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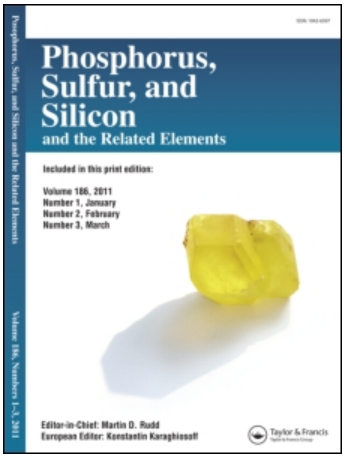

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COMPLEXING, REDOX AND EXTRACTIVE PROPERTIES OF CYCLIC AND ACYCLIC DERIVATIVES OF PHOSPHORUS DITHIOACIDS

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COMPLEXING, REDOX AND EXTRACTIVE PROPERTIES OF CYCLIC AND ACYCLIC DERIVATIVES OF PHOSPHORUS DITHIOACIDS

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Various types of acyclic and cyclic derivatives of phosphorus dithioacids form stable chelate complexes with nickel(II), cobalt(II) and silver(I) ions. Stability constants of these complexes and redox potentials of the systems disulfide/dithioacid have been determined. It has been shown that for each individual type of complex with dithiophosphoric, dithiophosphonic or dithiophosphinic ligands stability depends on the steric nature of the substituents at phosphorus. Correlations between the logarithm of stability constants and the sum of steric constants of substituents exist in these series. It is true also with regard both to a variation of redox potentials and reduction rate constants for copper(II) complexes.

Phosphorus dithioacids with cyclic substituents form less stable metal–ion complexes and can be used as selective extraction reagents.

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INTRODUCTION

Interest in transition metal complexes with sulfur-containing ligands is primarily caused by the needs of industry, biochemistry and agriculture.[1,2] Moreover, the process of complex formation is an interesting subject for theoretical research.

Among sulfur-containing ligands of great importance are the derivatives of phosphorus dithioacids. Phosphorus dithioacid anions are typical "soft" bases and form the most stable complexes with the metal ions belonging to the class of "soft" Lewis-type acids.[3]

Metal-ion chelate complexes with different types of phosphorus dithioacid derivatives have found extensive application and received widespread attention. Their structure, ESR, IR and UV spectra are being studied and theoretical calculations performed.[4–20]

As a rule, all the complexes of dithiophosphates studied with metals have a chelate structure with a pronounced delocalization of π-electron density in the chelate center.[7,8,12,18,19]

Complex compounds of phosphorus dithioacids with the ions of some metals at a high degree of oxidation are unstable owing to the markedly expressed reduction properties of dithioacids. In such cases, redox reactions occur and the corresponding disulfides are formed.[21–26]

Analysis of data concerning the complexation of metal ions with phosphorus dithioacids shows strong possibilities of using thiophosphorus derivatives as extractive reagents. It should be noted that for a number of specific problems of element isolation and separation it is necessary to study a broad range of this class of

compounds. In this respect phosphorus cyclic thioacids are of great interest. These compounds are known to form less stable complexes with a number of metals[16,17,27] owing to a higher electron-acceptor capacity of the dioxyalkylenic substituent, in comparison with alkoxy groups, at a phosphorus atom.[28] Their use can be expected to raise the selectivity of extraction and to produce new data for subsequent theoretical generalization concerning the complexation processes.

In the present communication, we have summed up the results of our previous investigations on the complexation of Ni(II), Co(II), Ag(I) and Cu(II) ions with a wide variety of acyclic and cyclic dithiophosphoric, dithiophosphonic and dithiophosphinic acids; their redox potentials are also presented.

All the acyclic and cyclic phosphorus dithioacids were synthesized as described in.[29-32] The procedures for spectrophotometric, potentiometric, calorimetric and kinetic determinations are described in.[17,33-38] The experimental values of stability constants ($\log\beta_2 \pm 0.07$) of Ni(II), Co(II) and Ag(I) complexes, redox potentials of the systems disulfide/dithioacid ($E^0 \pm 0.005$ V) and reduction rate constants for Cu(II) complexes are given in Table I.

