

## Preparation and Properties of Some Alkane-Soluble Liquid Transition Metal Complexes

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A series of nickel(II) compounds have been prepared which are derivatives of reported  $\beta$ -diketonates, *N,N*-dithiocarbamates, or *O,O'*-dithiophosphates. The transition metal ion complexes reported here are unusual in that they are liquids or low melting waxes that are very soluble in hydrocarbon solvents such as pentane and squalane. Because of their properties, techniques used for the isolation and subsequent purification of the complexes are different than those employed for the lighter homologues. The ligand substituents profoundly affect the properties of the compounds. In contrast to the reported complexes, the nickel(II) bis- $\beta$ -diketonates prepared in this study undergo the monomer-trimer transition close to room temperature. For example, in the compound in which the methyl groups of nickel(II) acetylacetonate are replaced by *n*-heptyl groups, the transition from diamagnetic purple solid monomer to paramagnetic green liquid trimer occurs at about 17 °C. It occurs at 42 °C for the *n*-nonyl derivative. The *t*-nonyl (1,1-dimethylheptyl) derivative melts at +2 °C since the bulky groups adjacent to the carbonyls prevent trimer formation and hinder crystallization.

### Introduction

Relatively few transition metal ion complexes are known that have appreciable solubility in aliphatic hydrocarbons. Such solubility properties are desirable for oil and gasoline additives [1, 2] investigation of fundamental acid-base interactions [3, 4], investigations of the role of metal ions in catalytic oxidations, polymer stabilization inhibitors for polymer degradation [2, 5–8] and as stationary phases with specific complexing ability utilized in gas-liquid chromatography [9]. We know of no systematic study of the modifications necessary in the standard chelating systems that would impart this property. We report here the synthesis of several complexes that have hydrocarbon chains that impart this unusual solubility property. The compounds were obtained in

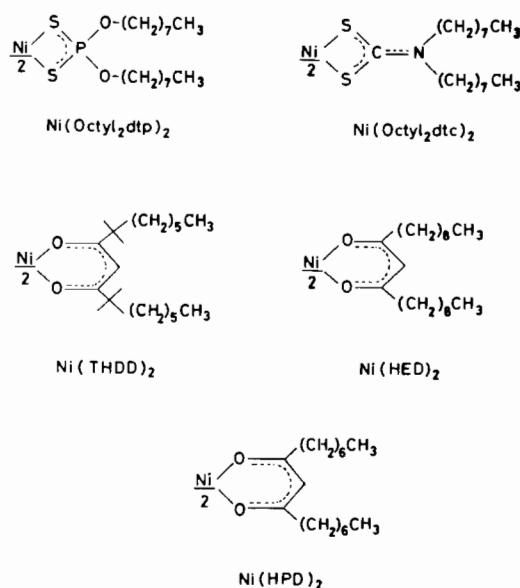


Figure 1. Compounds prepared in this study.

solution using synthetic procedures similar to those for the lower molecular weight homologues. However, because the products are liquids instead of crystalline materials, their isolation and subsequent purification is different than those employed for the lighter homologues.

The compounds consist of a nickel(II) center to which are coordinated two identical bidentate ligands, each of which possesses either one or two alkyl groups which contain a linear portion at least six carbons long. Structures of the compounds are given in Figure 1. Ni(Octyl<sub>2</sub>dtp)<sub>2</sub>, Ni(THDD)<sub>2</sub> and Ni(HPD)<sub>2</sub> are liquids at room temperature whereas Ni(Octyl<sub>2</sub>dtc)<sub>2</sub> and Ni(HED)<sub>2</sub> melt slightly above room temperature. The chain length also profoundly influences other physical properties of these materials.

During the course of this work we discovered that certain of the nickel bis- $\beta$ -diketonates undergo a monomer-trimer transition close to room temperature [10]. There are well established precedents for both monomeric and trimeric bis( $\beta$ -diketonate)-

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nickel(II) compounds [12–22]. The diamagnetic purple [23] monomers contain four-coordinate nickel(II) [17], whereas in the green trimers oxygen bridges permit the nickel ions to become six-coordinate [1]. The steric and electronic factors influencing the position of this equilibrium have long been established [13, 14]. We report here, by virtue of having liquid and hydrocarbon soluble transition complexes, systems in which the crystal lattice energy becomes dominant in determining the position of equilibrium.

