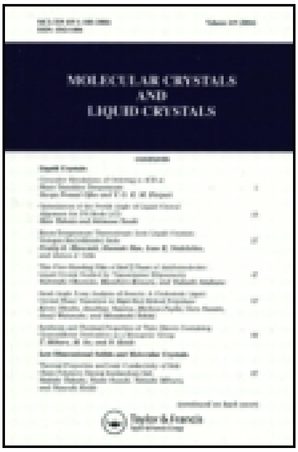


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Transition-Metal 1,2 Diheterolenes and Polyheterotetra-heterafulvalenes: Precursors of Conducting Solids

G. C. Papavassiliou [a] , V. C. Kakoussis [a] , D. J. Lagouvardos [a] & G. A. Mousdis [a]

[a] Theor.Phys.Chem.Institute, NHRF, 48, Vas.Constantinou Ave., Athens, 116/35, Greece

To cite this article: G. C. Papavassiliou , V. C. Kakoussis , D. J. Lagouvardos & G. A. Mousdis (1990): Transition-Metal 1,2 Diheterolenes and Polyheterotetra-heterafulvalenes: Precursors of Conducting Solids, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 181:1, 171-184

To link to this article: http://dx.doi.org/10.1080/00268949008036002

Mol. Cryst. Liq. Cryst., 1990, vol. 181, pp. 171–184
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

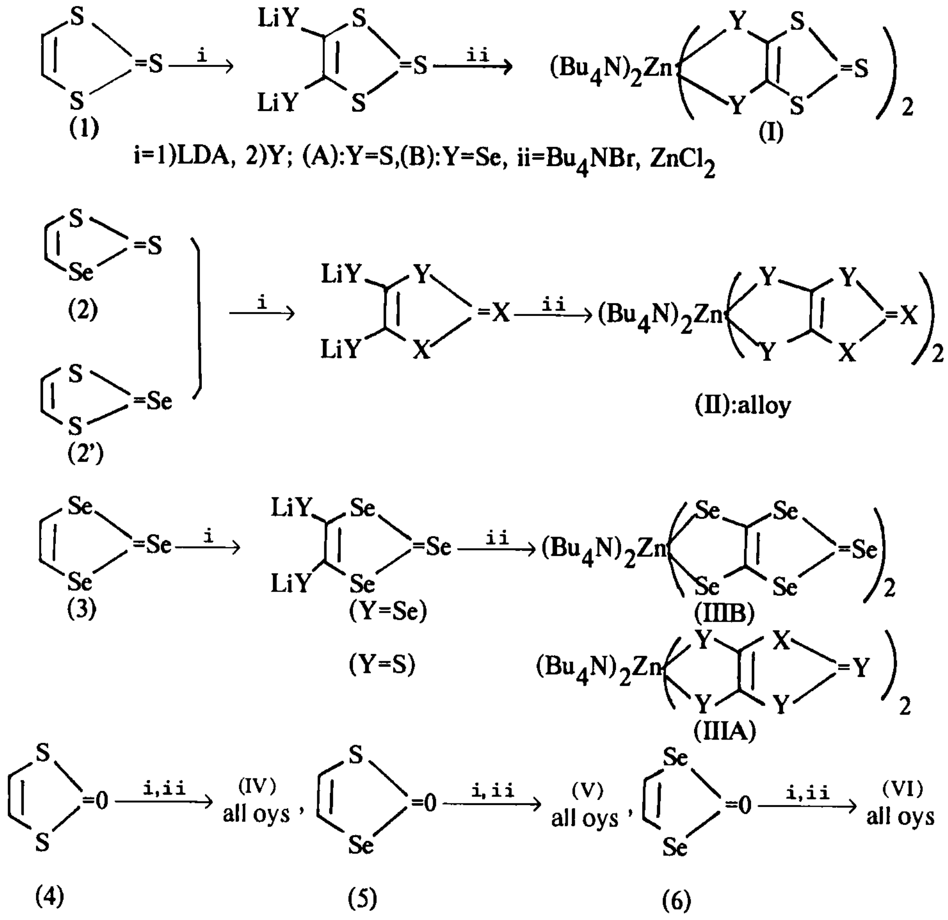
TRANSITION-METAL 1,2-DIHETEROLENES AND POLYHETEROTETRAHETERAFULVALENES: PRECURSORS OF CONDUCTING SOLIDS

G.C.PAPAVASSILIOU, V.C.KAKOUSSIS, D.J.LAGOUVARDOS AND G.A.MOUSDIS
Theor.Phys.Chem.Institute, NHRF, 48, Vas.Constantinou Ave., Athens 116/35, Greece

Abstract. Methods for synthesis and properties of oxygen-, sulfur-, selenium-, and nitrogen-containing transition-metal 1,2-diheterolenes and polyheterotetraheterafulvalenes are described. Also, the preparation and properties of some conducting salts based on these compounds are briefly discussed.

