Cobalt(II) and -(III) Complexes of 1,5-Dialkylpentane-2,4-diones[1]

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Based on the spectral studies in visible, ultraviolet as well as in infrared regions, the dimeric octahedral structure was proposed for bis(heptane-3,5-dionato)cobalt(II) monohydrate, $[Co(DNPM)_2 \cdot H_2O]$, bis(nonane-4,6-dionato)cobalt(II) monohydrate, $[Co(DNBM)_2 \cdot H_2O]$, bis(2,8-dimethylnonane-4,6-dionato)cobalt(II) monomethanolate, $[Co(DIVM)_2 \cdot CH_3OH]$, and bis(tridecane-6,8-dionato)cobalt(II) monomethanolate, $[Co(DNCM)_2 \cdot CH_3OH]$. The dimeric chelates of the type $[CoL_2 \cdot B]$, where B represented water or methanol, were stable in solid state, however, they freed the base B to form a tetrahedral monomeric complex in non-donating solvents. A red-pink solution of the cobalt(II) chelates were oxidized spontaneously in the period of a few days to give a green solution of cobalt(III) chelates of type $[CoL_3]$. Cobalt(III) chelates of 2,6-dimethylheptane-3,5-dione (DIBM) and 2,2,6,6-tetramethylheptane-3,5-dione (DPVM) in addition to the above ligands were synthesized and their spectra were discussed in comparison with the corresponding cobalt(II) chelates.

It has been well established by X-ray crystallography that anhydrous bis(pentane-2,4-dionato)cobalt(II), $Co(AA)_2$, existed as a tetramer in solid state, in which four octaheral units attached face-to-face and edge-to-edge linearly.[2] However, molecular weight determinations in non-donating solvents such as carbon tetrachloride or benzene indicated that the degree of polymerization varied between 1.3 and 3.5, and that the depolymerization proceeded with decreasing concentration.[3] The spectral characteristics of $Co(AA)_2$ in such solvents also indicated the reversible interconversion between an octahedral oligomer and a tetrahedral monomer. The spectrum of the highly diluted solution of $Co(AA)_2$ in non-donating solvents, is quite similar to that of bis(2,2,6,6-tetramethylheptane-3,5-dionato)cobalt(II), $Co(DPVM)_2$, which is known as a mononuclear tetrahedral complex.[4]

A unique tetrahedral structure of $Co(DPVM)_2$ among the cobalt(II) β-diketone chelates, is understood to be due to the steric hindrance of the terminal *t*-butyl groups which are bulky enough to prevent the association of mononuclear species in solid state as well as in solution state.[3,4] The similar effect was also observed in the case of bis(2,2,6,6-tetramethylheptane-3,5-dionato)-nickel(II), $Ni(DPVM)_2$, which is known to be a square planar mononuclear complex.[5-7]

In this respect, it is of great interest to investigate the effect of alkyl substitution at 1- and 5-carbon of pentane-2,4-dione upon the property of resulting complexes. In the previous paper, we reported on the nickel chelates of some 1,5-dialkyl-pentane-2,4-diones with terminal alkyl groups of various bulkiness and proposed an octahedral dimeric structure based on the spectral studies.[8]

This paper is to report on the syntheses and the structural studies of cobalt(II) and -(III) chelates of the following six pentane-2,4-dione analogues: 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).

Experimental

Preparation of Compounds. Details of the syntheses and the properties of 1,5-dialkyl-pentane-2,4-diones were described in the previous paper.[8]

Cobalt(II) chelates were prepared by the following general procedure. To a solution containing 1.5 g (0.005 mol) of cobalt(II) nitrate hexahydrate in 20 m*l* of aqueous methanol, was added a solution of 0.01 mol of the ligand in 5 m*l* of methanol. Then, 6 m*l* of 1.5 M aqueous sodium hydroxide was added with vigorous stirring to the mixture, from which a red-pink complex precipitated immediately along with a small amount of green precipitate. The red-pink cobalt(II) chelate was much less soluble in cold methanol than the green cobalt(III) chelate, and was readily separated by fractional dissolution in cold methanol. The cobalt(II) chelate was recrystallized from methanol as fine blood-red needles. Of the ligands investigated in the present work, attempts to prepare the DIBM and DPVM chelates were unsuccessful. The results of elemental analysis and the composition of the chelates, which were successfully synthesized, are summarized in Table 1.

