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## NEW SYNTHESIS AND THIN-LAYER CHROMATOGRAPHY OF TRIS-(ALKYLXANTHATO)COBALT(III) COMPLEXES

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### SUMMARY

A new method for the preparation of tris(alkylxanthato)cobalt(III) complexes,  $[\text{Co}(\text{S}_2\text{COR})_3]$ , involving the reaction of sodium hexanitrocobaltate(III) with alkylxanthates, is described. It has been established that the  $R_F$  values of these complexes, obtained by silica gel thin-layer chromatography, increase with increasing carbon number of the alkyl group, and that there is a linear relationship between this number of carbon atoms in an homologous series and the  $R_M$  values of the complexes. The mechanism of the chromatographic separations is thought to be based on adsorption.

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### INTRODUCTION

Jursik<sup>1</sup> established by thin-layer chromatography (TLC) that the  $R_F$  values of square-planar bis(aminocarboxylato)nickel(II) complexes increased with increasing length of the side chain. Liška *et al.*<sup>2</sup> observed a linear relationship between the number of carbon atoms in bis(dialkyldithiocarbamato)nickel(II) complexes and their  $R_M$  values.

Similar trends were found for *octahedral* aminocarboxylatocobalt(III) complexes by paper chromatography (PC)<sup>3</sup> and confirmed by TLC<sup>4</sup>. In all these studies, polycomponent solvent systems were used.

Continuing these investigations, we have studied the TLC of tris(alkylxanthato)cobalt(III) complexes, on silica gel using single component solvent systems.

### EXPERIMENTAL

#### *Synthesis*

In a 250-cm<sup>3</sup> round-bottomed flask, equipped with a stirrer, 100 cm<sup>3</sup> of the relevant alcohol were warmed to 50°C. A 2.0-g (0.05-mol) amount of ground sodium hydroxide and then 2.0 cm<sup>3</sup> of carbon disulphide were added, whereby a yellow solution containing the corresponding sodium xanthate was obtained. A solution of 7.0 g (0.017 mol) of sodium hexanitrocobaltate(III), in 10 cm<sup>3</sup> of water, was added

gradually and stirring continued for another 30 min. The reaction mixture obtained was kept overnight in a refrigerator and the green crystals which formed were filtered off. The crude product was recrystallized to constant melting point (Table I) from warm acetone. The complex of *n*-butylxanthate, obtained as a dense green liquid, was purified by chromatography on a column of silica gel (35 cm × 3 cm O.D.) with diethyl ether as the eluent. The purity of the products, after drying in vacuum at room temperature, was verified by microanalysis (C and H) and by electrogravimetric determination of the cobalt content. The results obtained are given in Table I.

### Solubility

The solubilities of the complexes were determined as follows: a saturated solution of the complex in carbon tetrachloride, prepared by shaking for 30 min at 22°C, was filtered. A 10-cm<sup>3</sup> volume of the filtrate was placed in a previously weighed flask and then evaporated to dryness in a vacuum evaporator at room temperature. The flask was left to stand overnight over sulphuric acid in a vacuum desiccator and then weighed again. The results obtained are presented in Table I.

### Thin-layer chromatography

Chromatographic separations were carried out by the ascending method on silica gel H (Merck, Darmstadt, F.R.G.). The preparation of the plates and the technique were as described previously<sup>4</sup>. The suspension was made from 50 g of silica gel H and 120 cm<sup>3</sup> of water. Solutions of the complexes in acetone were applied to the plate in the form of small drops. The solvents used were of p.a. purity and were dried over anhydrous sodium sulphate, except benzene which was dried over zeolite. The compositions of the solvent systems are presented in Table II. After the chromatographic development, green spots were obtained. All the investigations were carried out at 22 ± 2°C. The reproducibility of the  $R_F$  values was ± 0.02.

## RESULTS

As seen in the Experimental, a new, simple method for the preparation of tris(alkylxanthato)cobalt(III) complexes, in high yields, (43–96%), was developed. It

TABLE I

YIELDS (%), ANALYSES (%), MELTING POINTS (°C) AND SOLUBILITIES,  $s$  (g/100 cm<sup>3</sup>), OF THE COMPLEXES [Co(S<sub>2</sub>COR)<sub>3</sub>]

No.	R	Yield	Analyses						M.p.	$s$
			Co		H		C			
			Calc.	Found	Calc.	Found	Calc.	Found		
1	Methyl	70	15.49	15.36	2.39	2.63	18.94	20.15	—	1.7
2	Ethyl	96	13.95	13.79	3.58	3.74	25.58	26.24	120	5.2
3	<i>n</i> -Propyl	71	12.68	12.65	4.56	4.35	31.01	31.53	68	6.9
4	<i>n</i> -Butyl	43	11.63	11.53	5.38	5.38	35.55	34.35	—	11.3
5	Isobutyl	76	11.63	11.63	5.38	5.13	35.55	36.36	125	15.0
6	<i>sec.</i> -Butyl	64	11.63	11.27	5.38	5.49	35.55	35.99	103	12.4

TABLE II  
SOLVENT SYSTEMS USED

No.	Component	Development time (min)
1	Benzene	15
2	Toluene	30
3	Cyclohexane	40
4	Carbon tetrachloride	20
5	<i>n</i> -Hexane	15
6	<i>n</i> -Heptane	20
7	Ethyl acetate	30

consists of the reaction of sodium hexanitrocobaltate(III) with alkylxanthates. In this way, five crystalline products (Table I) were obtained. However, the corresponding complex with *n*-butylxanthate could not be prepared in a crystalline form as found previously<sup>5</sup>. On the other hand, the corresponding complex of *sec.*-butylxanthate could be prepared in the crystalline state although this could not be achieved by the previous methods<sup>5</sup>.