TABLE I

Logarithms of stability constants ($\log\beta_2$) for Ni(II), Co(II) and Ag(I) complexes, redox potentials (E^0), reduction rate constants for Cu(II) complexes (k_2^{298}) and sums of the steric constants of substituents at phosphorus (E_s^0) in the ligands

No.	Substituents at phosphorus R, RO, O—R—O	$\log\beta_2$ Ni	Co	Ag	E^0, V	k_2^{298}, L/(mol · sec)	$-\Sigma E_s^0$
1	2	3	4	5	6	7	8
			Ligand R_2PSS^-				
1	C_2H_5	6.55	5.99	—	0.166	—	1.08
2	C_3H_7	6.84	6.37	—	0.157	2000	2.24
3	C_4H_9	7.02	6.40	—	0.150	1900	2.36
4	i-C_4H_9	7.88	7.05	—	0.130	320	4.52
5	C_6H_5	4.94	—	—	—	290	—
			Ligand $(RO)CH_3PSS^-$				
6	CH_3O	6.08	5.02	15.60	0.198	—	0.54
7	C_2H_5O	6.60	5.50	—	0.188	—	1.12
8	C_3H_7O	6.71	5.58	—	0.183	—	1.18
9	i-C_3H_7O	7.49	6.05	16.47	0.159	36.0	2.26
10	C_4H_9O	6.79	5.55	—	—	84.0	1.20
11	s-C_4H_9O	7.81	6.53	—	—	—	2.34
12	c-$C_6H_{11}O$	7.71	6.27	16.58	0.156	34.0	2.36
			Ligand $(RO)_2PSS^-$				
13	CH_3O	4.42	4.03	14.91	0.271	14.9	1.08
14	C_2H_5O	5.53	4.55	15.41	0.241	7.37	2.24
15	C_3H_7O	5.68	4.70	15.60	0.233	6.50	2.36
16	i-C_3H_7O	7.22	5.73	15.90	0.209	1.52	4.52
17	C_4H_9O	5.94	4.78	15.72	0.228	4.59	2.40
18	i-C_4H_9O	6.12	4.83	—	0.229	3.83	2.20
19	s-C_4H_9O	8.35	6.00	16.56	0.170	0.65	4.68
20	t-C_4H_9O	10.22	8.06	16.65	0.136	0.13	7.76
21	c-$C_6H_{11}O$	7.35	5.83	16.02	0.195	1.77	4.72
22	$C_6H_5CH_2O$	4.54	—	—	0.276	3.20	—
23	$C_2H_5OC_2H_4O$	—	—	—	0.300	45.0	—
24	ClC_2H_4O	—	—	—	0.326	1000	—

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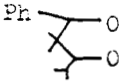
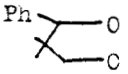
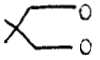
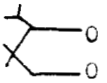
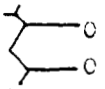
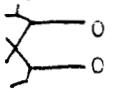
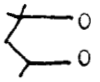
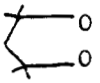
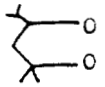
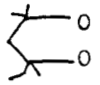
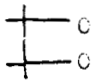
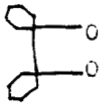
TABLE I (*Continued*)

No.	Substituents at phosphorus R, RO, O—R—O	$\log \beta_2$ Ni	Co	Ag	E^0, V	k_2^{298}, L/(mol · sec)	$-\Sigma E_s^0$
1	2	3	4	5	6	7	8
		Ligand R(O,O)PSS⁻					
25		< 3	< 3	—	0.325	57.0	—
26		< 3	< 3	—	0.330	230.0	—
27		4.20	3.52	14.84	0.315	151.0	—
28		4.41	3.99	15.24	0.267	58.3	—
29		4.07	3.05	—	0.347	—	—
30		3.95	3.55	15.02	0.307	47.8	—
31		4.40	3.75	—	0.274	44.6	—
32		3.89	3.64	—	—	—	—
33		5.86	4.84	15.66	0.218	21.0	—
34		7.33	5.67	15.85	0.187	4.40	—
35		6.14	4.80	—	0.202	12.0	—
36		7.49	5.78	—	0.175	1.66	—
37		4.27	—	—	—	—	—
38		6.22	4.60	15.37	0.271	0.05	—
39		7.02	5.32	—	—	—	—

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RESULTS AND DISCUSSION

Complexation of Ni(II), Co(II) and Ag(I) with Phosphorus Dithioacids

We have determined stability constants ($\log\beta_2$) in the series of phosphorus dithioacid complexes $M(SSPAB)_n$ (A and B = R, RO, O—R—O; M = Ni^{2+}, Co^{2+}, Ag^+; $n = 1, 2$).

These data are of great interest both for ascertaining the interrelation between the structure of the organophosphorus ligand and the properties of the complex compound and for predicting new analytical reagents.

Of interest in estimating the influence of substituents on stability constants in a series of similar complexes is the use of linear free-energy relationships in terms of the Hammett–Taft type equations that include σ, σ^{Φ}, E_s^0 and other constants of substituents at the phosphorus atom.

The experimental data (Table I) indicate that the reaction series in question are highly sensitive to the variation of substituents at the phosphorus atom. Comparison of the $\log\beta_2$ of Ni(II), Co(II) and Ag(I) complexes with $\Sigma\sigma^{\Phi}$ values for the constants of substituents at phosphorus[39] shows a marked tendency for the stability of complexes to decrease with the insertion of more acceptor substituents into the dithiophosphorus acid[14–17] (Eq. 1)

$$\log\beta_2 = \log\beta_2^0 + \rho\Sigma\sigma^{\Phi} \tag{1}$$

However, with the wide variety of available substituents (Table I), we do not observe a good correlation dependence (r 0.56).

