Complexes of Molybdenum(VI), (V) and (IV) with Macrocyclic Polythiaethers

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The complex formation of dioxodichloromolybdenum(VI), oxotrichloromolybdenum(V) and tetrachloromolybdenum(IV) with the macrocyclic polythiaethers: 1,4,8,11-tetrathiacyclotetradecane (TTP) and 1,4,7,10,13,16-hexathiacyclooctadecane (HTO) have been studied. The new complexes [MoO₂Cl₂(TTP)], [(MoO₂Cl₂)₂(HTO)], [(MoOCl₃)₂(TTP)(THF)₂], [MoOCl₃(TTP)], [(MoOCl₃)₂(HTO)], [(MoCl₄)₂(TTP)], [MoCl₄(TTP)] and [(MoCl₄)₂(HTO)] were isolated. The complexes were characterized on the basis of elemental analyses, magnetic measurements, IR and mass spectra. In the given complexes the bonding mode appears to be influenced by the number of sulphur atoms, as well as the size of the ring of the investigated macrocyclic polythiaethers.

Introduction

In recent years macrocyclic ligands containing oxygen or nitrogen atoms as donors have been widely studied because of their unusual metal binding properties [1].

Macrocyclic polythiaethers containing sulphur atoms as donors have drawn less attention, although investigations of some macrocyclic polythiaethers, and their complexes with a number of metals, have further extended the scope of macrocyclic chemistry [2–6].

Recent determinations of crystal structure have revealed different types of bonding for the potentially tetradentate macrocyclic ligand tetrathiacyclotetradecane (TTP). For example Alcock *et al.* [7, 8] found that the structures of mercury chloride and mercury perchlorate complexes with this ligand differ markedly, indicating both the flexibility of the ligand and the marked influence of the coordinative ability of the anion present. With the coordinating chloride anions the ligand adopts in the mercury complex a double bidentate bridging conformation, while with the noncoordinating perchlorate ions the ligand is tetradentate. On the other hand DeSimone *et al.* [9, 10] found that NbCl₅ complex contains two NbCl₅ units bridged by bis-unidentate ligand in the exo conformation.

In our previous studies we have shown that the stability of the complexes of silver and mercury chlorides, perchlorates and picrates with macrocyclic polythiaethers TTP and HTO depends on the number of sulphur atoms in the macrocyclic polythiaethers [11–15].

While we have a fairly good idea about the structures of the complexes with TTP as a ligand, we know considerably less about HTO, which being large and more flexible can fold into any number of conformations.

We have now extended our studies to the complex formation of molybdenum chlorides and oxychlorides of different oxydation states with potentially tetradentate and hexadentate polythiaethers TTP and HTO, respectively.

Experimental

Starting Materials

Reagent grade chemicals were used without further purification except in the cases noted. 1,4,8,11-tetrathiacyclotetradecane (TTP) and 1,4,7,10,13,16-hexathiacyclooctadecane (HTO) were prepared as described previously [14]. Solvents were purified by standard methods, dried and saturated with dry nitrogen before use. Dioxodichloromolybdenum(VI) was prepared by the chlorination of MoO₂ [30]. Oxotrichlorobis(tetrahydrofuran)molybdenum(V) was prepared by the reaction of molybdenum(V)-chloride with tetrahydrofuran [20]. Tetrachlorobis(butyronitrile)molybdenum(IV) was obtained by the method reported by Allen *et al.* [31].

Preparation of Complexes

All reactions and manipulations were carried out under a dry nitrogen atmosphere using a standard dry-box technique.

Conditions of preparations and analytical data for the complexes obtained are given in Table I and II. Most of the complexes were prepared several times. The analyses are the mean of the results on different preparations.

TABLE I. Conditions of Preparation for Molybdenum Complexes.

