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Note

Effect of the composition and the structure of cobalt(III) complexes on their R_F values obtained by partition paper chromatography

II. Linear dependence of R_M values on number of carbon atoms of aminocarboxylato-ligands

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In an earlier paper[1], we studied the effects of the position of nitro-groups and the chelate-ring size in cobalt(III) complexes on their R_F values in partition paper chromatography. In continuation of this work, we wished to study the effects of the nature of aminocarboxylato-ligands on the R_F values of mixed cobalt(III) complexes. It is known[2] that there is a linear relationship between the numbers of carbon atoms in homologous series of some organic compounds and their R_M values in paper chromatography. However, to our knowledge, such regularity has hitherto not been established for such compounds when co-ordinated in transition-metal complexes. Therefore, we have studied the effect of the number of carbon atoms of co-ordinated aminocarboxylato-ligands on the R_M values of cobalt(III) complexes.

EXPERIMENTAL

Preparation of the complexes

All the complexes studied were prepared according to known procedures (see Table I).

Chromatographic investigation

Chromatographic separations were carried out as described previously[1]; the solvent systems used are given in Table II.

RESULTS AND DISCUSSION

As can be seen from Table I, the linear dependence of R_M values on the number of carbon atoms in cobalt(III) complexes was studied with twenty-four cobalt(III) complexes containing some of the following ten ligands: nitro-group, glycine (gly), L-alanine (L-ala), L-aminobutyric acid (L-abu), L-norvaline (L-nva), L-valine (L-val), L-norleucine (L-nle), L-leucine (L-leu), L-isoleucine (L-ile), and ammonia. All these complexes are aminocarboxylato-complexes synthesized for the first time in our lab-

TABLE I

EFFECT OF CARBON-CHAIN SIZE OF CO-ORDINATED AMINO ACIDS ON THE R_F VALUES

No.	*Isomer*	*Complex*	*Ref.*	$R_F \times 100$*						
				1	*2*	*3*	*4*	*5*	*6*	*7*
1	*cis*-NO_2-*trans*-N	$[Cogly_2(NO_2)_2]^-$	3	20	10	41	3	—	—	—
2	(+)**-*cis*-NO_2-*trans*-N	$(L\text{-ala})_2$	3	28	21	60	10	—	—	—
3	(+)-*cis*-NO_2-*trans*-N	$(L\text{-abu})_2$	4	49	41	74	28	—	—	—
4	(+)-*cis*-NO_2-*trans*-N	$(ibu)_2$	4	52	32	76	31	—	—	—
5	(+)-*cis*-NO_2-*trans*-N	$(L\text{-nva})_2$	4	65	66	88	63	—	—	—
6	(+)-*cis*-NO_2-*trans*-N	$(L\text{-val})_2$	4	64	66	84	62	—	—	—
7	(+)-*cis*-NO_2-*trans*-N	$(L\text{-nle})_2$	4	73	85	94	88	—	—	—
8	(+)-*cis*-NO_2-*trans*-N	$(L\text{-leu})_2$	4	73	85	93	85	—	—	—
9	(+)-*cis*-NO_2-*trans*-N	$(L\text{-ile})_2$	4	76	81	94	83	—	—	—
10	*cis*-O-*trans*-NH_2	$[CoNH_3gly_2NO_2]$	5	—	—	—	—	23	16	14
11	(+)-*cis*-O-*trans*-NH_2	$(L\text{-ala})_2$	5	—	—	—	—	47	39	47
12	(+)-*cis*-O-*trans*-NH_2	$(L\text{-abu})_2$	6	—	—	—	—	67	80	70
13	(+)-*cis*-O-*trans*-NH_2	$(L\text{-nva})_2$	6	—	—	—	—	91	95	90
14	(+)-*cis*-O-*trans*-NH_2	$(L\text{-val})_2$	6	—	—	—	—	90	97	90
15	Meridional(1,2,6)	$[CoNH_3gly(NO_2)_3]^-$	7	—	—	—	—	44	54	68
16	(−)-Meridional(1,2,6)	L-ala	7	—	—	—	—	57	71	75
17	(−)-Meridional(1,2,6)	L-abu	7	—	—	—	—	69	79	82
18	(−)-Meridional(1,2,6)	L-nva	7	—	—	—	—	78	88	88
19	*cis*-NO_2-*trans*-NH_2,NH_3	$[Co(NH_3)_2gly(NO_2)_2]$	5	—	—	—	—	30	32	60
20	(+)-*cis*-NO_2-*trans*-NH_2,NH_3	L-ala	5	—	—	—	—	46	44	74
21	(+)-*cis*-NO_2-*trans*-NH_2,NH_3	L-abu	5	—	—	—	—	57	48	81
22	*trans*-NO_2-*cis*-NH_3	gly	5	—	—	—	—	18	13	31
23	*trans*-NO_2-*cis*-NH_3	L-ala	5	—	—	—	—	28	22	62
24	*trans*-NO_2-*cis*-NH_3	L-abu	5	—	—	—	—	39	32	76