Recent investigations have shown that the σ^{Φ} constants for RO groups at the phosphorus atom are complex, comprising the components of inductive, resonance and steric effects.[40–43] Each of these contributions can probably manifest itself in a specific way in the formation of complex compounds of chelate structure. Attempts at using sets of inductive (σ_I^{Φ}) or resonance (σ_R^{Φ}) constants of the substituents in equation (1) failed to produce the desired result.[39,43]

At the same time, in the series of nickel, cobalt and silver complexes with phosphorus dithioacids, an obvious tendency for their stability to increase with the

TABLE II

Parameters and characteristics of $\log\beta_2 = \log\beta_2^0 + \delta\Sigma E_s^0$ correlative dependences for ML_2 complexes

No. of series	L	M	$\log\beta_2^0$	δ	r	S_0	Nos. of points in Table I*
1	$(RO)_2PSS^-$	Ni(II)	3.81 ± 0.27	−0.831 ± 0.067	0.978	0.388	13–21
2	$(RO)_2PSS^-$	Co(II)	3.33 ± 0.12	−0.579 ± 0.031	0.990	0.179	13–21
3	$(RO)_2PSS^-$	Ag(I)	14.9 ± 0.2	−0.003 ± 0.047	0.904	0.266	13–17, 19–21
4	$(RO)CH_3PSS^-$	Ni(II)	5.65 ± 0.09	−0.875 ± 0.051	0.991	0.093	6–12
5	$(RO)CH_3PSS^-$	Co(II)	4.71 ± 0.14	−0.685 ± 0.079	0.968	0.143	6–12
6	R_2PSS^-	Ni(II)	6.06 ± 0.11	−0.400 ± 0.040	0.991	0.090	1–4
7	R_2PSS^-	Co(II)	5.67 ± 0.02	−0.301 ± 0.010	0.999	0.010	1–4

*In correlations are not included points Nos. 5, 22–24 having an electron-attracting groups at phosphorus.

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size and the degree of branching of the hydrocarbon radical in the ligand has been found.

Recent reports suggest that linear and branched alkyl groups differ but slightly in their electronic effect.[44,45] Stability variation in the above series (Table I) can be assumed to result mainly from steric effects.

This is confirmed by correlation with equation (2):

$$\log\beta_2 = \log\beta_2^0 + \delta\Sigma E_s^0 \qquad (2)$$

where δ is the reaction constant characterizing the sensitivity of a given reaction series to the steric effect of substituents in the ligand (ΣE_s^0). The ΣE_s^0 values for RO groups were calculated on the isostericity principle;[43,46] the parameters of correlation equations are shown in Table II.

The fact that the dependences are different for Ni(II) and Co(II) dithiophosphate, dithiophosphonate and dithiophosphinate complexes in the $\log\beta_2 - \Sigma E_s^0$ coordinates is associated with the difference between the electronic properties of alkyl and alkoxy radicals at phosphorus.

Negative δ values indicate that the stability of complexes increases with an increase in the steric effect of substituents in the ligand. It is possible that the steric factor can effectively manifest itself in the mutual repulsion of substituents in the ligands situated in the inner coordination sphere of the complex. The energy of such an interaction is primarily determined by geometric factors: the shape of the coordination center, the size of the central ion and of the ligands.

In particular, with an increase in the atomic radius of the central ion, the mutual repulsion of the ligands will decrease. This is in agreement with the decrease in the absolute value of δ in equation (2) as one passes from the Ni(II) (r ~ 1.24 Å) and Co(II) (r ~ 1.30 Å) series to the silver complexes (r ~ 1.44 Å). At the same time, a decrease in the correlation-constant value can be associated with the linear character of the coordination of ligands in the negatively charged complexes (ABPSS–Ag–SSPBA)$^-$, at which the substituents happen to be further away from the central ion than in planar-square and tetrahedral chelate Ni(II) and Co(II) complexes (ABP$\overset{S}{\underset{S}{\rightleftharpoons}}M\overset{S}{\underset{S}{\rightleftharpoons}}$PBA).[2]

An increase in complex stability following the introduction of a bulky substituent into the ligands can also be a result of a lesser solvation of the complex by the solvent molecules.[33] A study of the thermodynamic parameters of Ni(II) complexation with phosphorus dithioacids has shown that it is an endothermic process (ΔH = 36.8 – 54.5 kJ/mol) (Table III).

