NEW CONDUCTING SOLIDS BASED ON SOME SYMMETRICAL AND UNSYMMETRICAL π-DONORS

G.C. Mousdis, V.C. Kakoussis and G.C. Papavassiliou

Theoretical and Physical Chemistry Institute
National Hellenic Research Foundation
48, Vassileos Constantinou Ave., Athens
11635, Greece

INTRODUCTION

Recently, conducting and syperconducting crystals based on unsymmetrical π-donor molecules have been described [1]-[9]. In this paper we describe the preparation and preliminary studies of new conducting salts based on some unsymmetrical π-donors (1)-(13) (Table 1) [10]-[16] as well as on the following symmetrical π-donors: TTF (14), TMTSF (15), (BMDTTTF) (16), (BEDTTTF)(17), (BVDTTTF) (18) [17], (BPDTTF) (19) [18], (BDMETTF) (20) [19], (BMDSTTF) (21) [20], (BEDSTTFR) (22) [20] and (BTMDSTTF) (23) [20].

EXPERIMENTAL

The preparation of 1,3-dithiole-2-ones and selenium-analogs, precursors of unsymmetrical π-donors, is described in refs [10]-[16] and in the following paragraphs.

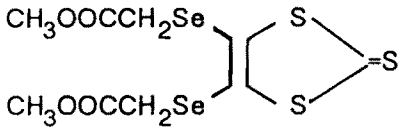
Preparation of 4,5-bis(methylacetate) diseleno-1,3-dithiole-2-thione (I)

This compound was prepared by a method similar to that reported for the preparation of its sulfur analog [13]: Treatment of bis(tetrabutylammonium) bis(1,3-dithiole-2-thione-4,5-diselenolato)-zincate [12] with methyl bromoacetate in boiling acetone, followed by cooling at -10°C and recrystallization of the resulting precepitate from boiling cyclohexane, gave a yellow crystalline solid ; mp=45°C; UV (CH_3CN):377, 280, 227 nm.

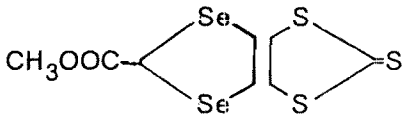
Preparation of 4,5-(methylacetatediseleno)-1,3-dithiole-2-thione (II)

This compound was prepared by a method similar to that reported for the preparation of its sulfur analog [14]: Treatment of bis(tetrabutylammonium) bis(1,3-dithiole-2-thione-4,5-diselenolato) -zincate [12] with methyl dichloroacetate in boiling acetone, followed by cooling at -10°C, and recrystallization of the resulting precipitate from boiling ethanol, gave a greenish-yellow solid; mp=171 °C; UV(CH_3CN): 418, 274 nm.

Lower-Dimensional Systems and Molecular Electronics
Edited by R.M. Metzger *et al.*, Plenum Press, New York, 1991



(I)

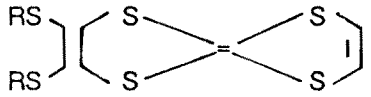


(II)

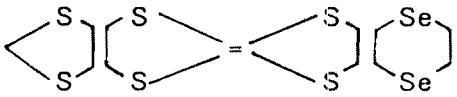
Preparation of 4,5-bis(methylacetate)diseleno-1,3-dithiole-2-one and 4,5-(methylacetatediseleno) -1,3-dithiole-2-one.

These compounds were prepared by treating the corresponding -2-thiones (I) or (II) with mercury acetate in a mixture of dichloromethane-acetic acid at refluxing temperature (see [12]-[14]). 4,5-Bis(methylacetate)diseleno-1,3-dithiole-2-one is a white solid; mp=18-20°C; UV(CH_3CN) 264 nm, and 4,5-(methylacetatediseleno)-1,3-dithiole-2 one is a white-yellow solid; mp=97 °C; UV(CH_3CN): 307 nm.

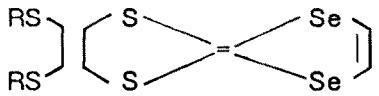
Table 1. Molecular formulas of unsymmetrical π-donors



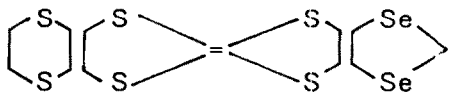
(1a)-(1g)



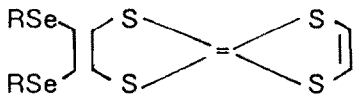
(8b)



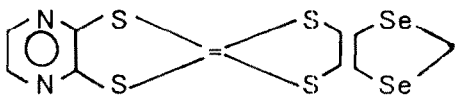
(2b)-(2c)



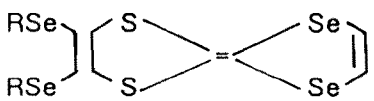
(9b)



