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Vacuum Sublimation Behavior of Nickel(II), Palladium(II), and Platinum(II) Chelates with Dimethylglyoxime

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Synopsis. A sublimation apparatus in perpendicular style with a continuous-temperature gradient (30—200 °C) along the glass tube (15—0cm) at 10^{-2} Torr (1 Torr=133.322 Pa) was used.

Dimethylglyoxime (DMG) and its chelates of nickel(II) and palladium(II) in milligram amounts were sublimed without any thermal decomposition, while platinum(II) chelate was accompanied by a remarkable thermal decomposition during the sublimation process. All metal chelates, $Ni(DMG)_2$ (brick-red), $Pd(DMG)_2$(yellow), and $Pt(DMG)_2$ (grayish violet), form needle-like crystals after purification with a sublimator under low pressure.

The vacuum sublimation method is useful for the purification of metal chelates.[1,2] After preliminary experiments on the vacuum-sublimation of chelates of iron(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), lead(II), palladium(II), and platinum(II) with dimethylglyoxime, only the chelates of nickel (II), palladium(II), and platinum(II) have been found to sublime by means of a sublimation apparatus in perpendicular style with a continuous temperature gradient (30—200 °C) along the tube (15—0 cm) at 10^{-2} Torr (1 Torr=133.322 Pa); their vacuum-sublimation behavior has been studied in detail with a continuous-temperature gradient under low pressure.

Experimental

Apparatus. The apparatus used were the same as those mentioned the previous report,[1] except for a model TBP_s Tokyo glass mantle heater; a model A-700 Takara thermistor; a model EPR-10B Toa Electric polyrecorder and a model PM-6 Olympus photomicrographic apparatus.

Materials. Dimethylglyoxime, purchased from the Kanto Chemical Co., was a guaranteed-grade material. Nickel and platinum dimethylglyoximates were prepared, as previously described.[2] Platinum dimethylglyoximate was prepared by the addition of 1% of an ethanolic solution of dimethylglyoxime to an aqueous solution containing excess $K_2[PtCl_4]$, adjusted to about pH 7 by adding each of 0.1—6 M (1 M=1 mol dm^{-3}) solutions of hydrochloric acid, ammonium acetate, and ammonia. After aging overnight the platinum(II) chelate on a water bath, the product was filtered off with a glass filter (1G4) under suction, followed by washing with hot distilled water, and finally dried in a desiccator under low pressure. These materials were purified by vacuum sublimation before use. The chelates of iron(II), cobalt(II), copper(II), zinc(II), cadmium(II), and lead(II), were soluble in an aqueous solutions. Then, the solutions having an excess of metals were evaporated off in air under low pressure by using an aspirator, and were used without further purification. The colors of the chelates were brick-red for iron(II), and nickel (II) chelates, yellow for palladium(II) chelate, grayish violet for platinum(II) chelate, brown for cobalt(II) and copper(II) chelates, and white for the chelates of zinc(II), cadmium(II), and lead(II). The sublimation behavior was ascertained by dissolving the sublimates in chloroform by means of an ordinary spectrophotometry.[2-4]

Sublimation Procedure. A sublimaltion apparatus in perpendicular style which provided a continuous temperature gradient (30—200 °C) along the tube (15—0 cm) at 10^{-2}

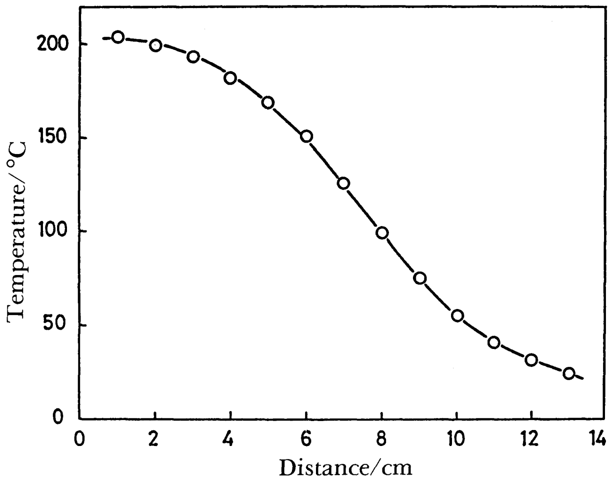


Fig. 1. Continuous temperature gradient along vacuum sublimator.

