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Vacuum Sublimation Behavior of Iron(III), Cobalt(II), Nickel(II), Copper(II), and Palladium(II) Chelates with Tetradentate *N,N'*-Disalicylideneethylenediamine and *N,N'*-Bis(1-methyl-3-oxobutylidene)ethylenediamine

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Synopsis. A vacuum sublimation apparatus with a continuous temperature gradient (25—200 °C) along the tube (50—0 cm) at 2×10^{-2} Torr (1 Torr = 133.322 Pa) was used. *N,N'*-disalicylideneethylenediamine, *N,N'*-bis(1-methyl-3-oxobutylidene)ethylenediamine and its metal chelates (Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, and Pd^{II}) were sublimed without thermal decomposition, while the chelates of Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, and Pd^{II} with *N,N'*-disalicylideneethylenediamine were thermally stable, but did not sublime completely.

The vacuum sublimation method is useful for the purification and separation of metal chelates of 4-anilino-3-penten-2-one, 2,4-pentanedione, dithiocarbamates, 8-quinolinol and its derivatives, dimethylglyoxime, diphenylthiocarbazone, 1-(2-pyridylazo)-2-naphthol, 5,10,15,20-tetraphenylporphyrin, and 1,1,1-trifluoro-4-(2-thienyl)-4-mercapto-3-buten-2-one.[1—3] Of the metal chelates described above, bidentate shiff base chelates of β-imino ketones, such as 4-anilino-3-penten-2-one, were accompanied by remarkable thermal decompositions during the sublimation process; however, the sublimation-recrystallization temperatures of these chelates were found in the lower-temperature region of all the chelates studied. The present research aims to investigate the tetradentate ligands of *N,N'*-disalicylideneethylenediamine and *N,N'*-bis(1-methyl-3-oxobutylidene)ethylenediamine for the purification of metals in milligram amounts (as their chelates) by a vacuum sublimator with a continuous temperature gradient under low pressure. Some of these chelates in nanogram amounts have already been evaluated by gas chromatography, mainly for Cu^{II}, Ni^{II}, and Pd^{II}.[4]

Experimental

Materials. The shiff bases of *N,N'*-disalicylideneethylenediamine and *N,N'*-bis(1-methyl-3-oxobutylidene)ethylenediamine were easily prepared by the condensation of ethylenediamine with salicylaldehyde in ethanol or with 2,4-pentanedione (directly), as described previously.[5]

Metal chelate compounds with these ligands were generally prepared by the addition of an ethanolic solution of the corresponding chelating reagent to an aqueous ammonia solution of each metal salt at room temperature, or by heating if necessary. This has been previously mentioned.[5,6] These materials were purified by recrystallization from ethanol or by vacuum sublimation before use.

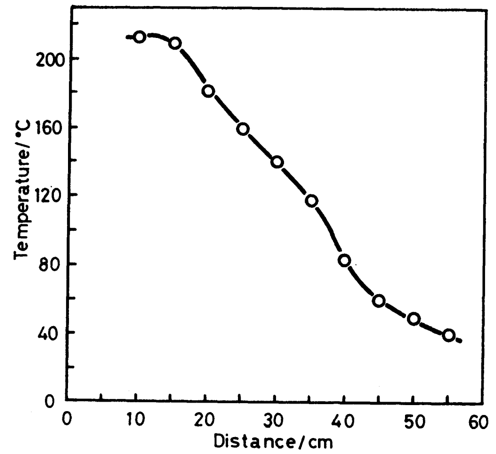


Fig. 1. Continuous temperature gradient along vacuum sublimator.

