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TETRAKIS (DEUTERIOMETHYL) TETRASELENAFULVALENE

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The preparation of >99% D tetramethyl tetraselenafulvalene is described. The synthesis involves hydrogen deuterium exchange of biacetyl followed by conversion to d_7-3-chloro-2-butanone. The latter was transformed to the title compound *via* known procedures. The physical properties of the salts $(d_{12}\text{—TMTSF})_2PF_6$ and $(d_{12}\text{—TMTSF})_2ClO_4$ are reported.

INTRODUCTION

The restoration of metallic conductivity below the metal to insulator transition temperature (T_{MI}) with low electric fields in the organic superconductor bis tetramethyl tetraselenafulvalenium hexaflurophosphate [$(TMTSF)_2PF_6$] has been interpreted as arising from depinning of spin density waves (SDW).[1] There have been attempts to corroborate this interpretation[2] and to find other elucidations for the above observations.[3] There is, however, only one *definitive* way to confirm the existence of SDW's and that is

by means of neutron scattering experiments. Since the background due to incoherent neutron scattering is much larger for protons than for deuterons, and since SDW's would be expected to be of weak intensity,[4] they would be more easily observed in $(d_{12}\text{–TMTSF})_2PF_6$. Therefore, it was necessary to prepare the fully deuterated analog of TMTSF. Also, since the carbon-deuterium bond is slightly shorter than the carbon-hydrogen bond, d_{12}–TMTSF is expected to be slightly smaller than TMTSF. This difference in size might have an effect on both the T_{MI} and the metal-to-superconductor (T_c) transition temperatures (under pressure[5] for the PF_6^- salt and atmospheric pressure for the ClO_4^- salt).[6] For the above reasons we decided to prepare d_{12}–TMTSF, and here we report on its preparation, spectroscopic properties and some physical properties of $(d_{12}\text{–TMTSF})_2PF_6$ and $(d_{12}\text{–TMTSF})_2ClO_4$ in comparison with the protio metals.

RESULTS AND DISCUSSION

Scheme I describes the most efficient synthetic approach for the preparation of d_7-3-chloro-2-butanone (3)[7], the key substance to the target molecule, d_{12}–TMTSF (4). The chloroketone thus obtained was converted to d_{12}–TMTSF (4) via our modification of the usual synthesis.[8,9] Precautions were taken to always keep the reaction medium fully enriched in deuterium; for example, the usual cyclization of the diselenocarbamate precursor to the 2-dimethylamino-1,3-diselenolium ion was performed in pure D_2SO_4. The final product (4) was twice gradient sublimed onto Teflon and analyzed spectroscopically. The UV-vis spectrum and cyclic voltammetry half-wave potentials were (within experimental error) identical to TMTSF. Infrared spectroscopy (*cf* Table I) revealed that (within experimental error, ± 5%) there was no absorption due to C-H stretching, and only absorption due to C-D stretching (2225-2050 cm^{-1}) and bending vibrations. Good spectra could only be obtained when samples were sublimed directly onto sodium chloride plates. The hexafluorophosphate and perchlorate salts were prepared electrolytically in the usual manner and subjected to the usual physical measurements. Results of these are shown in figures.

