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ON THE DIOXIMINE COMPLEXES OF TRANSITION METALS. PART XCVII. α-SUBSTITUTED OXIME DERIVATIVES IN THE SPECTROPHOTOMETRIC DETERMINATION OF COBALT[1]

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Abstract

The formation conditions, composition, stability and analytical application of some ternary complexes: Co(II):L^1:X=1:2:2(L^1=aliphatic and alycyclic α-dioximes; X=N_3^-, I^-), binary derivatives: Co(II):L^2=α-ketoximes: diacetylmonoxime, methyl-isopropyl dione monoxime, 1,2,3-cyclohexane trione dioxime (1,3)), Co(II): L^3=1:2 (L^3=condensation products of ketoximes with semicarbazide, thiosemicarbazide) and Co(II):L^4=Schiff's bases with ethylenediamine and hydrazine) were studied spectrophotometrically. The electronic spectra of these complexes were recorded and discussed.

Keywords: α-substituted oxime derivatives, spectrophotometric determination of cobalt.

Introduction

The interest in cobalt cheletes with α-substituted oxime derivatives is increased in a great extent in the last decades. The structure of the 'cobalamines' and other B_{12}-vitamine type cobalt derivetives is very similar to that of some cobalt compounds with α-dioximes. This phenomenon makes possible the study 'in vitro' of the biochemical activity of the abovementioned vitamin and other chelates of this class [1, 2].

Mixed cobalt(III)-dioximines of the type $Co(Diox.H)_2XY$ ($Diox.H_2$-aliphatic, Alycyclic dioximes, X=Y, X≠Y=Cl, Br, I, NO_2^-, N_3^-, SO_3^{-2}, NSC^-, $NSCe^-$) take part in various substitution reactions, which have been studied from kinetic point of view in our previous papers [3–9].

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The oxidation state of the central metal atom varies from Co(I) to Co(III) depending on the nature of anions, reducing agents present in solution, pH-value tec, and can be tessted, generally, by ESR measurements. The Co(II) gives a well defined ESR signal [10, 11].

Besides the α-dioximes, — from preparatiive and analytical point of view — only very little attention was given to the other α-substituted oxime chelating agents, α-amino-, ..hydroxy-, ketoximes and their condensation products with hydrazine, semicarbazide, thiosemicarbazide, etc. [12–15].

Results and Discussion

Cobalt(II)-α-dioxime Systems

Cobalt(II) salts give colour reactions with α-dioximes. The complexes can be stabilized in aqueous solutions in the absence of oxygen. The deaeration with inert gases (N_2, CH_4, argon) or the addition of reducing agents ensure favourable conditions for this purpose. Generally, in aqueous solutions and in solvent mixtures (water-alchohol, water-dioxane, water-acetone, DMF, DMSO, etc.) cobalt(II) derivatives of this type are oxidized rather rapidly, depending on the nature of the oxidizing agent (air, H_2O_2, free halogens, etc.). Some anions and neutral ligands with higher nucleophylic character (e.g. I^-, NCS^-, $NCSe^-$, phosphines) were observed to stabilize to some extent this oxidation state of cobalt [19, 20].

Spectrophotometric and potentiometric studies [21, 22] show that one can presume a monodeprotonation reaction with formation of $CoX_2(Diox.H)(Diox.H_2)$ and the stability of the complexes to increase in the order:

$$X: Cl < Br < I < NCS.$$

We have observed that the pH-value of the $CoX_2(Diox.H_2)$-solutions ($Diox.H_2$ = glyoxime, dimethylglyoxime, propoxime, alycyclic dioximes) influences the colour of the formed complexes. Higher pH-values promote the shift of the VIS absorption band towards lower frequency values and indcreases also the absorptivity of the solutions. In the case of the mixed dimethylglyoximine derivative: $Co(DH)_2(Ph_3P)_2$ a $Co(II) \longrightarrow Co(I) + Co(III)$ disproportion with colour change was mentioned [23] in strongly alkaline media:

$$Co(DH)_2(Ph_3P)_2 + HO^- \longrightarrow Co(DH)_2(Ph_3P) + Co(DH)_2(Ph_3P)(OH).$$

The IR spectral studies of some $Co(DH)_2A_2$ type derivatives isolated from organic solvents (A_2 – alcohols, dioxan, Ph_3P) prove an octahedral structure stabilized by two intramolecular O-H··O hydrogen bridges with a coplanar $Co(DH)_2$-grouping.

