obtained and the true symmetry remains a matter of conjecture.

The positions of the oxygens are not known but for lack of any evidence to the contrary (3) are assumed to be the same as in the ideal perovskite structure. The angle $Re^{VI}-O-Fe^{II}$ would be 180°. If the orthorhombic distortion found in the calcium compound should be analogous to that found in $GdFeO_3$,[6] this angle would be somewhat smaller. In either case, this juxtaposition of the paramagnetic cations with oxygen would appear to be most favorable for the superexchange phenomenon. A qualitative explanation of the magnetic properties of the manganese and iron compounds can be given in terms of the spin moment orientation suggested in Fig. 1. The progressive rise in the magnetic transition temperature in the iron compounds from barium through strontium to calcium suggests a stronger coupling due to the closer approach of the B cations to the oxygens. The comparatively low transition temperature for the manganese compound may also be attributable to the greater separation of the B cations due in this case to the difference in the ionic radii of the manganese (II) and iron (II) cations.

The absence of any ferromagnetic properties

in the case of the cobalt compound might be rationalized by assuming that the d-orbital splitting led in this case to a wider energy gap between the three lowest levels and the others. This would lead to one unpaired electron in the Co^{2+} ion which with the Re^{6+} ion might given an antiferromagnetic system. Such an explanation does not seem to be compatible with other oxide systems containing cobalt (II), but perhaps the close proximity of hexavalent rhenium ions might have some influence on the nature of the splitting brought about by the oxide ions.

Attempts to prepare compounds containing cadmium in the A-position with rhenium (VI) and iron (II) in the B-position led to the formation of a strongly magnetic phase but with an unknown structure. A similar phase containing zinc in place of the cadmium has been prepared. The investigation of these phases is being continued.

(6) S. Geller, *Acta Cryst.*, **9**, 563 (1956).

Molecular Association and Electronic Structures of Nickel(II) Chelates. I. Complexes of Pentane-2,4-dione and Some 1,5-Di-substituted Derivatives

By F. A. Cotton and J. P. Fackler, Jr.

A new phenomenon which can, under certain circumstances, account for anomalous magnetic and spectral behavior of planar nickel(II) complexes has been discovered. This is molecular association of the solute molecules in solvents of low coördinating power. It is shown that the magnetic moment and spectrum of bis-(2,6-dimethyl-3,5-heptanediono)-nickel-(II), Ni(DIBM)₂, dissolved in toluene, are dependent upon both temperature and concentration. Spectral and magnetic data over a temperature range of 0–50° and a concentration range of 0.24 to 0.010 M are reported and association constants and thermodynamic parameters of the association process evaluated therefrom. It is also shown that the more highly hindered, bis-(2,2,6,6-tetramethyl-3,5-heptanediono)-nickel(II), Ni(DPM)₂, remains diamagnetic under all conditions. Preliminary results show that bis-(2,4-pentanediono)-nickel(II) is associated in non-coördinating solvents at ordinary temperatures, with significant concentrations of red monomer occurring only at temperatures near 200° and above. Possible structures for the polymeric species are considered.

Introduction

Nickel acetylacetonate (for which we shall henceforth write Ni(AA)₂) has been the subject of considerable study over many years. The anhydrous solid has long been known to be paramagnetic (Asmussen[1] reported an effective moment of 3.04 B.M. at 20°; Holm[2] has recently obtained a value of 3.27 B.M. at 27°). In benzene, chloroform and methanol solutions, the moments at 27° are 3.24, 3.12 and 3.11 B.M., respectively.[2] It is also well known that the anhydrous compound readily forms a dihydrate which has a moment of 3.15 B.M. at 26°.[2] Although the eye distinguishes easily between the emerald green of the anhydrous compound and the aqua color of the dihydrate,

there is actually little difference between the visible spectra of the two compounds.[3] On comparing these spectra (considering both band energies and extinction coefficients) and the magnetic moments cited above with spectral and magnetic data[4] for compounds known or reliably assumed to contain tetrahedrally coordinated nickel, it is clear that the latter does not occur in Ni(AA)₂ under any known conditions.

Regarding the structure of Ni(AA)₂ and its dihydrate there is the following information in the literature. Bullen[5] has recently shown that Co-(AA)₂·2H₂O has a structure in which planar Co-(AA)₂ units with Co–O distances of 2.05 Å. bind

(1) R. W. Asmussen, Thesis, Copenhagen, 1944.

(2) R. H. Holm, Ph.D. Thesis, Massachusetts Institute of Technology, 1959.

(3) G. Maki, *J. Chem. Phys.*, **29**, 162 (1958).

(4) F. A. Cotton and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **82**, 2967 (1960), and references cited there.

(5) G. J. Bullen, *Acta Cryst.*, **12**, 703 (1959).

