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SPECTROSCOPIC STUDIES OF SOME METALLIC BIS-DITHIOPHOSPHONATES, $M(DTP)_2$, AND OF SOME ADDUCTS

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ABSTRACT. Metallic bis-[4-methoxyphenyl-O-methyl]-dithiophosphonate complexes (M^{II}=Fe, Ni, Cu, Zn, Cd, Hg, Sn) and the adducts with tertiary amines of Fe(II) and Ni(II) dithiophosphonates were prepared and investigated by UV-VIS, IR and EPR spectroscopies. The electronic spectra show the changes in coordination sphere of Fe(II) and Ni(II)-bis(4-methoxyphenyl-O-methyl-dithiophosphonates) by formation of the adducts. The characteristic frequencies of the PS_2 group confirm different coordination types of dithiophosphonate anion. EPR spectrum presents hyperfine and superhyperfine structure, suggesting a distorted D_{4h} symmetry.

Introduction

For several years we have studied the chemistry of transition metal phosphorodithioates, particularly the ability of nickel(II) phosphorodithioate to form adducts whith various donor ligands. Amine adducts of nickel(II) phosphorodithioates of the general formula $Ni[S_2P(OR)_2]_2 \cdot B$, where R=alkyl, phenyl, 1- and 2-naphtyl and B=mono- and di-amines were investigated [1-6]. We were also interested in coordination behaviour of some phosphonodithioates, such as $M[S_2(OR)(C_6H_4\text{-}O\text{-}CH_3\text{-}p)]_n$, where $M=VO^{2+}$,n=2, R=-CH_3, -C_2H_5, -$^iC_3H_7$, -$^nC_3H_7$, -$^nC_4H_9$, -$^iC_4H_9$, -$^sC_4H_9$[7], $M=Cr^{3+}$, n=3, R=-CH_3, -C_2H_5, -$^nC_3H_7$, -$^iC_3H_7$[8] and $Cr[S_2P(OCH_3)(C_6H_4\text{-}O\text{-}CH_2\text{-}CH_3\text{-}p)]_3$ and $Cu[S_2P(OCH_3)(C_6H_4\text{-}O\text{-}CH_2\text{-}CH_3\text{-}p)]$[9].

In the present paper we report the preparation and investigation of some metallic O-methyl-p-anisil-dithiophosphonates (dtp) of general formulae $M(dtp)_2$ (where M^{II}=Fe, Ni, Cu, Zn, Cd, Hg, Sn) and some of $Ni(dtp)_2$ and $Fe(dtp)_2$ adducts with tertiary amines, in order to follow the influence of different metallic ions and amines on the coordination behaviour of the O-methyl-p-anisil-dithiophosphonate ion.

Results and Discussion

Our compounds (table 1 and 5) were obtained with good yields, varying between 40 and 90%. It can be observed that the yields of simple metallic dithiophosphonate are greater than those of the corresponding adducts. Some of the compounds studied have sharp melting points, while the others do not present such behaviour, or undergo decomposition after melting (adducts with pyridine and picolines, $Hg(dtp)_2$, etc).

The compounds are relatively stable on storage; the relatively low melting points (table 1) suggest monomeric molecular structures, while the compounds whithout melting points may have a polymeric or, at least, a dimeric structure.

In order to gain some insight into the thermal behaviour of compounds, thermogravimetric curvers were recorded for selected compounds, considered as representatives from this point of view. Since the thermolysis curves were not recorded in an inert atmosphere, the presence of oxygen should be taken into account in the interpretation of data. Small endothermal efects, without weight loss are observed on all curves at melting temperature. The next thermal process is a weight loss accompanied by an exothermal effect, at temperatures immediately above the melting points, which corresponds to the elimination of the tertialy amines. This process takes place in two steps: the first molecule of pyridine and picolines is eliminated at 160° ($Ni(dtp)_2 \cdot pic)_2$), 165° ($Ni(dtp)_2(4\text{-}pic)_2$) and the second one at 190°, 180°, 200° respectively. The adducts of the type $Fe(dtp)_2 \cdot B_2$ (B=pyridine, 3-, 4-picoline) have the same behaviour; the loss of the tertiary amine takes place in an overlapping process, between 130-200°.