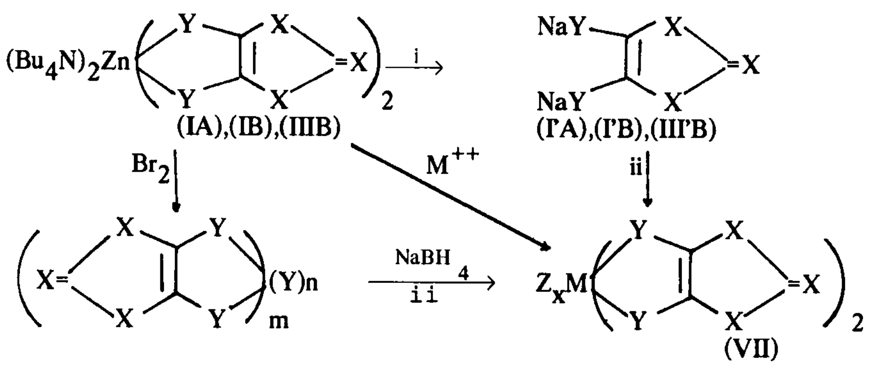
INTRODUCTION

During the last ten years a number of conducting solids based on transition-metal 1,2-diheterolenes and polyheterotraheterafulvalenes have been reported.[1-4] In this paper we describe the preparation of some oxygen-, sulfur-, selenium- and nitrogen-containing metal 1,2-diheterolenes and tetraheterafulvalenes. Also results on the preparation and properties of their conducting salts are briefly discussed. Metal 1,2-diheterolenes and tetraheterafulvalenes were prepared by procedures of Schemes 1-10. Starting from vinylene trithiocarbonate (1)[5], vinylene triselenocarbonate (3)[6], 1,3-thiaselenole-2-thione(2)[7], 1,3-dithiole-2-selone (2')[7], 1,3-dithiole-2-one(4)[8], 1,3-thiaselenole-2-one(5)[9], and 1,3-diselenole-2-one(6)[9], a number of zinc 1,2-diheterolenes (I)-(VI), nickel-, palladium-, etc-analogs can be obtained[10] by the procedure of Scheme 1. For the preparation of (IA), (IIIB) and (II), alternative methods based on the chemical or electrochemical reduction of CS_2, CSe_2 and CSSe have been described in the literature.[1,11-15] Purification of (I), (IIIB) and conversion from Zn to another metal (M) or from Bu_4N to another cation (Z) were performed by a several(1,2,3)-steps sequence[10-15] according to Scheme 2. Treatment of (IA), (IB), (IIIB) with an alkyl halide [16] gave the corresponding 1,3-dithiole-2-thione(7),(9), or 1,3-diselenole-2-selone (11). These compounds were transformed to the corresponding -2-ones (8),(10),(12) by treatment [16] with mercuric acetate according to Scheme 3. The alloys (II), (IIIA), (IV)-(VI) gave by similar procedures a number of mixtures (see for example Scheme 3). After chromatography separation, the compounds (13),(14) were obtained in a pure form. Compounds (7c)- (7g),



