

Short Communication

Thin-layer chromatography on silica gel of a homologous series of bis(alkylxanthato)nickel(II) complexes

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ABSTRACT

The direct synthesis of bis(alkylxanthato)nickel(II) complexes is described, consisting in the addition of nickel(II) chloride to a previously heated solution of sodium hydroxide and carbon disulphide in the corresponding alcohol. It was established that the R_F values of complexes obtained with non-aqueous solvent systems increased with increasing number of carbon atoms in the xanthato ligands used, but the opposite order was found using an aqueous solvent system. There is a linear dependence between the R_M values of complexes and the number of carbon atoms in the hydrophobic part of the ligands. In the former instance the proposed separation mechanism involves the formation of hydrogen bonds between strongly electronegative atoms of the ligands (O and S) and silanol groups of silica gel and in the latter a hydrophobic interaction mechanism was assumed. In this manner it was established that the previously found regularities for octahedral alkylxanthatocobalt(III) complexes can be applied also to the investigated square-planar alkylxanthatonickel(II) complexes.

INTRODUCTION

In previous papers, the chromatographic behaviour of octahedral tris(alkylxanthato)cobalt(III) complexes was investigated [1,2]. It was established that under conditions of normal-phase chromatography, the R_F values of these complexes obtained on thin layers of silica gel [1] and polyacrylonitrile (PANS) [2] increase with increasing number of carbon atoms in the alkyl substituents, and that there is a negative linear dependence between the number of carbon atoms and their R_M values. However, under the conditions of reversed-phase chromatography on thin layers of PANS [2], a reversed order of the complexes and a positive linear dependence be-

tween their R_M values and the number of carbon atoms in the alkyl substituents were obtained.

Continuing these investigations on thin layers of silica gel, in this work we wanted to establish whether the aforementioned regularities are applicable also to square-planar nickel(II) complexes.

EXPERIMENTAL

Syntheses

In a 250-cm³ erlenmeyer flask, equipped with a stirrer, 100 cm³ of the corresponding alcohol and 2.0 g (0.05 mol) of ground sodium hydroxide was heated to 50°C, then 2.0 cm³ of carbon disulphide were added, whereby a yellow solution was obtained. To this solution, a solution of 6.1 g (0.025 mol) of nickel(II) chloride hexahydrate in 10 cm³ of water was added in small portions with constant

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TABLE I

YIELDS AND ELEMENTAL ANALYSES OF THE COMPLEXES $[\text{Ni}(\text{S}_2\text{COR})_2]$, AND INDUCTIVE EFFECTS OF THE ALKYL GROUPS [2]

No.	R	Yield (%)	Analyses (%)				Inductive effect
			C		H		
			Calc.	Found	Calc.	Found	
1	Methyl	66	17.59	17.65	2.21	2.18	0.00
2	Ethyl	86	23.93	23.74	3.35	3.33	-0.10
3	<i>n</i> -Propyl	72	29.19	29.25	4.29	4.20	-0.115
4	<i>n</i> -Butyl	38	33.63	33.55	5.08	5.05	-0.130
5	<i>sec.</i> -Butyl	45	33.63	33.98	5.08	5.35	-0.210
6	Isobutyl	78	33.63	33.82	5.08	4.96	-0.125

stirring of the reaction mixture, which was prolonged for a further 30 min. The reaction mixture was left overnight in a refrigerator, then the precipitated yellow-brown crystals of the crude complex were separated by filtration under reduced pressure and recrystallized from warm acetone. The yields obtained and the corresponding results of elemental microanalyses are given in Table I.

Chromatography

Chromatographic investigation of the complexes obtained was carried out by ascending chromatography on thin layers of silica gel 60G (Merck, Darmstadt, Germany), on 5 × 5 cm plates. Freshly

prepared solutions of complexes in acetone (0.2 μl), having a concentration of 2 mg/cm³, were applied to the plates. Before development, the plates with starting spots were kept for 15 min in a 4 × 6 × 10 cm chromatographic chamber where development was performed. All solvents used were of analytical-reagent grade. The experiments were carried out at 20 ± 2°C. After development the coloured spots of the complexes were readily visible.

