Nickel(II), Cobalt(II), Palladium(II) and Beryllium(II) Chelates of 2,4,6-Heptanetrione[1]

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Divalent metal chelates of heptane-2,4,6-trione (H_2daa) were synthesized and their structures were discussed. Nickel(II), cobalt(II) and palladium(II) ions gave Ni(Hdaa)$_2$·2H_2O, Ni$_2$(daa)$_2$·4H_2O, Ni$_2$(daa)$_2$·4Py, Co(Hdaa)$_2$·2H_2O, Co$_2$(daa)$_2$·4H_2O, Co$_2$(daa)$_2$·4Py, Pd(Hdaa)$_2$ and Pd(Hdaa)$_2$·2H_2O respectively, while beryllium(II) ion unexpectedly gave bis(2-amino-2-heptene-4,6-dionato)beryllium(II) which resulted from an amino-derivative of the original ligand. Spectroscopic results suggested that the coordination structure of nickel(II) and cobalt(II) ions was octahedral hexacoordinate, that of palladium(II) ion square planar tetracoordinate and that of beryllium(II) ion tetrahedral tetracoordinate. NMR study of the palladium(II) chelate suggested partial enolization of an uncoordinated carbonyl group. It was also found that nickel, cobalt and platinum ions promoted catalytically the bimolecular-condensation of heptane-2,4,6-trione.

In previous papers we have reported on the syntheses and keto-enol tautomerism of heptane-2,4,6-trione (H_2daa) and its methylated derivatives,[2] and also on the properties and structures of their copper(II) chelates.[3] The characteristic feature of this particular β,δ-triketone is that the planar ligand behaves as either monobasic bidentate ligand or dibasic terdentate ligand depending upon the conditions of reaction as well as the kind of metal ion involved. Thus it is of interest to see how heptane-2,4,6-trione reacts with divalent metal ions of various coordination structures. This paper reports on the syntheses, and on the structures of palladium(II), nickel(II), cobalt(II) and beryllium (II) chelates of heptane-2,4,6-trione.

Experimental

Apparatus and Procedure. All the melting points were not corrected. NMR spectra were recorded on a Varian A-60, using tetramethylsilane as an internal reference. Spectral measurements in infrared and visible regions, and thermogravimetric analyses were carried out as described previously.[3]

Synthesis of the Chelates. a) Palladium Chelates. Bis(heptane-2,4,6-trionato)palladium(II). [*Pd(Hdaa)$_2$*]: In 50 ml of methanol were dissolved 0.30 g (0.0017 mol) of palladium(II) chloride and 3.0 g (0.021 mol) of heptane-2,4,6-trione, and the mixture was kept standing overnight at room temperature. The resulting yellow powdery precipitates were collected by filtration, and the product was purified through a silica gel column (Wakogel *Q*-23) in the form of a chloroform solution. Yield 0.12 g (18% from palladium chloride).

Found: C, 42.81; H, 4.76%. Calcd for $C_{14}H_{18}O_6Pd$: C, 43.26; H, 4.67%.

Bis(heptane-2,4,6-trionato)palladium(II) Dihydrate. [*Pd(Hdaa)$_2$·2H_2O*]. To 300 ml of tetrahydrofuran was added 0.30 g (0.0017 mol) of palladium chloride and the mixture was stirred at room temperature for 3 days to give a clear solution. To this was added 3.0 g(0.021 mol) of heptane-2,4,6-trione, and the pH of the solution was adjusted to 4 (on pH indicator paper) with aqueous ammonia. After being refluxed for 4—5 hr, the solution was kept standing overnight at room temperature to give yellow powdery precipitates. The product was recrystallized from tetrahydrofuran. Yield 0.30 g (42% from palladium chloride).