The results of our qualitative tests concerning the colour reactions in CoX_2-dioxime systems at various pH values are presented in *Table 1.*

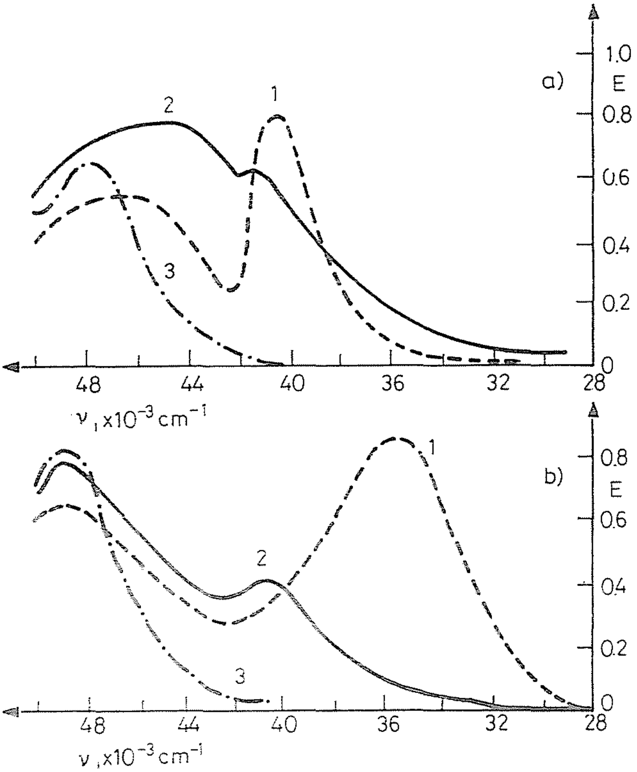

Fig. 1. Electronic spectra of 1. $[Co(DH)_2(N_3)_2]$; 2. $[Co(Furox.H)_2(N_3)_2]$; 3. $[Co(II)\text{-}(N_3)H_2O]$; *a*) pH = 3.29; *b*) pH = 9.62

As an example, the electronic spectra of the $Co(DH)_2(N_3)_2$ and $Co(Furox.H)_2(N_3)_2$ complexes – in comparison with those of the Co(II)-$(N_3)H_2O$-system are shown in *Fig. 1.*

The sensitivity of these colour reactions is the greatest in the presence of N_3^-, and they can also be used for analytical purposes. The formation of the azido-complexes was studied in the systems $Co(NO_3)H_2$-dioxime-NaN_3, by using Job's method. The curves shown in *Fig. 2* were recorded

Table 1
Colour reactions in Co^{2+}-Diox.H_2-X^- systems

Diox.H_2	X^-	pH	Medium	Colour
Glyoxime		3.29	In dil.	Colourless
	Br^-	6.80	ethanol	Green-yellow
(*Colourless)		9.62	0.5–1%	Yellow
		3.29		Light yellow
	I^-	6.80		Green-yellow
		9.62		Dark yellow
		3.29		Colourless
	NCS^-	6.80		Light yellow
		9.62		Yellow
		3.29		Light yellow
	N_3^-	6.80		Dark yellow
		9.62		Yellow-brown
Dimethyl		3.29	In dil.	Light yellow
glyoxime	Br^-	6.80	ethanol	Light yellow
(*Light yellow)		9.62	0.5–1%	Yellow
		3.29		Yellow
	I^-	6.80		Yellow
		9.62		Dark yellow
		3.29		Light yellow
	NCS^-	6.80		Yellow
		9.62		Yellow
		3.29		Yellow
	N_3^-	6.80		Reddish-yellow
		9.62		Brown
Furyldioxime		3.29	In dil.	Light yellow
	Br^-	6.80	ethanol	Light yellow
(*Light yellow)		9.62	0.5–1%	Dark yellow
		3.29		Light yellow
	I^-	6.80		Dark yellow
		9.62		Range
		3.29		Light yellow
	N_3^-	6.80		Reddish-brown
		9.62		Brown

