

yields no well-defined complexes with mercuric halides, and Drago⁵ reported the preparation of $\text{Hg}(\text{SCN})_2 \cdot 2(\text{CH}_3)_2\text{SO}$, a compound of undefined structure. No mercuric complex of $(\text{C}_6\text{H}_5)_3\text{PO}$ has been reported. Our preparation, then, of $[\text{Hg}(\text{C}_6\text{H}_5\text{NO})_6](\text{ClO}_4)_2$ is the first example of a well-defined mercuric complex of this type. Again, the attainment of a maximum coordination number should be noted.

An investigation of the reaction of pyridine N-oxide with other salts of these metals is in progress. We mention in particular the preparation of compounds which appear to have the formula $\text{M}(\text{NO}_3)_2 \cdot 2\text{C}_6\text{H}_5\text{NO}$, $\text{M} = \text{Cu}, \text{Ni}$. These compounds, which will be reported on in detail later, probably can be formulated as $[\text{M}(\text{C}_6\text{H}_5\text{NO})_2(\text{NO}_3)_2]$, with coordination by nitrate, as was found for the triphenylphosphine oxide complexes of metal nitrates.¹⁴

(14) E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 2276 (1960).

The intense charge transfer interaction that has been noted above appears to have been overlooked in the literature, for there is indeed a large number of strongly colored complexes whose color is due to this process. In order to examine this situation more closely, two paths of research are indicated. The complexes reported here contain central ions which have either a filled or an unfilled d shell; only the complexes of the latter type exhibit charge transfer bands close to the visible. Current work is directed toward preparing a larger selection of complexes with both types of metal ions, with the expectation that a correlation of strong charge transfer bands in complexes of metal ions with incomplete electronic shells will prevail. The other path being investigated concerns the complexes of alkylamine N-oxides. It is expected that the different environment of the nitrogen atom in these molecules will also affect the charge transfer process.

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Molecular Association and Electronic Structures of Nickel(II) Chelates. II. Bis-(3-Phenyl-2,4-pentanediono)-nickel(II) and High Temperature Studies of Nickel Acetylacetonate

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Additional support is given to the premise that association of molecules with one another must be considered in attempting to explain the spectral and magnetic behavior of Ni(II) complexes. Visible absorption spectra of bis-(2,6-dimethyl-3,5-heptanediono)-Ni(II), bis-(2,4-pentanediono)-Ni(II) and bis-(3-phenyl-2,4-pentanediono)-Ni(II) at 80, 120, 160 and 200° in diphenylmethane are described in terms of an equilibrium between monomers and polymers. The temperature and concentration dependent spectrum of bis-(3-phenyl-2,4-pentanediono)-Ni(II) in toluene has been analyzed in terms of monomer-trimer equilibria from 0–50°. Anhydrous bis-(3-phenyl-2,4-pentanediono)-Ni(II) and bis-(dibenzoylmethano)-Ni(II) have been isolated as solids in two forms, a green paramagnetic material (presumably polymerized) and a red diamagnetic material.

Introduction

X-Ray work² has established that crystalline anhydrous bis-(2,4-pentanediono)-nickel(II) ($\text{Ni}(\text{AA})_2$) contains trimeric molecules in which some of the pentanediono oxygen atoms serve as bridges between nickel ions in such a way that the nickel ions all become octahedrally coordinated. Molecular weight measurements are in accord with the view that these trimeric units are preserved when the compound is dissolved in non-coordinating solvents³ at room temperature and as high as at least 80° and the ultraviolet spectra of such solutions can best be understood using this assumption.⁴ It has also been shown⁴ that when the methyl groups in $\text{Ni}(\text{AA})_2$ are replaced by *t*-butyl groups, to give bis-(dipivaloylmethano)-nickel(II), $\text{Ni}(\text{DPM})_2$, steric hindrance completely prevents trimerization and the complex behaves as a spin-paired planar nickel(II) complex, whereas,

when the methyl groups are replaced by isopropyl groups, giving bis-(diisobutyrylmethano)-nickel(II) ($\text{Ni}(\text{DIBM})_2$), the complex exhibits partial, reversible and temperature-dependent association between 0 and 60°.

In this paper, we describe studies of the association equilibrium of $\text{Ni}(\text{DIBM})_2$ at temperatures above 60°, from which the molar extinction of the visible band characteristic of the monomer is obtained, studies of $\text{Ni}(\text{AA})_2$ at temperatures up to 200°, which show that the trimer of this complex also dissociates reversibly into monomers at sufficiently high temperatures, and finally studies of the reversible association of bis-(3-phenyl-2,4-pentanediono)-nickel(II)-($\text{Ni}(\text{PPD})_2$).