Compound	Starting Compound	Metal/ligand Ratio	Solvent
[MoO$_2$Cl$_2$(TTP)]	MoO$_2$Cl$_2$	1:1 2:1 2:1	Ether–CH$_2$Cl$_2$ Ether
[(MoO$_2$Cl$_2$)$_2$(HTO)]	MoO$_2$Cl$_2$	2:1	Ether
[(MoO$_2$Cl$_2$)$_2$(HTO)]·1/2CH$_2$Cl$_2$	MoO$_2$Cl$_2$	1:1 2:1 3:1	Ether–CH$_2$Cl$_2$
[(MoOCl$_3$)$_2$(TTP)(THF)$_2$]	MoOCl$_3$(THF)$_2$	2:1 1:1 2:1	CH$_2$Cl$_2$ Ether
[MoOCl$_3$(TTP)]	MoCl$_4$	1:1 2:1	Ether–CH$_2$Cl$_2$
[(MoOCl$_3$)$_2$(HTO)]	MoOCl$_3$(THF)$_2$ MoCl$_4$	2:1 2:1	Ether
[(MoOCl$_3$)$_2$(HTO)]·CH$_2$Cl$_2$	MoOCl$_3$(THF)$_2$ MoOCl$_4$	2:1 1:1 2:1	CH$_2$Cl$_2$
[(MoCl$_4$)$_2$(TTP)]	MoCl$_4$(PrCN)$_2$	4:1 5:1	CH$_2$Cl$_2$
[MoCl$_4$(TTP)]	MoCl$_4$(PrCN)$_2$	1:4 1:6	CH$_2$Cl$_2$
[(MoCl$_4$)$_2$(HTO)]·CH$_2$Cl$_2$	MoCl$_4$(PrCN)$_2$	1:1 2:1	CH$_2$Cl$_2$

TABLE II. Analytical Data for Molybdenum Complexes.

Compound	Mo%	Cl%	C%	H%	S%
[MoO$_2$Cl$_2$(TTP)]	20.62 (20.53)[a]	15.98 (15.17)	26.27 (25.70)	4.29 (4.31)	28.30 (27.44)
[(MoO$_2$Cl$_2$)$_2$(HTO)]	25.01 (25.30)	18.81 (18.70)	19.44 (19.00)	3.37 (3.19)	25.23 (25.37)
[(MoO$_2$Cl$_2$)$_2$(HTO)]·1/2CH$_2$Cl$_2$	23.89 (23.96)	18.71 (17.71)	18.84 (18.75)	3.23 (3.15)	22.21 (24.02)
[(MoOCl$_3$)$_2$(TTP)(THF)$_2$]	22.39 (22.59)	25.05 (25.05)	24.96 (25.45)	4.29 (4.27)	15.58 (15.10)
[MoOCl$_3$(TTP)]	19.69 (19.71)	23.00 (21.85)	23.42 (24.67)	3.75 (4.14)	25.37 (26.34)
[(MoOCl$_3$)$_2$(HTO)]	23.36 (24.07)	26.62 (26.68)	19.63 (18.08)	3.41 (3.03)	24.46 (24.13)
[(MoOCl$_3$)$_2$(HTO)]·CH$_2$Cl$_2$	21.15 (21.75)	24.01 (24.11)	18.02 (17.70)	2.99 (2.97)	22.56 (21.80)
[(MoCl$_4$)$_2$(TTP)]	25.94 (25.79)	35.78 (38.12)	16.89 (16.14)	2.64 (2.71)	17.19 (17.24)
[MoCl$_4$(TTP)]	19.59 (18.95)	28.36 (28.01)	22.23 (23.72)	3.70 (3.98)	22.34 (25.33)
[(MoCl$_4$)$_2$(HTO)]·CH$_2$Cl$_2$	20.58 (20.83)	30.84 (30.79)	17.65 (16.95)	2.70 (2.84)	20.40 (20.88)

[a] Calculated percentage in parentheses.

[MoO$_2$Cl$_2$(TTP)]

Dioxodichloromolybdenum(VI) (0.199 g, 1 mmol) was dissolved in dry diethyl ether (20 cm^3). The solution was filtered and the TTP (0.269 g, 1 mmol), dissolved partially in diethyl ether (20 cm^3) or completely in dichloromethane (20 cm^3), was slowly added. A yellow crystalline product immediately precipitated and after stirring for 3 h was filtered off and rinsed with diethyl ether or dichloromethane (2 × 10 cm^3).

