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HIGH-SPEED LIQUID CHROMATOGRAPHY OF METAL COMPLEXES*

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The chromatographic separations of several kinds of cobalt(III) and platinum(II) complexes were carried out by high-speed liquid chromatography. Among the geometric isomers of each complex, isomers of higher symmetry were more rapidly eluted. This method was applied to the analysis of reaction mixtures of *cis*- and *trans*-$[CoCl_2(en)_2]Cl$ in methanol and the first-order rate constant of isomerization was determined.

High-speed liquid chromatography has been rapidly developed in recent few years and extensively used in organic and biochemical researches. This chromatography is characterized by the rapid separation and the very high column efficiency. It has an advantage over gas chromatography in being applicable to non-volatile compounds. These advantages will make it possible to detect or isolate short-lived species in reacting solutions and equilibrium mixtures. Unfortunately, high-speed liquid chromatography has been little applied to inorganic compounds including metal complexes.

In the present study this chromatographic method has been successfully applied to the separations of geometric isomers of cobalt(III) complexes and organometallic platinum(II) compounds.

Measurements were carried out with a JASCO Model FLC-350 chromatographic instrument using a UV-254 spectrophotometric detector. A 500 mm × 2.3 mm column was used for all measurements.

(I) Separation of geometric isomers of several cobalt(III) complexes

Chromatographic separations were carried out with a JASCOREX CV-01(strongly acidic type) and a JASCOREX AV-02(strongly basic type) column on some series of geometric isomers of singly charged cobalt(III) complexes. The cationic and anionic complexes were eluted with a 0.02 M and a 0.002 M NaCl aqueous solution, respectively, at a flow rate of 1.0 ml/min(pressure: *ca.* 25 kg/cm^2).

Some typical elution curves of dianionotetraammine-type complexes are shown in Fig. 1, where $[Co(edta)]^-$ and *trans*-$[Co(NO_2)_2(en)_2]^+$ were used as markers determining nonsorbed times(t_0) for cationic and anionic complexes, respectively. Retention times of the complexes were measured from elution curves and their ratios to nonsorbed times are summarized in Table 1.

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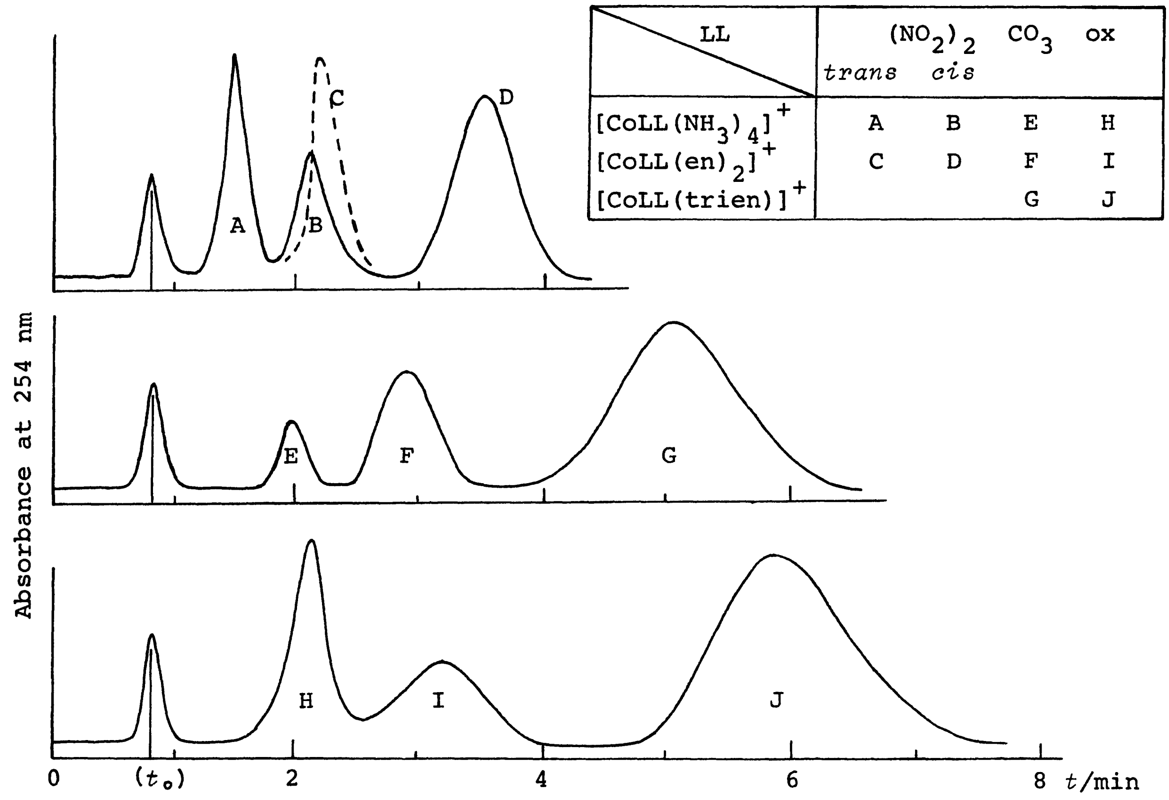

