Journal of Chromatography, 481 (1989) 471–476
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 21 766

Note

Effect of the chelate ring size of diamine cobalt(III) complexes on their R_F values obtained by paper chromatography

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(Received May 12th, 1989)

The effect of the chelate ring size of diamine cobalt(III) complexes on their R_F values obtained by paper chromatography has so far been investigated only in one instance, in which Ćelap *et al.*[1] chromatographed 35 cobalt(III) complexes containing five- and/or six-membered ligands. By the use of ten solvent systems it was established that enlargement of the chelate ring causes an increase in the R_F values of metal complexes. A linear dependence was found between the R_M values and the number of five-membered rings substituted by the corresponding six-membered rings. Continuing these investigations, in this work we studied the effect of seven-membered rings of the diamine type.

EXPERIMENTAL

All the investigated complexes were prepared according to procedures reported in the literature (Table I). Chromatographic separations were carried out by the ascending method on Whatman No. 1 paper strips (23 × 3 cm), as described in detail previously[2].

RESULTS AND DISCUSSION

As can be seen from Table I, the effect of the chelate ring size of diamine ligands of cobalt(III) complexes was studied by chromatographing 21 cationic and neutral complexes. With the exception of tris(diamine) complexes, the investigated complexes contained, in addition to diamine, some of the following ligands: glycinato, (*R*)-alaninato and/or nitro ligands. Chromatographic separations were achieved with 14 solvent systems containing an organic component and water, and sometimes also an electrolyte (mineral acid or salt). The composition of the solvent systems applied is given in Table II. As can be seen from Table I, in all the instances studied the R_F values of metal complexes increased with enlargement of the chelate ring size. A linear dependence was also found between the chelate ring size and the R_M values of the investigated complexes (Figs. 1–4). In all the instances studied the straight lines had a negative slope.

From the above, it can be concluded that the earlier established rule[1], according

0021-9673/89/$03.50

TABLE I

R_F VALUES OF THE INVESTIGATED COMPLEXES OBTAINED BY PAPER CHROMATOGRAPHY

No.	*Isomer*	*Absolute configuration*	*Complex*[a]	*Ref.*	$R_F \times 100$[b]													
					1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*
1	*cis*-(NO_2), *trans*-(NH_2)-		$[Co(NO_2)_2glyen]$	3	30	58	63	52	40	63	69	86	41	38	26	67	82	–
2			$[Co(NO_2)_2glytn]$	4	43	66	79	64	49	75	82	94	51	51	42	78	87	–
3			$[Co(NO_2)_2glytmd]$	5	56	73	86	75	59	88	90	98	60	64	68	84	92	–
4	*trans*-(NO_2)-		$[Co(NO_2)_2glyen]$	5	22	33	52	47	32	50	62	82	25	30	16	63	69	–
5			$[Co(NO_2)_2glytn]$	4	30	48	61	55	45	68	73	90	36	45	25	68	78	–
6			$[Co(NO_2)_2glytmd]$	5	40	64	67	62	58	81	81	95	51	59	36	72	87	–
7	*cis*-(NO_2)-		$[Co(NO_2)_2en_2]^+$	6	23	43	70	44	49	19	71	91	38	44	68	67	86	11
8			$[Co(NO_2)_2tn_2]^+$	7	41	62	80	62	65	31	76	–	55	61	87	82	94	19
9			$[Co(NO_2)_2tmd_2]^+$	5	66	80	90	83	78	52	83	–	72	77	97	96	98	30
10	*trans*-(NO_2)-		$[Co(NO_2)_2en_2]^+$	6	13	29	49	38	45	5	61	90	28	32	60	56	77	5
11			$[Co(NO_2)_2tn_2]^+$	7	32	41	64	55	63	10	72	–	45	56	87	72	90	13
12			$[Co(NO_2)_2tmd_2]^+$	5	43	77	84	66	76	29	82	–	64	70	94	84	95	26
13			$[Coen_3]^{3+}$	8	21	10	62	56	–	13	75	64	36	14	36	63	60	16
14			$[Cotn_3]^{3+}$	8	32	15	76	71	–	22	80	94	52	51	45	72	76	24
15			$[Cotmd_3]^{3+}$	9	52	24	87	85	–	46	87	–	72	83	58	82	89	32
16	*cis*-(NO_2)-	$-(+)_{589}-$	$[Co(NO_2)_2(R\text{-ala})en]$	10	39	64	76	52	47	80	85	94	58	47	37	71	91	35
17			$[Co(NO_2)_2(R\text{-ala})tn]$	10	55	78	86	68	62	85	90	98	70	63	51	83	95	49
18			$[Co(NO_2)_2(R\text{-ala})tmd]$	5	68	87	94	79	75	90	94	–	79	73	66	93	98	64
19	*trans*-(NO_2)-	$-(-)_{589}-$	$[Co(NO_2)_2(R\text{-ala})en]$	10	48	67	77	57	50	82	87	96	60	51	39	75	94	38
20			$[Co(NO_2)_2(R\text{-ala})tn]$	10	64	81	88	74	66	87	91	–	72	66	55	86	97	51
21			$[Co(NO_2)_2(R\text{-ala})tmd]$	5	76	90	95	82	78	94	95	–	82	79	70	94	–	66