Table 1. Sublimation-Recrystallization-Zone Temperatures, Amounts Remaining, and Colors of Dimethylglyoxime (DMG) and its Chelates of Nickel(II), Palladium(II), and Platinum(II) after Sublimation at 10^{-2} Torr

Metal chelates	Recrystallization-zone temperature °C	Color	Chelate taken mg	Metal compound remaining[a]
DMG	42—25	White	10.7	None
$Ni(DMG)_2$	135—50	Red	3.0	None
$Pd(DMG)_2$	145—50	Yellow	3.9	None
$Pt(DMG)_2$	150—60	Grayish violet	4.4	Much

a) None, 0—10%; a little, 10—30%; much, >30%. Chelates of iron(II), cobalt(II), copper(II), zinc(II), cadmium(II), and lead(II) with dimethylglyoxime (DMG) did not sublime.

Torr was used. The temperature gradient along the sublimator, which consists of a Pyrex glass tube (1.7 cm in outer diameter; 15 cm in length) covered with a heating mantle, is shown in Fig. 1; it was obtained after the thermal equilibrium had been kept for 1.5 h. This pattern was obtained by supplying an electric power of 40 V at 0.2 A through the heating mantle. A small glass sample-tube (Pyrex glass test-tube, 0.8 cm in inner diameter; 4 cm in length) containing an individual chelate (0—5 mg) and an attached long glass tube (0.6 cm in outer diameter; 10 cm in length), wrapped tightly with Teflon tape, were inserted into the higher-temperature end of the sublimator. Metal chelates were placed inside of the apparatus for 1 h after thermal equilibrium was established. The sublimate zone along the sublimation tube was determined from the color of the chelate and its 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 using another sublimation tube along with the metal chelates to be investigated. The sublimation-recrystallization temperatures of copper(II) acetylacetonate (in 5—10 mg amounts) were about 70—42 °C at 10^{-2} Torr, 88—45 °C at 1 Torr, and 135—60 °C at 10 Torr (bluish rectangular crystal).

Results and Discussion

The temperature range of the deposited zones, the recovery, and the colors of the chelates of nickel(II), palladium(II), and platinum(II) after sublimation at 10^{-2} Torr are summarized in Table 1. Dimethylglyoxime (DMG) and its chelates of nickel(II) and palladium(II) were sublimed without any thermal decomposition as has previously been observed with another vacuum sublimator,[2] while platinum(II) chelate was accompanied by remarkable thermal decomposition. The chelates of iron(II), cobalt(II), copper (II), zinc(II), cadmium(II), and lead(II), did not sublime at all. The sublimation-recrystallization zones for DMG, $Ni(DMG)_2$, $Pd(DMG)_2$, and $Pt(DMG)_2$ in milligram amounts (3.0—10.7 mg) at 10^{-2} Torr are graphically presented in Fig. 2. In cases where the recrystallization-zone pattern was not uniform, the deposition zones (where more than 90% of the materials were found) are indicated by thicker lines. No substantial difference in recrystallization-zone temperatures among three metal chelates was observed. However, these metal chelates can be separated completely from an uncombined DMG, and the highly sensitive spectrophotometry of nickel (II) as $Ni(DMG)_2$ without interference by DMG is possible

