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# Structure and Properties of Oxycations. IV. Spectroscopic Studies on Complex Compounds with Some Organophosphorus Ligands

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*In continuation of the studies on structure and properties of oxycationic compounds with the special emphasis on their spectroscopic properties, some new complexes of $Mo^{VI}$, $W^{VI}$, and $U^{VI}$ with organophosphorus ligands were obtained and characterized. Their electronic spectra were discussed as due to the transitions involving the oxycation entity and the ligand molecule. The UV phenyl bands were found in all the spectra of these compounds. The structure and bond type could be clearly explained in the case of uranyl compounds due to the uranyl vibronic structure in their UV-spectra. Infrared spectra supplied further evidence on these problems supporting some our conclusions.*

## Introduction

An important factor in the formation of complex compounds is the donor ability of a ligand, or more precisely of the atom which is linked to the central ion. The $P=O$ group as a ligand is of considerable importance here, no matter what type of a given compound is involved. Both the esters and oxides containing the above group are excellent and well known complexing agents, to mention only mono-, di- and tributylphosphate and triphenylphosphine oxide (or the oxides containing other radicals) which are of considerable significance in the extraction processes.

In the previous paper[1] it was demonstrated that triphenylphosphine and triphenylarsine oxides are good complexing agents for the $MoO_2^{2+}$ compounds. Some data relating to these compounds have been previously known[2,3] and Bartecki and Dembicka[1] have shown that the above ligands stabilize the halogenides ($MoO_2Cl_2$ and $MoO_2Br_2$) which in normal conditions undrego rapid decomposition.

One of the principal methods used in many works on complexes of various *d*-electron elements with the organophosphorus ligands was the infra-red spectroscopy.[3-8] This method enabled to obtain some essential data on the bonding and structure of these compounds on the basis of the P-O and Me-O frequency changes. It was shown, however,[1] that interesting ifnormation may also be obtained from the electronic spectra, especially if their structure in the ultra-violet is taken into account.

In the present work the complexes of $Mo^{VI}$, $W^{VI}$ and $U^{VI}$ with some new organophosphorus ligands have been examined which provided further information on the spectroscopic properties and structure of oxycationic compounds.

## Experimental Section

### 1. *Preparation of starting compounds.*

1.1. Preparation of $MoO_2Cl_2$ and $WO_2Cl_2$.

Molybdenyl chloride was prepared by the method previously described.[1] The procedure in case of $WO_2Cl_2$ was based on Spitzin's work.[9] Tungsten trioxide was placed in a quartz tube and dry, gaseous hydrogen chloride was passed at 400°C. $WO_2Cl_2$ contaminated with $WO_3$, condensed on cold parts of the tube. The reaction product was dissolved in dioxane and separated from insoluble $WO_3$.

1.2. Synthesis of phophorus esters.

In the present work, apart from triphenylphosphine oxides, the following phosphorus esters have been used:

1. ethylene-(P,P-diphenyl)-diphosphinic acid di-isopropyl ester-LP I
2. ethylene-(P,P-dibenzyl-diphosphinic acid di-isopropyl ester-LP II.
3. butylene 1,4(P,P-diphenyl)diphosphinic acid di-isopropyl ester-LP III.

The authors are indebted to Dr. Mastalerz[10-12] who has kindly agreed to synthesize and supply all the above compounds.

### 2. *Preparation of complexes.*

2.1. Preparation of $MoO_2Cl_2$ complexes with the organophosphorus esters.

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(2) S. M. Horner, S. Y. Tyree, *Inorg. Chem.*, *1*, 122 (1962).

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(12) P. Mastalerz, unpublished.

2.1.1. $MoO_2Cl_2$ dissolved in dioxane was treated with the LP I solution in dioxane at a molar ratio 1:2. The yellow precipitate was after 24 hours filtered off, washed with warm water and warm dioxane and then dried at room temperature. The composition of the product corresponded to the formula $MoO_2Cl_2$ . 2LP I. The analysis was made by the methods described previously.[1]

*Anal.* Calcd. Mo, 9.72; C, 48.64; H, 5.72. Found: Mo, 9.50; C, 47.51; H, 6.29.

