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Nickel(II) Complexes of 1,5-Dialkyl-2,4-pentanediones[1]

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Bis(heptane-3,5-dionato)nickel(II) monohydrate [Ni(DNPM)$_2$·H$_2$O], bis(nonane-4,6-dionato)nickel(II) monohydrate [Ni(DNBM)$_2$·H$_2$O], bis(2,6-dimethylheptane-3,5-dionato)nickel(II) monohydrate [Ni(DIBM)$_2$·H$_2$O], bis(2,8-dimethylnonane-4,6-dionato)nickel(II) monohydrate [Ni(DIVM)$_2$·H$_2$O] and bis(tridecane-6,8-dionato)nickel(II) monohydrate [Ni(DNCM)$_2$·H$_2$O] were prepared, and a dimeric octahedral structure was proposed for each of them by means of spectroscopic studies. These dimeric chelates, $(NiL_2 \cdot H_2O)_2$ were stable in solid state, however they disproportionated in non-coordinating solvents to afford dimeric monohydrates, $Ni_2L_4 \cdot H_2O$, and monomeric dihydrates, $NiL_2 \cdot 2H_2O$. DTA studies show that these monohydrates dehydrate in two steps and that the temperature of dehydration decreases in the order of the ligands, DNPM, DNBM, DIBM, DIVM, and DNCM. The dehydrated chelates are green in the neighborhood of room temperature while they changed into red at an elevated temperature. This thermochromism indicates that the chelates are in the trimeric octahedral form at low temperature and in monomeric tetra-coordinated square planar form at high temperature. On the other hand a nickel(II) chelate of 2,2,6,6-tetramethylheptane-3,5-dione (DPVM) was obtained as a penta-coordinated monodioxane adduct from aqueous dioxane. The coordinated dioxane was readily released to afford a monomeric tetra-coordinate square planar, red colored complex, Ni(DPVM)$_2$.

Extensive investigations have been worked out on nickel(II) chelates of pentane-2,4-dione, of which bis(pentane-2,4-dionato)nickel(II) dihydrate can be most easily obtained. The coordination structure of this dihydrate is known to be similar to that of bis(pentane-2,4-dionato)cobalt(II) dihydrate,[3] in which two water molecules coordinate to the central cobalt ion in a planar bis(pentane-2,4-dionato)cobalt unit on both sides along z axis.[4]

It is also well known that the dehydration of this chelate affords the anhydrous trimeric chelate, in which nickel ion is octahedrally coordinated.[5] However, when the terminal methyl groups in pentane-2,4-dione are replaced with *t*-butyl groups, the steric hindrance among the substituents completely prevents trimerization and the chelate behaves as a spin-paired, red colored planar chelate.[6] This structure is maintained in solid state as well as in non-coordinating solvents.

In this connection, it is of great interest to investigate on the chelating behavior and the properties of the chelates of pentane-2,4-dione derivatives, in which the terminal methyl groups are replaced by various alkyl groups such as ethyl, *n*-propyl, isopropyl, isobutyl, *tert*-

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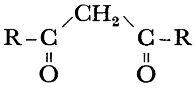
[3] R. H. Holm and F. A. Cotton, *J. Phys. Chem.*, **65**, 321 (1961).

[4] G. J. Bullen, *Acta Crystallogr.*, **12**, 703 (1959).

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

[6] F. A. Cotton and J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, **83**, 2818 (1961).

TABLE 1. ANALYSES OF 1,3-DIALKYLSUBSTITUTED ACETYLACETONE



$R-C(=O)-CH_2-C(=O)-R$

ligand	R	formula	C %		H %	
			found	calcd	found	calcd
DNPM	$-CH_2CH_3$	$C_7H_{12}O_2$	65.50	65.63	9.50	9.37
DNBM	$-CH_2-CH_2-CH_3$	$C_9H_{16}O_2$	69.00	69.24	10.31	10.25
DIBM	$-CH(CH_3)_2$	$C_9H_{16}O_2$	68.70	69.24	10.36	10.25
DIVM	$-CH_2-CH(CH_3)_2$	$C_{11}H_{20}O_2$	71.95	71.76	11.07	10.86
DPVM	$-C(CH_3)_2-CH_3$	$C_{11}H_{20}O_2$	71.77	71.76	10.96	10.86
DNCM	$-CH_2-CH_2-CH_2-CH_2-CH_3$	$C_{13}H_{24}O_2$	73.62	73.61	11.51	11.32