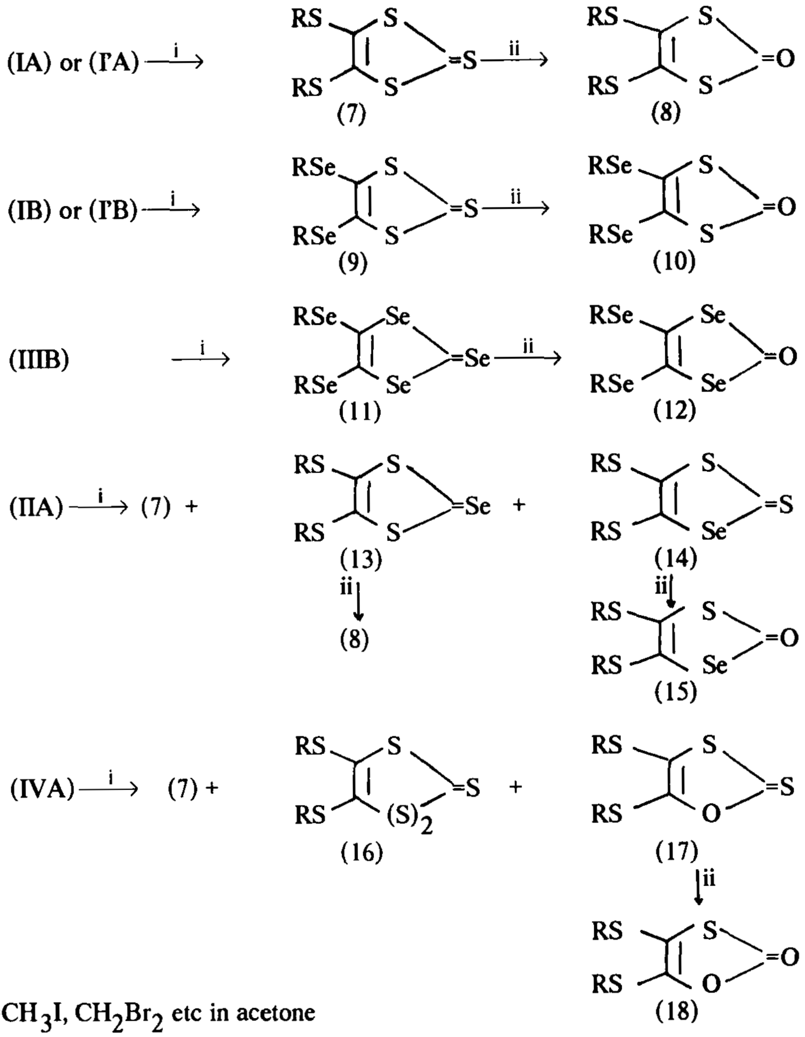
i=1)LDA, 2)Y; (A):Y=S,(B):Y=Se, ii=Bu_4NBr, $ZnCl_2$

SCHEME 1



i=1)PhCOCl, 2)$NaOC_2H_5$; ii=ZBr, M^{++}; Z=Me_4N, Et_4N etc.,
m,n=0,1,2...; x=2(under Ar), x=1 (under air)

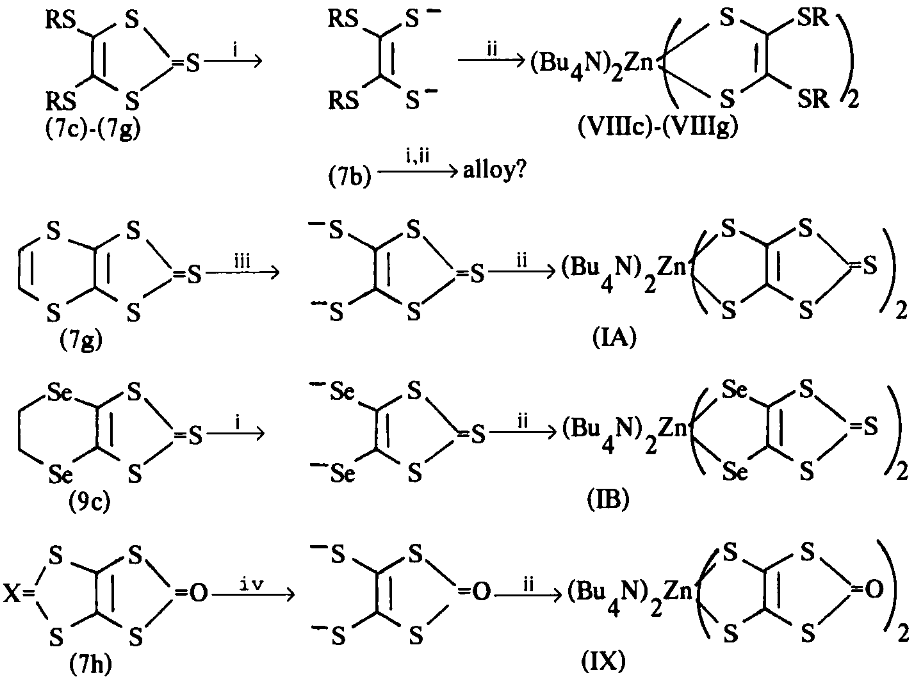
SCHEME 2



i=CH_3I, CH_2Br_2 etc in acetone
or BrCH=CHBr in CH_3CN
ii=$Hg(OAc)_2$ in CH_3COOH-CH_2Cl_2
(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, (h):2R=C=O