[a] glyH = glycine; *R*-alaH = (*R*)-alanine; en = 1,2-diaminoethane; tn = 1.3-diaminopropane; tmd = 1,4-diaminobutane.
[b] The compositions of the solvent systems are given in Table II.

TABLE II

SOLVENT SYSTEMS USED

No.	*Composition*	*Proportions*[a]
1	Isopropanol–water–conc. HNO_3	75:20:5 (v/v/v)
2	Ethyl acetate–ethanol–water	50:30:20 (v/v/v)
3	Acetone–water–conc. HNO_3	75:20:5 (v/v/v)
4	Ethanol water conc. HNO_3	75:20:5 (v/v/v)
5	Ethanol–water	80:20 (v/v)
6	Dioxan–water	80:20 (v/v)
7	Dioxan–water–KI	75:25:1 (v/v/w)
8	Phenol saturated with water	
9	Methanol–water–LiCl	90:10:5 (v/v/w)
10	Phenol–ethanol–water	10:70:20 (w/v/v)
11	Cyclohexanone–ethanol–water–KI	60:25:15:1 (v/v/v/w)
12	Tetrahydrofuran–water–conc. HNO_3	65:30:5 (v/v/v)
13	Pyridine–water–KI	80:20:1 (v/v/w)
14	Cyclohexanol–ethanol–water–conc. HNO_3	50:25:15:10 (v/v/v/v)

[a] v Refers to volume in millilitres; w refers to weight in grams.