Cobalt(III) chelates were prepared by the following method.[9] A suspension of 1.72 g of cobalt(II) carbonate (0.003 mol) and 0.01 mol of a ligand in 50 m*l* of water was heated at about 95°C. Then, 24 m*l* of 10% hydrogen peroxide was added dropwise to the hot mixture under effective stirring over a period of 1 hr. At the end of the reaction, the mixture was cooled to the room temperature and the dark green reaction product was extracted with 100—200 m*l* of benzene. After evaporating the solvent from the clear extract until dryness under reduced pressure, the green solid residue was recrystallized from an appropriate solvent.

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[1] Contribution No. 266 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University.

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[3] F. A. Cotton and R. H. Soderberg, *ibid.*, **3**, 1 (1964).

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[5] F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **5**, 1200 (1966).

[6] G. S. Hammond, D. C. Nonhebel, and C. H. S. Wu *ibid.*, **2**, 73 (1963).

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[8] I. Yoshida, H. Kobayashi, and K. Ueno, This Bulletin, **45**, 1411 (1972).

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Table 1. Elemental analysis of cobalt(II) chelate investigated

Complex	Molecular formula	Elemental analysis C % Found	C % Calcd	H % Found	H % Calcd	Yield (%)
$Co(AA)_2 \cdot 2H_2O$	$C_{10}H_{18}O_6Co$	40.77	40.97	6.20	6.14	60
$Co(DNPM)_2 \cdot H_2O$	$C_{14}H_{24}O_5Co$	50.68	50.78	7.35	7.25	70
$Co(DNBM)_2 \cdot H_2O$	$C_{18}H_{32}O_5Co$	55.52	55.84	8.34	8.27	70
$Co(DIVM)_2 \cdot CH_3OH$	$C_{23}H_{42}O_5Co$	60.43	60.43	8.94	9.19	40
$Co(DNCM)_2 \cdot CH_3OH$	$C_{27}H_{50}O_5Co$	63.95	63.19	9.88	9.74	50

Table 2. Elemental analyses, appearance, recrystalyzation solvents, and percent yields of the tris(β-diketonato)cobalt(III)

Complex	Molecular formula	Elemental analyses C % Found	C % Calcd	H % Found	H % Calcd	Solvent for recrystallization	Appearance	Yield %
$Co(AA)_3$	$C_{15}H_{21}O_6Co$	50.94	50.59	6.02	5.90	benzene+pet. ether	dark green needles	59
$Co(DNPM)_3$	$C_{21}H_{33}O_6Co$	57.51	57.30	7.50	7.50	water+methanol	dark green needles	95
$Co(DNBM)_3$	$C_{27}H_{45}O_6Co$	62.23	61.86	8.70	8.58	—	dark green liq.	35
$Co(DIBM)_3$	$C_{27}H_{45}O_6Co$	60.99	61.86	8.56	8.58	water+methanol	dark green plates	86
$Co(DIVM)_3$	$C_{33}H_{57}O_6Co$	65.30	65.16	9.46	9.37	water+methanol	dark green plates	55
$Co(DPVM)_3$	$C_{33}H_{57}O_6Co$	65.22	65.16	9.40	9.37	methanol +ethylacetate	dark green grains	25
$Co(DNCM)_3$	$C_{39}H_{69}O_6Co$	67.89	67.66	10.01	9.97	—	dark green liq.	75

Most of the ligands afforded crystalline cobalt(III) chelates, while DNBM and DNCM gave green oily chelates, which eventually had to be purified by a column chromatography. The crude oil was dissolved in a mixture of methanol and ether, and was passed through alumina and silica gel columns, of both 10 cm length, successively. The pure oily chelates were obtained from the eluates by evaporating the solvent. The results of elemental analysis, compositions, solvents for recrystallization as well as appearances of the chelates are summarized in Table 2.

Measurements. All solvents used in the spectral studies were of reagent grade, and were dried and distilled by the standard method prior to use.

Solid reflectance spectra were measured on a Hitachi EPU-2A spectrophotometer with a diffuse reflectance attachment. Absorption spectra in visible and ultraviolet regions were measured with Hitachi EPS-2 and Hitachi 124 spectrophotometers respectively. Infrared absorption spectra were measured with a JASCO–DS-403G spectrophotometer.