the two water molecules along the perpendicular axis through the Co atom with Co–OH$_2$ distances of 2.23 Å. Since Ni(AA)$_2$·2H$_2$O has been found to be isomorphous[6] with its cobalt analog, with virtually the same d spacings, we may conclude that the Ni(AA)$_2$·2H$_2$O molecule is isostructural and practically isometric with Co(AA)$_2$·2H$_2$O. Electron diffraction studies of gaseous Ni(AA)$_2$ have been reported; the results are stated to show that the molecule is flat with D$_{2h}$ symmetry,[7] but this does not appear to be very certain in view of the complexity of the molecule. Shibata[8] has also reported that Co(AA)$_2$, Zn(AA)$_2$ and Ni(AA)$_2$ are isomorphous, but Holm and Cotton[6] find this to be incorrect; no two of these three compounds are isomorphous. Bullen[9] has reported collecting three-dimensional X-ray diffraction data for single crystals of Ni(AA)$_2$ but was unable to educe from these data any structural information beyond the observation that nickel atoms occurred in essentially linear chains of three with Ni–Ni distances of about 2.8 Å. Very recently, Mason and Pauling[10] have succeeded in deducing the complete structure from Bullen's data. They find that the nickel atoms are bound together in symmetrical, linear chains of three by the acetylacetonato oxygen atoms in such a way that each nickel is surrounded by a distorted octahedron of oxygen atoms. The central octahedron shares each of two opposite triangular faces with the octahedra about the two end nickel atoms. An acetylacetonato oxygen stands at each apex, shared and unshared, of the chain of fused octahedra. An n-fold polymer (i.e., [Ni(AA)$_2$]$_n$) consisting of n octahedra fused together at triangular faces would contain altogether $3n + 3$ apices and $4n$ acetylacetonato oxygen atoms. The only value of n for which the equality $3n + 3 = 4n$ is satisfied is $n = 3$. Thus the only polymer which can be formed with the particular kind of bridging found in the trimer is the trimer itself. We shall refer to this fact later. For convenience in later discussion, a schematic sketch of the structure of the trimer is given in Fig. 1. The six chelate rings are number 1–6. The oxygen atoms of the nth ring are called On1 and On2, the ring carbon atoms adjacent to each of these will be numbered Cn1 and Cn2 respectively, and the unique carbon atom in the nth ring will be numbered Cn.

Nothing has been reported concerning the structures of the other two nickel chelates studied in this work, which are bis-[2,6-dimethyl-3,5-heptanediono)-nickel(II) and bis-(2,2,6,6-tetramethyl-3,5-heptanediono)-nickel(II). In fact, it does not appear that these compounds have ever been isolated before although their formation in aqueous dioxane has been studied.[11] In this medium they may be assumed to exist as dihydrates according to the results given below. Since 2,6-dimethyl-3,5-heptanedione may also be called diisobutyryl-methane, we shall abbreviate the rather cumber-
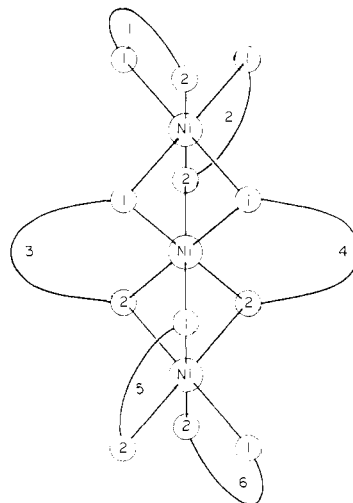
(6) R. H. Holm and F. A. Cotton, J. Phys. Chem., **65**, 321 (1961).

(7) S. Shibata, Bull. Chem. Soc., Japan, **30**, 753 (1957).

(8) S. Shibata, ibid., **30**, 842 (1957).

(9) G. J. Bullen, Nature, **177**, 537 (1956).

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

(11) G. S. Hammond and G. A. Guter, J. Am. Chem. Soc., **81**, 4686 (1959).

Fig. 1.—Schematic diagram of the structure of the bis-(2,4-pentanediono)-nickel(II) trimer, [Ni(AA)$_2$]$_3$ as reported by Bullen, Mason and Pauling.[10] The numbering system used by them is indicated.

some systematic names for it and its nickel complex as DIBM and Ni(DIBM)$_2$, respectively. Similarly, since 2,2,6,6-tetramethyl-3,5-heptanedione can be called dipivaloylmethane, we shall use the abbreviations DPM and Ni(DPM)$_2$ for it and its nickel chelate.

Experimental

Preparation of Compounds.—Melting and boiling points are uncorrected. Microanalyses are by S. M. Nagy, MIT, and Schwartzkopf Microanalytical Laboratories, Long Island.

White label grade acetylacetone was purchased from Distillation Products Industries. Freshly distilled samples (b.p. 138–140°) were used.

2,6-Dimethyl-3,5-heptanedione.—The sodium amide condensation described by Adams and Hauser[12] was used. In a typical experiment, 7.5 g. (0.33 mole) of sodium, 300 ml. of liquid ammonia, 24.2 g. (0.29 mole) of methyl isopropyl ketone and 33.8 g. (0.29 mole) of ethyl isobutyrate were used. The dione was isolated in 21% yield as 11.4 g. of the crude copper(II) chelate. The free dione was obtained on decomposing the copper complex with 3N H$_2$SO$_4$, extraction with ether and distillation, affording 8 g. of liquid, b.p. 82.0–83.1° (19 mm.) (lit.[12,13] 80.5–81.4 (17 mm.)). It was further identified by forming the copper(II) chelate which melted 125–127° (lit.[13] 127–129°).

Anal. Calcd. for C$_{18}$H$_{30}$CuO$_4$: C, 57.81; H, 8.09. Found: C, 57.74, 58.04; H, 8.08, 8.21.

2,2,6,6-Tetramethyl-3,5-heptanedione.—This was also prepared by the Adams and Hauser procedure from pinacolone (Matheson) and ethyl pivalate (Columbia Organic Chemicals). It boiled at 90.0–92.5° (16 mm.) (lit.[13] 94.0–94.5° (20 mm.)) The copper(II) complex melted at 187–189° (lit. 190–191°).

Anal. Calcd. for C$_{22}$H$_{38}$CuO$_4$: C, 61.36; H, 8.90. Found: C, 62.72, 60.40; H, 8.43, 8.64.

Bis-(2,4-pentanediono)-nickel(II).—This was prepared as directed by Charles and Pawlikowski.[14] It was obtained as the blue-green dihydrate (Found: C, 39.76; H, 6.31; Ni, 19.1). The deep green anhydrous compound was obtained by heating the dihydrate at 80° in vacuum overnight. (Found: C, 46.38; H, 5.46; Ni, 22.5.)

Bis-(2,6-dimethyl-3,5-heptanediono)-nickel(II).—1.5 g. of nickel(II) acetate tetrahydrate was dissolved in 10 ml. of

(12) J. T. Adams and C. R. Hauser, ibid., **66**, 1220 (1944).