Table 1
continued

Diox.H_2	X^-	pH	Medium	Colour
Propoxime	Br^-	4.10		Light yellow
		9.62		Yellow
	I^-	4.10		Orange
		9.62		Dark orange
	NCS^-	4.10		Light yellow
		9.62		Yellow
	N_3^-	4.10		Reddish
		9.62		Brown-orange
1,2-Cyclopentane-dione dioxime	Br^-	4.10		Colourless
		9.62		Light yellow
	I^-	4.10		Light yellow
		9.62		Dark yellow
(*Colourless)	NCS^-	4.10		Colourless
		9.62		Light yellow
	N_3^-	4.10		Reddish-brown
		9.62		Dark brown
1,2-Cyclohexane-dione dioxime	Br^-	4.10		Colourless
		9.62		Yellow
	I^-	4.10		Yellow
		9.62		Orange
(*Colourless)	NCS^-	4.10		Colourless
		9.62		Yellow
	N_3^-	4.10		Dark orange
		9.62		Brown

*$Co(NO_3)_2$+Diox.H_2 in the absence of nucleophilic anions at pH∼ 4

by mixing $Co(NO_3)_2$ solutions with equimolecular binary solutions of the corresponding α-dioximes and NaN_3.

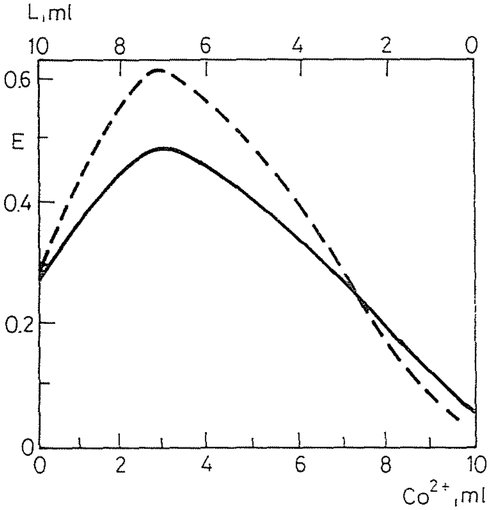

Fig. 2. Job curves of - - - $[Co(DH)_2(N_3)_2]$; —— $[Co(Furox.H)_2(N_3)_2]$; at pH = 2.56

The maximum absorption (at 35000 (38000) cm^{-1}) corresponds to a molar ratio of 1:2. This result is in good agreement with the formation of $Co(Diox.H)_2(N_3)_2$ type complexes.

To stabilize the Co(II)-chelate forms we have added an excess of Na_2SO_3 or $NH_2OH.HCl$ and Britton-Robinson buffer solutions to the systems studied.

Cobalt(II)-α-ketoxime and Condensation Derivatives Systems

The qualitative tests for the colour reactions at various pH values in the presence and absence of nucleophilic anions in $Co(NO_3)_2$-chelating agent systems are presented in *Table 2.*

The data in the Table show that the intensity of the colour generally increases with increasing pH also in the absence of nucleophilic anions. Nucleophilic anions (I^-, N_3^-) modify the optical properties only with α-ketoximes. In such cases one can presume the formation of ternary complexes (formation of Co-L-X). When using the condensation products of the ketoximes for this reaction the mentioned changes cannot be observed in the optical properties of the systems with the exception of the ethylenediamine derivative (presumably formation of Co-L only).

For our spectrophotometric studies diacetylmonoxime, methyl-iso-propyl-2,3-diione-monoxime(2), 1,2,3-cyclohexane-trione-dioxime(1,3) and their condensations products with semicarbazide, thiosemicarbazide and ethylendiamine were used.