Found: C, 40.08; H, 5.15%. Calcd for $C_{14}H_{18}O_6Pd$·2H_2O: C, 39.59; H, 5.22%.

b) Nickel Chelates. Bis(heptane-2,4,6-trionato)nickel(II) Dihydrate. [*Ni(Hdaa)$_2$·2H_2O*]. *Procedure A*: To 30 ml of an ether solution containing 2.80 g(0.0197 mol) of heptane-2,4,6-trione was added 0.30 g (0.0011 mol) of anhydrous bis(acetylacetonato)nickel(II), and the clear solution was left for 1 hr at room temperature to give blue powdery precipitates. The product was collected by filtration, washed with ether and air-dried. Yield 0.17 g (39% from the nickel acetylacetonate).

Found: C, 44.60; H, 6.01; Ni, 15.57%. Calcd for $C_{14}H_{18}O_6Ni$·2H_2O: C, 44.60; H, 5.88; Ni, 15.57%. $\bar{\nu}_{max}$ in 95% methanol (ε): 15.8 (6.3), 13.6 (shoulder) (2.9), and 9.3 kK (5.7). $\bar{\nu}_{min}$: 19.2 (0.9) and 12.2 kK (1.4).

Procedure B: A mixture of 0.98 g (0.0021 mol) of bis-(heptane-2,4,6-trionato)dinickel(II) tetrahydrate and 3.0 g (0.021 mol) of heptane-2,4,6-trione was carefully warmed at 55—60°C (slightly above the melting point of the ligand, mp 42.5—43.5°C). The green molten paste was kept at this temperature for 90 min with occasional stirring. After the reaction, 100 ml of ether was added portionwise to this reaction mixture to precipitate the pale green nickel chelate. Excess ligand was removed by filtration. The product was finally washed with ether and air-dried and was identified by IR spectral comparison with the nickel chelate obtained by procedure A. Yield 0.68 g (43% from the 2 : 2 nickel chelate)

Bis(heptane-2,4,6-trionato)dinickel(II) Tetrahydrate. [*Ni$_2$(daa)$_2$·4H_2O*]. *Procedure A*: To 50 ml of methanol was added 1.0 g (0.007 mol) of heptane-2,4,6-trione and 2.0 g (0.0069 mol) of nickel(II) nitrate hexahydrate, and pH of the solution was adjusted to about 7 with aqueous methanolic ammonia (1 : 1 by volume) to give bright green powdery precipitates. The product was collected by filtration, washed with water and dried under reduced pressure. Yield 1.5 g (93%).

The sample thus obtained is fairly soluble in various organic solvents such as methanol, chloroform and tetrahydrofuran. Recrystallization from methanol gave green crystallites. Thermogravimetric analysis on the recrystallized chelate showed 16% of weight decrease in the region between 100 and 160°C, which corresponded to the loss of four molecules of water (Calcd as a tetrahydrate: 15.3%).

Found: C, 35.10; H, 5.22; Ni, 25.03%. Calcd for C_{14}-

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1) Contribution No. 254 from the Department of Organic Synthesis, Kyushu University.

2) F. Sagara, H. Kobayashi, and K. Ueno, This Bulletin, **45**, 900 (1972).

3) F. Sagara, H. Kobayashi, and K. Ueno, *ibid.*, **45**, 794 (1972).

$H_{16}O_6Ni_2 \cdot 4H_2O$: C, 35.80; H, 5.15; Ni, 25.00%.

$\bar{\nu}_{max}$ in 95% methanol (ε): 24.1 (shoulder) (530), 16.8 (16), 13.7 (shoulder) (11) and 10.0 kK (15). $\bar{\nu}_{min}(\varepsilon)$: 17.7 (13) and 12.2 kK (8.8).

Procedure B: A methanol solution (3 ml) containing 1.0 g (0.0027 mol) of bis(heptane-2,4,6-trionato)nickel(II) dihydrate was heated at 50°C for 30 min, to give blue powdery precipitates. The product was collected by filtration, washed with ether and air-dried. Yield 0.42 g (66%). The nickel chelate was found to be identical with the sample obtained by procedure A by infrared spectral comparison.

Pyridine Adduct of Bis(heptane-2,4,6-trionato)dinickel(II). [$Ni_2(daa)_2 \cdot 4Py$]. *Procedure A*: A mixture of 2.0 g (0.0043 mol) of bis-(heptane-2,4,6-trionato)dinickel(II) tetrahydrate and 50 ml of pyridine was stirred for several hours, and the resulting blue powdery precipitates were collected by filtration and air-dried. Yield 1.0 g (33%).