[(MoO$_2$Cl$_2$)$_2$(HTO)]

The HTO ligand (0.361 g, 1 mmol) was suspended in diethyl ether (25 cm^3), and a filtered solution of

MoO_2Cl_2 (0.398 g, 2 mmol) in diethyl ether (20 cm^3) was added. The reaction occurred immediately and after stirring for two hours the yellow powdered product was filtered off and washed with diethyl ether (2 × 10 cm^3). If dichloromethane was used as solvent a yellow crystalline complex [$(MoO_2Cl_2)_2$·(HTO)]·1/2CH$_2$Cl$_2$ was formed.

[(MoOCl$_3$)$_2$(TTP)(THF)$_2$]

A solution of TTP (0.134 g, 0.5 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added to a green solution obtained by dissolving MoOCl$_3$(THF)$_2$ (0.363 g, 1 mmol) in CH$_2$Cl$_2$ (20 cm^3). After a few minutes the product started to precipitate. The reaction mixture was left for 3 days in a dry-box. The small green crystals formed were filtered off, rinsed with dichloromethane (2 × 10 cm^3) and dried. Diethyl ether can also be used as solvent, but because of low solubility of the reactants, continuous stirring for 5 h was necessary.

[MoOCl$_3$(TTP)]

Tetrachloromolybdenum(IV) (0.238 g, 1 mmol) ('Alfa', for chemical purposes) was dissolved in diethyl ether (40 cm^3) by stirring at room temperature in stoppered reaction flask. To the green solution formed a solution of TTP (0.269 g, 1 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added. The mixture was stirred for 3 h; the green crystalline product formed was filtered, washed up with diethyl ether (10 cm^3) and dichloromethane (10 cm^3), and dried.

[(MoOCl$_3$)$_2$(HTO)]

Oxotrichlorobis(tetrahydrofuran)molybdenum(V) (0.726 g, 2 mmol) was suspended in diethyl ether (35 cm^3) and HTO (0.361 g, 1 mmol) partially dissolved in diethyl ether (30 cm^3) was added. After stirring for 2 h a green product was filtered off, washed with diethyl ether (2 × 10 cm^3) and dried. The same product was formed when tetrachloromolybdenum(IV) (0.476 g, 2 mmol) was used as starting material.

[(MoOCl$_3$)$_2$(HTO)]·CH$_2$Cl$_2$

The HTO (0.180 g, 0.5 mmol) dissolved in CH$_2$Cl$_2$ (10 cm^3) was slowly added to a solution of MoOCl$_3$(THF)$_2$ (0.363 g, 1 mmol) in CH$_2$Cl$_2$ (10 cm^3). Green crystals immediately formed; they were filtered off and washed with CH$_2$Cl$_2$ (2 × 10 cm^3). The same adduct was obtained by the reaction of MoOCl$_4$ with HTO.

[MoCl$_4$(TTP)]

A solution of MoCl$_4$(PrCN)$_2$ (0.376 g, 1 mmol) in CH$_2$Cl$_2$ (20 cm^3) was slowly added to a solution of ligand TTP (1.074 g, 4 mmol) in CH$_2$Cl$_2$ (20 cm^3). Although a brown product started to form immediately, the stoppered reaction flask was allowed to

stand overnight to complete the reaction. The crystalline complex precipitated was filtered, washed with CH$_2$Cl$_2$ (5 × 10 cm^3) and dried.

[(MoCl$_4$)$_2$(TTP)]

A solution of TTP (0.269 g, 1 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added to filtered solution of MoCl$_4$-(PrCN)$_2$ (1.504 g, 4 mmol) in CH$_2$Cl$_2$ (40 cm^3). The rection mixture was stored for 3 days in a stoppered flask under nitrogen, yielding brown crystals which were filtered, washed with CH$_2$Cl$_2$ (5 × 10 cm^3) and dried.

[(MoCl$_4$)$_2$(HTO)]·CH$_2$Cl$_2$

MoCl$_4$(PrCN)$_2$ (0.752 g, 2 mmol) was dissolved in CH$_2$Cl$_2$ (20 cm^3). The dark red solution obtained was slowly added to a solution of HTO (0.361 g, 1 mmol) in CH$_2$Cl$_2$ (10 cm^3). After three days the brown crystalline product formed was filtered off, washed with CH$_2$Cl$_2$ (2 × 10 cm^3) and dried.