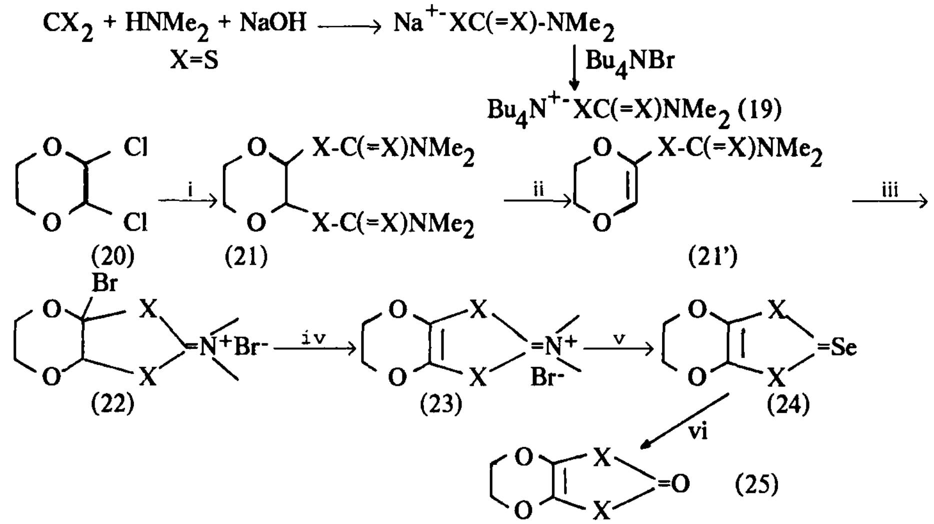
SCHEME 3

(7h), (8h), (9c) can be transformed to the corresponding metal 1,2-diheterolenes by two-steps sequences[10-20] according to Scheme 4. 4,5-Ethylenedioxo-1,3-dithiole-2-one (25) was obtained from 2,3-dichlorodioxane (19) by a six-steps sequence[21,22] according to Scheme 5. Pyrazino-, dimethypyrazino-1,3-dithiole-2-one and selenium analogs (29) have been prepared[23] from 2,3-dichloropyrazine and 5,6-dimethyl-2,3-dichloropyrazine, respectively, according to Scheme 6. Cross-coupling of (8) and (10) with (25) via triethylphosphite gave the corresponding unsymmetrical tetrathiafulvalenes (30) and (31) according to Scheme 7. Cross-coupling of (8),(10), (12) and (25) with (19) via triethyl phosphite gave[23,24] the corresponding unsymmetrical tetraheterafulvalenes (32) according to Scheme 8. The unsymmetrical compounds (35) were prepared from (8), (10), (12),(25) and (33) by a two-steps sequence[1,10,24] according to Scheme 9. Similar tetraheterafulvalenes based on (15), (18) and (25) (X=Se) as well as metal 1,2-diheterolenes based on (25) and (29)[23] were not prepared yet in a pure form. Also oxygen addition (Scheme 1, Y=O) is possible but the corresponding dioxolenes were not prepared yet. Metal 1,2-dithiolenes (X) and polyheterotetraheterafulvalenes (38), (39) were prepared by similar methods[22,25] according to Scheme 10. Cation deficient metal 1,2-dihe terolenes (VII, 0<x<1), charge transfer complexes and cation radical salts of (30)-(32), (35), (39) were obtained by chemical or electrochemical procedures.[1-3]



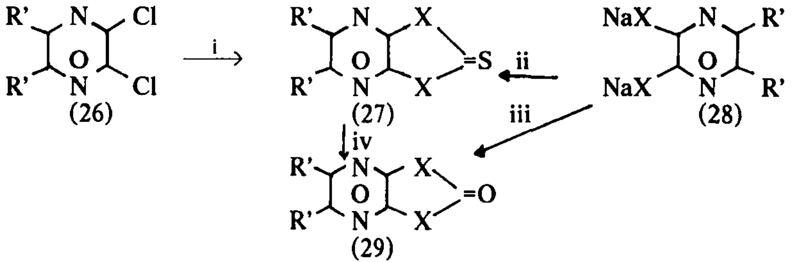
i=NaOC$_2$H$_5$ or KOH, ii=Bu$_4$NBr, ZnCl$_2$, iii=LDA at -70°C,
iv=NaOCH$_3$(X=O) or electroreduction (X=O,S)

SCHEME 4



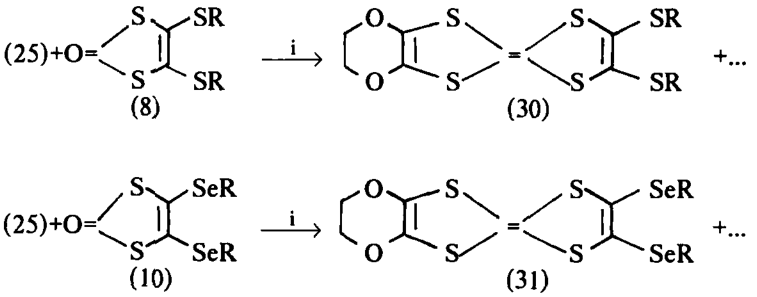
i=(19) in CH_3CN, Δ ; ii=DMSO,110°C;iii=Br_2 in CH_2Cl_2,0°C;iv=110°C, 25 Torr v=H_2Se in MeOH; vi=$Hg(OAc)_2$ in CH_3COOH-CH_2Cl_2