TABLE 2. ELEMENTAL ANALYSES, APPEARANCE, RECRYSTALYZATION SOLVENTS AND PERCENT YIELDS OF THE BIS(DIALKYLACETYLACETONATO)NICKEL(II) MONOHYDRATE

complex	molecular formula	Elemental analyses				recrystalyzation solvent	appearance	Yield (%)
		C %		H %				
		found	calcd	found	calcd			
$Ni(DNPM)_2 \cdot H_2O$	$C_{14}H_{24}O_5Ni$	50.90	50.81	7.44	7.25	C_2H_5OH	light green needles	60
$Ni(DNBM)_2 \cdot H_2O$	$C_{18}H_{32}O_5Ni$	56.49	55.87	8.52	8.27	C_2H_5OH	light green[a] needles	95
$Ni(DIBM)_2 \cdot H_2O$	$C_{18}H_{32}O_5Ni$	56.03	55.87	8.70	8.27	C_2H_5OH	light green plates	85
$Ni(DIVM)_2 \cdot H_2O$	$C_{22}H_{40}O_5Ni$	60.40	59.66	9.21	9.03	C_2H_5OH	light green needles	100
$Ni(DPVM)_2 \cdot$dioxane	$C_{26}H_{46}O_6Ni$	60.62	60.87	9.05	8.97	C_2H_5OH+dioxane or dioxane	light blue needles	100
$Ni(DNCM)_2 \cdot H_2O$	$C_{26}H_{48}O_5Ni$	62.54	62.59	9.70	9.62	C_2H_5OH	light green[a] needles	95

a) These were exist as needles at the low temperature in the ethanol, however, melted at the room temperature.

butyl, and *n*-pentyl group.

Although these ligands are reported in the literature, and some of their nickel(II) chelates have been synthesized, very few detailed investigations have been carried out.[6] This paper is to report on the synthesis of nickel(II) chelates of the following six ligands; heptane-3,5-dione (or dipropionylmethane, DNPM), nonane-4,6-dione (or di-*n*-butyrylmethane, DNBM), 2,6-dimethylheptane-3,5-dione (or diisobutyrylmethane, DIBM), 2,8-dimethylnonane-4,6-dione (or diisovalerylmethane, DIVM), 2,2,6,6-tetramethylheptane-3,5-dione(or dipivaloylmethane, DPVM) and tridecane-6,8-dione(or di-*n*-caproylmethane, DNCM), and on the structural studies concerning these chelates chiefly by spectroscopic methods.

Experimental

Synthesis of Ligands. The ligands were synthesized by the standard procedure described by Adams and Hauser[7] with slight modifications. The corresponding methyl-ketone and ethyl ester were condensed in the presence of sodium amide, and the resulting crude diketone was isolated as a copper(II) chelate, from which the diketone was liberated by decomposing with 10% sulfuric acid, followed by extraction with ether and fractionation. The results of elemental analyses of the ligands are summarized in Table 1.

Preparation of Nickel(II) Chelates. All chelates were prepared by the procedure as described below. To a solution containing 1.5 g (0.005 mol) of nickel nitrate hexahydrate in 12 m*l* of water and 8 m*l* of methanol, was added a solution of 0.01 mol of a ligand in 5 m*l* of methanol. Then, 6 m*l* of 1.5M sodium hydroxide solution was added to the mixture with vigorous stirring, from which green complex precipitated immediately. The product was recrystallized from an appropriate solvent and was dried over phosphorous pentoxide in vacuum at room temperature. The appearance, solvent used for recrystallization, yield, and the result of elemental analyses of each chelate are summarized in Table 2.

A careful dehydration of the hydrated chelates at about 180°C in vacuum afforded the anhydrous chelates, which were also green and were hygroscopic.