Physical Measurements

Infrared spectra of the complexes in the range of 4000–625 cm^{-1} were recorded on Perkin-Elmer Model 257 spectrophotometer, as either KBr pellets or nujol mulls.

Magnetic susceptibilities were determined by standard Gouy method at 295 K using CuSO$_4$·5H$_2$O as calibrant.

Mass spectra were obtained on a Varian CH-7 mass spectrometer, using an ionization current of 100 μA, an electron energy of 70 eV, and an ion accelerating voltage of 3 kV. All samples were introduced into the ion source on a direct insertion probe.

ESR spectra were obtained by Varian E-3 ESR Spectrometer operating at a microwave frequency of about 9.15 GHz.

Results and Discussion

We have investigated the complexes formed by the reaction of molybdenum chlorides and oxychlorides with macrocyclic polythiaethers TTP and HTO. The methods of prepration, analytical data, physical and spectroscopic properties of the compounds isolated are listed in Tables I–IV. The complexes are formulated on the basis of chemical analysis and physical measurements. They were not purified or recrystallized before analyses. The solubility of the complexes was too low for their molecular-weight determinations and conductivity measurements. The structures postulated for the complexes were based on the observed chemical and physical properties. In the absence of more exact measurements such as X-ray crystal structure analyses, the postulated structures must therefore be regarded as tentative.

TABLE III. Physical and Spectroscopic Properties of Molybdenum Complexes.

Compound	Colour	$\nu(M = O)$, cm^{-1}	μ_{eff}, B.M.	g_{iso}
[MoO$_2$Cl$_2$(TTP)]	Yellow	935s, 910s		
[(MoO$_2$Cl$_2$)$_2$(HTO)]	Yellow	940s, 910s		
[(MoO$_2$Cl$_2$)$_2$(HTO)] · 1/2CH$_2$Cl$_2$	Yellow	940s, 910s		
[(MoOCl$_3$)$_2$(TTP)(THF)$_2$]	Green	985s	1.66	
[MoOCl$_3$(TTP)]	Green	973s	1.65	1.954
[(MoOCl$_3$)$_2$(HTO)]	Green	970s	1.70	1.954
[(MoOCl$_3$)$_2$(HTO)] · CH$_2$Cl$_2$	Green	970s	1.69	1.954
[(MoCl$_4$)$_2$(TTP)]	Brown		2.32	
[MoCl$_4$(TTP)]	Brown		2.21	
[(MoCl$_4$)$_2$(HTO)] · CH$_2$Cl$_2$	Brown		2.31	

TABLE IV. Characteristic IR Bands (cm^{-1}) of Macrocyclic Polythiaethers and Their Complexes.

Probable Assignments	$\nu(C-S)$		*trans* CH$_2$-rock. or $\nu(C-S)$		gauche CH$_2$-rock.		*trans* CH$_2$-twist.	*trans* CH$_2$-wag.
TTP	675s	692vs	730vw		....	....	1140s	1208vs
[MoO$_2$Cl$_2$(TTP)]	670m	690m	725m		855m	a	1140m	1207m
[MoOCl$_3$(TTP)]	655m	680m	715m		838w	923s	1140m	1208m
[(MoOCl$_3$)$_2$(TTP)(THF)$_2$]	665m	688w	720w		b	920m	1140m	1208m
[MoCl$_4$(TTP)]	....	692w		737s	843m	941m	....	1209m
[(MoCl$_4$)$_2$(TTP)]	....	....	730m		855m	919m	....	....
[HgCl$_2$(TTP)]	668s	686s	723m		846vw	914w	1131s	1200s
[(HgCl$_2$)$_2$(TTP)]	668m	687m	730m		851s	918s	1134m	1193m
HTO	660s	683s	730vw	743vw	842m	928w	1151s	1195vs
[(MoO$_2$Cl$_2$)$_2$(HTO)]	651w	683w		735m	859m	a	1155m	1203m
[(MoOCl$_3$)$_2$(HTO)]	655w	683m	728vs	735s	858s	920m	1155m	1206s
[(MoCl$_4$)$_2$(HTO)]	....	682m	728vs		854m	918m	1150w	1199m
[(HgCl$_2$)$_2$(HTO)]	669s	690s	727s	736m	844s	918m	1154w	1200s
[HgCl$_2$(HTO)]	670w	687m		738w	858m	923w	1152w	1205s

[a] Overlapped with ν_{as}(Mo = O) band.   [b] Overlapped with ν_{as}(C−O−C) band of coordinated THF.