SCHEME 5



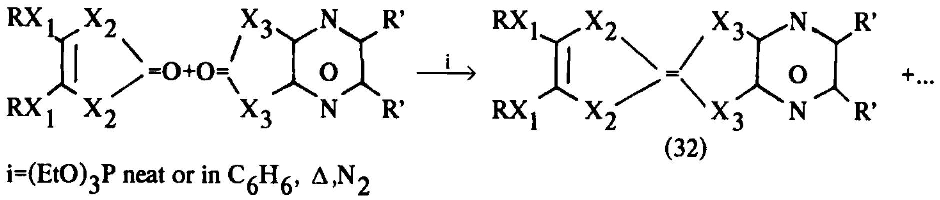
i=NaS-(C=S)-SNa, ii=Cl_2C=S, iii=Cl_2C=O, iv=$Hg(OAc)_2$ in CH_3COOH-CH_2Cl_2
(a'):X=S, R'=H; (b'):X=S, R'=CH_3; (c'):X=Se, R'=H; (d'):X=Se, R'=CH_3.

SCHEME 6



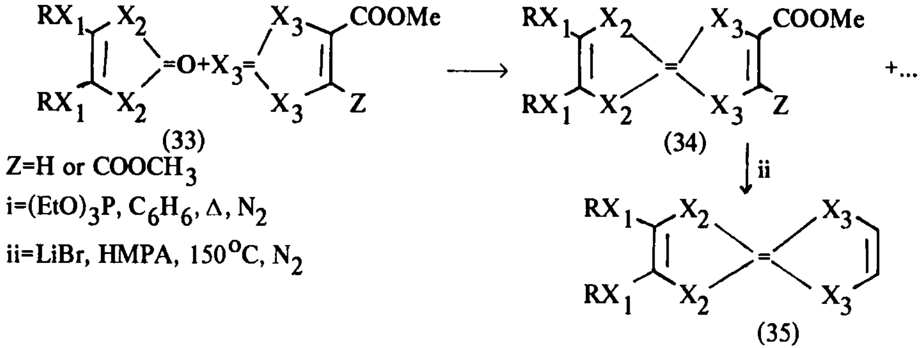
i=$(EtO)_3P$, ≈ 150°C, N_2

SCHEME 7



i=$(EtO)_3P$ neat or in C_6H_6, Δ,N_2

SCHEME 8

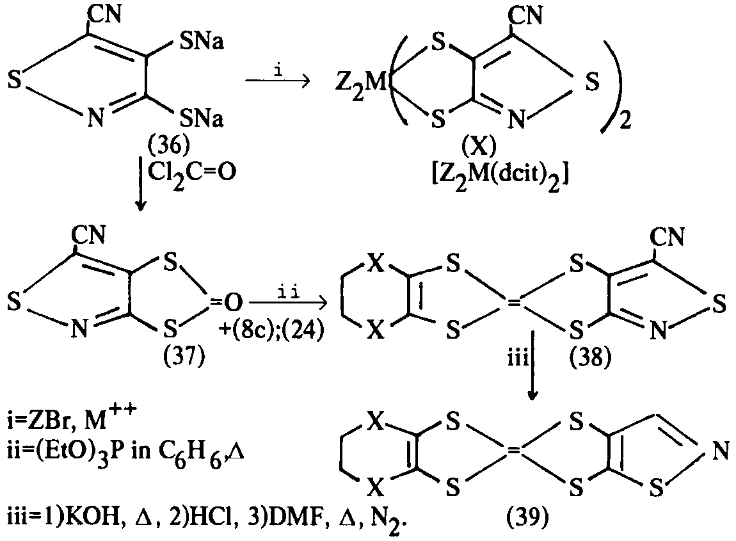


Z=H or $COOCH_3$

i=$(EtO)_3P$, C_6H_6, Δ, N_2

ii=LiBr, HMPA, 150°C, N_2

SCHEME 9



i=ZBr, M^{++}

ii=$(EtO)_3P$ in C_6H_6,Δ

iii=1)KOH, Δ, 2)HCl, 3)DMF, Δ, N_2.

SCHEME 10

EXPERIMENTAL

Preparation of Bis(tetrabutylammonium)-bis(1,3-dithiole-2-thione-4,5-dithiolato)-zincate (IA) [:$(Bu_4N)_2Zn(dmit)_2$] and Similar Compounds (IB),(II)-(VI).