The pyridine adduct is fairly soluble in various organic solvents and can be recrystallized from methanol. Thermogravimetric analysis showed 44% weight decrease in the range 90—140°C, which indicated the loss of four pyridine molecules (Calcd: 44.2%).

Found: C, 57.12; H, 5.04; N, 8.16; Ni, 16.44%. Calcd for $C_{14}H_{16}O_6Ni_2 \cdot 4(C_5H_5N)$: C, 57.19; H, 5.08; N, 7.85; Ni, 16.44%.

Procedure B: To a hot solution of 490 mg (0.001mol) of bis(heptane-2,4,6-trionato)dinickel(II) tetrahydrate in 100 ml of methanol was added 100 ml of pyridine at 60°C. The green solution was kept at this temperature for 2 hr, when a small amount of glittering flaky precipitate was obtained. The solution was allowed to cool to room temperature for 3 hr. The resulting precipitate was collected by filtration and washed with a small amount of chilled methanol and air-dried. Yield 390 mg (52%). IR spectral comparison showed that the flaky product was identical with the powdery pyridine adduct from procedure A.

c) Cobalt Chelates. Bis(heptane-2,4,6-trionato)cobalt(II) Dihydrate. [$Co(Hdaa)_2 \cdot 2H_2O$]: A mixture of 0.67 g (0.0014 mol) of bis(heptane-2,4,6-trionato)dicobalt(II) tetrahydrate and 2.0 g (0.014 mol) of heptane-2,4,6-trione was treated at 52—54°C for an hour in a similar manner to that in procedure B for preparation of the 1 : 2 nickel chelate. The product was light pink powder. Yield 0.62 g (58% from the 2 : 2 cobalt chelate).

Found: C, 44.52; H, 6.09%. Cacld for $C_{14}H_{18}O_6Co \cdot 2H_2O$: C, 44.57; H, 5.88%.

When the dihydrate was dried at room temperature in a vacuum (0.3—0.4 mmHg) for a few hours, it turned from light pink to pink, affording a dehydrated product whose composition was found to be $C_{14}H_{18}O_6Co \cdot 1/4H_2O$ by elemental analysis.

Bis(heptane-2,4,6-trionato)dicobalt(II) Tetrahydrate. [$Co_2(daa)_2 \cdot 4H_2O$]. The 2 : 2 chelate was synthesized according to procedures essentially similar to those described for the 2 : 2 nickel chelate, either procedure A or B.

The 2 : 2 cobalt(II) chelate was obtained as brown powder from 2.5 g (0.018 mol) of heptane-2,4,6-trione and 5.13 g (0.018 mol) of cobalt(II) nitrate hexahydrate in methanol-water at 55—60°C with the final pH values 6—8. Yield 2.9 g (70%).

Thermogravimetric analysis on the tetrahydrate chelate revealed that a gradual weight loss due to four moles dehydration took place from room temperature to 180°C, leaving an anhydrous chelate $Co_2(daa)_2$ which decomposed spontaneously at 235°C.

Found: C, 35.94; H, 5.09; Co, 25.2%. Calcd for $C_{14}H_{16}O_6Co_2 \cdot 4H_2O$: C, 35.76; H, 5.15; Co, 25.07%.

The same 2 : 2 chelate was obtained by refluxing a methanol solution of bis(heptane-2,4,6-trionato)cobalt(II) dihydrate.

Pyridine Adduct of Bis(heptane-2,4,6-trionato)dicobalt(II). [$Co_2(daa)_2 \cdot 4Py$]. One gram of 2 : 2 cobalt chelate (tetrahydrate) was dissolved in a methanol-pyridine mixture, and the clear solution was concentrated by evaporation to give yellow brown crystalline precipitates. The product was collected by filtration and dried over phosphorus pentoxide and activated charcoal at room temperature under reduced pressure. Yield 1.2 g (80%).