Complexes of Dioxodichloromolybdenum(VI)

Complexes of MoO$_2$Cl$_2$ with monodentate and bidentate oxygen or nitrogen donor ligands have been extensively studied [16–18]. We succeeded in preparing the complexes of dioxodichloromolybdenum(VI) with macrocyclic polythiaethers. All the complexes formed are very air- and moisture-sensitive yellow crystalline solids.

We found that TTP as ligand always forms adduct [MoO$_2$Cl$_2$(TTP)] with the 1:1 metal/ligand ratio, regardless of the experimental conditions used. On the other hand HTO forms only a 2:1 adduct [(MoO$_2$Cl$_2$)$_2$(HTO)], with the ligand acting as a bridge between the two dioxodichloromolybdenum-(VI) units. With this ligand some of the complexes

were obtained as solvates, from which the solvate molecules were not removable by prolonged pumping at room temperature. The presence of dichloromethane was confirmed by examination of mass spectra. The lack of solubility of these complexes in common organic solvents precludes any solution chemistry. In addition, the extreme air and moisture sensitivity further limits characterization.

IR spectra of these complexes exhibit two expected strong bands at 940 and 910 cm^{-1}, consistent with terminal Mo = O stretching vibrations. The presence of two Mo−O$_t$ bands in virtually all the 6-coordinate MoO$_2^{2+}$ compounds is strongly indicative of the *cis*-dioxo structure [19]. Coordination of sulphur to the metal atom causes both a decrease in

the frequencies and lowering of the intensity of the C–S–C stretching modes, which appear as very strong split bands in the 692–675 cm^{-1} and 683–660 cm^{-1} region in the infrared spectra of the ligands TTP and HTO respectively.

On the basis of the obtained results and the fact that MO_2Cl_2 and $MOCl_3$ usually react in the absence of reduction or solvolysis to form six-coordinate adducts [25], it can be proposed that dioxodichloromolybdenum(VI) complex with TTP has structure(I) (Fig. 1) in which the ligand acts as bidentate.
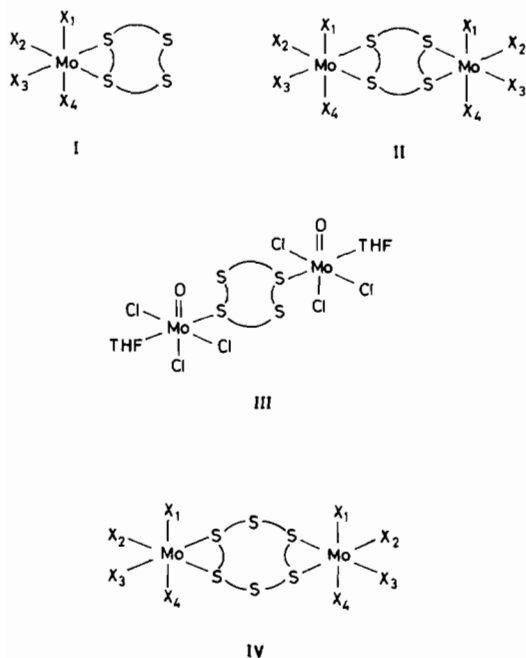

Fig. 1. Proposed structures of molybdenum complexes with macrocyclic polythiaethers. For the complexes of MoO_2Cl_2: $X_1 = X_4 = Cl$, $X_2 = X_3 = 0$; $MoOCl_3$: $X_1 = X_3 = X_4 = Cl$, $X_2 = 0$; $MoCl_4$: $X_1 = X_2 = X_3 = X_4 = Cl$.

On the contrary our results suggest that HTO forms complex [$(MoO_2Cl_2)_2(HTO)$] in which two molybdenum atoms achieve an octahedral configuration (structure IV, Fig. 1) with the ligand functioning as a bridge between them in a double bidentate manner.