The loss of coordinated amines is followed by the combustion of the organic groups, with the py_2), 150° ($Ni(dtp)_2$(3- thermal effects partially overlapping with one another. After the combustion of the organic components of the molecules, the inorganic residue exhibits some minor exothermal effects between 550-700°, probably due to some polymorphic transformations. Such a thermal behaviour of our complexes resembles the one observed in other similar compounds[6,10].

Table 1

Elemental Analysis and Some Properties of Compounds

Compound	Colour	Mp ° (dc)	Elemental Analysis (found/calc.)			
			% M	% P	% S	% N
NH_4dtp	white					
$Fe(dtp)_2$	reddish-brown	293 dark-brown	10.35/10.70	11.53/11.88	23.95/24.52	-
$Fe(dtp)_2{\cdot}py_2$	white-yellow	147-150	8.35/8.21	8.85/9.11	18.32/18.82	3.84/4.11
$Fe(dtp)_2{\cdot}(2,2`\text{-dipy})$	cherry-red	145	8.40/8.23	8.83/9.14	18.24/18.87	3.97/4.13
$Fe(dtp)_2$ (o-phen)$_2$	red	120 brown	6.52/6.32	7.23/7.03	14.22/14.51	6.21/6.35
$Ni(dtp)_2$	violet	178	11.35/11.18	12.15/11.81	23.95/24.39	-
$Ni(dtp)_2{\cdot}py_2$	green	148-151	8.35/8.60	9.30/9.08	18.38/18.74	3.82/4.10
$Ni(dtp)_2{\cdot}(3\text{-pic})_2$	green	138-140	7.90/8.86	8.50/8.72	17.70/18.01	3.80/3.94
$Ni(dtp)_2{\cdot}(4\text{-pic})_2$	green	150-152	8.15/8.26	8.90/8.72	17.65/18.01	3.75/3.94
$Ni(dtp)_2{\cdot}(2,2`\text{-dipy})$	green	130	8.70/8.62	9.37/9.10	18.70/18.80	4.02/3.97
$Ni\ (2,2`\text{-dipy})_3{\cdot}(dtp)_2$	pink	56-60 (90)	5.68/5.91	6.38/6.24	12.55/12.90	-
$Ni(dtp)_2{\cdot}(o\text{-phen})$	green	145	8.54/8.33	8.95/8.79	18.46/18.16	3.82/3.97
$Ni(o\text{-phen})_3{\cdot}(dtp)_2$	pink	177-180 (185)	5.35/5.14	6.01/5.82	11.75/12.02	-
$Cu(dtp)_2$	beige-yellow	190 orange	12.35/12.00	11.25/11.70	23.75/24.17	-
$Zn(dtp)_2$	white	140	12.66/12.30	11.33/11.66	23.80/24.08	-
$Cd(dtp)_2$	white	155-157*	19.19/19.43	11.00/10.71	21.82/22.13	-
$Hg(dtp)_2$	yellow-greenish	100-101 117-120 orange	29.75/30.09	9.75/9.30	18.88/19.20	-
$Sn(dtp)_2$	yellow	>200 beige	20.50/20.29	10.88/10.60	22.00/21.89	-

* 195^0 re-solidifies; 225^0 greenish; 245-255^0 re-melts

Electronic Spectra

The changes in iron(II) and nickel(II) coordination induced by adding the amine ligands are clearly shown by the features of the electronic spectra. The electronic transitions in the spectra of the adducts are strongly dependent on the nature of the amine ligands.

Electronic spectra for $Fe(dtp)_2$ and its adducts were recorded and spectral data were listed in table 2.

For $Fe(dtp)_2$ the recorded spectrum is only qualytative because of the insolubility of this compound in solvents without donor properties. The spectrum was recorded on a freshly-prepared solution by the reaction of metallic iron with O-methyl-p-anisil dithiophosphonic acid, before the precipitations should have become quatitative. In the electronic spectrum, two bands are resolved, located at 19 300 and 16 400 cm^{-1}.

The data in table 2 certify the formation of complex combinations: in the UV domain two bands appear located between 43 000 and 34 000 cm^{-1}, wich represent intraligand transitions and have high values of molar extinction coefficient. These bands will be shifted towards lower values in complexes as compared to the free dithiophosphonate ion, thus certifying the structural modifications which occur by the shift of the negative charge density towards the central ion through coordination.

Table 2.