(13) G. S. Hammond, W. G. Borduin and G. A. Guter, ibid., **81**, 4683 (1959).

(14) R. G. Charles and M. A. Pawlikowski, J. Phys. Chem., **62**, 440 (1958).
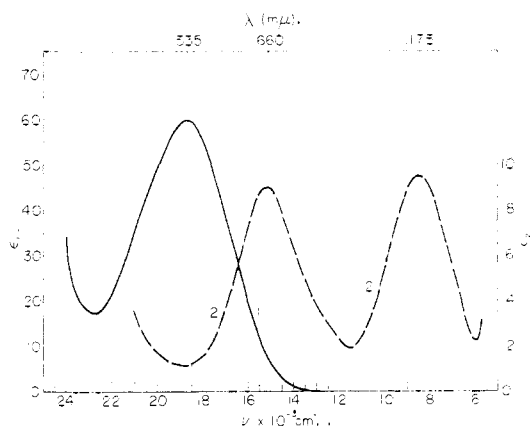
Fig. 2.—The visible absorption spectra of Ni(DPM)₂, bis-(2,2,6,6-tetramethyl-3,5-heptanediono)-nickel(II) (1), and Ni(AA)₂, bis-(2,4-pentanediono)-nickel(II) (2), in cyclohexane at 20°.

warm absolute methanol. This solution was added slowly to 5 ml. of methanol containing a slight excess of the freshly distilled ligand. 5 ml. of water was then added to complete precipitation of the light blue complex. It was filtered off and dried thoroughly over P₂O₅ at 100° in vacuum. As this crude complex, presumably the dihydrate, dries, it changes from blue to green, very much as does the acetylacetonate.

After drying, it was recrystallized by dissolving 2 g. in 10 ml. of warm dichloroethane. The warm solution was red, but on cooling, the complex crystallized out as long green needles. The complex was then sublimed twice in vacuum at 150°. The pure complex[15] melts sharply (sealed tube) at 155°, giving a dark green melt.

Anal. Calcd. for C₁₈H₃₀NiO₄: C, 58.57; H, 8.11. Found: C, 58.48; H, 8.29.

Bis-(2,2,6,6-tetramethyl-3,5-heptanediono)-nickel(II).— The crude complex, as the dihydrate, was prepared as described above for the 2,2-dimethyl-3,5-heptanedione complex. On drying, the light blue material turned pink. It was purified by cooling a hot saturated solution of the dry material (~1.0 g.) in 5 ml. of dichloroethane, whence large red crystals were obtained, m.p. 217-221°.

Anal. Calcd. for C₂₂H₃₈NiO₄: C, 62.14; H, 8.92. Found: C, 61.98; H, 8.92.

The powdered compound slowly changes from pink to blue on standing in moist air, presumably due to formation of the dihydrate.

Physical Measurements.—Magnetic Measurements.— Magnetic susceptibilities were measured using a sensitive Gouy balance. Split tubes for solids were calibrated with Mohr's salt and copper sulfate pentahydrate using the values for these given by Selwood.[16] In each case, measurements were made at three field strengths (~6,000, ~8,000, ~10,000 oersteds). In no case was any dependence on field strength observed. All measurements were made at least twice; the duplicate measurements involved a repacking of the tube.

Solution measurements were made using a split tube so constructed that pure solvent could be placed in the lower portion.[17] The tube was calibrated using aqueous nickel chloride.[16] The gram susceptibility of the toluene (saturated with O₂) was measured to be −0.71 × 10⁻⁶ c.g.s.u. × g.⁻¹ (lit.[18] −0.774 × 10⁻⁶ c.g.s.u. × g.⁻¹). Temperature control for solution measurements was accomplished by circulating thermostated water through a large condenser

(15) When the ligand used was not freshly distilled, it was found that even repeated recrystallizations would not give a pure product. However, sublimation will effect purification. Upon sublimation of complex prepared from undistilled ligand, a yellow residue is obtained.

(16) P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 25.

(17) B. N. Figgis and J. Lewis, "Modern Coördination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p. 415.

(18) W. R. Angus and W. K. Hill, *Trans. Faraday Soc.*, **39**, 188 (1943).

which completely surrounded the Gouy tube. The bath temperature varied less than 0.5° from the temperature of the return water over the range 0-60°. Again measurements were made at 3 field strengths (~4,500, ~6,000, and ~8,000 oersteds).

Visible Spectra.—Spectra at room temperature were recorded with a Beckman Model DK-2. The temperature dependence of the spectrum of bis-(2,6-dimethyl-3,5-heptanediono)-nickel(II) was determined using a Beckman DU spectrophotometer equipped with a thermostated cell housing of local design. Temperature was fixed by circulation of water from a regulated bath.

Results

Immediately on isolating anhydrous Ni(DPM)₂, it was noted that this compound is red, while Ni(AA)₂ and Ni(DIBM)₂ are green. The red color of Ni(DPM)₂ was found to persist in solutions in non-coördinating solvents such as cyclohexane, carbon tetrachloride, etc. Figure 2 shows the visible absorption spectra of Ni(DPM)₂ and Ni(AA)₂ in cyclohexane, from which it is clear that the difference in color is due to a fundamental difference in the absorption spectra. The one absorption peak shown by Ni(DPM)₂, at 535 mμ, has a molar extinction coefficient about an order of magnitude greater than those for the absorption bands of Ni(AA)₂. Numerical parameters for these and several other spectra at 20° are tabulated in Table I. The magnetic susceptibility of Ni(DPM)₂ was then measured, and the compound was found to be diamagnetic, whereas Ni(AA)₂ has two unpaired electrons.