The electronic spectra of the coloured complexes were recorded in dilute ethanol (1:3) in the presence of Na_2SO_3 or $NH_2OH.HCl$ as reducing agents. The spectral data are presented in *Table 3.*

The electronic spectra of Co(II)-diacetyl-monoxime-thio-semicarbazone, Co(II)-bis-diacetylmonoxime-ethylendiimine and Co(II)-bis-1,2,3-cyclo-hexane-trione-dioxime(2)-ethylendiimine at various pH values are presented in *Figs 3–5.*

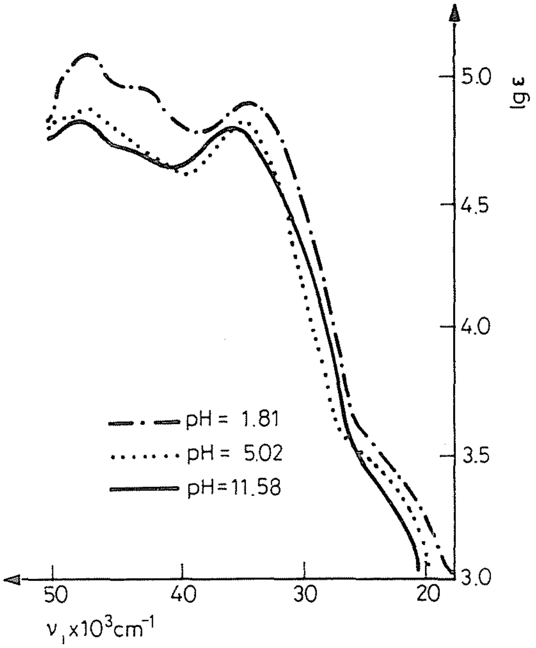

Fig. 3. Electronic spectra of Co(II)-diacetylmonoxime-thiosemicarbazone at various pH-values

The spectra indicate that the position, and in some cases also the number of the absorption bands show differences in acidic and basic media. This phenomenon suggest the existence of some protolytic equilibria in the studied systems. Further spectrophotometric and potentiometric measurements are required to the clarify this problem.

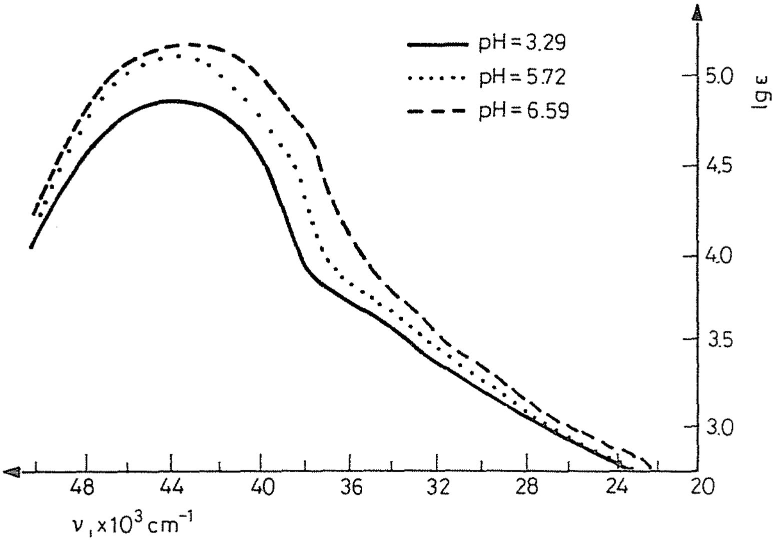

Fig. 4. Electronic spectra of Co(II)-bis-diacetylmonoxime-ethylenediimine at various pH-values

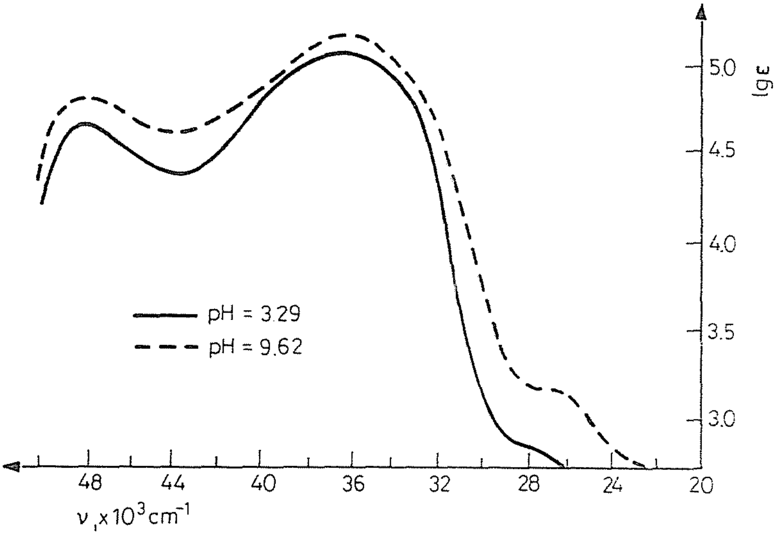

Fig. 5. Electronic spectra of Co(II)-bis-1,2,3-cyclohexane-trione-dioxime(1,3)-ethylenediimine(2) at various pH-values

