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Some Thermal Properties of Metal Chelates of *o*-Acylphenols and of Their Ketimine Derivatives[*1]

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The beryllium chelates of 2-hydroxy-3-methylacetophenone, 2-hydroxy-3-isopropylisobutyrophenone and 2-hydroxyacetophenone, and the copper- and nickel chelates of the ketimine derivatives of 2-trifluoroacetylphenol and 2-hydroxyisobutyrophenone in addition to the above *o*-acylphenols were synthesized. The thermal stability and relative volatility of these chelate compounds, measured by means of a thermogravimetric method, were found to be strongly increased by introduction of bulky alkyl or trifluoromethyl groups.

In relation to the application of gas-chromatography to the analysis of metal chelates, the great numbers of volatile metal chelates of β-diketones,[1)] and of *N*-alkylsalicylaldimines[2)] have been synthesized, and especially concerning the homologues of β-diketone, the correlation between the molecular structure of ligands and the volatility of their metal chelates has been intensively investigated.[3)] Although no conclusive general rules governing the volatility of metal chelates have been attained yet, an observation has been made that introduction of trifluoromethyl or *t*-butyl group into a β-diketon skeleton strongly increased the volatility of its metal chelates. Except on the β-diketone homologues, however, very few works have been made on volatility of metal chelates and its correlation to the molecular structures of the ligands.

In the hope of obtaining a new type of volatile metal chelates, we synthesized the metal chelate compounds containing aromatic nuclei fused to the chelate rings in a molecule, *e. g.*, metal chelates of salicylaldehyde and of *o*-acylphenols, and investigated their volatilities and thermal stabilities in relation to the effects of aromatic nuclei, and of alkyl groups attached closely to the chelate ring.

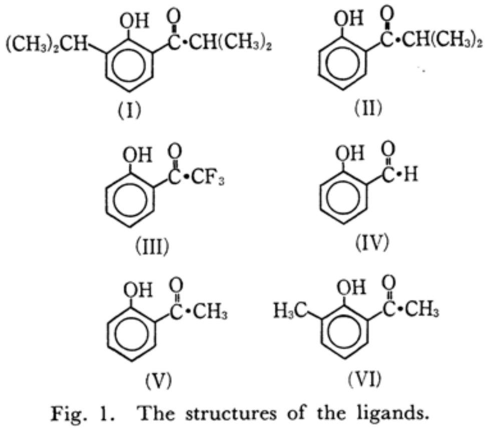

Fig. 1. The structures of the ligands.

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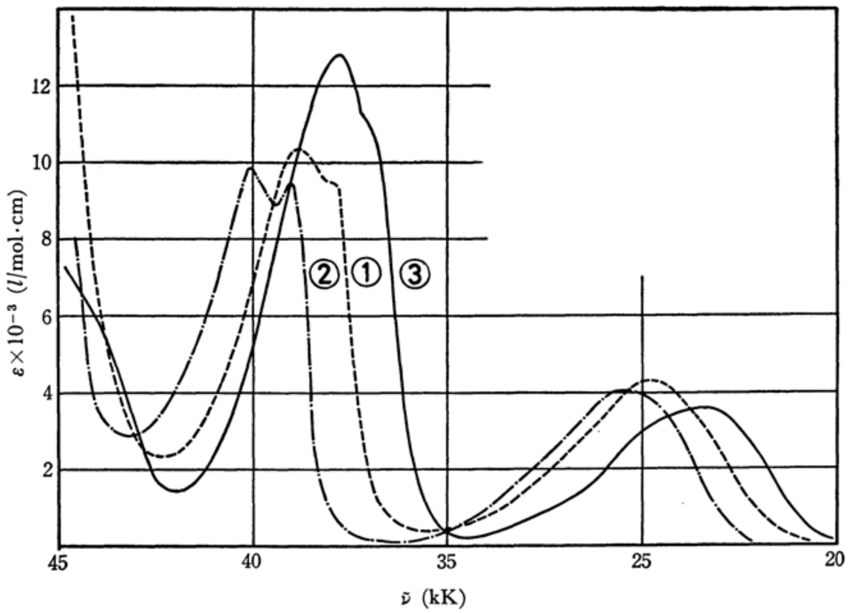


Fig. 2. Ultraviolet spectra of the ligands: Curve 1 for I, 2 for II, and 3 for III, respectively.