Spectral Measurements. Solid reflectance spectra were measured with a Hitachi EPU-2A spectrophotometer with

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[7] J. T. Adams and C. R. Hauser, *J. Amer. Chem. Soc.*, **66**, 1220 (1944).

a diffuse reflectance attachment. Absorption spectra in visible and ultraviolet regions were measured with a Hitachi EPS-2 and Hitachi 124 spectrophotometer respectively. Visible absorption spectra of the anhydrous chelates in toluene at elevated temperature were measured with a Hitachi 139 spectrophotometer with a high temperature attachment. Infrared absorption spectra were measured with a JASCO-DS-403G spectrophotometer on Nujol mull samples.

Molecular Weight Measurement. Molecular weight of the chelates was determined in toluene at 37°C with a Mechlolab's 301A vapour pressure osmometer. The standard material for the caribration curve was $Cu(DNBM)_2$, which was analytically pure and it's molecular weight was checked previously using α-naphthol as a primary standard.

Results and Discussion

Structural Study on DNPM, DNBM, DIBM, DIVM-, and DNCM Chelates. The result of elemental analysis of the nickel(II) chelates (except dipivaloylmethanato-nickel to be described later) agrees well with a molecular formula of $NiL_2 \cdot H_2O$ where L represents a β-diketonato monoanion. A sharp, relatively strong absorption band in 3350—3400 cm^{-1} region is observed in IR spectra of these chelates as shown in Fig. 1, indicating the presence of coordinated water. Although the above results seem to suggest a penta-coordinate structure, the diffuse reflectance spectra of solid samples, which are shown in Fig. 2 and Table 3, are very much similar to that of bis(pentane-2,4-dionato)nickel(II) dihydrate which is a typical hexa-coordinate octahedral nickel(II) chelate. Thus, it is reasonable to assume that the chelates are of dimeric structure, in which two $NiL_2 \cdot H_2O$ units are joined by two bridging oxygens as shown in Fig. 5 (I). Other possibility such as the double deck structure proposed for DNBM chelate of trimethyl platinum(IV),[8] can not be accepted in this case because the ionic radius of nickel(II) ion is too small in comparison with the van der Waals radius of terminal alkyl groups which prevents the approach of second unit from above or below of the nickel(II) ion in the first unit.

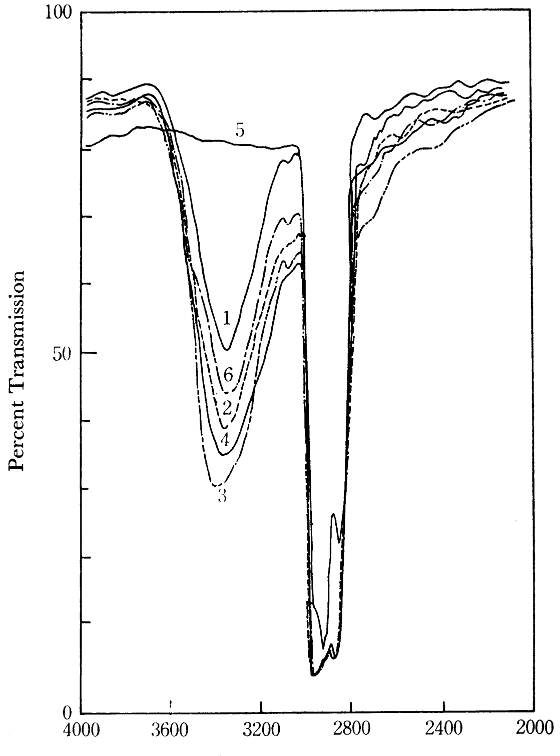

Fig. 1. Infrared spectra of the $Ni(DNPM)_2 \cdot H_2O$ (1), $Ni(DNBM)_2 \cdot H_2O$ (2), $Ni(DIBM)_2 \cdot H_2O$ (3), $Ni(DIVM)_2 \cdot H_2O$ (4), $Ni(DPVM)_2 \cdot$dioxane (5) and $Ni(DNCM)_2 \cdot H_2O$ (6) in 4000—2000 cm^{-1} region. (In Nujol mull)

