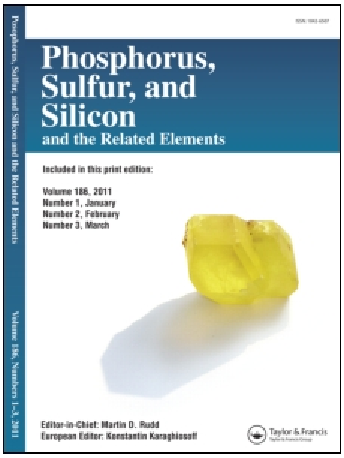

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Yu. I. Murinov[a]
[a] USSR Acad. Sci. Bashkirian Branch Inst. Chem., Ufa, USSR

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COMPLEX FORMATION OF D- AND F-ELEMENTS WITH SULPHUR ORGANIC COMPOUNDS IN EXTRAKTION EQUILIBRIA

Yu. I. MURINOV
USSR Acad. Sci. Bashkirian Branch Inst. Chem., Ufa, USSR

Abstract The regularities in reactivities of some mono- and polydentate organosulphur compounds have been established for complex formation with metal salts in extraction-sorption equilibria. Their reactivities have been shown to depend upon the spatial arrangement of donor centres in an extractant. New classes of polydentate extractants (keto sulphides, amino-sulphides, keto-aminosulphides) have been suggested.

Chemical properties of coordinative extractions and sorptions have been investigated for d- and f-elements to be the most intrinsic for the above mentioned class. The keto group has been found to affect the electron density of sulphur in the keto sulphides, thus preventing undesirable redox reactions between an extractant and the isolated metal ion. The coordination character and properties of extracted and sorbated complexes of d- and f-elements with organosulphur compounds have been determined.

The donor centres of polydentate organosulphur ligands in the process of complex formation with d- and f-elements have been detected by IR-,.ESR-, PMR-, and Raman spectral analyses.

Introduction

The most actual problem in the field of extraction and sorption equilibria is the problem to elucidate the reactivity of polydentate organic compounds and its dependence on the nature of the functional groups. During the last decade this aspect acquired the highest interest due to both the ever-growing application of extraction and sorption processes in hydrometallurgy and the increasing use of the bulk of poor and complex ores. This lead to a search for new reagents and their synthesis. The sulphur-organic extractants and sorbents attracted special interest due to the characteristics of the sulphur atom in complex formation reactions and to the existence of raw materials rich in sulphur-organic compounds. The extraction and sorption abilities of reagents with different structures may be estimated by employing the mass-action-law and some equilibrium methods. However, the most detailed investigation of extraction and sorption process mechanism and the quantitative interpretation of extractant donor abilities demand proper comparison of the results obtained by the equilibrium data and the information on the compositions and structures of the extracted complexes formed.

While the extraction equilibria assisted by sulphur-organic compounds as reagents are intensively investigated both in our country and abroad, the development of sulphur organic coordination chemistry has been, by far, not so much advanced as the chemistry of N- and P-organic compounds as ligands. Most investigations are known for coordination compounds where compounds with low molecular weight (TMS, DMS, DMSO, and TMSO series) or aromatic sulphides and sulphoxides are used as ligands. Information on the ligand properties of sulphides and sulphoxides with high molecular weight is scanty. Almost no studies have been carried out into the complex forming features of polyfunctional sulphur organic compounds. Therefore, the investigations of compositions, structures, and reactivities of extracted d- and f-element complexes with mono- and polydentate sulphur organic compounds will expand our theoretical evaluations in the field of the coordination chemistry and will afford the insight into the complex formation phenolena in extraction and sorption processes. These processes are characterized by the emergence of electron-donor-acceptor complexes formed by v-acceptors (d- and f-element nitrates and halogenides possessing a vacant d- or f-orbital) together with n-donors with an unshared electron pair (donor sulphur and oxygen atoms of a sorbent or an extractant). The n- and v-orbital electron densities are to be estimated to give quantitative characteristics of the EDA-bonding. Such exact electron density calculations and evaluations of molecular orbital energies in multiatom molecules are not possible by present-day methods. Therefore, physical chemistry methods such as UV/VIS-, IR-, NMR-, and Raman spectroscopy, electro- and dielectrometry, thermogravimetry, and the determination of molecular masses of extracted complexes have been employed for the EDA-interaction evaluations as well as for the estimation of the complex structures and compositions.

The process of coordination extraction of a metal by sulphur organic compounds can be described by stoichiometric equations of the following type,

$$M^{z+}_{(aq)} + zA^{-}_{(aq)} + qL_{(s)} \longrightarrow MA_zLq(s) \qquad (1)$$

where K is the equilibrium constant of the coordination extraction, or

$$\Delta G_{ex} = -RT\ln K_{ex} \qquad (2)$$

ΔG_{ex} consists of contributions by the complex formation in the organic phase, by the hydration in the aqueous phase (ΔG_{aq}) and by the interactions of the extractant, the extracted complex and the solvent (ΔG_s) in the organic phase.

$$-RT\ln K_{ex} = \Delta G_{ex} = \Delta G_{complex} - \Delta G_{aq} + \Delta G_s \qquad (3)$$

If the extracted compound and the solvent are held constant, a change in the extraction constant value specifies the complex formation properties of sulphur organic reagents, i.e. K_{ex} is a measure for the complex formation of metals with ligands in extraction equilibria. The method of interphase distribution of d- and f-element salts between aqueous and organic phases has been used as the basic one for investigating some regularities in complex formation of d- and f-elements with mono- and polydentate sulphur organic compounds, the quantitative interpretation of the results being based on the mass-action-law.

COMPLEX FORMATION PROPERTIES OF POLYDENTATE ORGANIC SULPHIDES IN D-ELEMENT EXTRACTION AND SORPTION

The selective extraction and separation of noble metal ions (soft acids by Pearson's conception) demands a certain class of sulphur organic compounds in which sulphur reveals its donor properties and forms an EDA-complex with the metal extracted. Different thioester derivatives or organic sulphides[1] belong to such a class of sulphur organic compounds. Vacant d-orbitals allow the sulphur atom to play the role as an acceptor in a π-dative bond. Besides, there exist two unshared pairs (UP) of electrons. Thus, two types of interactions are possible in sulphides: between sulphur atom UP-electrons and radical p-orbitals, and between the radical π-electrons and sulphur atom d-orbitals. The electron density distribution in such sulphur compounds has been asserted to determine the sulphur atom donor properties towards the complex forming ions: An increase in the electron density at a sulphur atom results in a decrease in the sulphide redox potential and in increasing the polarizabilities of both the sulphide and the complex forming ion, it causes the oxidation of the sulphide in the extracts to the sulphoxide and the reduction of the metal ion to a lower valence state and sometimes, to the metal. Here, an alternative arises: either the sulphur atom electron density should be increased to lead to growing extractant effectivity and to a lower redox potential (which would influence the process selectivities, for the sulphoxides formed in the oxidation of the sulphides are less selective); or the extractant effectivity should be lowered and chemical stability raised. The "stabilization" of electron densities has been viewed as the simplest way out.

The stabilization is possible if another functional group possessing a slight negative inductive effect is introduced into the molecule. A ketone group is suitable in this case[2]. The presence of a sulphur atom and a carbonyl group in the extractant molecule results in stabilizing electron densities at the sulphur atom.

Feeble pπ-dπ-interactions between ketone group oxygen and sulphur in sulphides have been first observed in interpreting the photoelectron- and mass-spectra of keto-sulphide negative ions. The ionization potentials for unshared pairs of oxygen and sulphur atoms are 9.45 and 8.51 eV in the ketosulphide 3-(ethyl-thiomethyl)-butanon-2. The increase in the ionization potential of the sulphur unshared pair in the keto-sulphide as compared with that of dialkyl sulphides (8.32 eV for dipropyl sulphide) is evidence of a weak inductive effect of the ketone group. However, the exchange of the ethyl group in the keto-sulphide for the butyl group leads to a decrease in the ionization potential of the sulphur UP down to 8.45 eV and to an increase of the ionization potential of the oxygen UP up to 9.55 eV, which may serve as a symptom for interactions of sulphur and oxygen atom orbitals to result in an intramolecular redistribution of electron densities. The value for the cross-section of dissociative electron trapping (DET) found for ketosulphides proves once more the existence of interactions of the atoms: 3.8 $10^{-19} cm^2$, while dialkyl sulphides give o.6 $10^{-19} cm^2$.

The nonadditive value of DET cross-section for keto-sulphides indicates possible pπ-dπ intramolecular interactions of the ketone group oxygen and the sulphur in sulphides. The stabilization of electron density at a ketosulphide sulphur atom is corroborated by the redox potentials of the systems dihexyl sulphoxide - dihexyl sulphide and octylthiomethylacetophenone sulphoxide - octylthiomethylacetophenone sulphide as determined by potentiometry technique. Thus, E^o = -o.41 ± o.o1 V for the first system (DHSO/DHS), relative to the Ag/Ag^+ pair, and E^o = +o.25 ± o.o1 V relative to $H_2/2H^+$, and for the second system (keto sulphoxide/keto sulphide) E^o = -o.11 ± o.o1 V and E^o = +o.55 ± o.o2 V, respectively: Dialkyl sulphides are easier oxidized than keto sulphides.

The introduction of a tertiary nitrogen with pronounced nucleophilic properties into a sulphide influences the kinetics of ligand substitution in platinum metal extractions. This is the reason for the synthesis of polyfunctional sulphides containing keto and amino groups and for testing them in the extraction and separation of noble metals.