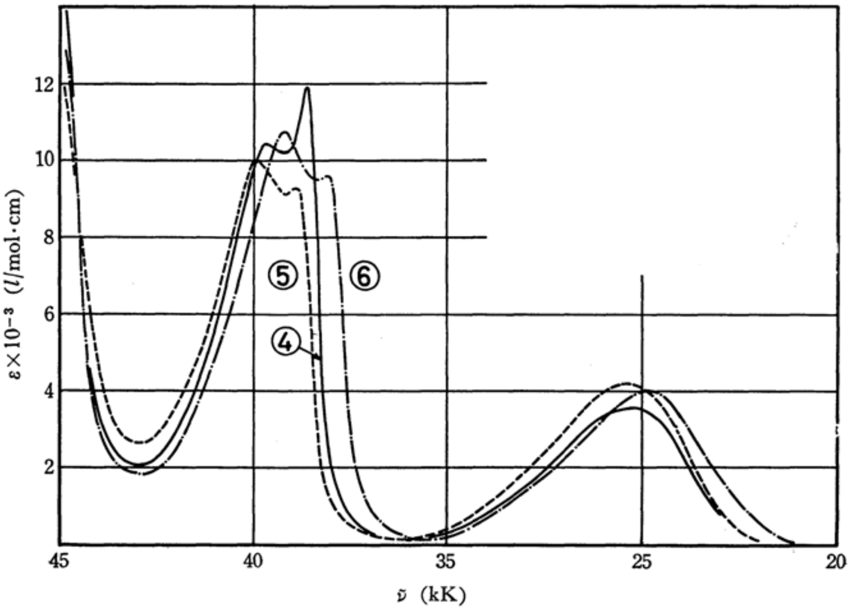


Fig. 3. Ultraviolet spectra of the ligands: Curve 4 for IV, 5 for V, and 6 for VI, respectively.

Results and Discussion

The new ligands synthesized in the present work are 2-hydroxy-3-isopropylisobutyrophenone (I), 2-hydroxyisobutyrophenone (II), and 2-trifluoroacetylphenol (III). In addition to the above, salicylaldehyde (IV), 2-hydroxyacetophenone (V) and 2-hydroxy-3-methylacetophenone (VI) are used as ligands in order to make a comparison with the new ones. The structures of these ligands are shown in Fig. 1.

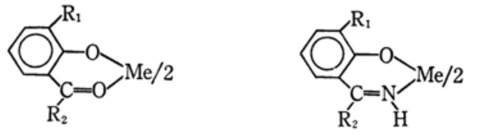
The new *o*-acylphenols, I, II and III, were synthesized by Fries rearrangement reaction from corresponding phenol acylates, accompanied by formation of isomeric *p*-acylphenols.

Infrared spectrum of I shows a broad diffused band at 3500—2500 cm^{-1} in good contrast with the sharp strong hydroxy band of the isomeric *p*-acylphenol observed at 3310 cm^{-1}. The character and position of this band allow it to be assigned to the stretching vibration of hydroxy group involved in intramolecular hydrogen bond with carbonyl group sited at *ortho*-position. This is in good agreement with the observation of carbonyl band of I at 1630 cm^{-1} which is at a position of lower wave number as compared with that of the *p*-substituted isomer at 1650 cm^{-1}. 1,2,3-Trisubstituted phenyl moiety in I is ascertained by the nuclear magnetic resonance spectrum, in which three protons on an aromatic nucleus show themselves in a typical ABX pattern ($\delta_A=7.30$ ppm, $\delta_B=7.55$ ppm, $\delta_X=6.70$ ppm, $J_{AX}=J_{BX}=8$ cps, $J_{AB}=2$ cps); a quite similar pattern is observed also concerning three protons in aromatic ring of VI.

Infrared spectra of II and of III also show respectively a broad diffused band assigned to a hydroxy group in an intramolecular hydrogen bond and a band assigned to a lowered carbonyl stretching frequency in comparison with that of each *p*-substituted isomer. The spectra of II and of III reveal respectively a strong band characteristic to *o*-disubstituted benzene ring at about 750 cm^{-1}, and the presence of this band, together with the intramolecular hydrogen bond between the hydroxy and the carbonyl group, indicates *ortho*-acylphenol structures of II and III, which are also ascertained by their abilities of chelate formation with metal ions.

As observed in Figs. 2 and 3, characteristic resemblance to each other in the ultraviolet spectra of all these ligands also indicates that these ligands have the same arrangement of chromophores on a benzene nucleus.

Metal chelates of the *o*-acylphenols were prepared by using beryllium(II), copper(II) and nickel(II) salts. Beryllium ion gave 1 : 2 (metal ion : ligands) chelate compounds (VII) for I, V and VI as shown in Fig. 4, attempts to prepare complexes of III and of IV being unsuccessful. On the other hand, in the cases of copper(II)- and ncikel-(II) ions, usual procedures trying to prepare the complexes of an *o*-acylphenolate afforded, contrary to our intentions, 1 : 2 chelate compounds in which the ligands coordinated in the forms of ketimine derivatives as VIII in Fig. 4. The ketimines seem to arise on the process of chelate formation from the *o*-acylphenols and ammonia added into the reaction media to adjust its pH. Attempts to prepare *o*-acylphenolato-chelate compounds have been unsuccessful.



(VII) (VIII)

Fig. 4. The structures of the metal chelates.

Thermogravimetric curves of the metal chelates described above are shown in Figs. 5, 6 and 7.

