

The effect of β -ketoiminato ligand substituents of copper(II) and nickel(II) complexes on R_F values obtained by thin-layer chromatography on silica gel

RADA M. BAOŠIĆ and ŽIVOSLAV Lj. TEŠIĆ*

Faculty of Chemistry, University of Belgrade, Studentski trg 16, P.O.Box 550, YU-11001 Belgrade, Yugoslavia

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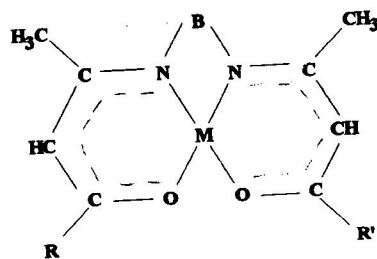
The effect of β -ketoiminato ligand substituents on the R_F values of 36 metal complexes of Cu(II) and Ni(II) obtained by thin-layer chromatography on silica gel, was investigated. The chelate ligand was prepared by condensing a diamine with a β -diketone. Three series of complexes were prepared (Fig. 1) in which the ligand contained ethylenediamine (en) as the amine part, whereas acetylacetone (acac) and/or benzoylacetone (phacac); acetylacetone and/or trifluoroacetylacetone (tfac) and benzoylacetone and/or trifluoroacetylacetone were used as β -diketones. In addition, three analogous series containing propylenediamine (pn) instead of ethylenediamine were also prepared. Finally, the separation mechanism for the investigated complexes is discussed.

The effect of β -ketoiminato ligand substituents on the R_F values of metal complexes obtained by thin-layer chromatography on silica gel has hitherto not been investigated. Several papers have dealt with the separation of these complexes by the HPLC method,¹⁻⁴ mainly by the reversed-phase mode,¹⁻³ the normal-phase mode being applied only in one paper.⁴ Thus, using HPLC, Clark *et al.*⁴ separated on silica gel columns (Spherisorb SGP 8 μ m and Partisil 10 μ m) (25 cm \times 4 cm) tetradentato- β -ketoiminato complexes of the type $[M(acac_n tfac_{2-n} dm)]$, where M = Cu(II), Ni(II) and Pd(II); dm = 1,2-diaminoethane or 1,2-diaminopropane; acac = 2,4-pentanedionato ion; tfac = 1,1,1-trifluoro-2,4-pentanedionato ion; and $n = 0-2$. These authors found that non-fluorinated chelates of the three metals are much more strongly retained than semi-fluorinated or fully fluorinated analogs. Besides, the substitution of a single CF₃-group was found to greatly reduce the column interaction, while a second group substitution only marginally reduced retention further.

The effect of β -diketonato ligand substituents of (tris)- β -diketonato complexes of Co(III), Cr(III) and Ru(III), was also investigated by thin-layer chromatography on silica gel.⁵ It was found that the substitution of acetylacetone ligands by dibenzoylmethanato ligands caused an increase in the R_F values of the investigated complexes if nonaqueous solvent systems were used. These findings were explained by the corresponding adsorption separation mechanism. However when aqueous solvent systems

* Author for correspondence

were applied, a reversed order of complexes was obtained. In this manner it was shown that nonmodified silica gel can also be used for the reversed-phase chromatography.



R	R'	B	
CH ₃	CH ₃	en	M(acac ₂ en)
CH ₃	CF ₃	en	M(acactfacen)
CH ₃	CF ₃	en	M(1fac2en)
CF ₃	CF ₃	en	M(acacphacacen)
CH ₃	C ₆ H ₅	en	M(phacac ₂ en)
C ₆ H ₅	C ₆ H ₅	en	M(phacactfacen)
C ₆ H ₅	CF ₃	pn	M(acac ₂ pn)
CH ₃	CH ₃	pn	M(acactfacpn)
CH ₃	CF ₃	pn	M(1fac2pn)
CF ₃	CF ₃	pn	M(acacphacacpn)
CH ₃	C ₆ H ₅	pn	M(phacac ₂ pn)
C ₆ H ₅	C ₆ H ₅	pn	M(phacactfacpn)
C ₆ H ₅	CF ₃	pn	

en = -CH₂CH₂-; pn = -CH(CH₃)CH₂-; M = Cu(II), Ni(II)

Fig. 1. General structure of investigated tetradentate β -ketoimine complexes.

In this work we wanted to examine the effect of β -ketoiminato ligand substituents of Cu(II) and Ni(II) complexes, using a greater number of complexes and applying a greater number of solvent systems for their chromatographic separation on thin-layers of silica gel, as well as to compare the results of these investigations with those obtained on HPLC columns⁴ and silica gel thin-layers.⁵

EXPERIMENTAL

Syntheses

All ligands and complexes were prepared according to the earlier described procedures cited in Table I.