2.1.2. If the complex discused under 2.1.1. was synthesized from the reagents heated up to 70°C at the ratio 1:1 and then heated for a short time in water bath, the precipitate became orange. The precipitate, as previously, was filtered off after 24 hours, washed and dried. The composition of that complex corresponds to the formula $MoO_2Cl_2$ . LP I.

*Anal.* Calcd. 16.17. Found: Mo, 16.05.

2.1.3. The reactions of molybdenyl chloride acc. to 2.1.1. with the ligands LP II enable to obtain similar complex compounds of a formula $MoO_2Cl_2$ . 2LP III.

*Anal.* Calcd. Mo, 15.45; C, 42.53; H, 4.60. Found: Mo, 14.65, C, 41.80; H, 5.15.

2.2. Preparation of $WO_2Cl_2$ complexes with the organophosphorus esters.

The reaction of tungstenyl chloride with the LP I ligand acc. to 2.1.1. resulted in a yellow compound of a formula $Wo_2Cl_2$ . 2LP I. In this complex W, C and H contents have been determined. The percentage of W has been determined by calcinating the complex to $WO_3$ and that of other elements by burning in an electric furnace.

*Anal.* Calcd. W, 18.19; C, 45.09; H, 5.26. Found: W, 17.56; C, 46.26; H, 5.72.

2.3. Preparation of $UO(NO_3)_2$ complexes with the organophosphorus ligands.

Unranyl nitrate « Anala R » grade was used without further purification. Complexes with the LP I, LP II and LP III ligands were synthesized by method 2.1.2. with excess uranyl nitrate being used in the reaction. The compounds obtained were assigned the following formulae:

$2\,UO_2(NO_3)_2$ . LP I
$2\,UO_2(NO_3)_2$ . LP II
$2\,UO_2(NO_3)_2$ . LP III

In the above compounds U, C and H have been determined. The percentage of U was determined by calcination of the sample and weighing as $U_3O_8$.

| *Anal.* | Found | Calcd. |
|---|---|---|
| $2\,UO_2(NO_3)_2$ . LP I | U, 39,99 | 40.26 |
| $2\,UO_2(NO_3)_2$ . LP II | U, 39,33 | 39.22 |
| $2\,UO_2(NO_3)_2$ . LP III | U, 39.33 | 39.11 |

3. *The absorption and reflection spectra of complex compounds.*

The absorption and reflection spectra over the range 200 to 800 nm were made in an Unicam SP500 spectrophotometer and up 1000 nm in an Unicam SP 700. The infra-red spectra were measured in a Zeiss UR 10 spectrophotometer over the range 400-5000 cm$^{-1}$.

## Results and Discussion

1. *The electronic spectroscopy of the complexes with organophosphorus ligands.*

1.1. Complexes with the molybdenyl group $MoO^{2+}{}_2$.

The spectroscopic properties of the Mo$^{VI}$ compounds with the $MoO_2^{2+}$ group have been discussed in the papers[1,13] by Bartecki and Dembicka. The results of studies on both the complex compounds and aqueous solutions of molybdates have shown that these properties are manifested by the appearance of the so called « molybdenyl » band whose average energy amounts to about 29 kK.

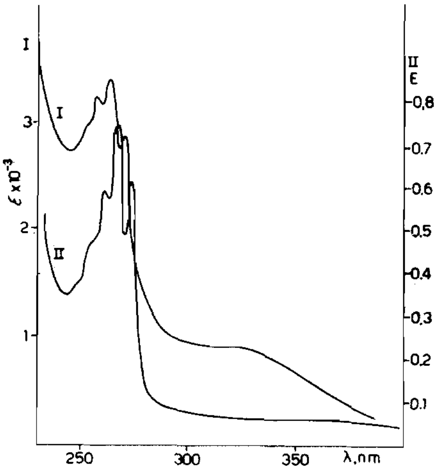

Figure 1. Absorption spectra of $MoO_2Cl_2$ . LP I in ethanol (I) (c = 1.1×10$^{-3}$ *M*) and in dioxane (II).