Electronic Spectra of $Fe(dtp)_2$ Adducts

Compound	c (mol/L)	Bands (cm^{-1})	ε ($l \cdot mol^{-1} \cdot cm^{-1}$)	Transitions
NH_4 dtp	$7.9 \cdot 10^{-6}$	42 640 41 773	$1.15 \cdot 10^4$ $1.27 \cdot 10^4$	n-π^* (L)
$Fe(dtp)_2 \cdot py_2$	$3 \cdot 10^{-6}$	40 325 35 800 18 400 16 500	$6.8 \cdot 10^4$ $6.1 \cdot 10^4$ $5 \cdot 10^3$ $2 \cdot 10^2$	n-π^* (L) t_{2g}(Fe)-π^*(L)
$Fe(dtp)_2 \cdot$dipy	$9 \cdot 10^{-6}$	38 462 37 981 21 792 19 948	$5.29 \cdot 10^4$ $5.38 \cdot 10^4$ $5.1 \cdot 10^3$ $5.9 \cdot 10^3$	n-π^* (L) t_{2g}(Fe)-π^*(L)
$Fe(dtp)_2 \cdot (o\text{-phen})_2$	$9 \cdot 10^{-6}$	41 827 34 616 22 915 21 792 20 509	$9.23 \cdot 10^4$ $2.1 \cdot 10^4$ $3.67 \cdot 10^3$ $4.44 \cdot 10^3$ $4.91 \cdot 10^3$	n-π^* (L) t_{2g}(Fe)-π^*(L)

In the visible range, bands appear between 22 300-16 900 cm^{-1}, bands whose molar extinction coefficients have lower values; yet, these values are not low enough to be associated with *d-d* transitions, they are due to metal-ligand transitions (t_{2g} (Fe)-π^*(L)). The values of these transitions decreases from the o-phenantroline adduct to the one with pyridine. The presence of these bands in the spectra represents another proof of the formation of complex combination an they

are responsable for the colour of the compounds. One may notice that the values of the t_{2g}-π^* transitions increase from the pyridine adduct to the one with o-phenantroline, which corresponds to the peculiar structures of organic ligands.

The electronic spectrum of $Cu(dtp)_2$ exhibits the following bands in UV: 41 900 cm^{-1} and 38 000 cm^{-1} (n-π^*), 29 070 cm^{-1} (π-π^*), all of them being intraligand transitions. There are also some bands in visible: 23 800 cm^{-1} (t_{2g}-π^*(L)), 21 690 cm^{-1} and 15 105 cm^{-1} ($^2B_{1g}\rightarrow{}^2E_g$ and $^2B_{1g}\rightarrow{}^2A_{1g}$ respectively). Similar bands are observed also for other Cu(II)-dithiophosphonates[11]; their positions indicate a distorted square-planar geometry arround the copper atom involved in the CuS_4 chromophore.

The electronic transitions in the spectra of $Ni(dtp)_2$ adducts are dependent on the nature of the amine ligands (table 3). $Ni(dtp)_2$ exhibits two bands in the visible region situated at 14 400 cm^{-1} ($^1A_{1g}\rightarrow{}^1B_{1g}$) and at 18 600 cm^{-1} ($^1A_{1g}\rightarrow{}^1B_{2g}$), usually values for NiS_4 chromophores[12].

The assigment of transitions is in accordance with a (more or less distorted) O_h symmetry[13]. The Lever`s method[14] was used to calculate the crystalline field splitting parameter (10 Dq), the Racah parameter (B) and the nephelauxetic parameter β (table 3). The calculates values of 10 Dq depend on the type of chromophore (higher for NiN_6 than for NiS_4N_2, i.e. 9 380 cm^{-1} and 9 420 cm^{-1} for $Ni(dipy)_3\cdot(dtp)_2$ and $Ni(o\text{-}phen)_3\cdot(dtp)_2$ respectively). The covalent contribution of the dithiophosphonic ligand is reflected by the values of the β nephelauxetic parameter; this parameter is lower when the sulphur atoms are coordinated and slightly higher when only nitrogen atoms are coordinated to the nickel atom (table3).

Table 3.