Various keto sulphides have been prepared by the reaction of a ketone with formaldehyde and a mercaptane in the presence of sodium hydroxide [3]:

$$R\text{-}COCH_2R_2 + CH_2O + R^3SH \longrightarrow R\text{-}COCHR^2CH_2SR^3$$

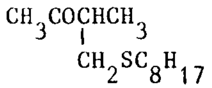
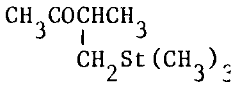
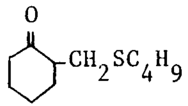
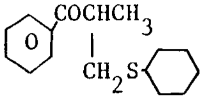
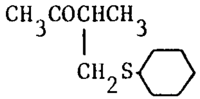
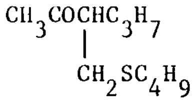
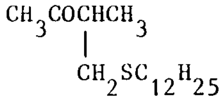
Table 1 presents the synthesized keto sulphides and their physico-chemical properties.
The structures of the keto sulphides were confirmed by their ^{1}H-NMR-spectrum, elemental analysis, and IR spectrum assignments of their derivatives, i.e. sulphones and dinitrophenyl hydrazones, the compounds were 98-99% pure. The obtained keto sulphides reveal high stability in oxidative processes. Thus, the production of aliphatic keto sulphides needs more rigid conditions (temperature, catalyst) than those under which the corresponding sulphides are oxidized by hydrogen peroxide to sulphoxides.

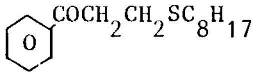
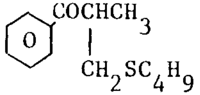
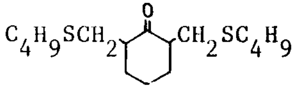
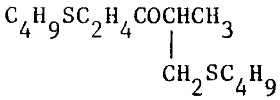
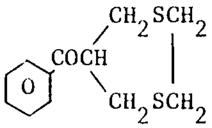
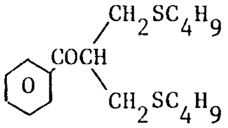
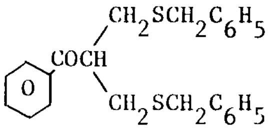
SILVER NITRATE EXTRACTIONS

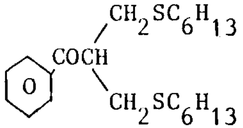
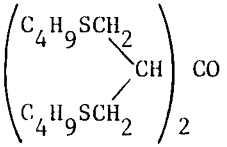
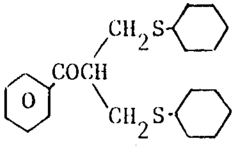
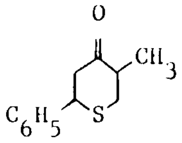
The extraction properties of all keto sulphides were investigated by silver nitrate extraction from o.1 mole/l nitric acid. Reagents 1,2,3,5,6,1o,11 (see Table 1) and silver nitrate appeared to form complexes of high solubility in the aqueous phase. Reagents 4,9 and 12 gave complexes insuble in organic solvents. Reagents 7 and 18 revealed their low extraction activity because of steric factors for the former and of the negative inductive effects of the carbonyl group in paraposition to the sulphur atom for the latter.

Fig. 1 shows the isotherms of silver nitrate extraction by keto sulphides, petroleum sulphides (PS), and dihexylsulphide (DHS). OTMA appears to be the best monosulphide for silver nitrate extraction as compared to PS and DHS; however, STBMA is the most effective. An increase in the extractant dentate ability for a sulphur results in a proportional growth of its capacity for the silver. The ratio one silver atom per sulphur atom is proved by the method of saturation. A more detailed investigation of

TABLE 1 Some properties of the synthesized keto sulphides

Formula	Structure	b.p. °C	Density	n_D^{20}
1	2	3	4	5
1. 3-(octylthiomethyl)-butanon-2	 $CH_3COCH(CH_3)CH_2SC_8H_{17}$	174-175 (5 mm)	0.9100	1.4680
2. t3-(tertbutylthiomethyl)-butanon-2	 $CH_3COCH(CH_3)CH_2St(CH_3)_3$	85-87 (5 mm)	0.9270	1.4650
3. 2-(butylthiomethyl)-cyclohexanone		132-133 (1 mm)	1.0036	1.4990
4. 2-(cyclohexylthio-methyl)-propiophenone		183-186 (1 mm)	1.0594	1.5540
5. 3-(cyclohexylthiomethyl) butanon-2		114-114.5 (1 mm)	0.9932	1.4970
6. 3-butylthiomethyl-hexanon-2	 $CH_3COCH(C_3H_7)CH_2SC_4H_9$	151-152 (7 mm)	0.9211	1.4672
7. 3-(dodecylthiomethyl) -butanon-2	 $CH_3COCH(CH_3)CH_2SC_{12}H_{25}$	150-152 (1 mm)	0.9129	1.4760

1	2	3	4	5
8. octylthiomethyl-acetophenone ([illegible]		213-214 (3 mm)	1.0017	1.5280
9. 2 -(butylthiomethyl) propyophenone		192-193 (5 mm)	1.0207	1.5358
10. 2,6-bis(butylthio-methyl)-cyclohexanone		-	1.0231	1.5170
11. 1,3-bis(butylthio-methyl)-butanon-2	 $C_4H_9SC_2H_4COCHCH_3$, $CH_2SC_4H_9$	-	0.9954	1.5100
12. 3-benzoyl-1,5-di-thiocycloheptane		m.p.=120°	-	-
13. bis(butylthiomethyl)-propyophenone		244-245 (1 mm)	1.0354	1.5435
14. bis(benzylthiomethyl) -acetophenone (BBTMA)		-	1.1532	1.6187

1	2	3	4	5
15. bis(hexylthiomethyl)-acetophenon (BHTMA)		271-272 (0.5 mm)	1.0012	1.5298
16. symmetric tetrakis-(buthylthiomethyl)acetone (STBTMA)		259-261 (2 mm)	1.0050	1.5160
17. bis(cyclohexylthiomethyl)acetophenone (BCHTMA)		172-173 (3 mm)	1.0369	1.5410
18. 2-phenyl-4-oxy-5-methyl-thiocyclohexane		m.p.=62.5-63°	-	-

the silver nitrate extraction was carried out with OTMA. The solvation number was determined by the equilibrium shift technique to change from 3 to 1. Several types of complexes were supported to exist in the organic phase. This assumption was ascertained by the absence of correlation between the solvation numbers determined by the above-mentioned methods. The compositions of those complexes depended on the aqueous and organic phase activity: $AgNO_3 \cdot L$, $AgNO_3 \cdot 2L$, $AgNO_3 \cdot 3L$, where L is an OTMA molecule.

It should be noted than an increase of the silver concentration in the aqueous phase and a decrease of the free OTMA concentration lead to a reduction of the solvation number from 3 to 1.

The correlation between the NMR spectra of free OTMA and those of the extraction phases made it possible to observe a change in the chemical shift of protons α to the sulphur atom (ca. o.16 ppm for saturated extracts, ca. o.o9 ppm at the middle point of the isotherm line, and ca. o.o7 ppm for the starting point). A similar change in the chemical shift was also found for protons α to the C=O bond (o.2 ppm) for the organic phase saturated with silver nitrate. The IR-spectrum of the saturated extraction phase showed a shift of the C=O band of 2o-3o cm^{-1} to lower frequency. All these results point to a favoured EDA interaction of silver and sulphur in the solvates and to an additional coordination of the carbonyl group by oxygen in the case of the monosolvates.

The data obtained led us to assume that the silver nitrate extraction by keto sulphides proceeds according to the mechanism,

$$Ag^+ + NO_3^- + qL \longrightarrow AgNO_3 \cdot qL \qquad (1-2)$$

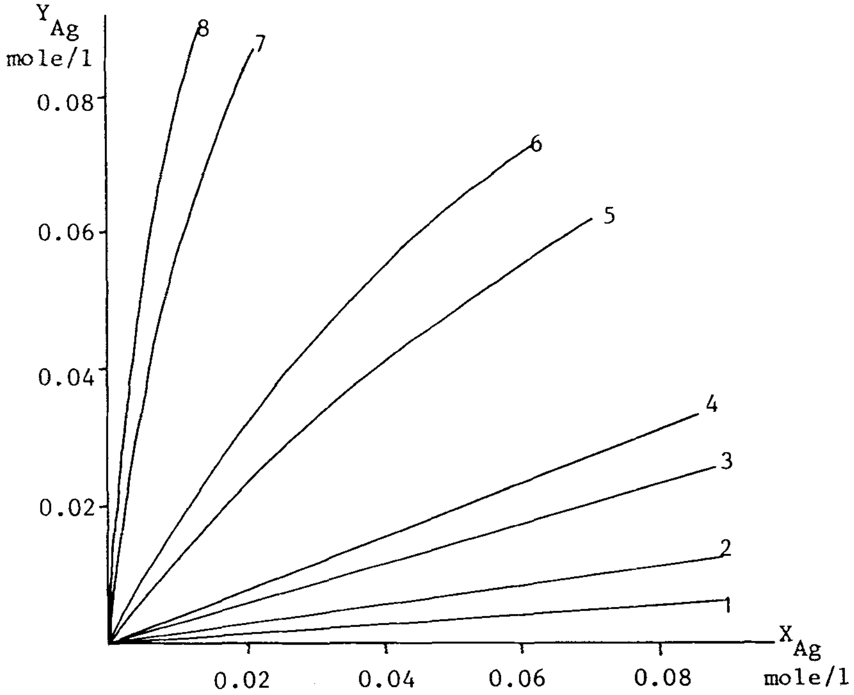


FIGURE 1 Isotherm lines for silver nitrate extractions from 0.1 mole/l of HNO_3 by 0.1 mole/l of an extractant solution in o-xylene.