* The compositions of solvent systems 1–7 are shown in Table II.
** The sign of optical rotation at 589 nm.

oratory. The chromatography was carried out with seven solvent systems containing, in addition to water, some of the following components: ethanol, isopropanol, ethyl acetate, dioxan, phenol, hydrochloric acid, nitric acid, and potassium iodide.

The R_F values obtained are listed in Table I. From the results obtained, it might be concluded that, for the five homologous series of complexes, which contain three to nine members, there is a linear relationship between the R_M value and the

TABLE II

SOLVENT SYSTEMS USED

No.	*Composition*	*Component ratio*	*Development time (h)*
1	Phenol saturated with 2 *M* HCl		12
2	Ethyl acetate–ethanol–water	70:20:10 (v/v/v)	6
3	Dioxan–water	80:20 (v/v)	6
4	*n*-Butanol–ethanol–water	70:20:10 (v/v/v)	12
5	Isopropanol–water–conc.HNO_3	75:20:5 (v/v/v)	14
6	Ethyl acetate–ethanol–water	60:25:15 (v/v/v)	6
7	Dioxan–water–KI	85:15:1 (v/v/w)	6

number of carbon atoms in co-ordinated aminocarboxylato-ligands; the same dependence was established with three or four solvent systems (Figs. 1–5)*. This conclusion is valid for either normal or branched amino acids. Moreover, because of the relatively small differences in the R_F values of the complexes containing aminocarboxylato-ligands with normal chains and those having branched chains with the same number of carbon atoms (an analogous phenomenon has been established with

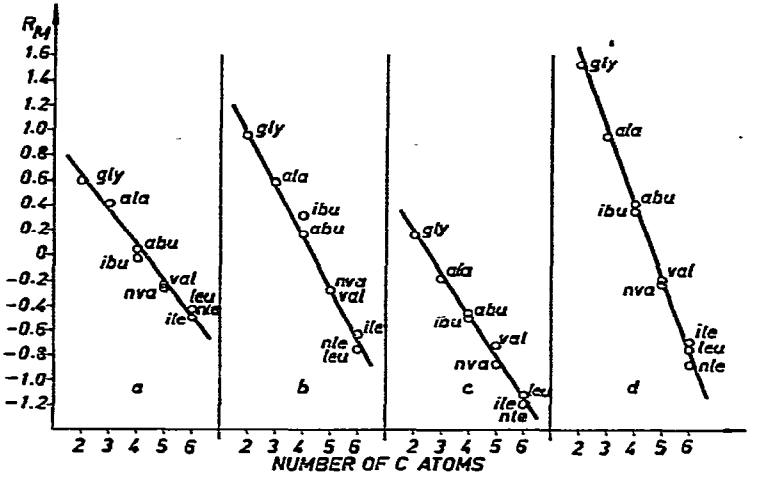

Fig. 1. Dependence of R_M value on the number of carbon atoms in one of the coordinated amino acids in the $(+)_{589}$-*cis*(NO_2),*trans*(N)-$[CoAm_2(NO_2)_2]^-$ complex. Solvent system used: (a) 1; (b) 2; (c) 3; (d) 4 (see Table II).

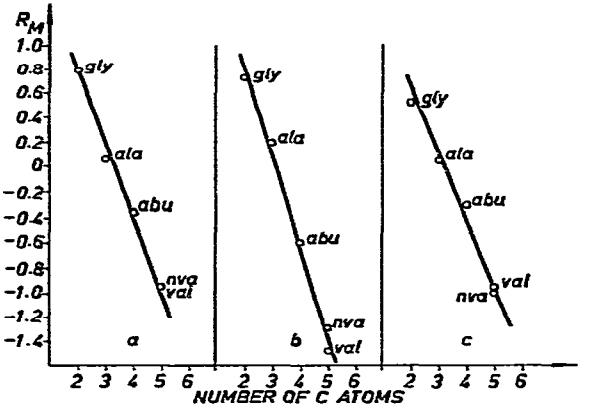

Fig. 2. Dependence of R_M value on the number of carbon atoms in one of the coordinated amino acids in the $(+)_{589}$-*cis*(O),*trans*(NH_2)-$[CoNH_3Am_2NO_2]$ complex. Solvent system used: (a) 7; (b) 6; (c) 5 (see Table II).

