REACTION OF TETRAMETHYLTHIONYLAMIDE AND TRISDIMETHYLAMINOPHOSPHINE SULPHIDE WITH Nb(V), Mo(V) AND Ta(V) CHLORIDE

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Summary

Complexes of the type MCl_5L (where $L \equiv (Me_2N)_2SO$, $(Me_2N)_3PS$, Ph_3PS ; $M \equiv Nb$, Mo and Ta) have been prepared by reaction of the parent chloride MCl_5 with appropriate ligands.

1. Introduction

During the period 1949–1965, Fairbrother and his coworkers reported the preparation and properties of the halides of niobium and tantalum and a large number of complexes of these halides [1, 2]. Tetramethylthionylamide and trisdimethylaminophosphine sulphide were not among the ligands investigated, although complexes of some sulphineamides (RR'NS(O)CH₃, where $R \equiv R' \equiv H$, $R \equiv H$, $R' \equiv CH_3$ and $R \equiv R' \equiv CH_3$) have been reported for various transition metals [3].

We now report the preparation and characterization of a number of complexes having the general formula MCl_5L , where $N \equiv Nb$, Mo, Ta; $L \equiv Ph_3PS$, $(Me_2N)_3PS$ and $(Me_2N)_2SO$.

2. Experimental details

The complexes were prepared and handled in a dinitrogen free dry-box.

2.1. Materials

NbCl₅ (Koch-Light), TaCl₅ (Alfa), MoCl₅ (Alfa), $(Me_2N)_3PS$ (Alfa), SOCl₂ (BDH) and Me₂NH (Hopkin and Williams) were dried and purified by the standard methods.

2.2. Analytical determination

Analysis of niobium, tantalum, molybdenum, chlorine, sulphur, nitrogen, carbon and hydrogen were carried out in the microanalytical laboratory of the Manchester University Chemistry Department by Mr. M. Hart.

2.3. Preparation of compounds

2.3.1. Preparation of ligands

Triphenylphosphine sulphide and tetramethylthionylamide were prepared as described in refs. 4 - 6.

2.3.2. Preparation of $NbCl_5(Me_2N)_3PS$

 $NbCl_5(Me_2N)_3PS$ was prepared by the direct reaction of a yellow suspension of $NbCl_5$ in dichloromethane with the stoichiometric amount (1:1 molar ratio) of ligand in dichloromethane, which resulted in orange-yellow microcrystals. $NbCl_5(Me_2N)_3PS$ required: Nb, 19.98%; Cl, 38.13%, S, 6.87%; P, 6.60%; N, 9.02%; C, 15.46%; H, 3.88%. Analysis found: Nb, 20.2%; Cl, 37.25%; S, 6.7%; P, 6.7%; N, 8.7%; C, 15.2%; H, 3.6%.

2.3.3. Preparation of $MoCl_5(Me_2N)_3PS$

 $MoCl_5(Me_2N)_3PS$ was prepared by the direct reaction of a reddishbrown solution of $MoCl_5$ in dichloromethane with the stoichiometric amount (1:1 molar ratio) of ligand in dichloromethane which resulted in the formation of a precipitate of the complex. $MoCl_5(Me_2N)_3PS$ required: Mo, 20.49%; Cl, 37.8%; S, 6.8%; P, 6.61%; N, 8.96%; C, 15.36%; H, 3.84%. Analysis found: Mo, 21.0%; Cl, 36.6%; S, 6.4%; P, 6.61%; N, 8.8%; C, 15.8%; H, 4.0%.

2.3.4. Preparation of NbCl₅Ph₃PS

NbCl₅Ph₃PS was prepared by the following routes.

(a) The orange complex was prepared by the direct reaction of a yellow suspension of $NbCl_5$ in dichloromethane with triphenylphosphine sulphide in dichloromethane. The reddish-orange solution was concentrated to half of the original volume and, when left in a dry-box for two days, resulted in the formation of a precipitate of the complex.

(b) The green complex was prepared by the direct reaction of a yellow solution of NbCl₅ in a mixture of CH_2Cl_2 -MeCN with Ph₃PS in dichloromethane. The reddish-orange solution was left in a dry-box for two days, by which time the colour had changed to green and the green complex had precipitated out.

NbCl₅Ph₃PS required: Nb, 16.46%; Cl, 31.4%; S, 5.67%; P, 5.48%; C, 38.29%; H, 2.67%. Analysis found: Nb, 15.8%; Cl, 30.9%; S, 5.9%; P, 4.8%; C, 38.0%; H, 28%.

