Chem. Pharm. Bull. 27(4)1045—1048(1979)

UDC 541.49.08 : 543.544.2.06

Behavior of Copper and Nickel Chelates of β-Ketoimines and Related Compounds in Electron Capturing Detector-Gas Chromatography(ECD-GC)

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(Received November 11, 1978)

The behavior of copper and nickel chelates of β-ketoimines and the related 3-bromo-β-diketone were investigated by electron capturing detector–gas chromatography (ECD–GC). The chelate, bis(4-imino-2-pentanono)-nickel (II) gave the most sharp gas chromatogram among the chelates examined. The β-ketoimine chelates showed to be less sensitive towards ECD–GC than the chelates of the original β-diketone and the related 3-bromo-β-diketone.

Approximate values of detection limits for metals were also obtained by ECD–GC on some of the copper and nickel chelates here examined.

Keywords——metal chelate; β-ketoimine; gas chromatography; electron capturing detector; detection limit

In recent developments of gas chromatography of metal chelates, an attempt has been reported on the gas chromatographic separation of copper and nickel chelates of some β-ketoimines.[2] Further studies on this subject have revealed that two types of β-ketoamine or β-ketoimine compounds are suitable to be used as ligands to complex with metal ions; a) a compound derived from condensation of one molecule of amine with one molecule of β-diketone and b) a compound derived from condensation of one molecule of diamine with two molecules of β-diketone.

In the type a) compounds, there are 4-aminopent-3-en-2-one[2,3] (AP) and 4-amino-1,1,1-trifluoro-3-en-2-one[4] (ATFP), while bisacetyl-acetone-1,2-propylenediimine (AAPD) and its homologues[4–6] and bistrifluoroacetylacetone-ethylenediimine (TFAED or enTFA$_2$) and its derivatives[3,4,6,7] are reported as the type b) compounds. These β-ketoamino or β-ketoimino compounds are known to have more strong affinities to metal ions such as copper (II), nickel (II), palladium (II) and platinum (II) than the original β-diketones, and the metal chelates are found to show definite and sharp gas chromatograms.

This report deals with examination of behavior of some β-ketoimine chelates previously mentioned[2] and of the related 3-bromo-β-diketone chelates on ECD–GC which have not yet been described in recent investigations.

Experimental

Materials——The metal chelates used in this study were synthesized by analogous methods reported in the literatures.[8–12] However, the chelates III and V were synthesized as follows.

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Bis(3-bromo-4-imino-2-pentanono)-copper (II) III——1.30 g of I was added to 75 ml of CCl_4 and the mixture was stirred for 30 min at room temperature. To the solution, was added 1.78 g of pulverized N-bromosuccinimide and the mixture was kept for 30 min at room temperature. The solution was filtered and the filtrate was evaporated under reduced pressure to remove the solvent. The residue was dried *in vacuo* and recrystallization of the residue from benzene–hexane (2:1) gave 1.01 g (48.4%) of crystals.

Bis(4-methylamino-3-penten-2-onato)-copper (II) V——This chelate was prepared by the modification of the method of Everett.[11] 1.95 g of potassium metal was dissolved in 150 ml of *t*-BuOH which was dried absolutely with sodium metal, and the solution was heated to 80°. To this solution 5.65 g of freshly prepared 4-methylamino-3-penten-2-one[8] was added and the mixture was kept at 50° under stirring for 10 min. To the mixture 18.0 g of $[(C_2H_5)_4N]_2[CuBr_4]$ was added and the whole mixture was vigorously stirred for 3 hr at room temperature. The mixture was evaporated to remove the solvent under reduced pressure by trapping it with a dry ice–acetone cooled trap. The residue was extracted with 200 ml of *n*-hexane and the hexane extract was filtered with a glass filter G3. The filtrate was evaporated under reduced pressure to give a solid and the solid was desiccated over $CaCl_2$ for a night. Recrystallization of the solid from dry *n*-hexane gave 3.84 g (53.4%) of crystals.

The melting points and elemental analyses of the synthesized chelates are listed in Table I. Bis(2,4-pentanedionato)-copper (II) VIII was purchased from Dojindo Co., Ltd., Research Laboratories, and was used without further purification.

