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PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS
XXVII*. LITHIUM PENTAKIS (PENTAFLUOROPHENYL)TUNGSTEN

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SUMMARY

The synthesis and some properties of $LiW(C_6F_5)_5 \cdot 2Et_2O$ are described. Thermal decomposition of this etherate gives the volatile $W(C_6F_5)_5$ in low yield.

The simple alkyl and aryl derivatives of the heavier transition elements are, in general, unstable and poorly characterized; for example, $Li_2W(C_6H_5)_6 \cdot 3Et_2O$ has been isolated from the reaction of tungsten pentabromide and phenyllithium, and is described as a black, pyrophoric and diamagnetic powder[2]. We report the preparation of lithium pentakis (pentafluorophenyl) tungsten as the dietherate $LiW(C_6F_5)_5 \cdot 2Et_2O$ which we have found to be more amenable to study.

When a solution of (pentafluorophenyl)lithium is stirred in ether with tungsten hexachloride the solution assumes a green colour. Removal of the precipitated lithium chloride followed by crystallization under an inert atmosphere gives bright green crystals of $LiW(C_6F_5)_5 \cdot 2Et_2O$ in high yield; decafluorobiphenyl is also produced in the reaction, presumably during the reduction of W^{VI} to W^{IV}. The solid dietherate slowly decomposes over a period of weeks when held in sealed tubes at room temperature but it can be stored for many months at −10°; the stability in solution depends on the solvent used: for example, in benzene the decomposition is essentially instantaneous but in ether takes some hours to go to completion. [When $LiW(C_6F_5)_5 \cdot 2Et_2O$ is dissolved in a strongly coordinating ether solvent such as tetrahydrofuran (THF) the diethyl ether is replaced and on crystallization $LiW(C_6F_5)_5 \cdot 2THF$ is obtained.] $LiW(C_6F_5)_5 \cdot 2Et_2O$ reacts with mercuric chloride to give bis(pentafluorophenyl)mercury and with iodine to give iodopentafluorobenzene; hydrolysis produces C_6F_5H.

The magnetic moment of the dietherate is 2.70 B.M. at room temperature; the variation of the magnetic moment with temperature (Fig. 1) suggests a spin-orbit coupling constant of about 100 cm^{-1}. Many W^{IV} compounds are diamagnetic and even those that are paramagnetic have moments which are considerably reduced from the spin-only value unless a high distortion occurs in the molecule or ion; *e.g.* K_2WCl_6 has magnetic moment of 1.42 B.M.[3] compared to 2.2 B.M.[3] for K_2W-

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[*] For Part XXVI see ref. 1.

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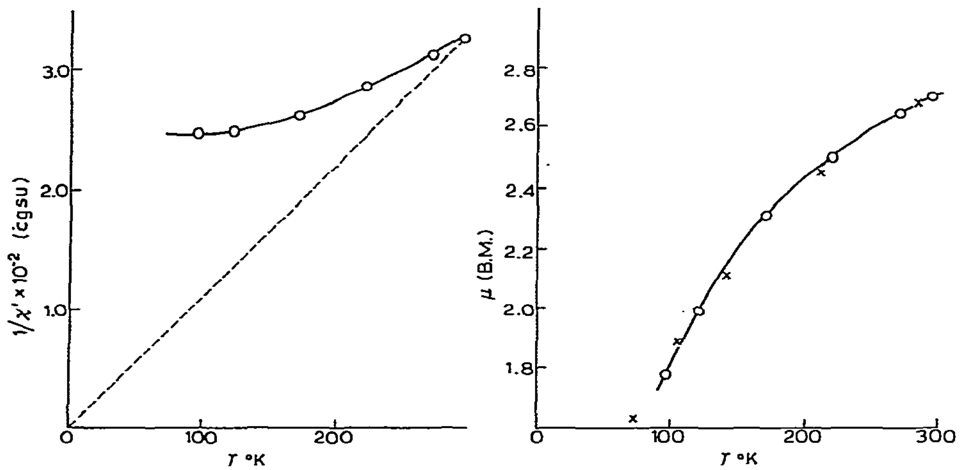

Fig. 1. Plots of $1/\chi$ vs. T and μ vs. T for $LiW(C_6F_5)_5 \cdot 2Et_2O$. O, experimental; ×, theoretical (ref. 3).