TABLE I: PHYSICAL PROPERTIES OF h_{-12} TMTSF vs d_{-12} TMTSF

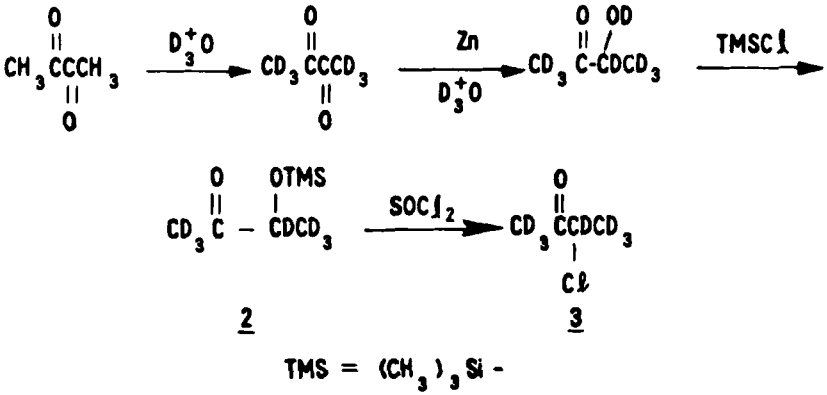
INFRA RED[a]		RAMAN[b]		ULTRA VIOLET VISIBLE[c]	CYCLIC VOLTAMMETRY[d]
h_{12}	d_{12}	h_{12}	d_{12}	h_{12} d_{12}	h_{12} d_{12}
2970 (m)	2225 (m)	1537	1537	508 ± 5	$E_{1/2}^{1}$ = 430 ± 10
2902 (s)	2190 (m)	1496	1496	299 ± 1	$E_{1/2}^{2}$ = 730 ± 10
2840 (m)	2095 (m)	680	—		
	2050 (m)	453	453		
1617 (m)	1599 (m)	274	296		
1438 (vs)	1170 (m)				
1145 (m)	1108 (m)				
1062 (s)	1036 (s)				
665 (s)	1007 (m)				
	942 (vs)				
	742 (w)				
	658 (m)				

(a) cm^{-1}

(b) totally symmetric modes; k. iwahana et al[11]

(c) nm

(d) mV vs SCE



Scheme I: Synthesis of d_7-3-chlorobutanone (3)

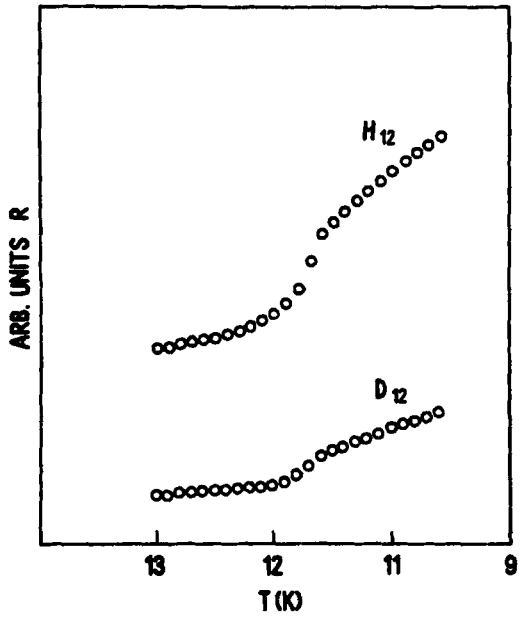


Figure 1: D.C. resistivity of $(TMTSF)_2PF_6$ and $(d_{12}-TMTSF)_2PF_6$ vs. temperature.

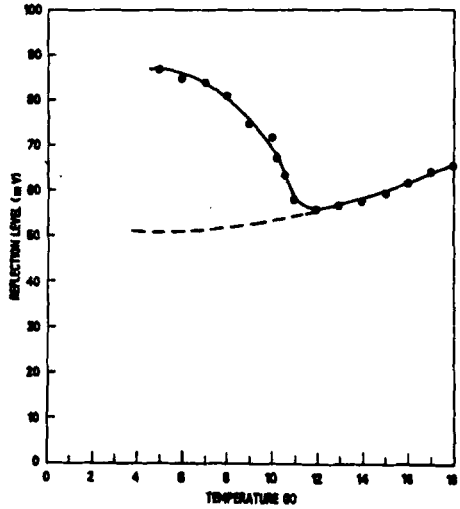


Figure 2: The microwave reflection level of $(TMTSF)_2PF_6$ (dashed curve) and of $(d_{12}-TMTSF)_2$ as a function of temperature indicating pinning of the SDW state in the deuterated salt.