Found: C, 56.46; H, 5.05; N, 7.76%. Calcd for $C_{14}H_{16}O_6Co_2 \cdot 4(C_5H_5N)$: C, 57.19; H, 5.08; N, 7.84%.

d) Beryllium Chelate. Bis(2-amino-2-heptene-4,6-dionato)beryllium(II). [$Be(aho)_2$]: Beryllium nitrate trihydrate (1.5 g, 0.008 mol) dissolved in ethanol (10 ml) was added to an ethanol solution (20 ml) of heptane-2,4,6-trione (2.31 g, 0.0163 mol) at 40°C. To the resulting pale pink solution was added 12 ml of a mixture of ethanol-aqueous ammonia (1 : 1 by volume) at 30—40°C and the solution was stirred for 10 min. After being left standing for an additional 40 min, the resulting pale yellow crystalline precipitates were collected by filtration and recrystallized from acetonitrile. Yield 1.73 g(75%). The product was found to be a 1 : 2 beryllium chelate of 2-amino-2-heptene-4,6-dione which resulted from the amination of terminal carbonyl oxygen of heptane-2,4,6-trione.

Found: C, 58.13; H, 6.97; N, 9.54%. Calcd for $C_{14}H_{20}O_4N_2Be$: C, 58.12; H, 6.97; N, 9.68%.

Results and Discussion

Synthetic Conditions of the Chelates. The 2 : 2 chelates of nickel(II) and cobalt(II) can be synthesized by procedures similar to those employed in the synthesis of bis(heptane-2,4,6-trionato)dicopper(II), either by subjecting the corresponding metal ion to the reaction with an equimolar amount of heptane-2,4,6-trione in methanol at pH about 7, or by heating a methanol solution of the corresponding 1 : 2 chelate.[3] The nickel(II) and cobalt(II) chelates were obtained as tetrahydrates.

On the other hand, the 2 : 2 chelate of palladium (II) could not be obtained despite our efforts to employ various reaction conditions including those mentioned above. The chelate obtained from the reaction mixtures was always 1 : 2 palladium(II) chelate, anhydrous or dihydrate, depending upon the reaction conditions. The main reason for the difficulty of forming a 2 : 2 palladium(II) chelate could be understood to be due to the larger ionic size of palladium(II) ion than that of copper(II), nickel(II) or cobalt(II) ion. Palladium(II) ion can hardly be accomodated in the binuclear centers of the 2 : 2 chelate.

It is interesting to note that the 1 : 2 palladium(II) chelate can be obtained in a dihydrate form as well as in an anhydrous form, while the chelates of copper(II), nickel(II) and cobalt(II) are obtained only in a dihydrate form. The dehydration of the latter chelates, even at reduced pressure and at lower temperature, always resulted in rearrangement into the corresponding 2 : 2 chelates. The relative stability of 1 : 2 palladium(II) chelate in an anhydrous form might be con-

Table 1. Catalytic condensation of heptane-2,4,6-trione

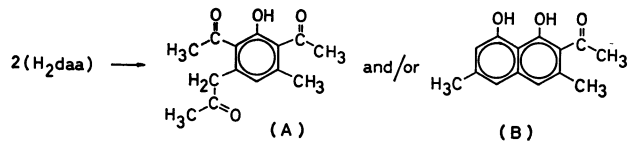
Complex	Reaction conditions			Reaction product	
	Solvent	Temperature	Duration		Yield
$Ni_2(daa)_2 \cdot 4H_2O$	H_2daa	70°C	2 days	A[a)]	52%
$Co_2(daa)_2 \cdot 4H_2O$	H_2daa	70	1 hr	A	67
K_2PtCl_4	Water-methanol	Room temp.	1 hr	A	23
	Water-methanol	70	2 hr	B[a)]	34

a) Products A and B melted at 113 and 182°C, respectively. They were identified with the reported compounds by their melting points and elemental analyses. A. J. Birch, D. W. Cameron, and R. W. Rickards, *J. Chem. Soc.*, **1960**, 4395.

nected with the difficulty of forming 2 : 2 chelate as discussed above.