High positive ΔS values (269 to 317 J/mol · K) seem to be associated with the destruction of the solvate shell in the $Ni^{2+}_{solv.}$ ion that enters a complexation reaction with formation of a less solvated chelate complex.[47–49] Such positive entropic-factor values in the complexation of some metal cations have been noted in ref. 50.

As it follows from the experimental data, the $\log\beta_2$ values for Ni(II), Co(II) and Ag(I) complexes with cyclic dithiophosphorus ligands are, in general, smaller than for the complexes of acyclic ligands containing the same number of carbon atoms in the radicals. This is apparently associated with a lower steric effect of spatially fixed cyclic dioxyalkylenic substituents at phosphorus. When, however, one examines the stability of complexes with five-membered cyclic dithiophosphate ligands (Nos. 37–39, Table I), it is necessary to take into account, in addition to the screening

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TABLE III

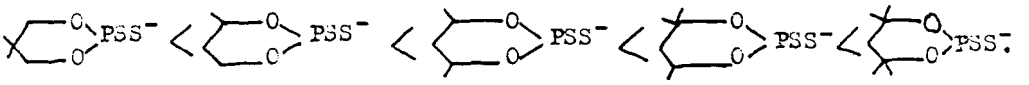
Thermodynamic parameters of the formation of $Ni(SSPBA)_2$ complexes* (μ = 0.01, propanol–water 9 : 1, T = 293 ± 2 K)

A and B	$\log\beta_2$	$\Delta G \pm 1$, kJ/mol	$\Delta H \pm 0.6$, kJ/mol	$\Delta S \pm 7$, J/(mol · K)
C_3H_7	6.84	−38.4	54.5	317
i-C_4H_9	7.88	−44.2	47.2	312
CH_3 and C_2H_5O	6.60	−37.0	42.0	269
CH_3 and *s*-C_4H_9O	7.81	−43.8	36.5	274
CH_3 and *c*-$C_6H_{11}O$	7.71	−43.3	39.4	282
i-C_3H_7O	7.22	−40.5	39.9	274
s-C_4H_9O	8.35	−46.9	37.4	287
$OC(CH_3)_2CH_2C(CH_3)(C_2H_5)O$	7.49	−42.0	36.8	269
$OC(CH_3)_2CH_2CH(i\text{-}C_3H_7)O$	6.14	−34.5	49.6	287

*Refined data.[34,38]

effect, a certain contribution of the ring-strain factor which is capable of imparting higher electron-acceptor properties to this type of ligand.

The stability of metal complexes with six-membered cyclic substituents at phosphorus in the ligands is primarily controlled by the number of alkyl groups in position 4 and 6 of the 1,3,2-dioxyphosphorinanic ring. Stability of complexes increases in the following series of ligands:



The most pronounced stability increase is noted upon the insertion of heme-dialkyl groups into the above-mentioned positions of the cycles. This is, possibly, associated with a change in the conformational features of the six-membered cycle, caused by the strong 1,3-repulsion arising between the alkyl substituents and the coordinately bound sulfur atoms in the $>P\overset{S}{\underset{S}{<}}$ triad. In such cases, the so-called "steric assistance" to the electron effect is brought about, classified for heterocyclic systems as the stereoelectronic effect.[51]

Redox Processes in the Complexation of Phosphorus Dithioacids

Redox potential values are an important characteristic of substances and are of interest in ascertaining the mutual effect of substituents in organic molecules, as well as predicting their behavior in nucleophilic addition, complexation, substitution and other reactions.

We have determined the redox potentials for a wide variety of systems $(ABPSS)_2/2$ $ABPSS^-$ in aqueous propanol (9 : 1 PrOH to H_2O, by volume) using potentiometric titration of dithioacid salts with iodine.[35] The E^0 values for all $ABPSS^-$ are given in Table I.

It can be seen that an increase in electron-acceptor properties of substituents A and B in the ligands leads to a decrease in the reductive ability of phosphorus dithioacids.

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A and B in $ABPSS^-$	$(ClC_2H_4O)_2$	$(C_3H_7O)_2$	$CH_3(i\text{-}C_4H_9O)$	$(C_4H_9)_2$
E^0, V	0.325	0.233	0.159	0.150

However, the relationships between E^0 magnitudes and the sum of steric or isosteric constant substituents at phosphorus in the series of dithiophosphinic (Eq. 3, Nos. 1–4), dithiophosphonic (Eq. 4, Nos. 6–9, 12) and dithiophosphoric (Eq. 5, Nos. 13–21) derivatives also exist:

$$E^0 = (0.002 \pm 0.003) + (0.10 \pm 0.001)\Sigma E_s^0 \quad (3)$$
$$r = 0.988, \quad S_0 = 0.003, \quad n = 4$$

$$E^0 = (0.212 \pm 0.002) + (0.023 \pm 0.001)\Sigma E_s^0 \quad (4)$$
$$r = 0.997, \quad S_0 = 0.002, \quad n = 5$$

$$E^0 = (0.280 \pm 0.008) + (0.019 \pm 0.002)\Sigma E_s^0 \quad (5)$$
$$r = 0.962, \quad S_0 = 0.012, \quad n = 9.$$