2.3.5. Preparation of MoCl₅Ph₃PS

The procedure was similar to that used in the preparation of $MoCl_5$ - $(Me_2N)_3PS$. $MoCl_5Ph_3PS$ required: Mo, 19.902%; Cl, 31.1%; S, 5.6%; P,

5.46%; C, 38.6%; H, 2.07%. Analysis found: Nb, 18.94%; Cl, 31.5%; S, 5.5%; P, 5.2%; C, 37.5%; H, 2.65%.

2.3.6. Preparation of $NbCl_5(Me_2N)_2SO$

The procedure was similar to that used in the preparation of NbCl₅- $(Me_2N)_3PS$. NbCl₅ $(Me_2N)_2SO$ required: Nb, 22.76%; Cl, 43.66%; S, 7.87%; N, 6.66%; C, 11.80%; H, 2.95%. Analysis found: Nb, 21.9%; Cl, 43.1%; S, 6.9%; N, 6.7%; Cl, 12.3%; H, 3.1%.

2.3.7. Preparation of $TaCl_5(Me_2N)_2SO$

 $TaCl_5(Me_2N)_2SO$ was prepared by the direct reaction of a white suspension of $TaCl_5$ in CH_2Cl_2 which resulted in the formation of a precipitate of the complex. $TaCl_5(Me_2N)_2SO$ required: Ta, 36.60%; Cl, 35.86%; S, 6.47%; N, 5.66%; C, 9.7%; H, 2.43%. Analysis found: Ta, 38.06%; Cl, 34.7%; S, 5.9%; N, 5.4%; C, 10.2%; H, 2.7%.

2.4. Physical measurements

2.4.1. IR spectra

IR spectra were recorded using Perkin–Elmer Model 257 (4000 - 625 cm^{-1}) and Perkin–Elmer model 225 (625 - 200 cm^{-1}) instruments. Nujol mulls were prepared in a dry-box.

2.4.2. Raman spectra

Raman spectra of the powdered samples were recorded using a Cary 82 laser Raman spectrophotometer.

2.4.3. X-ray powder photographs

Photograps were obtained using a Debye–Scherrer camera of diameter 5.37 cm. In all cases Cu K α radiation was used.

3. Result and discussion

Niobium, tantalum and molybdenum pentachlorides yield the expected 1:1 complexes when they are reacted in dichloromethane with the stoichiometric amount of ligands. Tetramethylthionylamide and trisdimethylaminophosphine sulphide are of particular interest in that there are three and two possible coordination sites respectively.

All of these complexes are soluble in common organic solvents such as CH_2Cl_2 , $CHCl_3$, MeCN, CCl_4 and are highly moisture sensitive.

In contrast, the reaction of excess triphenylphosphine oxide and hexamethylphosphoramide with niobium(V) and molybdenum(V) chlorides results in trichloro-oxometal(V) complexes, and it is significant that sulphur is not abstracted from Ph₃PS and $(Me_2N)_3PS$, although the dissociation energy of the P=S bond is much less than that of the P=O bond. This emphasizes the much greater avidity of niobium(V) and molybdenum(V) chlorides for oxygen. Brown et al. [7] have reported that a lowering of the v(P=S) vibration on coordination occurs owing to the overall decrease in the bond order, probably due to a decreased p—d bonding, also the shift in the v(P=S) vibration is less than that for v(P=O). They have reported the preparation of some metal(V) thiophosphoryl complexes with a shift in the P=S vibration of as much as 53 cm⁻¹ for NbCl₅Ph₃PS.

The recorded infrared spectrum of Ph₃PS shows a strong absorption at 638 cm⁻¹ which has been assigned to the ν (P=S) stretching vibration, which upon coordination has been shifted to 580 and (576, 584) cm⁻¹ with a lowering of 58 and (62, 54) cm⁻¹ for NbCl₅Ph₃PS and MoCl₅Ph₃PS respectively.

The $\nu(P=S)$ vibration of trisdimethylaminophosphine sulphide has been assigned to be at 743 cm⁻¹ [8], which on coordination with NbCl₅ and MoCl₅ is shifted to 656 and 655 cm⁻¹, respectively.

The infrared spectra of some halothiocomplexes of niobium and tantalum indicated the existence of terminal M=S or bridging M-S-M bonds. Some of these assignments have been confirmed by crystal structure studies.

TaSX₃2L (where $L \equiv MeCN$, dimethylsulphide, tetrahydrothiophene; $X \equiv Cl$ and Br) showed strong absorption in the range 504-510 cm⁻¹ and TaSCl₃(PHSCH₂SPH), which crystallizes in the monoclinic system with space group $P2_1/C_1$, showed very strong absorption at 508 and 512 cm⁻¹ which are assigned to the tantalum sulphur stretching vibration [9]. The Nb=S bond length in monomer NbSCl₃Ph₃PS is shorter than in the dimer because of the influence of trans chlorine in the dimer, but this difference is not reflected in the IR and Raman spectra, which both show a single band at 536 and 537 cm⁻¹, respectively [10].

