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ADDUCTS OF TUNGSTEN OXIDE TETRAFLUORIDE WITH 1,8 - NAPHTHYRIDINE AND 2,7 -DIMETHYL - 1,8- NAPHTHYRIDINE : PREPARATION AND CHARACTERIZATION OF WOF_4.napy AND WOF_4.dmnapy

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SUMMARY

The adducts WOF_4.napy and WOF_4.dmnapy were prepared from the reaction of WOF_4 with 1,8-naphthyridine (napy) and 2,7-dimethyl-1,8-naphthyridine (dmnapy) in dichloromethane . Both adducts were characterized by elemental analysis, X- Ray powder data and infrared absorption spectroscopy. Their solubility in the usual organic solvents was found to be negligible and the trace amounts of species present in the solutions were identified as ionic derivatives originating from side-reactions.

INTRODUCTION

As part of a general study of the tungsten (VI) oxide fluoride nitrogen-base - systems, [1,2] , the interaction of WOF_4 with 1,8-naphthyridine (napy) and 2,7-dimethyl-1,8- naphthyridine (dmnapy) was investigated. Although the chelate bite in

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1,8-naphthyridine is 2.2 Å [3] and the nitrogen lone pair orbitals are parallel to each other, a large number of transition metals are now known to form four-membered chelate rings with 1,8-naphthyridine and its substituted derivatives [3-11] . Methylation of the 1,8-naphthyridine was expected to increase the solubility of the adducts in the common solvents, thus allowing more information to be obtained through NMR and single crystal X-ray investigations. In fact, the gain in solubility, if any, was still insufficient for these investigations to be achieved. However, the tungsten (VI) adducts obtained were fully characterized by elemental analysis, X - ray powder diffraction, and infrared absorption spectroscopy.

EXPERIMENTAL

General procedure, characterizations and materials. Volatile materials were purified and transferred in a glass vacuum line designed to handle highly moisture-sensitive materials. Solid products were handled in a glove box flushed with dry nitrogen. Infrared spectra were recorded in the range 4000-200 cm^{-1} on a Perkin - Elmer Model 283 spectrophotometer. Spectra of the solids were obtained by pressing the powders between AgCl windows in an Econo press (Barnes Engineering Co). The NMR spectra were recorded on a Bruker Model AC 200 spectrometer at 200 MHz for ^1H and 188.2 MHz for ^{19}F. Samples were referenced externally with respect to $Si(CH_3)_4$ or $CFCl_3$ with positive shifts being downfield from the standards. X-ray powder diffraction patterns of the samples sealed in 0.3 mm o.d. glass capillaries were obtained by using a Phillips camera (diameter 11.46 cm) and Ni-filtered CuKα radiation. Elemental analyses were performed by Mikroanalytische Laboratorien Elbach, Germany. Tungsten oxide tetrafluoride was obtained by the literature procedure [12] and purified by sublimation *in vacuo* at ca. 50°C. Tungsten hexafluoride used for this preparation was obtained from Comurhex, napy and dmnapy were obtained by the literature procedure [13] . Methylene chloride (Prolabo) and CD_2Cl_2 (99.6% D, CEA) were dried over Na-Pb alloy under reflux. Acetonitrile (Prolabo) and CD_3CN (99.3% D, CEA) were dried over P_2O_5 followed by treatment and storage over 5A molecular sieves.

Preparation of WOF_4.napy. Solutions of WOF_4 (1.252 mmol) and napy (1.252 mmol) in 10 cm^3 of CD_2Cl_2 were first cooled to 0°C and then mixed together at this temperature. The white crystalline powder that instantly precipitated was filtered and dried by pumping at room temperature.
Anal. calcd. for WOF_4 $C_8H_6N_2$: W 45.28, F 18.72, C 23.67, H 1.49, N 6.90 ; found : W 45.50, F 18.75, C 23.58, H 1.51 , N 6.80.

Preparation of WOF_4.dmnapy. Solutions of WOF_4 (0.697 mmol) and dmnapy (0.320 mmol) in 10cm^3 of CD_2Cl_2 were treated as above. The purple, white crystalline powder that precipitated was washed under vacuum with CD_2Cl_2 to remove the excess of WOF_4, filtered and dried by pumping at room temperature m.p. 220° d.
Anal. calcd. for $WOF_4.C_{10}H_{10}N_2$: W 42.36, F 17.51, C 27.67, H 2.32, N 6.45 ; found : W 42.10, F 17.22, C 27.41, H 2.28 , N 6.31.

RESULTS

The treatment of WOF_4 with the nitrogen-bases napy and dmnapy in CD_2Cl_2 gives the new adducts WOF_4.napy and WOF_4.dmnapy . When performed in CH_3CN the reaction leads to a more complicated system in which the solvent is probably involved as attested by the infrared specta of the solids obtained which displayed characteristic bands of coordinated acetonitrile. The use of other strong donors compounds was therefore disregarded in the search for a solvent of these adducts. Both WOF_4.napy and WOF_4.dmnapy were found to be moisture sensitive . Owing to the lack of suitable solvents and limited thermal stability, the crystal structures of the adducts have not been determined. The X-ray powder data are listed in Table I.