Complexes of Oxotrichloromolybdenum(V)

Some reactions of mono and bidentate thiaether ligands, as well as open-chain tetrathiaethers with $MoOCl_3$, have been recently investigated [20–22]. We prepared some complexes of $MoOCl_3$ with macrocyclic polythiaethers. Oxotrichloromolybdenum(V) reacts with thiaether ligands giving green crystalline solids. The products are air and moisture sensitive, but in dry nitrogen atmosphere they are stable for several months. It has been found that the

complexes with HTO are more stable than complexes with TTP. All the complexes are insoluble in most organic solvents, or react with strong donor solvents liberating the ligand.

The reaction of oxotrichlorobis(tetrahydrofuran)molybdenum(V) with the tetrathiaether TTP in 2:1 and 1:1 metal/ligand ratio always yields a binuclear complex [$(MoOCl_3)_2(TTP)(THF)_2$], in which two molecules of tetrahydrofuran are bound. The two $MoOCl_3$ units are probably bridged by a bis-unidentate ligand. The IR spectrum of the complex exhibits strong $\nu(Mo = O)$ stretching vibration at 985 cm^{-1} consistent with terminal Mo = O bond. The spectrum also indicates that coordination of the tetrahydrofuran is through the oxygen atom because the symmetric and asymmetric $\nu(C-O-C)$ stretching vibrations of the free THF which have appeared at 1078 and 909 cm^{-1} are split and lowered to 1007 and 846 cm^{-1} [23]. It seems that for this complex an alternative structure(III) (Fig. 1) involving coordination of THF molecules is more likely.

Starting from tetrachloromolybdenum(IV) we have obtained 1:1 complex [$MoOCl_3(TTP)$]. This complex has magnetic moment 1.65 B.M. and its infrared spectrum exhibits strong Mo = O stretching vibration at 973 cm^{-1}. It can be postulated that this complex has a structure(I) (Fig. 1) in which TTP acts as a bidentate ligand.

HTO as ligand always forms with $MoOCl_3$ a 2:1 complex [$(MoOCl_3)_2(HTO)$], regardless of the experimental conditions and starting materials used (Table I). If dichloromethane was used as organic solvent it goes to its incorporation into the complex. IR spectrum of [$(MoOCl_3)_2(HTO)$] exhibits strong band at 970 cm^{-1} which can be assigned to the (Mo = O) stretching vibration of the terminal molybdenum–oxygen bond. The magnetic moment of this complex is 1.70 B.M. per molybdenum atom. The powder e.s.r. spectra recorded at room temperature give g_{iso} values of 1.954 (Table III), very close to those found for a series of oxotrichloromolybdenum(V) complexes with open-chain tetrathiaethers [21]. In the [$(MoOCl_3)_2(HTO)$] complex HTO probably acts in a double bidentate bridging manner between two molybdenum units, and it can thus be presumed that the molybdenum here has an octahedral configuration (structure IV, Fig. 1).

Complexes of Tetrachloromolybdenum(IV)

Complexes of molybdenum(IV) have recently become common in molybdenum chemistry [19]. At the same time little is known about tetrachloromolybdenum(IV) complexes with sulphur containing ligands. Westland *et al.* prepared a complex of $MoCl_4$ with tetrahydrothiophene $MoCl_4(THT)_2$ [24]. Levason *et al.* reported the preparation of $MoCl_4$ complexes with open-chain tetrathiaethers [21]. They have supposed that tetrathiaethers yielded

seven-coordinate MoCl₄(ligand) complexes in which the thiaethers acted as tridentate ligands. We have obtained some complexes of $MoCl_4$ with macrocyclic polythiaethers, using $MoCl_4(PrCN)_2$ as the starting compound. The reaction between $MoCl_4(PrCN)_2$ and thiaethers immediately gives brown crystalline solids. It has been established that the complexes of molybdenum(IV) are stabilized by sulphur containing ligands, compared with the complexes of molybdenum(VI) and (V) with the same ligands. If we compare the ligands influence on the stability of the molybdenum complexes it appears that HTO forms more stable complexes than does TTP.