Results and Discussion

Reflectance and Absorption Spectra in Visible Region. The result of elemental analyses of the cobalt(II) chelates, with an exception of pentane-2,4-dionate, agrees well with a molecular formula of $CoL_2 \cdot B$, where L and B represent β-diketonate anion and water or methanol respectively. Interestingly, DNPM and DNBM chelates were obtained as a monohydrate while DIVM and DNCM chelates as a monomethanolate. While the above compositions seem to suggest a pentacoordinate structure, the reflectance spectra on solid samples, which are shown in Fig. 1 and Table 3, are very similar to those of bis(pentane-2,4-dionato)-cobalt(II) dihydrate or tetrameric anhydrous bis(pentane-2,4-dionato)cobalt(II), both being known to

Table 3. Characteristics of solid reflectance and absorption spectra of cobalt(II) chelates

Chelate	Peak in solid reflectance spectra (kK) ν_1	ν_2	Absorption peaks (kK) and molar absorptivities ($mol^{-1}\ l\ cm^{-1}$) in pyridine solution ν_1	ε	ν_2	ε	ν_3	ε
$Co(AA)_2 \cdot 2H_2O$	20.2	~ 8.3	21.3	(35.0)	19.6sh	(~22)	18.5sh	(~18)
$Co(DNPM)_2 \cdot H_2O$	20.8	~ 8.3	21.1	(39.5)	19.3sh	(~28)	18.2sh	(~21)
$Co(DNBM)_2 \cdot H_2O$	20.8	~ 8.3	20.7	(42.5)	19.3sh	(~32)	18.2sh	(~22)
$Co(DIVM)_2 \cdot CH_3OH$	20.8	~ 8.3	20.5sh	(~55)	19.2sh	(~39)	18.1sh	(~30)
$Co(DNCM)_2 \cdot CH_3OH$	20.5	~ 8.3	20.5sh	(~81)	19.2sh	(~55)	18.1sh	(~43)

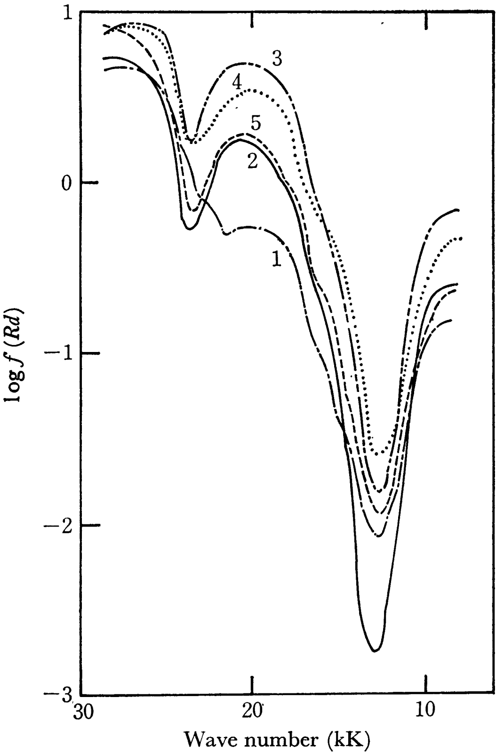
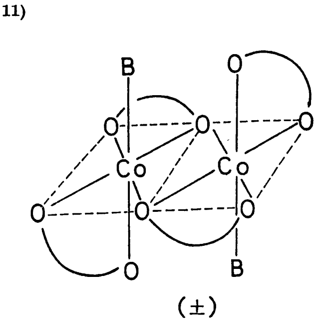


Fig. 1. The reflectance spectra of solid coblat(II) chelates: (1): $Co(AA)_2 \cdot 2H_2O$, (2): $Co(DNPM)_2 \cdot H_2O$, (3): $Co(NDBM)_2 \cdot H_2O$, (4): $Co(DIVM)_2 \cdot CH_3OH$, (5): $Co(DNCM)_2 \cdot CH_3OH$.

be octahedral hexacoordinate.[2,10] In the wave number range higher than 8.3 kK, two peaks can be observed at about 20 and 8.3 kK, which are assignable to the transitions of ${}^4T_{1g}(P)\leftarrow{}^4T_{1g}(F)$ and ${}^4T_{2g}(F)\leftarrow{}^4T_{1g}(F)$ respectively.[11]



(±)

Proposed dimeric structure on the mono-base adduct complexes of bis(1,5-dialkyl-pentane-2,4-dionato)cobalt(II).