* It is known that the R_F values might be determined with an experimental error of $\pm 0.01\ R_F$. In order to facilitate estimation of whether the differences in R_M values between individual points are within the limits of experimental error, we have given in Fig. 6 the errors in R_M value corresponding to the afore-mentioned R_F errors. This has been achieved by using the following equation for the propagation of determinate error[5]: $\Delta R_M = -[0.434/R_F(1 - R_F)] \cdot \Delta R_F$.

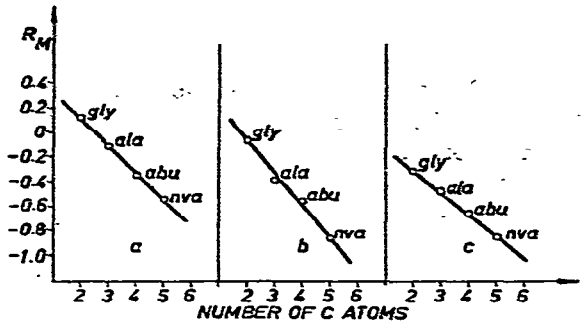

Fig. 3. Dependence of R_M value on the number of carbon atoms in one of the coordinated amino acids in $(-)_{589}$-meridional-$[CoNH_3Am(NO_2)_3]^-$ complex. Solvent system used: (a) 5; (b) 6; (c) 7 (see Table II).

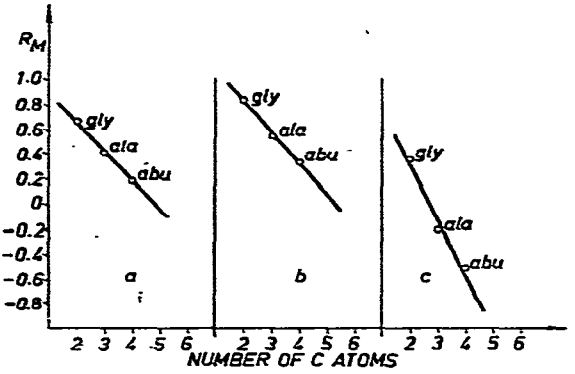

Fig. 4. Dependence of R_M value on the number of carbon atoms in one of the coordinated amino acids in the *trans*(NO_2),*cis*(NH_3)-$[Co(NH_3)_2Am(NO_2)_2]$ complex. Solvent system used: (a) 5; (b) 6; (c) 7 (see Table II).

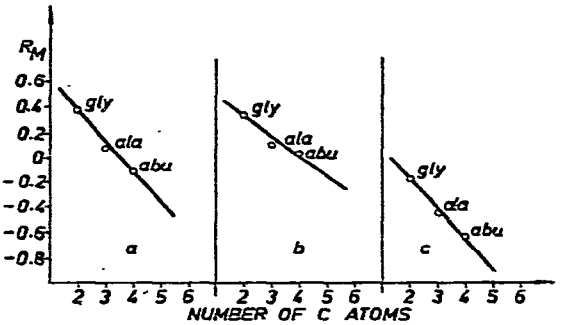

Fig. 5. Dependence of R_M value on the number of carbon atoms in one of the coordinated amino acids in $(+)_{589}$-*cis*(NO_2),*trans*(NH_3,NH_2)-$[Co(NH_3)_2Am(NO_2)_2]$ complex. Solvent system used: (a) 5; (b) 6; (c) 7 (see Table II).

some non-coordinated amino acids), the R_M values of all the complexes investigated in one homologous series lie approximately on one straight line.

The most important statistical data concerning these investigations are shown in Table III. On the basis of calculated correlation coefficients (from —0.9992 to