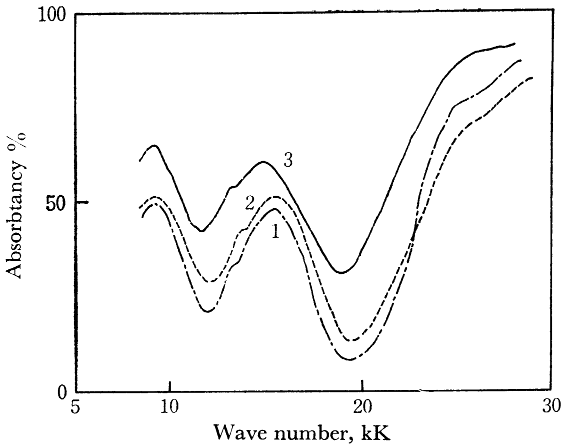

Fig. 2. Electronic reflectance spectra of the solid $Ni(DNPM)_2 \cdot H_2O$ (1), $Ni(DIBM)_2 \cdot H_2O$ (2) and $Ni(DIVM)_2 \cdot H_2O$ (3).

TABLE 3. SPECTROSCOPIC DATA FOR $NiL_2 \cdot H_2O$ (L=DNPM, DNBM, DIBM, DIVM) AND $NiL_2 \cdot$DIOXANE (L=DPVM)

L	solid. $\nu_{max}(cm^{-1})$	in toluene ν_{max} (cm^{-1})	ε_{max}
DNPM	9200	8340	6.9
	13000 (sh)	13200 (sh)	3.8
	15400	15300	6.3
DNBM		8320	5.8
		13300 (sh)	3.5
		15400	6.1
DIBM	9100	8340	3.9
	13300 (sh)	13200 (sh)	2.2
	15400	15400	4.3
DIVM	9100	8500	5.5
	12900 (sh)	13200 (sh)	3.7
	15300	15200	6.8
DNCM		8600	4.5
		13200 (sh)	2.9
		15200	4.9
DPVM	7900		
	10000 (sh)		
	11000		
	13500	18800	45.2
	16400		

It has been known that the chloroform solution of trimeric bis(pentane-2,4-dionato)nickel(II) shows two bands in ultraviolet region at 33800 and 37700 cm^{-1}, and they merge into a single band at 34000 cm^{-1} when

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[8] A. G. Swallow and M. R. Truter, *Proc. Roy. Soc.* (London), **254A**, 205 (1960).

ethanol is added to the chloroform solution.[9] According to Cotton and Fackler,[6] this spectral change is related with the coordination of ethanol to nickel ion resulting in the depolymerization of trimeric nickel chelate to give a mononuclear $NiL_2 \cdot 2EtOH$. The two bands of the trimeric form are assigned to two types of chelate rings, *i.e.* one is the non-bridging chelate ring and the other the bridging chelate ring, respectively. The single band observed in the mononuclear ethanol-adduct is, as being obvious from its coordination structure, ascribable to the non-bridging chelate ring.

TABLE 4. ULTRAVIOLET SPECTROSCOPIC DATA FOR $NiL_2 \cdot H_2O$ (L=DNPM, DNBM, DIBM, DIVM) AND NiL_2·DIOXANE (L=DPVN)

L	in cyclohexane		in 10% ethanol+ 90% cyclohexane	
	ν_{max} (cm^{-1})	ε_{max}	ν_{max} (cm^{-1})	ε_{max}
DNPM	33200	11500	33800	14200
	36600	10300		
DNBM	33000	12100	33700	13900
	36500	10600		
DIBM	33000	11600	36400	14600
	37200	16300		
DIVM	32700	14200	33600	17500
	36600	18200		
DPVM	37300	32600	36500	17000
Ni(AA)$_2$[7]	33800[a]	12400	34000[b]	23700
	37700	15200		

a) in chloroform. b) in ethanol.

As shown in Table 4, the UV spectra of the 1,5-dialkyl-2,4-pentanedionatonickel(II) chelates in cyclohexane solutions are very much similar to that of trimeric bis(pentane-2,4-dionato)nickel(II) in chloroform. The spectral change which is observed when ethanol is added to these cyclohexane solutions is also quite similar to that of the pentane-2,4-dionato chelate described above. The result, combined with their compositions and the spectral evidences in the visible and infrared regions, supports strongly the dimeric structure of bis(1,5-dialkyl-2,4-pentanedionato)nickel of type $NiL_2 \cdot H_2O$.