Electronic Spectra of $Ni(dtp)_2$ Adducts

Compound	ν_2 (cm^{-1}) $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$	ν_3 (cm^{-1}) $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$	B (cm^{-1})	β	ν_1= 10Dq (cm^{-1}) $^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$
$Ni(dtp)_2\cdot py_2$	13 800	22 140	664	0.63	8 630
$Ni(dtp)_2\cdot(3\text{-}pic)_2$	13 650	21 700	620	0.59	8 060
$Ni(dtp)_2\cdot(4\text{-}pic)_2$	13 750	22 200	660	0.63	8 580
$Ni(dtp)_2\cdot$dipy	13 900	22 300	669	0.64	8 690
$Ni(dipy)_3\cdot(dtp)_2$	15 000	24 050	721	0.68	9 380
$Ni(dtp)_2\cdot$o-phen	14 000	22 700	681	0.65	8 850
$Ni(o\text{-}phen)_3\cdot(dtp)_2$	15 100	24 150	724	0.69	9 420

EPR Spectrum of $Cu(dtp)_2$

The powder EPR spectrum of Cu(II)-bis[4-mothoxyphenyl-O-methyl]-dithiophosphonate at room temperature is typical for square planare CuS_4 species (figure 1). The shape of the spectra shows the presence of hyperfine and superhyperfine structure.

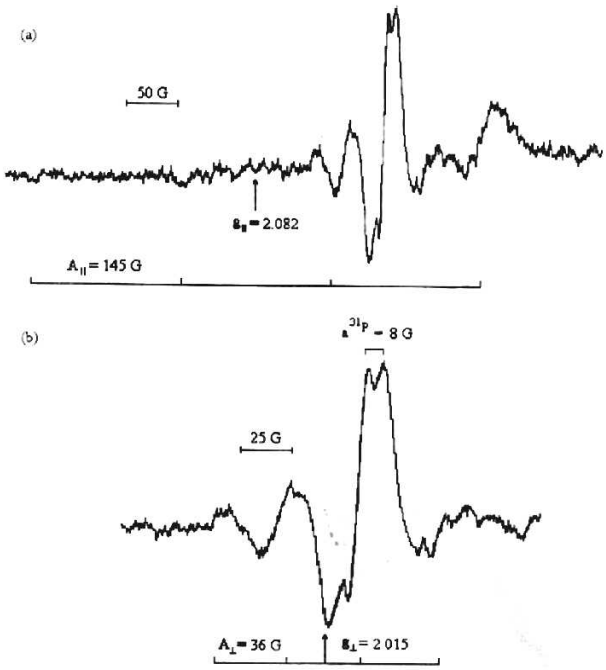


Figure 1. EPR spectrum of $Cu(dtp)_2$

The spin Hamiltonian used for the studied complex is:

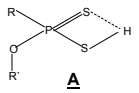
$$H=\beta[g_{\parallel} B_Z S_Z + g_{\perp}(B_X S_X + B_y S_y)] + A_{\parallel} S_Z I_Z + A_{\perp}(S_X I_X + S_y I_y) + S \sum_{n=1}^{2} a^{31}P I_p$$

where $g_{\parallel}$ and $g_{\perp}$ are the principal values of the g tensor, β is the Bohr magneton, B_x, B_y and B_z are the components of the external magnetic field, S_x, S_y and S_z are the components of the electron magnetic moments S, I_x, I_y and I_z are the components of the nuclear spin moment of ^{63,65} Cu and I_p-the nuclear spin moment of ^{31}P and $a^{31}P$ the superhyperfine tensor.

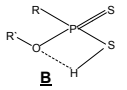
Using the experimental EPR parameters (figure 1) and optical spectral data we have estimated, according to Kivelson and Neiman[15] the covalency degree of the σ in plane bonding (α^2=0.52) and the delocalisation degree of the paramagnetic electron in 3*s* orbital of phosphorous atoms (c_s^2=0.002). Both values are tipicaly for distorted CuS_4 chromophores[9].

Infrared Spectra

The interpretation of IR spectrum of O-methyl-*p*-anisildithiophosphonic acid was based on the literature data[16-21] concerning phosphoro- and phosphonodithionate acids. Thus, two bands in ν_{SH} region, situated at 2 593 and 2 526 cm^{-1} were observed, corresponding to A, respectively to B isomers.



A



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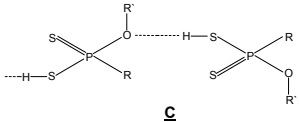
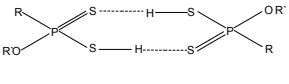


C



D

The intramolecular hydrogen bond in both A and B structures was responsable for splitting of ν_{SH} band. The difference between the two bands in our spectrum and that of the literature[21] can be correlated with influence of organic radical directly bonded to the phosphorous atoms ($-C_6H_4-O-CH_3$ comparatively to $-CH_3$). The bands at 593 cm^{-1} and 526 cm^{-1} were assigned to $\nu_{P=S}$ and ν_{P-S} respectively. The smaller value of $\nu_{P=S}$ related to $\nu_{P=S}$(620 cm^{-1}) in 4-methoxyphenyl-thionophosphine sulfide can be a consequencies of the involvment of SH group to hydrogen bonding (structures A-D).