## Experimental

### *Bis(O,O'-di-n-octyldithiophosphato)nickel(II), Ni(Octyl<sub>2</sub>dtp)<sub>2</sub>*

The compound was obtained in solution in a manner similar to that given by Livingstone and Mihkelson [25]. **CAUTION: Hydrogen sulfide and hydrogen chloride are evolved.** To phosphorus pentasulfide (22.2 g, 0.10 mol) under a nitrogen atmosphere was added 1-octanol (75 ml). After the mixture was stirred 1 hour with gentle heating, nickel(II) chloride hexahydrate (30 g, 0.13 mol) was added, the mixture turning purple. After 10 minutes of additional heating and a cooling period of 30 minutes, the purple solution was decanted from the residual solid. The solution was extracted 3 times with methanol to remove excess 1-octanol. The purple liquid which remained was dissolved in petroleum ether (bp 60–68°) and extracted three times with water. The solvent was removed, leaving 15 g (20%) of the crude purple liquid.

The purple liquid was eluted from a 9 × 33 cm silica gel column with carbon tetrachloride. The first 100 ml of eluant was discarded, the purple eluant being collected in 500 ml fractions. The solvent was removed from the first and second 500 ml fractions to yield a combined weight of 10 g (13%) of purple liquid. Characteristic infrared bands include those at 995(s) (P–O), 666(s) (P–S), 570(s) (P–S), 365(s) (Ni–S) cm<sup>-1</sup>. Mw(cyclohexane): Calculated: 766. Found: 755.

*Anal.* Calcd for C<sub>32</sub>H<sub>68</sub>O<sub>4</sub>S<sub>4</sub>P<sub>2</sub>Ni: C, 50.19; H, 8.95; S, 16.75; P, 8.09; Ni, 7.67. Found: C, 50.05; H, 8.80; S, 16.77; P, 8.15; Ni, 7.71.

### *Bis(N,N-di-n-octyldithiocarbamato)nickel(II), Ni(Octyl<sub>2</sub>dtc)<sub>2</sub>* [24]

This preparation was patterned after that given by Hendrickson *et al.* [26]. Carbon disulfide (0.68 ml, 11 mmol) was added to a rapidly stirred suspension of sodium hydroxide (0.43 g, 11 mmol), di-n-octylamine (2.41 g, 10 mmol), and 50 ml water in a flask fitted with reflux condenser. More water was then added to soften the thick white mass which had formed. After 1 hour, the suspension was added to a

rapidly stirred solution of nickel(II) chloride hexahydrate (1.19 g, 4.8 mmol) in 100 ml of water. A brown-green precipitate formed along with some brown oil. The precipitate was collected on a sintered glass funnel, the supernatant being clear and colorless. The material was dried in the presence of anhydrous calcium sulfate for two weeks. The brown-green material is a wax which melts and freezes at about room temperature. The infrared spectrum has a characteristic strong peak at 1505 cm<sup>-1</sup> which compares well with the C–N stretch at 1512 cm<sup>-1</sup> in bis-(diethyldithiocarbamato)nickel(II) [4].

*Anal.* Calcd for C<sub>34</sub>H<sub>68</sub>N<sub>2</sub>S<sub>4</sub>Ni: C, 59.02; H, 9.91; N, 4.05; Ni, 8.49. Found: C, 58.91; H, 9.71; N, 4.12; Ni, 8.80.