LL	$(NO_2)_2$ *trans*	$(NO_2)_2$ *cis*	CO_3	ox
$[CoLL(NH_3)_4]^+$	A	B	E	H
$[CoLL(en)_2]^+$	C	D	F	I
$[CoLL(trien)]^+$			G	J

Fig. 1. Elution curves of dianionotetraammine-type cobalt(III) complexes.

Table 1. Retention times of singly charged cobalt(III) complexes

Complexes		t/t_0	Complexes		t/t_0
$[Co(NO_2)_2(NH_3)_4]^+$	*trans*	1.6	$[Co(CO_3)(NH_3)_4]^+$	*(cis)*	2.4
$[Co(NO_2)_2(NH_3)_4]^+$	*cis*	2.4	$[Co(CO_3)(en)_2]^+$	*(cis)*	3.5
$[Co(NO_2)_2(en)_2]^+$	*trans*	2.8	$[Co(CO_3)(trien)]^+$	*cis*-α	5.6
$[Co(NO_2)_2(en)_2]^+$	*cis*	4.0	$[Co(CO_3)(trien)]^+$	*cis*-β	6.0
$[Co(NO_2)_2(trien)]^+$	*trans*†	5.1			
$[Co(NO_2)_2(trien)]^+$	*cis*-α	7.2	$[Co(ida)(dien)]^+$	*mer*	2.9
$[Co(NO_2)_2(trien)]^+$	*cis*-β	7.8	$[Co(ida)(dien)]^+$	*s-fac*	4.7
$[Co(ox)(NH_3)_4]^+$	*(cis)*	2.6	$[Co(ida)(dien)]^+$	*u-fac*	4.9
$[Co(ox)(en)_2]^+$	*(cis)*	3.8			
$[Co(ox)(trien)]^+$	*cis*-α	6.2	† See the text.		
$[Co(ox)(trien)]^+$	*cis*-β	7.0			
$[Co(ox)_2(NH_3)_2]^-$	*cis*	2.2	$[Co(edta)]^-$		3.6
$[Co(ox)_2(en)]^-$	*(cis)*	2.4	$[Co(ida)_2]^-$	*trans*	2.1
$[Co(CO_3)_2(NH_3)_2]^-$	*cis*	1.6	$[Co(ida)_2]^-$	*cis*	3.2
$[Co(CO_3)_2(en)]^-$	*(cis)*	1.6			

The results give the following elution orders of the complexes.

1) *trans* complex ⟶ *cis* complex
2) tetraammine complex ⟶ bis(en) complex ⟶ trien complex
3) carbonato complex ⟶ oxalato complex ⟶ dinitro complex
4) *cis*-α complex ⟶ *cis*-β complex (for trien complexes)
5) *mer* complex ⟶ *s-fac* complex ⟶ *u-fac* complex (for $[Co(ida)(dien)]^+$)

It is seen that the complex with charge distribution of higher symmetry is eluted more rapidly. The newly found isomer ($t/t_0 = 5.1$) of $[Co(NO_2)_2(trien)]^+$ listed in Table 1 was assigned to *trans* isomer on the basis of the elution order. Each order is consistent with the results obtained from the ordinary liquid chromatography.[1),2)] The high-speed liquid chromatographic method has great advantages of short elution time and micro quantities of samples.

The extention of this method to multivalent complex ions is now in progress.

(II) Application to kinetic studies

As an example of application of this method to kinetic studies, the rate of isomerization of *cis*-$[CoCl_2(en)_2]^+$ in methanol was measured. The experiment was made at 35 °C with a solution of the *cis* complex of the initial concentration of 0.002 M. For the chromatographic separation, a Pellidon(pellicular-type polyamide) column was prepared and a 0.03 M NaCl methanol solution was used as the eluent at a flow rate of 1.5 ml/min (pressure: *ca.* 12 kg/cm^2). After dissolving the *cis* complex in methanol, portions of the reacting solution were withdrawn at timed intervals and then chromatographed.

Fig. 2 shows the elution curve measured 20 minutes after initiating the reaction. The peak area for each complex is proportional to the absorption coefficient times concentration of each complex in the reacting solution. The notations, S_{trans} and S_{cis}, are used to designate peak areas for the *trans* and *cis* complexes, respectively, and α the *trans*-to-*cis* ratio in the absorption coefficient at 254 nm.