The infrared spectra can provide useful information concerning the coordination of the PS_2 groups. The IR absorption bands containing the higest PS_2 contributions, namely ν_a (PS_2) and ν_s (PS_2) are listed in table 4. The combinations with other normal modes (especially ν_{P-O} and ν_{P-C}) have some influence upon the behaviour of these bands. The atributions were made accroding to the literature data[22] and by comparison with NH_4dtp spectrum (table 4).

Table 4.

Infrared Spectra of Compounds

Compound	ν_a (PS_2)	ν_s (PS_2)	$\Delta\nu$	Coordination type of the PS_2 group
NH_4dtp	627	556	71	ionic
Fe(dtp)$_2$	627 653	531 546	96 107	anisobidentate bridge
Fe(dtp)$_2$·py$_2$	633	533	100	anisobidentate
Fe(dtp)$_2$·dipy	633	543	90	anisobidentate
Fe(dtp)$_2$·(o-phen)$_2$	643	520	123	monodentate
Ni(dtp)$_2$	620	552	68	isobidentate
Ni(dtp)$_2$·py$_2$	628	550	78	iso-anisobidentate
Ni(dtp)$_2$·(3-pic)$_2$	628	550	78	iso-anisobidentate
Ni(dtp)$_2$·(4-pic)$_2$	628	543	85	iso-anisobidentate
Ni(dtp)$_2$·dipy	635	546	89	anisobidentate
Ni(dipy)$_3$·(dtp)$_2$	629	559	70	ionic
Ni(dtp)$_2$·o-phen	632	542	90	anisobidentate
Ni (o-phen)$_3$·(dtp)$_2$	622	553	69	ionic
Cu(dtp)$_2$	647	534	113	bridge
Zn(dtp)$_2$	621	540	81	iso-anisobidentate
Cd(dtp)$_2$	622 642	521 541	101 101	anisobidentate bimetallic triconective bridge
Hg(dtp)$_2$	634	536	98	anisobidentate
Sn(dtp)$_2$	610 655	525 539	85 116	iso-anisobidentate bridge

On analysing the data in the table 4 and the refrence in the literature[22] according to which the mode of coordination of the PS_2 group can be established in keeping with the values of the $\Delta\nu = \nu_a(PS_2) - \nu_s(PS_2)$ difference, i.e.:

$60 < \Delta\nu < 70$ cm^{-1} (isobidentate coordination)

and $90 < \Delta\nu < 100$ cm^{-1} (anisobidentate coordination),

we find that:

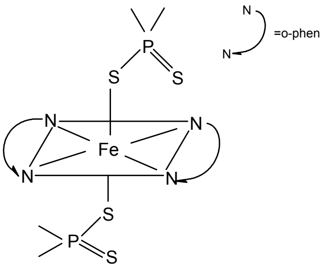
a) The O-methyl-*p*-anisildithiophosphonic anion may be *ionically bonded* in compounds having the formula $Ni(dtp)_2 \cdot B_3$ (B=dipyridil (dipy) and ortho-phenantroline (o-phen)), for which the ν_a and ν_s (PS_2) and $\Delta\nu$ values are close to the once found in the IR spectrum of NH_4dtp.

b) The phosphonodithioate anion may achive a *monodentate coordination* (structure I) like in the case of $Fe(dtp)_2(o\text{-phen})_2$ when the double character of the P=S bond is strenghtened, while the P-S bond is weakned, which leads to an increase of the ν_a frequency and to the decrease of the ν_s frequency as related to the corresponding values for NH_4dtp compound. In fact ν_a becames $\nu_{P=S}$, while ν_s - ν_{P-S}; $\Delta\nu$ assumes the highest value (table 4).