TABLE 5. MOLECULAR WEIGHTS OF $NiL_2 \cdot H_2O$ IN TOLUENE AT 37°C

molecular formula	calcd	found	found/calcd
$(Ni(DNPM)_2 \cdot H_2O)_2$	661.82	532	0.81
$(Ni(DNBM)_2 \cdot H_2O)_2$	773.82	588	0.77
$(Ni(DIBM)_2 \cdot H_2O)_2$	773.82	618	0.80
$(Ni(DIVM)_2 \cdot H_2O)_2$	885.86	575	0.65
$(Ni(DNCM)_2 \cdot H_2O)_2$	997.82	708	0.71

The molecular weights of these chelates, however, show somewhat odd values in toluene at 37°C as summarized in Table 5. The values are about 0.75± 0.1 of dimeric molecular weights. Thus, a certain kind of rearrangement of the chelate might occur even in a

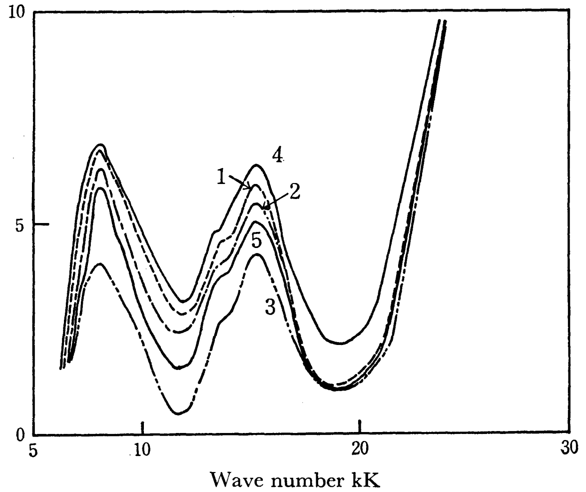

Fig. 3. Electronic absorption spectra of the $Ni(DNPM)_2 \cdot H_2O$ (1), $Ni(DNBM)_2 \cdot H_2O$ (2), $Ni(DIBM)_2 \cdot H_2O$ (3), $Ni(DIVM)_2 \cdot H_2O$ (4) and $Ni(DNCM)_2 \cdot H_2O$ (5) in toluene.

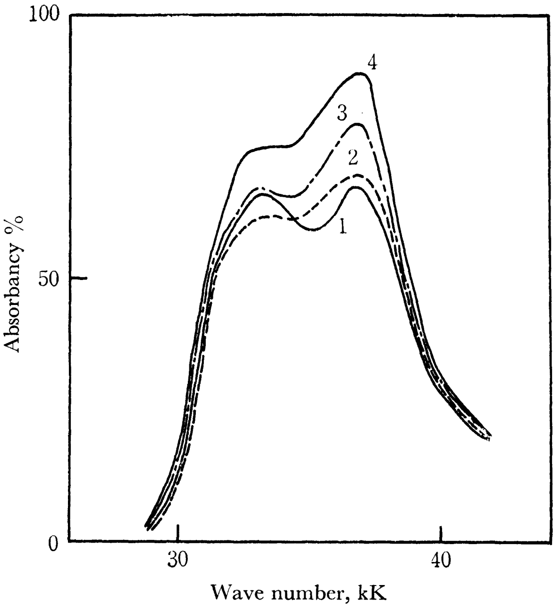

Fig. 4. Time dependency of UV absorbancy of the $Ni(DIVM)_2 \cdot H_2O$ in cyclohexane.
$Ni(DIVM)_2 \cdot H_2O = 9.56 \times 10^{-5}$M
1:3 min, 2:6 min, 3:17 min, 4:40 min

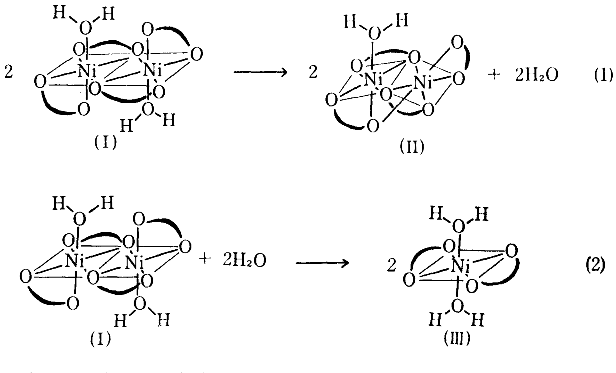

Fig. 5. Proposed dimeric structure and their rearrangements in non-coordinative solvents.