Vinylene trithiocarbonate (1) (5g,37mmol) in THF (70 ml) was converted to (IA) by a three-steps sequence [8,26]: treatment with lithium diisopropylamide (LDA) (75 mol) at -75°C, addition of powdered sulfur (2.4 g, 75 mmol) and treatment with $ZnCl_2$ in methanol in presence of Bu_4NBr (13g) at room temperature. The solution was poured into water and the brown precipitate was filtered, washed with water, ether-isopropanole (1:1, 70 ml), ether, benzene and dried in air. Then, it was dissolved in acetone (150 ml), dried over $MgSO_4$ and precipitated with isopropanol at -15°C to give 12.5 g of (IA) (71% based on (1)). This is a red solid, mp=174 °C (lit[11] 177-8 °C); UV-visible (CH_3COCH_3 516 nm, CH_3OH 480 nm: solvent effect). Same procedure was applied for the preparation of (IB)[10], (II)-(VI) and similar compounds with Ni, Pd etc. instead of Zn. Preparative data are listed in Table I. Some of these compounds have been prepared by alternative methods. [11-15, 25, 27]

Preparation of Bis(tetrabutylammonium)-bis(5,6-dihydro-1,4-dithin-2,3-dithiolato)-zincate (VIIIc)[:$(Bu_4N)_2$ Zn(dddt)$_2$] and Similar Compounds.

To a freshly prepared solution of sodium methoxide in methanol 0.4 mol.equiv. of 4,5-ethylenedithio-1,3-dithiole-2-thione was added and the mixture was heated with stirring at reflux temperature for 1 hour under nitrogen atmosphere. Then, the appropriate amounts of $ZnCl_2$ and Bu_4N Br in methanol were added and the stirring was continued for 30 min. The mixture was treated as in the procedure of previous paragraph to give (VIIIc) as a yellow-orange solid not isolated in a pure form.

Similar methods were applied for the preparation of (VIIId)-(VIIIg), (IA), (IB), (IX) from (7d)-(7g), (7g), (9c), (9h), respectively, except that LDA at -70°C instead of sodium methoxide was used for the preparation of (IA) from (7g) and KOH instead of sodium methoxide for the preparation of (VIIIg)[28,19] from (7g). Also electroreduction procedure[28] can be used for the preparation of (IX) from (7h) or (8h). Compounds (X) were prepared from (36) by a similar method.[25] Preparative data are listed in Table I. Compound (7b) gave a dark-brown solid (M=Zn, mp=138°C; UV-visible: in acetone 495, 622nm; in methanol 474, 592nm). Perhaps, this is a mixed-ligand complex.

Preparation of Tetrabutylammonium-bis(1,3-dithiole-2-thione-4,5-dithiolato)-nickelate (VII, Z=Bu_4N, x=1, M=Ni, Y=X=S)[:$(Bu_4N)_1$Ni(dmit)$_2$] and Similar Compounds.

To a solution of $(Bu_4N)_2Zn(dmit)_2$ or Hg-analog[20,27] in acetone a solution of $NiCl_2$ in methanol was added dropwise with stirring. Crystals were obtained after slow evaporation of the solvent in air. They washed with water and methanol and recrystallized from acetone; black crystals in yield 86%; mp=189°C. They can be obtained by an alternative method from $(Bu_4N)_2Ni(dmit)_2$ after oxidation with the appropriate amount of iodine in an organic solvent.

The compounds $(Bu_4N)_1Ni(dsit)_2$,$(Bu_4N)_1Ni(dsis)_2$,$(Bu_4N)_1Ni(dmid)_2$, etc.[13,18,19,28,29] were obtained by the same procedures. Preparative data are listed in Table I.