Experimental

The high temperature spectra were run using a Cary Model 14 spectrophotometer equipped with a special heated cell housing designed at the Argonne National Laboratory for spectral study of molten salt solutions. Our use of this instrument, at the Argonne Laboratory, was made possible by the generosity and assistance of Dr. D. M. Gruen and Mr. R. L. McBeth. The temperatures reported in this work are believed to be reliable to within $\pm 1^\circ$. Spectra were recorded from 400 to 1500 $\text{m}\mu$; the solvents have a

(1) Alfred P. Sloan Foundation Fellow.

(2) G. J. Bullen, R. Mason and P. Pauling, *Nature*, **189**, 291 (1961).

(3) R. Soderberg, unpublished work. Ebullioscopic measurements in benzene and carbon tetrachloride give association factors of, respectively, 2.96 ± 0.2 and 2.90 ± 0.1 .

(4) F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961).

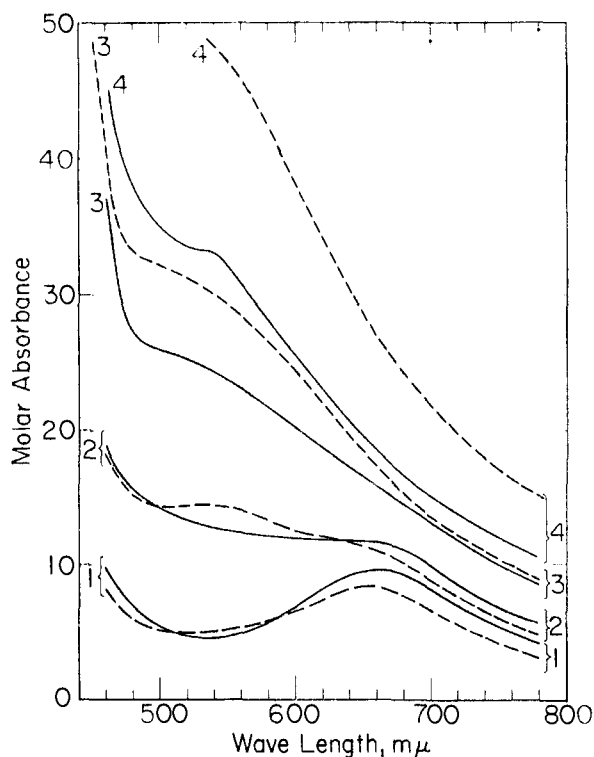


Fig. 1.—The visible spectrum of bis-(acetylacetonato)-nickel(II) in diphenylmethane at two concentrations and four temperatures. Solid lines are for an 0.0385 *M* solution; dashed lines are for an 0.0208 *M* solution. Temperatures are: (1) 80°; (2), 120°; (3), 160°; (4), 200°.

strong peak at about 1150 $m\mu$ which prevented a study of the decay of the low energy band ($\sim 1160 m\mu$)⁴ of the polymeric species.

The solvent used in this work was diphenylmethane (Eastman), distilled under reduced pressure. Solutions were prepared by weighing accurately appropriate amounts of the complex in 10-ml. volumetric flasks. Solvent was added to the mark at room temperature ($\sim 30^\circ$, m.p. of $(C_6H_5)_2CH_2$ 26–27°) and the weight recorded. Rectangular quartz cells with a long neck that extended out of the furnace were filled to a level above the optical surface and corked. In order to determine concentrations at higher temperatures, the density of the diphenylmethane was determined pycnometrically at several elevated temperatures with the results

<i>T</i> (°C.):	26	80	120	160	200
<i>d</i> (g.-cm. ⁻³):	1.001	0.9599	0.9291	0.8967	0.8653

In order to ensure temperature equilibrium between the solutions and the cell compartment of the furnace, the samples were kept at the desired temperature for 10 min. prior to placing them in the previously equilibrated cell compartment. They remained in the cell compartment at least five minutes before a spectrum was obtained. Temperature equilibrium was verified by repeating a spectrum after the solution remained an additional 10 min. in the cell compartment. A base line was determined at 80° with solvent in each of the cells.

The visible spectrum of $Ni(PPD)_2$ was observed from 0–50° in toluene at various concentrations. A Beckman DU spectrophotometer was used with a cell compartment thermostated by circulating water as previously described.⁴ Samples were prepared by dissolving appropriate amounts of the pure complex in toluene and diluting to 10 ml. The true concentrations are the concentration at 25° times the ratio of the density of toluene at selected temperatures to that at 25°.⁵

(5) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y.