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[9] R. H. Holm and F. A. Cotton, *J. Amer. Chem. Soc.*, **80**, 5658 (1958).

non-coordinating solvent such as toluene, while the octahedral structure is retained as suggested by the visible absorption spectra which are shown in Fig. 3. The structural change of the chelate after dissolution in such solvents can be traced also by observing the time dependence of the UV spectral change in cyclohexane which is also one of the non-coordinating solvents, as shown in Fig. 4. Although we are not successful in identifying the rearrangement products in solution, one of the possible scheme of the rearrangement may be such as shown in Fig. 5. As to the binuclear chelate (II) in Fig. 5, a similar structure was assigned to pyridine-tetrakis(pentane-2,4-dionato)dinickel, $[(NiL_2)_2 \cdot Py]$, which was isolated as a reaction intermediate when trimeric nickel chelate was dissolved in pyridine.[10] If it is assumed that the reactions (1) and (2) proceed until completion, three moles of $(NiL_2 \cdot H_2O)_2$ give each two moles of (II) and (III), thus the resulting solution giving an apparent molecular weight of three quarters of the formular weight of $(NiL_2 \cdot H_2O)_2$.

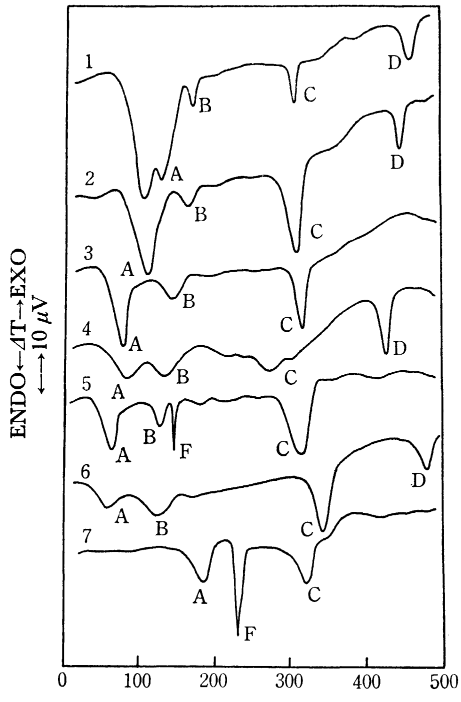

Fig. 6. DTA curves of nickel chelates in nitrogen atmosphere.
1: $Ni(AA)_2 \cdot 2H_2O$, 2: $Ni(DNPM)_2 \cdot H_2O$,
3: $Ni(DNBM)_2 \cdot H_2O$, 4: $Ni(DIBM)_2 \cdot H_2O$,
5: $Ni(DIVM)_2 \cdot H_2O$, 6: $Ni(DNCM)_2 \cdot H_2O$,
7: $Ni(DPVM)_2$·dioxane
Heating rate=15°C/min.

In addition to the structural change in solution, it is of interest to see if the dehydration of binuclear $NiL_2 \cdot H_2O$ chelate affords polymeric anhydrous nickel(II) chelate in solid state in a similar manner to the case of pentane-2,4-dionato chelate. In this connection, the dehydration process of the solid chelates was followed by differential thermal analysis (DTA) in nitrogen atmosphere with combined use of infrared spectroscopy. Although thermogravimetric analysis was also attempted, the present nickel chelates sublimed so easily, that no quantitative result on dehydration process could be obtained. As shown in Fig. 6, the DTA curves of the nickel chelates are characterized with four endothermic peaks, A, B, C, and D. When DTA was carried out in air, intense exothermic peak was observed generally in the range of 300—380°C which could be assigned to the oxidative decomposition of the sample. Of the four peaks, the first two seem to be related with the dehydration of the chelate, since the sample decreased the intensity of ν_{OH} band at 3300 cm^{-1} region when it was heated above the temperature corresponding to the peaks A and B. The resulting nickel chelate, which was still green, is considered to be polymeric structure such as trimeric bis(pentane-2,4-dionato)nickel(II). The latter two peaks, C and D, may be related with some sort of structural change of anhydrous chelates, however, little more informations could be obtained except that all four peaks were found to be irreversible ones. It is interesting to note, with this respect, that the respective temperatures corresponding to the peaks A and B decrease with increasing size of alkyl groups introduced to pentane-2,4-dione. This result may be interpreted as an effect of the hydrophobic nature of alkyl groups surrounding the coordinated water molecule. It is also safe to conclude that the replacement of terminal methyl groups of pentane-2,4-dione with higher alkyl groups except *t*-butyl group, is not a decisive factor to prevent the formation of an oxygen-bridged polymeric octahedral nickel chelate. An additional peak F of $Ni(DIVM)_2 \cdot H_2O$ and $Ni(DPVM)_2$·dioxane, was definitely due to the melting of samples as verified