Preliminary observations showed the behavior of Ni(DIBM)₂ to be still more surprising. This compound is green in the solid state at room temperature. It is also paramagnetic in the solid state with a moment of 3.41 B.M. at 24°. However, it dissolves in non-polar solvents to give solutions which have a dirty red color at room temperature. The red color becomes clearer and more intense when the solutions are heated, and it fades to light green when they are cooled. The spectrum in toluene at 20° is recorded in Table I. It is evident from these data that the spectrum is approximately a superposition of those of Ni(AA)₂ and Ni(DPM)₂, with the band of the latter at 535 mμ having considerably reduced intensity. The last of the preliminary observations, and the most important of all, was that the color of solutions of Ni(DIBM)₂ in non-coördinating solvents was dependent not only on temperature but on concentration as well. The more dilute solutions are reddest; the more concentrated ones greenest. Thus it seemed that Ni(DIBM)₂ was capable of existing in two forms, in one of which its electronic structure closely resembles that of Ni(AA)₂, while in the other it closely resembles that of Ni(DPM)₂, and that the equilibrium between the two forms is temperature dependent and also concentration dependent. Experiments were therefore carried out to characterize this behavior quantitatively.

The solvent selected for studies of the temperature dependence of the magnetic and spectral properties of Ni(DIBM)₂ was toluene. The results of susceptibility measurement over a temperature range of about 0° to about 53° are presented in Table II along with the other magnetic data being reported. The qualitative meaning of

TABLE I

VISIBLE SPECTRA OF SEVERAL NICKEL(II) COMPLEXES AT 20°

Ligand	Solvent	Concentration, mole/l.	Absorption maxima, mμ; ϵ_M values in parentheses
2,4-Pentanedione (AA)	Cyclohexane	0.0183	665(9.0); 1180(9.5)
2,4-Pentanedione (AA)	75% Dioxane–water	.0429	635(5.00); ~735(sh. 2.2) 1090(4.25); 1520(2.95)
2,2,6,6-Tetramethyl-3,5-heptanedione (DPM)	Cyclohexane	.0236	535(60)
2,6-Dimethyl-3,5-heptanedione (DIBM)	Toluene	.0102	535(13); ~660(sh, ~6); 1250(6.0)

the results is most easily seen in Fig. 3 where the calculated apparent magnetic moments are plotted as a function of temperature for several concentrations. Each of the curves individually shows the
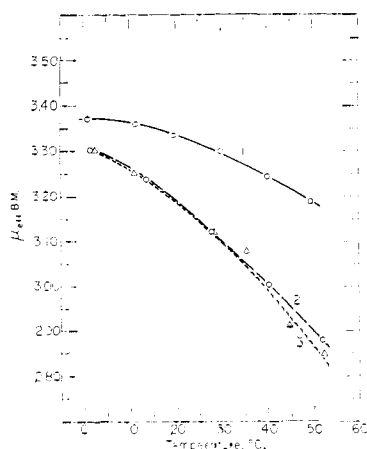

Fig. 3.—The apparent magnetic moment of Ni(DIPM)$_2$, bis-(2,6-dimethyl-3,5-heptanediono)-nickel(II), in toluene solution as a function of temperature and concentration; (1) 0.2373 M, (2) 0.06371 M, (3) 0.04365 M.
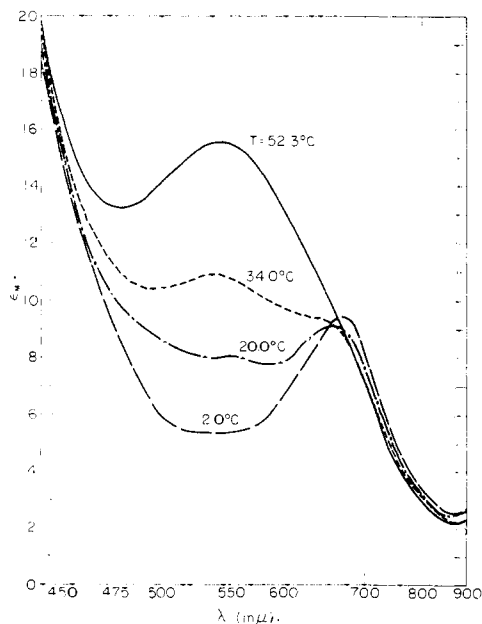

Fig. 4.—Visible spectra of Ni(DIBM)$_2$, bis-(2,6-dimethyl-3,5-heptanediono)-nickel(II), in toluene at various temperatures, concentration 0.04365 M.

temperature dependence of the apparent moments, while the difference between the curves, both in position and curvature, shows the effect of concentration. It appears that all of the curves are asymptotically approaching a limiting ordinate value of about 3.38 B.M. with decreasing temperature. No attempt has been made to use these magnetic data to determine the magnitudes of association constants, however, since they are not sufficiently accurate or extensive for this purpose. It is shown later that they are consistent with results obtained from spectral data.
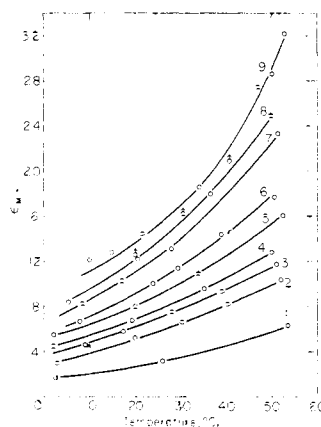

Fig. 5.—True molar absorbances, A, of the nine solutions listed in Table III plotted against temperature.