In the case of beryllium chelate, the use of ammonia to adjust the pH of reaction medium resulted in the amination of terminal carbonyl group in heptane-2,4,6-trione, so that only 1 : 2 chelate of the amino derivative was obtained. Attempts to obtain a 2 : 2 beryllium(II) chelate using various reaction conditions were unsuccessful.

In contrast to the relative easiness of obtaining 2 : 2 chelates with nickel(II) and cobalt(II), the corresponding 1 : 2 chelates could not be obtained by the standard procedures which were employed in the synthesis of 1 : 2 copper(II) chelate. During the course of an investigation on the synthesis of 1 : 2 chelates of nickel (II) and cobalt(II), it was found that the bimolecular condensation of heptane-2,4,6-trione was accelerated in the presence of 2 : 2 nickel or cobalt chelate according to the following reaction scheme.



Scheme 1.

A similar effect was also observed with platinum(II) salt, but neither copper(II) ion nor copper(II) chelate was effective for promoting such condensation reactions. When pure heptane-2,4,6-trione was heated above its melting point, no cyclized condensation product has obtained. However, when an excess of the ligand was brought into contact with such metal chelates, especially at an elevated temperature, the cyclized product A or B was obtained in the reaction mixture depending upon the condition of reaction. Table 1 summarizes the result.

Thus, when nickel(II) or cobalt(II) ion was allowed to react with excess heptane-2,4,6-trione with the purpose of obtaining a 1 : 2 chelate, the reaction products were always a 2 : 2 chelate and cyclized by-products but no 1 : 2 chelate. Accordingly, the 1 : 2 chelates had to be prepared by the ligand exchange reaction between a bis(acetylacetonato)-metal chelate and heptane-2,4,6-trione in anhydrous ether, or by the reaction between 2 : 2 metal chelates and molten heptane-2,4,6-trione at a temperature slightly above its melting point.

Structures of Nickel(II)- and Cobalt(II) Chelates. The infrared spectra of 1 : 2 chelates of nickel(II) and

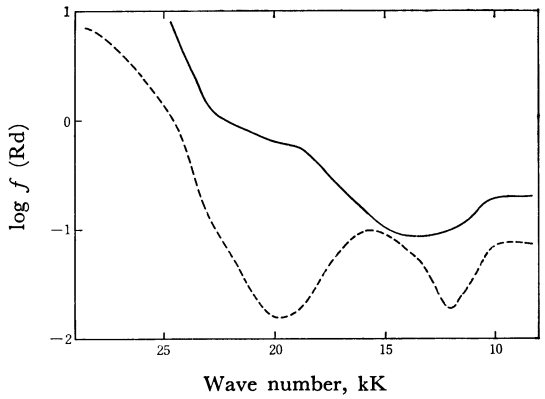


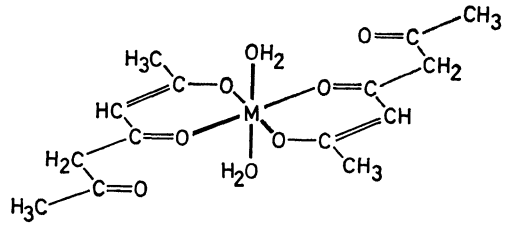
Fig. 1. Diffuse reflectance spectra of $Ni(Hdaa)_2 \cdot 2H_2O$ (----) and $Co(Hdaa)_2 \cdot 2H_2O$ (——).

cobalt(II), [$Ni(Hdaa)_2.2H_2O$ and $Co(Hdaa)_2.2H_2O$], show characteristic bands in 3000—3400 cm^{-1} and 1500—1700 cm^{-1} regions. A broad band with a maximum at 3280 cm^{-1} for the nickel- and 3400 cm^{-1} for the cobalt chelates can be assigned to the hydrated water. This makes a sharp contrast with those observed in the 1 : 2 copper(II)- and palladium(II) dihydrate chelates, where a sharp band at 3530 cm^{-1} and a multiplet weak band with maxima at about 3420, 3350 and 3260 cm^{-1} appear. The broad band of 1 : 2 nickel(II)- and cobalt(II) chelates suggests a rather strong coordination of water molecules to the central metal ion along the z axis, while the ligand molecules coordinate along the x—y plane. On the other hand, a multiplet band with fine structure of 1 : 2 copper(II) and palladium(II) chelates indicates the weaker interaction of hydrated water molecules with metal ion.