Table 2

Colour reactions of $Co(NO_3)_2$ with α-ketoxime derivatives

Oxime	Anion	pH	Medium	Colour
Diacetylmonoxime (*Colourless)	Br^-	4.10	In dil. (1:3) ethanol	Light yellow
		9.62		Light yellow
	I^-	4.10		Yellow
		9.62		Yellow
	NCS^-	4.10		Colourless
		9.62		Light yellow
	N_3^-	4.10		Violet
		9.62		Violet
Methyl-isopropyl-2,3-dione-monoxime(3) (*Colourless)	I^-	4.10		Yellow
		9.62		Yellow
	N_3^-	4.10		Violet
		9.62		Violet
Diacetylmonoxime thiosemicarbazone (*Yellow)	I^-	4.10		Yellow
		9.62		Orange
	N_3^-	4.10		Yellow
		9.62		Orange
1,2,3-Cyclohexane-trione dioxime(1,3) (*Yellow)	I^-	4.10		Dark yellow
		9.62		Orange
	N_3^-	4.10		Reddish-brown
		9.62		Brown
1,2,3-Cyclohexane-trione dioxime semicarbazone(2) (*Yellow)	I^-	4.10		Yellow
		9.62		Yellow
	N_3^-	4.10		Yellow
		9.62		Yellow
1,2,3-Cyclohexane-trione dioxime thiosemicarbazone(2) (*Brown)	I^-	4.10		Brown
		9.62		Brown
	N_3^-	4.10		Brown
		9.62		Brown
Ethylene-diimino-bis-diacetylmonoxime (*Yellow)	Br^-	4.10		Light yellow
		9.62		Yellow
	I^-	4.10		Reddish-orange
		9.62		Orange
	NCS^-	4.10		Light yellow
		9.62		Yellow
	N_3^-	4.10		Red-violet
		9.62		Red-brown

Table 2
continued

Oxime	Anion	pH	Medium	Colour
Ethylene-diimino-bis-1,2,3-cyclohexane trione dioxime(2)	Br^-	3.29	In dil. (1:3) ethanol	Dark yellow
		6.80		Yellow
		9.62		Orange
	I^-	3.29		Orange
(*Orange)		6.80		Orange
		9.62		Reddish-orange
	NCS^-	3.29		Orange
		6.80		Orange
		9.62		Orange
	N_3^-	3.29		Orange
		6.80		Reddish-orange
		9.62		Red-brown

*$Co(NO_3)_2$+oxime derivatives in the absence of nucleophilic anions

Table 3
Electronic spectral data of some Co(II)-α-substituted oxime derivatives (pH = 3–5)

Ligand	$\tilde{\nu}_1.10^{-3}$ cm^{-1}	log ε_1	$\tilde{\nu}_2.10^{-3}$ cm^{-1}	log ε_2	$\tilde{\nu}_3.10^{-3}$ cm^{-1}	log ε_3
Diacetylmonoxime thiosemicarbazone	21-22	3.1-3.3	34-35	4.70	43-44	4.60
Methyl-isopropyl-2,3-dione-monoxime(2) thiosemicarbazone(3)	21-22.5	3.0-3.15	34-35	4.65	44-45	4.60
bis-1,2,3-Cyclo hexane-trione dioxime(1,3) ethylene-diimine	24-26	3.0-3.25	33-36	4.80	47-48	4.70
bis-diacetyl monoxime ethylene-diimine	21-23$_i$	2.6-2.8	26-29$_i$ 34-36$_i$	3.2-3.75	43.5-46	4.50

i = inflexion point

The composition of the chelates formed was determined also by means of the continuous variation method. The Job curves of the Co(II)-ketoxime systems (n derivatives) are presented in *Fig. 6.*

Analogous measurements with the condensation products of aliphatic and alicyclic ketoximes with thiosemicarbazide, ethylenediamine and hydrazine are presented in *Figs 7–9.*