$(OH)Cl_5$. It is possible that one of the ether molecules is bound to the tungsten atom giving the metal a distorted octahedral structure.

Controlled thermal decomposition of $LiW(C_6F_5)_5 \cdot 2Et_2O$ at 100° under vacuum gives very low yields of the orange-red pentakis(pentafluorphenyl)tungsten, $W(C_6F_5)_5$. This thermally stable compound was isolated by fractional sublimation in sealed, evacuated tubes and was identified by mass spectrometry (the four main tungsten isotopes give a highly characteristic pattern to any tungsten-containing ions in the mass spectrum). The mass spectrum of the other decomposition products suggests the presence of $W(C_6F_5)_4$ but we have been unable to isolate this compound in the pure state*.

EXPERIMENTAL

All preparations and manipulations of the materials described in this work were carried out either in a vacuum or under dry, oxygen-free nitrogen.

Preparation of $LiW(C_6F_5)_5 \cdot 2Et_2O$

Butyllithium (37.8 ml, 1.56 *M* solution in hexane) was dissolved in freshly distilled, dry ether (80 ml) and the mixture cooled to −78°; bromopentafluorobenzene (14.1 g, dried over molecular sieves, 4A) was added slowly and the mixture stirred at −78° for 30 min. Sublimed tungsten hexachloride (3.3 g) was then added to the stirred mixture and the temperature allowed to rise slowly to ambient. The precipitated LiCl was filtered off and about 50 ml of solvent removed by vacuum distillation; cooling the remaining solution yielded a green solid which was collected and recrystallized from ether. [Found: C, 38.5; H, 1.7; F, 30.75; Li, 0153, 0.55; W, 15.6; oxidation state of W, 4.2. $C_{38}H_{20}F_{25}$ LiW calcd.: C, 38.85; H, 1.7; F, 40.5; Li, 0.60; W, 15.7%; oxidation state of W, 4.0] Yield 5.5 g, 73%; m.p. 110–115° with decomposition.

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* In similar experiment involving (pentafluorophenyl)niobium compounds we have isolated $Nb(C_6F_5)_4$ as a photosensitive, volatile solid. (Found: C, 38.2; F, 50.5; $C_{24}F_{20}Nb$ calcd.: C, 37.8; F, 49.9%.)

Reaction of $LiW(C_6F_5)_5 \cdot 2Et_2O$ with $HgCl_2$

The dietherate (0.21 g) was dissolved in dry ether and mercuric chloride (0.117 g) added with stirring. After 2 h the solution was filtered, the solvent removed and bis(pentafluorophenyl)mercury (0.243 g, 104%) sublimed onto a weighed probe.

Thermal decomposition of $LiW(C_6F_5)_5 \cdot 2Et_2O$

$LiW(C_6F_5)_5 \cdot 2Et_2O$ (1.2931 g) was heated to 90° in a closed system under high vacuum when vigorous decomposition occurred. The colourless liquid product (identified as diethyl ether by IR, NMR and mass spectroscopy) was distilled through a U-trap held at −78° and collected in a weighed bulb [weight of ether collected, 0.1646 g; weight of ether expected from decomposition of $LiW(C_6F_5)_5 \cdot 2Et_2O$, 0.1630 g]. The white solid which collected in the cooled U-trap was decafluorobiphenyl (m.p. 67.5–69°; infrared spectrum identical to that of an authentic sample). From the residue of the decomposition it was possible to sublime a red solid at 150° (10^{-4} mm). This material was handled entirely under high vacuum conditions using all-glass "break-seal" systems; on fractional sublimation along a tube having a temperature gradient from 130 to 180° small, orange-red crystals were obtained. These were introduced into an AEI MS 902 mass spectrometer equipped with a glove-bag purged by dry nitrogen; the mass spectrum identified the crystals as $W(C_6F_5)_5$.