TABLE I. Preparative data for (I)-(X) and similar compounds

Compound	Yield(%)	mp(°C)	λ/nm : (Solvent)*
(IA):$(Bu_4N)_2Zn(dmit)_2$	71	174	516(α) 480(β)
(IB):$(Bu_4N)_2Zn(dsit)_2$	80	163	498(α) 472(β)
(IIA)	60	171	542(α) 514(β)
(IIIA)	64	172	519(α) 494(β)
(IIIB):$(Bu_4N)_2Zn(dsis)_2$	70	178	562(α) 496(β)
(IVA)	53	≥120	565(α) 516(β)
(IVB)	28		544(α) 488(β)
(VA)	33	130	480(α) 415(β)
$(Me_4N)_2Zn(dmit)_2$	53	179	508(α) 476(β)
$(Et_4N)_2Zn(dmit)_2$	61	198	512(α) 484(β)
(VIIIc):$(Bu_4N)_2Zn(dddt)_2$	48		479(α) 426(β)
(IX):$(Bu_4N)_2Zn(dmid)_2$	≥30	137	372(α) 354(β)
$(Bu_4N)_2Hg(dmit)_2$	62	165	517(α) 485(β)
$(Bu_4N)_2Ni(dmit)_2$	58	≥200	615(α) 530(β)
$(Me_4N)_2Ni(dmit)_2$	57	>260	628(α) 558(β)
$(Bu_4N)_2Ni(dcit)_2$	80	170	465-505(β)
$(Bu_4N)_2Pd(dmit)_2$	67	211	580(α) 528(β)
$(Me_4N)_2Pd(dmit)_2$	62	>260	580(α) 528(β)
$(Bu_4N)_2Pt(dmit)_2$	66	≥210	622(α) 543(β)
$(Bu_4N)_1Ni(dmit)_2$	86	189	1030(α)
$(Bu_4N)_1Ni(dsit)_2$	90	215	1067(α)
$(Bu_4N)_1Ni(dsis)_2$	94	>250	925(α)
$(Bu_4N)_1Ni(dmid)_2$	87	149	1045(α)
$(Bu_4N)_1Ni(dddt)_2$	85	189	1040(α)
$(Bu_4N)_1Pt(dmit)_2$	84	212	1135(α)

* First low frequency visible-near IR absorption maximum in (α)CH_3COCH_3 and (β)CH_3OH. See also refs.11-15, 25,27.

Preparation of compounds (7)-(18)

The compounds (7a)-(7d) were prepared from $(Bu_4N)_2Zn(dmit)_2$ by adaptation of the method reported for the preparation of (7e)[11], except that silica-gel column chromatography was used for the isolation of (7b) from the subproducts. Compound (7f) was prepared by same method and by a method reported in the literature[30]. Compound (7g) was prepared by treatment of (I'A) with BrCH=CHBr in acetonitrile[31]. Compound (7h) was prepared by treating a suspension of powdered (IA) in benzene with phosgene. Compounds (9), (11)[32,33] were prepared from $(Bu_4N)_2Zn(dsit)_2$ and $(Bu_4N)_2Zn(dsis)_2$, respectively by adaptation of the method reported for the preparation of (9b)[10]. Same method was used for the preparation of (13), (14) as well as (16), (17) except that silica gel column chromatography was used for the separation of the products. Compounds (8), (10), (12), (15), (18) were prepared from (7), (9), (11), (14), (17), respectively, after treatment with mercuric acetate in CH_3COOH-CH_2Cl_2 (1:1).[10,11] Preparative data for (11)-(15) are listed in Table II; (16)-(18) were not prepared yet in a pure form.

TABLE II. Preparative data for (11)-(15)

Compound	Yield(%)	mp(°C)	UV-visible(λ/nm) in CH_3CN
(11b)	42	182	214,300-322, 470
(12b)	70	113	280(w), 306
(11c)	77	160(lit 125)[33]	208, 242, 302-324, 442
(12c)	87	110(lit 109)[33]	250, 288
(13b)	14	176	270(w), 312(w), 458
(13c)	28	138	214(sh), 274, 312, 442
(14b)	18	152	269, 288(sh), 430
(14c)	33	116	274, 300(sh), 407
(15c)	70	105	230, 270

Preparation of 4,5-Ethylenedioxo-1,3-dithiole-2-one (25)

Tetrabutylammonium N,N'-dimethyldithiocarbamate instead of sodium-analog[34] was used for the preparation of (24)[21]. To a concentrated aqueous solution of sodium N,N'-dimethyldithiocarbamate[34] obtained from 9.5g (0.21 mol) of dimethylamine, a solution of Bu_4NBr (68g) in water 40 ml was added and the precipitate was filtered, washed with a small amount of cold water and air dried to give 50 g (66 %) of (19) (X=S); mp=125-127°C; UV(CH_3CN):372 nm. To a solution of (19) (15g) in acetonitrile (20ml) the appropriate amount of dichlorodioxane (20)[35] was added and the mixture was heated at reflux temperature for 1 hour. The mixture was cooled at -15°C and the precipitate was filtered, washed with a small amount of cold methanol (5ml) and then with water and air-dried to give 3.5 g (53 %) of (21) (X=S). This is a yellowish solid; mp=165-166 °C; UV(CH_3CN): 330nm; IR(KBr): 1500cm^{-1}(broad). A solution of (21) (3.5 g) in dimethylsulfoxide (20ml) was heated at 110 °C for 1 hour. The mixture was poured into water, extracted with dichloromethane and the organic extract was dried over $MgSO_4$. After evaporation of the solvent, 2.0 g (91%) of (21') (X=S) were obtained. This is a white solid; mp=171 °C; UV(CH_2Cl_2): 244(sh), 279 nm. To a solution of (21') (2.0 g) in CH_2Cl_2 (10ml) a solution of bromine (1ml) in CH_2Cl_2 (10ml) was added drop-wise into 15 min with stirring at 0 °C under dry atmosphere. The stirring was continued for 30 min at room temperature and the solvent was evaporated to drynees to give 3.2 g(88%) of (22) (X=S). This is a white solid; mp=105°C; UV(CH_3CN): 202, 218, 240 nm. It was pyrolised[36] at 110°C under reduced pressure (25 Torr) to give (23) (X=S) as a brown solid; UV(CH_2Cl_2): 270, 360 nm. To a solution of (23) in methanol (25 ml) hydrogen selenide carried in a stream of argon to give 1.8 g of (24) (43%, based on (21)); red needles of mp=151-155 °C; UV-visible (CH_3CN): 217, 242, 287, 455 (s) nm. To a solution of (24) (1g) in CH_2Cl_2 (200 ml) and CH_3COOH (250 ml) 2g of mercuric acetate was added and the mixture was stirred for 20 min at room temperature. It was filtered and the filtrate was washed with water. The organic fraction was dried over $MgSO_4$, and the solvent evaporated to give 0.6 g (81%) of (25) (X=S); mp=85-87 °C; UV(CH_3CN): 310 nm. Selenium analogs (24), (25) (X=Se) were not prepared yet by this method.[22]