1- dihexyl sulphide (DHS)
2- petroleum sulphides (PS)
3- octylthiomethyl acetophenone(OTMA)
4- bis(benzylthiomethyl)acetophenone
5- bis(butylthiomethyl)acetophenone
6- bis(hexylthiomethyl)acetophenone
7- bis(cyclohexylthiomethyl)acetophenone
8- symm.tetrakis(butylthiomethyl)acetone (STBMA)

The concentration constant of extraction was calculated as,

$$\tilde{K} = \frac{[AgNO_3\ qL]}{[Ag^+]\ [NO_3^-]\ [L]^q} = \frac{Y_{Ag}}{x_{Ag}(x_{H^+} + x_{NO_3^-})(L_o - qY_{Ag})^q} \qquad (1-3)$$

where x and Y are the silver equilibrium concentrations in the aqueous and organic phases, respectively; $Y=Y_1+Y_2+Y_3$; Y_1 - for mono-, Y_2 - for di-, and Y_3 - for tri-solvate. $L = L_o-Y_1-2Y_2-3Y_3$ - the OTMA free concentration; and x_{H^+} - the nitric acid concentration (o.1 mole/l). Thus, the nitric acid silver extraction by OTMA may be described as follows,

$$Y = Y_1+Y_2+Y_3 = x_{Ag}(x_{H^+} + x_{Ag^+}).L(\tilde{K}_1 + \tilde{K}_2 L + \tilde{K}_3 L^2) \qquad (1-4)$$

The highest degree of validity may be reached by calculating $\tilde{K}_1$ and $\tilde{K}_3$ constants for the initial point of the isotherm line, where mono- and tri-solvates prevail (Y_1=Y or Y_3Y, respectively). Then the method of gradual approximation should be used for calculating the concentration constant of the disolvate as well according to equation (1-4). Thus, all the equilibrium forms could be found for silver nitrate in an organic phase.

The equilibrium concentration of the nitric acid/silver system calculated by the above method for the OTMA extractions (o.o5; o.1o; o.21; o.29 mole/l) in xylene satisfied the experimental data with K_1 = 1 ± o.o8, K_2 = 4o ± 7, K_3 = 1ooo ± 6o.

The keto sulphide extraction activity for the silver nitrate is lowered by a temperature rise. The temperature dependence of extraction was used at high excess of extractant ($L \gg Y_{Ag}$), which led to the trisolvate only to calculate the thermodynamic functions of the silver extraction by OTMA.

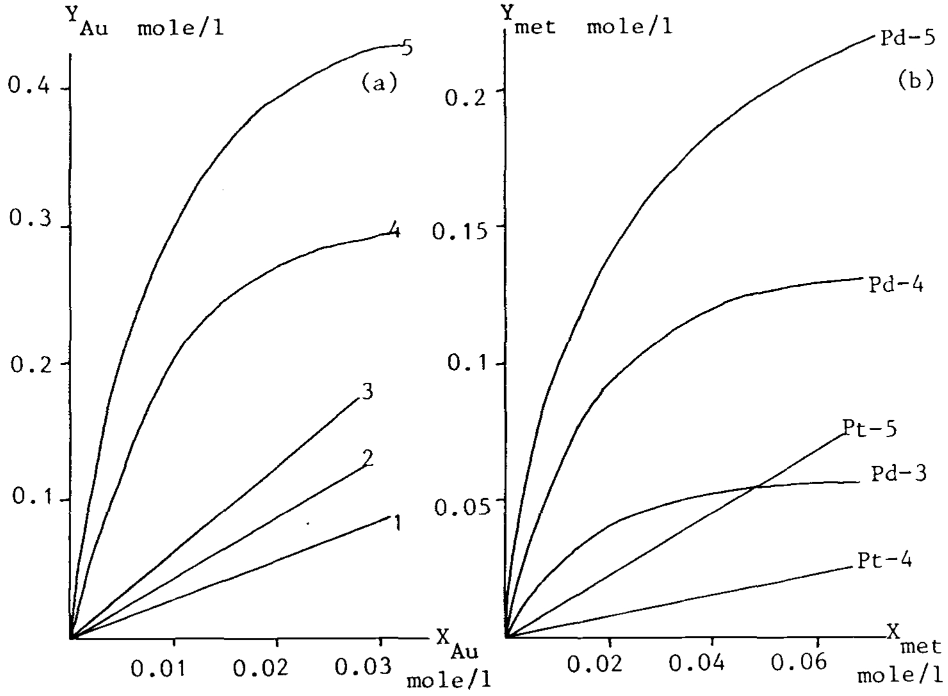


FIGURE 2 Extraction isotherms for a)gold(Au), b)platinum and palladium(Pt and Pd) from 0.5 mole/l of HCl by 0.1 mole/l of keto sulphide solutions in o-xylene (20°C).

1- DHS; 2- PS; 3- OTMA; 4- BCTMA; 5- Sym.TBTMA.

The calculated changes of thermodynamic functions in the extraction were estimated as follows:

$\Delta H = -45 \pm 0.05$ kJ/mole,

$\Delta G = -17.0 \pm 0.3$ kJ/mole,

$\Delta S = -9.6 \pm 0.1$ J/mole.

The values of enthalpy changes are evidence for strong EDA interactions between silver and sulphur in keto sulphides. The lower the substituent electronegativity at a sulphur atom, the higher its donor activity and, thus, the higher the extractability of keto sulphides compared to dialkyl sulphides (c.f. the silver nitrate extraction isotherms with BBTMA, BHTMA, BCHTMA).

GOLD(III), PALLADIUM(II), AND PLATINUM(IV) EXTRACTIONS FROM HYDROCHLORIC SOLUTIONS

Preliminary experiments afforded an estimation of the time necessary for reaching the interphase equilibria to be 2, 1o, and 3o min for each metal in extractions of gold(III), palladium(II), and platinum(IV), respectively, by keto sulphides from hydrochloric acid solutions. Fig. 2 shows the isotherms of extractions of gold(III), palladium(II), and platinum(IV) by different keto sulphides. The most effective is STBMTA. As seen in Fig. 2, the keto sulphide "dentateness" is growing with its capacity increase. The solvation numbers were determined by the equilibrium shift method and appeared to be 1 (for gold), 2 (for palladium and platinum) at the initial points of the isotherm line, these values being independent of the extractant dentateness.

The values for the solvation numbers were further confirmed by studies of the complexes isolated from the extractive phase. These experiments gave no evidence for Pd and Pt forming any cycles with di- and tetraketo sulphides in extractions from hydrochloric acid solutions. Consequently, di- and tetraketo sulphides associate in the organic phase and precipitate with an increase in Pd and Pt concentration. The so-called "stepped complex formation" is also observed with gold to be determined by increasing the number of donor atoms. The steric factor (i.e. spatial positioning of sulphur atoms in a molecule) seems to grovern the extraction equilibria.

Gold, palladium and platinum extractions decrease with increasing concentration of hydrochloric acid, as well as of chloride ion at constant acidities in the aqueous phase. The ratio of metal to chloride ions in the extractive phase 1:3, 1:2, 1:4, respectively; the IR spectra demonstrated no shifts of the carbonyl stretching band (17oo cm^{-1}). The extractive phase PMR spectra gave a change of the chemical shift for methylene protons α-positioned to C-S bond (o.3 ppm). This allows the assumption that metal coordination proceeds by the keto sulphide sulphur.

From the quantitative analyses of extracts, IR- and PMR-spectrum interpretations, and taking into account the dependences of metal extractions on the concentrations of chloride ions and of extractants, the mechanism given below may be suggested for the extraction of these metals from hydrochloric acid solutions. According to this mechanism the extraction proceeds by substitution of a chloride ion by a keto sulphide to form a neutral complex.It should be noted that the equilibrium data are valid for metal extractions by di- and tetra-keto sulphides for the initial points of the isotherm line only, i.e. $C_{met} \ll C_L$.

$$AuCl_4^- + L \longrightarrow AuCl_3L + Cl^-;$$

$$\tilde{K}_{Au} = \frac{[AuCl_3L]_S[Cl^-]_{aq}}{[AuCl_4^-]_{aq}[L]_S^2} = \frac{Y_{Au}\cdot C_{Cl}}{x_{Au}\cdot C_L} \qquad (1\text{-}5)$$

$$PdCl_4^{--} + 2L \longrightarrow PdCl_2\cdot 2L + 2Cl^-;$$

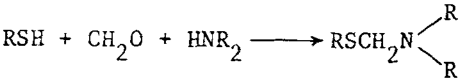
$$\tilde{K}_{Pd} = \frac{[PdCl_2\cdot 2L]_S[Cl^-]_{aq}^2}{[PdCl_4^{--}]_{aq}[L]_S^2} = \frac{Y_{Pd}\cdot C_{Cl}^2}{x_{Pd}\cdot C_L^2} \qquad (1\text{-}6)$$

$$PtCl_6^{--} + 2L \longrightarrow PtCl_4\cdot 2L + 2Cl;$$

$$\tilde{K}_{Pt} = \frac{[PtCl_4\cdot 2L]_S[Cl^-]_{aq}^2}{[PtCl_6^{--}]_{aq}[L]_S^2} = \frac{Y_{Pt}\cdot C_{Cl}^2}{x_{Pt}\cdot C_L^2} \qquad (1\text{-}7)$$

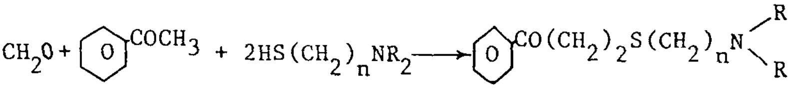
EXTRACTION PROPERTIES OF AMINO SULPHIDES

Unsufficient effectivity of platinum and rhodium extractions by keto sulphides is caused by the slow procedure of substituting chloride ions by ligands in the acid complexes of these metals. Temperature variation and various labilizing agents were employed for increasing the ligand exchange rate in the extraction by keto sulphides. Another way, instead of increasing the temperature, consists in the introduction of a more effective nucleophilic atom into the sulphur containing extractant, tertiary nitrogen being such an atom. A new class of sulphur containing extractants, namely amino sulphides, attractive by their properties, was obtained by the following reactions



$$RSH + CH_2O + HNR_2 \longrightarrow RSCH_2N\begin{matrix}R\\R\end{matrix}$$

(1-8)