### *Heneicosane-10,12-dione*

The method of Kopecky *et al.*, was used in this preparation [25]. Anhydrous conditions were employed and provisions were made to measure the amount of gas evolved. Ethyl decanoate (20.0 g, 0.100 mol) and 57% sodium hydride in mineral oil (8.4 g of suspension, 0.20 mol of NaH) were added to 150 ml of dimethoxyethane. The sodium hydride was washed with pentane to remove the oil before the addition. 2-undecanone (18.3 g, 0.102 mol) in 20 ml dimethoxyethane was added dropwise to the stirred refluxing mixture over a 1.5 hour period. Gas evolution continued after the ketone addition was complete. After 5 liters of gas were evolved, the reaction mixture was cooled and placed in a large beaker. Concentrated hydrochloric acid (12.5 ml, .27 mol) was added as rapidly as possible, producing white precipitate and foam. **CAUTION:** Since the reaction mixture is heterogeneous, uneven stirring during the addition of the acid may result in sudden foaming. The mixture was then poured onto a mixture of 250 ml of water and 70 ml of petroleum ether (bp 60–68°). The aqueous layer was extracted with petroleum ether, the combined petroleum ether extracts then being washed with five 70-ml portions of water and then dried over anhydrous sodium sulfate. The solvent was removed, yielding 23.2 g (71%) of a yellow oil, which, upon cooling, formed white crystals. The β-diketone was then purified through preparation of the copper chelate.

Copper(II) acetate monohydrate (14.2 g, 17 mmol) was dissolved in 120 ml of water, heated almost to boiling, filtered to remove copper metal, and then added to a stirred boiling mixture of the β-diketone in 40 ml of ethanol. The solution was then allowed to cool without stirring. A waxy blue solid layer formed on top of the solution. This was collected by vacuum filtration. The solid was added to boiling ethanol and then heated for 5 minutes, after which fine blue needles formed. These were collected by vacuum filtration and washed with methanol until the supernatant was colorless,

effectively removing the more soluble green chelates of the ester, ketone, and/or carboxylic acid. 13.5 g (36%) of the blue-grey copper chelate was obtained. This was recrystallized from petroleum ether (bp 60–68°), giving blue-grey needles, mp 106 °C.

*Anal.* Calcd for  $C_{42}H_{78}O_4Cu$ : C, 70.99; H, 11.06. Found: C, 70.89; H, 11.16.

#### Isolation of free Ligand

The  $\beta$ -diketone was then obtained by decomposing the copper chelate. The complex was shaken with a mixture of 10% sulfuric acid and pentane until the blue color was completely transferred to the aqueous phase. The aqueous layer was extracted with pentane, and the combined pentane layers washed twice with water, then dried over anhydrous sodium sulfate. The pentane was removed, yielding a white solid which was dried *in vacuo* over night, mp 38.5–39.0. The strong peak at  $1600\text{ cm}^{-1}$  in the infrared spectrum of the nujol mull is indicative of the  $\beta$ -diketone.

*Anal.* for  $C_{21}H_{40}O_2$ . C, 77.72; H, 12.42. Found: C, 77.80; H, 12.52.

#### *Bis(heneicosane-10,12-dionato)nickel(II), Ni(HED)<sub>2</sub>*

The  $\beta$ -diketone (1.85 g, 5.70 mmol) was placed in a beaker with 15 ml methanol and heated to boiling. Nickel(II) chloride hexahydrate (0.678 g, 2.85 mmol) dissolved in 10 ml boiling methanol was added dropwise to the rapidly stirred  $\beta$ -diketone solution. Then, sodium hydroxide (0.233 g, 5.70 mmol) in 50 ml boiling methanol was added dropwise to the rapidly stirred solution. As the addition neared completion, a green oil and white precipitate formed. The solution was allowed to cool with continued stirring, at which time the green oil solidified. The mixture was extracted with pentane which was extracted with water, then dried over anhydrous sodium sulfate. The pentane was removed, the last traces of volatiles being removed by heating at 130 °C and 0.05 torr for 2 hours on a rotary evaporator. A green oil was recovered, 1.7 g (85%). In about 0.5 hour, this solidified to form a purple solid, mp = 42–45°, i.r.  $1530, 1560\text{ cm}^{-1}$  (strong), indicative of a chelated  $\beta$ -diketone. The visible spectra of the solid showed a peak at 5350 Å, indicative of the monomeric bis( $\beta$ -diketonate)nickel(II).

*Anal.* for  $C_{42}H_{78}O_4Ni$ . C, 71.48; H, 11.14; Ni, 8.32. Found: C, 71.32; H, 10.95; Ni, 8.60.