Thus, in order to satisfy these requirements, it is reasonable to assume that the chelates are of dimeric structure, in which two octahedral CoL_2B units are jointed together by two bridging oxygens as shown in the structure (I). This structure may be indirectly supported by the similar dimeric structure which has been assigned to bis(pentane-2,4-dionato)cobalt(II) monohydrate by the X-ray diffraction study.[12] We have also proposed the similar structure for bis(1,5-dialkyl-pentane-2,4-dionato)nickel(II) monohydrate.[8]

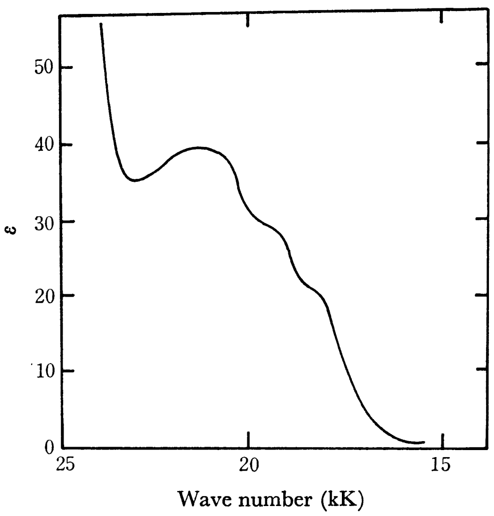


Fig. 2. The pyridine solution spectrum of the $Co(DNPM)_2 \cdot H_2O$ at room temperature.

The blood-red cobalt(II) chelates could dissolve easily into pyridine affording a pink solution. The absorption peaks of the cobalt(II) chelates in pyridine are summarized in Table 3. A typical example is shown in Fig. 2, in which three absorption peaks are observed at 21.1, 19.5, and 18.5 kK respectively, and the spectrum can be referred to an octahedral cobalt(II) chelate.[10,11,13] Accordingly, the dimeric chelate must be cleaved therein to afford the monomeric octahedral *trans* bis-pyridine adducts.[13,14]

It has been known that the alkyl substitution on the 3-carbon of pentane-2,4-dione leads to the metal complex being a weaker Lewis acid,[15,16] and a similar effect may also be expected on the 1,5-dialkyl substitution on pentane-2,4-dione. The decrease in the acidity of CoL_2 unit may weaken the axial ligation by a base such as pyridine. Resulting elongation of the bond along z-axis leads to lowering the symmetry of octahedral pyridine adducts, and eventually to increase the absorption intensity. There may also operate the steric interaction between pyridine molecule and cobalt(II) chelate. In our previous paper on the copper(II) complexes of 1,5-dialkyl-pentane-2,4-diones, we proposed that the terminal alkyl groups extended above or below of the xy-plane of copper(II) chelates.[17] If it is also true in this case, the elongation of the bond along z-axis may be more pronounced on the chelates with more bulky alkyl substituents. Thus, the combined inductive and steric effects of alkyl substituents may be responsible for the increase of the absorption intensity. The fact that the extent of increase in molar absorptivity is parallel to the bulkiness of alkyl substituents, positively favors our proposal.

On the other hand, absorption spectra of the present

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[12] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **5**, 423 (1966).

[13] J. P. Fackler, Jr., *ibid.*, **2**, 266 (1963).

[14] D. P. Graddon, *Coordin. Chem. Rev.*, **4**, 1 (1969).

[15] D. P. Graddon and K. B. Heng, *Aust. J. Chem.*, **24**, 1059 (1971).

[16] D. P. Graddon and K. B. Heng, *ibid.*, **24**, 1781 (1971).