As already mentioned, the strong reductive properties of phosphorus dithioacids determine the instability of their complexes with some metal ions. In particular, it is known that copper(II) dithiophosphate complexes are converted in polar media into polynuclear copper(I) compounds.[17,21–26]

The kinetics of this redox reaction has been studied spectrophotometrically.[37] When the solutions of copper(II) nitrate(10^{-5}–10^{-4} mol/L) and of phosphorus dithioacid salts (10^{-2} mol/L) are mixed, $Cu(SSPBA)_2$ complexes are formed practically instantaneously; the electronic spectra of these compounds have a charge-transfer band ($\varepsilon = 10^4$, $\lambda = 420$ nm) whose intensity diminishes with time in the course of reaction (Eq. 6):

$$2\,Cu(SSPBA)_2 \rightarrow Cu_2(SSPBA)_2 + (ABPSS)_2 \quad (6)$$

The investigation was performed in aqueous propanol (10 vol.% H_2O at 288 to 318 K).

The reduction rate is described by a second-order kinetic equation; at a 100-fold excess of the ligand, the reaction order (with respect to the complex) is equal to 2.

The experimental rate constants at 298 K are shown in Table I; activation parameters of the reaction for some acyclic and cyclic phosphorus dithioacids are given in Table IV.[37]

The data presented in Table I reveal a parallelism in the variation of the redox-process rate constants and the redox potentials of the dithiophosphate systems (Nos. 13–28, 30–31, 33–36; in the correlation, points corresponding to phosphinic, phosphonic and phospholanic derivatives are not included) (Eq. 7):

$$\log k_2^{298} = (-2.86 \pm 0.44) + (16.52 \pm 1.73)E^0$$
$$r = 0.906, \quad S_0 = 0.451, \quad n = 22 \quad (7)$$

Taking into account this fact, as well as the fulfillment of Leffler's criterion,[52] from the results presented in Table III (Eq. 8)

$$E_a = (64.4 \pm 1.4) + (0.218 \pm 0.021)\Delta S^{\ddagger}$$
$$r = 0.969, \quad S_0 = 2.23, \quad n = 9 \quad (8)$$

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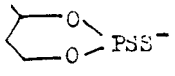
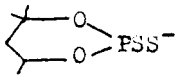
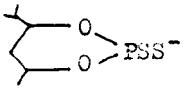
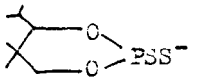
TABLE IV

Rate constants and activation parameters for the reduction reaction of CuL_2 complexes

L	k_2^{298}, L/(mol · sec)	E_a, kJ/mol	$\Delta S^{\ddagger}$, J/(mol · K)
$(C_2H_5O)_2PSS^-$	7.37	52.6	−59.4
$(C_3H_7O)_2PSS^-$	6.50	52.3	−62.7
$(i\text{-}C_3H_7O)_2PSS^-$	1.52	48.9	−84.9
$(C_4H_9O)_2PSS^-$	4.59	43.9	−93.6
$(i\text{-}C_4H_9O)_2PSS^-$	3.83	40.1	−107.4
	151.0	61.0	−7.1
	21.0	48.9	−59.8
	44.6	68.6	−8.8
	47.8	51.4	−48.1

it can be concluded that there exists a common associative mechanism (with the participation of two complex species) for all the acyclic and cyclic compounds of the reaction series studied.

At the same time, there is an obvious tendency for the reactivity of Cu(II) complexes with acyclic dithiophosphate ligands to decrease (Table III) with a decrease in the activation energy of the process, and the reaction is mainly controlled by the entropic factor. The latter fact determines the fulfillment of the correlation dependence between the values of $\log k_2^{298}$ and those of ΣE_s^0—the constants (Table I, Nos. 13–21) characterizing the steric effect of alkoxy substituents at the phosphorus atom in the ligand (Eq. 9)

$$\log k_2^{298} = (1.441 \pm 0.109) + (0.298 \pm 0.027)\Sigma E_s^0$$
$$r = 0.973, \qquad S_0 = 0.156, \qquad n = 9 \tag{9}$$

It is significant that copper complexes with cyclic dithioacids in which the phosphorus atom is included in the cycle are capable of even faster reduction. However, insertion of bulky alkyl radicals into the ring exerts a considerable effect upon the reaction rate.