This band, according to the results of all our previous studies, has a considerable halfwidth. This most probably means that not only a strongly antibonding excited state is involved in the transition but also that apart from the molybdenyl band (corresponding to a transition in the $MoO_2^{2+}$ group) another trasition in which Cl$^-$ is involved occurs here (from the π orbital).[13]

The energies of the particular transitions are given in Table I.

Table I shows that in case of LP I the molybdenyl band undergoes a considerable hypsochromic shift in the mixture of ethanol and chloroform, as compared to that in dioxane. The same situation occurs both in the complexes with simple triphenylarsine and triphenylphosphine oxides and in the molybdenyl halogenides.[1] This regularity may be explained as due to the donor-acceptor character of the complexes in which molybdenyl chloride retains its own properties and also to the effect of the polar solvent on the dissociation process. This second factor has been previously expressed by the following equation:

$$MoO_2Cl_2(S)_2 \rightleftarrows MoO_2(S)_2^{2+} + 2Cl^-$$

in which S denotes polar solvents.

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(13) A. Bartecki, D. Dembicka, *J. Inorg. Nucl. Chem.*, *29*, 2907 (1967).

**Table I.** Electronic absorption spectra of $MoO_2Cl_2$ and $WO_2Cl_2$ with organophosphorous ligands.

| Compounds | Solvent | Transition energy kK | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $MoO_2Cl_2$ | dioxane | 27.4 | | | 38.0 | | | 44.6 |
| $MoO_2Cl_2$ . LP I | ethanol-chloroform | 30.7 | 36.3 | 37.2 | 38.0 | 39.0 | 40.0 | 44.2 |
| $MoO_2Cl_2$ . 2LP I | dioxane | (27.0) | 36.5 | 37.5 | 38.3 | 39.0 | 40.2 | 46.0 |
| $MoO_2Cl_2$ . LP III | dioxane | 29.3 | 36.4 | 37.4 | 38.2 | 39.0 | 40.3 | 46.0 |
| $MoO_2Cl_2$ . LP III | reflection | 23.2 | | | 37.2 | | | |
| $WO_2Cl_2$ | dioxane | 25.0 | | | (39.0) | | | 44.0 |
| $WO_2Cl_2$ . 2LP I | dioxane | 29.0 | 36.6 | 37.3 | 38.4 | 39.0 | 40.0 | 44.0 |

One of the characteristic features of the absorption spectra of the compounds containing phenyl group in their ligands is the vibrational structure found in the region of about 250 to 270 nm. This structure is very typical for simple oxides (both phosphine and arsine) since the transition resulting from the excitation of the electron from a free electron pair in the P atom which occur in the phosphines and disturb the spectrum are not, of course, found in the phosphine oxides. The phenyl structure in the ligands used in the present work is also well defined for the same reasons.

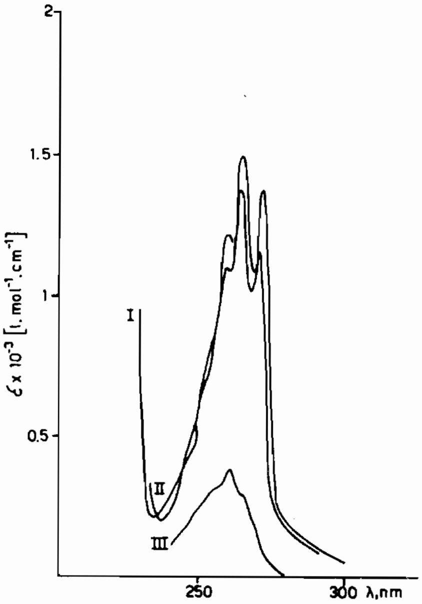

Figure 2. Absorption spectra of LP I (I) in ethanol of LP II (II) in dioxane and of LP III (III) in dioxane (in all cases c = $10^{-3}M$).

