

CHROM. 12,961

## Note

### Resolution of neutral complexes of transition metals by stereoselective adsorption on optically active complexes

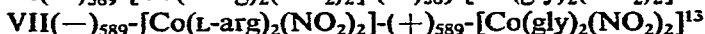
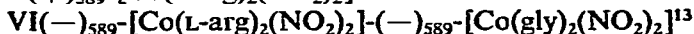
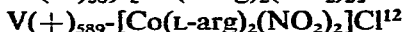
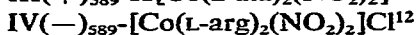
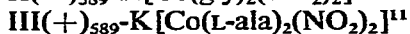
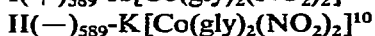
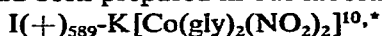
#### I. Partial resolution of tris(acetylacetonato)cobalt(III) and tris(acetylacetonato)chromium(III) on cobalt(III) complexes

M. B. ČELAP\*, I. M. HODŽIĆ and T. J. JANJIĆ

*Institute of Chemistry, Faculty of Sciences, University of Beograd, P.O. Box 550, 11001 Beograd (Yugoslavia)*

(First received March 18th, 1980; revised manuscript received May 22nd, 1980)

A large number of papers have described the chromatographic resolution of metal complexes into enantiomers<sup>1,2</sup>. However, only a few of them refer to the resolution of neutral complexes by stereoselective adsorption on dissymmetric adsorbents such as quartz<sup>3</sup>, sodium chlorate<sup>4</sup>, lactose<sup>5,6</sup>, alumina treated with (+)-tartaric acid<sup>7</sup>, D-sorbitol and D-manitol<sup>8</sup> and starch<sup>9</sup>. None of the studies employed an optically active complex of a transition metal as adsorbent. Hence we have investigated the resolution of neutral complexes using seven optically active cobalt(III) complexes that had been prepared in our laboratories for the first time, *i.e.*:



All these complexes represent very stable *cis*(NO<sub>2</sub>)-*trans*(N) geometrical isomers which suffer neither physical nor chemical changes in the course of time. The neutral complexes investigated were tris(acetylacetonato)cobalt(III) and tris(acetylacetonato)chromium(III), which had been prepared according to known procedures<sup>14,15</sup>. These complexes were chosen because they are soluble in benzene, whereas the compounds used for their resolution are insoluble.

The procedure involved the dissolution of 0.20 g of the neutral complex in 5 cm<sup>3</sup> of benzene. The resulting solution was passed through a column of diameter 1 cm and adsorbent height 60 cm, the adsorbent grain size ranging from 50 to 100 mesh. The complex was first adsorbed to the column and then eluted with benzene. Fractions of 15 drops were collected and then diluted up to 3 cm<sup>3</sup> with benzene. The concentration of solutions coming off the column was determined spectrophotometri-

\* glytt = Glycine; alat = alanine; arg = arginine.

cally at a wavelength of 577 nm, using a Beckman DU-2 spectrophotometer. Optical rotation of solutions was measured by means of a Perkin-Elmer 141-MC polarimeter at a wavelength of 546 nm.

## RESULTS AND DISCUSSION

From the results given in Table I it may be seen that a partial resolution of the two neutral complexes has been achieved in all the cases investigated.

TABLE I  
MAXIMAL VALUES OF APPARENT MOLECULAR ROTATIONS

Adsorbent	Experi- ment	$M_{546}$ (degrees)			
		$Co(C_5H_7O_2)_3$		$Cr(C_5H_7O_2)_3$	
I	1	+ 179.9	- 420.4	- 48.6	+ 66.8
	2	+ 188.3	- 356.0	- 55.6	+ 71.8
II	1	- 136.0	+ 379.9	+ 50.4	- 61.6
	2	- 172.4	+ 369.9	+ 52.4	- 58.2
III	1	+ 219.3	- 291.2	- 54.1	+ 58.9
	2	+ 228.2	- 275.2	- 58.2	+ 55.3
IV	1	- 346.6	+ 295.4	+ 71.2	- 72.6
	2	- 306.0	+ 302.6	+ 68.7	- 79.2
V	1	- 226.4	+ 358.8	+ 69.8	- 52.5
	2	- 209.3	+ 335.7	+ 65.4	- 53.4
VI	1	+ 278.3	- 548.7	- 64.5	+ 50.8
	2	+ 283.8	- 559.7	- 66.3	+ 40.2
VII	1	+ 284.1	- 169.9	- 55.3	+ 51.4
	2	+ 280.2	- 159.6	- 52.8	+ 48.7

The maximal values of the apparent molecular rotations obtained in the resolution of tris(acetylacetonato)cobalt(III) were higher than those obtained with tris(acetylacetonato)chromium(III), using the same adsorbent. This may be due either to a higher actual molecular rotation of the cobalt(III) complex or to its more complete resolution. However, since the same phenomenon was observed with other adsorbents<sup>5,6</sup>, the most likely explanation is a higher molecular rotation of the cobalt(III) complex relative to that of the chromium(III) complex.

