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Research Article

SPECTROPHOTOMETRIC STUDY OF COBALT(II) COMPLEX FORMATION WITH QINAZOLONE-4

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ABSTRACT

This article discusses spectrophotometric study of cobalt(II) complex formation with qinazolone-4.

KEYWORDS

Methanol, qinazolone-4, spectrophotometric study.

INTRODUCTION

Methanol solutions of sulfate, nitrate and chloride of cobalt(II) in the region of 400-700 nm have one absorption band at about 515 nm with a molar absorption coefficient Ɛ=8 (Fig. 1). The light absorption law is observed for solutions at least up to a cobalt concentration of 0.12 M. In the visible region of the spectrum, methanol solutions of quinazolone-4 and its potassium salt do not absorb.

THE MAIN RESULTS AND FINDINGS

When KHz solutions and cobalt salts are mixed, an intense violet color of the solutions appears, the absorption spectra of which have a maximum at 560 nm (Fig. 1), which indicates the complex formation of cobalt ions with quinazolone.

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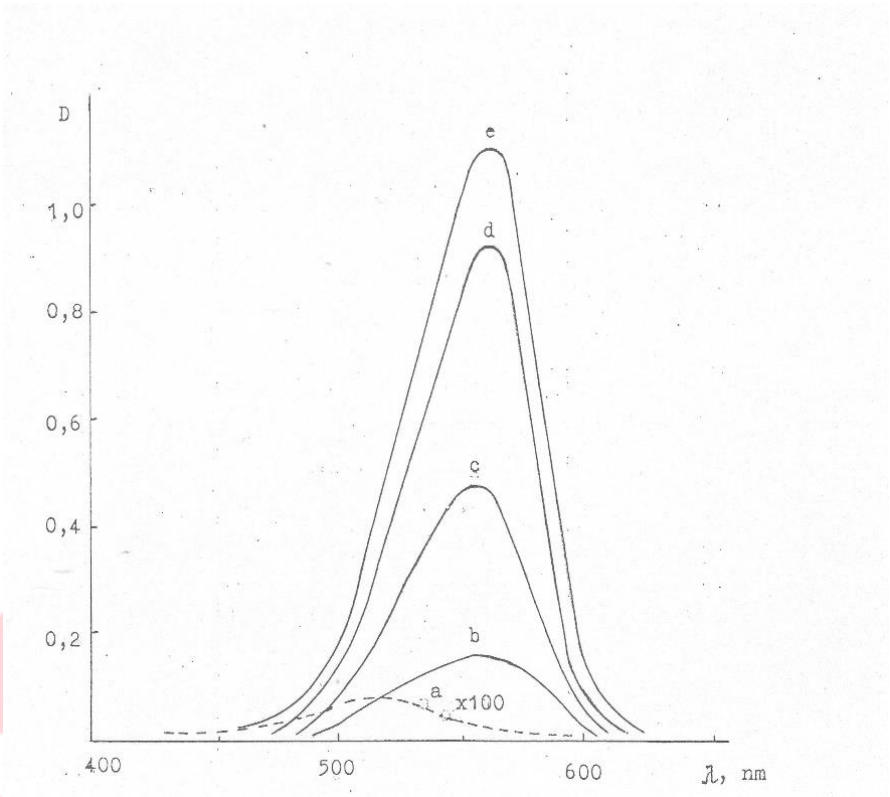

Рис. 1. ЭСП $CoCl_2.6H_2O$ (a) и в присутствии KHz (b-e) в метаноле.

CCo=10-3 M, CKHz=0 (a); 0,02 M (b); 0,035 M (c); 0,05 M (d) и 0,15 M (e).

To determine the composition and stability of the complex, the dependence of the optical density of the absorption band maximum of the complex on the ligand concentration at a constant metal concentration was studied. With an increase in the Hz content in the solution, the optical density of the complex increases and reaches its maximum at a 100-fold excess of the ligand, regardless of the chosen metal salt (Fig. 2). Obviously, in this case, the entire cobalt ion is bound into a complex and its concentration will be equal to the concentration of the initial metal. Therefore, the molar absorption coefficient of the complex is Εком=Do/CM.L. In all three cases, close values are calculated Εком=(1,1±0,1).103. This value is more than 100 times higher than the values of the extinction of solutions of the initial cobalt salts.