The spectra of solutions of Ni(DIBM)$_2$ of various concentrations were measured at temperatures from about 0° to about 53° in the range 400 to 900 mμ. Typical results are shown in Fig. 4. The apparent molar absorbances (A') of the 535 mμ band are tabulated in Table III. These data were treated in the following way: (1) The A' values, which are the ratios of optical density (log I_0/I) at the temperature of measurement to the concentration (moles of monomer per liter of solution at 25°), were multiplied by the ratios of the density of toluene at 25° to the density of toluene at the temperature of measurement to give true molar absorbances, A's. (2) These A values were plotted against temperature, as shown in Fig. 5, where the solutions are numbered as in Table III. (3) From this plot A values at selected temperatures (10, 25, 40 and 50°) were obtained, and these were plotted against the true concentrations (the "25° concentrations" of Table III times the ratio of density of toluene at the selected temperature to that at 25°). One of these plots is shown in Fig. 6. (4) Each point was used to evaluate the constant K_T, defined as

$$3Ni(DIBM)_2 = [Ni(DIBM)_2]_3 \qquad (1)$$

$$K_T = \frac{[Trimer]}{[Monomer]^3} \qquad (2)$$

<p align="center">TABLE II</p>
<p align="center">MAGNETIC DATA FOR β-DIKETONE COMPLEXES OF NICKEL(II)</p>

Ligand	Solvent	Conc. (M)	Temp., °K.	χ^Mcorr. $\times 10^6$	Dia., corr.	μ_{eff} ($\theta = 0$)
Acetylacetone[a]	Solid	.....	300.0	4433	−125	3.27
Acetylacetone[a]	C_6H_6	?	299.9	4337	−125	3.24
Acetylacetone[a]	$CHCl_3$	?	300.2	4009	−125	3.12
Acetylacetone·$2H_2O$[a]	Solid	.....	299.3	4098	−151	3.15
Diisobutyrylmethane[b]	Solid	.....	297.4	4863	−219	3.41
Diisobutyrylmethane	$C_6H_5CH_3$	0.2373	275.0	5106	−219	3.37
Diisobutyrylmethane	$C_6H_5CH_3$	.2373	283.4	4940	−219	3.36
Diisobutyrylmethane	$C_6H_5CH_3$	.2373	293.2	4670	−219	3.33
Diisobutyrylmethane	$C_6H_5CH_3$	.2373	303.2	4442	−219	3.30
Diisobutyrylmethane	$C_6H_5CH_3$	.2373	313.2	4146	−219	3.24
Diisobutyrylmethane	$C_6H_5CH_3$	.2373	323.2	3902	−219	3.19
Diisobutyrylmethane	$C_6H_5CH_3$	.06371	274.9	4910	−219	3.30
Diisobutyrylmethane	$C_6H_5CH_3$	.06371	287.2	4535	−219	3.24
Diisobutyrylmethane	$C_6H_5CH_3$	.06371	300.8	4013	−219	3.12
Diisobutyrylmethane	$C_6H_5CH_3$	.06371	313.5	3571	−219	3.00
Diisobutyrylmethane	$C_6H_5CH_3$	.06371	325.4	3169	−219	2.88
Diisobutyrylmethane[c]	$C_6H_5CH_3$	.04365	274.6	4899	−219	3.30
Diisobutyrylmethane	$C_6H_5CH_3$	.04365	284.2	4626	−219	3.25
Diisobutyrylmethane	$C_6H_5CH_3$	.04365	302.0	4009	−219	3.12
Diisobutyrylmethane	$C_6H_5CH_3$	.04365	308.6	3814	−219	3.08
Diisobutyrylmethane	$C_6H_5CH_3$	.04365	317.9	3301	−219	2.91
Diisobutyrylmethane	$C_6H_5CH_3$	.04365	325.6	3098	−219	2.85
Dipivaloylmethane	Solid	.....	297.4	Diamagnetic		

[a] R. H. Holm.   [b] Analysis slightly low in C and H for sample used.   [c] Accuracy of the method reduced due to small concentrations.

In order to do this the trimer was assumed to be transparent at 535 mμ and the monomer was assumed to have a molar extinction coefficient of 42.5, on the basis of results obtained both in toluene at temperatures up to 80° and in diphenylmethane at temperatures up to 200°.[19]   The equilibrium
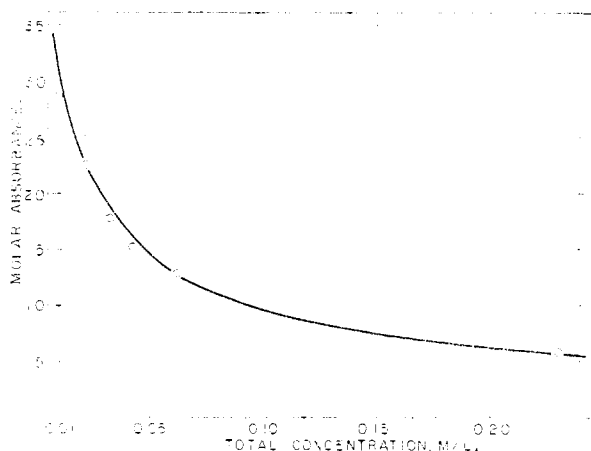

Fig. 6.—The variation of molar absorbance with concentration at 50° for Ni(DIBM)₂ in toluene: the circles represent measured values; the curve represents values calculated from eq. 1 with K_T equal to 2.25 $\times$ 10³ liters² moles⁻².

constants, K_T, for trimerization are recorded in Table IV. From these constants, the following thermodynamic parameters of the trimerization process (eq. 1) at 25° were calculated

(19) These experiments together with others on the complex of 3-phenylpentanedione and on Ni(AA)₂ were carried out on special equipment at the Argonne National Laboratory through the courtesy of Dr. Dieter Gruen and will be described in a later paper.

$\Delta F = -5.7 \pm 0.3$ kcal./mole

$\Delta H = -15.0 \pm 1.0$ kcal./mole

$\Delta S = -31 \pm 5$ cal. deg.⁻¹ mole⁻¹.

The consistency of the spectral and magnetic measurements is shown by the results given in Table V. Assuming the moment of a paramagnetic nickel ion in the trimer to be 3.38 B.M. (vide supra) and using the equilibrium constants in Table IV, the expected apparent magnetic moments for various solutions at several temperatures were calculated. These are recorded in Table V along with the observed apparent magnetic moments. The agreement is fairly good, and within experimental uncertainties, which are about 0.1 BM for the observed moments and probably about the same for those calculated from the spectral data.