We then chromatographed six members of the homologous series obtained, using seven one-component solvent systems (Tables II and III). It was established that the  $R_F$  value of the complex increased with increasing number of carbon atoms in the ligand side chain. There is also a linear relationship between the carbon numbers in the *n*-series and the  $R_M$  values of the complexes (Fig. 1).

Finally, it was found that the solubilities of the complexes parallel their  $R_F$  values (Tables I and III).

## DISCUSSION

### Synthesis

Two methods have hitherto been reported for the preparation of tris(alkylxan-

TABLE III

$R_F$  VALUES OF TRIS(ALKYLXANTHATO)COBALT(III) COMPLEXES,  $[Co(S_2COR)_3]$ , ON SILICA GEL

Solvent systems as in Table II.

No.	R	$R_F \cdot 100$						
		1	2	3	4	5	6	7
1	Methyl	86	82	8	34	3	9	88
2	Ethyl	89	89	11	42	5	12	90
3	<i>n</i> -Propyl	92	93	15	56	7	17	93
4	<i>n</i> -Butyl	95	95	25	68	11	25	96
5	Isobutyl	95	96	29	69	12	27	96
6	<i>sec.</i> -Butyl	93	95	18	60	8	20	94

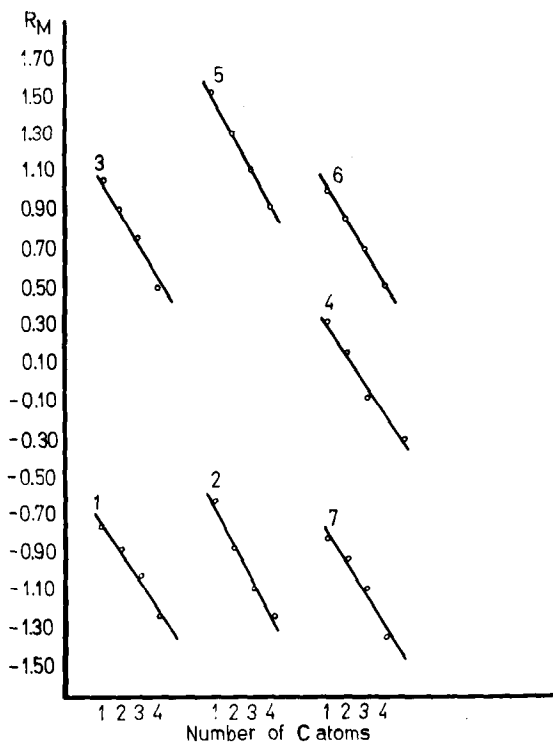


Fig. 1. Dependence of the  $R_M$  values on the number of carbon atoms in the  $n$ -alkyl group of the  $[\text{Co}(\text{S}_2\text{COR})_3]$  complexes. The numbers on the lines refer to the solvent systems used (see Table II).

thato)cobalt(III) complexes. The first, by Delépine and Compin<sup>6</sup>, consists of the reaction of alkylxanthates with cobalt(II) salts; in our experience, this method gives impure products in relatively low yields. The second method, by Watt and McCormic<sup>7</sup>, involves a relatively long period of heating of previously prepared solid hexamminecobalt(III) xanthates.

As is seen in the Experimental, we have prepared tris(alkylxanthato)cobalt(III) complexes by adding a solution of sodium hexanitrocobaltate(III) to the reaction mixture employed for the preparation of sodium xanthates. Our method has advantages over those previously employed since it involves an easily available cobalt(III) complex and requires neither the isolation of the sodium alkylxanthates, nor any other reaction intermediate. Besides, the yields obtained are high (43–96%).

#### Chromatographic

Since the results of the chromatographic separations of the tris(alkylxanthato)cobalt(III) complexes are consistent with our previous results for aminocarboxylato complexes, it might be concluded that the relationship which we have established between the number of carbon atoms in an homologous series of complexes and their  $R_M$  values is of wider applicability.

### *Separation mechanism*

In view of the fact that the neutral complexes were separated by means of single component solvent systems, it might be concluded that the separation mechanism does not involve ion exchange, nor partition, but adsorption. As the adsorption energy of the  $-\text{CH}_2-$  group is known to be small<sup>8</sup>, the separation of members of an homologous series is not expected to be achieved on the basis of differences in their adsorption energies. This means that in the present case, the differences in the solubility of the complexes in the solvent systems studied are sufficiently high to cause differences in the adsorption of the complexes and in their chromatographic separation. Thus the solubility of the complexes in the solvent by means of which the best separations were achieved (carbon tetrachloride) parallels their  $R_F$  values (Tables I and III).

### CONCLUSIONS

It can be assumed that the linear correlation between the number of carbon atoms in the side chain of an homologous series of complexes and the  $R_M$  values is valid regardless of whether paper or thin-layer chromatography is used, or whether the separation mechanism is based on partition or adsorption. In addition, square-planar and octahedral complexes with aminocarboxylato, alkylxanthato or dialkyl-dithiocarbamate ligands give analogous results. Finally of interest is the similar trend observed by Lederer<sup>9</sup> upon replacement of a 1,2-diaminoethane ring by a 1,2-diaminopropane one.

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