Inorganica Chimica Acta, 201 (1992) 1–3

Inorganica Chimica Acta

LETTER

Preparation and structure of $(Ph_3P)_2N[WSF_5]$

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(Received March 19, 1992)

Chalogenide fluorides of molybdenum, tungsten and rhenium have been prepared by several methods and in part characterized by X-ray structure determinations [1–8]. Anionic fluoro species, like WSF_5^- or $W_2S_2F_9^-$ and others, have been identified only by NMR spectroscopy [1, 5], but have not been characterized further until very recently [9]. We have now prepared three salts of the WSF_5^- ion using PPh_4^+, Na(15-crown-5)$^+$ and $(Ph_3P)_2N^+$ as counterions. In order to study the bonding in these compounds and to compare it with the bonding in the related oxofluoro compounds, we determined their crystal structures. During the course of this work, Dehnicke and coworkers reported the preparation and spectroscopic characterization of Na(15-crown-5)$[WSCl_nF_{5-n}]$ with $n=4$, 2 and 0 [9].

Experimental

Syntheses

All manipulations were performed under N_2 in Schlenk tubes or in a nitrogen filled dry box. CH_3CN was dried with CaH_2 and distilled under N_2. NaF was desiccated at 800 °C *in vacuo*. $WSCl_4$ was prepared by literature methods [10].

Na(15-crown-5)[WSF₅] (1)

NaF (4.70 g, 112 mmol) was added to a red solution of $WSCl_4$ (3.57 g, 10.0 mmol) in CH_3CN (30 ml). Then 15-crown-5 (1.99 ml, 10 mmol) was added to the suspension, using a syringe. A green solution was formed; its color changed to yellow after 12 h. The solid residue of NaF/NaCl was filtered off, and the volume of the solution concentrated to 15 ml. Crystals formed were dissolved by heating the solution up to 50 °C. Subsequent crystallization at −30 °C yielded large yellow crystals of Na(15-crown-5)$[WSF_5]$, which were washed with CCl_4 (2×5 ml). Yield 3.66 g (66%).

Anal. Calc. for $C_{10}H_{20}F_5NaO_5SW$: C, 21.67; H, 3.64. Found: C, 21.53; H, 3.65%.

PPh₄[WSF₅] (2)

$WSCl_4$ (5.39 g, 15.1 mmol), NaF (5.04 g, 120 mmol) and 15-crown-5 (3.59 ml, 18.1 mmol) were treated as above in CH_3CN (75 ml). After 12 h the solids were filtered off. Then a solution of $(PPh_4)Br$ (6.32 g, 15.1 mmol) in CH_3CN (25 ml) was slowly added. Crystallization for 1 h at 0 °C yielded 6.6 g (67%) of $PPh_4[WSF_5]$, which was washed with cold CH_3CN (2×5 ml).

(Ph₃P)₂N[WSF₅]·MeCN (3)

This salt was prepared by a similar procedure, using $[(Ph_3P)_2N]Cl$ (8.67 g, 15.1 mmol) instead of $(PPh_4)Br$.

Structure determinations

Data were collected for **1** on a Enraf-Nonius CAD4 diffractometer at room temperature, for **2** and **3** on a Syntex $P2_1$ diffractometer at 140 K. Crystal data and data collection parameters for **3** are collected in Table 1. **1** crystallizes tetragonally in space group $I\bar{4}$ with $a=12.424(3)$ and $c=7.403(1)$ Å. Structure determination showed that the $[WSF_5]^-$ anions are disordered; so no individual values for the W–S and W–F bond lengths could be determined. **2** crystallizes triclinic in

TABLE 1. Crystal data and data collection parameters

Formula	$C_{38}H_{33}N_2F_5P_2SW$
Formula weight	890.55
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	12.051(2)
b (Å)	12.269(2)
c (Å)	14.056(2)
α (°)	70.72
β (°)	65.92(1)
γ (°)	74.25(1)
V (Å^3)	1768.8
Z	2
D_{calc} (g/cm^3)	1.67
μ(Mo Kα) (cm^{-1})	35.3
Absorption correction	semi-empirical
Radiation (Å)	0.71069
Scan method	ω–2θ
Collection range, 2θ (°)	4–54
Unique data: total	7770
with $I>2\sigma(I)$	7257
No. parameters	570
R	0.027
R_w	0.028

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0020-1693/92/$5.00

space group $P1$ with one formula unit per unit cell (with a volume of 424 Å^3). The structure could be refined with 2493 reflections and 205 variables to $R = 0.048$. But the bond distances obtained were in part unreasonable probably due to a poor data set. The WSF_5^- anion was well resolved, finally, in the structure of $(Ph_3P)_2N[WSF_5]$ (**3**).