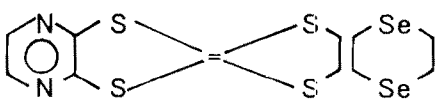
(3b)-(3d)



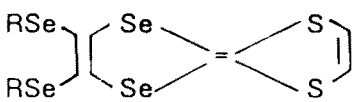
(10b)



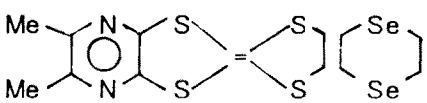
(4c)



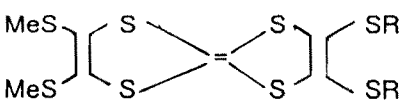
(10c)



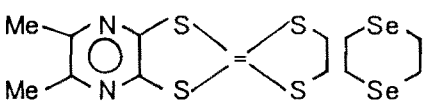
(5b)-(5c)



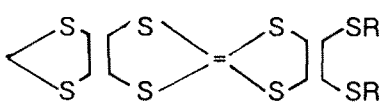
(11b)



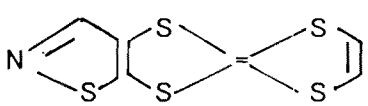
(6b)-(6g)



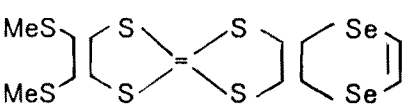
(11c)



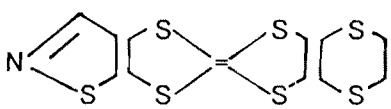
(7a)-(7f)



(12)



(8a)



(13c)

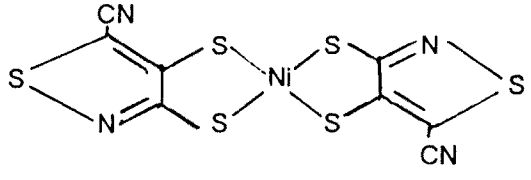
(a):R=CH_3, (b):2R=CH_2, (c):2R=CH_2CH_2, (d):2R=$CH_2CH_2CH_2$, (e):2R=$CH(CH_3)CH_2$, (f):2R=$CH(CH_3)CH(CH_3)$, (g):2R=CH=CH

Table 2. Salts, their method of preparation and their appearance.

$(1b)_2AuBr_2$	EL	black plates	$(6f)_xIBr_2$	CH	black needles
$(1b)_xNi(dcit)_2$	EL	black μ-crystals	$(6f)_xTCNQ$	CH	black needles
$(1c)_2AuBr_2$	EL	black plates	$(6d)_xI_3$	CH	golden μ-crystals
$(1c)_2Ag(CN)_2$	EL	black needles	$(6d)_xIBr_2$	CH	black plates
$(1c)_xNi(dcit)_2$	EL	black μ-crystals	$(7c)_xIBr_2$	EL	bronze plates
$(1g)_xAuI_2$	EL	black needles	$(7c)_xI_3$	EL	bronze-blackplates
$(1g)_xIBr_2$	EL	black needles, plates	$(8a)_xI_3$	CH	black μ-crystals
$(1g)_xNi(dcit)_2$	EL	black μ-crystals	$(8a)_xIBr_2$	CH	black μ-crystals
$(2b)_xIBr_2$	CH	bronze needles, plates	$(9b)_xTCNQ$	CH	black μ-crystals
$(2c)_xIBr_2$	EL	black needles, plates	$(9b)_xI_3$	CH	needles
$(3b)_xTCNQ$	CH	black needles	$(10b)_xI_3$	CH	dark-copper
$(3b)_xI_3$	CH	copper plates	$(10b)_xIBr_2$	CH	dark-copper
$(3b)_xIBr_2$	CH	bronze needles	$(10b)_xBr_3$	CH	brown chips
$(3b)_xAuI_2$	CH	black plates	$(10c)_xI_3$	CH	golden needles
$(3c)_xTCNQ$	CH	black μ-crystals	$(10c)_xIBr_2$	CH	brown μ-crystals
$(3c)_xI_3$	CH	black μ-crystals	$(10c)_xBr_3$	CH	golden brown
$(3c)_xIBr_2$	CH	golden μ-crystals	$(11b)_xIBr_2$	EL	black plates
$(3c)_xIBr_2$	EL	black, golden plates	$(11b)_xI_3$	CH	golden chips
$(3d)_xTCNQ$	CH	black μ-crystals	$(11b)_xIBr_2$	CH	copper chips
$(3d)_xI_3$	CH	needles, μ-crystals	$(11b)_xI_3$	EL	bronze plates
$(3d)_xIBr_2$	CH	black μ-crystals	$(11c)_2TCNQ$	CH	dark blue plates
$(3d)_xI_3$	EL	black needles, μ-crystals	$(11c)_xI_3$	CH	dark bronze
$(4c)_xI_3$	CH	bronze needles	$(11c)_xIBr_2$	CH	black plates
$(5c)_xTCNQ$	CH	black μ-crystals	$(11c)_xIBr_2$	EL	black plates
$(5c)_xI_3$	CH	golden needles	$(11c)_xAuI_2$	EL	black plates
$(5c)_xI_3$	EL	black needles, plates	$(12)_xTCNQ$	CH	brown μ-crystals
$(5c)_xIBr_2$	CH	black needles	$(13c)_xBr_3$	CH	black μ-crystals
$(5c)_xAuI_2$	EL	black μ-crystals	$(14)_x$-$(15)_xNi(dcit)_2$	EL	black μ-crystals
$(6e)_xIBr_2$	CH	black μ-crystals	$(16)_xNi(dcit)_2$	EL	red-black chips
$(6g)_xIBr_2$	CH	black μ-crystals	$(17)_x$-$(23)_xNi(dcit)2$	EL	black μ-crystals