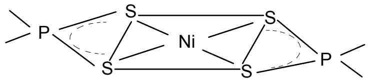
c) *The bidentate coordination* of the $^{-}S_2P(OCH_3)(C_6H_4OCH_3)$ ion may be of two types: *isobidentate* (structure II) which is found in $Ni(dtp)_2$; both frequencies ν_a and ν_s will shift to lower values as related to those of NH_4dtp, as a consequence of sulphur coordinatin to the central atom. *Anisobidentate* coordination takes place whitout delocalisation of the π system of electrons over the whole PS_2 group (structure III), with a $\Delta\nu$ difference located within the ~90-100 cm^{-1} interval. This occurs in $Hg(dtp)_2$ and in the $Fe(dtp)_2 \cdot B$ (B=2py, dipy) or the $Ni(dtp)_2 \cdot B$ (B=dipy, o-phen) adducts (structure IV). There are compounds in which the ν_a and ν_s (PS_2) frequences assume intermediary values, between those specific to isobidentate and anisobidentate coordinations, as is the case with the $Ni(dtp)_2 \cdot B_2$ (B=py, 3- and 4-pic) adducts (structure V) and for $Zn(dtp)_2$.

In the case of bidentate coordination of the anion, the frequencies characteristic of the PS_2 group vibrations will undergo the following changes: ν_a shifts to higher values, while ν_s - to lower once compared to the values of the frequences characteristic of the parent compound, $Fe(dtp)_2$, respectively $Ni(dtp)_2$. Such shifts can be explained by the fact that, as a consequence of the coordination of tertiary amines. The density of negative charge arround the central ion increases, which induces a weakening of the metal-sulphur bond and, concomitantly, the strengthening of the phosphorous-sulphur bond.

d) For the $M(dtp)_2$ (M^{II}=Fe, Cu, Cd, Sn) compounds, there are two pairs of bands in the range of νPS_2 (700-500 cm^{-1}) which may attributed to different types of dithiophosphonate ions coordination; they correspond to structures VI-VIII. In order to discriminate these structures one can appeal to the $\Delta\nu$ values and thermal behaviour of the compounds. Thus for $Fe(dtp)_2$, $\Delta\nu$=96 cm^{-1} suggests the PS_2 group bound by chelation, while $\Delta\nu$=107 cm^{-1} can be correlated with bridge coordination. Since the compound is decomposed generating a black waxy oil product only over 300^{o} (table 1), it means that this compound is at least dimeric, taking a VI type structure. For $Cd(dtp)_2$ the two values of $\Delta\nu$ are equal (table 4), but the ν_a and ν_s values undergo such shifts that the structure of the compound can be associated with a model in which a sulphur atom of two PS_2 group is bonded bimetallic triconective[23] (structure VII).



I



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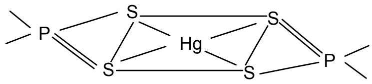

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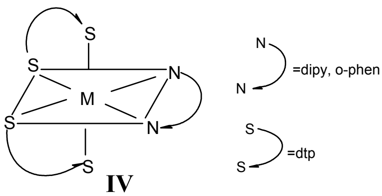

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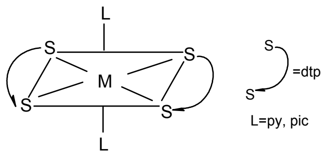
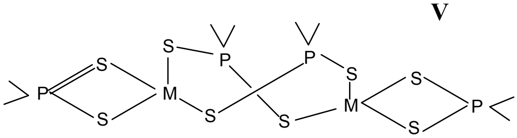
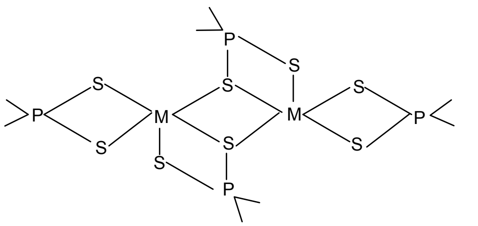


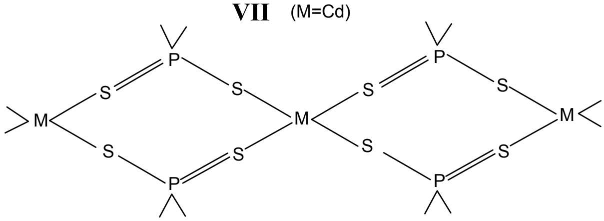
V



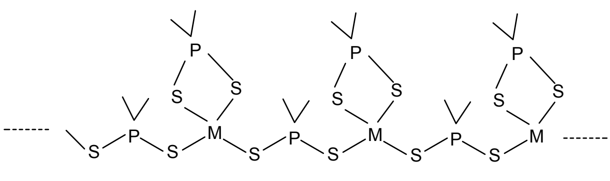
VI (M=Fe)