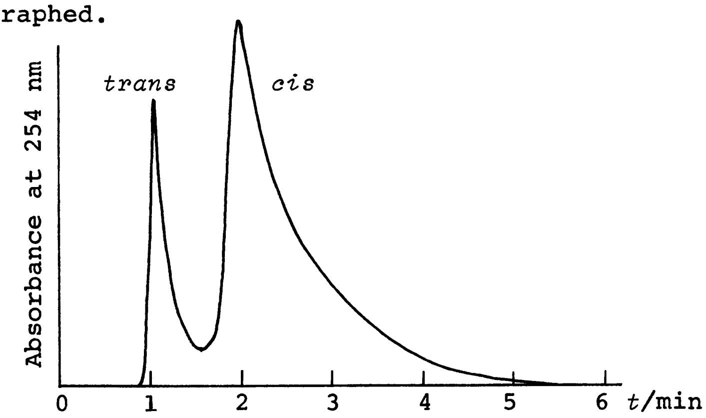

Fig. 2. Typical elution curve of the reaction mixture.

The reaction is known to be of the first order and the rate is represented by the equation

$$-\frac{dC_{cis}}{dt} = k\,C_{cis} \qquad \text{or} \qquad k\,t = -2.303 \log \frac{C_{cis}}{C^{\circ}_{cis}} \qquad (1)$$

where C_{cis} and C°_{cis} are concentrations of the *cis* complex at time t and zero, respectively, and k the first-order rate constant. By using the values of S_{trans} and αS_{cis}, Eq. (1) is rewritten as

$$k\,t = -2.303 \log \frac{\alpha S_{cis}}{S_{trans} + \alpha S_{cis}} \qquad (2)$$

On plotting the right-hand side of Eq. (2) *vs.* t, the experimental data showed a linear relationship. The value of k obtained from the slope, $5 \times 10^{-3}\ \mathrm{min}^{-1}$, is in agreement with the result of Tobe *et al.*3)

This method will be effective for the analysis of multicomponent reaction systems with half-lives of a few hours.

(III) Separation of geometric isomers of organometallic compounds

Newly prepared *cis*- and *trans*-$[PtY(CH_2CN)(PPh_3)_2]$ (Y = Cl, NCO, N_3, NO_2)4) with known configurations were chromatographically investigated. A JASCOGEL (pellicular-type silica gel) column was prepared, and chloroform was used as the eluent at a flow rate of 1.0 ml/min(pressure: *ca.* 10 kg/cm^2). Fig. 3 shows the elution curve of the mixture of geometric isomers of $[Pt(NCO)(CH_2CN)(PPh_3)_2]$. Each peak was identified by separate chromatographing.

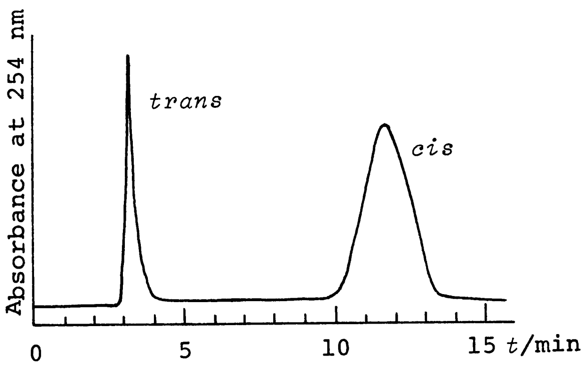

Fig.3. Elution curve of the mixture of *cis*- and *trans*-$[Pt(NCO)(CH_2CN)(PPh_3)_2]$.

Table 2. Retention times of *cis*- and *trans*-$[PtY(CH_2CN)(PPh_3)_2]$

Y	*trans* (min)	*cis* (min)
NCO	3.3	11.5
N_3	2.7	7.0
NO_2	2.7	5.6
Cl	2.4	(2.4)

Table 2 lists the retention times of the compounds. It was confirmed that the *trans* isomer is eluted faster than the *cis* isomer —— the same result as that for the cobalt(III) complexes. An apparent exception is the result for $[PtCl(CH_2CN)(PPh_3)_2]$ isomers. The retention time obtained for the *cis* isomer(2.4 min) would possibly be attributed to the *trans* isomer produced on the adsorbent, since the *cis* isomer easily isomerizes, for example, by refluxing in benzene solution.

From this experiment of the platinum(II) complexes, it appears possible to separate geometric isomers of other organometallic compounds by high-speed liquid chromatography.

REFERENCES

1) M. Mori, M. Shibata, and M. Nanasawa, *Bull. Chem. Soc. Japan*, 29, 947 (1956).
2) J.I. Legg and D.W. Cooke, *Inorg. Chem.*, 5, 594 (1966).
3) B. Bosnich, C.K. Ingold, and M.L. Tobe, *J. Chem. Soc.*, 1965, 4074.
4) K. Suzuki and M. Sakurai, unpublished result. The compounds used were kindly supplied by them.

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