3-Phenyl-2,4-pentanedione.—The acid acetylation of methyl benzyl ketone with acetic anhydride and boron trifluoride⁶ gave $\sim 53\%$ yield of steam distilled product.

Bis-(3-phenyl-2,4-pentanediono)-Ni(II).—Fourteen g. of nickel (II) acetate tetrahydrate in 30 ml. of warm methanol was added to 21 g. (0.12 mole) of 3-phenyl-2,4-pentanedione in 30 ml. of methanol. The solution was warmed and 40 ml. of 1:1 dioxane-water was added. Upon cooling, 21 g. (85% yield) of the crude blue-green solvated complex was obtained. The complex dried under vacuum to a red material. It was purified by crystallization from dioxane-water and dried under vacuum at 80°; m.p. $\sim 182^\circ$.

Anal. Calcd. for $NiC_{22}H_{22}O_4$: C, 64.59; H, 5.42. Found: C, 64.31; H, 5.60. The red material changes irreversibly to a green form at $\sim 160^\circ$ without melting or at room temperature under mechanical pressure. The green form may also be obtained by sublimation. *Anal.* Found: C, 64.47; H, 5.88.

Results and Discussion

Bis-(diisobutyrylmethano)-nickel(II).—The new results obtained on this system are collected in Table I. The complex in the very dilute solution in toluene at 80° should be almost fully dissociated ($\sim 95\%$) into monomers according to the thermodynamic parameters of the equilibrium previously determined⁴ and the molar extinction coefficient of 42.4 should therefore be very close to the value for the pure monomer. This is confirmed by the data for the diphenylmethane solution where the values of ϵ_{max} rise to 42 ± 0.5 at temperatures of 160 and 200°.

The difference between the ϵ_{max} values at 160 and 200° is probably just within experimental error, although it is possible that the ϵ_{max} value could be slightly lower at 200 than at 160° if thermal broadening of the band takes place without any increase in total intensity. Our estimates of the half widths of the bands give no support to this hypothesis, but the accuracy is not high enough to be conclusive. The data for $Ni(DIBM)_2$ in diphenylmethane also show a small but consistent bathochromic shift with increasing temperature.

Bis-(acetylacetonato)-nickel(II).—We have reported before⁴ that solutions of this compound in high boiling, non-coordinating solvents turn red at temperatures around 200° and revert to green again on cooling. In order to be certain whether this thermochromic effect was really due to the growth of a band characteristic of the $Ni(AA)_2$ monomer at $\sim 540 m\mu$, solutions of $Ni(AA)_2$ in diphenylmethane were studied spectrophotometrically from 80 to 200°. The results, which cannot be meaningfully summarized in tabular form, are shown in Fig. 1. It is evident that while a part of the thermochromic effect may be attributed to an increase in absorption between 400 and 800 $m\mu$ by the tail of strong ultraviolet absorption, there are also just the specific changes to be expected on comparison with the results previously⁴ reported for the $Ni(DIBM)_2$ system.

At 80° the weak ($\epsilon_{max} \sim 4$) absorption band at 650–660 $m\mu$, characteristic of the octahedrally coordinated nickel(II) ions in the trimeric molecules, is clearly observed. As the temperature is raised this band becomes undiscernible while

(6) C. R. Hauser and J. T. Adams, *J. Am. Chem. Soc.*, **66**, 345 (1944).

TABLE I

VISIBLE ABSORPTION BY BIS-(DIISOBUTYRYLMETHANO)-Ni(II) AND BIS-(3-PHENYL-2,4-PENTANEDIONO)-Ni(II)

Sample	Solvent	Temperature, °C.	Concn., M/l. ^a	λ_{\max} (m μ)	ϵ_{\max}	Half width ^b
Ni(DIBM) ₂	Toluene	80	0.00877	540	42.4	2.8×10^3
	Diphenylmethane	80	.02869	534	24.8	2.9×10^3
	Diphenylmethane	120	.02869	540	36.8	2.7×10^3
	Diphenylmethane	160	.02869	543	42.5	2.6×10^3
	Diphenylmethane	200	.02869	548	41.5	2.6×10^3
Ni(PPD) ₂	Diphenylmethane	80	.03014	530	28.7	3.2×10^3
	Diphenylmethane	120	.03014	530	45.4	3.0×10^3
	Diphenylmethane	160	.03014	528	49.0	3.0×10^3
	Diphenylmethane	200	.03014	524	46.5	3.5×10^3