Although a rigorous discussion of volatility of a compound necessitates vapor pressure data at various temperatures and other thermodynamic data, the thermogravimetric method employed in the present work, roughly approximate though it may be, is a convenient procedure for the measurement of thermal stability of a compound and its relative volatility. Results of preliminary experiments on subliming behaviors of the chelates under reduced pressures indicated that the beryllium chelates of I, V and VI were readily sublimed at 150°C/0.5 mmHg, and that the copper- and nickel ketimine chelates of I and III were sublimed at

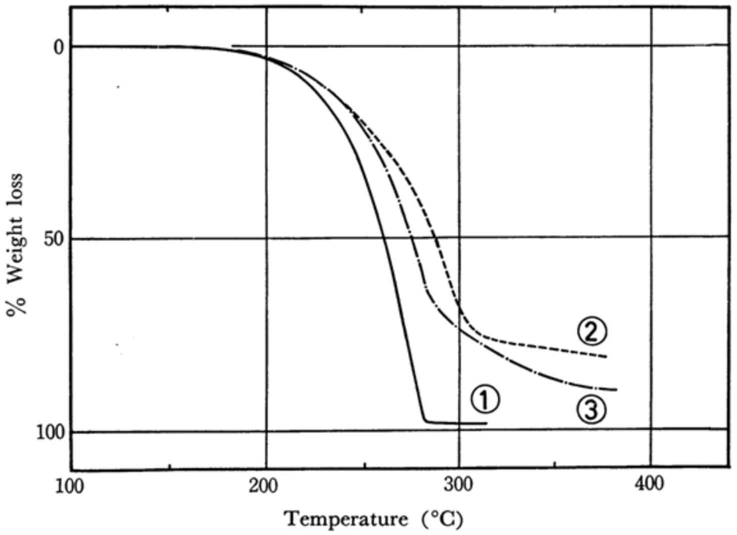


Fig. 5. Thermogravimetric curves of the beryllium chelates: Curve 1 for that of I, 2 for of V, and 3 for of VI, respectively.

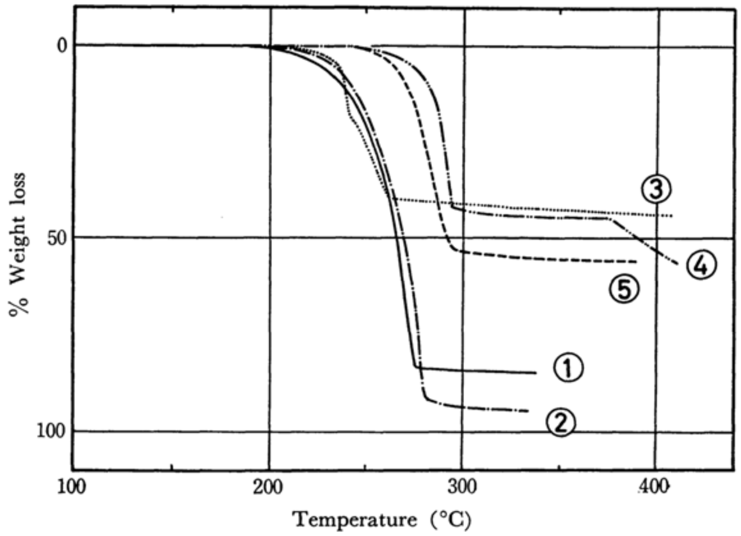


Fig. 6. Thermogravimetric curves of the copper chelates of the ketimine derivatives: Curve 1 for that of I, 2 for of III, 3 for of IV, 4 for of V and 5 for of VI, respectively.

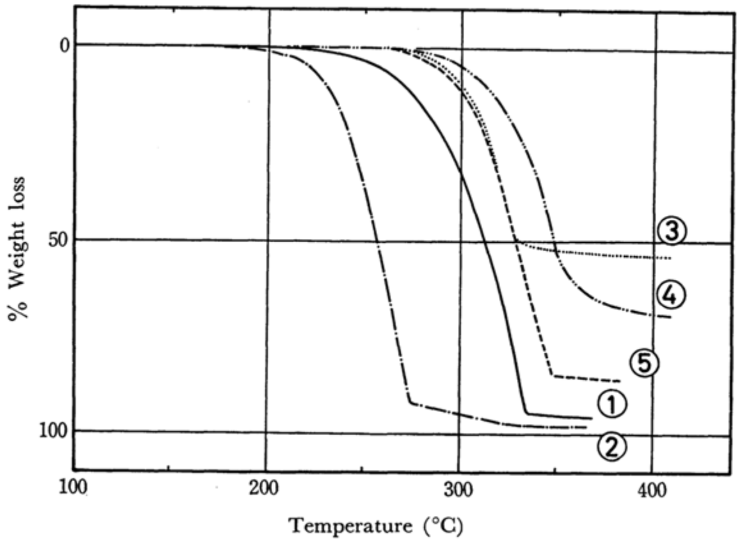


Fig. 7. Thermogravimetric curves of the nickel chelates of the ketimine derivatives: Curve 1 for that of I, 2 for of III, 3 for of IV, 4 for of V, and 5 for of VI, respectively.

about 160°C/0.4 mmHg without any decomposition, while those of IV, V and VI were less sublimable or the sublimation was accompanied with their thermal decomposition.