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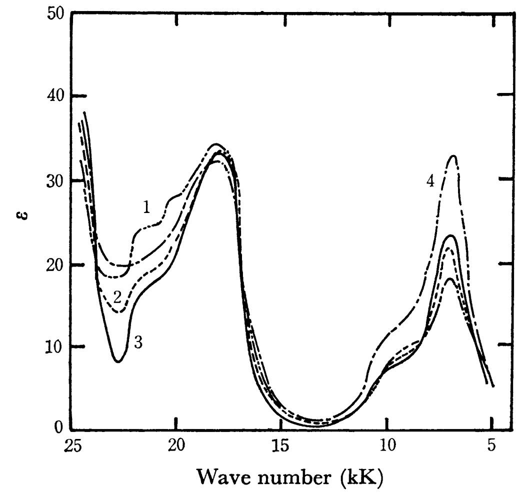

Fig. 3. The absorption spectra of $Co(DNPM)_2 \cdot H_2O$ in chloroform:
(1): 0.02 M, (2): 0.01 M, (3): 0.005 M (14°C), (4): 0.02 M (46°C).

complexes in non-donating solvents are quite different from the reflectance spectra of solid samples or the absorption spectra of pyridine solutions. As an example, Fig. 3 shows the absorption spectra of $Co(DNPM)_2 \cdot H_2O$ in chloroform in a range of concentration and of temperature. The spectral characteristics in dilute solution are very much similar to that of $Co(DPVM)_2$, which is known as a monomeric tetrahedral complex.[4] Two absorption peaks at 18.0 and 7.0 kK may be assigned to ${}^4T_1(P) \leftarrow {}^4A_2$ and ${}^4T_1(F) \leftarrow {}^4A_2$ transitions, respectively.[18] These spectral features due to a tetrahedral structure are enhanced with decreasing the chelate concentration and with elevating temperature.

It is clear, therefore, that the dimeric 1 : 1 base adduct dissociates into a corresponding monomeric tetrahedral cobalt(II) complex and a free base in equilibrium in a chloroform solution as shown in Eq. (1).

$$[CoL_2 \cdot B]_2 \rightleftharpoons 2[CoL_2] + 2B \qquad (1)$$

As expected, the bulkiness of the alkyl substituents on the ligands seems to favor the abundance of the monomeric form in the equilibria in solution phases. However, no quantitative study was undertaken owing to an undesirable oxidative side reaction, which will be described below.

Finally, the solutions of the present complexes in non-donating solvents gradually change their color from red-pink to green. Figure 4 shows the absorption spectra of such solutions measured at 24 hr after dissolution in toluene. It is interesting to note that the rate of the color change is parallel to the bulkiness of the alkyl substituents on the ligands. Thus, after 24 hr, the solution of $Co(DIVM)_2 \cdot CH_3OH$ is of an intense green color, while that of $Co(DNPM)_2 \cdot H_2O$ still remains in a pale-pink color. However, after one week standing at room temperature, the solution of cobalt(II) chelates changed to green color completely and their spectra were superimposable to those of the corresponding cobalt(III) chelates which were synthesized in separate routes. The spectral data of the cobalt(III) chelates are summarized in Table 4. Accordingly, these cobalt(II) chelates were oxidized spontaneously to cobalt(III) chelates, and the relative easiness of oxidation was again in parallel with the bulkiness of the alkyl substituents. As the oxidation proceeded even in the atmosphere of nitrogen, some redox reaction must have occurred in this system. However, further detailed investigation was not undertaken to elucidate the reaction mechanism.

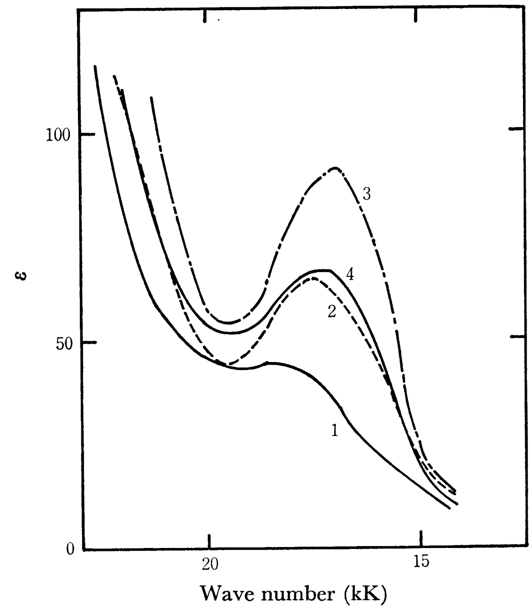

Fig. 4. The absorption spectra of coblat(II) chelates in toluene, measured at 24 hr after dissolution:
(1): $Co(DNPM)_2 \cdot H_2O$, (2): $Co(DNBM)_2 \cdot H_2O$, (3): $Co(DIVM)_2 \cdot CH_3OH$, (4): $Co(DNCM)_2 \cdot CH_3OH$. Absorption coefficient was evaluated from the above structures.

