2)$ solubility in supercritical CO₂ at a density of 0.874 g mL⁻¹ versus Fedors' calculated solubility parameter of the free ligand.**Figure 3.** Measured and predicted values of Cr(acac)₃ solubility in supercritical CO₂ from regular solutions theory.

Predicted and measured solubilities for the Cr(acac)₃ complex are shown in Figure 3, along with the ideal solubility.

Discussion

The experimental solubilities of Table 4 conform to the commonly observed linear relationship between $\log(y_2)$ and fluid density.³⁹ The solubility measurements suggest that substituting trifluoromethyl for methyl groups as substituents increases solubility, while substituting phenyl groups decreases solubility. Substitution of *tert*-butyl for methyl groups also increases solubility, as seen in the progression Cu(acac)₂, Cu(dmhd)₂, and Cu(thd)₂. The plot in Figure 2 shows a good correlation between the calculated solubility parameter and the experimentally measured mole fraction solubility of both the copper(II) and chromium(III) β -diketonates in supercritical CO₂. For the nine copper(II) complexes plotted in Figure 2, a linear relationship ($R = 0.980$) is exhibited over 4 orders of magnitude. Given that (a) the copper β -diketonates crystallize in square planar

structure,⁴⁰ (b) the central copper ion is in a similar environment based on the nearly equal Cu–O bond distances, (c) the spectral shifts in nondonor solvents are small, and (d) the solution and reflection spectra are nearly identical,⁴¹ the observed trend based on the ligand moiety is not surprising. Others have observed experimentally that increasing fluorine substitution on the ligands bound to metals increases the solubility of the chelates in supercritical CO₂^{12,13,42,43} and decreases retention times of the β -diketonates in gas chromatography.¹⁰

Figure 2 also illustrates the relationship between the measured solubility in supercritical CO₂ for the octahedrally coordinated β -diketonate complexes of chromium(III). Again, a linear relationship ($R = 0.995$) is observed between the experimentally determined mole fraction solubility and the solubility parameter of the complex periphery. Though unsymmetrical copper(II) β -diketonates are capable of possessing *cis* and *trans* isomers in solution and will interchange rapidly to form racemic mixtures in supercritical CO₂, the *cis* (facial) and *trans* (meridional) isomers of Cr(tfa)₃ are kinetically inert on the time scale of the solubility measurement; therefore, their individual solubilities were determined in supercritical CO₂. All of the CF₃ groups of *cis*-Cr(tfa)₃ reside on the same side of the complex, which results in the *cis* isomer being more polar than the *trans* isomer of Cr(tfa)₃. Fay and Piper^{32,44,45} have previously demonstrated that the more polar *cis* isomers of octahedrally coordinated trivalent metals are more soluble than the *trans* isomers in polar solvents such as ethanol. The solubility of *trans*-Cr(tfa)₃ isomer was, on the average, 65% higher than the solubility of the *cis* isomer over the entire solubility isotherm in supercritical CO₂, as might be expected from the nonpolar nature of the CO₂ molecule. In the SFC separation of *cis*-Cr(tfa)₃ and *trans*-Cr(tfa)₃ on an octadecylsilane column using supercritical CO₂ as the mobile phase, the longer retention time of the *cis* isomer was ascribable to both stationary phase interactions and the lower solubility of the *cis* isomer in the mobile phase.⁴⁶ The higher solubilities of the complexes of chromium(III) over the corresponding complexes of copper(II) is probably attributable to the increased extent of contact of the surrounding ligand with the solvent.

On the basis of solubility parameters of the free ligand alone, one would predict the order acac < dmhd < dibm < tod < thd

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for increasing solubility in CO₂ of the copper(II) β -diketonates with alkyl peripheral moieties. However, the Cu(tod)₂ complex was observed experimentally to exhibit the highest solubility in supercritical CO₂, and this mirrors what was previously observed in *n*-hexane.⁴ A possible explanation for the observed trend may be found by examination of the crystal structure of the complex. While most unsymmetrical β -diketonate complexes of copper(II) crystallize in the nonpolar *trans* square planar configuration,⁴⁷ the Cu(tod)₂ complex crystallizes in a *cis* square planar configuration in which a small permanent dipole exists.⁴ Though the complex will racemize to form *cis* and *trans* isomers in solution, if the *cis* configuration is favored in solution, a permanent dipole will exist in the complex that cannot be accounted for by the ligand group-contribution method of Fedors.

Cu(hfa)₂ exhibits a statistically significant higher solubility than the monohydrated Cu(hfa)₂ complex. The structure of the monohydrated complex is assumed to be a five-coordinate, square pyramidal structure rather than four-coordinate square planar, as all of the other copper(II) chelates are presumed to be.

From the data presented in Figure 3, one can conclude that the regular solutions theory framework provides a poor predictive model when applied to supercritical fluid solubility of the complexes studied in this work. The large discrepancy between predicted and experimental solubilities can potentially be explained by some of the simplifying assumptions in regular solution theory. The geometric mean assumption for the δ_{12} term may not be valid for the molecular interactions between components so dissimilar as CO₂ and Cr(acac)₃. The volume change of the pure liquid components on mixing is assumed to be zero, however, especially for conditions about the critical point, this is possibly a poor assumption due to clustering. It has been well established that solvent clustering about solute molecules exists in dilute supercritical fluid mixtures.^{28,48-50} The clustering effect in supercritical fluids consists of three re-

gions: (1) gas-phase solute-solvent clustering, (2) clustering in the near critical region, and (3) "liquid-like" solvation.²⁸ The predicted solubility for Cr(acac)₃ approaches the measured solubility at higher pressures, where the fluid phase better resembles that of a pure liquid. The volume change of the pure liquid components on mixing is assumed to be zero, however, for conditions about the critical point, this is possibly a poor assumption due to clustering. Qualitatively, it is important to note that the measured solubility is lower than the ideal solubility. The ideal solubility is the maximum solubility achievable, since nonidealities increase γ , resulting in a decrease in γ_2 . If there is specific chemical solvation of the solute by the solvent, such as in hydrogen bonding or ion pair formation, the observed solubility can exceed the ideal solubility. This is not the case in the pressure region measured, indicating that there are no strong specific forces between Cr(acac)₃ and CO₂.

Conclusions

The solubilities of copper(II) and chromium(III) β -diketonates were measured and examined as a function of the solubility parameter of the free ligand calculated from a group-contribution approach. A trend was observed relating substitution about the periphery of the complex to the measured solubilities in supercritical CO₂ through the use of a calculated solubility parameter. Regular solutions theory applied to Cr(acac)₃ appears to be limited in the quantitative prediction of solubility in a supercritical fluid due to simplifying assumptions such as a zero mixing volume.

Acknowledgment. The assistance of Bill Ingino and Eric Cravens is gratefully acknowledged. A.F.L. gratefully acknowledges the financial support of the Professional Research Experience Program (PREP) at NIST.

IC950234X

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