Benton *et al.* have shown that [11] the reaction of acetonitrile complexes of niobium(IV) chloride and bromide with Sb_2S_3 results in the formation of dihalosulphide niobium(IV) complexes. The crystal structures of $(\{NbSCl_2(MeCN)_2\}_2)2MeCN$ and $(\{NbSCl_2(MeCN)_2\}_2)MeCN$ show them to be crystallized in the triclinic system with *P* space group and contain niobium sulphur bridging. The absorptions at 476, 4705 (doublet) and 330 (sh) in the spectrum of $(\{NbSCl_2(MeCN)_2\}_2)$ and strong absorptions at 468 and 321 in the IR spectrum of $(\{NbSCl_2(MeCN)_2\}_2)$ have been assigned with great conficence to Nb-S-Nb-S vibrations. The same workers have also shown that [12] the reaction of trihalosulphide niobium(V) with tetrahydrothiophone results in the formation of complexes of the type NbSBr_32tht and Nb_2S_3-X_44tht (where $X \equiv Cl$, Br). The existence of terminal Nb=S and bridging Nb-S-Nb have been confirmed by crystal structure studies of NbSBr_32tht and Nb_2S_3X_44tht, respectively.

The reaction of NbSCl₃ with Ph₄PCl resulted in the formation of [Ph₄P][NbSCl₄] which crystallizes in the tetragonal system with space group P4/n. The absorptions at 552 and 548 cm⁻¹ in the IR spectra of [Ph₄P]-[NbSCl₄] and [Ph₄P][Nb³⁴SCl₄] have been assigned, respectively, to the ν (Nb=S) stretching vibration [13].

Do et al. [14] have compared the differences in the IR spectra of $MS(S_2CNEt_2)_3$ (where $M \equiv Nb$, Ta) and have concluded that the $\nu(M=S)$ is



less than or equal to $\nu(M=S)$. Finally, by crystal studies of NbS(S₂CNEt₂)₃ and comparing with the other known crystal structures of halosulphide complexes of Nb(V), they have assigned the absorptions at 493 cm⁻¹ and 479 cm⁻¹ in the spectra of NbS(S₂CNEt₂)₃ and TaS(S₂CNEt₂)₃, respectively, to the $\nu(M=S)$ stretching vibration [15].

The reaction of NbCl₅ with Ph₃PS in a solvent containing a few drops of acetonitrile resulted in the formation of a green complex whose analysis corresponds to 1:1 NbCl₅ to ligand, but the IR spectrum of this green compound is not identical with that of NbCl₅Ph₃PS, and shows a medium strong absorption at 517 cm⁻¹, which is completely absent from the spectrum of NbCl₅Ph₃PS. Therefore, with respect to the above discussion it may be concluded that the green compound may be formulated as [Ph₃PCl][NbSCl₄] with an Nb=S stretching vibration at 517 cm⁻¹ by analogy with that of [(Me₂N)₂CCl][NbSCl₄] [16] and [Ph₄P][NbSCl₄] [13].

Cotton *et al.* [17], from a study of the infrared spectra of transition metal complexes, have suggested that when dimethylsulphoxide coordinates through the oxygen atom this results in a shift to a lower frequency of the $\nu(S=O)$ stretching vibration and when coordination is via the sulphur atom the $\nu(S=O)$ frequency increases.

Complexes of some sulphineamides $(RR'NS(O)CH_3)$, where $R \equiv R' \equiv H$; $R \equiv H$, $R' \equiv CH_3$; $R \equiv R' \equiv CH_3$) have been prepared for various transition metal compounds containing the non-coordinating anions perchlorate and tetrafluoroborate [5]. In these complexes, oxygen rather than sulphur or nitrogen coordination is indicated on the basis of their IR spectra.

In the recorded IR spectra, the strong absorption at 1125 cm⁻¹ in the spectrum of $(Me_2N)_2SO$ is assigned to the $\nu(S=O)$ vibration which on coordination with NbCl₅ and TaCl₅ has been shifted to 962 and 960 cm⁻¹ respectively.

The IR spectra of NbCl₅Ph₃PS, MoCl₅Ph₃PS, NbCl₅(Me₂N)₃PS, MoCl₅(Me₂N)₃PS and TaCl₅(Me₂N)₂SO showed strong absorptions at (367, 346), (366, 344), 337, (366, 336) and (304, 288) cm⁻¹, respectively, which are assigned to (M-Cl) stretching vibrations. The IR spectra of phosphine sulphide complexes is shown in Fig. 1.

X-ray powder measurement results indicate that these complexes appear to possess low symmetry, but they have not been interpreted in detail.

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