^a Concentrations given in column apply at 25°. The ϵ_{\max} values were calculated at the higher temperatures using concentrations obtained from these by correcting these with the density ratio of the solvent at 25° and at the temperature of measurement. ^b Half-width at half height. Probably reliable to $\pm 10\%$.

at the same time there is the unmistakable growth of a band around 540 m μ and a rise in absorption by the ultraviolet tail. These observations are qualitatively in accord with the postulation of a trimer-monomer equilibrium having a positive enthalpy of dissociation. If it be assumed that the intrinsic ϵ_{\max} for the 540 m μ band of the Ni(AA)₂ monomer is at least 40, an assumption supported by the observed values of 42, 60 and 42 in Ni(DIBM)₂, bis-(dipivaloylmethano)-nickel (II) and bis-(3-phenyl-2,4-pentanediono)-nickel (II), respectively, we can also conclude that in the temperature range 160–200°, at the concentrations used, dissociation is incomplete. For example, at 160° the more dilute solution shows a net ϵ_{\max} (allowing for the ultraviolet tail) of only about 10, which suggests about 25% dissociation.

Bis-(3-phenyl-2,4-pentanediono)-Ni(II).—Scale molecular models indicated that the phenyl group in Ni(PPD)₂ cannot become coplanar with the chelate ring of the complex due to steric hindrance with the methyl groups and that the out-of-plane phenyl groups would offer some interference with the association of Ni(PPD)₂ into polymers. The red-brown anhydrous material obtained by vacuum drying the solvated complex was found to be diamagnetic with an absorption band at 535 m μ , Fig. 2. This is in accord with the data presented previously⁴ for Ni(DPM)₂. Rearrangement of the molecules in the solid state occurs at $\sim 165^\circ$ or under mechanical pressure to give the paramagnetic material. Hydrocarbon solutions also showed a temperature and concentration dependent polychroism similar to that shown by solutions of Ni(DIBM)₂.⁴

The results obtained for the visible spectrum of Ni(PPD)₂ in diphenylmethane at elevated temperatures are summarized in Table I for an 0.03014 M solution and are shown in Fig. 2 for an 0.01327 M solution. The visible spectrum of Ni(PPD)₂ in toluene was observed at various concentrations and temperatures from 0 to 51°. The apparent molar absorbance A' (liter mole⁻¹ cm.⁻¹)⁷ and the density-corrected true molar

(7) Defined as the ratio of $\log I_0/I$ to the concentration in gram atoms Ni per liter at 25° for a 1 cm. cell path length. The spectra of the monomer and trimer cannot be entirely independent of temperature as implicitly assumed in our treatment of the data here.

absorbance A of the 535 m μ band are listed in Table II. These data were treated in the same way as were the data for Ni(DIBM)₂⁴; from a plot of A against temperature, the molar absorbance at selected temperatures (10, 25, 30, 50°) was ob-

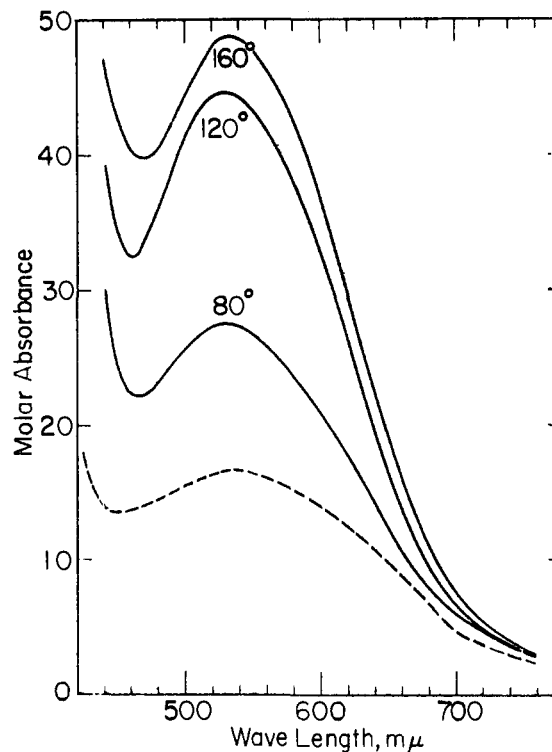


Fig. 2.—Spectra of bis-(3-phenyl-2,4-pentanediono)-nickel (II). Solid curves are spectra of an 0.01327 M solution in diphenylmethane at the temperatures indicated. The lower, dashed curve is the reflectance spectrum of the red modification of the solid at room temperature. The molar absorbance scale applies to the solution spectra only.