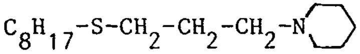
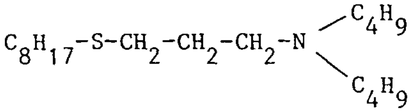
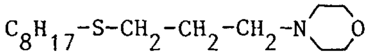
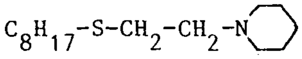
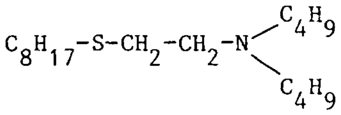
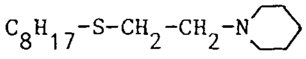
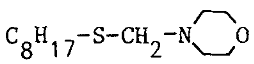
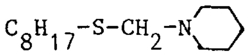
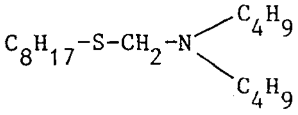
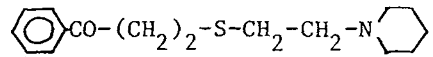
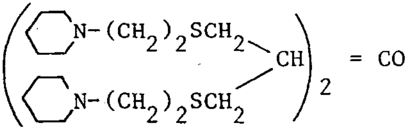


(1-9)

Table 2 shows the amino sulphides and amino keto sulphides obtained by these reactions. The elemental and mass-spectrometric analysis data ascertained the purities of the products to be 97%. Extractions of Pd and Pt from hydrochloric and sulphuric acid solutions were taken as models for the determination of amino sulphide extraction properties.

Platinum is well extracted by amino sulphides while thioesters are unsuited under such conditions. The method of equilibrium shifts gives a solvation number 2 for platinum in case of a high reagent excess. When the free reagent concentration is lowered (the organic phase being metal saturated) the solvation number tends to be

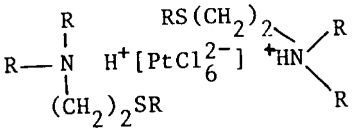
TABLE 2 Amino sulphide structures and extraction properties

Structures	Coefficients of distribution between Pt aqueous and organic phases (D_{Pt})
1. 	6.5
2.  $C_8H_{17}-S-CH_2-CH_2-CH_2-N(C_4H_9)_2$	6.3
3. 	6.1
4. 	6.2
5.  $C_8H_{17}-S-CH_2-CH_2-N(C_4H_9)_2$	5.9
6. 	6.5
7. 	2.7
8. 	2.0
9.  $C_8H_{17}-S-CH_2-N(C_4H_9)_2$	2.1
10. 	5.7
11. 	7.8

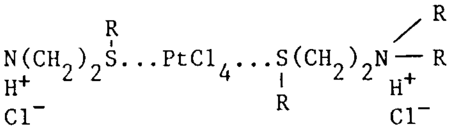
lowered. The metal-to-ligand relation in the complexes isolated from the extraction phase corresponds to the values of solvation numbers obtained if $Y_{met} \ll L$.

The PMR spectra of these complexes shows a change of the chemical shift of o.33-o.4 ppm for the protons in α-position to the sulphur atom. This corresponds to a metal ion coordination with the sulphur atom. The labilizing action of the amino sulphide tertiary nitrogen is supported to proceed in the following way.

is formed as presented below.



Second, a chloride ion in the acid complex is split off and is substituted by a sulphur atom to form the extracted complex composed as



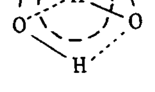
The steric structure of the amino sulphide is considered to be a factor influencing the intermediate complex formation. The ligand ability to form five- and six-membered rings should promote an increase in amino sulphide extraction properties as well as a decrease in the time for ligand exchange. This mechanism is well manifested for the Pt(IV) extraction by amino sulphides of different structures as a function of the phase contact period (Fig. 3).

The rate of interphase equilibration is fastest for a reagent with two methylene groups between the sulfur and the nitrogen atoms. The introduction of other donor atoms possessing negative induction effects into an amino sulphide molecule reduces the nitrogen nucleophilic properties if these atoms are placed in near proximity to the nitrogen, as in the morpholine sulphide, or it decreases the sulphur donor ability (as in the case of a phenyl radical instead of an aliphatic one) to lower the amino sulphide extraction properties for platinum.

THE RELATION BETWEEN THE STRUCTURES OF ORGANIC SULPHIDES AND THEIR EXTRACTION PROPERTIES. THE RELATIVE POSITION OF KETO AND AMINO SULPHIDES IN A SERIES OF NEUTRAL SULPHUR ORGANIC EXTRACTANTS.

While uranyl nitrate is employed as a probe for elucidation the sulphoxide extraction activity, the extraction of Au(III) from hydrochloric acid solutions (0.1 mole/l of HCl) is regarded to be the most appropriate probe for investigating and comparing the sulphide extraction properties. The solvation numbers were determined by the methods of saturation and equilibrium shift for all the extractants used. The solvation numbers for monodentate sulphides are equal to 1. The existence of complexes with various structures in the organic phase is possible for the polydentate ligands.

Of interest is the decreasing induction effect in the formation of intramolecular hydrogen bonds in hydroxyl substituted sulphides. Intermolecular bonds were observed for reagent 2 (Table 3), but intramolecular bonds for reagent 15. The following ring is formed in this case,



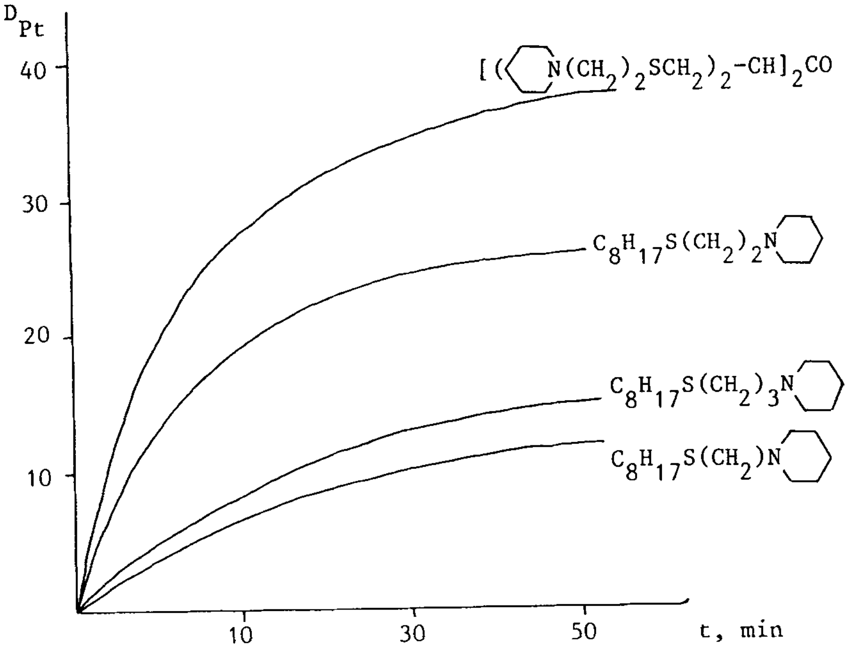
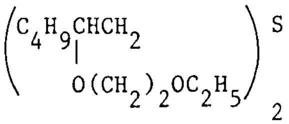
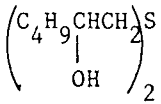
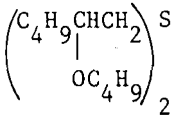
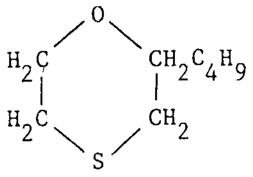
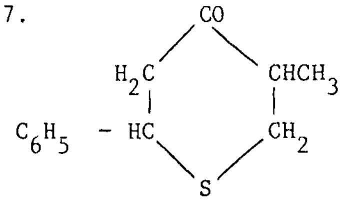
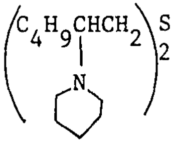
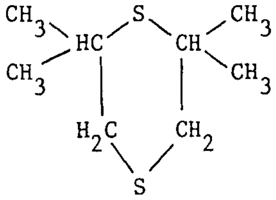
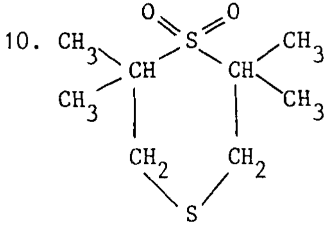
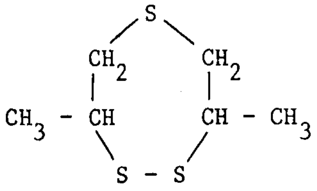
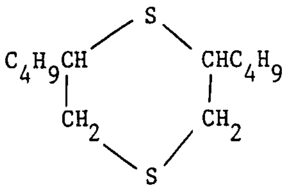
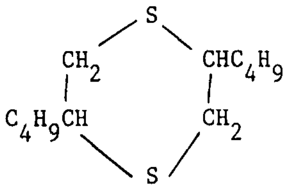
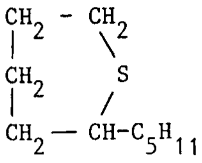


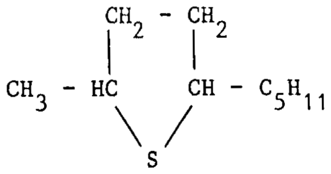
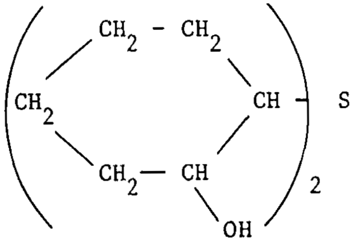
Figure 3: The influence of the phase contact period on Pt(IV) extraction by 0.01 mole/l of amino sulphides (o-xylene, 20°C, C_{HCl} = o.5 mole/l, C_{met} = 0.0001 mole/l).