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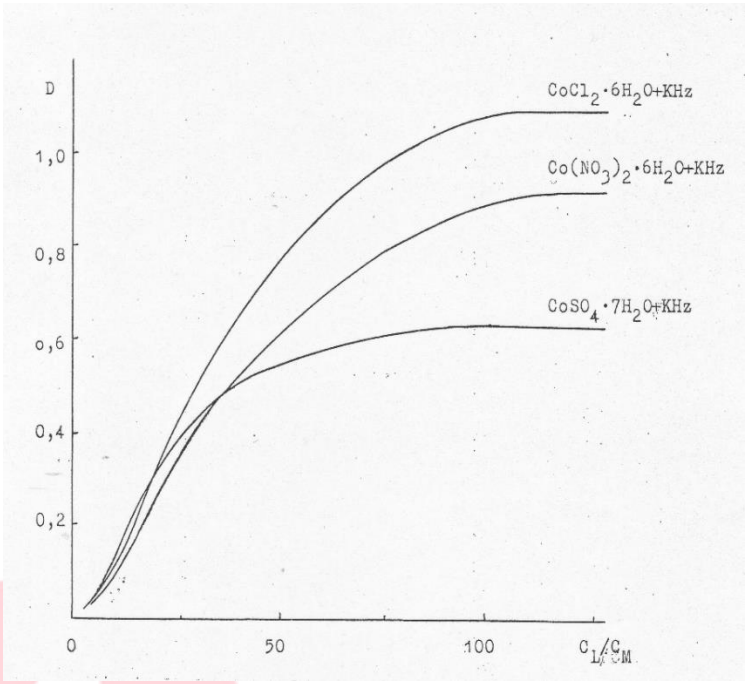

Rice. 2. Absorption saturation curve (λ=560 nm).

The above experiment makes it possible to determine the composition and stability of the complex by the methods of equilibrium shift, Babko and Foster [1]. In table. Tables 1-3 show the spectrophotometric parameters of the complex formation of quinazolone-4 with chloride, sulfate, and cobalt(II) nitrate, necessary for calculating the composition and stability by these three methods.

According to the equilibrium shift method (Fig. 3), the dependence of the optical density of the complex on the concentration of the ligand at a constant metal concentration coordinates lgD/Do – D и lg[C] represents parallel straight lines with an angle of inclination tgα=2, which indicates the formation of a complex of composition Me:L=1:2.

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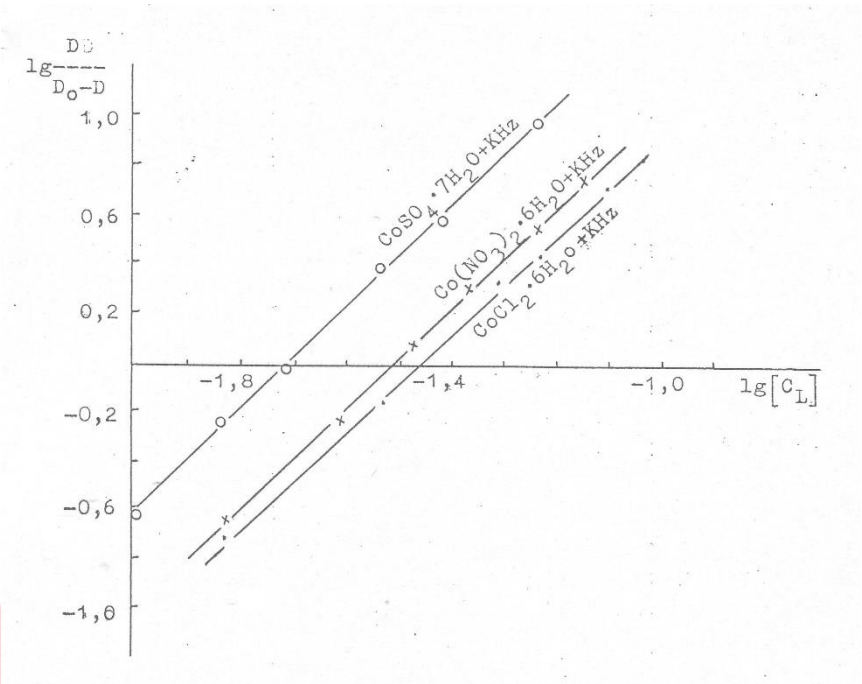

Рис. 3. Dependency Plots lgD/Do-D от lg [CL].

This composition is also confirmed by the Foster method. Dependencies D/CLn from D only in case n=2 (composition of the complex) are straight lines (рис. 4), т.е. two independent methods confirm the formation of a composition complex 1:2.

Since, regardless of the chosen cobalt salt, one complex is formed, which has an absorption band at 560 nm, it becomes obvious that the complex does not include anions SO42-, Cl-, NO3-. Therefore, quinazolone-4 enters complex formation in the form of a monobasic anion.

For the potassium salt Hz, it was found that the metal replaces the nitrogen proton in position 3 [2]. On this basis, for the cobalt complex with quinazolone-4, one can assume the formation of an ionic bond with nitrogen and a coordination bond with carbonyl oxygen to form a four-membered metallocycle.