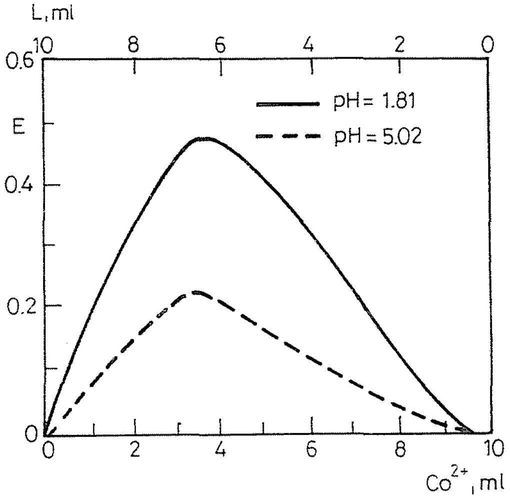

Fig. 6. Continuous variation curves for the system Co(II)-diacetyl-monoxime

The experimental data are shown in *Table 4.*

The α-ketoximes act as bidentate ligands and form Co : L = 1:2 type chelates with pentaatomic heterocycles.

The condensation products of the above mentioned ketoximes with semicarbazide and thiosemicarbazide are tridentate ligands and the complexes formed have also a Co : L = 1:2 composition in a wide pH range.

The chelating agents derived from ketoximes and 1,2-diamines (en, pn, hydrazine) are tetradentate and hexadentate ligands, respectively (the latter in the case of 1,2,3-cyclohexane-trione-dioxime derivatives). The Job curves in *Figs 8–9* are in agreement with the formation of Co : L = 1:1 complexes. The increase in colour intensity by addition of NaI or NaN_3 suggests also in these cases formation of ternary Co-L-X complexes, probably with octahedral structure.

Presumably, in the case of the hexadentate ligands, the free oxime group promotes the formation of dimeric and polymeric structures, especially in basic media.

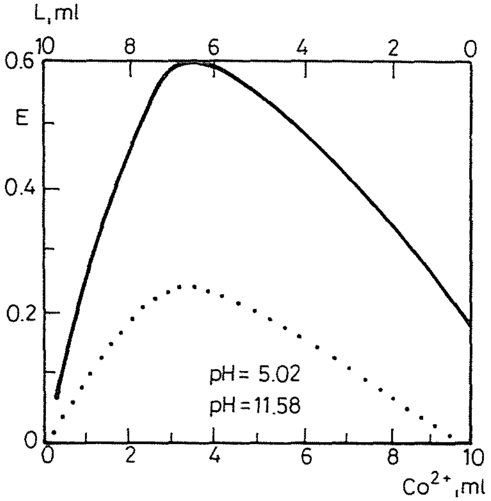

Fig. 7. Continuous variation curves for the system Co(II)-1,2,3-cyclohexane trione dioxime (1,3) thiosemicarbazone (2)

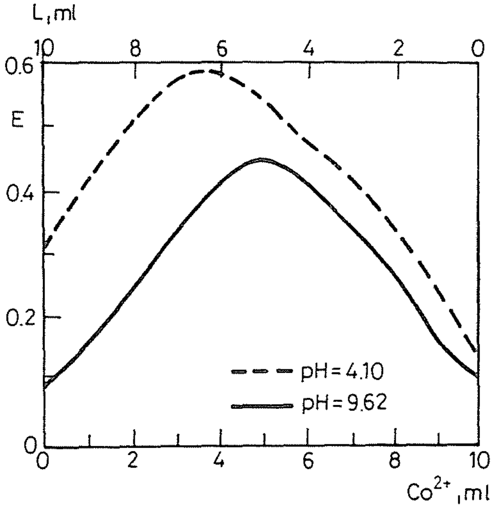

Fig. 8. Continuous variation curves for the system Co(II)-bis-diacetylmonoxime-ethylenediimine

The shape of the Job curves enabled us to determine the stability constant only for the Co(II)-bis-diacetylmonoxime-azine system (*Fig. 10*).