In the thermogravimetric experiments of these chelate compounds except those of IV, there was observed the deposition of crystalline substances onto the inner wall of the tubular glass part of the apparatus in the initial stage of the weight decrease, and the deposited substance in each experiment was confirmed to be the respective original one intact by infrared spectral comparison. This means that the initial weight decrease is not due to decomposition but to sublimation of the chelate compounds.

Thermogravimetric curves show that the introduction of a methyl group into V to give VI results in slightly easy vaporization of the chelates, and that replacing the methyl groups in VI with isopropyl groups to give I lowers the temperature where vaporization of the chelates begins and subsequently decreases their thermal decomposition as seen in Fig. 5. Thus, among the beryllium chelates only that of I could vaporize completely at a lower temperature without any thermal decomposition. Similar tendencies are observed on the ketimine chelates of copper and of nickel as seen in Figs. 6 and 7; the copper chelate of IV begins to decompose at about 200°C and no vaporization is observed, the behavior of the nickel chelate also being not far different. Introduction of methyl- or isopropyl groups in the position adjacent to the donor groups in IV to give V, VI or I, makes their chelate compounds increasingly volatile as well as thermally stable, although the vaporization was still accompanied with slight thermal decomposition.

On the other hand, the introduction of trifluoromethyl group lowers the temperature at which vaporization of the complexes begins, as well as suppressing thermal decomposition, as observed in the complexes with the chelating agent III, which shows no thermal decomposition within the temperature range studied here.

Thus, as far as volatility is concerned, the *o*-acylphenols seem to show similar tendencies as those observed in the β-diketones; namely the more crowded groups around the donor atoms in a ligand make its chelate compound more volatile and more stable thermally, and in addition, the introduction of perfluoroalkyl groups into a ligand also makes its metal chelate strongly volatile as well as

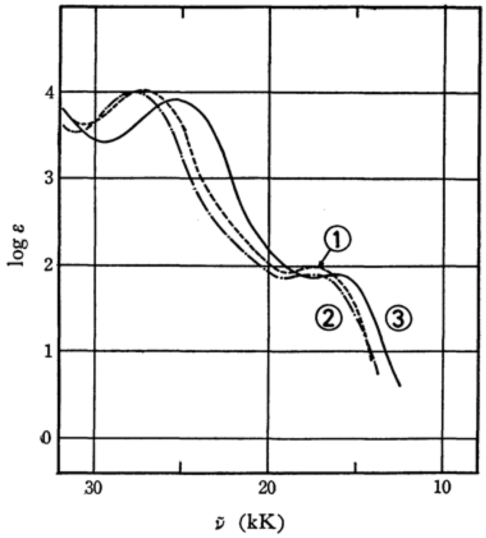


Fig. 8-A

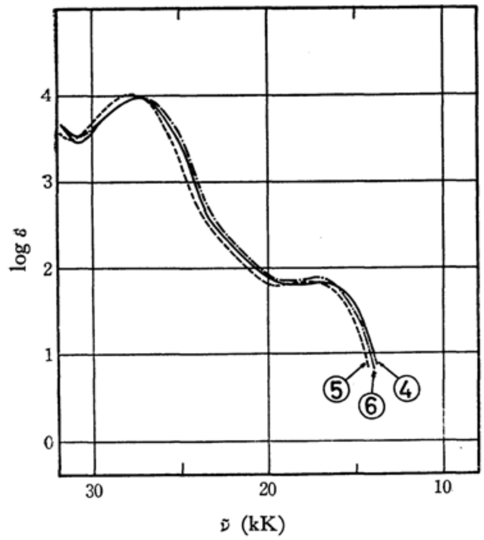


Fig. 8-B

Fig. 8-A, B. Visible spectra of the copper chelates of the ketimine derivatives: Curve 1 for that of I, 2 for of II, 3 for of III, 4 for IV, 5 for of V, and 6 for of VI, respectively.