Infrared spectrum of $LiW(C_6F_5)_5 \cdot 2Et_2O$

In nujol and hexachlorobutadiene mulls: 3000 m, 2960 m, 2920 m, 1635 m, 1600 sh, 1540 sh, 1520 sh, 1465 s, 1450 sh, 1430 m, 1395 w, 1385 w, 1355 m, 1342 sh, 1310 w, 1265 m, 1252 m, 1185 w, 1153 w, 1130 w, 1095 sh, 1078 s, 1066 s, 1050 sh, 1022

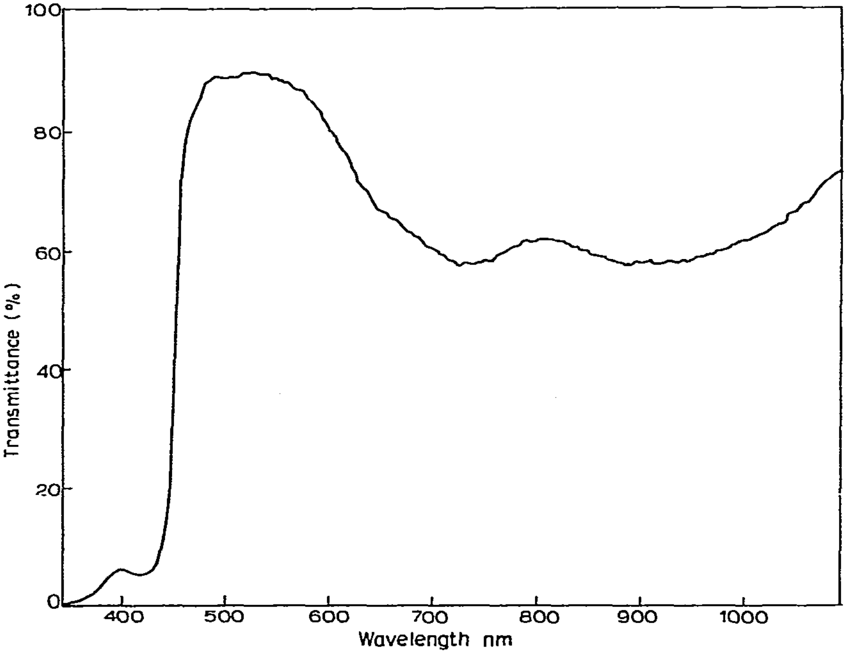

Fig. 2. Visible spectrum of $LiW(C_6F_5)_5 \cdot 2Et_2O$ in ether solution.

w, 1002 w, 965 s, 950 s, 920 sh, 900 sh, 840 w, 790 m, 757 w, 738 sh, 723 w, 618 w, 610 w, 602 w, cm^{-1}. The visible spectrum of $LiW(C_6F_5)_5 \cdot 2Et_2O$ in ether solution is shown in Fig. 2.

Reaction of $LiW(C_6F_5)_5 \cdot 2Et_2O$ with tetrahydrofuran

When $LiW(C_6F_5)_5 \cdot 2Et_2O$ was recrystallized from tetrahydrofuran the diethyl ether was found to have been completely replaced by tetrahydrofuran: 803.4 mg of the green THF complex were heated to 90° in a closed system and the tetrahydrofuran collected and weighed (92 mg of THF recovered; calculated for $LiW(C_6F_5)_5 \cdot 2THF$, 98 mg). No diethyl ether could be detected in the tetrahydrofuran using vapour phase chromatography.

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