As far as vibrational spectroscopy is concerned, no Raman data could be obtained since the solids were decomposed by the available exciting lines (argon and krypton lasers) so that only the infrared absorption spectra, the data of which are given in Table II, were obtained. Several changes in the spectra of the organic ligand regarding the frequency and relative intensity of the bands are brought about

TABLE I
X-ray Powder Data[a] for WOF_4.napy and WOF_4. dmnapy

WOF_4.napy		WOF_4.dmnapy	
d, Å	intensity	d, Å	intensity
8.2	w	8.9	w
7.3	s	7.4	m
6.45	w	5.6	s
5.9	mw	4.42	m
5.6	vs	3.8	m
4.96	s	3.69	vvw
4.62	vs	3.59	m
4.38	s	3.21	mw
4.08	s	3.09	vw
3.76	s,br	3.	w
3.2	s	2.78	vw
3.05	w	2.73	w
2.97	mw	2.65	mw
2.79	ms	2.6	w
2.72	vw	2.45	mw
2.62	vvw	2.32	vw
2.56	w	2.3	mw
2.47	mw	2.25	vw
2.43	w	2.22	vw
2.348	m	2.2	vw
2.275	m	2.1	m
2.1	w	2.02	w
2.15	w	1.99	m
2.06	m		

[a] s=strong, m=medium, w=weak, v=very, br=broad

TABLE II

Infrared Data [a] for WOF$_4$.napy and WOF$_4$.dmnapy : Comparison with those of napy and dmnapy

WOF4.napy	napy	WOF4. napy	napy	WOF4.dmnapy	dmnapy	WOF4.dmnapy	dmnapy
310 s,br		1145 s	1127 s	**331** s,br	347 s	1155 s	1132 ms
385 s	403 s	1155 s	1192 m	375 ms		1164 ms	1157 s
455 ms	470 ms	1226 s	1227 s	405 s	445 s	1224 ms	1210 ms
	478	1253 s	1275 m	457 mw	480 s	1257 ms	1245 s
517 m	532 ms	1310 mw	1295 s	515 s	530 vw	1315 ms	1315 vs
545		1327 mw		**547**	587 s	1326 ms	
570 vs,br	605 s	1365 m	1397 ms	**590** vs,br		1380 s	1372 ms
635	632 w	1420 s,br	1416 m	**635**	625 s	1410 ms	1390 mw
710 mw,br		1465 mw	1460 m	**710** s,br	680 ms	1433 ms	1447 s
	758 s		1478 m	785 s	782 vs	1515 ms	1507 s
800 s	810 s	1508 s	1492 ms	795 vs	810 vs	1570 mw	1543 ms
820 s	837 s	1585 s	1560 m	827 s		1605 ms	
852 s		1608	1603 s	874 s	853 vs	1620	1610 vs,br
940 m	935 m	1630 s		935 ms	930 w	1630 s	
	954 m	1645		955 ms	951 mw	1660 w	1700 mw
973 s,br	970 m	1675 mw	1730 mw	**975** vs,br		1695 w	1800 mw
	985 m	1780 mw	1795 mw		993 ms	1745 w	1845 mw
	998 ms	1840 mw	1820 mw	1005 w		1867 w	1990 ms
1025 s	1027 ms	1960 m	1980 s		1015 mw	1950 mw	
1040 ms	1045 ms	2025 m	2992 ms	1030 ms	1040 s	2010 mw	2022 ms
1087 m	1105 m		3010 ms			2940 m	2920 s
		3080 s	3060 s			3005 m	3010 vs
		3100	3100 ms			3090 s	3060 s

[a] frequency in cm^{-1}, s=strong, m=medium, w=weak, br=broad; bands with intensity weaker than a few % of the strongest ones have been omitted, frequencies in bold refer to vibrations involving only W, O, and / or F atoms.

by the coordination to the tungsten atom. However, if, the skeletal modes of the free ligand napy (observed here at 403 , 605 , 758 , 1027 , 1045 , 1127 , and 1560 cm $^{-1}$) which were claimed [10,11] to be the most affected upon coordination, are considered , their shifts in WOF_4.napy are different from those found in the adducts M $(napy)_n$ $(ClO_4)_3$ where M= La--- Pr (n=6), Nd---Eu(n=5), and $Fe(napy)_4(ClO_4)_2$, [11]. The ionic character of these adducts compared with the mainly covalent bonding expected in WOF_4.napy and WOF_4.dmnapy, certainly accounts for this discrepancy.