Reagents——All reagents used in this study were analytical reagent-grade ones, and 2,4-pentanedione used to prepare β-ketoimines was distilled to collect a fraction of bp 137°—140° before use. Twice-distilled water was used to make metal solutions.

Apparatus——Melting points were measured on a Yanagimoto Micro Melting Point Apparatus and were uncorrected. A Shimadzu Gas Chromatograph Model GC 3 BE (Shimadzu Co., Ltd.) equipped with an electron capturing detector (^{63}Ni, 15 mc) was used. The column was 3 mm (i.d.) × 1 m glass tubing packed with 1% SE-52 on Gas Chrom Z (60—80 mesh). A 0.5—2 μl of the chelate solution (0.02—0.5% in benzene) was injected into the gas chromatograph.

Table I. Metal Chelates used in ECD–GC

No.	Metal chelate	mp (°C)	Formula	Analysis (%) Calcd. (Found) C	H	N
I	Bis(4-imino-2-pentanono)-copper(II)	196—197	$C_{10}H_{16}CuN_2O_2$	46.23 (46.33	6.21 6.20	10.78 10.89)
II	Bis(4-imino-2-pentanono)-nickel(II)	248—248.5 (dec.)	$C_{10}H_{16}N_2NiO_2$	47.11 (46.98	6.33 6.24	10.99 10.98)
III	Bis(3-bromo-4-imino-2-pentanono)-copper(II)	141—142 (dec.)	$C_{10}H_{14}Br_2CuN_2O_2$	28.76 (29.06	3.38 3.45	6.71 6.72)
IV	Bis(3-bromo-2,4-pentane–dionato)-copper(II)	216—217 (dec.)	$C_{10}H_{14}Br_2CuO_4$	28.62 (28.72	2.88 2.85)	
V	Bis(4-methylamino-3-penten-2-onato)-copper(II)	92— 93.5	$C_{12}H_{20}CuN_2O_2$	50.07 (50.14	7.00 7.25	9.73 9.66)
VI	Bis(4-methylamino-3-penten-2-onato)-nickel(II)	122—123 (dec.)	$C_{12}H_{20}N_2NiO_2$	50.93 (50.65	7.12 7.37	9.90 9.84)
VII	Bis(N-methylsalicylaldimine)-copper(II)	158—158.5 (dec.)	$C_{16}H_{16}CuN_2O_2$	57.91 (57.68	4.86 4.68	8.44 8.57)

Results and Discussion

Gas Chromatograms, Detection Limits, and Sensitivities of the Metal-Chelates in ECD-GC

Gas chromatograms of some of the metal chelates of β-ketoimines and the related 3-bromo-β-diketones are shown in Fig. 1. Among the metal chelates examined, some of them (I, II, IV, V, and VIII) showed definite gas chromatograms enough to use identification or detection, but the others (III, VI, and VII) did not show sharp peaks at the working conditions. The

11) G.W. Everett and R.H. Holm, *J. Am. Chem. Soc.*, 87, 2117 (1965).