TABLE 3 Some physico-chemical characteristics of sulphides and concentration constants of gold(III) chloride extractions

Formula	Name	b.p. t°C	n_D	d_4^{20}	$K_{ex}(Au)$
1.  $(C_4H_9CH(O(CH_2)_2OC_2H_5)CH_2)_2S$	3,6,12,15-tetraoxy-7,11-dibutyl-9-thiaheptadecane	-	1.4656	-	170
2.  $(C_4H_9CH(OH)CH_2)_2S$	5,9-dioxy-7-thiatridecane	-	1.4856	-	80
3.  $(C_4H_9CH(OC_4H_9)CH_2)_2S$	5,6-dibutoxy-7-thiatridecane	-	1.4581	-	220
4. $C_6H_5CO(CH_2)_2SC_8H_{17}$	octylthiamethylacetophenone	213-214 (3mm)	1.5280	1.0017	530
5. $(C_6H_{13})_2S$	dihexylsulphide	260 (760mm)	1.4590	-	350
6. 	2-n-butyl-1,4-oxythiane	82-83 (3mm)	1.4865	0.9778	27

1	2	3	4	5	6
7. 	2-phenyl-5-methyl-4-oxy-1-thia-cyclohexane	62.5-63	-	-	190
8. 	5,9-dipyridino-7-thiatridecane	-	1.4960	-	13
9. 	2,2,6,6-tetramethyl-1,4-dithiane	92.3-93.5	-	-	270
10. 	2,2,6,6-tetramethyl-1,4-dithian-1,1-dioxide	120-121.5	-	-	8

1		2	3	4	5	6
11.		3,6-dimethyl-1,4-5-trithiacycloheptane	104-106 (5mm)	-	-	17
12.	 	2,5- and 2,6-dibutyldithian-1,4	140-146 (2mm)	1.65091	-	240
13.		2-amylthiacyclohexane	109-110	1.4850	0.9044	320

1	2	3	4	5	6
14. 	2-n-amyl-5-methylthiacyclopentane	105-106.5 (11mm)	1.4740	0.8900	310
15. 	bis(2-hydroxycyclohexyl) sulphide	88-89	-	-	210

thereby the sulphur donor properties change (it is probable that this occurs at the expense of a partial delocalizing of the electron density inside the ring): K = 8o for reagent 2 and K = 21o for reagent 15.

The extraction properties are almost unchanged by going from dialkyl sulphides to cyclic compounds: K = 35o for dihexyl sulphide, K = 32o for 2-amylthiacyclohexane, and K = 31o for 2-n-amyl-5-methyl thiacyclopentane. However, the introduction of other functional groups into a ring influences the sulphur donor properties.

The ether oxygen gives an unimportant decrease of the sulphur donor properties when it is introduced in β-position of dialkyl sulphides (K = 22o), while its introduction into a ring causes a distinct change in the sulphide extraction abilities (K = 27). Another sulphur atom in para- or ortho-position in a ring does not influence much the sulphide extraction abilities but, at the same time, increases the capacity of an extractant to become bi-dentate. Reagent 12 has $\tilde{K}$ = 24o, for reagent 9 $\tilde{K}$ = 27o.

The sulphur donor abilities in a sulphide are lowered by the introduction of a disulphide sulphur (reagent 11). A sulphonyl group also decreases the sulphur extraction properties as well as the sulphur donor abilities in a sulphide (reagent 1o).

The electronegativities of radicals in cyclic extractants have a less pronounced influence on the sulphide sulphur. Thus, a carbonyl oxygen in γ-position and a phenyl radical in α-position have only a weak influence on the sulphur donor activity (reagent 7), while the change of an alkyl radical for a phenyl in dialkyl sulphides gives a sharp reduction of the extraction properties[8].

The presence of a tertiary nitrogen in a sulphide produces an acceleration of the ligand exchange at the expense of the intermediate complex formation to raise the relative reagent extraction activity. However, in the case where steric effects prevent a nitrogen to produce an intermediate complex with an extracted metal, this atom has a small induction effect on the sulphur atom thus diminishing the reagent extraction activity (Table 3, no. 8).

The dependence on the extraction activity for gold(III) chloride of some sulphides on their structures **are** shown below (concentration constants are given in brackets). Trithianes (K = 1o5o) and tetrakissulphides (K = 75o) are considered the most promising of all the reagents studied in terms of their solubilities, selectivities, and extraction activity.

A similar sequence as in Fig. 4 is observed for Pd(II) and Pt(IV) extraction from hydrochloric acid solutions. This sequence is evidently valid for those metal extractions, where the formation of EDA complexes and the ligand substitution of a chloride ion for an extractant are the determining factors for the process.

The correlation between the gold and palladium extraction constants from hydrochloric acid solutions verifies the hypothesis given above (Fig. 5). This correlation is described by the equation,

$$\lg K_{Au} = 1.166 \cdot \lg K_{Pd} - o.3oo \qquad (1\text{-}1o)$$

In accordance with these assumptions the activation energy of the ligand exchange should increase in a reverse relationship.

The values of the activation energy changes were calculated for the process of extracting gold(III), palladium(II), and platinum(IV) from the aqueous into an organic phase,

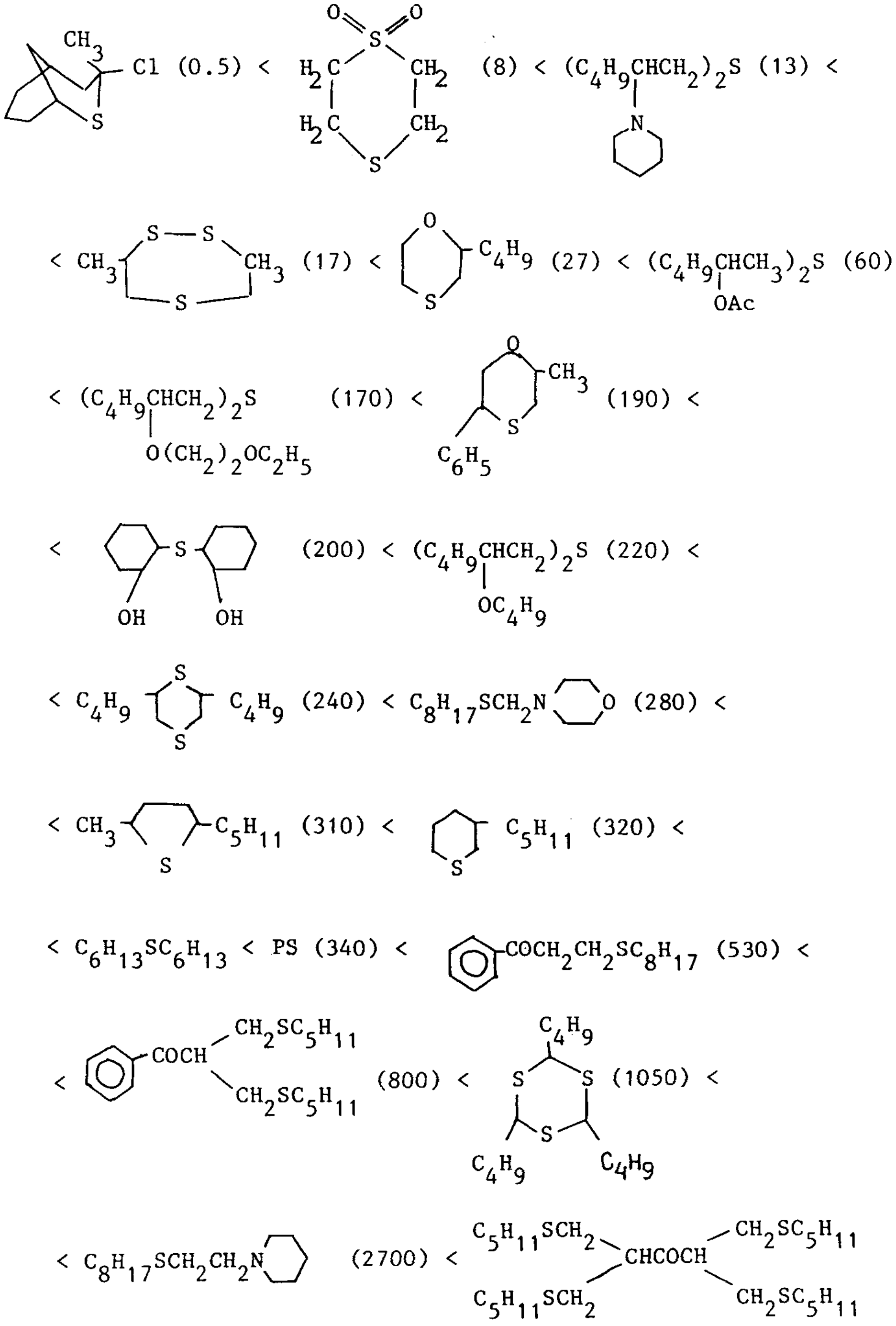


Figure 4: Extraction of gold(III) chloride by sulphides

the calculations being based on temperature dependences (2o-6o°C) of the concentration pseudo-constants of these metal extractions (Table 4). The data confirm the earlier assumptions. In most cases a decrease in the activation energy is observed with increasing polydentate sulphide extraction activity, i.e. the reagent labilizing effect on the ligand exchange kinetics should be treated as a determining factor in extracting gold and platinum metals, the increase of sulphide sulphur activity being not important.