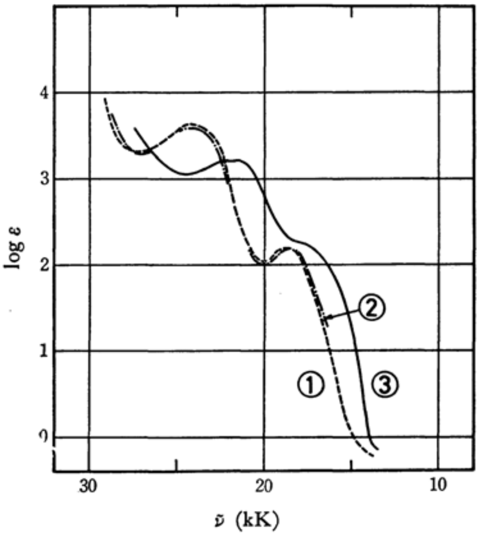


Fig. 9-A

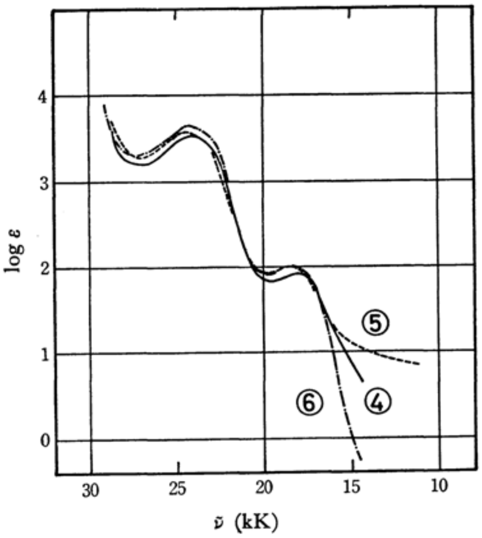


Fig. 9-B

Fig. 9-A, B. Visible spectra of the nickel chelates of the ketimine derivatives: Curve 1 for that of I, 2 for of II, 3 for of III, 4 for of IV, 5 for of V, and 6 for of VI, respectively.

thermally stable.

Ultraviolet spectra of the ligands given in Figs. 2 and 3 show that replacing a formyl group with an acyl group (IV→V, *etc.*) causes a characteristic shift on the spectra, although different acyl groups give no significant differences, and the introduction of an alkyl group into the aromatic nucleus (V→VI, or II→I) causes the bathochromic effect, which is still not so intensive as that observed with trifluoromethyl on III. Trifluoromethyl group causes not only strong bathochromic but also hyperchromic effects which are apparent by a comparison of the spectrum of III with that of V.

General features of visible spectra of the copper- and of the nickel ketimine chelates given respectively in Figs. 8 and 9 indicate that they are of a square planar configuration[4] and, although their molecular weights have not been determined, they seem to be all monomeric. Comparisons of their spectra reveal that introduction of alkyl groups into the ligands gives also very little effects on the electronic spectra of their metal complexes, while trifluoromethyl group causes a strong bathochromic shift.

Increased volatility of the chelate compound containing bulky alkyl groups, therefore, seems to be ascribed not to electronic effects by the alkyl groups, but mainly to their steric effects; namely the bulky alkyl groups sterically hinder the polar, or polarizable moieties such as aromatic, and chelate ring from being intermolecularly close to each other, so that consequent intermolecular forces among the chelate molecules seem to decrease to a large extent.

On the other hand, with respect to trifluoromethyl group, the nickel ketimine chelate of III is much more volatile than that of I, and therefore, bulkiness of the ligand or congestion around the central metal ion can not be only a responsible factor for the volatility. In preliminary solubility measurements in chloroform, which is known as one of the nonpolar solvents, the copper ketimine chelate of III has much less solubility than those of I, II, V and VI, though comparable with that of IV. The electronic spectrum of the copper ketimine chelate of III shows the strong red-shift, and the increased volatility of this chelate compound, therefore, must be ascribable not only to steric effects but also particular electronic effects of a trifluoromethyl group.

Whole mechanism of the increased volatility observed here should be very complicated and there remains much to be elucidated.

Experimental

Apparatus and Procedures. All melting points measured are uncorrected. The ultraviolet and visible spectra were measured with a Hitachi EPS-2 recording spectrophotometer, by using *n*-hexane as the solvents for the ligands and chloroform for the metal chelates respectively. The infrared spectra were measured with a JASCO DS-301 recording spectrophotometer. The nuclear magnetic resonance spectra were recorded with a Varian A-60 operating at 60 Mc, by using tetramethylsilane as the internal reference and carbon tetrachloride as the solvent. Thermogravimetric curves were obtained with a Shimadzu automatic recording thermobalance TB-10B under atmospheric pressure. A sample (about 40 mg) was held in a nitrogen stream (flow rate; about 60 m*l*/min) and heated at a rate of 5°C per minute. Temperatues were measured by alumel chromel thermocouples which were calibrated by the melting points of benzoic acid, succinic acid and anthraquinone.