Table 4. Spectral characteristics of cobalt(III) chelates in visible and ultraviolet regions

Chelate	Peak (kK) and molar in visible region (in carbon tetrachloride)	absorptivity (mol^{-1} l cm^{-1}) in ultraviolet region (in cyclohexane)	
$Co(AA)_3$	16.7 (144)	— —	— —
$Co(DNPM)_3$	16.8 (152)	38.4 (35500)	43.5 (40000)
$Co(DNBM)_3$	16.9 (157)	38.2 (35500)	43.2 (39500)
$Co(DIBM)_3$	16.9 (176)	38.0 (37500)	43.2 (43000)
$Co(DIVM)_3$	16.9 (153)	37.9 (37500)	43.1 (42000)
$Co(DPVM)_3$	17.0 (182)	37.9 (39000)	43.1 (43500)
$Co(DNCM)_3$	16.9 (158)	38.0 (36000)	43.1 (39000)

Absorption peaks of the cobalt(III) chelates, as shown in Table 4, shift slightly to higher energy side with increasing bulkiness of the alkyl substituents, probably due to the increased basicity of the ligands.

Ultraviolet Absorption Spectra. Tetrameric octahedral bis(pentane-2,4-dionato)cobalt(II) is known to dissociate to form a monomeric tetrahedral complex in non-donating solvents,[3] showing a single absorption peak at 292 nm in a diluted chloroform solution, for example.[19] On the other hand, the octahedral mono-

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[18] A. B. P. Lever, "Inorganic Electronic Spectroscopy", American Elsevier, Pub. Co., New York (1968), p. 323.

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

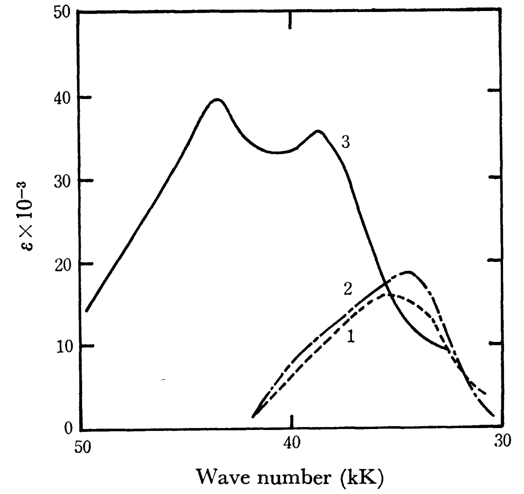

Fig. 5. Typical UV absorption spectra of cobalt(II) and -(III) chelates:
(1): $Co(DNPM)_2 \cdot H_2O$ in methanol, (2): $Co(DNPM)_2 \cdot H_2O$ in cyclohexane, (3): $Co(DNPM)_3$ in cyclohexane.

meric species of bis(pentane-2,4-dionato)cobalt(II), regardless of the kind of bases or donating solvents, always gave rise to an absorption peak at around 280 nm.

Concerning the present complexes also, as summarized in Fig. 5 and Table 5, the mono-solvent adducts shows a single absorption peak at 288—291 nm region upon dissolved in cyclohexane to a high dilution. Combined with the result of the visible spectral studies, these complexes are considered to exist as tetrahedral monomeric species in cyclohexane. On the other hand, the spectra of these complexes in methanol exhibit a single absorption peak at 282—283 nm region, which indicates the predominance of the solvent coordinated octahedral species, again being consistent with the visible spectral observations. Thus, in the ultraviolet absorption spectra of bis(pentane-2,4-dionato)cobalt(II) and its analogues, such extent of difference in wave number may be utilized as a criterion in discriminating their coordination structures. The cobalt(III) chelates, $Co(III)L_3$, show two UV absorption peaks in a much shorter wavelength region as shown in Table 4, and can be readily distinguished from those of the cobalt(II) chelates.