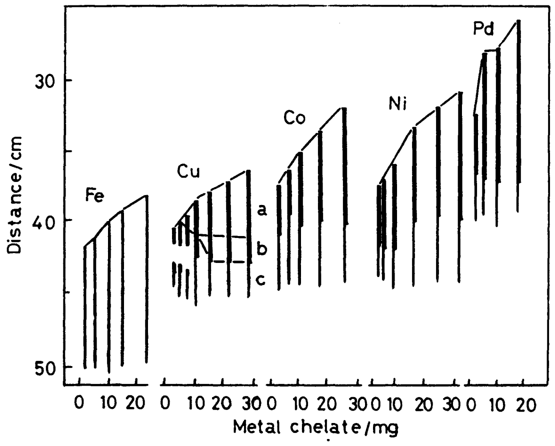


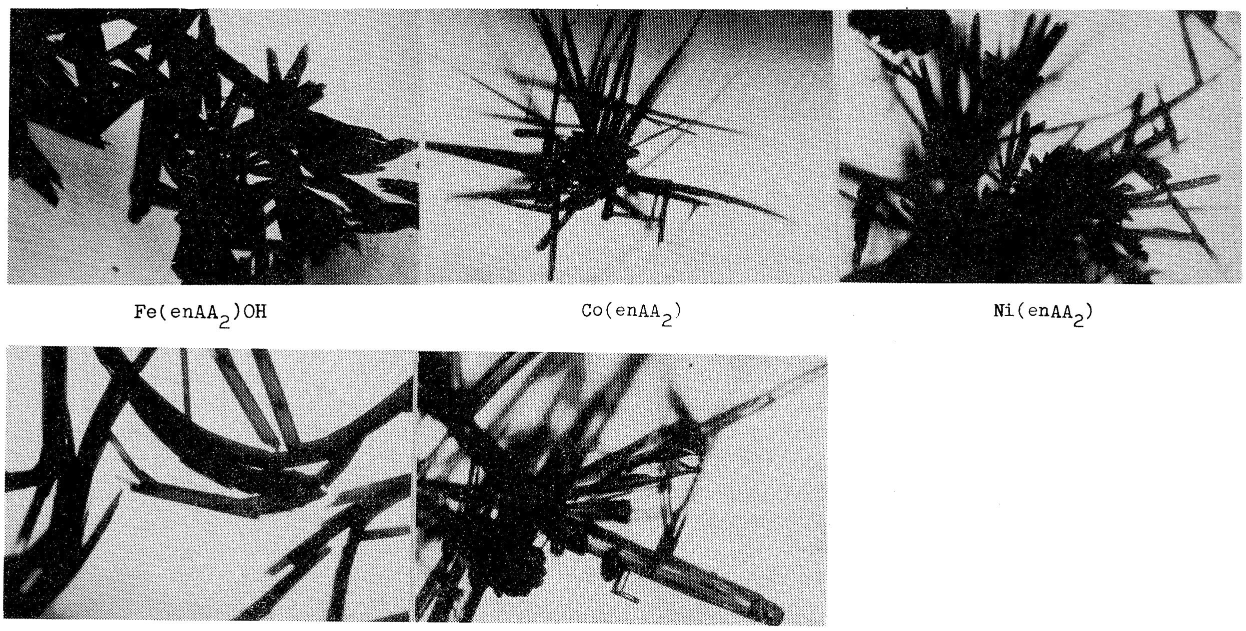
Fig. 2. Sublimation-recrystallization zone of metal chelate compounds of *N,N'*-bis(1-methyl-3-oxobutylidene) ethylenediamine in various quantities. Color of copper chelate: a green, b green and purple mixture, c purple.

Sublimation Procedure. A vacuum sublimation apparatus which provided a continuous temperature gradient (25—200 °C) along the tube (50—0 cm) at 2×10^{-2} Torr was used, as previously described.[1] The temperature gradient along the sublimator is shown in Fig. 1; this was obtained after thermal equilibrium for 4 h. These patterns were obtained by supplying the following electric power through the heating mantle, 16V, 8V, and 3V at 1.0A. Metal chelates were placed inside the apparatus for 5.5 h after establishing thermal equilibrium. The sublimate zone along the sublimation tube was decided from the color of the chelate and its deposition position. The thermal conditions of the sublimator were always checked from the sublimation zone of a definite amount of copper(II) acetylacetonate after sublimating it by another sublimation tube with the metal chelates to be investigated. The sublimation-recrystallization zone temperatures of copper(II) acetylacetonate (in 12-mg amounts) were 89—60 °C at 0.02 Torr, 120—66 °C at 0.1 Torr, and 162—158 °C at 7 Torr, respectively.