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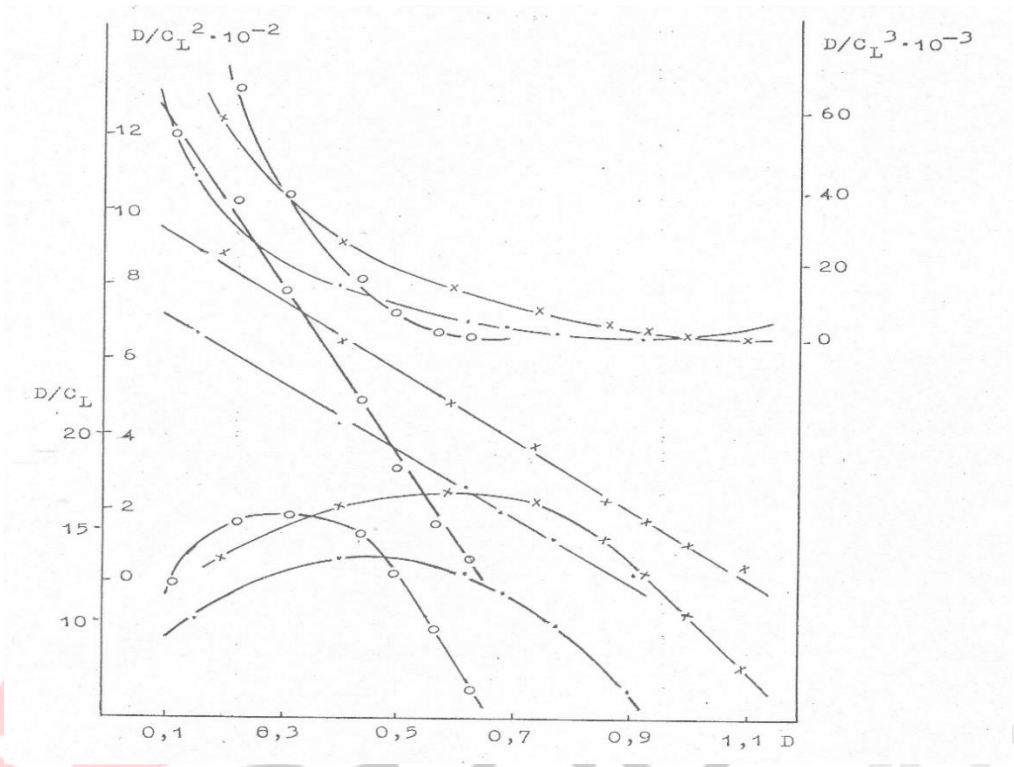

Рис. 4. Dependency Plots D/CLn от D. – o – CoSO4.7H2O + KHz,

– . – Co(NO3)2.6H2O + KHz, – x – CoCl2.6H2O + KHz.

Table 1.

Spectrophotometric parameters of complexation

CoCl2.6H2O+nKHz в метаноле. Co=10-3M, λмак=560 нм, L=1см.

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C_L, 10^{-2} M	D	$[C_k]$, 10^{-4} M	$[C_L]$, 10^{-2}	$Lg[C_L]$	$lgD_i/(D_0-D_i)$	$(lg[C_L])^2$	$lgD_i/D_0-D_i \cdot lg[C_L]$	C_L^2, 10^{-4} M^2	C_L^3, 10^{-6} M^2	D/C_L, M^{-1}	D/C_L^2, 10^2 M^2	D/C_L^3, 10^3 M^3
15,0	1,10	6,00	14,940									
7,5	0,93	5,07	7,399	-1,131	0,74	1,29	-0,84	56,25	421,9	12,40	1,65	2,20
6,0	0,86	4,69	5,90	-1,229	0,54	1,52	-0,67	36,00	216,0	14,33	2,39	3,98
4,5	0,74	4,04	4,42	-1,355	0,31	1,85	-0,42	20,25	91,13	16,44	3,65	8,12
3,5	0,59	3,22	3,43	-1,464	0,06	2,15	-0,09	12,25	42,88	16,86	4,82	13,76
2,5	0,40	2,18	2,45	-1,610	-0,24	2,60	0,39	6,25	15,63	16,00	6,40	25,59
1,5	0,20	1,09	1,48	-1,830	-0,65	3,36	1,19	2,25	3,38	13,33	8,89	59,17
	3,32		25,09	-8,620	0,76	12,77	-0,437		89,36	27,80	112,82	

C_L, 10^{-2} M	D_i	$[C_k]$, 10^{-4} M	$[C_L]$, 10^{-2}	$lg[C_L]$	lgD_i/D_0-D_i	$(lg[C_L])^2$	$lgD_i/D_0-D_i \cdot lg[C_L]$	C_L^2, $10^{-4}M^2$	C_L^3, 10^{-6} M^2	D/C_L, M^{-1}	D/C_L^2, 10^2M^2	D/C_L^3, 10^3M^3
15,0	0,92	6,00	14,880	-0,827								
8,0	0,77	5,02	7,900	-1,102	0,71	1,22	-0,78	64,00	512,0	9,63	1,20	1,50