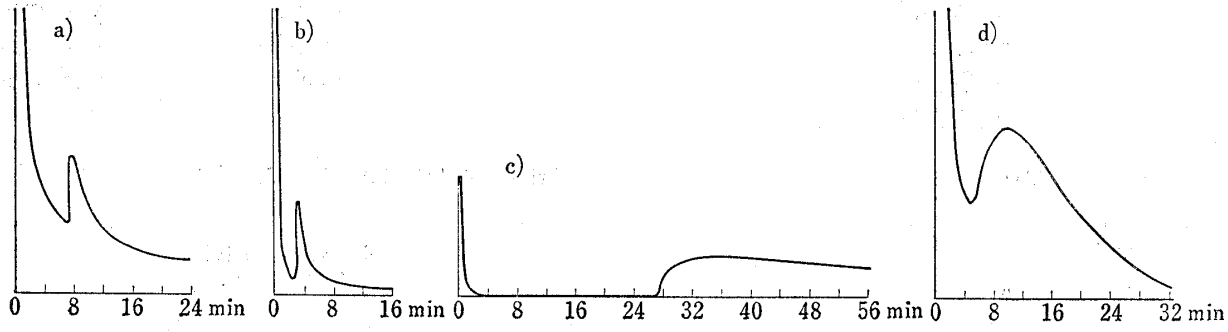


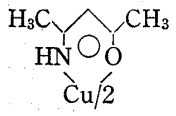
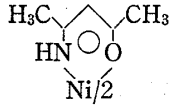
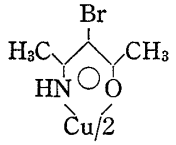
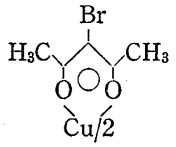
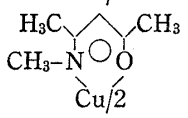
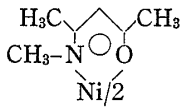
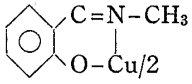
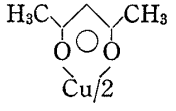
Fig. 1. Gas Chromatograms of Metal Chelates by ECD–GC

Experimental conditions are given in Table II.
a) I, *b*) II, *c*) III, *d*) IV.

copper chelates seemed to be partially decomposed, while the nickel chelate II was hardly decomposed during the ECD-GC procedure.

Therefore, the nickel chelate II showed the most sharp gas chromatogram and its behavior was similar to that of II in thermoconductivity detector–gas chromatography (TCD–GC) as reported previously.

Table II. Metal Chelates and Their Detection Limits in ECD–GC

Metal chelate No.	Structure	Detection limit as a metal (g)	Temperature (°C) Column	Temperature (°C) Injection	Carrier N_2 (ml/min)
I		1.3×10^{-8} —2.2×10^{-8}	150	170	40
II		2.4×10^{-10}—4.8×10^{-10}	160	185	50
III		*a*)	100	120	100
IV		7.8×10^{-10}—7.8×10^{-9}	150	170	40
V		1.1×10^{-8} —5.5×10^{-8}	90	100	50
VI		*a*)	105	120	50
VII		*a*)	150	178	75
VIII		7.3×10^{-10}—3.6×10^{-9}	150	170	40

a) A definite value was not obtained at the experimental conditions.

As for the detection limits of the metal chelates in ECD–GC, there have been very scarce studies on the sensitivities of β-ketoimine and the related 3-bromo-β-diketone metal chelates in ECD–GC. The detection limits and comparison of sensitivities of the metal chelates in ECD–GC are given in Tables II and III.

Table III. Comparison of Sensitivities of the Metal Chelates in ECD–GC

Chelate A	Chelate B	Relative sensitivity A/B (mean)
I	II	54—46 (50)
I	IV	17— 3 (10)
I	V	1— 0.4 (0.8)
I	VIII	18— 6 (12)
IV	VIII	2— 1 (1.5)

As are seen in Table II, the copper chelate I was found to be less sensitive than VIII, the original β-diketone chelate. The nickel chelate II was most sensitive to ECD–GC among the chelates examined and the detection limit for II was about one-fiftieth of that of I. The chelate III had a broad tailing in its gas chromatogram, and could not give a definite detection limit. Comparing the ECD–GC behavior of IV with VIII, it was proved that both of the chelates had almost the same sensitivites in this experiment. The chelate V had almost a similar limit value to that of I in detecting them by ECD–GC. The chelate VII did not show a sharp gas chromatogram, while V decreased its sensitivity for detection. From the results obtained, it might be deduced that the introduction of bromine atom at C_3 position of β-ketoimine molecule does not seem to enhance its sensitivity towards ECD–GC. Similar observations have been reported recently by Tanikawa on the gas chromatography of metal chelates,[13] and the sensitivities of the metal chelates of β-diketones are found generally to be not depended on the properties of the ligands, but did mainly on the species of the central metals involved in the metal chelates.

Acknowledgement The authors thank to Mr. S. Nagai of Hokuriku University for his advices and to Mr. Y. Itatani and Miss. Y. Arano of this Faculty for elemental analyses.

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