EFFECT OF THE CENTRAL ION OF OCTAHEDRAL TRANSITION METAL COMPLEXES ON THEIR THIN-LAYER CHROMATOGRAPHIC R_F VALUES

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SUMMARY

The R_F values of twenty complexes of Cr^{III}, Co^{III}, Ru^{III}, Rh^{III}, Fe^{II}, Co^{II}, Ni^{II} and Zn^{II} containing ligands such as ethylenediamine-N,N'-diacetato-N,N'-di-3-propionato (eddadp), ethylenediaminetetra-3-propionato (edtp), 2,4-pentanedionato (acac), 1-phenyl-1,3-butanedionato ion (bzac) or α,α'-dipyridyl (dipy), were determined by thin-layer chromatography. Development was carried out with 22 single-component solvents. The results obtained for anionic and neutral complexes can best be explained by using the polarization power of the central ions of the complexes, assuming an adsorption separation mechanism.

INTRODUCTION

In previous studies we investigated the effect of various factors on the R_F values of transition metal complexes obtained by thin-layer chromatography (TLC) on silica gel and/or aluminium oxide. The effects of the geometric configuration of octahedral[1], square-planar[2] and facial-meridional isomers[3], of the chelate ring size[1], of the absolute configuration of a complex[4] and of the length of the coordinated ligand side-chain were studied[1,5].

In this work we examined the effect of the central ion. Many papers[6] have dealt with TLC separations on different adsorbents of various transition metal complexes containing the same ligands. However, the aim in almost all of those studies was simply to achieve the chromatographic separation, and not to establish the regularities in the chromatographic behaviour of the complexes. In most instances the complexes of various metals were not previously isolated in the solid state, the chromatographic separations being carried out using solutions containing simple salts and the corresponding ligands.

In only two of the papers published so far were attempts made to correlate the nature of the central ion of the complexes with the R_F values[7,8]. Subbotina *et al.*[7] separated β-diketonato complexes of lanthanides on thin layers of aluminium oxide using multi-component solvent systems. On the basis of few examples it was concluded that the R_F value of a complex decreases with increasing radius of the central ion, although in some instances deviations from this rule were observed. Haworth and Hung[8] chromatographed mixtures of transition metal 2,4-pentanedionato complexes on thin layers of microcrystalline cellulose using multi-component solvent systems. The order of the R_F values of complexes containing different central ions varied, and this was ascribed to the competition of two factors essential for the separation, *viz.*, the size of the metal ion and the solubility of the complex in the solvent system used.

We decided to examine in more detail the effect of the central ion on the R_F values of complexes obtained on silica gel thin layers, as previous separations were performed on cellulose and aluminium oxide. For development we applied single-component solvents, resulting in an adsorption mechanism; previous separations were performed with multi-component solvent systems, which may involve a partition separation mechanism[1].

TABLE I

EFFECT OF THE CENTRAL ION OF TRANSITION METAL COMPLEXES ON THE R_F VALUES

No.	Isomer	Complex	Metal (M)	Ref.	r (nm)	$Z^*/r \cdot 10^{-10}$ (m^{-1})
1	*trans*(O_5)	$[M(eddadp)]^-$	Co	9	0.052	13.0
2			Rh	10	0.066	10.4
3			Cr	11	0.061	8.1
4		$[M(edtp)]^-$	Co	12, 13	0.052	13.0
5			Rh	14	0.066	10.4
6			Cr	15	0.061	8.4
7		$[M(acac)_3]$	Co	16	0.052	13.0
8			Rh	17	0.066	10.4
9			Ru	18	0.068	9.2
10			Cr	19	0.061	8.1
11	Facial	$[M(bzac)_3]$	Co	16	0.052	13.0
12			Rh	20	0.066	10.4
13			Cr	20	0.061	8.1
14	Meridional	$[M(bzac)_3]$	Co	16	0.052	13.0
15			Rh	20	0.066	10.4
16			Cr	20	0.061	8.1
17		$[M(dipy)_3]^{2+}$	Zn	21	0.074	11.4
18			Ni	21	0.070	10.3
19			Co	22	0.065	10.1
20			Fe	22	0.061	9.7

[a] Solvents 1–22 are given in Table II. Thin layers: K_1 = commercial silica gel SIL-G on an aluminium sheet; K_2 = commercial silica gel SIL-G on a plastic sheet; A = aluminium oxide; G = silica gel G; H = silica gel H.

EXPERIMENTAL

Thin-layer chromatography

The complexes were synthesized according to literature procedures (Table I). The purity of the products was checked by microanalysis. Chromatographic development was carried out by the ascending method on silica gel H (Merck, Darmstadt, F.R.G.) or G (Riedel-de Haën, Hannover, F.R.G.), aluminium oxide (Merck) and commercially prepared silica gel SIL-G (Machery, Nagel & Co., Düren, F.R.G.) plates.

The preparation of the plates and all the other experimental data were described in a previous paper[1]. Before development, the complexes were dissolved in the corresponding solvent systems. The solvents (analytical-reagent grade) were dried with anhydrous sodium sulphate, except benzene, which was treated with dehydrated zeolite.

The solvents used are listed in Table II. All the substances were coloured and hence could be detected visually on the plates.