Discussion

The results reported here are of considerable import in the full understanding of the electronic structures of planar four-coördinate nickel(II) complexes, particularly those which exhibit anomalous magnetic and spectral properties as a function of temperature and the solvent in which they may be dissolved.[20–26] It appears certain that the hypothesis of configurational equilibria between diamagnetic planar and paramagnetic tetrahedral

(20) H. S. French, M. Z. Magee and E. Sheffield, J. Am. Chem. Soc., 64, 1924 (1942).

(21) B. Willis and D. P. Mellor, ibid., 69, 1237 (1947).

(22) H. C. Clark and A. L. Odell, J. Chem. Soc., 3431 (1955).

(23) H. C. Clark and A. L. Odell, ibid., 520 (1956).

(24) H. C. Clark and R. J. O'Brien, Can. J. Chem., 37, 436 (1959).

(25) L. Sacconi, P. Paoletti and G. Del Re, J. Am. Chem. Soc., 79, 4092 (1957); L. Sacconi, R. Cini, M. Ciampolini, F. Maggio, ibid., 82, 3487 (1960).

(26) W. D. Phillips and R. E. Benson, J. Chem. Phys., 33, 607 (1960).

TABLE III

MOLAR ABSORBANCES OF SOLUTIONS OF BIS-(DIISOBUTYRYL-METHANO)-NICKEL(II) AT VARIOUS TEMPERATURES IN TOLUENE SOLUTION

No.	Solution conc., mole/l. at 25°	Temp. of measurement, °C.	Apparent molar absorbance, A'	Corr. molar absorbance, A
1	0.2373	53.5	6.15	6.33
		25.9	3.16	3.16
		2.7	1.73	1.69
2	.1086	52.0	10.0	10.3
		40.0	8.06	8.19
		30.2	6.63	6.67
		20.1	5.25	5.22
		2.9	3.16	3.09
3	.09531	50.8	11.4	11.7
		38.9	9.19	9.31
		28.1	7.44	7.44
		17.6	5.90	5.88
		8.9	4.78	4.70
4	.06371	50.0	12.5	12.8
		35.1	9.41	9.50
		19.3	6.80	6.77
		2.1	4.72	4.61
5	.04365	52.3	15.5	16.0
		34.0	10.8	10.9
		20.0	8.04	8.00
		2.0	5.38	5.25
6	.03340	50.6	17.2	17.7
		38.7	14.1	14.2
		23.8	9.97	9.96
		7.9	6.77	6.65
7	.02254	51.1	22.7	23.4
		39.0	17.3	17.5
		28.2	13.1	13.1
		17.0	10.4	10.3
		7.8	8.30	8.15
8	.02051	50.0	24.2	24.9
		36.5	17.8	18.0
		20.4	12.2	12.1
		5.7	8.53	8.36
9	.01015	10.0	12.3	12.1
		15.0	12.9	12.8
		20.0	12.6	12.5
		21.5	14.5	14.4
		30.5	16.0	16.1
		34.0	18.3	18.5
		41.0	20.5	20.9
		47.0	26.9	27.5
		50.5	27.9	28.7
		53.0	31.2	32.1

TABLE IV

TRIMERIZATION CONSTANTS OF Ni(DIBM)$_2$ IN TOLUENE AT VARIOUS TEMPERATURES

Temp., °C.	K_T, l.^{2} mole^{-2}
10	5.27×10^4
25	1.50×10^4
40	5.22×10^3
50	2.23×10^3

TABLE V

COMPARISON SHOWING THE CONSISTENCY OF THE SPECTROSCOPICALLY DERIVED EQUILIBRIUM CONSTANTS AND THE MAGNETIC DATA

Temp., °C.	Concn., mole/l.^{a}	Apparent magnetic moments B.M.	
		Calcd.^{b}	Obsd.^{c}
10	0.2372	3.30	3.36
25		3.26	3.32
50		3.14	3.19
10	.06371	3.16	3.27
25		3.07	3.15
50		2.83	2.90
10	.04365	3.12	3.27
25		3.03	3.15
50		2.72	2.87

^{a} Moles of the monomeric unit Ni(DIBM)$_2$ per liter of toluene at 25°. ^{b} See text. ^{c} Interpolated from Fig. 3.

predominantly cubic field. In this case the energy separation between the lowest singlet state and the lowest triplet state may decrease to a value comparable with kT and either state might be the ground state. In the limit, essentially perfect cubic symmetry may be achieved, in which case the triplet level will drop below the singlet level, and the magnetic and spectral properties will be those typical of any normal octahedral complex of nickel(II).[30]

The results of the present study show that, in addition to the possibility of lessening tetragonality of the ligand field by coördination of solvent molecules (or other ligands), *association of solute molecules with one another* may accomplish the same end, as with Ni(DIBM)$_2$ in toluene. Molecular association is thus established as a possible cause of anomalous spectral and magnetic behavior and must in the future be so considered unless definitely ruled out by experimental evidence. Upon this premise, Holm has conducted some important experiments with nickel(II) complexes of Schiff bases and his results show that in various cases there is molecular association which runs parallel to the anomalous paramagnetism, within the limits of experimental error.[31]

Another result of the present study which is of considerable significance is the observation that Ni(DPM)$_2$ is diamagnetic. Beginning with the pioneer studies of Mellor and Craig,[32] the view has developed that, among planar four-coördinate nickel(II) complexes, those of the Ni–O$_4$ type are paramagnetic, those of the types Ni–S$_4$, Ni–S$_2$N$_2$ and at least most of those of the Ni–N$_4$ type are diamagnetic, while those of the Ni–O$_2$N$_2$ type ex-

forms may in general be abandoned.[27] It has been shown by G. Maki[28] and by Ballhausen and Liehr[29] using both the weak field[29] and strong field[29] approaches that if a planar diamagnetic nickel(II) complex coördinates two molecules of a donor solvent, the ligand field about the nickel(II) ion will change from one with strongly tetragonal symmetry, in which the singlet ground state lies well below the lowest triplet state to one in which there is only a small tetragonal perturbation upon a

(27) See for example references and discussion given by R. H. Holm, J. Am. Chem. Soc., **82**, 5632 (1960).