RESULTS AND DISCUSSION

As can be seen from Table I, the earlier described [3–5] series of six bis(alkylxanthato)nickel(II) com-

TABLE II

SOLVENT SYSTEMS USED

No.	Composition	Proportions (v/v)
1	<i>n</i> -Hexane	
2	Cyclohexane	
3	Carbon tetrachloride	
4	Benzene	
5	Toluene	
6	<i>n</i> -Hexane-toluene	80:20
7	<i>n</i> -Hexane-benzene	80:20
8	<i>n</i> -Hexane-chloroform	80:20
9	<i>n</i> -Hexane-carbon disulphide	80:20
10	<i>n</i> -Hexane-dioxane	80:20
11	<i>n</i> -Hexane-tetrahydrofuran	80:20
12	Cyclohexane-chloroform	85:15
13	Cyclohexane-carbon tetrachloride	80:20
14	Cyclohexane-toluene	80:20
15	Tetrahydrofuran-water-NiCl ₂ ·6H ₂ O	50:50:1 (v/v/w)

TABLE III

 R_F VALUES OF BIS(ALKYLXANTHATO)NICKEL(II) COMPLEXES $[\text{Ni}(\text{S}_2\text{COR})_2]$ OBTAINED BY TLC

No.	R	$R_F \times 100^a$														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Methyl	8	13	45	71	82	26	30	43	19	46	36	29	21	34	77
2	Ethyl	11	17	50	78	88	34	42	53	25	53	47	43	29	43	66
3	<i>n</i> -Propyl	15	22	57	81	90	41	50	60	28	57	55	50	36	54	57
4	<i>n</i> -Butyl	19	28	62	84	93	47	59	67	32	61	64	57	42	63	50
5	<i>sec.</i> -Butyl	21	23	58	78	89	41	53	64	32	61	55	53	39	57	58
6	Isobutyl	23	28	62	78	93	50	60	69	38	61	61	56	44	64	51

^a The compositions of the solvent systems are given in Table II.

plexes were obtained for first time by direct synthesis in yields ranging from 38 to 86%, with respect to the crude reaction product.

The chromatographic investigation of these complexes was performed with fourteen non-aqueous solvent systems (five one-component and nine two-component) and with a three-component aqueous solvent system (Table II).

From the results obtained (Table III), it is seen that in chromatographic separations of the aforementioned square-planar complexes with non-aqueous solvent systems their R_F values increase with increasing number of carbon atoms in the side-chain of the *n*-alkylxanthato ligands. This behaviour is in agreement with results obtained previously in chromatographic separations of a homologous series of octahedral alkylxanthatocobalt(III) complexes on thin layers of silica gel [1] and PANS [2].

From Table III it is also seen that with the investigated square-planar isomeric butylxanthato complexes using non-aqueous solvent systems, the complex containing a secondary butylxanthato ligand, as a rule, exhibits the lowest R_F value, whereas the values for the other two isomers are most often very close or identical with one another, which is in accordance with their inductive effects (Table I). This is also in accordance with results obtained for octahedral tris(alkylxanthato)cobalt(III) complexes in their chromatographic separations on silica gel [1] and PANS [2].

As regards the explanation for the first-mentioned regularity, it was assumed that the dominant mechanism of complex separation is the generally

accepted mechanism of hydrogen bond formation between strongly electronegative atoms of the ligand (O, S) and silanol groups of the silica gel [6]. However, it is known that with increasing side-chain length the positive inductive effect of an alkyl group is also increased (Table I), which causes an increase in the electron density on the electronegative oxygen and sulphur atoms, and this would lead to a strengthening of hydrogen bonds between these atoms and hydrogens of the silanol groups of silica gel. The latter would, however, give rise to a reversed order of complexes relative to that which is obtained (Table III). Therefore, in considering the dependence of the complex mobility on the type of the substituent in the alkylxanthato ligand, attention should be also devoted to their steric effects. These effects, with increasing side-chain length, are manifested in a more difficult approach of strongly electronegative atoms of complexes to silanol groups of silica gel, with which hydrogen bonds might be formed. This would cause a decrease in the strength of complex adsorption with increasing side-chain length, which in fact was experimentally established for the investigated *n*-alkylxanthato complexes (Table III). This phenomenon was already noticed earlier in chromatographic separations of homologous series of transition metal complexes containing the same [1,2] or related [7–14] ligands.