Table 1. Sublimation-Recrystallization Zone Temperatures, Amounts Remaining, and Colors of Various Metal Chelates with *N*,*N*′-Disalicylideneethylenediamine and *N*,*N*′-Bis(1-methyl-3-oxobutylidene)ethylenediamine after Sublimation at 2×10^{-2} Torr

Metal chelates	Recrystallization zone temperature/°C	Color	Chelate taken mg	Metal Compound remaining[a)]
N,*N*′-Disalicylidene-ethylenediamine	90—55	Yellow	6.8	None
Fe^{III}	About 200	Brown	3.4	Much
Co^{II}	171—160	Brown	1.8	Much
Ni^{II}	178—160	Dark red	10.9	Much
Cu^{II}	172—160	Grayish green	3.9	Much
Pd^{II}	171—158	Pale yellow	6.0	Much
N,*N*′-Bis(1-methyl-3-oxo-butylidene)ethylenediamine	105—60	White	7.0	None
Fe^{III}	83—46	Red	10.0	None
Co^{II}	118—60	Orange yellow	10.0	None
Ni^{II}	116—60	Dark red	10.0	None
Cu^{II}	94—78	Green	10.0	None
	78—58	Purple		
Pd^{II}	150—80	Yellow	10.0	None

a) None, 0—10%; much, >30%.



Fe(enAA$_2$)OH Co(enAA$_2$) Ni(enAA$_2$)

Cu(enAA$_2$) Pd(enAA$_2$)

Fig. 3. Microphotographs of metal chelates.
H_2 (en AA$_2$): *N*,*N*′-Bis(1-methyl-3-oxobutylidene)ethylenediamine.
Photograph: 40 times.

Results and Discussion

The temperature range of the deposited zones, the recovery, and the colors of the various metal chelates after sublimation are summarized in Table 1.

N,*N*′-Disalicylideneethylenediamine, and *N*,*N*′-bis(1-methyl-3-oxobutylidene)ethylenediamine and its metal chelates (Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, and Pd^{II}) were sublimed without any thermal decomposition, while the chelates of Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, and Pd^{II} with *N*,*N*′-disalicylideneethylenediamine were thermally stable, but did not sublime completely. This fact may have been caused by the rate of sublimation of the chelate compounds, which depends upon the temperature established at the high-temperature end of the sublimator. The sublimation-recrystallization temperature of individual chelates generally increased in the following order: Fe^{III}< Cu^{II}<Ni^{II}, Co^{II}<Pd^{II}. The sublimation-recrystallization zones for metal chelates of Fe^{III}, Cu^{II}, Co^{II}, Ni^{II}, and Pd^{II} with *N*,*N*′-bis(1-methyl-3-oxobutylidene)ethylenediamine in varying quantities are graphically presented in Fig. 2. In general, the sublimation-recrystallization distance gave shorter values with an increase in quantity of the chelates. In cases where the recrystallization-zone pattern was not uniform, the deposition zones (where over 90% of the chelates were

found) are indicated by a thicker lines.

Representative photomicrographs of metal chelates with *N,N′*-bis(1-methyl-3-oxobutylidene)ethylenediamine deposited on the glass wall inside the sublimation tube are given in Fig. 3. Metal chelates of Co^{II}, Ni^{II}, and Pd^{II} form stereoradial needle-like crystals, and Fe^{III} chelate forms hexahedral crystals. A copper chelate forms two kinds of crystals; a purple planar needle-like crystal at the lower-temperature side, and a green plate crystal at the higher-temperature side, when sublimating it in more than 5 mg amount. Both crystals are purple in their powder states. Therefore, it is clear that sublimation is useful for the purification of milligram amounts of each metal chelate since large-sized crystals can be obtained.

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