It may also be seen (Table I) that the two complexes exhibit opposite elution sequences of the optically active isomers, using the same adsorbent. Fig. 1 shows that the first fractions coming off the column exhibit the greatest values of the apparent molecular rotation, which gradually decreases. Middle fractions are inactive, and they are followed by fractions with increasing molecular rotation of opposite sign to that of the first fractions.

Thus in the course of these experiments, only a partial resolution of the tris(acetylacetonato) complexes of cobalt(III) and chromium(III), has been achieved. A similar partial resolution of these complexes has also been effected by the use of

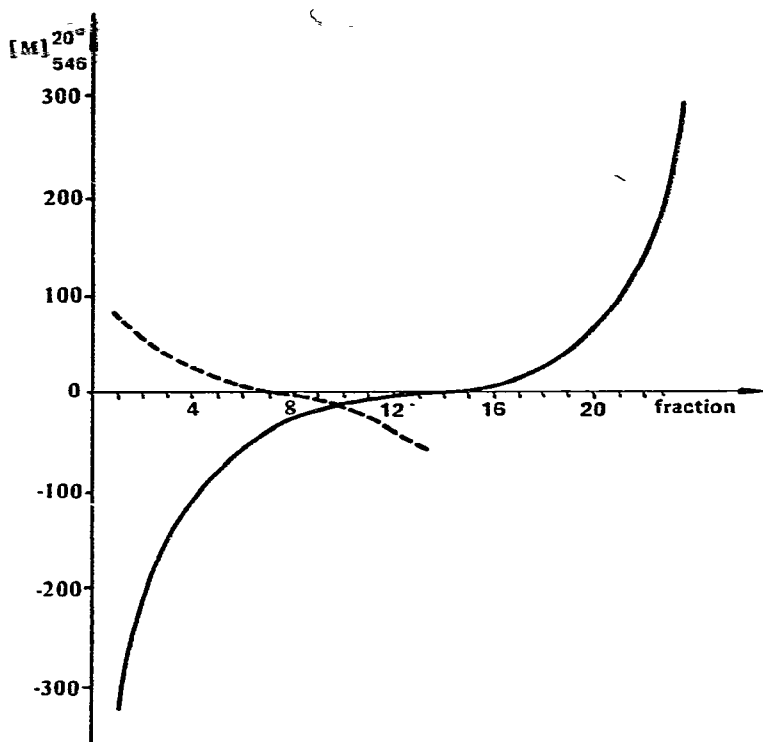


Fig. 1. Functional dependence of the apparent molecular rotation for tris(acetylacetonato)cobalt (III) (—) and tris(acetylacetonato)chromium(III) (---) on fraction number in the course of separation on a column packed with *cis*(NO<sub>2</sub>)-*trans*(N)-(—)<sub>589</sub>-[Co(L-arg)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]Cl.

adsorption columns of lactose<sup>6</sup>, alumina treated with (+)-tartaric acid<sup>7</sup>, D-sorbitol and D-mannitol<sup>8</sup>. The achievement of only partial resolution cannot be due to racemization in the course of the separation, since we have established experimentally that these complexes do not racemize upon standing in benzene solution even for a time-period longer than that required for the elution in our resolution experiments. One reason for the incomplete resolution is the relatively low plate number of the system used due to the large grain size of the adsorbent. However, the use of adsorbents of smaller grain size was not possible since the elution was not performed under high pressure. Experiments aimed at increasing the efficiency of the column are now being made.

#### REFERENCES

- 1 Y. Yoshikawa and K. Yamasaki, *Coord. Chem. Rev.*, 28 (1979) 205.
- 2 S. Yamazaki, T. Yukimoto and H. Yoneda, *J. Chromatogr.*, 175 (1979) 317.
- 3 R. Tsuchida, M. Kobayashi and A. Nakamura, *Bull. Chem. Soc. Jap.*, 11 (1936) 38.
- 4 E. Ferroni and R. Cini, *J. Amer. Chem. Soc.*, 82 (1960) 2427.
- 5 T. Moeller and E. Gulyas, *J. Inorg. Nucl. Chem.*, 5 (1958) 245.
- 6 J. P. Collman, R. P. Blair, R. L. Marshall and S. Slade, *Inorg. Chem.*, 2 (1963) 576.
- 7 T. S. Piper, *J. Amer. Chem. Soc.*, 83 (1961) 3908.
- 8 N. S. Bowman, V. Gčeva and G. K. Schweitzer, *Inorg. Chem. Lett.*, 2 (1966) 251.

- 9 H. Krebs and R. Rasche, *Naturwissenschaften*, 41 (1954) 63.
- 10 M. B. Čelap, D. J. Radanović and T. J. Tanjić, *Inorg. Chem.*, 4 (1965) 1494.
- 11 M. B. Čelap, D. J. Radanović, T. I. Nikolić and T. J. Janjić, *Inorg. Chim. Acta*, 2 (1968) 52.
- 12 B. A. Kamberi, M. B. Čelap and T. J. Janjić, *Glas. Hem. Druž., Beograd*, 43 (1978) 149.
- 13 M. B. Čelap, P. N. Radivojša and G. Djinović, in preparation.
- 14 L. F. Audrieth, (Editor), *Inorg. Syn.*, 5 (1950) 188.
- 15 L. F. Audrieth (Editor), *Inorg. Syn.*, 5 (1950) 130.