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6,0	0,68	4,43	5,911	-1,278	0,45	1,51	-0,55	36,00	216,0	11,33	1.89	3,15
5,0	0,62	4,04	4,920	-1,307	0,32	1,71	-0,42	25,00	125,0	12,40	2,48	4,96
3,0	0,40	2,61	2,948	-1,530	-0,11	2,34	0,17	9,00	27,0	13,33	4,44	14,81
1,5	0,15	0,98	1,480	-1,830	-0,71	3,35	1,30	2,25	3,4	10,00	6,67	44,12
	2,62		23,16	-6,99	0,66	10,13	-0,29			56,69	16,68	68,54

Table 3

Spectrophotometric parameters of complexation

$CoSO_4 \cdot 7H_2O$+nKHz в метаноле. Co=10^{-3}M, $\lambda_{мак}$=560 нм, L=1см.

C_L, 10^{-2} M	D_i	$[C_K]$, 10^{-4} M	$[C_L]$, 10^{-2}	$lg[C_L]$	lgD_i/D_0-D_i	$(lg[C_L])^2$	$lgD_i/D_0-D_i lg[C_L]$	C_L^2, $10^{-4}M^2$	C_L^3, 10^{-6} M^2	D/C_L, M^{-1}	D/C_L^2,10^2M^2	D/C_L^3,10^3M^3
11,0	0,63	6,00	8,880	-1,052								
6,0	0,57	5,40	5,892	-1,230	0,98	1,51	-1,20	36,00	216,0	9,50	1,58	2,64
4,0	0,50	4,76	3,905	-1,408	0,58	1,98	-0,82	16,00	64,0	12,50	3,13	7,81
3,0	0,44	4,19	2,916	-1,535	0,38	2,36	-0,58	9,00	27,0	14,67	4,89	16,29
2,0	0,31	3,00	1,940	-1,712	0,00	2,93	0,00	4,00	8,0	15,75	7,88	39,37
1,5	0,23	2,19	1,456	-1,837	-0,24	3,37	0,44	2,25	3,4	15,33	10,22	67,65
1,0	0,12	1,14	0,977	-2,010	-0,63	4,04	1,27	1,00	1,0	12,00	12,00	120,0
	2,80		23,97	-10,774	1,07	16,19	-0,89			79,75	39,70	253,76

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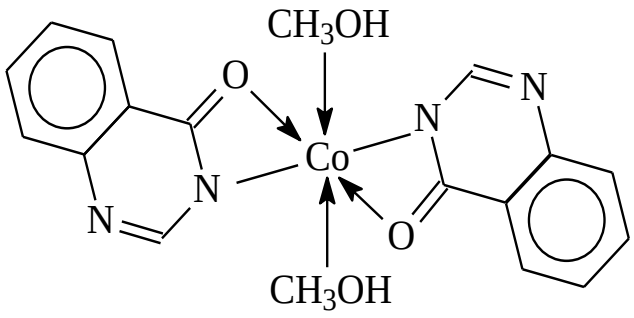
The most probable octahedral structure in solution is formed due to the coordination of two solvent molecules to the axial positions of the square planar complex.



The observed band at 560 nm corresponds to the most intense transition $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ octahedral cobalt complex [3]. The remaining two weak transition bands $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ и $^4T_{1g} \rightarrow {}^4T_{1g}(F)$ in the region of 1250 and 500 nm, we did not detect them due to the impossibility of recording the spectrum with this device, as well as due to overlapping by a strong band at 560 nm.

As expected, the instability constant of the complex, determined by the three methods, gives close values corresponding to low-stability complexes.

Table 4

Logarithm of the instability constant (lgK) of the complex Co(Hz)2.2CH3OH

Комплексообразование хиназолона-4 с	По Фостеру	По Бабко	По сдвигу равновесия
$CoSO_4 \cdot 7H_2O$	-3,38	-3,41	-3,42
$CoCl_2 \cdot 6H_2O$	-2,97	-3,02	-3,00
$Co(NO_3)_2 \cdot 6H_2O$	-2,92	-2,94	-2,92

CONCLUSION

Thus, based on the study of the complexation of the potassium salt of quinazolone-4 with sulfate, chloride and cobalt nitrate by the photometric method, the formation of an unstable complex Co(Hz)2.2CH3OH. The maximum light absorption of the methanol solution of the complex is observed at 560 nm, the molar light absorption coefficient – 1,1.103. An octahedral structure of the complex with two molecules of the quinazolone-4 anion in the equatorial plane and two molecules of methanol in the axial

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positions of the complex is proposed. The ligand is bidentately coordinated through oxygen and nitrogen atoms, forming a four-membered metallocycle [4].

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