VII (M=Cd)



VIII (M=Cu)



IX (M=Sn)

For $Cu(dtp)_2$, $\Delta\nu$=113 cm^{-1} suggests a bridged-bonded dithiophosphonate anion as in the structure VIII, which fits with no melting point of these substance. For $Sn(dtp)_2$, there are two values for $\Delta\nu$ (table 4): one of them suggests a bidentate anion and the other - a bridged one, like in structure IX; this compound have no melting point also. The last two compounds undergo changes of colour by increasing of the temperature (table 4), so a polymeric structure is expected.

However, it is hard to assume, relying only on data provided by IR spectra whether the bridge achived is iso- or anisobidentate.

Experimental

Reagents and Procedures

The reagents used here were analitycal grade purity.

4-Methoxy-phenylthiophosphine sulfide was obtained by Lecher`s method[23] and used for preparation of *O-methyl-p-anisildithiophosphonic acid*: 4g disulfide was refluxated, under stirring with 100 mL anhydrous methanol for 30 minutes. The acid was separated by vaccuum distilation as an incolour viscous liquid. Yield: 88.6%: acidic constant, k_a, is 1.4 · 10^{-4} mol/l. Other acids were obtained by the same procedure with different alcohols, ROH (R=-C_2H_5, *n*- and *i*-C_3H_7, *n*-, *i*-, *sec*- and *t*-C_4H_9; -CH_2-CH_2OPh, -CH_2-CH_2-OMe, -CH_2Ph, -C_5H_{11}, -C_6H_{11}, α- and β-$C_{10}H_7$, but here we report only O-methyl derivative and some coordination properties of it.

Ammonium O-methyl-p-anisil-dithiophosphonte was obtained by refluxing 4g methoxy-phenyl-thionophosphine sulfide in 50 mL anhydrous benzene and the stoechiometric amount (0.5 mL) of anhydrous methanol, at 40-60°, under stirring, for 30 minutes. In the benzenic solution of O-methyl-*p*-anisil-dithiophosphonic acid thus obtained, was bubbled a current of dry ammonia. The bulky, white precipitate resulted was filtred, washed with benzene and dried in vaccuum. Elemental analysis: %P found(calc) 12.15(12.35): %S found(calc) 22.25(22.50); Mp°=152-158 (with decomposition), η%=70.

Table 5.

Synthesis and Yields of Compounds

Compound	$MX_2 \cdot nH_2O$ (g) solvent (mL)	NH_4dtp (g) solvent (mL)	$M(dtp)_2$ (g) solvent (mL)	Base (g) solvent (mL)	Yield (%)
$Fe(dtp)_2$[a]	$(NH_4)_2 \cdot Fe(SO_4)_2 \cdot 6H_2O$ (0.4) water (20)	(0.5) water (25)	-	-	60
$Fe(dtp)_2 \cdot py_2$[b]	$(NH_4)_2 \cdot FeSO_4 \cdot 6H_2O$ (0.4) water (20)	(0.5) water (25)	-	py (0.2) MeOH (10)	62
$Fe(dtp)_2$·2,2`dipy[b]	$(NH_4)_2 \cdot FeSO_4 \cdot 6H_2O$ (0.4) water (20)	(0.5) water (25)	-	dipy (0.154) MeOH (20)	51
$Fe(dtp)_2$·o-phen[b]	$(NH_4)_2 \cdot FeSO_4 \cdot 6H_2O$ (0.4) (20)	(0.5) water (25)	-	o-phen (0.36) MeOH (25)	40

Table 5.