In the 1500—1700 cm^{-1} region, there are observed a sharp band at 1720 cm^{-1} for the nickel(II)- and 1695 cm^{-1} for the cobalt(II) chelates and a strong band with several shoulders at 1500—1600 cm^{-1} for the both chelates. These bands can be assigned to an uncoordinated carbonyl group and a coordinated carbonyl group in conjugated chelate ring system respectively as in the case of 1 : 2 copper(II) chelate.

The power reflectance spectra of the 1 : 2 chelates of nickel(II) and cobalt(II) are shown in Fig. 1. In the case of $Ni(Hdaa)_2.2H_2O$, two broad bands at 9300 and 15800 cm^{-1} with a shoulder at 25000 cm^{-1} were observed, and in the case of $Co(Hdaa)_2.2H_2O$, a band at 19000 cm^{-1} and a broad band at 9000—9500 cm^{-1} were observed. These spectra are found to be very much similar to those of bis(acetylacetonato)nickel-

(II) dihydrate[4] or -cobalt(II) dihydrate[5] respectively. These results strongly suggest the octahedral coordination structure around the central metal ion for both 1 : 2 chelates as proposed in structure I.



Structure I. M=Ni(II) or Co(II).

As to the 2 : 2 chelates of nickel(II) and cobalt(II), [$Ni_2(daa)_2.4H_2O$ and $Co_2(daa)_2.4H_2O$], infrared spectra were characterized with a broad band at 3200—3400 cm^{-1} and a band with shoulders at 1500—1600 cm^{-1}, which could be assigned to hydrated water and coordinated carbonyl groups in the conjugated chelate ring system, respectively. Absence of a band due to the uncoordinated carbonyl groups indicates that all carbonyl groups are involved in the coordination to the metal ions.

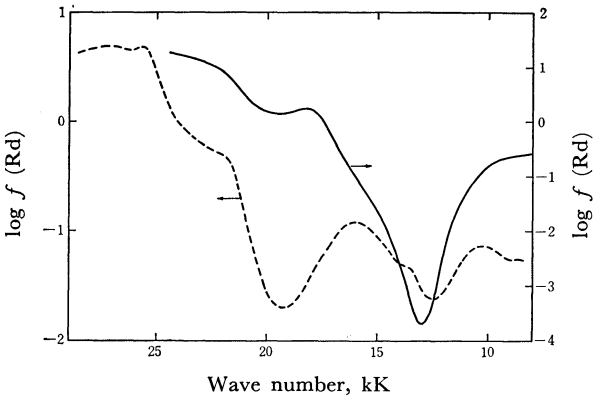
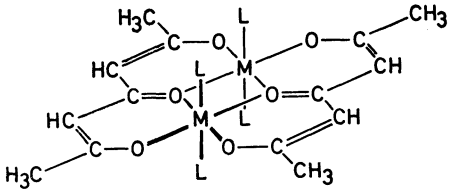


Fig. 2. Diffuse reflectance spectra of $Ni_2(daa)_2 \cdot 4H_2O$ (----) and $Co_2(daa)_2 \cdot 4H_2O$ (——).

The solid reflectance spectra of these hydrated chelates in visible region are shown in Fig. 2. They show two bands at 10400 and 16000 cm^{-1} with shoulders at 13500 and 22000 cm^{-1} for nickel(II) chelate, and a single band at 18200 cm^{-1} with shoulders at 9000 and 23000 cm^{-1} for cobalt(II) chelate. The results suggest that the coordination structure around nickel(II) or cobalt(II) ion is also octahedral.

The molecular weight of anhydrous 2 : 2 nickel(II) chelate in methanol, determined by the vapor pressure osmometer, was found to be 410 which is close to the calculated value of 397.7 for $Ni_2(daa)_2$. Consideation of these observations leads to the conclusion that the structures of $Ni_2(daa)_2.4H_2O$ and $Co_2(daa)_2.4H_2O$ can be assigned to structure II, in which four molecules of hydrated water coordinate to the central metal ions along the z axis.