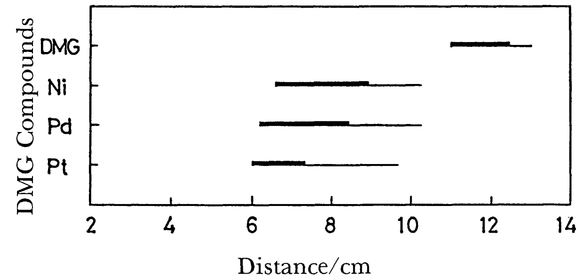
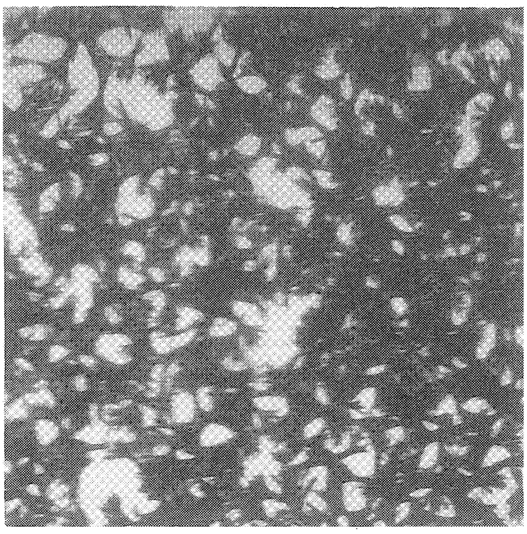
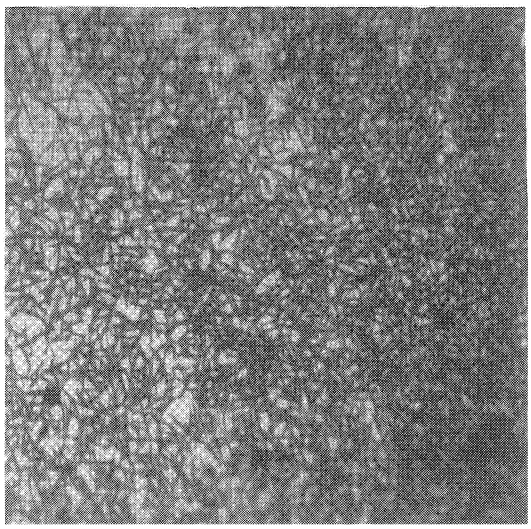


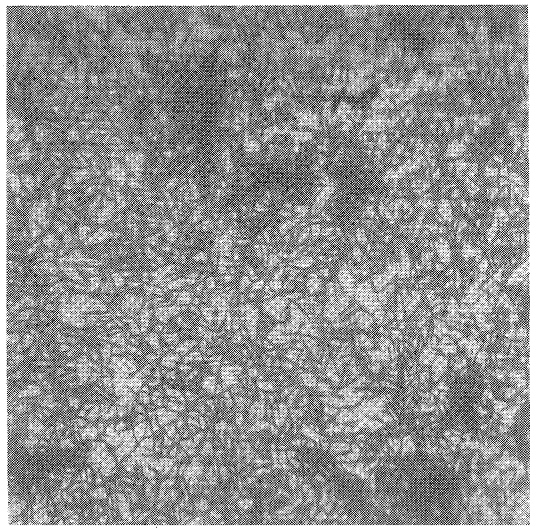
Fig. 2. Sublimation recrystallization zone of dimethylglyoxime and its metal chelates of nickel(II), palladium(II), and platinum(II).



$Ni(DMG)_2$



$Pd(DMG)_2$



$Pt(DMG)_2$

Fig. 3. Microphotographs of metal chelates. DMG: dimethylglyoxime, Magnification: ×40.

by means of solvent extraction and vacuum sublimation;[4,5] the maximum wavelength of $Ni(DMG)_2$ in chloroform being 262 nm (ε=23,500 $cm^2 l mol^{-1}$). The sensitivity is about 7-times that obtained by an ordinary method,[4] in which the absorptivity is 3,200 at 370 nm owing to the higher reagent blank. By using this method, nickel(II) can be completely separated from copper(II) and cobalt(II) coextracted in chloroform.

Representative photographs of $Ni(DMG)_2$, $Pd(DMG)_2$, and $Pt(DMG)_2$ deposited on the glass wall inside the sublimation tube are given in Fig. 3. All of the metal chelates were purified as needle-like crystals after vacuum sublimation by means of the present experimental apparatus.

References

1) T. Honjo and S. Kawasaki, *Bull. Chem. Soc. Jpn.*, **61**, 2247 (1988).

2) T. Honjo, H. Imura, S. Shima, and T. Kiba, *Anal. Chem.*, **50**, 1545 (1978).

3) G. Basu, G. M. Cook, and R. L. Belford, *Inorg. Chem.*, **3**, 1361 (1964).

4) Y. Hirano, "Inorganic Applied Spectrophotometry," Kyoritsu Shuppan, Tokyo (1975).

5) E. Shirakawa, T. Honjo, and K. Terada, *Fresenius Z. Anal. Chem.*, **334**, 37 (1989).