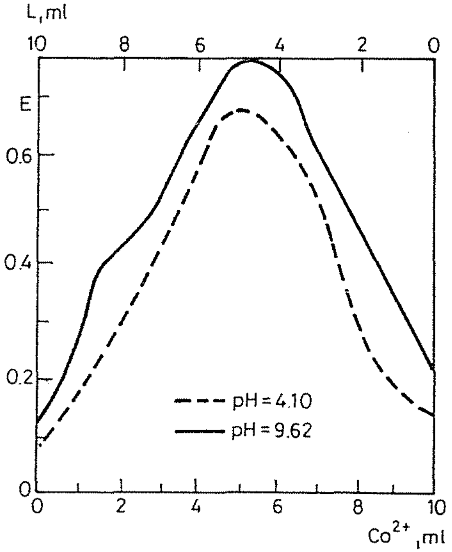

Fig. 9. Continuous variation curves for the system Co(II)-1,2,3-cyclohexane trione dioxime (1,3)-ethylenediimine

Since the curve indicates a molar ratio of 1:1 for the complex, by adding V ml of 10^{-2} mol/l solution of Co(II) to (5-V)ml of 10^{-2} mol/l solution of the ligand L the concentration of the different species in the expression of the stability constant

$$K = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]}$$

can be calculated as

$$[\mathrm{ML}] = \frac{E}{2E_\infty}10^{-2};\ [\mathrm{M}] = \Big(\frac{V}{5} - \frac{E}{2E_\infty}\Big)10^{-2};\ [\mathrm{L}] = \Big(\frac{5-V}{5} - \frac{E}{2E_\infty}\Big)10^{-2};$$

respectively, where E means the absorptivity of the sample and E_∞ the absorptivity corresponding to the intersection of the extrapolations straight line portions of the Job curves constructed for the extreme compositions (pure components).

The results are presented in *Table 5.*

Analytical applications. The binary (Co-L) and ternary (Co-L-X) complexes studied are reagents of medium sensitivity for the analytical detection of cobalt(II).

Table 4
Compositions of Co(II)-α-substituted oxime chelates

Ligand	Composition	Method	
	Co : L	Job	Molar ratio
Diacetyl-monoxime	1:2	1:2	1:2
Methyl-isopropyl-2,3-dione-monoxime(2)	1:2	1:2	1:2
Diacetyl-monoxime thiosemicarbazone	1:2	1:2	—
Methyl-isopropyl-2,3-dione-monoxime(2)1:2 thiosemicarbazone	1:2	—	
bis-Diacetylmonoxime-azine	1:1	1:1	1:1
bis-Diacetylmonoxime-ethylene-diimine	1:1	1:1	1:1
bis-Methyl-isopropyl-2,3-dione-monoxime(2) ethylene-diimine	1:1	1:1	—
bis-1,2,3-Cyclohexane trione dioxime(1,3) ethylene-diimine	1:1	1:1	1:1

(pH-range = 3.3–11)

Table 5
Stability constant of the CoL^4-chelate from spectrophotometric data (20 °C)

λ_{max}	E_∞	E	V, ml	$K.10^{-2}$	$\bar{K}$
400 nm	1.4	0.48	1.0	1.54	
		0.58	1.5	1.05	
		0.63	2.0	1.01	
		0.66	2.5	1.16	1.5×10^{-2}
		0.62	3.0	1.31	
		0.54	3.5	1.60	
		0.42	4.0	2.31	
		0.20	4.5	2.15	
440 nm	0.57	0.28	1.5	2.14	
		0.30	2.0	1.55	
		0.33	2.5	1.72	1.8×10^{-2}
		0.27	3.0	1.51	