#### Heptadecane-8,10-dione

The method of preparation was identical to that employed for the previous  $\beta$ -diketone. The impure product was obtained as a liquid and used to prepare the copper chelate (21%), mp 107 °C.

*Anal.* Calc for  $C_{34}H_{62}O_4Cu$ : C, 68.24; H, 10.44; Cu, 10.62. Found: C, 68.50; H, 10.25; Cu, 10.79.

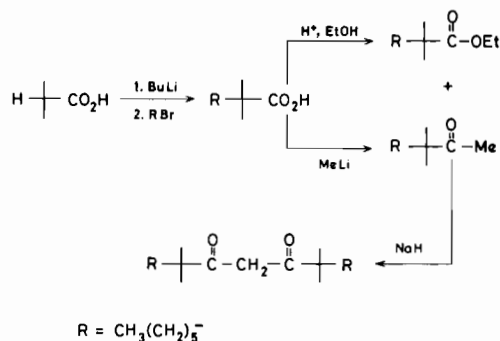


Figure 2. Synthetic route for 7,7,11,11-tetramethylheptadecane-8,10-dione.

The free  $\beta$ -diketone, which in this case is a liquid, was obtained as before from the copper salt.

*Anal.* Calcd for  $C_{17}H_{32}O_2$ : C, 76.06; H, 12.12. Found: C, 75.87; H, 12.05.

#### *Bis(heptadecane-8,10-dionato)nickel(II), Ni(HPD)<sub>2</sub>*

The method employed was similar to that used to prepare the nickel complex, Ni(HED)<sub>2</sub>. The dark green nickel complex was obtained as a liquid, which did not solidify upon standing at room temperature.

*Anal.* Calc for  $C_{34}H_{62}O_4Ni$ : C, 68.80; H, 10.53; Ni, 9.89. Found: C, 68.72; H, 10.40; Ni, 9.99.

#### 7,7,11,11-tetramethylheptadecane-8,10-dione

The preparation of Ni(THDD)<sub>2</sub> is outlined in Figure 2.

#### 2,2-Dimethyloctanoic acid

The method of Creger was used [28]. The crude liquid acid was distilled at 0.1 torr, the clear, colorless fraction boiling at 83–86 °C being retained, 67 g (78%). Characteristic bands existed in the infrared at 3000 (broad) and 1700 (s)  $\text{cm}^{-1}$ .

*Anal.* Calc for  $C_{10}H_{20}O_2$ : C, 69.72; H, 11.70. Found: C, 69.73; H, 11.74.

#### Ethyl-2,2-dimethylhexanoate

The method given by Vogel [29] was used to convert about half of the 2,2-dimethyloctanoic acid to the ethyl ester. The crude liquid ester was distilled at 23 torr. The clear, colorless fraction at 116–118 °C was retained, 28.5 g (80%). A characteristic band existed in the infrared at  $1720\text{ cm}^{-1}$  (s).

*Anal.* Calc for  $C_{12}H_{24}O_2$ : C, 71.95; H, 12.08. Found: C, 71.90; H, 12.33.

#### 3,3-Dimethyl-2-nonanone

The method given by Jorgenson for 4-t-butyl-cyclohexyl methyl ketone [30] was used to convert about half of the 2,2-dimethyloctanoic acid to the methyl ketone. The crude liquid ketone was distilled

at 18 torr. The fraction distilling at 107–109 °C was retained, 29 g (73%). The material contained a characteristic infrared band at 1710  $\text{cm}^{-1}$  (s).

*Anal.* Calc for  $\text{C}_{11}\text{H}_{22}\text{O}$ : C, 77.58; H, 13.02. Found: C, 77.41; H, 12.78.

The same technique as used to prepare the previous  $\beta$ -diketone was used to condense ethyl-2,2-dimethylhexanoate and 3,3-dimethyl-2-nonanone to form the  $\beta$ -diketone. The yellow oil so obtained was vacuum distilled at 0.04 torr on a Nester-Faust spinning band column. The fraction at 135° was retained, 26.0 g (57%). (Purification *via* the copper chelate was not feasible since it appeared to be a liquid.) The infrared contained a symmetrical band at 1600  $\text{cm}^{-1}$ ; no peaks were observed in those regions normally assigned to ester and ketone adsorptions.