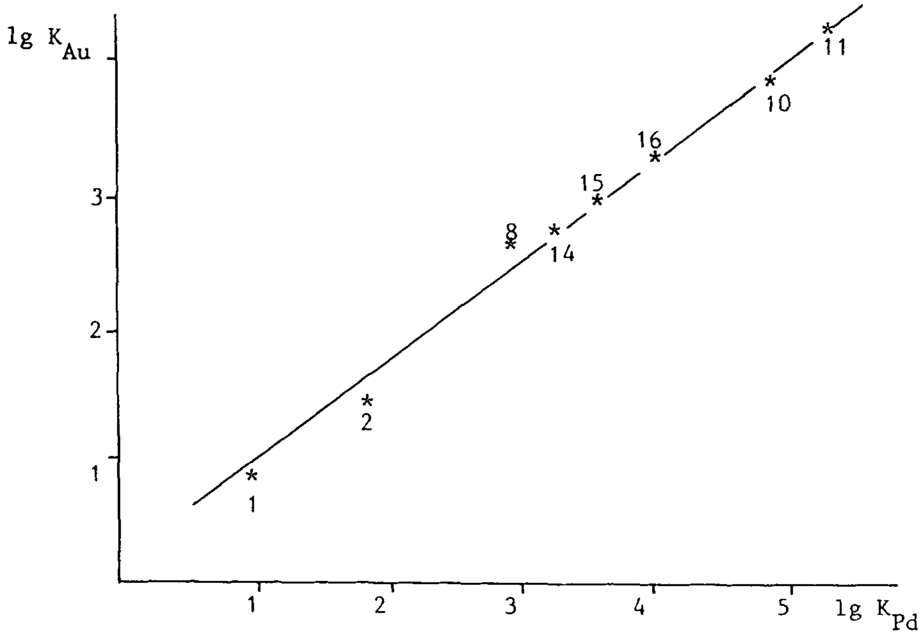


Figure 5: Correlation between Au and Pd extraction constants for the extraction by neutral sulphur organic compounds:

1, 2, 8, 14, 15, 16 - taken from Table 3;

1o, 11 - taken from Table 2;

TABLE 4 Activation energy changes in Pt(IV), Au(III), Pd(II), and Ag extractions by different sulphides (kJ/mole)

Extracted metal and extractant	DHS	OTMA	BCHTMA	STBTMA	Amino sulphides 3 and 10 from Table 3
Ag(I) from 0.1mole/l of HNO_3	-56±2	-50±3	-64±2	-76±2	-63±3
Au(III) from o.1mole/l of HCl	28±1	23±1	21±2	18±1	13±0.5
Pd(II) from 0.1mole/l of HCl	30±1	-	-	20±2	11±1
Pt(IV) from 0.1mole/l of HCl	69±3	46±2	-	38±2	32±1
Pt(IV) from 0.1mole/l of HCl in the presence of 0.00015mole/l of Fe(II)	-	25±1	-	20±1	-

NOBLE METAL SORPTIONS BY OPEN-CHAIN HETERO-SUBSTITUTED SULPHUR ORGANIC SORBENTS.

The weak induction effect of sulphur atoms if they are separated by one methylene group (as it is seen for the polydentate sulphide extraction activity in Table 3) led us to synthesize a "heterochained polymer" of the $[-(CH_2)_nS-]_m$ type, where n = 1,2, with high sorption capacity and selectivity for noble metals.

These syntheses were successfully developed in the Laboratory of Polycondensation of the USSR Academy of Sciences, Bashkirian Branch Institute of Chemistry. Polymethylene monosulphide $[-CH_2-S-]_m$ (PMMS) and polyethylene monosulphide $[-CH_2CH_2-S-]_m$ (PEMS) were prepared $^{5-6}$. PMMS and PEMS represent highly dispersed white powders with molecular masses about 15oo, soluble neither in aqueous acid and alkali nor in organic solvents such as alcohols, ketones, ethers, aromatic or other hydrocarbons. Table 5 presents the elemental analyses of the products.

TABLE 5 Elemental analysis of heterochained polymers.

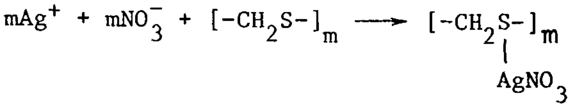
Compound	Fragment	Elemental analysis					m.p. t°C
		S	C	H	Cl	ash	
Polymethylene monosulphide (PMMS)	$(-CH_2-S-)$	68.05	25.21	4.95	-	1.76	190-210
Polyethylene monosulphide (PEMS)	$(-CH_2CH_2-S-)$	49.63	36.75	6.27	2.15	2.27	185-200

The "heterochained polymers" were washed with 1 mole/l of nitric acid, then water and acetone, and dried at 6o°C before use.

The sorption properties of PMMS and PEMS were investigated employing Ag nitric acid solutions and Hg(II), Pt(IV), and Au(III) hydrochloric acid solutions. Sorptions were carried out by the method of isolated shots under static isothermal conditions and stirring, the ratio of liquid and solid phase being 15o. The degree of sorption was defined by changes in the initial metal concentration in the liquid phase. The optimal period for the heterophase equilibrium was found experimentally. That period depended on the individual characteristics of the metal salt extracted.

SILVER SORPTION.

The time for reaching the interphase equilibrium in extracting silver nitrate from nitric acid solution was short, only 5-7 min. The isotherms of the silver nitrate sorptions were plotted against the aqueous phase acidities and temperatures. The higher the acidity and temperature, the lower was the sorption for both polymers. The capacity of PMMS for silver (2.3 g/g) was larger than that of PEMS (1.7 g/g) because the sulphide sulphur content was higher in the former compound, i.e. the saturation of the sorbent proceeded to the Met:S ratio equal to 1. The silver nitrate sorption may be described by the following equation,



$$mAg^+ + mNO_3^- + [-CH_2S-]_m \longrightarrow [-CH_2\underset{AgNO_3}{\underset{|}{S}}-]_m \qquad (1\text{-}11)$$

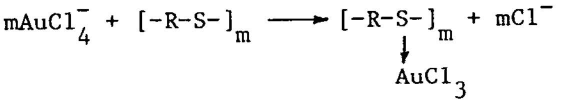
MERCURY, GOLD, PALLADIUM, AND PLATINUM SORPTIONS FROM HYDROCHLORIC ACID SOLUTIONS.

Mercury(II), gold(III), Palladium(II), and platinum (IV) chlorides were extracted from hydrochloric acid solutions containing 0.61 and 1 mole/l of HCl. The times for reaching the heterogeneous equilibrium were: 15 min (for Au(III)), 30 min (for Hg(II) and Pd(II)), and 200 min (for Pt(IV)). The higher the acidity, the lower were the sorptions of the metal chlorides, the same as for the extraction by sulphides. A temperature increase led to increased sorption. At room temperature, rhodium(III) and iridium(III) were actually unextractable, platinum was hardly extractable, while gold(III), palladium(II), and mercury(II) have fair results. At 100°C all platinum metals were well extracted by both sorbents. As for the silver sorption, the PMMS capacities for the platinum metals were larger that those of PEMS: PMMS sorption capacities were 4 g/g (Au), 1.2 g/g (Pd) and those of PEMS were 2.3 and o.7 g/g, respectively. The elemental analysis of the sorbent saturated by Au, Pd, and Hg chlorides gave the following ratios of Met : Cl : L : 1 : 3 : 1 (Au), 1 : 2 : 2 (Pd, Hg), which corresponds to the formation of $MetCl_3L$ and $MetCl_2L_2$ complexes.

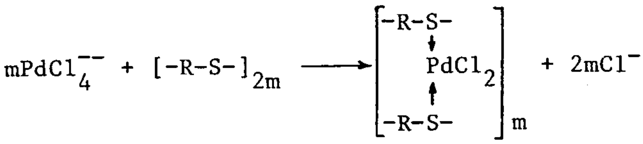
The sorption capacities of both sorbents appeared to be much lower for platinum chloride than for palladium chloride. Such differentiation between the sorption of platinum and that of palladium and gold may be explained by the structures of the initial complex anions $PtCl_6^{--}$, $PdCl_4^{--}$, and $AuCl_4^{-1}$, because the hexachloroplatinate anion was of larger capacity than $PdCl_4^{--}$ and $AuCl_4^{--}$.

The interaction of the planar complex anion $PdCl_4^{--}$ and the sulphide sulphur was not prevented by any steric effects allowing a smooth introduction of the former into the sorbent, while the octahedral complex anion $PtCl_6^{--}$ (with larger capacity) interacted difficultly with the inner region of the sorbent.