CH= chemical method, EL= electrochemical method

$Ni(dcit)_2$ =



The unsymmetrical π-donors (1)-(13) were prepared from the corresponding pı cursors by methods reported in refs. [10]-[16]. A number of salts based on the π-c nors (1)-(23) was prepared by chemical or electrochemical procedures. These sal their method of preparation, and their appearance are summarized in Table 2.

RESULTS AND DISCUSSION

Conductivity measurements on polycrystalline compressed pellets or on sinç crystals performed at room temperature in the salts of Table 2 showed that these a conducting salts. Some of them, such as $(1b)_2AuBr_2$, $(1b)_xNi(dcit)_2$, $(1c)_2AuBı$ $(1g)_xIBr_2$, were found to be metallic down to low temperatures. These preliminary r sults indicate that the compounds are worthy of further studies.

REFERENCES

1. G.C.Papavassiliou, G.A.Mousdis, J.S.Zambounis, A.Terzis, A.Hountas, B.Hilti, C.W.Mayer and J.Pfeiffer , Synth.Metals 27 B379 (1988).
2. A.Terzis, A.Hountas, A.E.Underhill, A.Clark, B.Kaye, B.Hilti, C.Mayer, J.Pfeiffer, S.Y.Yiannopoulos, G.A.Mousdis and G.C.Papavassiliou, Synth.Metals 27 B97 (1988).
3. A.Terzis, A.Hountas, and G.C.Papavassiliou, Sol.St. Commun., 66, 1161 (1988)
4. A.Hountas, A.Terzis, G.Papavassiliou, B.Hilti and J.Pfeiffer, Acta Cryst., C, in press.
5. A.Hountas, A.Terzis, G.C.Papavassiliou, B.Hilti, N.Bürkle, C.W.Mayer, and J.S.Zambounis, Acta Cryst. C, in press.
6. A.Terzis, A.Hountas, G.C.Papavassiliou, B.Hilti and J.Pfeiffer, Acta Cryst., in press.
7. B.Hilti et al , to be published.
8. A.M.Kini et al ,Sol.St.Commun., 69, 503 (1989).
9. A.Kobayashi, R.Kato, and H.Kobayashi, to be published.
10. G.C.Papavassiliou, V.C.Kakoussis and G.A.Mousdis to be published:(5c)(orangı mp=210°C), (8a) (yellow, mp=105°C), (9b)(orange-brown, mp=189° C),(1C (orange-red, mp=244°C), (10c) (orange mp=209°C), (11b) (yellow-orange, mp=240°C), (11c)(yellow, mp>240°C), (13)(yellow, mp=197°C) have been pre pared by methods similar to those reported in refs [11]-[16] herein.
11. G.C.Papavassiliou, this volume.
12. G.C.Papavassiliou, V.C.Kakoussis, J.S.Zambounis, and G.A.Mousdis, Chem.Scripta, in press (1989).
13. G.C.Papavassiliou, V.C.Kakoussis, G.A.Mousdis, J.S.Zambounis and C.W.Mayer, Chem.Scripta, in press (1989).
14. G.C.Papavassiliou, G.A.Mousdis, S.Y.Yiannopoulos, and J.S.Zambounis, Chem.Scripta 28, 365 (1988).
15. G.C.Papavassiliou, G.A.Mousdis, S.Y.Yiannopoulos, V.C.Kakoussis and J.S.Zambounis, Synth.Metals 27, B373 (1988).
16. G.C.Papavassiliou, J.S.Zambounis, G.A.Mousdis, V.Gionis and S.Y.Yiannopoulos, Mol.Cryst.Liq.Cryst., 156, 269 (1988).
17. K.Inone et al Chem.Lett. 781 (1986): K.S.Varma et al Physica 143B, 321 (1986).
18. G.C.Papavassiliou et al Chem.Scripta, 27, 261 (1987).
19. J.D.Wallis et al Helv.Chim.Acta 69, 69 (1986).
20. P.J.Nigrey et al Synth.Metals, 27, B481 (1988).