The order of the investigated square-planar complexes described is reversed when an aqueous solvent system is applied (Table III, No. 15). This phenomenon might be explained by a change in the separation mechanism, *i.e.*, by non-specific hydro-

phobic interactions [15], as had been shown in previous work [16] for the octahedral transition metal tris(β -diketonato) complexes. These interactions are the greater the larger is the hydrocarbonaceous surface area [17], on account of which it is expected that the R_F values of complexes will decrease with increasing side-chain length of the alkylxanthato ligand, as was experimentally obtained.

In all instances investigated a linear dependence between the R_M values of the investigated square-planar complexes and the number of carbon atoms in the n -alkylxanthato ligands was established (Fig. 1), which is in accordance with the results obtained in previous work in which we investigated the corresponding octahedral cobalt(III) complexes using a non-aqueous solvent system in thin layer chromatographic separations on silica gel [1] and aqueous and non-aqueous solvent systems in separations on polyacrylonitrile [2].

In order to show quantitatively the difference in the selectivity [16,18] among the solvent systems used in this work, Fig. 2 shows the dependence between the R_M values of the investigated nickel(II) complexes, obtained by means of fourteen solvent systems, and their R_M values obtained by using n -hexane–dioxane (80:20, v/v), which gives the smallest difference in R_M values between the outermost members of the homologous series. From these data it might be concluded that in normal-phase chromatography high selectivity is achieved using solvent systems 5, 7, 11, 12 and 14, the selectivities of which do not differ much.

Finally, it might be concluded that the earlier es-

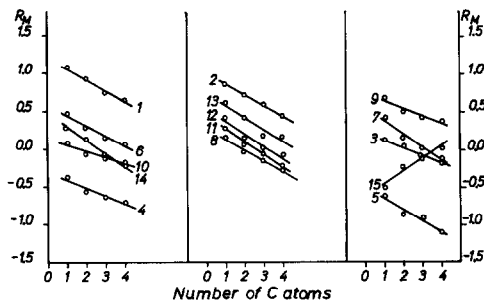


Fig. 1. Dependence of the R_M values on the number of carbon atoms in the n -alkyl group of the $[\text{Ni}(\text{S}_2\text{COR})_2]$ complexes. The numbers against the lines refer to the solvent system used (see Table II).

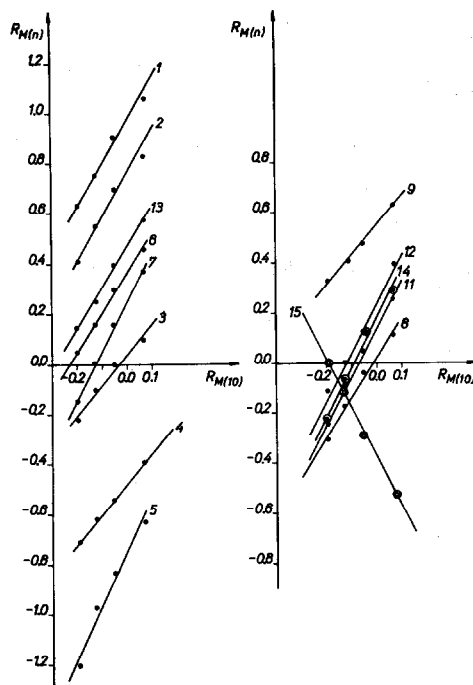


Fig. 2. Correlation between the R_M values of the investigated Ni(II) chelates obtained on a thin layer of silica gel with a given solvent system and solvent system 10. $R_{M(n)}$ = R_M values obtained with the solvent system by the number against the lines (see Table II); $R_{M(10)}$ = the same for solvent system 10.

tablished regularities for octahedral alkylxanthato-cobalt(III) complexes are also valid for square-planar alkylxanthatonickel(II) complexes.

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