The vibrational phenyl structure appears in all complexes with the molybdenyl group which indicates that in these cases no change of the electron density in the P-O bond occurs. This, however, is valid only for solutions.

The above phenyl structure does not occur in the reflection spectra. This may be explained as due to a strong interaction between the ligand molecule and $MoO^{2+}{}_2$ group in the crystal lattice. Such conclusion in also supported by the results of infra-red studies.

## 1.2. Complex with the $WO_2^{2+}$ group.

Only a complex with the LP I ester has been studied in dioxane solution. The general properties of the spectra are very similar to those of the molybdenyl complexes with the structure of the phenyl radical retained. The band which should be assigned to one of the O→W transition appears at about 25 kK. The problem related to this transition are much less discussed in the literature than in case of molybdenyl compounds. Bartecki[14] has shown that this band should rather be assigned to the low energy transition in the oxycation entity.

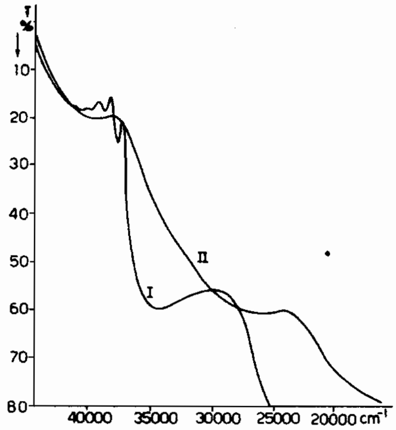

Figure 3. Absorption spectrum in dioxane (I) and reflection spectrum (II) of $MoO_2Cl_2$ . LP II.

## 1.3. Complexes with the $UO_2^{2+}$ group.

More extensive spectrophotometric studies were made on the complexes obtained in the reaction between uranyl nitrate and suitable esters and also with triphenylphosphine and triphenylarsine oxides. A characteristic vibrational structure found in uranyl compounds could also have been used for the analysis of the spectra. According to our studies (Figure 4, Figure 5, Table II and III) there is much stronger interaction in the complexes of uranyl nitrate with organophosphorus ligands than in the compounds previously described.

First, one should notice that the blurring off of the vibrational structure related to the phenyl radical takes place even in dioxane solutions, as well as in the reflection spectra. This is also typical (though to a lesser extent) for the oxide complexes.

The vibrational structure related to the transitions in the uranyl group undergoes significant changes depending on the surrounding medium. This structure

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(14) A. Bartecki to be published, Symposium on Coordination Chemistry in Bratislava (1967).

**Table II.** Electronic absorption spectra of $UO_2(NO_3)_2$ complexes with organophosphorous ligands in dioxane

| Compounds | | | | | | Transition energy kK | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $UO_2(NO)_2 . 2Ph_3PO$ | | | | | | 29.0 | | | | | | | | 36.60 | 37.20 | 38.50 | 39.30 | 44.20 |
| $2UO_2(NO_3)_2 . LP$ I | 20.53 | 21.35 | 22.03 | 22.97 | 23.58 | 24.00 | 24.58 | 25.30 | 26.03 | 27.10 | 27.83 | 28.80 | | | | 38.80 | | 47.00 |
| $2UO_2(NO_3)_2 . LP$ II | 20.50 | 21.30 | 22.00 | 22.95 | 23.50 | 24.00 | 24.60 | 25.25 | 26.00 | 27.00 | 27.80 | 28.70 | 29.40 | | | 40.80 | | 46.20 |
| $2UO_2(NO_3)_2 . LP$ III | 20.50 | 21.32 | 22.00 | 22.96 | 23.50 | 24.00 | 24.59 | 25.27 | 26.00 | 27.00 | 27.82 | 28.80 | 29.50 | | | 40.50 | | 46.00 |