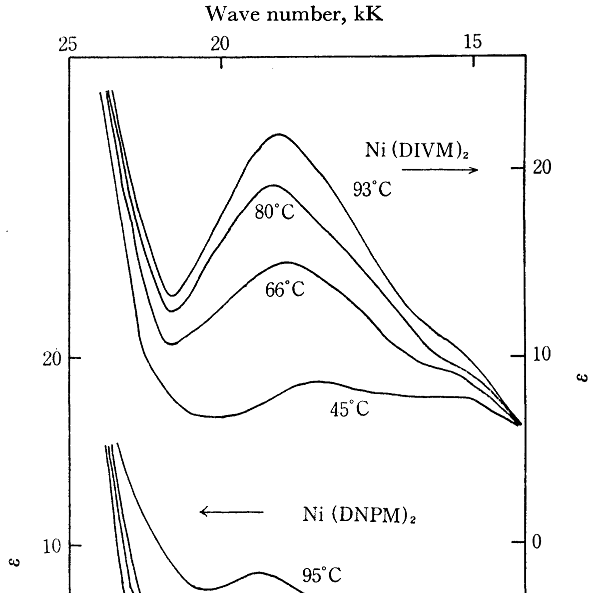

Fig. 7. Visible spectra of $Ni(DNPM)_2$ and $Ni(DIVM)_2$, in toluene at four temperatures, concentration about 1/100M.

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[10] J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, **84**, 24 (1962).

by melting point measurement.

As described in the experimental section, the anhydrous octahedral green nickel(II) chelates could be obtained by heating the hydrated chelates in vacuum. Although the molecular weights of the anhydrous chelates at room temperature could not be determined because of the experimental difficulty, the spectral evidence for the octahedral structure and the metal-ligand ratio strongly suggest the polymeric structure similar to bis(pentane-2,4-dioanto)nickel(II).

Absorption spectra were measured on the anhydrous chelates of the present ligands in toluene over the temperature range of 45—95°C. Typical examples are illustrated in Fig. 7. The peak at 650 nm, which is observable at lower temperature, is most distinct for pentane-2,4-dionato chelate, and becomes less distinct when the terminal methyl groups are replaced with bulkier alkyl groups. With elevating temperature, a new peak becomes noticable at around 520 nm and overshadows the peak at 650 nm in the extreme case.

A similar thermochromic effect has been reported by Cotton and Fackler$^{6)}$ with Ni(DIBM)$_2$, and was rationalized by reversible interconversion between polymeric octahedral and monomeric square planar structures.

The pentane-2,4-dionato- and dipivaloylmethanato chelates, however, show no spectral change in this temperature range; the former shows a single peak at 650 nm while the latter only at 520 nm throughout the temperature elevation. Of the remaining chelates, the spectral changes increase in the order of Ni(DNPM)$_2$<Ni(DNBM)$_2$< Ni(DNCM)$_2$<Ni(DIVM)$_2$<Ni(DIBM)$_2$, which parallels to the bulkiness of the terminal alkyl groups. These results clearly indicate that the peak at around 520 nm is assignable to the monomeric square planar structure, while the peak at 650 nm is due to the polymeric octahedral one, and that bulkier alkyl groups introduced on the 1- and 5-positions of pentane-2,4-dione favor the square planar configuration of the nickel chelates. In the extreme case of dipivaloylmethane, which has *t*-butyl groups on the both ends, the nickel chelate, Ni(DPVM)$_2$, takes a square planar structure even at room temperature.

Structural Study on DPVM Chelate. The properties of nickel DPVM chelate are different in many respects from those of other alkyl substituted pentane-2,4-dione. The result of elemental analysis on the light blue chelate agrees with a formula of NiL$_2$·dioxane. Infrared absorption spectrum also supports the existence of dioxane and the absence of water.