Synthesis of the Ligands. *2-Hydroxy-3-isopropylisobutyrophenone (I).* 2-Isopropylphenyl isobutyrate[5] (14.7 g) was added dropwise into a suspension of aluminum chloride (10.9 g) in carbon disulfide (20 m*l*) with stirring for 30 min. The mixture was heated with gentle refluxing for an additional hour. After the solvent was distilled, which took about two hours, the temperature of the reaction mixture was gradually raised to 170°C during 30 min, and the mixture was heated keeping this temperature for subsequent 40 min. After cooled to room temperature, the resulting mixture was decomposed with aqueous hydrochloric acid (*ca.* 5 N) and steam-distilled. An organic layer separated from the aqueous distillate was taken into 500 m*l* of ether, and the ethereal solution was washed with 2 N aqueous sodium hydroxide (500 m*l*). The remaining ether layer afforded oily 2-hydroxy-3-isopropylisobutyrophenone (5.3 g) boiling at 109.0—111.0°C/2 mmHg. Found: C, 75.66; H, 8.82%. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%. IR (liquid film): a broad band spreading over during 3500 and 2600 cm^{-1}, a triplet at 2982, 2950, and 2880 cm^{-1}, a sharp carbonyl band having some shoulders at 1632 cm^{-1}, and a sharp singlet at 746 cm^{-1}. NMR (*c* 0.77 M): a doublet at 1.17 and 1.28 ppm (12 protons), a multiplet spreading from 3.0 to 3.8 ppm (2 protons), a triplet centered at 6.70 ppm splitted with 8 cps of *J*-value (1 proton), two quartets (2 protons) centered at 7.30 and 7.55 ppm respectively, each of which is splitted into a quartet with two *J*-values (2 and 8 cps), and a singlet at 12.80 ppm (1 proton). Attempts to prepare a semicarbazone derivative were unsuccessful.

The residue remaining in a still-pot upon the steam-distillation gave the colorless crystals melting at 98.5—99.9°C (from petroleum ether). This crystalline compound was also separated from the alkaline washings after acidified (*ca.* 1 g). Found: C, 75.73; H, 9.01%. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%. IR (potassium bromide disc): a strong band at 3310 cm^{-1}, a doublet at 2974 and 2880 cm^{-1}, a sharp carbonyl band at 1651 cm^{-1}, a prominent doublet at 1608 and 1585 cm^{-1}, and a strong sharp band at 819 cm^{-1}. Semicarbazone is readily formed, mp 199.0—203.0°C. This crystalline compound, though seemed to be 3-isopropyl-4-hydroxyisobutyrophenone, was not confirmed.

2-Hydroxyisobutyrophenone (II). Phenyl isobutyrate[6]

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[4] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y. (1962).

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[6] E. H. Man, F. W. Swamer and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 901 (1951).

(40 g) was added dropwise into a suspension of aluminum chloride (37.3 g) in carbon disulfide (40 m*l*) with stirring. The mixture was heated in the similar way just as described above. The resulting mixture was decomposed with aqueous hydrochloric acid, and steam-distilled. An organic layer separated from the aqueous distillate was taken into ether, dried and distilled to give a fraction boiling at 79.3—79.5°C/3.5 mmHg (yield: 16.1 g, 40% of the theoretical). IR (liquid film): a broad band spreading over between 3400 and 2600 cm^{-1}, a triplet at 2980, 2940, and 2870 cm^{-1}, a carbonyl band at 1645 cm^{-1}, and two strong bands at 822 and 754 cm^{-1}. Analysis was satisfactory as the metal chelate derivatives, *vide infra*.

2-Trifluoroacetylphenol (III). Phenyl trifluoroacetate[7] (57 g) was added dropwise into a suspension of aluminum chloride (46 g) in carbon disulfide (60 m*l*) with stirring at room temperature for an hour. The mixture was heated with gentle refluxing for an additional hour. After the solvent was distilled out, which took one and half hour, the temperature of the reaction mixture was gradually rasied to 115°C during 15 min, and the mixture was cooled to 90°C, being kept at this temperature for one and half hour. The resulting mixture, after cooled to room temperature, was decomposed with aqueous hydrochloric acid, and steam-distilled. An organic layer separated from the aqueous distillate was taken into ether, and the ethereal extract was evaporated off. A residual oil was treated with copper acetate and ammonia in aqueous ethanol, giving a copper ketimine chelate (VIII) of the trifluoroacetylphenol (35 g). The ketimine chelate was decomposed with aqueous hydrochloric acid, giving a free ligand, which was extracted with ether, and was rectified to give an oily fraction boiling at 92°C/55 mmHg (yield: 23.8 g, 42% of the theoretical). Found: C, 50.65; H, 2.78%: Calcd for $C_8H_5O_2F_3$: C, 50.54; H, 2.65%. IR (liquid film): a broad band at 3240 cm^{-1}, a carbonyl band at 1684 cm^{-1}, three strong sharp bands at 1155, 950, and 755 cm^{-1}. NMR (*c*, 0.7 M): a triplet at 6.88, 7.03, and 7.17 ppm, a quartet having fine structures at 7.53, 7.67, 7.80, and 7.94 ppm, and a singlet at 11.12 ppm.