**Table III.** Electronic reflection spectra of $UO_2(NO_3)_2$ complexes

| Compounds | | | | | | | | | (kK) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $UO_2(NO_3)_2 . 2Ph_3AsO$ | 15.00 | | | 20.30 | 21.00 | 21.80 | 22.40 | 23.15 | 23.60 | 24.20 | 24.85 | 25.60 | | | | | | 30.40 | 38.00 |
| $UO_2(NO_3)_2 . 2Ph_3PO$ | 15.00 | 17.80 | 19.20 | 20.40 | 21.00 | 21.75 | 22.50 | 23.15 | 23.60 | 24.40 | 25.00 | 25.70 | 26.85 | 27.90 | | | | 30.00 | 37.00 |
| $2UO_2(NO_3)_2 . LP$ I | | | | 20.38 | 21.05 | 22.00 | 22.70 | 23.25 | 23.95 | 24.60 | 24.90 | 25.60 | 26.60 | 27.50 | | | | | |
| $2UO_2(NO_3)_2 . LP$ II | | | | | 20.65 | 21.45 | 22.10 | 22.85 | 23.45 | 24.05 | 24.80 | 25.45 | 26.2 | 27.20 | 27.90 | 28.60 | 29.50 | | 37.00 |
| $2UO_2(NO_3)_2 . LP$ III | 17.30 | | | 20.45 | 21.20 | 22.05 | 22.80 | 23.35 | 24.00 | 24.65 | 25.25 | 26.00 | 27.00 | | | | | | |

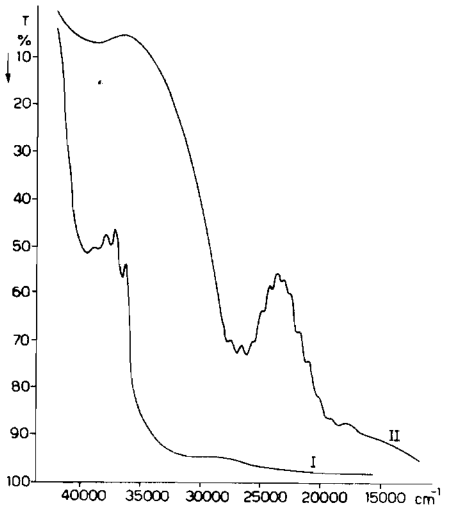

Figure 4. Absorption spectrum in dioxane (I) and reflection spectrum (II) of $UO_2(NO_3)_2 . 2Ph_3PO$.

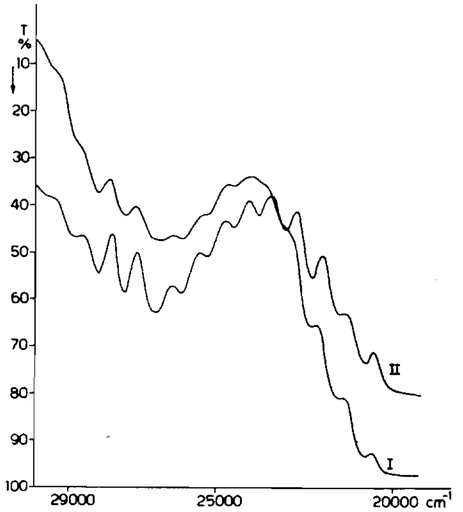

Figure 5. Absorption spectrum in dioxane (I) and reflection spectrum (II) of $UO_2(NO_3)_2 . 2LP$ II.

is not found in dioxane in case of simple oxides whereas it becomes quite evident in the solid phase (reflection spectra). On the contrary, the uranyl structure in the spectra of complexes with LP I, LP II and LP III ligands is found both in solution and in solid phase.

These phenomena may be explained as due to the different roles af solvents (particularly of the donor solvents as dioxane) in case of the $UO_2^{2+}$ complexes for one part and $MoO_2^{2+}$ and $WO_2^{2+}$ for another part. These problems are discussed in p. 3.