tained for each concentration. These values were in turn plotted against the true concentration. Each experimental value at 50, 30 (not shown) and 10° was used to evaluate the constant K defined as

$$3\text{Ni}(\text{PPD})_2 = [\text{Ni}(\text{PPD})_2]_3$$

$$K = [\text{Trimer}]/[\text{Monomer}]^3$$

Since there is some background absorption at 535 $m\mu$ due to the ultraviolet tail, this was assumed to contribute a value of 7 liter mole⁻¹ cm.⁻¹ to the molar absorbance at this wave length. Since the trimer does not absorb radiation appreciably at 535 $m\mu$, it was assumed to contribute only from the ultraviolet tail, and a correction for this was estimated visually from the spectrum at 25°. The results obtained in diphenylmethane at elevated temperatures indicate that the apparent extinction coefficient for the monomer is ~ 42 . The equilibrium constants thus calculated are recorded in Table III. Assuming constant enthalpy and entropy changes over the 0–50° temperature range, these thermodynamic parameters were evaluated and equilibrium constants K' re-determined at 10, 25 and 50°.

As in the case of Ni(DIBM)₂, the spectral evidence cannot conclusively eliminate monomer-dimer or monomer-dimer-trimer equilibria. Polymerization similar to that described for trimethyl-platinum(IV) acetylacetonate⁴ is not likely since in such a structure the phenyl group must nearly be coplanar with the chelate ring. Steric hindrance would be considerably less in the other two modes of association described previously.⁴

It is particularly interesting to note that polymerization does not occur upon drying the solvated complex. Since the red material cannot be re-crystallized without polymerizing and readily undergoes an irreversible transition to the polymeric form upon heating or under mechanical pressure, the red form apparently is metastable. The transition also was found to occur when the material in a desiccator was subjected to a month of summer heat. No evidence for a similar metastable state was found for the anhydrous Ni(DIBM)₂.

Bis-(dibenzoylmethano)-Ni(II) also has been isolated in two magnetically and spectrally different forms.⁸ The anhydrous red diamagnetic material changes to the green paramagnetic form at 185° without melting. The green material can also be obtained with mechanical pressure. Here again the bulky phenyl groups apparently are forced into a configuration which allows polymerization of the complex, the energy gained from bonding being enough to offset the energy required to confine the molecules to a particular configuration.

(8) R. Soderberg, unpublished work.

TABLE II

MOLAR ABSORBANCES OF SOLUTIONS OF BIS-(3-PHENYL-2,4-PENTANEDIONO)-Ni(II) AT VARIOUS TEMPERATURES IN TOLUENE SOLUTION

Concn., mole/l. at 25°	Temperature of measurement, °C.	Apparent absorbance A' (l./mole cm.)	Corrected absorbance, A
0.01513	50.3	35.3	36.3
	50.3	33.3	34.3
.0220	37.6	28.8	29.2
	25.1	23.3	23.3
	3.4	17.0	16.6
	50.3	28.6	29.4
.03647	37.6	25.4	25.8
	25.1	21.1	21.1
	3.5	14.4	14.1
	50.7	23.1	23.8
.06275	37.9	21.4	21.7
	23.5	17.6	17.6
	5.8	13.3	13.0
	50.3	18.6	19.1
.08908	37.6	16.8	17.0
	25.1	15.3	15.3
	3.3	12.1	11.8
	50.3	18.2	18.2
.1037	37.6	16.6	16.6
	25.1	15.2	15.2
	3.6	11.6	11.3

TABLE III

THERMODYNAMIC PARAMETERS OF TRIMERIZATION

Temp., °C.	$K \times 10^{-3}$, l. ³ mole ⁻³	ΔF cal./mole	K_T^a	$\Delta F'$ (cal./mole) ^b
50	1.13 ± 0.19^d	-4512	1.12×10^3	-4505
30	3.47 ± 0.52^d	-4910	3.70×10^3	-5058
25	5.10×10^3	-4949
10	15.0 ± 1.9^d	-5407	14.6×10^3	-5394

$$\Delta H^\circ = -10.3 \text{ kcal./mole}$$

$$\Delta S^\circ = -18.0 \text{ kcal./mole degree}$$

$$\Delta F_{25}^\circ = -4.9 \text{ kcal./mole}$$

^a Calculated from $\Delta F'$. ^b Determined from a plot of ΔF against temperature. ^c Values probably good to $\pm 10\%$. ^d Average deviation of four best values.

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