L^4 = hydrazine-bis-diacetylmonoxime

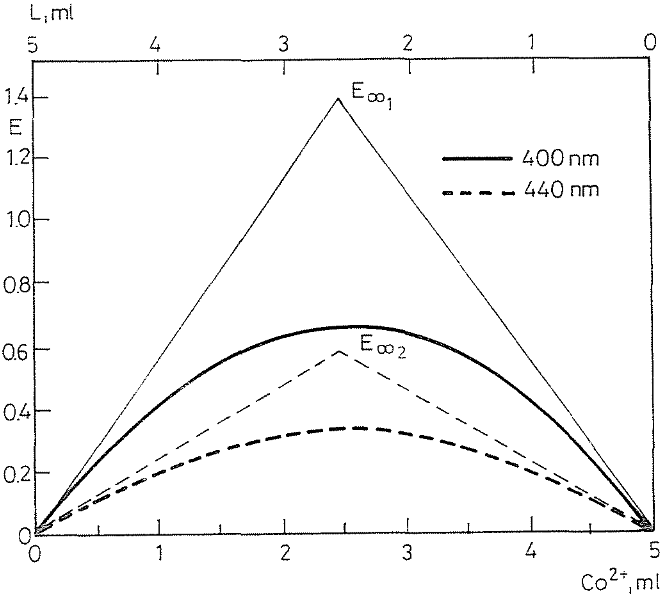

Fig. 10. Deriving of the stability constant from the continuous variation curves of the system at 20 °

	Detection limits	
Reagent	acidic media pH=3-4.5	basic media pH=8-9
Dimethylglyoxime+NaN_3	10-14 ppm	10 ppm
Furyldioxime+NaN_3	10 ppm	8 ppm
Diacetylmonoxime+NaN_3	15 ppm	10 ppm
Diacetylmonoxime thiosemicarbazone	15 ppm	10 ppm
bis-diacetylmonoxime ethylene-diamine+NaN_3	10 ppm	8 ppm
bis-1,2,3-Cyclohexane-trione dioxime(1,3) ethylene-diamine	10 ppm	8 ppm

The yellow to reddish-brown coloured solutions of the Co(II)-oxime systems obey Beer's law in mildly acidic and mildly basic solutions in a concentration range of $(0.2\text{-}10)\times10^{-4}$mol/l.

The spectrophotometric measurements were made in the presence of an excess of Na_2SO_3 to reduce interference from oxygen. The colour has a higher stability in mildly acidic media. The spectrophotometric measurements must be performed after 5 min standing. In the presence of air, during 4-5 hours the optical densities increase and eventually attain their maximum values corresponding to the completion of the oxidation: Co(II)⟶Co(III). Alkali, alkaline earth, Zn(II), Cd(II), Mn(II) and actinoid ions do not influence this analytical procedure.

Cu(II), Fe(II) and some heavy metals in the platinum group interfere with the determination of Co(II).

Experimental

The α-ketoximes: diacetylmonoxime, methyl-isopropyl-dione-(2,3)-monoxime(2), and 1,2,3-cyclohexane-trione-dioxime(1,3) were prepared by isonitrozation of the corresponding monoketones by gaseous ethylnitrite [16,17]. The crude products were recrystallized from water.

The condensation products with semicarbazide, thiosemicarbazide, hydrazine and diamines (en, pn) were obtained at room temperature (in some cases by boiling in alcoholic or aqueous solutions). The molar ratios of the components were: α-ketoxime: L = 1:1, and 2:1 (hydrazine, diamines) [18].

Electronic spectra in the visible ($c = 1 - 2 \times 10^{-3}$ mol/l) and UV regions ($10^{-4} - 10^{-5}$ mol/l) were recorded in ethanol-water mixtures (1:1) in the presence of Britton-Robinson buffer solutions and some crystals of Na_2SO_3 or $NH_2OH.HCl$, with a SPECORD Carl Zeiss spectrophotometer VSU (Germany). The colorimetric measurements were made with a FEK-colorimeter (USSR).

The series (isomolar and molar ratio) of sample solutions was prepared from 10^{-3} mol l^{-1} $Co(NO_3)_2$ and 10^{-3} mol l^{-1} reagent in aqueous-alcoholic media in the presence of 5-5 ml Britton-Robinson solutions and 2-2 ml Na_2SO_3 or $NH_2OH.HCl$ (2%) in 50-50 ml volume.

We mention that all pH values indicated in the present paper mean the pH of the Britton-Robinson buffer added and not the real pH of the solution, the latter being modified by the presence of ethanol. In the case of the isomolar series this modification is not very significant since the ethanol content did not exceed 10%.

In this paper the formation conditions of some cobalt(II)-chelates of the type $Co(Diox.H)_2$ -$X_2(Diox.H)_2$-α-dioxime, $X = Br^-, I^-, NCS^-, N_3{}^{-1}$) and some Co(II) derivatives with aliphatic and alicyclic α-ketoximes and their condensation products were studied by spectrophotometry.

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