4) G. Maki, *J. Chem. Phys.*, **29**, 162 (1958).
5) F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, **3**, 1 (1964).



Structure II. M=Ni(II) or Co(II), L=H_2O or Pyridine.

Pyridine Adducts of 2 : 2 Chelates. Coordinated water in 2 : 2 nickel- and cobalt(II) chelates can easily be replaced by pyridine, affording the pyridine adducts having the formula $M_2(daa)_2.4Py$, where M denotes Ni(II) or Co(II).

The absence of infrared absorption band due to free carbonyl group at around 1700 cm^{-1} indicates that the coordination structure of heptane-2,4,6-trione remained intact and the addition of pyridine merely caused the replacement of coordinated water with pyridine.

The solid reflectance spectra of pyridine adducts in visible region shown in Fig. 3 are characterized by two

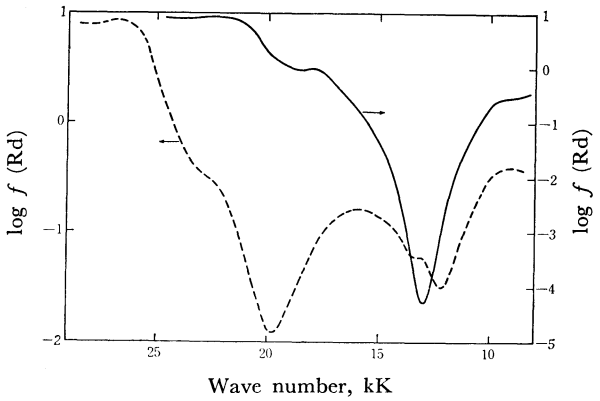


Fig. 3. Diffuse reflectance spectra of $Ni_2(daa)_2 \cdot 4Py$ (----) and $Co_2(daa)_2 \cdot 4Py$ (——).

broad bands at 9200 and 16000 cm^{-1} and shoulders at 13000 and 22500 cm^{-1} for nickel(II) chelate and at 9000, 18200 and 22000 cm^{-1} for cobalt(II) chelate, indicating the octahedral hexacoordinate structure around nickel(II) or cobalt(II) ion as shown in structure II.

Thermogravimetric analysis of the pyridine adducts as well as hydrates of 2 : 2 chelates revealed that pyridine or water dissociated above 90°C, leaving anhydrous 2 : 2 chelates.

Structure of Palladium(II) Chelate. The 1 : 2 palladium(II) chelate could be obtained either as dihydrate or anhydrous form. Infrared absorption spectrum of the anhydrous sample was characterized with a weak multiplet band at 3400 cm^{-1} region, a sharp strong band at 1730 cm^{-1} due to uncoordinated carbonyl groups, and complex bands in 1500—1600 cm^{-1} region due to coordinated carbonyl groups conjugated with olefinic chelate ring.

The NMR spectrum of the anhydrous chelate in $CDCl_3$ (1.0 M solution) is shown in Fig. 4. Peaks at δ=2.12, 2.24, 3.42 and 5.47 ppm can be assigned to methyl(a), methyl(b), methylene(c) and methine(d)

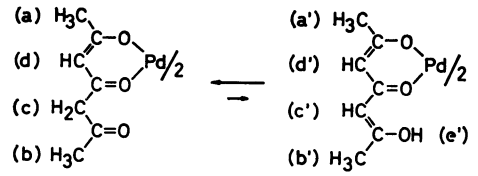


Fig. 4. NMR spectrum of the 1 : 2 palladium chelate and its tautomers. Assignments of the NMR peaks correspond to the protons indicated by alphabetical letters in the above structural formulae.

protons, respectively. However, weak peaks are also observed at $\delta=1.93$, 4.97, 5.13 and 11.85 ppm. If we consider the partial enolization of uncoordinated carbonyl groups, these weak peaks can be reasonably assigned to the protons of enolized chelate as indicated in Fig. 4.