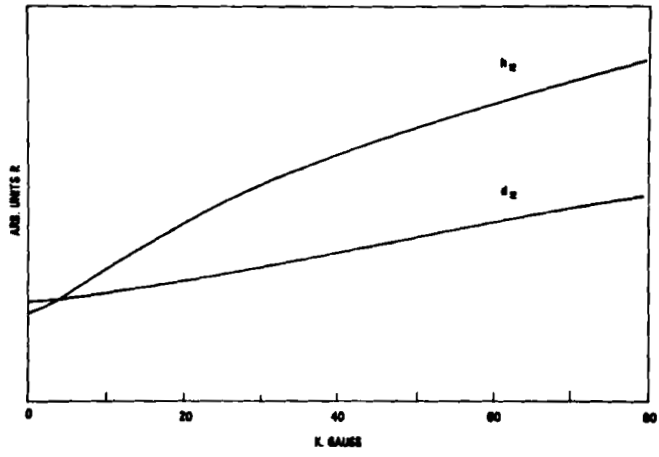


Figure 3: Magneto-resistance of $(TMTSF)_2PF_6$ and of $(d_{12}-TMTSF)_2PF_6$ at 4.4 k.

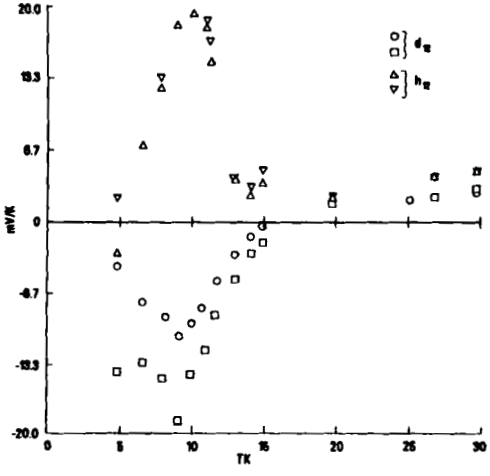


Figure 4: Thermopower of $(TMTSF)_2PF_6$ and of $(d_{12}-TMTSF)_2PF_6$ vs. temperature.

The D.C conductivity of $(d_{12}-TMTSF)_2PF_6$ and $(TMTSF)_2PF_6$ at atmospheric pressure shown in figure 1 indicates no isotope effect on T_{MI} within experimental error ± 0.2 K. On the other hand EPR (Figure 2), magnetoresistance (Figure 3) and thermopower (Figure 4) measurements are different for both metals. These differences are attributed to disorder due to residual protons in the samples and probably not to an isotope effect.

The $(d_{12}-TMTSF)_2ClO_4$ salt in comparison to its protonated analog shows a broader transition before becoming superconducting.[6] This again can be interpreted as due to the disorder mentioned above. A possible isotope effect on T_c of the order of 90 mk is suggested from the magnetization measurements.[10] The heavier, deuterated, salt shows a lower T_c as would be expected from BCS theory (Figure 5).

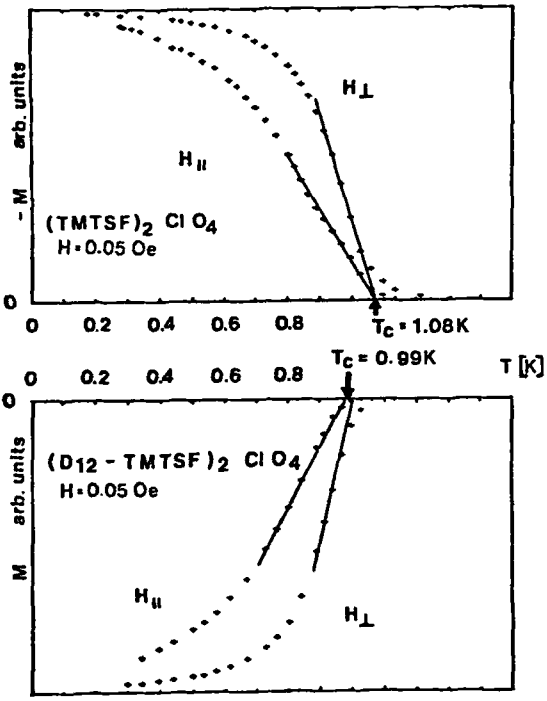


Figure 5: Magnetization behavior of $(TMTSF)_2ClO_4$ and $(d_{12}-TMTSF)_2ClO_4$ vs. temperature.

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