*Anal.* Calcd for  $\text{C}_{21}\text{H}_{40}\text{O}_2$ : C, 77.70; H, 12.44. Found: C, 77.74; H, 12.21.

*Bis(7,7,11,11-tetramethylheptadecane-8,10-dionato)-nickel(II), Ni(THDD)<sub>2</sub>*

This was prepared in the same manner as previously described for the nickel chelate, Ni(HED)<sub>2</sub>. A purple liquid was obtained, 8.0 g (100%) with infrared bands at 1525 (s) and 1540 (s)  $\text{cm}^{-1}$ , indicative of a nickel(II)  $\beta$ -diketone chelate. The extinction coefficient in squalane at 5350 Å is 58. M.W. in cyclohexane: Calcd: 706. Found: 707.

*Anal.* Calcd for  $\text{C}_{42}\text{H}_{78}\text{O}_4\text{Ni}$ : C, 71.48; H, 11.14; Ni, 8.32. Found: C, 71.21; H, 10.91; Ni, 8.45.

## Results and Discussion

The high solubility in hexane and squalane was achieved using ligands possessing long linear alkyl chains. The critical nature of the length of the alkyl group is illustrated by the fact that we have found that the nickel(II) bis xanthate is much more soluble when the alkyl group is octyl [31] than when it is octadecyl [32]. Similarly, the *n*-octyl derivative of the nickel(II) dithiocarbamate is much more soluble in squalane than the *n*-butyl derivative [33]. Bis(2,4-pentanedionato)nickel(II) and bis(2,2,6,6-tetramethylheptane-3,5-dionato)nickel(II) [34] are insoluble in squalane whereas the nickel  $\beta$ -diketonates reported here are very soluble.

The liquid compounds we have prepared are *squalane* soluble whereas the solids are not. The solid, monomeric form of Ni(HED)<sub>2</sub> is not immediately soluble in squalane, but the liquid trimeric form is. Evidently, very small crystal stabilization energy [35] suffices to produce squalane insolubility. The smaller size of the pentane molecule apparently leads to better solubility in *pentane* than squalane since the solid form of Ni(HED)<sub>2</sub> immediately dissolves in

*pentane*, forming the solvated trimer. The weak packing forces are also evidenced by the low melting points of these materials.

The copper complexes of the  $\beta$ -diketonates are much less soluble in alkanes. This may be related to the fact that the copper species exist as monomers in solution, with no stabilization from trimerization in solution to compensate for the loss of crystal stabilization energy upon dissolving. The ability to form trimers is related to the Lewis acidity of the metal center and the Lewis basicity of the oxygens. The metal center is apparently more acidic in the nickel(II) than in the copper(II) complex.

The fact that the trimers are often liquids whereas the corresponding monomers are solids may be rationalized on the basis of the structures of the two species. The trimers exist as bulky masses from which twelve alkyl chains protrude. This unit is not expected to pack into an organized crystalline form, hence the compound remains liquid. However, the square planar Ni(THDD)<sub>2</sub> is a soluble liquid, but is monomeric. In this case, aggregation is prevented by the bulky tertiary alkyl groups, eliminating the trimerization process. The combination of the tertiary nature and the long alkane chain again may make it difficult to form an organized crystalline material. This, coupled with the degree of hydrocarbon character of the compound, essentially makes it soluble in itself.