Some interesting results may be obtained from a detailed analysis of the vibronic transitions. In Table II and III the energies of particular vibronic transitions are given (approximated to hundreds of $cm^{-1}$). The number of vibronic bands are found to be different in various complexes, in general however the structure is better defined in solid phase (reflection spectra) than in solutions.

The literature on the spectroscopic of uranyl compounds is very extensive and it was recently discussed by Rabionowitsh and Belford.[15] One of the authors of the present work (A.B.) and B. J. Trzebiatowska have also published a number of papers on the subject.[16]

One of the factors which the latter authors considered as very important was the estimation of the vibrational structure and its dependence on various parameters. In these papers it was shown that this structure is well explained by assuming the vibronic mechanism in which the entire spectrum in the visible and UV range corresponds to one progression $0''$-$v'$ derived from the transitions in $UO_2^{2+}$ as an anharmonic oscillator. By using the Birge-Sponer extrapolation it was possible to determine approximately not only the dissociation energy in the excited state but also the number of possible vibrational energy levels. The value was equal to 13 but the probably error was as high as 20 per cent. Jørgensen[17] reported the energy values of vibronic bands assuming the occurrence of two systems. One should emphasize, however, that only 11 bands are usually recorded in the absorption spectra of solutions.

Thirteen distinct bands have been found to appear in the reflection spectra from 20.4 to 29.5 kK. In

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(15) Rabinowitsch, R. L. Belford. Spectroscopy and Photochemistry of Uranyl Compounds, Pergamon Press, Oxfgord 1963.

(16) B. Jezowska-Trzebiatowska, A. Bartecki, *Spectrochimica Acta 18*, 799 (1962) and other papers cited there.

(17) C. K. Jørgensen, *Acta Chim. Scand.*, *11*, 116 (1957).

**Table IV.** Infra-red spectra of some $Mo^{VI}$, $W^{VI}$ and $U^{VI}$ complex compounds

| Compound | Me—O | V | P—O—C | P=O | Reference |
|---|---|---|---|---|---|
| $Ph_3PO$ | | | | 1193 | 3 |
| $MoO_2Cl_2$ | 903, 945 | 42 | | | 1 |
| $MoO_2Cl_2 . 2Ph_3PO$ | | | | 1140, 1162 | 3 |
| $MoO_2Br_2 . 2Ph_3PO$ | 903, 946 | 43 | | 1147, 1175 | 3 |
| $WO_2Cl_2$ | 923, 963 | | | | |
| $WO_2Cl_2 . 2Ph_3PO$ | 913, 960 | 47 | | 1162, 1170 | 3 |
| $WO_2Br_2 . 2Ph_3PO$ | 907, 954 | 47 | | 1159, 1190 | 3 |
| $UO_2Cl_2 . 2Ph_3PO$ | | | | 1064, 1125 | 3 |
| $UO_2(NO)_3)_2 . 2Ph_3PO$ | | | | 1079, 1134 | 3 |
| LP I | | | 990 | 1182, 1239 | |
| $MoO_2Cl_2 . 21P$ I | 907, 950 | 43 | 992 | 1166, 1180, 1209, 1235 | |
| $MoO_2Cl_2$ . LP I | 914, 952 | 38 | 998 | 1170, 1187, 1211, 1239 | |
| $WO_2Cl_2$ . 2LP I | 910, 952 | 42 | 992 | 1166, 1183, 1206, 1240 | |
| $UO_2(NO_3)_2$ . LP I | 930 | | 990, 1003 | 1160, 1198, 1280 | |
| LP III | | | 980 | (1175), 1200 | |
| $MoO_2Cl_2$ . LP III | 917, 956 | 39 | 995 | 1167, 1198, 1248 | |
| $UO_2(NO_3)_2$ . LP III | 930 (850) | | 980, 1010 | 1157, (1185), 1270 | |

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some cases the lower energy bands are also observed and these are assigned to the transitions from higher vibrational levels of the ground state, $V'' = 1$ and 2. The energy of the 0—0 transition is then equal to 20.4 - 20.7 kK which is in agreement with all experimental data for the above complexes.