Infrared Absorption Spectra. A sharp, relatively strong ν_{OH} band is observed in a region of 3350—3360 cm^{-1} on each of the monohydrate complexes in nujol mull. The corresponding peak appears at a higher frequency region in non-donating solvents such as carbon tetrachloride or chloroform as summarized in Table 6. The ν_{OH} band shifts to a higher wave number region with the decreasing chelate concentration, approaching to that of free water molecule at 3710 cm^{-1}. This result suggests that the interaction between the coordinated water and the chelated cobalt(II) ion becomes weaker in non-donating solvents than in solid state, being in good agreement with the result of visible and ultraviolet spectral studies.

The monomethanol adducts show a ν_{OH} band at 3550—3540 cm^{-1}, appearing at a little lower wave number region than that of the free ν_{OH} band of primary alcohol (3640 cm^{-1}). The result again suggests the interaction between methanol and the chelated cobalt(II) ion.

As stated previously, when the hydrated cobalt(II) chelates were recrystallized from methanol, DIVM and DNCM chelates came out as monomethanol adducts, while DNPM and DNBM chelates as monohydrates. Therefore, DIVM and DNCM chelates accept methanol as a second ligand in preference to

TABLE 5. CHARACTERISTICS OF ULTRAVIOLET ABSORPTION SPECTRA OF COBALT(II) CHELATES

Chelate	Absorption peak (kK and nm) and molar absorptivity (mol^{-1} l cm^{-1})					
	in methanol[a)]			in cyclohexane[a)]		
	ν, kK	λ, nm	ε	ν, kK	λ, nm	ε
$Co(AA)_2 \cdot 2H_2O$	35.4	(282)	16000	34.2[c)]	(292)	16200
$Co(DNPM)_2 \cdot H_2O$	35.3	(283)	16000	34.7	(288)	18500
$Co(DNBM)_2 \cdot H_2O$	35.3	(283)	17500	34.4	(291)	19500
$Co(DIVM)_2 \cdot CH_3OH$	35.4[b)]	(282)	20500	34.4	(291)	19000
$Co(DNCM)_2 \cdot CH_3OH$	35.4[b)]	(282)	19500	34.6	(289)	21000

a) Measurements were carried out on 2—4×10^{-5}M solutions.
b) Observed in a methanol-cyclohexane (9:1) mixed solvent.
c) Reported value for $Co(AA)_2$ in chloroform.[18)]

TABLE 6. INFRARED SPECTRA OF COBALT(II) CHELATES

Chelate	in Nujol mull		in Carbon tetrachloride	in Chloroform
	ν (C=O)	ν (O-H)	ν (O-H)	ν (O-H)
$Co(AA)_2 \cdot 2H_2O$	1605	3420	—	—
$Co(DNPM)_2 \cdot H_2O$	1592	3350	3530 (0.1M)	3420 (0.25M) 3430 (0.08M)
$Co(DNBM)_2 \cdot H_2O$	1589	3360	3520 (0.1M)	3420 (0.25M)
$Co(DIVM)_2 \cdot CH_3OH$	1585	3552	—	—
$Co(DNCM)_2 \cdot CH_3OH$	1586	3540	—	—

water. Although it seems contradictory that DIVM and DNCM chelates accepts a weaker base such as methanol in preference to a stronger base such as water, the result could be explained by the hydrophobic repulsion by non-polar alkyl substituents against polar water molecule, if one remind that DIVM and DNCM have more bulky alkyl substituents than those of DNPM and DNBM.

There is still remained to be elucidated a question why the alkyl substituents on the 1- and 5-positions of pentane-2,4-dione favors the formation of a dimeric form of the mono-solvent adduct in their cobalt(II) as well as nickel(II) complexes[8] rather than forming a mononuclear bis-adduct octahedral complex as observed in the parent pentane-2,4-dionates. However, this tendency may partly be ascribed to the mutual repulsion between solvent molecules and alkyl substituents, and partly to the increased basicity of coordinated carbonyl oxygen atoms which could eventually coordinate to the neighboring cobalt(II) or nickel(II) complex unit by forming the oxygen bridged binuclear complex.