TABLE III

STATISTICAL DATA*

Data from Fig. No.	*Equation of regression line*	*Correlation coeff.*	*R_F values calculated (found) ×100*
1a	$R_M = -0.2693(C)^{**} + 1.1281$	−0.9889	20, 32, 47, 47, 62, 62, 75, 75, 75 (20, 28, 49, 52, 64, 65, 73, 73, 76)
1b	$R_M = -0.4281(C) + 1.8729$	−0.9927	9. 21, 41, 41, 65, 65, 83, 83, 83 (10, 21, 41, 32, 66, 66, 85, 85, 81)
1c	$R_M = -0.3315(C) + 0.8359$	−0.9949	40, 59, 76, 76, 87, 87, 93, 93, 93 (41, 60, 74, 76, 88, 84, 94, 93, 94)
1d	$R_M = -0.5729(C) + 2.6620$	−0.9982	3, 10, 30, 30, 61, 61, 86, 86, 86 (3, 10, 28, 31, 63, 62, 88, 85, 83)
2a	$R_M = -0.5624(C) + 1.8501$	−0.9960	16, 41, 72, 90, 90 (14, 47, 70, 90, 90)
2b	$R_M = -0.7233(C) + 2.2533$	−0.9931	13, 45, 81, 96, 96 (16, 39, 80, 95, 97)
2c	$R_M = -0.4998(C) + 1.5614$	−0.9932	22, 46, 73, 90, 90 (23, 47, 67, 91, 90)
3a	$R_M = -0.2188(C) + 0.5372$	−0.9996	44, 57, 69, 78 (44, 57, 69, 78)
3b	$R_M = -0.2574(C) + 0.4260$	−0.9955	55, 69, 80, 88 (54, 71, 79, 88)
3c	$R_M = -0.1795(C) + 0.0462$	−0.9975	67, 76, 82, 88 (68, 75, 82, 88)
4a	$R_M = -0.2321(C) + 1.1173$	−0.9992	18, 28, 39 (18, 28, 39)
4b	$R_M = -0.2491(C) + 1.3149$	−0.9981	13, 21, 32 (13, 22, 32)
4c	$R_M = -0.4241(C) + 1.1503$	−0.9833	33, 57, 78 (31, 62, 76)
5a	$R_M = -0.2452(C) + 0.8407$	−0.9922	31, 44, 58 (30, 46, 57)
5b	$R_M = -0.1463(C) + 0.5945$	−0.9574	33, 41, 49 (32, 44, 48)
5c	$R_M = -0.2268(C) + 0.2604$	−0.9915	61, 72, 82 (60, 74, 81)

* Calculation were made by means of a Texas Instruments Programmable Slide-rule Calculator SR-56.

** Number of carbon atoms in one of the co-ordinated amino acids.

TABLE IV

CARBON-INCREMENTS OF SOME OF THE HOMOLOGOUS SERIES OF COMPLEXES

Solvent system	*Complex*			
	(+)-cis-O-trans-NH_2 $[CoNH_3Am_2NO_2]$	*(−)-Meridional(1,2,6) $[CoNH_3Am(NO_2)_3]^-$*	*(+)-cis-NO_2-trans-NH_2,NH_3 $[Co(NH_3)_2Am(NO_2)_2]$*	*(+)-trans-NO_2-cis-NH_2 $[Co(NH_3)_2Am(NO_2)_2]$*
5	−0.250	−0.219	−0.245	−0.232
6	−0.362	−0.257	−0.146	−0.249
7	−0.281	−0.180	−0.227	−0.424

−0.9574), for all the complexes studied, there might be established a very high degree of negative correlation between the R_M values and the number of carbon atoms in coordinated aminocarboxylato-ligands. Table III also shows the good agreement between the experimental and calculated R_F values (using the regression-line equation).

From Table IV, it can be seen that the carbon-increments obtained with the same solvent system for different homologous series of complexes are different, even for homologous series of different geometrical isomers. This is evident from the results obtained with solvent systems 6 and 7. However, the results obtained with solvent system 5 show that, in some cases, similar increments are obtained for complexes having different compositions or showing different geometrical isomerism.

Thus, for the first time, we have shown that the previously established linear relationship between the number of carbon atoms in homologous series of some organic compounds and their R_M values in paper chromatography is also valid for aminocarboxylato-ligands in mixed cobalt(III) complexes.

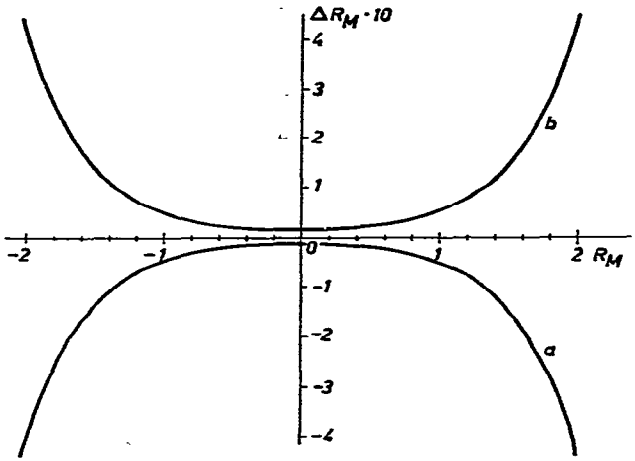

Fig. 6. R_M value errors corresponding to: (a) +0.01 R_F value error; and (b) −0.01 R_F value error.

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