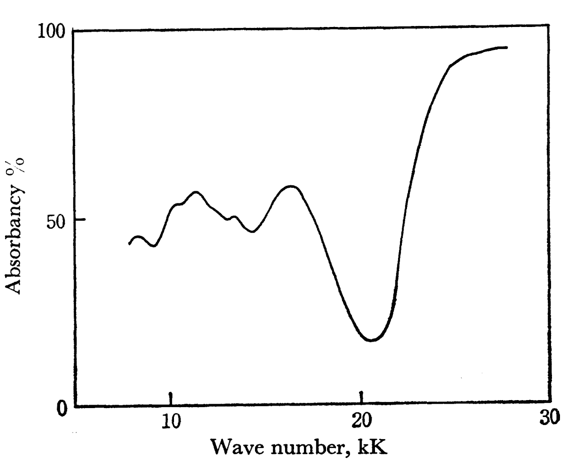

Fig. 8. Electronic reflectance spectrum of the solid Ni(DPVM)$_2$·dioxane.

A diffuse reflectance spectrum of the solid dioxane adduct in visible region which is shown in Fig. 8 and in Table 3, is quite different from the spectra which are typical to octahedral, tetrahedral or planar nickel(II) complexes. According to the result by Ciampolini who analyzed the energy levels of penta-coordinate nickel(II) complex of D_{3h} or C_{4h} symmetry,$^{11)}$ the spectrum of Ni(DPVM)$_2$·dioxane is similar to that of C_{4v} symmetry, indicating that the chelate is monomeric penta-coordinate square pyramidal structure.

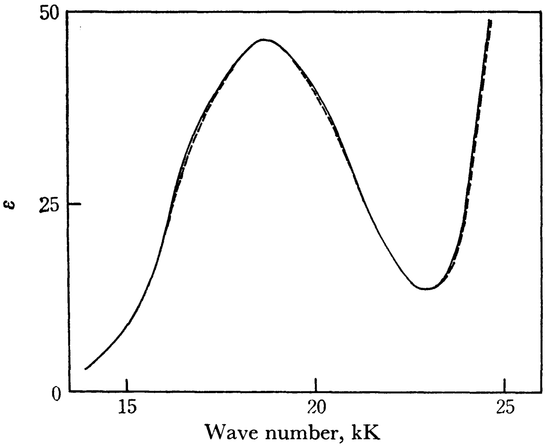

Fig. 9. Electronic absorption spectra of the Ni(DPVM)$_2$·dioxane (----) and Ni(DPVM)$_2$(——) in tolene.

When the light blue dioxane adduct is dissolved in toluene, it turned red, giving a spectrum as shown in Fig. 9. If the dioxane adduct is heated at 100°C in vacuum, it afforded a red chelate of the formula of Ni(DPVM)$_2$ with a monomeric molecular weight. The visible absorption spectrum of the toluene solution of red chelate was found to be identical with that obtained by dissolving light blue dioxane adduct in toluene as shown in Fig. 9. According to Cotton, this spectrum can be assigned to a diamagnetic tetra-coordinate square planar complex.$^{6)}$ Thus, the dissolution of dioxane adduct in non-coordinating solvent at room temperature, results in the dissociation of coordinated dioxane, and no further rearrangement of the chelate could be observed.

Interestingly, Ni(DPVM)$_2$ does not accept coordinated water but does dioxane which is known to be much weaker ligand than water. A DTA study indicated that the coordinated dioxane dissociated at 188°C (peak A) and the resulting Ni(DPVM)$_2$ melted at 230°C (peak F). The preference of dioxane to water molecule as a secondary ligand to Ni(DPVM)$_2$ is again indicative that the hydrophobic dioxane molecule may receive less repulsion from the neighboring *t*-butyl groups than does water molecule. The relative easiness of dissociation in non-coordinating solvents, which is contrary to the result observed by DTA study, may be

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11) C. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966).

explained by the solvation of dissociated dioxane. The formation of red planar chelate after the dissociation of dioxane also suggests that the terminal *t*-butyl groups are bulky enough to prevent the formation of oxygen-bridged polymeric structure even at room temperature.

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