If we take into account that 13 vibronic bands appearing in the spectrum of the complex with ligand LP II form the vibronic system then the mean value of the vibrational quantum amounts to 733 $cm^{-1}$, that is, it is almost equal to that for the spectra of uranyl nitrate in organic solvents.[16] Besides, the energy of the last band would correspond to the dissociation energy since in the other part of the spectrum no absorption related to the $UO_2^{2+}$ group occurs. The value of 733 $cm^{-1}$ is due to the total-symmetric vibration of the uranyl ion, $\nu_1$.[16]

2. *Vibrational spectroscopy of the complexes with organophosphorus ligands.* As was stated previously, one of the most popular methods used in the studies on complexes with organophosphorus ligands is the infra-red spectroscopy. In general, it is not difficult to asign the particular bands to the corresponding frequencies.

The results of absorption measurements in the infra-red are very important since the frequency shifts in the groups of atoms corresponds to the changes in bonding and interatomic distances. No detailed analysis based on the absorption measurements was attempted in the present work. Only the values of the particular frequencies and their splittings in the spectra of complexes have been determined in comparison to the values in ligands.

The frequency values for the P=O, P—O, Me—O and in some cases for the phenyl group have been considered as most important.

Table IV shows the data obtained in the present work and also, for comparison, some data reported by other authors.

It is evident from the table that even the P=O frequencies in the oxide are comprised within the range of about 10 $cm^{-1}$ according to various sources. The changes which occur in the corresponding bands on complexation are, however, more essential. This realtes to both their energy changes and splitting value.

The esters used in this work exhibit two strong absorption bands within the range corresponding to the P=O group frequencies, for instance in LP I with energies 1182 and 1239 $cm^{-1}$. The appearance of these two bands is related to the change in symmetry of the P=O group and to the coupling with other frequencies in esters in comparison to the tertiary oxide. Both these bands are evidently split in complex compounds, the splittings for the first band amounting to 14-17 $cm^{-1}$ and for the second one 26-34 (for LP I).

According to many authors [18-20] the splitting value of the band corresponding to the stretching symmetric P=O frequencies is closely related to the properties of the coordinating molecule as an acceptor. For transition metals, Cotton and others[19] have assumed that it is the reduction of the $p\pi$—$d\pi$ bond contribution which is essential. This effect clearly exceeds those resulting from an increase of the P—O $\sigma$ bond and Me—O interaction which might considerably increase the P=O frequency. Cousins and Hart[20] suggest that in lanthanides the $\pi$-electrons become more polarized in the P=O bond as the ionic radius of Me increases. For the lanthanides with lesser ionic radii, however, coupling with the Me—O vibrations is important.

It was not possible to determine how the coordinating molecule (with a definite ligand) affects the P=O frequencies for the complex compounds studied in the present work. It seems, however, that there are two characteristic factors: (i): $MoO_2^{2+}$ compounds show lower frequencies of the split bands than $WO_2^{2+}$ compounds, (ii): for the same oxycation an increase occurs in the bromide complex in comparison to the chloride complex.

The first factor might be explained as due to the change in the ionic radius of $Me^{VI}$. The fact that this problem is not so clear in the complexes with the LP I ligand may result from a lesser significance of

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(18) M. J. Frazer, W. Gerrard, R. Twalts, *J. Inorg. Nucl. Chem.*, *25*, 637 (1963).

(19) F. A. Cotton, R. D. Barnes, E. Bannister, *J. Chem. Soc.*, 1499 (1965).

(20) O. R. Cousins, F. A. Hart, *J. Inorg. Nucl. Chem.*, *29*, 1745 (1967).

the coupling between the Me–O and P=O vibrations in these cases.