Results and discussion

1 could be prepared in acetonitrile by fluorination of $WSCl_4$ with NaF in the presence of a crown ether under rather mild conditions. This type of fluorination has been developed and successfully applied recently by Dehnicke and coworkers [9]. By metathesis with $(PPh_4)Br$ and $[(Ph_3P)_2N]Cl$ **1** can be transformed to **2** and **3**. All compounds are rather stable in air. **1** reacts rapidly with water and develops H_2S, **2** and **3** are insoluble in water.

The IR spectrum of **1** contains bands at 662(s), 607(vs,b), 526(s), 472(s,b) cm^{-1}, which have to be assigned in this series to $\nu_s WF_4$, $\nu_{as} WF_4$, $\nu W{=}S$ and $\nu WF'$. In the Raman spectrum $\nu_s WF_4$ and $\nu W{=}S$ are observed at 662(m) and 525(vs) cm^{-1}, respectively. Caused by the negative charge of WSF_5^-, these bands are shifted to lower frequencies in comparison to WSF_4. A similar shift of $\nu W{=}S$ (from 566 to 526 cm^{-1}) has been observed between $WSCl_4$ and $WSCl_5^-$ [10]. The ^{19}F NMR spectrum of **1** in CD_3CN shows a doublet at -62.8 and a quintet at -116.2 ppm, $^2J(F–F)$ is 75.6 Hz. So no exchange occurs between the axial and equatorial ligands.

The WSF_4^- ion has a distorted octahedral structure (see Fig. 1 and Table 2). The W=S bond, 2.123(1) Å, is considerably shorter than the sum of the covalent single bond radii of 2.33 Å, indicating strong π-bonding interactions. A slightly shorter W=S bond distance has been observed so far only in $WSCl_4$ with 2.10 Å [10]. In the related dimeric anion $[WOSF_3]_2^{2-}$ the W=S distance is 2.148(3) Å [9]. With a mean value of 1.873 Å the axial W–F bonds are also rather short. In WF_6 the mean bond length is 1.833 Å [11]. Due to the *trans* effect of the W=S bond, the axial bond W–F(1) is lengthened to 1.963(3) Å.

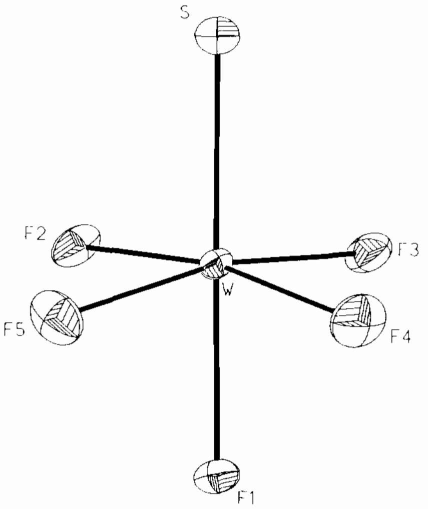

Fig. 1. Structure of the WSF_5^- anion (ellipsoids with 30% probability).

TABLE 2. Selected bond distances (Å) and bond angles (°) in $(Ph_3P)_2N[WSF_5]\cdot MeCN$ (**3**)

W–S	2.123(1)	W–F(4)	1.854(3)
W–F(1)	1.963(3)	W–F(5)	1.863(2)
W–F(2)	1.889(3)	P(1)–N	1.590(3)
W–F(3)	1.886(2)	P(2)–N	1.589(4)
S(1)–W–F(1)	178.1(1)	F(2)–W–F(4)	168.3(1)
S(1)–W–F(2)	96.6(1)	F(3)–W–F(4)	89.9(1)
S(1)–W–F(5)	95.4(1)	F(1)–W–F(2)	85.1(1)
S(1)–W–F(3)	97.4(1)	F(1)–W–F(5)	83.8(1)
F(1)–W–F(3)	83.5(1)	F(2)–W–F(5)	88.8(1)
F(2)–W–F(3)	86.8(1)	F(3)–W–F(5)	166.8(1)
S(1)–W–F(4)	94.9(1)	F(4)–W–F(5)	91.9(1)
F(1)–W–F(4)	83.4(1)	P(1)–N–P(2)	132.4(2)

W=S π-bonding and the attached *trans* effect lead to a considerable distortion of the WSF_5^- octahedron. The central atom is situated 0.20 Å above the equatorial plane. The mean $S–W–F_{eq}$ angle is 96.1°. A slightly larger distortion was observed for the WOF_5^- ion in $AsPh_4[WOF_5]$ [8]. But due to disorder in the solid state, the individual bond lengths of the axial ligands could not be determined in this study. Finally, based on Dehnicke's work and our own, it can be stated, that the structural properties and the bonding pattern, including the strength of the *trans* effect, only gradually change from oxo- to thiofluoroanions.

Supplementary material

Tables of complete crystallographic data, bond distances and angles, and thermal parameters are available from the authors on request.

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