In the course of the redox reaction, electrons are obviously transferred from the ligand to the central ion (the possibility of a single-electron transfer is not confirmed by the ESR data). That is why we are justified in the assumption that an increase in the acceptor capacity of substituents will cause a decrease in the observed k_2^{298} value. If, however, we examine the values of reduction rate constants for Cu(II) complexes with ligands in which the substituents at phosphorus have a comparable

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steric influence but a different electronic effect, it can be stated that there is no unambiguous interrelationship between the structural and the electronic effects upon the overall rate of the process: with an increase in acceptivity the reaction rate at first decreases and then increases:

L^-	$(C_4H_9)_2PSS^-$	$CH_3(i-C_3H_7O)PSS^-$	$(C_3H_7O)_2PSS^-$	$(ClC_2H_4O)_2PSS^-$
k_2^{298}, L/(mol · sec)	1900	36	6.50	1000

This is probably associated with the multistage nature of the reaction process, in which the replacement of the limiting stage of the reaction is possible with the variation in the electronic nature of the ligands. The following mechanism of the reduction of $Cu(SSPBA)_2$ complexes may be proposed (Eq. 10):

$$2\,Cu(SSPBA)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Cu_2(SSPBA)_4 \xrightarrow{k_2} Cu_2(SSPBA)_2 + (ABPSS)_2 \qquad (10)$$

At the first stage, there is a possibility for an intermediate dimeric Cu(II) complex to be formed. Formation of similar binuclear Cu(II) complexes with carboxylic acids is known from the literature,[53] with the position of monomer ⇄ dimer equilibrium being shifted towards the latter and accompanied by a decrease of the monomeric complex stability.

Reactions proceeding in accordance with Eq. 10 are described by the second-order kinetic equation (Eq. 11) in which

$$k_{obs} = \frac{k_1 \cdot k_2}{k_{-1} + k_2} \qquad (11)$$

Taking into account the high lability of the complexes, i.e. $k_{-1} \gg k_2$, Eq. 11 can be presented in the form (Eq. 12):

$$k_{obs} = \frac{k_1 \cdot k_2}{k_{-1}} = K_{eq} \cdot k_2, \qquad (12)$$

where $K_{eq} = k_1/k_{-1}$.

Variations of the electronic and the steric nature of substituents can thus have a two-way action on the observed k_2^{298}.

The activation parameters presented in Table IV are effective values, although entropic control in the given reaction series is obviously preferable.

Extractive Properties of Cyclic Derivatives of Phosphorus Dithioacids

As already noted, cyclic dithiophosphoric acids, because of a lower steric and higher electron-acceptor effect of dioxyalkylene substituents at phosphorus, form less stable complexes with Ni(II), Co(II) and Ag(I) ions. The application of this class of dithiophosphorus derivatives could be assumed to raise the selectivity of the extractive separation of metal ions.

It is known[54] that selective extraction of copper can be achieved with help of dithiophosphoric acids, in particular, *i*-butyl 2-ethylhexyl dithiophosphoric acid (IBEHDTPA) or its derivatives. However, a rather high stability of the copper ion complex with this reagent hinders the re-extraction process, whereas its strong reductive properties ($E^0 = 0.2$ V) cause partial formation of disulfides of this acid.

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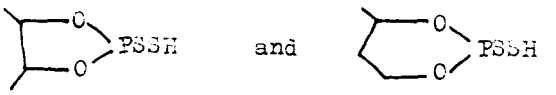
A search for compounds having weaker reductive properties and that form less stable complexes with copper ions has resulted the choice of isomeric cyclic 2,3- and 1,3-butylene dithiophosphoric acids (BDTPA)[55] as extractive reagents:



It was established[55] that copper(II) is quantitatively (99.8%) extracted by these acids in chloroform within a wide range of the aqueous solution acidity. In a study of solutions of synthetic mixtures that contained Mn(II), Zn(II), Ni(II) and Fe(III) ions, the extraction of these ions did not exceed 0.1–0.8%. An exception is Fe(III) whose extraction amounted to 8–10%. Treating solutions of a similar composition with IBEHDTPA has shown that, in comparison with BDTPA, acyclic dithiophosphate is a less selective reagent: the extraction of Fe(III) and Ni(II) amounted to 46 and 90%, respectively.

When the process of copper re-extraction was studied, it was also noted that cyclic dithiophosphorus reagents are preferable to acyclic ones. Quantitative copper re-extraction (99.9%) is achieved in the first case in 0.5–1.0 mol/L thiourea solution in the presence of 2.5 mol/L H_2SO_4. Re-extraction of copper with acyclic reagent requires a larger amount of thiourea under the same conditions.

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CONCLUSIONS

The results of the investigation carried out thus make it possible to draw some inferences regarding the interrelation between the structure of cyclic and acyclic phosphorus dithioacids, their complexing, redox and extractive properties.