The liquid nature of these nickel compounds can also be predicted from a purely empirical approach based on trends in the homologous series. The dialkyldithiophosphate butyl, isoamyl, and decyl compounds have melting points of 16, 24, and 20 °C respectively [1]. Hence, the octyl derivative, Ni(Octyl<sub>2</sub>dtp)<sub>2</sub>, might be expected to be a liquid at room temperature. The dialkyldithiocarbamate complexes have decreasing melting points as the *n*-alkyl groups increase in length: methyl, 275 (dec); ethyl, 234; propyl, 134; butyl, 95; pentyl, 80 °C [36]. Continuing this trend, we find that the *n*-octyl derivative Ni(Octyl<sub>2</sub>dte)<sub>2</sub> melts at about 30 °C. Finally, for the  $\beta$ -diketonates, those containing short alkyl group derivatives are solids, but the pentyl derivative is found to be a liquid [37]. The heptyl derivative Ni(HPD)<sub>2</sub> is a liquid and the nonyl derivative, Ni(HED<sub>2</sub>), supercools to exist as a liquid.

The green liquid Ni(HPD)<sub>2</sub> dissolves in squalane forming a green solution which is converted to a red-brown solution at 250 °C. The change is reversible with temperature variation. A monomer–trimer equilibrium is evident with a temperature dependence similar to that of Ni(AA)<sub>2</sub>. Ni(HPD)<sub>2</sub> is unlike Ni(AA)<sub>2</sub> in that analytically pure samples remain liquid at room temperature. Ni(DNCM)<sub>2</sub> ( $R_1 = R_3 = n$ -pentyl,  $R_2 = H$ ) is also reported to be a liquid, green trimer at room temperature [19]. Apparently, the larger  $R_1$  and  $R_3$  groups destabilize the crystalline

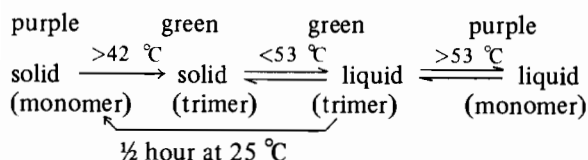
TABLE I. Effect of R Group on Properties of Compound at Room Temperature.

Compound	R Group	Isomer	State	Color	$\mu_{\text{eff}}$ , B.M.	Trans. Temp. <sup>d</sup>
Ni(AA) <sub>2</sub>	methyl	trimer	solid	green	3.3 <sup>a</sup>	...
Ni(HPD) <sub>2</sub>	n-heptyl	trimer	liquid <sup>b</sup>	green	3.3	17
Ni(HED) <sub>2</sub>	n-nonyl	monomer	solid	purple	0 <sup>c</sup>	42
Ni(THDD) <sub>2</sub>	t-nonyl	monomer	liquid	purple	0	...

<sup>a</sup>References 13. <sup>b</sup>Ni(HPD)<sub>2</sub> slowly forms a purple solid below 0 °C. At 17 °C, it starts to form solid trimer, and at 19 °C becomes viscous enough to flow. <sup>c</sup>The supercooled green trimer has a moment of 3.4 B.M. <sup>d</sup>The temperature (°C) at which solid monomer is converted to trimer.

lattice of the trimer, but do not destabilize the trimeric structure itself.

It is of interest to determine the influence of chain length and branching of the alkyl substituents on the properties of the compound. Ni(HED)<sub>2</sub> exists in an unusual balance among several physical states. It is isolated as a purple solid which starts to turn to a green solid upon heating to 42 °C with no purple liquid observed. Between 42 and 45 °C, a mixture of green liquid, green solid, and purple solid appear to coexist and, between 45 and ~53 °C, only green solid and green liquid appear to exist. Apparently, when the purple monomeric solid is heated, a green solid trimer is formed at about 42 °C, which in turn becomes liquid at a slightly higher temperature. If the green liquid is left standing at room temperature for about half an hour, it reverts to the solid purple monomer:



Above 53 °C, the usual monomer–trimer equilibrium exists in the melt and in solution [38].