(28) G. Maki. J. Chem. Phys., (a) **28**, 651 (1958); (b) **29**, 162 (1958); (c) **29**, 1129 (1958).

(29) C. J. Ballhausen and A. D. Liehr, J. Am. Chem. Soc., **81**, 538 (1959).

(30) A. D. Liehr and C. J. Ballhausen, Annals of Phys., **2**, 134 (1959).

(31) R. H. Holm and T. M. McKinney. J. Am. Chem. Soc., **82**, 5506 (1960).

(32) D. P. Mellor and D. P. Craig, J. Proc. Roy. Soc. N. S. Wales **74**, 475 (1940).

hibit anomalous magnetic behavior.[27] The fact that Ni(DPM)$_2$, which belongs to the Ni–O$_4$ class, is diamagnetic immediately brings into question the general validity of these correlations; and in the light of all of the results reported here and by Holm,[31] it seems evident that molecular association, especially in the crystalline compounds usually studied, may have played a part in causing paramagnetism in complexes of the Ni–O$_4$ and Ni–O$_2$N$_2$ types.[33]

As will be discussed presently the implication of our results on Ni(DIBM)$_2$ and Ni(DPM)$_2$ is clearly that Ni(AA)$_2$ exists in non-coördinating solvents as a polymer in which the nickel(II) ions are surrounded by fields of essentially octahedral symmetry due to coördination by sharing of atoms. In this way, the great similarity between the spectra of Ni(AA)$_2$·2H$_2$O and the anhydrous compound in non-coördinating solvents,[28,34] *i.e.*, the observation of Klixbüll Jorgensen that "anhydrous Ni(AA)$_2$ seems. . . to be mainly octahedral" receives an explanation without the rather unlikely assumption that molecules of solvents such as benzene, carbon tetrachloride or chloroform can enter the coördination sphere and transform an otherwise highly tetragonal ligand field to an essentially octahedral one.

We must now consider the nature of the polymers formed by Ni(DIBM)$_2$ in toluene solution. The most obvious possibility to consider is that there exists a monomer–trimer equilibrium as indicated in eq. 1 and 2 with the trimer having presumably the same structure as that of [Ni(AA)$_2$]$_3$ in the crystal. All of our experimental evidence is consistent with this proposal. The trimerization constants evaluated at various temperatures may be used to calculate curves of molar absorbance *vs.* concentration which fit the experimental points within the experimental uncertainties, as illustrated in Fig. 6 for the data at 50°. The ΔH and ΔS values for this trimerization process, obtained from the K_T's at various temperatures, have magnitudes which appear to us to be reasonable. Moreover, the apparent complete association of Ni(AA)$_2$ at ordinary temperatures,[35] the partial, temperature- and concentration-dependent association of Ni(DIBM)$_2$ and the non-association of Ni(DPM)$_2$ are consistent with this structure. This was demonstrated by means of a scale model built using the molecular dimensions found by Bullen, Mason and Pauling and other appropriate bond lengths and bond angles. Inspection of the model showed immediately that only four pairs of substituents on the rings could give rise to steric hindrance with any of the ring substituents, –CH$_3$, –CH(CH$_3$)$_2$ and –C(CH$_3$)$_3$, used; by symmetry, all of these pairs are equivalent. Using the numbering system de-

scribed above and illustrated in Fig. 1, the four pairs of substituents concerned are those on the following pairs of ring carbon atoms: C21–C41, C22–C42, C31–C51, C32–C52. Measurements on the scale model gave the distance between centers of these pairs as 4.7 ± 0.2 A. Thus when the ring substituents are methyl groups, as in Ni(AA)$_2$, there is no significant hindrance, since twice the van der Waals radius of a methyl group is only ~4.0 A.[36] However, the van der Waals radius of a *t*-butyl group, the ring substituent in Ni(DPM)$_2$, must be about 3.5 A., so that the required distance, ~7 Å., is greatly in excess of that available in the structure. For Ni(DIBM)$_2$ association is possible because the asymmetric isopropyl groups can orient themselves so as to minimize repulsion, but this is done only at the expense of rotational freedom of the isopropyl groups and evidently the balance of forces favors the latter at higher temperatures so that the polymers are forced to dissociate.

It is to be noted that, while we believe that all our experimental data are consistent with the hypothesis of monomer–trimer equilibrium in Ni(DIBM)$_2$ solutions, and that this is the most likely explanation, we cannot offer any conclusive proof of the correctness of this equilibrium. In fact, the precision of the experimental data is such that curves can be calculated assuming monomer–dimer and monomer–dimer–trimer equilibria which fit about as well as the monomer–trimer curves.[37] As noted in the introduction, the trimeric structure for [Ni(AA)$_2$]$_3$ of Bullen, Mason and Pauling is specific for the trimer. In a system containing dimers, or in one involving statistical distribution among monomers, dimers, trimers, etc., other modes of association could be conceived. Planar molecules could come together with their planes parallel so that each nickel atom would be coördinated by an oxygen atom of the other molecule, thus attaining five-coördination which could quite conceivably result in stabilization of a triplet ground state. Very probably association of this general structural type occurs in the Schiff base complexes studied by Holm,[31] and its occurrence in similar crystalline materials has been demonstrated in the dimeric structures of bis-(salicylaldehydo-ethylenediimino)-copper(II)[38] and bis-(dimethylglyoxime)-copper-(II)[39] and in the infinite polymer structure of bis-(methylethylglyoxime)-copper(II) and -nickel-(II).[40] Still another conceivable alternative, although a somewhat improbable one, is the formation of dimers and higher polymers having structures similar to those found by Truter[41] in β-diketone complexes of trimethylplatinum(IV).[42] It will be noted that both of these alternative struc-

(33) We recognize that a similar uncertainty now arises concerning the genuineness of the spin-free square planar complexes of Co(II) recently described (F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, 82, 2979 (1960)), and further investigations of these compounds have been undertaken.