Synthesis and Yields of Compounds

Compound	$MX_2 \cdot nH_2O$ (g) solvent (mL)	NH_4dtp (g) solvent (mL)	$M(dtp)_2$ (g) solvent mL)	Base (g) solvent (mL)	Yield (%)
$Ni(dtp)_2$[c]	$NiCl_2 \cdot 6H_2O$ (4.75) MeOH (20)	(10.04) MeOH (20)	-	-	78
$Ni(dtp)_2 \cdot py_2$	-	-	$Ni(dtp)_2$ (0.52) acetone (50)	py (0.2) acetone (10)	86
$Ni(dtp)_2 \cdot (3\text{-pic})_2$	-	-	$Ni(dtp)_2$ (0.52) acetone (50)	3-pic (0.2) acetone (10)	40
$Ni(dtp)_2 \cdot (4\text{-pic})_2$	-	-	$Ni(dtp)_2$ (0.52) acetone (50)	4-pic (0.2) acetone (10)	60
$Ni(dtp)_2 \cdot dipy$	-	-	$Ni(dtp)_2$ (0.52) acetone (50)	dipy (0.156) acetone (20)	41
$Ni(dipy)_3 \cdot (dtp)_2$	-	-	$Ni(dtp)_2$ (0.52) acetone (50)	dipy (0.465) acetone (30)	62
$Ni(dtp)_2 \cdot o\text{-phen}$	-	-	$Ni(dtp)_2$ (0.52) acetone (50)	o-phen (0.18) acetone (10)	45
$Ni(o\text{-phen})_3 \cdot (dtp)_2$	-	-	$Ni(dtp)_2$ (0.52) acetone (50)	o-phen (0.54) acetone (30)	80
$Cu(dtp)_2$[d]	$CuSO_4 \cdot 5H_2O$ (0.25) water (20)	(0.25) water (20)	-	-	61
$Zn(dtp)_2$[e]	$ZnSO_4 \cdot 7H_2O$ (0.29) water (20)	(0.5) water (15)	-	-	70
$Cd(dtp)_2$	$Cd(NO_3)_2 \cdot 4H_2O$ (0.308) water (20)	(0.5) water (10)	-	-	75
$Hg(dtp)_2$	HgI_2 (0.455) MeOH (20)	(0.5) MeOH:H_2O 1:1 (20)	-	-	30
$Sn(dtp)_2$	$SnCl_2 \cdot 2H_2O$ (0.23) slightly acidulated water (30)	(0.5) water (25)	-	-	67

a) Iron (II) O-methyl-*p*-anisildithiophosphonate was also obtained by another method, namely, the reaction between Hdtp and iron powder: 0.4g *p*-anisil-tiophosphine sulfide in 20 mL anhydrous methanol with an excess of iron powder were refluxated for 90 minutes. A brown-greenish solution was obtained, from which a brown-reedish compound, $Fe[S_2P(OCH_3)(C_6H_4OCH_3)]_2$ was separated on cooling. The precipiate was filtred, washed with methanol (5-7 mL) and ether (5-7 mL) and was dried in air. Elemental analysis: %Fe found(calc): 10.50(10.70); %P found(calc): 11.52(11.88); %S found(calc): 24.13(24.52); η=50%. It does not present melting point, it decomposes up to 300°.

b) Iron (II) O-methyl-*p*-anisilphosphonodithioate adducts can not be obtained directly from $Fe(dtp)_2$ due to its insolubility in usualy solvents. However, these adducts were prepared also by following method: the solutions obtained in a,

were separated by decantation over the methanolic solutions containing the amounts of tertiary amines listed in table 5. Under stirring the corresponding adducts precipitated. The precipitates were filtred, washed with 2 mL methanol and 3 mL ether, then were dried in air.

c) Nickel (II) O-methyl-*p*-anisildithiophosphonate can be obtained also by reaction of 4g *p*-anisil-thionophosphine sulfide in 20 mL anhydrous methanol and an excess of nickel powder. It was refluxed, under stirring, during 90-120 minutes. The violet precipitate of $Ni[S_2P(OCH_3)(C_6H_4OCH_3)]_2$ was separated, filtred washed with methanol (5-10 mL) and ether (5-10 mL). The same product was obtained by the reaction of Hdtp with other nickel salts.

d) NH_4dtp solution was added to the $CuSO_4$ solution (table 5), drop by drop, under continuous stirring for 30 minutes.

e) $Zn(dtp)_2$ can be obtained also by the methods described at a and c.

The metallic compounds and their adducts were obtained according to the known procedure[1-8] and are listed in table 5.

The compounds were analysed by classical methods[25] and the results were listed in table 1.

Thermolysis curves were recorded using a MOM Erdely-Paulik derigratograph. Electronic spectra were recorded in methanol, chloroform or methylene chloride with a JASCO V-530 UV-VIS aparatus, infrared spectra - in KBr pellets, with a FT-IR JASCO-615 instrument and the powder EPR spectrum was recorded at 9.4 GHz (X band) using a standard JEOL-JES-3B equipment with a magmetic field modulation of 100 kHz.

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