The stability of dithiophosphate, phosphonate and phosphinate Ni(II), Co(II) and Ag(I) complexes increases with an increase in the size of alkyl, alkoxyl and cyclic dioxyalkylenic substituents at phosphorus in the ligand.

In our opinion, this can be associated both with a lower solvatibility of the complex by an aqueous organic solvent, in comparison with the solvation of initial metal salts and phosphorus dithioacids, and with a decrease in the coordination number of the central ions in the course of complex formation.

A study of the redox potentials of disulfide/dithioacid anion systems, as well as the reduction kinetics for the corresponding Cu(II) complexes, has shown that the redox properties of dithioacids undergo appreciable changes depending on the nature of substituents in the $ABPSS^-$ anion. The latter fact determines the complex mechanism of redox processes taking place with the participation of type $M(SSPBA)_2$ complexes.

The regularities characterizing the interrelation between the structure of phosphorus dithioacids and the stability of metal complexes formed by them can in future be used for a rational approach to the choice of organophosphorus extractive analytical reagents. An instance of this are cyclic derivatives of phosphorus dithioacids that have a sufficiently high selectivity by virtue of the specific character of dioxyalkylenic substituents at the phosphorus atom.

REFERENCES

1. A. I. Busev and M. I. Ivaniutin, *Trudy komissii po analiticheskoy khimii AN SSSR*, **11**, 172 (1960).
2. J. R. Wasson, G. M. Wolterman and H. J. Stoklova, *Forsch. Chem. Forsch.*, **35**, 65 (1973); F. A. Cotton and G. Wilkinson, F.R.S., Advanced Inorganic Chemistry, Moskow, Mir Publishers, Part III (1969) (in Russian).
3. R. G. Pearson and J. Songestadt, *J. Am. Chem. Soc.*, **85**, 1827 (1967).
4. S. L. Lawton and G. T. Kokotailo, *Inorg. Chem.*, **8**, 2410 (1969).
5. T. Ito, T. Igarashi and H. Hagihara, *Acta Cryst.*, **B25**, 2303 (1969).
6. V. Kastalsky and J. F. McConnel, *ibid.*, **B25**, 909 (1969).
7. E. A. Gilinskaya and M. A. Porai-Koshits, *Kristallografiya*, **4**, 241 (1959).
8. Q. Fernando and C. D. Grien, *Inorg. Nucl. Chem.*, **29**, 647 (1967).
9. N. S. Garifyanov and B. M. Kozyrev, *Zh. strukt. khim.*, **6**, 773 (1965).
10. N. S. Garifyanov and B. M. Kozyrev, *ibid.*, **9**, 529 (1968).
11. L. A. Bylinskaya, I. V. Ovchinnikov, R. A. Cherkasov and V. V. Ovchinnikov, *Zh. neorg. khim.*, **19**, 420 (1974).
12. J. Silaghi-Dimitrescu and J. Haiduc, Intern. Conference on Phosphorus Chemistry, GDR, Halle, 1979, p. 457.
13. R. Micu-Semeniuc, J. Silaghi-Dimitrescu and J. Haiduc, *Inorg. Chim. Acta*, **33**, 281 (1979).
14. V. F. Toropova, R. A. Cherkasov, N. I. Savelyeva, V. N. Gorshkova and A. N. Pudovik, *Zh. obshch. khim.*, **40**, 1043 (1970).
15. V. F. Toropova, R. A. Cherkasov, N. I. Savelyeva, N. V. Sliusar and A. N. Pudovik, *ibid.*, **42**, 1485 (1972).
16. V. F. Toropova, R. A. Cherkasov, N. I. Savelyeva, L. A. Grigoryeva, I. V. Shergina and V. V. Ovchinnikov, *ibid.*, **41**, 1673 (1971).
17. V. V. Ovchinnikov, A. R. Garifzyanov, N. I. Savelyeva and V. F. Toropova, *Izv. VUZ. Khimiya i khim. tekhnologiya*, **22**, 654 (1979).
18. S. V. Larionov, V. M. Shulman and P. A. Podolskaya, *Zh. neorg. khim.*, **12**, 2456 (1967).
19. A. T. Pilipenko, L. I. Savransky and A. I. Zubenko, *Koord. khim.*, **7**, 25 (1981).
20. D. V. Sokolsky, L. M. Kurashvili and N. A. Zavorokhina, MS. depos. at VINITI, No. 2015 (1976).
21. R. N. Mukherje, V. V. Krishna and J. Gupta, *Indian J. Chem.*, **4**, 209 (1966).
22. W. Kuchen and H. Hertel, *Angew. Chem.*, **B81**, 127 (1969).
23. W. Kuchen and H. Magatepic, *Chem. Ber.*, **B101**, 127 (1968).
24. J. R. Wasson, *Inorg. Chem.*, **10**, 1531 (1971).
25. H. Bode and W. Arnewald, *Z. Anal. Chem.*, **B185**, 179 (1962).
26. A. I. Busev and M. I. Ivaniutin, Vestnik MGU, ser. mathematiki, mechanici, astronomii, fiziki i khimii, No. 5, 157 (1957).
27. V. F. Toropova, R. A. Cherkasov, N. I. Savelyeva and E. I. Petrova, *Zh. obshch. khim.*, **44**, 531 (1974).
28. R. A. Cherkasov, V. V. Ovchinnikov, M. A. Pudovik and A. N. Pudovik, *Usp. khimii*, **51**, 1305 (1982).
29. P. S. Pishchimuka, *Zh. russk. fiz.-khim. obshchestva*, **44**, 1406 (1913).
30. J. P. Chupp and R. E. Nevallis, *J. Org. Chem.*, **47**, 3832 (1962).
31. T. A. Mastryukova, A. S. Shipov and M. I. Kabachnik, *Zh. obshch. khim.*, **31**, 507 (1961).
32. V. V. Ovchinnikov, A. R. Garifzyanov, A. M. Polozov, R. A. Cherkasov and V. F. Toropova, *ibid.*, **51**, 1922 (1981).
33. V. V. Ovchinnokov, A. R. Garifzyanov, R. A. Cherkasov, A. N. Pudovik and V. F. Toropova, *Organic Reactivity*, **17**, 54 (1980).
34. V. V. Ovchinnokov, A. R. Garifzyanov, V. F. Toropova and R. A. Cherkasov, *Zh. obshch. khim.*, **52**, 1323 (1982).
35. I. A. Kakovsky, B. A. Stepanov, O. F. Ryazantseva and N. V. Serebryakova, *Zh. fiz. khim.*, **33**, 1830 (1955).
36. V. V. Ovchinnikov, A. R. Garifzyanov, R. A. Cherkasov and V. F. Toropova, *Zh. obshch. khim.*, **50**, 67 (1980).
37. V. V. Ovchinnikov, A. R. Garifzyanov and V. F. Toropova, *Izv. VUZ. Khimiya i khim. Tekhnologiya*, **25**, 244 (1982).
38. V. V. Ovchinnikov, A. R. Garifzyanov, R. A. Cherkasov and V. F. Toropova, *Zh. obshch. khim.*, **53**, 1262 (1983).
39. T. A. Mastryukova and M. I. Kabachnik, *Usp. khimii*, **38**, 1751 (1969).
40. B. I. Istomin, V. A. Baransky, A. D. Lobanov and Ye. F. Grechkin, *Organic Reactivity*, **12**, 69 (1975).
41. V. A. Baransky and B. I. Istomin, *ibid.*, **12**, 83 (1975).
42. M. Charton and B. J. Charton, *J. Org. Chem.*, **43**, 2383 (1978).
43. L. F. Kasukhin and Yu. G. Gololobov, *Organic Reactivity*, **15**, 477 (1978); V. I. Galkin and R. A. Cherkasov, *ibid.*, **18**, 113 (1981).