Ni(HED)<sub>2</sub> is unusual in that both the solid state monomer–trimer transformation and the melting of the green trimer occur close to room temperature, much lower than those in other systems. For the compound where R<sub>1</sub> = R<sub>3</sub> = phenyl and R<sub>2</sub> = H and the compound where R<sub>2</sub> = phenyl and R<sub>1</sub> = R<sub>3</sub> = methyl, the monomer–trimer transformation occurs in the solid state, without melting, at 185° and 160 °C, respectively [14]. As mentioned above, this transformation occurs at about 42 °C for Ni(HED)<sub>2</sub>. For systems such as R<sub>1</sub> = aryl, R<sub>2</sub> = H, R<sub>3</sub> = tert-butyl [21]; R<sub>1</sub> = R<sub>3</sub> = aryl, R<sub>2</sub> = H [16]; and R<sub>1</sub> and R<sub>2</sub> = -(CH<sub>2</sub>)<sub>n</sub>, n = 3,4,5, R<sub>3</sub> = methyl [16]; both monomeric and trimeric forms can be isolated, their melting points being grouped around 200 °C for the monomers and 100 °C for the trimers [39]. In contrast, the green solid trimer of Ni(HED)<sub>2</sub> starts to

melt at about 45 °C, much lower than the systems just described. The reduction in chain length results in a reduction of the temperature at which the monomeric red solid is converted to a green solid trimer. For example, compare Ni(HPD)<sub>2</sub> and Ni(HED)<sub>2</sub> where the decreased bulk of n-heptyl compared to n-nonyl results in a lowering of the transition temperature from 42° to 17 °C. The lack of formation of a purple liquid during the melting of Ni(HED)<sub>2</sub> and Ni(HPD)<sub>2</sub> indicates this form is less stable than either the solid monomer or the liquid trimer. The purple solid monomer is stabilized by crystal packing forces, and the compound upon melting forms a liquid trimer which is stabilized by nickel-oxygen bond formation.

With substituents that have very bulky groups adjacent to the carbonyl, trimer formation is not an available option so that only monomeric forms exist in the liquid. The compound bis(7,7,11,11-tetramethylheptadecane-8,10-dionato)nickel(II) (R<sub>1</sub> = R<sub>3</sub> = -C(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>, R<sub>2</sub> = H), Ni(THDD)<sub>2</sub>, has been isolated in our laboratory as an analytically pure purple monomeric liquid [24]. Like Ni(THD)<sub>2</sub>, the tertiary carbons adjacent to the carbonyls prevent trimer formation, but the rigid planar structure from which four long hydrocarbon chains protrude must be difficult to organize into a crystalline form; its melting point is +2 °C.

The new compounds reported here illustrate how alkyl groups with similar inductive properties can dramatically affect the properties of the compounds. This is summarized in Table I. Proper choice of R<sub>1</sub> and R<sub>3</sub> should allow one to design a molecule such that the desired chemical and physical properties (magnetic, color, physical state, monomer vs. trimer) can be attained at the temperature of interest.

A modification of the usual synthetic procedure is required when the desired transition metal complex is a liquid rather than a solid. For example, one normally attempts to purify an inorganic complex by recrystallization, but this technique is not applicable in this case. On the other hand, purification of liquids usually is done by distillation, but the compounds described here are non-volatile. Although

Ni(Octyl<sub>2</sub>dtp)<sub>2</sub> was purified by column chromatography, Ni(THDD)<sub>2</sub> decomposed under similar conditions. The best approach involves preparations which initially lead to pure isolated compound, *vide infra*. The approach we have used is to perform the metal complexing reaction stoichiometrically, using analytically pure reagents in such a manner that no side products will be formed. This approach is evident in several of our syntheses. In the isolation of Ni(Octyl<sub>2</sub>dtp)<sub>2</sub>, the solvent 1-octanol was removed by extraction. When the nickel β-diketonates were made, it was critical that the free ligands be analytically pure since no reasonable means of separating alkane soluble impurities could be used in the subsequent work up. Even if the usual impurities could be eliminated, it would be difficult to eliminate the ester and ketone used to prepare the β-diketone since they could form adducts with the Lewis acid, metal complex.

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- It is difficult to determine how many liquid transition metal complexes are known because this aspect of a compound's physical nature is often not emphasized. For example, the compound bis(tridecane-6,8-dionato)nickel(II) was reported [11], but mention of the fact that it is a liquid was only made in a footnote in another paper by the same authors (see reference 37).
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- If R<sub>1</sub> = R<sub>3</sub> = methyl and R<sub>2</sub> = alkyl or aryl, except for *o*-tolyl, the compound is isolated as a red monomer (references 5, 7, 9).