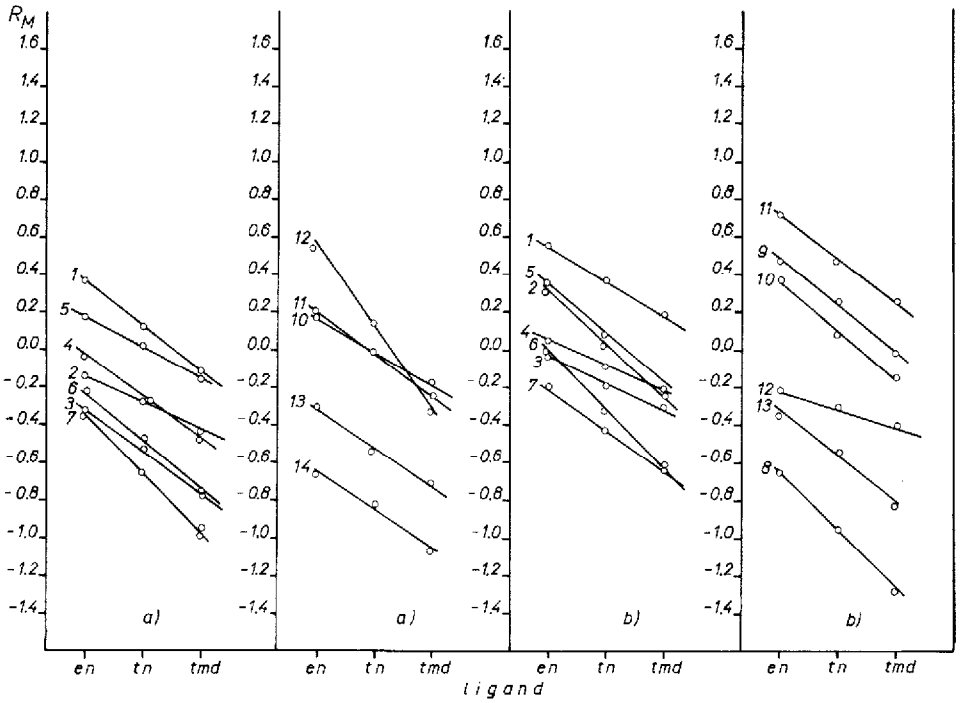

Fig. 1. Dependence of the R_M values on the chelate ring size of the following complexes (see Table I): (a) 1–3; (b) 4–6. The numbers on the lines refer to the solvent systems used (see Table II).

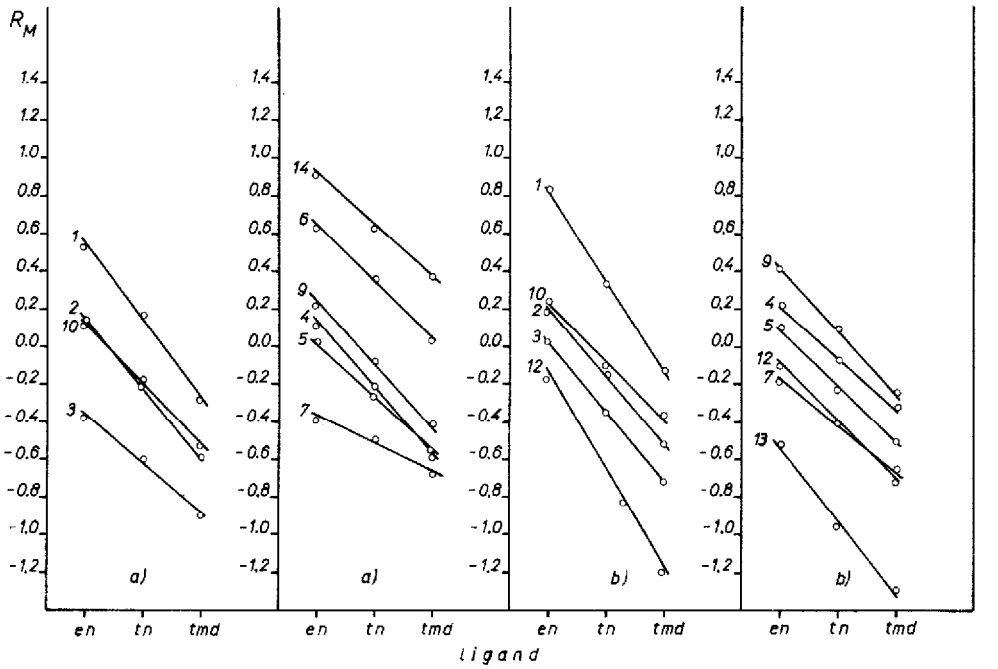

Fig. 2. Dependence of the R_M values on the chelate ring size of the following complexes (see Table I); (a) 7–9; (b) 10–12. The numbers on the lines refer to the solvent systems used (see Table II).