Chromatography

Chromatographic separations were carried out by horizontal thin-layer chromatography on silica gel plates (5×10 cm) (HPTLC Fertigplatten Kieselgel 60 für die Nano-DC, Merck, Germany). For this purpose a Camag HPTLC Chamber under the Tank Configuration Developing Conditions was used. Standard solutions (2 mg/cm³) of the investigated complexes were prepared in acetone and the plates were spotted

TABLE I. hR_F values of investigated complexes

No	Complex ^a	Ref. for synth.	hR_F^b																											
			1	2	3	4	5	6	7	8	9	10	11	12	13	14														
			Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni										
1	M(acac ₂ en)	6,7	19	19	4	7	10	8	18	22	41	44	28	30	12	16	25	41	15	22	7	13	5	12	36	36	12	17	27	31
2	M(acacphacac ₂ en)	8	40	42	7	15	19	14	29	26	72	53	40	43	16	27	39	46	31	42	26	34	13	27	48	55	31	40	52	53
3	M(phacac ₂ en)	7,8	59	55	11	22	33	28	46	45	83	78	49	53	36	40	53	54	53	56	59	60	26	35	67	69	56	58	63	59
4	M(acac ₂ en)	6,7	21	21	4	7	9	10	20	24	43	42	28	29	12	18	23	43	17	20	7	13	6	14	36	36	10	17	29	31
5	M(acactfac ₂ en)	4,8	48	45	11	14	21	19	35	30	60	56	42	45	25	31	42	47	44	44	34	39	14	30	52	56	40	46	54	55
6	M(tfac ₂ en)	6,9	54	54	14	18	24	29	44	40	64	66	46	50	30	39	48	56	49	52	44	50	20	34	65	48	54	60	58	
7	M(tfac ₂ en)	6,9	53	56	12	17	25	30	46	40	66	68	48	48	28	38	47	57	47	54	44	51	20	32	64	69	54	63	58	
8	M(tfacphacac ₂ en)	8	57	56	12	24	35	30	46	47	81	76	48	54	38	38	55	57	51	54	60	61	26	37	68	69	54	60	63	58
9	M(phacac ₂ en)	7,8	57	56	12	24	35	30	46	47	81	76	48	54	38	38	55	57	51	54	60	61	26	37	68	69	54	60	63	58
10	M(acac ₂ pn)	6,7	20	20	4	7	10	9	19	23	44	44	28	28	14	16	25	40	18	22	9	13	6	12	35	34	12	17	30	31
11	M(acacphacac ₂ pn)	8	48	46	9	14	25	16	33	38	79	56	46	43	26	27	42	48	40	45	31	37	21	37	48	65	34	46	51	55
12	M(phacac ₂ pn)	7,8	60	60	14	30	35	29	48	50	87	82	57	54	44	44	57	59	66	66	28	47	72	72	58	61	63	61		
13	M(acac ₂ pn)	6,7	19	21	5	7	11	10	17	22	42	42	30	30	15	17	25	41	18	20	10	15	6	12	37	34	12	19	31	32
14	M(acactfac ₂ pn)	4,8	50	49	11	14	28	23	37	39	68	58	48	46	28	33	44	49	48	47	44	49	23	35	55	67	45	49	52	55
15	M(tfac ₂ pn)	6,8	58	55	14	21	33	30	47	41	70	67	52	51	40	40	51	57	54	56	53	57	28	45	68	69	56	62	57	
16	M(tfac ₂ pn)	6,8	60	54	14	19	34	31	46	42	69	68	51	49	38	38	50	59	54	58	51	55	60	47	70	58	60	63	57	
17	M(tfacphacac ₂ pn)	8	60	58	14	28	34	31	46	49	87	83	58	56	44	44	58	59	57	58	64	64	30	47	70	58	60	63	59	
18	M(phacac ₂ pn)	7,8	60	58	14	28	34	31	46	49	87	83	58	56	44	44	58	59	57	58	64	64	30	47	70	58	60	63	59	

^aen = 1,2-diaminoethan; pn = 1,2-diaminopropan; acac = 2,4-pentanedionato ion, i.e., acetylacetonato ion; phacac = 1-phenyl-1,3-butanedionato ion, i.e., benzoylacetonato ion; tfac = 1,1,1-trifluoro-2,4-pentanedionato ion, i.e., trifluoroacetylacetonato ion.

^bCompositions of solvent systems in Table II; $hR_F = 100 \times R_F$

TABLE II. Solvent systems used

No	Composition	Proportions (v/v)
1	Dichloromethane	
2	1,2-Dichlorbenzene	
3	1,2,3,4-Tetrahydronaphthalene	
4	Chloroform	
5	<i>n</i> -Amyl acetate	
6	Benzene-tetrahydrofuran	70 : 30
7	Chloroform – carbon tetrachloride	90 : 10
8	Acetone – benzene	30 : 70
9	Benzene – dichloromethane	10 : 90
10	Toluene – dichloromethane	40 : 60
11	Toluene – dichlorbenzene	20 : 80
12	Benzene – ethyl methyl ketone	20 : 80
13	Dichloromethane – carbon tetrachloride	80 : 20
14	Acetonitrile – benzene	20 : 80

with 0.2 μ l aliquots of freshly prepared solutions. Before development, the spotted plates were saturated with vapours of the solvent system being used (Table II). All solvents used were of analytical reagent grade. After development, the spots of individual complexes were visible, owing to their natural colours.