(34) C. Klixbüll Jorgenson, *Acta Chem. Scand.*, 9, 1369 (1955).

(35) This statement is based upon extensive spectral studies up to about 200°[11] and upon some molecular weight determinations made by Mr. R. Soderberg. Ebullioscopic measurements in benzene gave an association factor of 2.96 ± 0.2 and in carbon tetrachloride 2.90 ± 0.1 for Ni(AA)$_2$.

(36) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed.' Cornell University Press, Ithaca, New York, 1960, p. 260.

(37) Measurements at lower concentrations should serve to distinguish conclusively between these alternative equilibria, but the experimental difficulties involved in making reliable measurements would be formidable, and such studies are not contemplated.

(38) D. Hall and T. N. Waters, *J. Chem. Soc.*, 2644 (1960).

(39) E. Frasson, R. Bardi and S. Bezzi, *Acta Cryst.*, 12, 201 (1959).

(40) E. Frasson, C. Panattoni and R. Zannetti, *Ricerces sci.*, 29, 783 (1959).

(41) A. G. Swallow and M. R. Truter, *Proc. Roy. Soc. (London)*, 254A, 205 (1960); A. C. Hazell and M. R. Truter, *ibid.*, 254A, 218 (1960).

tural types for polymers would probably show the observed steric sensitivity to substituents.

A final point worthy of note concerns the explanation of a rather striking observation previously reported.[43] It was found that the ultraviolet absorption spectrum of Ni(AA)$_2$ in chloroform was very different from that in methanol, as shown here in Fig. 7. In methanol there is no doubt that the solute is present entirely as the solvated species Ni(AA)$_2$·2CH$_3$OH, and it thus shows an ultraviolet band quite typical of those found[43] in other acetylacetone complexes containing ordinary chelate rings. The anomalous spectrum found in chloroform can now be explained by the presence of both normal, nonbridging rings and bridging rings in the trimer. The former presumably give rise to the band at $\sim$ 300 mμ while the bridging rings cause the absorption at lower wave lengths.

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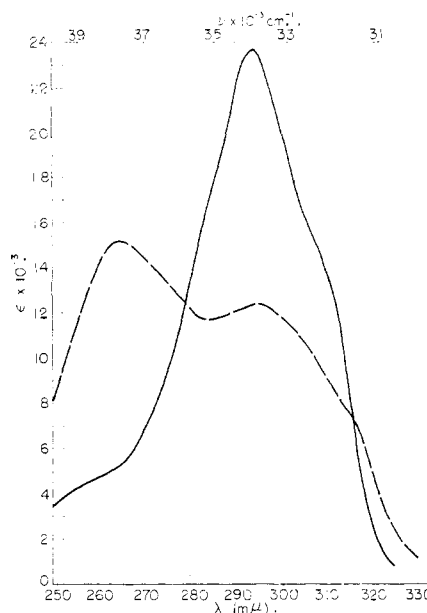
Fig. 7.—The ultraviolet spectrum of bis-(acetylacetonato)-nickel(II) in methanol (solid line) and in chloroform (broken line).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

The Mechanism of the Exchange of Chromium(III) and Chromium(VI) in Acidic Solution[1-3]

BY CARL ALTMAN AND EDWARD L. KING

The rate of exchange of chromium(III) and chromium(VI) in acidic aqueous solution at 94.8° is governed by the rate law: Rate = $[Cr(OH_2)_6^{+3}]^{1/3} [H_2CrO_4]^{2/3} \{k[H^+]^{-2} + k'\}$. On the basis of this rate law one concludes that the rate-determining step in the exchange is a reaction of chromium(III) and chromium(V), chromium(V) being in chemical equilibrium with chromium(III) and chromium(VI). The chromium-(III)–chromium(VI) exchange is completed by the relatively rapid exchange of chromium(V) and chromium(VI). The values of k and k' for solutions of ionic strength = 0.92 M are 6.6 × 10^{-7} moles l.$^{-1}$ sec.$^{-1}$ and 1.4 × 10^{-6} mole^{-1} l. sec.$^{-1}$, respectively. (In arriving at the conclusions stated in this summary, the probable presence of appreciable amounts of dimeric chromium(VI) in the reaction solutions was neglected and a relatively uncertain value of the first dissociation constant of monomeric chromic acid was used.)

The rate of exchange of chromium(III) and chromium(VI) in acidic aqueous solution is very low. At 45° and a total chromium concentration of 0.02 gram atoms per liter, 43% exchange is observed in 1200 hours.[4] The slowness of this process is expected; the chromium species differ by three units in oxidation state and the coördination number of chromium differs in the two species,

(1) Taken in part from the Ph.D. thesis of Carl Altman, University of Wisconsin, 1957.

(2) Supported in part by grants from the United States Atomic Energy Commission (Contract AT(11-1)-64, Project No. 3) and the Research Committee of the Graduate School, University of Wisconsin.

(3) Presented at the 133rd National Meeting of the American Chemical Society, San Francisco, California, April 13–18, 1958.

(4) H. E. Menker and C. S. Garner, *J. Am. Chem. Soc.*, **71**, 371 (1949).

chromium(III) exhibiting coördination number 6 in aquochromium(III) ion and chromium(VI) exhibiting coördination number 4 in chromate ion and dichromate ion. These factors suggest not only that the exchange rate may be low but also that the rate law may be more complicated than the usual second order rate laws exhibited by many exchange reaction systems. The objective of the present study was the elucidation of those features of the exchange reaction mechanism which are discernible from the form of the rate law.

Experimental Methods and Results

Reagents.—All solutions used in this work were prepared with doubly distilled water, the second distillation being from an alkaline permanganate solution using a Barnstead still.