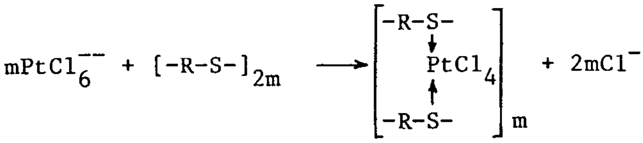
The kinetic properties of the complexing metal chloride anions explain the increase in sorption with temperature and its decrease with an increase in the hydrochloric acid concentration. Temperature rise and chloride ion concentration lowering in the aqueous phase led to accelerating the substitution of chloride ions by a sulphide sulphur in Pt, Pd, and Au acid complexes. The extraction of the metals from hydrochloric acid solutions was of the substitution type and may be described by the following equations,



$$mAuCl_4^- + [-R-S-]_m \longrightarrow \begin{array}{c}[-R-S-]_m \\ \downarrow \\ AuCl_3\end{array} + mCl^- \qquad (1\text{-}12)$$

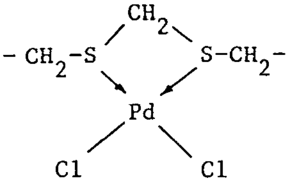


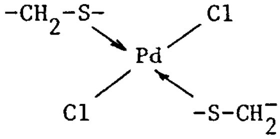
$$mPdCl_4^{--} + [-R-S-]_{2m} \longrightarrow \left[\begin{array}{c} -R-S- \\ \downarrow \\ PdCl_2 \\ \uparrow \\ -R-S- \end{array}\right]_m + 2mCl^- \qquad (1\text{-}13)$$



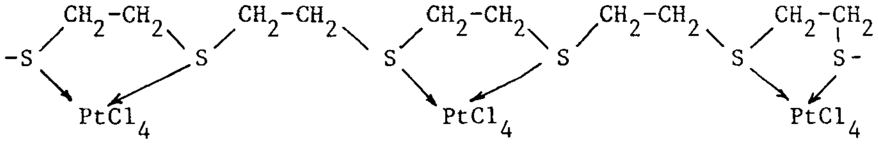
$$mPtCl_6^{--} + [-R-S-]_{2m} \longrightarrow \left[\begin{array}{c} -R-S- \\ \downarrow \\ PtCl_4 \\ \uparrow \\ -R-S- \end{array}\right]_m + 2mCl^- \qquad (1\text{-}14)$$

where R is a methylene or an ethylene bridge. Here, the EDA interactions of Pt and Pd ions may proceed in the same way as in the case with sulphide sulphur atoms of one sorbent polymer molecule as well as with other atoms,

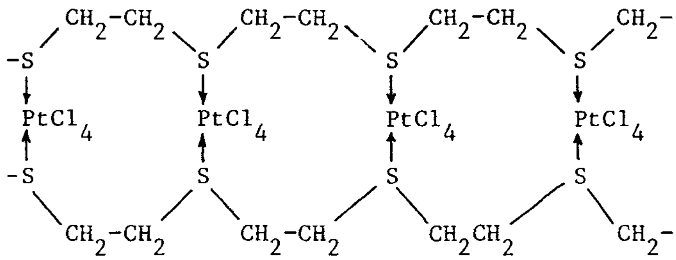




in palladium sorption by PMMS



in platinum sorption by PEMS



other platinum metals (rhodium, iridium) gave quantitative yields at temperatures of aqueous solutions of 1oo°C. The use of different labilizing additions accelerated the substitution reaction of chloride ions for a sulphide sulphur to raise the platinum metal sorptions.

The comparison of the sorption properties of "heterochained polymer" sorbents, PMMS and PEMS, with other known sorbents is in favor of these compounds in terms of their higher effectivities, selectivities, and capacities for the noble metals. PMMS and PEMS are well applicable for concentrating noble metals and for separating these from nonferrous metals as well as for silver and gold affinage.

SULPHOXIDE COMPLEX FORMATION PROPERTIES IN EXTRACTION OF D- AND F-ELEMENTS

The polydentate sulphides are quite effective and selective for noble metal extractions, while metal salt extractions (hard acids in Pearson' classification) need another class of sulphur organic compounds to act as hard bases. The oxidized sulphides, i.e. sulphoxides, present such a class. The presence of two donnor atoms in a sulphoxide promotes the extraction of metal salts of both hard and soft acids. But in most cases they behave as hard bases.

Before a consideration of the experimental aspect of the sulphoxide extraction chemistry the position of sulphoxides in a series of neutral acid-containing extractants (organic oxides) of R_nXO type was investigated. The complexes of these compounds with metal salts are formed in accordance with the mechanism of electron-donor-acceptor (EDA) interactions. The extraction activity of R_nXO compounds depends on the electron density on the oxygen atom and the molecular geometric parameters which determine the entropy effect. The present state of quantum chemistry makes a precise analysis of electron densities for multiatomic R_nXO molecule where X = P, S, N, Se etc. impossible, thus the basicity is regarded the best characteristics for the oxygen donor activity in these compounds. It defines the protonation free energies of P=O, S=O, N=O, and other groups. The correlation between basicity and extraction activity affords an accurate estimation of the position of sulphoxides in the oxide series: between ketones and phosphine oxides. The reactivity increase for SO groups as compared to that of CO groups is also explained by the size of the sulphur atom which is larger than the carbon atom (r_S = 1.o4 Å, r_C = o.77 Å) and therefore leads to a lower binding energy with oxygen ($E = r_e^{-m}$, where $m > 1$) and to a reduced force constant K_e(SO). The correlation between sulphoxide basicity and their extraction ability for uranyl nitrate is described by the following equation[7],

$$\lg K_U = -11.88 + 5.6\ pK_S \qquad (2-1)$$

The oxygen basicity increases going from dialkyl sulphoxides to cyclic sulphoxides, thus enhancing their extraction activity.

The extractability for cyclic sulphoxides increases with the ring size ($6 > 5 > 4$) in accordance with the basicity[7] and with the ligand exchange. The petroleum sulphoxides consist preferably of cyclic structures and their extractivities are larger than that of dialkyl sulphoxides and TBP, approximately the same as that of phosphonates. The extractabilities of open chain sulphoxides may be predicated by the electronegativities ($\sum X$) or by the induction constants (σ^X) of the substituents at sulphur,

$$\lg K_U = 2.33 - 2.54\,\sigma^X = 3.04 - 5.23\sum X \qquad (2\text{-}2)$$

Sulphoxides possess higher sensitivities towards changes in the substituent extraction activity and electronegativities as compared to the neutral phosphorous organic compounds (NPOC). Thus, the substitution of an aliphatic radical (X = 2.0) for a phenyl group (X = 2.34) in NPOC reduces the uranium extraction by a factor of 17, while in the case with sulphoxides it is lowered 40 times. The extraction activity of the sulphoxides cannot be predicted by their IR spectra, another difference between sulphoxides and NPOC. The SO-group stretching frequency is actually unchanged by the introduction of aromatic substituents whereas the PO group stretching frequency increases in phosphorous organic compounds,

DMSO	$(CH_3\text{-}SO\text{-}CH_3)$	1069 cm^{-1}
DBSO	$(C_6H_5\text{-}CH_2\text{-}SO\text{-}CH_2C_6H_5)$	1056 cm^{-1}
BPSO	$(C_6H_5\text{-}SO\text{-}CH_2\text{-}C_6H_5)$	1054 cm^{-1}
DPSO	$(C_6H_5\text{-}SO\text{-}C_6H_5)$	1052 cm^{-1}
TBP	$(C_4H_9O)_3PO$	1274 cm^{-1}
TPP	$(C_6H_5O)_3PO$	1306 cm^{-1}
TBPO	$(C_4H_9)_3PO$	1160 cm^{-1}
TPPO	$(C_6H_5)_3PO$	1195 cm^{-1}

The increase of the extraction activity going from aliphatic to cyclic sulphoxides was assumed to be influenced by the entropy factor [8] and independent of bond energy increase of the complexes formed.

Metal chlorides may be extracted by sulphoxides as coordinative-solvated complexes,

$$M^{Z+} + ZCl^- + qL \longrightarrow MCl_Z \cdot qL \qquad (2\text{-}3)$$

and as complexed anions in the ion associates,

$$M^{Z+} + MH^+ + (Z + m)\ Cl^- + qL \longrightarrow H_mMCl_{Z+m} \cdot qL \qquad (2\text{-}4)$$

Extraction with reproducing metal complex acids is often assisted by water (i.e. the hydration-solvation mechanism is implemented). The quantitative interpretation of the results is complicated by these factors. So, the behaviour of a given system demands a thorough analysis and a consideration of many factors such as aqueous phase states, acidity effects, the type of the salting agent at constant ion strength, and the aqueous state activity.

BISMUTH(III), ANTIMONY(III), TIN(II,IV), VANADIUM(V), AND CHROMIUM(IV) EXTRACTIONS BY SULPHOXIDES

The extraction chromatography technique was employed to investigate the extraction and separation of the above named metals by sulphoxides from various media. The formation of an EDA-complex of the metal salts with the sulphoxides determines the extraction. There are maxima in the curves plotting the metal distribution coefficients (D) vs. the acid concentration in the aqueous phase (Fig. 6). The presence of maxima is explained by three factors,

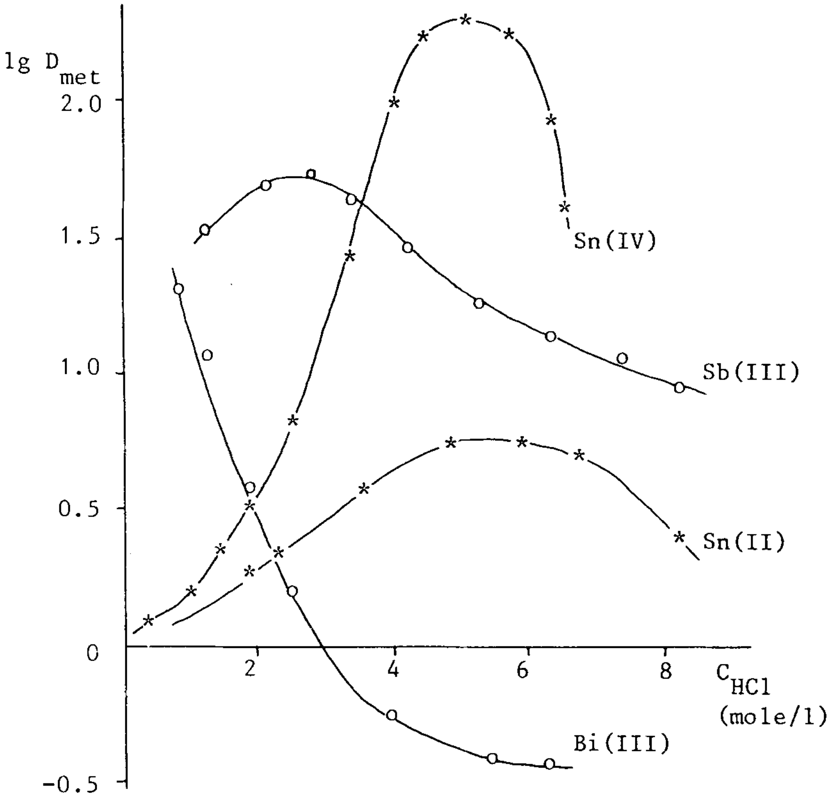


FIGURE 6 Dependences of Sn(II,IV), Bi(III), Sb(III) chloride extractions on hydrochloric acid concnetrations in extractions by 0.05 mole/l of DHSO in xylene ($C_{met}=10^{-3}$mole/l, 20°C).