The P–O–C (aliph) frequency which we have identified on the basis of [21] seems to be much less sensitive. It is only natural since this group of atoms is merely indirectly depending on the coordination process.

Another important factor determining this process is the absorption related to the Me–O frequencies. Numerous literature data indicate that the stretching vibrations occur in the range 900-950 $cm^{-1}$ for $Mo^{VI}$ and $W^{VI}$. Considering the $MeO^{2+}{}_2$ group as nonlinear entity ($C_{2v}$-symmetry), the simultaneous occurrence of two stretching vibrations symmetric and antisymmetric, should be expected. In simple compounds like $MoO_2Cl_2$, their energies amount to 903 and 945 $cm^{-1}$,[3] in $WO_2Cl_2$ to 923 and 963 $cm^{-1}$.[22] If the group is linear ($D_{\infty p}$-symmetry) then only the total-symmetric vibration should occur in the infra-red and the antisymmetric one in the Raman spectrum. This situation corresponds, in fact, to the uranyl compounds although the cancellation of the selection rules by the crystal lattice results in many cases in the simultaneous occurence of these two vibrations.

The table shows that, as was expected, the frequencies $\nu_1$ and $\nu_3$ (for an isolated oxycationic group) decrease considerably but their differences are only slightly increasing. This probably corresponds to the change in angle in the Me–O–Me system but the change in the Me–O distance resulting from coordination is not significant. Similar values have also been found for other complexes of the above oxycationic compounds, like $MoO_2Cl_2 . 2DMP$.[23]

3. *The structure of complexes with organophosphorus ligands.* The results of spectroscopic studies suggest some conclusions related to the structure of the above complexes. In our previous paper on the molybdenyl complexes with tertiary phosphine and arsine oxides the spectroscopic studies enabled us to suggest the structure considering the addition character of these compounds.

The donor character of the P=O group may be lesser in esters, the occurrence of two such groups, however, results in a certain tendency to form chelated complexes. According to the analyses, in some cases the quantitative ratio of an acceptor molecule ($MoO_2Cl_2$) to an ester molecule (LP I) is equal to 1:1 which may be explained only assuming a chelated structure. This is also in agreement with the higher stability of the above compound in comparison to the complex of a formula 1:2 in which no chelation process occurs.

The structure 1:1 of the Mo-complex is a result of the strong tendency to reach coordination number 6 which is proved by the numerous addition compounds of a formula $MoO_2Cl_2 . 2L$. One should assume that the ester molecule acts as a unidentate ligand although it has two donor groups P=O. If, however, this molecule acted as a bidentate ligand, as in case of the 1:1 complex, then the structure of the compound would be characterized by two multimembered ringe (for LP I - 8). As a result of this, the Cl atoms must be placed beyond the coordination sphere. It seems significant that in the 1:1 complex both the Me–O and P=O frequencies are higher than in the 1:2 complex. Nevertheless, these data are not sufficient to draw definite conclusions on the structure of the compounds.

Some other problems are essential in case of the uranyl nitrate complexes with the above organophosphorus ligands. The analysis shows that the main form is the compound of formula $2\,UO_2(NO_3)_2 . LP$. The situation is then quite different than in case of Mo ando W since the esters act as unidentate ligands, with both the P=O groups being equally active. This means, however, that the coordination number of $U^{VI}$ is being changed. A very distinct vibrational structure of the electronic spectra (as was discussed previously) might then correspond to such structure in tri-nitrate ions where these ions act as bidentate ligands. Under such assumption the coordination number of U with each $NO_3$-group being bicoordinative amounts to 7 and it is known to appear sometimes in uranyl compounds.

It should be noted that Katzin[24] has found that the organophosphorus ligands result rather in lowering of the coordination number. If we, however, assume the coordination number of U as 5 then it would be difficult to explain the distortion of the uranyl vibrational structure in solid phase in case of the 1:1 complex. This structure became very clear in the 2:1 complexes.

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