Semicarbazone derivative melting at 185.3—188.8°C (from aqueous ethanol). Found: C, 43.60; H, 3.27; N, 16.88%. Calcd for $C_9H_8N_3O_2F_3$: C, 43.73, H, 3.26; N, 17.00%.

From the fraction which did not form a copper ketimine chelate, a small amount of a seemingly *p*-substituted isomeric compound was separated, which was recrystallized from benzene to give colorless needles melting at 105.5—106.0°C. Found: C, 50.48; H, 2.80%. IR (potassium bromide disc): a sharp peak at 3480 cm^{-1} a carbonyl band at 1687 cm^{-1}, and four strong sharp bands at 1160, 951, 855, and 766 cm^{-1}.

2-Hydroxy-3-methylacetophenone (VI).[8,9] It was obtained from *o*-cresyl acetate in a similar manner to that of the ligand II, with accompanied by the *p*-substituted isomer: bp 91.7—91.9°C/5 mmHg. Semicarbazone derivative: mp 240.8—42.6°C.[9] NMR: two singlets at 2.20 and 2.51 ppm (3 protons each), a triplet centered at 6.54 ppm splitted with 7 cps of *J*-value (one proton), two doublets having fine structures, centered at 7.1 and 7.4 ppm respectively, each of which is splitted with 7 cps of *J*-value (one proton each), and a singlet at 12.18 ppm (one proton).

Salicylaldehyde (IV). used here was a commercially available one.

2-Hydroxyactophenone (V) was synthesized from phenyl acetate in a standard procedure, boiling at 113.5—113.8°C/33 mmHg.

Synthesis of the Metal Chelates of Copper and of Nickel. Salicylaldimine chelates of copper and of nickel were synthesized as following. A bis(salicylaldehydato)metal chelate (the copper chelate; 0.50 g, the nickel chelate; 0.50 g), which was prepared according to Tyson and Adams,[10] was added into 10% aqueous ammonia (90 m*l* for the former chelate and 70 m*l* for the latter, respectively) and the resulting suspension was stirred at room temperature until the color of the precipitates was changed, which took about an hour. The precipitates, collected by filtration, was washed with methanol, dried and recrystallized from an appropriate solvent. (Yield; 0.50 g for the copper chelate, and 0.41 g for the nickel chelate, respectively). The ketimine chelates of copper and of nickel were synthesized in either of the following procedures.

(A) Into an aqueous alcoholic solution of an ammine metal complex, which was prepared from the aqueous solution of the corresponding metal ion and ammonia in alcohol, was added an alcoholic solution of two moles of an *o*-acylphenol, and the solution was left to stand for a required period of time. Resulting precipitates, collected by filtration, was washed with ammonia and alcohol successively, dried and recrystallized from an appropriate solvent.

(B) Into an aqueous solution of a metal acetate, two moles of an *o*-acylphenol was added, and then alcohol was added so that the mixture made just a homogeneous solution. An appropriate amount of 28% ammonia diluted with alcohol was added into the above solution, and it was left at room temperature until the metal ketimine chelates were precipitated. The resulting precipitates were treated in the similar way just as described above. The details of the amounts of the reagents, the yields and the properties of the chelates are tabulated in Tables 1, 2, 3, and 4.

Synthesis of the Beryllium Chelates. *Bis(2-hydroxy-3-methylacetophenonato)beryllium(II).* 2-Hydroxy-3-methylacetophenone (1.51 g) dissolved in methanol (5 m*l*) and 3% methanolic ammonia (8 m*l*) were added successively into a mixture of a 50% aqueous solution of beryllium nitrate (0.88 g) and methanol (10 m*l*).

The resulting mixture, after refluxed for several hours, was evaporated to dryness under reduced pressure. The residual solid was dissolved in chloroform, washed with water, and again solidified by evaporation of the solvent. The second solid was recrystallized from petroleum ether to give yellow grains (740 mg) melting at 163.9—65.6°C. Found: C, 70.32; H, 6.04%. Calcd for

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[10] G. N. Tyson, Jr., and S. C. Adams, *J. Am. Chem. Soc.*, **62**, 1228 (1940).

TABLE 1. CONDITIONS EMPLOYED TO SYNTHESIZE THE COPPER KETIMINE CHELATES AND THE RESULTS

Ligand	Procedure	Amounts of the reactants and solvents used					Yield (% yield)
		Metal acetate[a]	Ligand	Water	Ethanol	28% Ammonia	
I	B	1.00 g	2.06 g	20 ml	80 ml	20 ml	1.16 g (49%)
II	A	1.00	1.64	25	60	20	1.75 (90)
III	B	0.50	0.96	15	9	1	0.72 (33)
V	B	1.00	1.37	30	—	15	1.38 (83)
VI	A	1.00	1.50	25	70[b]	20	1.70 (94)

a) Copper acetate was in the form of a monohydrate.
b) Methanol was used in the place of ethanol.