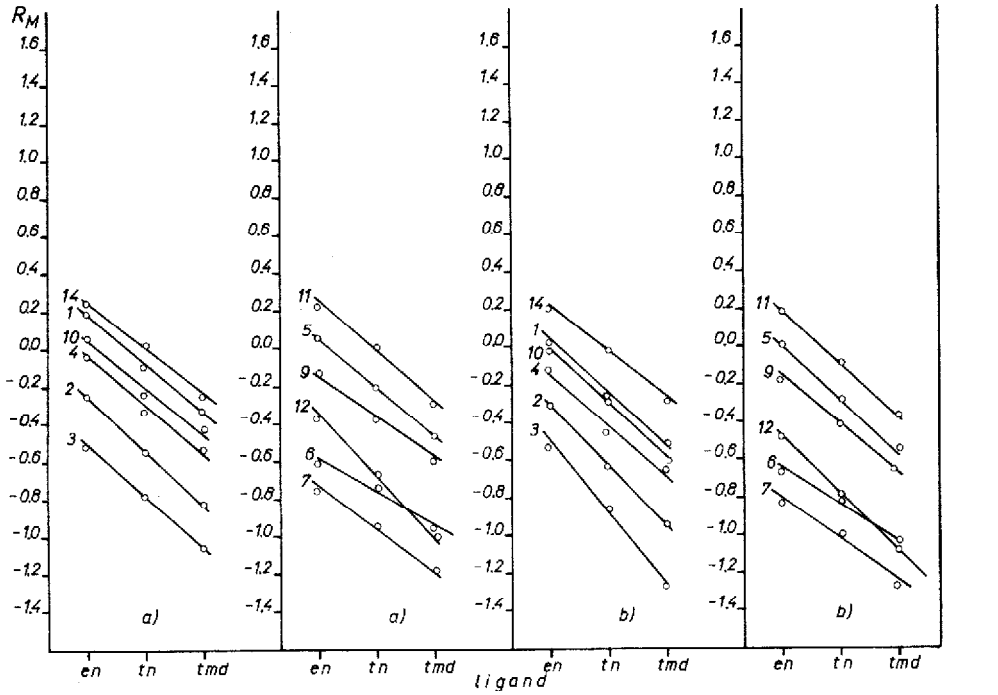

Fig. 3. Dependence of the R_M values on the chelate ring size of the following complexes (see Table I): (a) 13–15; (b) 16–18. The numbers on the lines refer to the solvent systems used (see Table II).

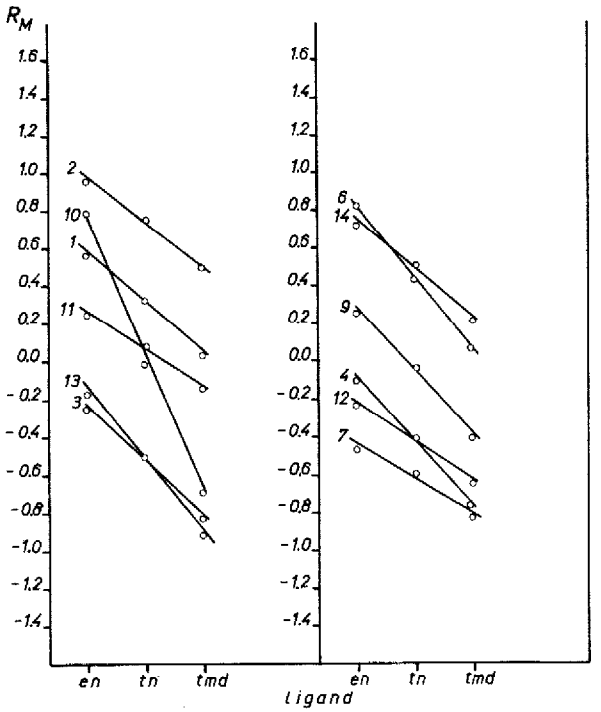

Fig. 4. Dependence of the R_M values on the chelate ring size of complexes 19–21 (see Table I). The numbers on the lines refer to the solvent systems used (see Table II).

to which the R_F values obtained by paper chromatography increase with enlargement of the chelate ring size of metal complexes, is valid also for seven-membered rings. It is worth mentioning that this regularity had already been established in thin-layer chromatographic separations on silica gel by the use of single-component solvent systems, with the exception of water[11]. As regards the mechanism of the separation on paper performed in this study it may be assumed that "normal" phase partition chromatography is involved, as it is known that analogous compounds possessing a larger hydrophobic part exhibit higher R_F values, owing to their greater solubility in the mobile phase[12]. Hence a new possibility is offered for the determination of the composition of the corresponding complexes.

ACKNOWLEDGEMENT

The authors are grateful to the Serbian Research Fund for financial support.

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