A comparison of the vibration frequencies of these skeletal modes between those observed for M $(napy)_n$ $(ClO_4)_3$ and $Fe(napy)_4$ $(ClO_4)_2$ the crystal structure of which was known , allowed the authors [10,11] to conclude that the ligands were coordinated in a bidentate manner in M $(napy)_n$ $(ClO_4)_3$ as well. Owing to the discrepancy mentioned above, such a conclusion cannot similarly be extended to WOF_4.napy and WOF_4.dmnapy. However, the W=O vibrational mode of these adducts is informative because its frequency can be compared with that of previously studied similar adducts [1] with the monodentate ligand py (pyridine) . This mode has been found at 997 cm^{-1} and 973 cm^{-1} for WOF_4.py, and WOF_4.2 py respectively. The crystal structure determination of these adducts had shown that the tungsten atom was surrounded by a pentagonal bipyramid of ligands in WOF4. 2 py, whereas in WOF_4.py the tungsten atom was surrounded by a distorted octahedron of ligands. The W=O vibration mode was also found to be located at 968 cm $^{-1}$ in the adduct of WOF_4 with the bidentate ligand bipy (2,2'- bipyridyl) [2] . Consequently, the frequency of the corresponding vibration mode, observed at 973 cm^{-1} for WOF4.napy and at 975 cm $^{-1}$ for WOF_4.dmnapy, is in line with an hepta-coordination of the tungsten atom with the organic ligand in the expected bidentate form.

In order to gain more information regarding the molecular structure of these adducts, many attempts were made to obtain ^{19}F and ^{1}H NMR data on their solutions. Unfortunately, the solubility of both adducts in the usual solvents was found to be negligible as attested for instance by the great number of accumulation required to obtain ^{19}F and ^{1}H signals of significant signal / noise ratios.

Furthermore, as described below, the species to which the signals had to be assigned, were found to be mainly due to side-reactions. However, owing to the uncommon species which were studied, a brief description of the NMR observations is given. The results reported below were obtained on mother-solutions or saturated solutions of the solids in CD_2Cl_2 at room temperature.

The ions WOF_5^- and $W_2O_2F_9^-$ were identified in the ^{19}F NMR spectra by their characteristic lines [14]. For WOF_5^-, a doublet at ϕ 49.4 with $J_{W\text{-}F}$ = 70.4 Hz, $J_{F\text{-}F}$ = 52.4 Hz and an unresolved multiplet at ϕ -83. For $W2O2F_9^-$, a doublet at ϕ 62.2 with $J_{W\text{-}F}$ = 71.5 Hz, $J_{F\text{-}F}$= 58 Hz and an unresolved multiplet at ϕ -145.2. When an excess of WOF_4 was present (ϕ 67.2) , aging of the solution was found to increase the relative concentration of WOF_5^- vs that of $W_2O_2F_9^-$. This is readily explained by an increase in F^- concentration upon storage and the equilibria which have been shown to take place between these species [14] . Based upon a comparison with data presented for adducts of tungsten oxide fluorides including MO_2F_2 (M = W, Mo) [15] with special attention to the adduct WO_2F_2 $(OPh_3)_2$ (ϕ -60. 20, $J_{W\text{-}F}$ = 112 Hz) , a singlet at ϕ -64 with $J_{W\text{-}F}$ = 90 Hz which was also observed here, was tentatively assigned to WO_2F_2 bond to the ligand.

TABLE III

NMR Data for Saturated Solutions of WOF_4. napy and WOF_4. dmnapy in CD_2Cl_2. Comparison with the Free Ligands

	Chemical Shift (ppm)				Coupling constant (Hz)		
	δ_2	δ_3	δ_4	δ_{Me}	J_{23}	J_{24}	J_{34}
napy	9.09	7.50	8.22		4.19	2.01	8.19
WOF4.napy	9.55	7.95	8.70		4.64	1.78	8.33
dmnapy		7.32	8.04	2.74			8.28
WOF4.dmnapy		7.76	8.58	3.03			8.45

The ^1H NMR spectra showed that the proton signals were shifted downfield from those of the free ligand (see Table III) . A broad line observed at δ=12.6 and 14.6, was assigned to an NH+ species [16] . It is possible to rationalize these observations by assuming that the species originated from traces of water brought in by the organic ligands and / or the solvent. Under these circumstances, H_2O presence may result in the formation of HF , (which may also have been brought in with WOF_4) and tungsten oxide fluoride anions. Since the solutions were contained in glass tubes , long period storage resulted in attack on this material by HF as attested by spectra of old solutions which displayed weak lines assigned to the ions SiF_6^{2-} (ϕ -138.5) [17] and HF_2^- (ϕ -145.6 to -149.3) [18]. The downfield shift observed for the ^1H NMR spectra of the ligand when compared with those of its free form in the same solvent, indicated that the ligand is involved in some kind of bonding and that the protons are deshielded. The absence of other cationic species like OH_3^+ [19] to balance the anionic charges, as well as the deshielding of the protons's ligand , and the appearance of the NH^+ line indicate that the organic base is, at least partially, protonated in these media. A fast proton exchange may explain that only one set of ligand lines was observed and that the triplet expected for NH + was not resolved.

Based upon the NMR experimental conditions used to observe their signals, and those used for solutions of known concentration, the species described above were estimated to be present at the approximate molar concentration level of 10^{-6}. Even at this detection level no evidence was found for the presence of species which would have resulted from partial fluorination of the ligands.

CONCLUSION

As a whole this study has shown that the nitrogen- bases napy and dmnapy were able to yield one-to-one bidentate adducts with WOF_4. Unlike the corresponding monodentate hepta-coordinate adduct WOF_4. 2py, these adducts are not labile at room temperature.

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