RESULTS AND DISCUSSION

The chromatographic investigation of the aforementioned substituent effect was carried out with 36 complexes of Cu(II) and Ni(II). For chromatographic separations, 14 solvent systems were applied, five single component and nine two-component (Table II). The obtained R_F values are given in Table I.

As seen from Table I, the substitution of acetylacetone by trifluoroacetylacetone and benzoylacetone, respectively, in the ligand of β -ketoiminato complexes, gives rise to an increase in the R_F values of the investigated complexes. This increase is considerably greater in the case of substituting a single acetylacetone and much smaller in the case of substituting a second acetylacetone. The same trend was observed in the substitution of trifluoroacetylacetone by benzoylacetone in the ligand of β -ketoiminato complexes.

The results obtained are in agreement with those reported by Clark *et al.*⁴ in chromatographic separations of β -ketoiminato complexes in which acetylacetone was substituted by trifluoroacetylacetone, in conditions of HPLC, as well as with results obtained by Tešić *et al.*⁵ in thin-layer chromatography on silica gel of (tris)- β -diketonato complexes of Co(III), Cr(III) and Ru(III) in which acetylacetone was substituted by dibenzoylmethane. These findings are consistent with the generally accepted separation mechanism for complexes on silica gel¹⁰ in conditions of normal phase chromatography, based on the specific interactions of these complexes with the

sorbent which include the formation of hydrogen bonds between the silanol groups of silica gel and ligator atoms (O, N) of the chelates. For the investigated complexes, the strength of the hydrogen bonds is affected by two factors, namely by inductive and steric effects.¹¹ Thus, due to the negative inductive effects of CF₃- and C₆H₅- groups, the electron density on ligator oxygens of β -ketoiminato ligands is smaller than in the case of acetylacetone, and that causes the formation of weaker hydrogen bonds with the sorbent and the greater mobility of the investigated complexes. Also, the substitution of acetylacetone by trifluoroacetylacetone and benzoylacetone, respectively, due to the presence of CF₃- and C₆H₅- groups gives rise to steric hindrance so that the approach of the ligator oxygen and nitrogen to silanol groups of silica gel is rendered more difficult which results in the increased mobility of such complexes.

In addition, in all the investigated cases it was found that the β -ketoiminato complexes which contain propylendiamine instead of ethylendiamine, exhibited higher R_F values than the corresponding complexes with ethylendiamine. It is known in the TLC separations that when monocomponent solvent systems are used the R_F values of the investigated complexes depend on two factors: the strength of the adsorption of the dissolved substance to the adsorbent and the solubility of the substance in the solvent system used.¹²⁻¹⁴ As can be seen from Table I, in chromatographic separation of the investigated β -ketoiminato complexes using non aqueous solvent systems the first factor had the major influence because of their similar solubility in organic solvents.¹⁵

Finally, from Table I it is also seen that in most cases the R_F values of β -ketoiminato complexes of Ni(II) are higher than those of the corresponding Cu(II) complexes.

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ИЗВОД

УТИЦАЈ СУПСТИТУЕНТА β -КЕТОИМИНАТО ЛИГАНДА КОМПЛЕКСА БАКРА(II) И НИКЛА(II) НА R_F -ВРЕДНОСТИ КОЈЕ СУ ДОБИВЕНЕ ХРОМАТОГРАФИЈОМ НА ТАНКОМ СЛОЈУ СИЛИКА-ГЕЛА

РАДА М. БАОШИЋ И ЖИВОСЛАВ Љ. ТЕШИЋ

Хемијски факултет Универзитета у Београду, Студентски трг 16, п.пр. 158, 11001 Београд

Испитиван је утицај супституента β -кетоиминато лиганда на R_F -вредности 36 металних комплекса Cu(II) и Ni(II) које су добивене хроматографијом на танком слоју силика-гела. Хелатни лиганд је добивен кондензацијом диамин са β -дикетоном. Награђене су три серије комплекса (Слика 1) у којима је лиганд као амински део садржавао етилендиамин (en) док је као β -дикетон узиман ацетил-ацетон (асас) и/или бензоил-ацетон (phasас), ацетил-ацетон и/или три-флуороацетил-ацетон и бензоил-ацетон и/или трифлуороацетил-ацетон. Поред ових награђене су и три аналоге серије које су уместо етилендиамина садржавале пропилендиамин (pn). Најзад, дискутован је механизам одвајања испитиваних комплекса.

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