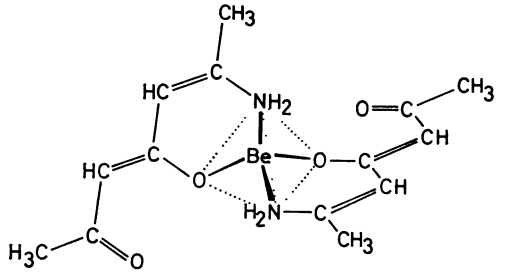
Thus the weak multiplet infrared absorption band at 3400 cm^{-1} region can also be assigned to the enol hydroxyl group. The relatively weak intensity of the signals due to the enolic isomer, in the infrared and NMR spectra, indicates that the extent of enolization in the 1 : 2 palladium(II) chelate is rather small.

Thus, the anhydrous 1 : 2 palladium(II) chelate $Pd(Hdaa)_2$ can be assigned to structure I, but with no water. As to dihydrate chelate $Pd(Hdaa)_2 \cdot 2H_2O$, the most probable structure is I, with water molecules weakly coordinated to palladium(II) ion along z axis.

Structure of Beryllium(II) Chelate. Despite our effort to obtain a 1 : 2 beryllium(II) chelate of heptane-2,4,6-trione by the reaction of beryllium(II) ion with free ligand in an ethanol–ammonia medium, a 1 : 2 beryllium chelate of 2-amino-2-heptene-4,6-dione was obtained unexpectedly.

The result of elemental analysis indicates that it is a 1 : 2 chelate of monoamino derivative of heptane-2,4,6-trione. Two sharp infrared absorption bands at 3390 and 3300 cm^{-1}, which appeared at a relatively lower frequency region than usual primary amines, suggest that the primary amino group may coordinate to beryllium(II) ion.[6] Other characteristic bands at 1635 and 1525 cm^{-1} may be assigned to uncoordinated and coordinated carbonyl groups, respectively, though the frequency of the former band is slightly lower than that expected for $\alpha,\beta : \gamma,\delta$-unsaturated ketones.

Although there is no positive evidence, structure III is most likely to be assigned to bis(2-amino-2-heptene-4,6-dionato)beryllium(II) based on the following observations.



Structure III.

When acetylacetone was brought into reaction with beryllium(II) ion in the presence of ammonia, only bis(acetylacetonato)beryllium(II) was obtained. When 2-methoxy-2-heptene-4,6-dione[3] was brought into reaction with beryllium(II) ion in the presence of ammonia, the product was bis(2-methoxy-2-heptene-4,6-dionato)beryllium(II). Thus, the amination seems to be characteristic to β,δ-triketones. It does not proceed on β-diketones nor β,δ-triketones in which the terminal carbonyl group is fixed in the form of an enol ether. Thus, it is reasonable to assume that the chelation occurs between heptane-2,4,6-trione and beryllium(II) ion to give bis(heptane-2,4,6-trionato)-beryllium(II) as an intermediate product, which in turn reacts with ammonia to afford 2-amino-2-heptene-4,6-dionato chelate. When heptane-2,4,6-trione reacts with ammonia in the absence of metal ion, it is known that amination occurs on the terminal carbonyl group, affording 2,6-dimethyl-4-pyridone as a cyclization product.[7] Thus, it is likely that amination occurs on the chelated ligand but not on the free ligand, and that the position of amination may be on the terminal carbonyl group. As regards whether the 1 : 2 beryllium chelate is an *O,O*-coordinated structure with the amino group uncoordinated, or the rearrangement occurs after amination resulting in an *O,N*-coordinated structure with the carbonyl group uncoordinated, the latter seems probable. This is supported by the fact that 2-amino-2-heptene-4,6-dione is stable only in the form of beryllium chelate, and attempts to recover the free aminated ligand from the beryllium(II) chelate were unsuccessful, only giving the original heptane-2,4,6-trione. Therefore, the amino group might be protected by the coordination to the metal ion.

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7) R. J. Light and C. R. Hauser, *J. Org. Chem.*, **25**, 158 (1960).