The reaction of TTP with $MoCl_4(PrCN)_2$ in the metal/ligand molar ratios 2:1 or 1:1 results in the precipitation of a brown solids, but the results of the analyses have indicated that more than one type of complex was formed. Only when we used $MoCl_4$-$(PrCN)_2$ in fourfold excess we obtained the well defined complex $[(MoCl_4)_2(TTP)]$. The effective magnetic moment of this complex is 2.32 B.M. per Mo atom, consistent with a high-spin d^2 system with strong spin-orbit coupling. The strong bands at 692 and 675 cm^{-1} in the IR spectrum of TTP which correspond to the C–S–C stretching modes disappeared completely in the spectra of the $[(MoCl_4)_2$-(TTP)] complex (Table IV). In this complex TTP plausibly behaves as a double bidentate bridging ligand (structure II, Fig. 1). When we used the ligand TTP in the fourfold excess we obtained the 1:1 complex $[MoCl_4(TTP)]$, which had a magnetic moment of 2.21 B.M. Although no X-ray structural information is available, there is little doubt of a 6-coordinate octahedral $MoCl_4$ complex in structure (I) (Fig. 1).

HTO as a ligand forms with $MoCl_4$ only a 2:1 complex $[(MoCl_4)_2(HTO)]$, as in the case of its complexes with molybdenum(VI) and (V). It seems that the number of sulphur atoms, as well as the flexibility of the macrocyclic ring, favours the formation of such a type of complexes. In this complex there is also an incorporation of solvent dichloromethane, and its presence was confirmed by examination of mass spectrum. $[(MoCl_4)_2(HTO)]$ complex has a magnetic moment of 2.31 B.M. per molybdenum atom, consistent with the results published for the other complexes of molybdenum(IV) [19]. The assumption that in this complex HTO also acts as a double bidentate ligand is more likely (structure IV, Fig. 1).

Infrared Spectra (1200–625 cm⁻¹)

The assignation of the infrared spectra was restricted to some characteristic CH₂- and C–S vibrations in the range of 1200–625 cm^{-1}, where significant differences between the macrocyclic polythiaethers TTP and HTO and their molybdenum complexes may be noted. The observed absorption bands

and the proposed assignments are summarized in Table IV. Some data on the complexes HgCl₂(TTP), HgCl₂(HTO), (HgCl₂)₂(HTO) [32] and (HgCl₂)₂-(TTP), for which the crystal structure was determined [7], are also given for comparison.

Regarding the complexity of these spectra a more detailed analysis is not attempted at present. The free ligands TTP and HTO exhibit the strong bands at 1208 and 1195 cm^{-1} respectively attributed to the *trans* CH₂-wagging vibration. In their complexes these bands regulary show a noticeable decrease in intensity, while in the spectrum of the complex $[(MoCl_4)_2$-(TTP)]$ they are absent. Similar changes are observed with the absorption bands present in the free ligands at 1140 and 1151 cm^{-1} respectively, presumably arising from the *trans* CH₂-twisting vibration.

Considerable changes are observed in the range between 940 and 830 cm^{-1}. In the spectra of all the investigated complexes two absorption bands appear at 940–915 cm^{-1} and 855–835 cm^{-1}, with various intensities assigned to the gauche CH₂-rocking vibrations [26–29]. These bands are absent in the spectrum of the free TTP and are of very low intensity in the spectrum of HTO, indicating that considerable conformation changes appeared upon their complex formation.

The free macrocyclic polythiaethers exhibit one or two weak bands in the region between 740–715 cm^{-1}. These bands are also found in the spectra of their complexes but an increase in intensity is observed. Absorption bands found in this region could not be detected with certainty, because some authors attribute bands between 740 and 735 cm^{-1} to the *trans* CH₂-rocking vibrations [26–27], while others think that the absorption in the region of 735–720 cm^{-1} arises from one mode of the C–S stretching vibrations [27, 28, 33].

As previously mentioned two strong bands at 692 and 675 cm^{-1} for TTP and at 682 and 675 cm^{-1} for HTO are assigned to the C–S stretching modes. In the spectra of the complexes these bands exhibit a decrease in frequency and intensity while in the spectrum of the complex $[(MoCl_4)_2(TTP)]$ the bands have not been observed.

All differences in CH₂-rocking deformation and C–S stretching vibrations between the spectra of macrocyclic polythiaethers and their molybdenum complexes indicate that there are considerable conformation changes in the ligands upon their complex formation.

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