$R_F \cdot 100^a$

1	2	3	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
K_1	A	K_2	G	K_2	G	G	K_2	G	K_1	H	H	A	G	G	G	G	G	K_1	K_1	G	H	H
—	—	—	—	—	73	14	—	15	—	18	8	85	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	77	17	—	36	—	22	15	88	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	79	35	—	44	—	43	18	91	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	48	18	48	13	78	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	51	24	59	24	80	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	57	32	52	15	86	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	20	10	—	—	—	—	—	—	—	—	71	71	43	70	89	68	79	86	53	50
—	—	—	22	11	—	—	—	—	—	—	—	—	74	72	44	69	95	74	85	94	58	59
—	—	—	27	14	—	—	—	—	—	—	—	—	75	77	48	71	98	77	87	96	60	60
—	—	—	23	17	—	—	—	—	—	—	—	—	79	80	57	75	95	74	84	96	59	58
4	—	44	—	12	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
7	—	50	—	20	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
9	—	46	—	15	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
12	20	60	64	36	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
18	26	67	70	54	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
20	28	62	66	48	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	18	—	83	28	—	—	—	31	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	17	—	84	32	—	—	—	36	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	5	—	78	17	—	—	—	9	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	2	—	75	14	—	—	—	13	—	—	—	—	—	—	—	—	—	—

Solubility

The solubilities of the complexes were determined as described previously[5].

Calculation of Z*/r values

The polarization power of an ion (ρ) is proportional to the ratio of the effective charge ($Z - S$) and the radius of the ion (r): $\rho \propto (Z - S)/r$, where Z is the atomic number, S Slaiter's shielding constant and r the ionic radius according to Shanon and Prewit[23].

RESULTS AND DISCUSSION

Table I gives the R_F values for 20 cationic, anionic and neutral complexes obtained with the 22 solvents listed in Table II.

For all the anionic and neutral complexes, the Co^{III} complex had a smaller R_F value than the corresponding Cr^{III}, Ru^{III} and Rh^{III} complexes. In addition, in most instances the following order of R_F values was observed: Co^{III} < Rh^{III} < Ru^{III} < Cr^{III}.

In order to interpret these results we first considered the correlation between the R_F values and the radii of the corresponding metal ions (Table I). This made it possible to explain why a Co^{III} complex always has the smallest R_F value, as its radius is much smaller than those of the other metal ions. However, it is not possible on this basis to explain the order of R_F values of complexes whose central ions have similar radii.

However, taking into account that the radius of the ion affects the distribution of the complex charge via the polarization power of the central ion, we thought that this polarization power might be a better parameter to provide an explanation of the order of the R_F values. We therefore compared the R_F values with the $Z*/r$ values ($Z*$ is the effective charge and r the radius of the central ion), which are proportional to the polarization powers of the central ions.

In this way we established that the order of the R_F values of the complexes containing central ions with a large difference in their radii can be well explained by

TABLE II

SOLVENTS USED

No.	Solvent	Time of development (min)	No.	Solvent	Time of development (min)
1	Benzene	15	12	Ethylene glycol	120
2	Carbon tetrachloride	20	13	*sec.*-Butanol	85
3	Chloroform	15	14	*n*-Butanol	65
4	Methylene chloride	10	15	*n*-Hexanol	80
5	Distilled water	15	16	*n*-Pentanol	120
6	Methanol	15	17	Acetylacetone	60
7	Formic acid	30	18	Methyl *n*-propyl ketone	15
8	1,2-Propanediol	16 h	19	Methyl ethyl ketone	12
9	Formamide	10	20	Cyclohexanone	60
10	1,3-Propanediol	10 h	21	Isobutanol	70
11	Ethylene glycol monomethyl ether	55	22	Cyclohexanol	6 h

means of the polarization power of the central ion (e.g., Co^{III} and other metals). Moreover, by means of this parameter it is possible to explain in most instances the order of the R_F values of complexes whose central ions have similar radii. For example, in the series of $[M(eddadp)]^-$ and $[M(edtp)]^-$ complexes (Table I), on the basis of the central ion radii, the order of the R_F values of the complexes $Co^{III} < Cr^{III} < Rh^{III}$ would be expected, but this order was not in agreement with the experimental results. However, on the basis of the polarization power the order of the R_F values of these complexes should be $Co^{III} < Rh^{III} < Cr^{III}$, which agreed with the experimental results. Nevertheless, in some instances when the difference between the polarization powers of central ions was small, deviations from the expected order were observed, pointing to the existence of some other factors that affect the R_F values. Therefore, we determined the solubility of three complexes in three solvent systems (Table III). It can be seen that in some instances the chromatographic behaviour of the complexes is in accordance with their solubilities, whereas in others it is not, indicating that some other factors are operating.

TABLE III

SOLUBILITIES (s, mol dm^{-3}) OF SOME OF TRIS(ACETYLACETONATO) TRANSITION METAL COMPLEXES AND THE CORRESPONDING R_F AND Z^*/r VALUES

Complex	$Z^*/r \cdot 10^{-10}$ (m^{-1})	Chloroform		n-Butanol		Acetylacetone	
		s	$R_F \cdot 100$	s	$R_F \cdot 100$	s	$R_F \cdot 100$
[Co(acac)$_3$]	13.0	0.259	20	0.0418	71	0.0947	89
[Ru(acac)$_3$]	9.2	0.324	27	0.0449	77	0.177	98
[Cr(acac)$_3$]	8.1	0.304	23	0.0795	80	0.213	95

As regards the separation mechanism, we consider that with anionic and neutral complexes, the greater the polarization power of the central ion the more the ligand is polarized; hence the negative charge on the ligator is higher and stronger hydrogen bonds with silanol groups are formed.

With cationic complexes, in all instances the R_F value of the Zn^{II} complex was greater that those of the Co^{II} and Fe^{II} complexes, whereas there was no regularity in the order of the R_F values of Co^{II}, Fe^{II} and Ni^{II} complexes.

As the order of the R_F values of these complexes cannot be explained on the basis of either ionic radii or polarization power, we have assumed that in this instance, in addition to the adsorption mechanism, ion exchange may be also involved, as silica gel is known to behave also as a cation exchanger[24].

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