1. the acid salting out effect (D_{met} is increasing with C_{HCl}).
2. the extraction of the acid (thermodynamic extractant activity reduction)
3. the non-identities in extracting different complex ions from a solution.

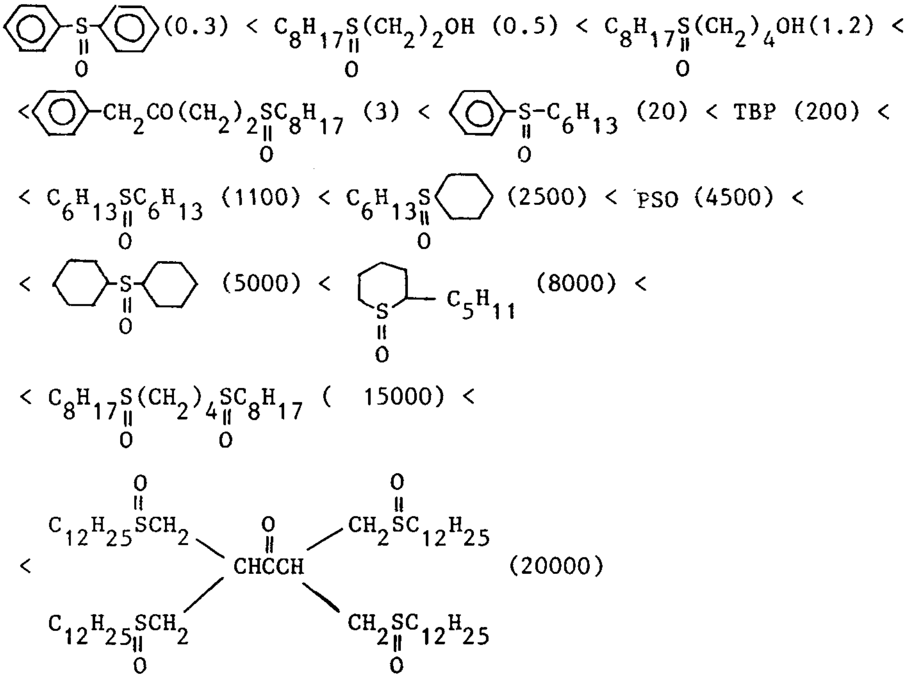
The most complete extraction from nitric acid solution may be achieved with Bi(III), UO_2^{+2}, Hf(IV), Fr(IV) in comparison to other metals (Sb, Cu, Zn, Co, Ni, Pb, and Fe).

THE POSITION OF POLYDENTATE SULPHOXIDES IN A NEUTRAL EXTRACTANT SERIES.

The extraction activity of polydentate sulphoxides was investigated most thoroughly. Di-sulphoxides, keto-, hydroxy-, and amino-sulphoxides were synthesized and investigated in our laboratory. An increase in the number of sulphoxide groups leads to a rise in extractant capacity and effectivity. The presence of additional donor centres in a sulphoxide in appropriate positions allows to form a ring between the complex forming ion and the ligand, this ring formation resulting in a gain of the extraction free energy (in fact, of the complex formation free energy). Extraction entropy and enthalpy effects together afford the true value of extraction activity of polydentate sulphoxides. The uranyl nitrate extraction from o.1 mole/l of HNO_3 was assumed to be a suitable probe to make a comparative evaluation of the extraction activity of mono- and polydentate sulphoxides of different structures. The aqueous phase activities and distribution constants for uranyl nitrate between aqueous and organic phases have been observed by extracting microquantities of uranyl nitrate. It should be noted, that the investigated polydentate sulphoxides are practically insoluble in the aqueous phase and unassociative in an organic phase at $1o^{-3}$ mole/l concentration. In this case the extraction constants should characterize the relative magnitude of EDA interactions between the uranyl group and the oxygen of the sulphoxide group, thus representing the characteristic for the oxygen donor activity in an extractant.

All the sulphoxides studied produce disolvates (with uranyl microconcentrations), a mono-solvate (for disulphoxides), and a semi-solvate (for the keto tetrakissulphoxide) on **saturation of the** organic phase with uranyl nitrate. Di-solvate formation is possible only if the oxygen atoms are trans-positioned to each other both in di- and keto tetrakissulphoxides. The atomic orbitals of uranyl ions cannot be fitted into the extractant geometry, therefore the formation of a ring is possible only by an additional activity for reorienting the oxygen donor atoms which is not compensated by the chelate effect.

A di-solvate may act as an extractant with increasing the uranyl nitrate concentration to promote the extracted complex association in the organic phase. Consequently, effective constants for the uranyl nitrate extractions (K_U) were calculated with its micro-concentration increasing. The extraction activity increases in the following series:



This shows nicely the influence of the induction effect of sulphur radicals on the sulphoxide group donor activity. Keto tetrakissulphoxides possess the highest extraction activity.
However, the extracted complex with uranyl nitrate is strongly associated in the organic phase and therefore insoluble in the organic solvents employed as diluents.

The IR spectra of the complexes reveal a shift of the SO-stretching vibration band of 3o-1oo cm^{-1} to lower frequency to evidence the coordination of the central atom with the sulphoxide oxygen. Besides, another SO band shifted by 5-1o cm^{-1} is observed. This band is assigned to a sulphoxide group coordinated in the outer sphere, i.e. the complex starts to solvate. The small shift of this band indicate weak interaction of the complex with the excess sulphoxide.
The metal chloride and nitrate complexes with petroleum sulphoxides (PSO) and cyclic sulphoxides (HTSO, TCHSO, etc.) are viscous transparent liquids showing the same colour as the metal salts. The complexes of metal chlorides with aliphatic and aromatic sulphoxides were isolated as solids (exception: the liquid iron chloride(III) complex).

The elemental analysis data of both the extracted complexes and those obtained by a direct synthesis show that the chlorides and nitrates of (II)-valence d- and f-elements produce $MetX_3 (H_2O)_3 L_3$, and iron chloride $MetX_3 \cdot L_2$.
To confirm the compositions of the coordination compounds and to get relative values of their stabilities molecular mass measurements were carried out for the complexes in benzene and acetone by the "thermal condensation effect measurement" (TCEM) method. The complex concentration was varied from o.1 to o.oo1 mole/l, the temperature from

2o to 5o^{o}C. A solution of an n-paraffinic hydrocarbon of approximately the same molecular mass was used as a standard. Molecular mass determinations revealed the absence of any significant dissociation in benzene and acetone within the whole range of concentrations. With increasing concentration up to o.2 mole/l some association of the complexes in benzene was observed. In this case we found an increase of the complex molecular masses by 1o-15% of the calculated value. The changes of electric conductivity of the complexes in dry acetone at o.o1 mole/l did not demonstrate those complexes to be electrolytes, i.e. no acid displacement to the outer coordination sphere took place.

Special attention should be paid to the sulphoxide complex with iron(III) chloride which differs from other coordination compounds by its unusual composition ($FeCl_3$ 2L), low solubilities in aromatic hydrocarbons (o.oo2 mole/l), and its state of aggregation (liquid), its molecular mass being 8oo and 59o in benzene and acetone, respectively. The electric conductivity of this complex has the value of 3o.3 cm^2 ohm^{-1} $mole^{-1}$. If an ion-associate structure is assumed for the iron chloride complex, its electric conductivity is calculated to be 6o.6 cm^2 ohm^{-1} $mole^{-1}$ corresponding to an electrolyte ratio 1:1. The increase in the molecular mass value in acetone is caused by ion association.

The structures of the extracted complexes of d- and f-elements with sulphoxides were established by IR-, and Raman spectra, the absorption band relations taking into account the ESP and crystal field parameters. Besides the dipole moments were measured and calculated for 18 probable complex configurations.

Considerations of the whole scope of results makes it

possible to conclude that sulphoxide coordination complexes with (II)-valence metal chlorides are of quasi-tetrahedral structures, where the tetrahedron is narrowed along the Z axis, especially with $CuCl_2$ 2 DHSO. This results from electrostatic interactions of like-charged ligands. Sulphoxide molecules are not fixed rigidly but rotate freely around the Met-O bond in the coordination sphere of the complex forming ion. PMR spectra of the complexes indicate also free rotations. The C_{2v} symmetry type of the complexes indicates also free rotations. The C_{2v} symmetry type was assigned for the $BiCl_3 \cdot 2L$ and $SbCl_3 \cdot 2L$ complexes, it corresponds to a deformed square bipyramid accounting for an unshared pair of antimony ($5S^2$) and bismuth ($6S^2$) electrons.
Nitrate complexes of (II)-valence metals with sulphoxides possess cis-octahedral structures for manganese (Mn), copper (Cu), and cobalt (Co), and trans-structures for uranyle (UO_2), nickel (Ni), and Zinc (Zn). In all these complexes the sulphoxide molecules are fixed more rigidly than in the chloride complexes. This is evidently due to an ion-nitrate volume factor.

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