TABLE 2. CONDITIONS EMPLOYED TO SYNTHESIZE THE NICKEL KETIMINE CHELATES AND THE RESULTS

Ligand	Procedure	Amounts of the reactants and solvents used					Yield (% yield)
		Metal acetate[a]	Ligand	Water	Ethanol	28% Ammonia	
I	A	1.25 g	2.06 g	—	35 ml	10 ml	0.82 g (35%)
II	A	1.24	1.64	20 ml	50	10	1.8 (94)
III	B	1.24	1.92	15	18	1.7	1.8 (83)
V	A	1.24	1.37	20	10[b]	10	1.25 (77)
VI	B	2.48	3.00	20	46	4	2.1 (59)

a) Nickel acetate is in the form of a dihydrate.
b) Methanol was used in the place of ethanol.

TABLE 3. APPEARANCE, MELTING POINTS AND ELEMENTAL ANALYSES OF THE COPPER KETIMINE CHELATES

Ligand	Appearance (Solvent used for recryst.)	Mp or (dp) °C	Molecular formula	Elemental analyses					
				Found			Calcd		
				C%	H%	N%	C%	H%	N%
I	G-l(E)[a]	167—170	$C_{26}H_{36}N_2O_2Cu$	66.21	7.79	5.87	66.14	7.69	5.93
II	DG-p(E)[a]	(253—255)	$C_{20}H_{24}N_2O_2Cu$	61.84	6.40	7.13	61.89	6.24	7.23
III	G-n(E)[a]	(260∼)	$C_{16}H_{10}N_2O_2F_6Cu$	43.48	2.54	6.28	43.70	2.29	6.37
IV	G-l(E)[a]	(160—170)	$C_{14}H_{12}N_2O_2Cu$	55.74	3.98	9.16	55.35	3.98	9.22
V	G-l(E)[a]	(270—280)	$C_{16}H_{16}N_2O_2Cu$	57.85	4.87	8.46	57.91	4.86	8.44
VI	DG-n(C)[a]	(270—274)	$C_{18}H_{20}N_2O_2Cu$	60.15	5.30	7.73	60.07	5.60	7.78

a) G, green; DG, dark green; l, leaflets; p, fine plates; n, needles; E, ethanol; C, chloroform

TABLE 4. APPEARANCE, MELTING POINTS AND ELEMENTAL ANALYSES OF THE NICKEL KETIMINE CHELATES

Ligand	Appearance (Solvent used for recryst.)	Mp or (dp) °C	Molecular formula	Elemental analyses					
				Found			Calcd		
				C%	H%	N%	C%	H%	N%
I	R-l(E)[a]	163—166	$C_{26}H_{36}N_2O_2Ni$	67.10	7.81	6.04	66.83	7.77	5.99
II	R-g(C)[a]	higher than 300	$C_{20}H_{24}N_2O_2Ni$	61.76	6.09	7.29	62.68	6.32	7.32
III	B-n(C)[a]	(270—280)	$C_{16}H_{10}N_2O_2F_6Ni$	44.12	2.44	6.76	44.18	2.32	6.44
IV	R-l(E)[a]	(280—300)	$C_{14}H_{12}N_2O_2Ni$	55.96	4.00	9.48	56.24	4.05	9.37
V	R-g(C)[a]	higher than 300	$C_{16}H_{16}N_2O_2Ni$	58.30	4.96	8.57	58.77	4.93	8.57
VI	R-g(C)[a]	higher than 300	$C_{18}H_{20}N_2O_2Ni$	61.03	5.42	7.94	60.91	5.64	7.89

a) R, red; B, brown; l, leaflets; g, grains; n, needles; E, ethanol; C, chloroform

$C_{18}H_{18}O_4Be$: C, 70.34; H, 5.90%.

Bis(2-hydroxy-3-isopropylisobutyrophenonato)beryllium(II). 2-Hydroxy-3-isopropylisobutyrophenone (1.05 g) and a 50% aqueous solution of beryllium nitrate (0.45 g) were treated in the same way just as described above to give yellow grains (250 mg) melting at 149.6—52.6°C. Found: C, 74.52; H, 8.24%. Calcd for $C_{26}H_{34}O_4Be$: C, 74.43; H, 8.24%.

Bis(2-hydroxyacetophenonato)beryllium(II). Into a mixture of a 50% aqueous solution of beryllium nitrate (1.3 g), 2-hydroxyacetophenone (2.05 g) and ethanol (5 m*l*) was added a mixture of 28% ammonia (1.2 m*l*) and ethanol (3.8 m*l*). The resulting solution was refluxed for a half an hour, and the solvents were removed as an azeotropic mixture with benzene. The residual solid was recrystallized from benzene, and from a mixture of petroleum ether and benzene successively, to give pale yellow grains (110 mg) melting at 173.1—74.3°C. Found: C, 68.43; H, 5.55%. Calcd for $C_{16}H_{14}O_4Be$: C, 68.81; H, 5.05%.

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