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44. M. Charton, *J. Am. Chem. Soc.*, **99**, 5687 (1977).
45. F. D. Detar, *ibid.*, **102**, 7988 (1980).
46. V. A. Palm, Fundamentals of the Quantitative Theory of Organic Reactions, Leningrad, Khimiya Publishers (1977) (in Russian).
47. K. B. Yatsimirsky, *Theor. i Eksp. khim.*, **16**, 34 (1980).
48. R. T. Mayers, *Inorg. Chem.*, **17**, 952 (1978).
49. Z. Holtsbecher, L. Divish, M. Kral and L. Shukha, Organic Reagents in Inorganic Analysis, Moscow, Mir Publishers (1979) (in Russian).
50. V. Ye. Mironov and A. K. Piartman, *Usp. Khimii*, **52**, 1468 (1983); S. A. Aleksandrova and V. P. Vasilyev, Abstracts of Papers at II All-Union Conference "Problems of Solvation and Complexation in Solutions", Ivanovo, 1981, p. 167.
51. P. Deslongchamps, *Tetrahedron*, **31**, 2463 (1975).
52. J. F. Leffler, *J. Org. Chem.*, **31**, 533 (1966).
53. A. Jingst and D. H. McDaniel, *Inorg. Nucl. Chem.*, **28**, 2919 (1966).
54. Yu. A. Zolotov, G. Ye. Vlasova, Ye. V. Rybakova, V. V. Sher and Ye. I. Markova, Tsvetniye metally, No. I, 14 (1978).
55. G. Ye. Vlasova, Ye. V. Rybakova, A. R. Garifzyanov, V. V. Ovchinnikov, R. A. Cherkasov, V. F. Toropova and Yu. A. Zolotov, *Zh. neorg. khim.*, **26**, 2204 (1981).

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