Preparation of Tetraheterafulvalenes (30)- (32), (35), (39)

Ethylenediselenodithiadiselenafulvalene (EDSDTDSF) (35:X_1=X_2=Se, X_3=S; 2R=CH_2CH_2), ethylenedioxotetrathiafulvalene (EDOTTF) (35: X_1=O, X_2=X_3=S; 2R=CH_2CH_2) and ethylenedioxodiselenadithiafulvalene (EDODSDTF) (35: X_1=O, X_2=S, X_3=Se; 2R=CH_2CH_2) were prepared by adaptation of the method reported for the preparation of methylene dithiotetrathiafulvalene (MDTTTF) (35:X_1=X_2=X_3=S; 2R=CH_2) and similar compounds,[1,10,24,37] according to Scheme 9. Pyrazinoethylenedioxotetrathiafulvalene (PEDOTTF) (32: X_1=O, X_2=X_3=S;

$2R=CH_2CH_2$, $R'=H$), dimethylpyrazinoethylenedithiotetrathiafulvalene (DMPEDOTTF) ($32{:}X_1=O, X_2=X_3=S$; $2R=CH_2CH_2$, $R'=CH_3$), and pyrazinoethylenedioxodiselenadithiafulvalene (PEDODSDTF) ($32{:}X_1=O$, $X_2=S$, $X_3=Se$; $2R=CH_2CH_2$, $R'=H$) were prepared by adaptation of the method reported for the preparation of pyrazinoethylenedithiotetrathiafulvalene (PEDTTTF) ($32{:}X_1=X_2=X_3=S$, $2R=CH_2CH_2$, $R'=H$) and similar compounds[1,23,2438,39] according to Scheme 8. That is cross-coupling of the corresponding 1,3-dichalcogeno-2-ones followed by chromatography separation (silica, dichloromethane). Same method was applied for the preparation of ethylenedioxoethylenedithiotetrathiafulvalene (EDOEDTTTF) ($30{:}2R=CH_2CH_2$) and ethylenedioxoethylenediselenotetrathiafulvalene ($31{:}2R=CH_2CH_2$) (Scheme 7) except that benzene-cyclohexane was used instead of dichloromethane. Isothiazoloethylenedioxotetrathiafulvalene (ITAEDOTTF) ($39{:}X=O$) was prepared by adaptation of the method reported for the preparation of isothiazoloethylenedithiotetrafulvalene (ITAEDTTTF) ($39{:}\ X=S$) and similar compounds[25,40] according to Scheme 10. However, it was not obtained yet in a pure form. Preparative data of these new tetraheterafulvalenes are listed in Table III. It was found that half-wave oxidation potential values of (1)-(8) are close to those of BEDTTTF.

TABLE III. Preparative data of some new tetraheterafulvalenes

Compound	Yield(%)	mp(°C)	UV-visible(λ/nm) in CH_3CN
EDSDTDSF(1)	20	210	240(sh), 297-320(sh),360(sh), 486(w)
EDOTTF (2)	2.5	92	246(w), 296(sh)-308, 483(w)
EDODSDTF(3)	<1	>90	248(w), 302, 492(w)
PEDOTTF (4)	6	209	240(sh), 294(sh)-311, 430
DMPEDOTTF(5)	4	>280	218(sh), 238(sh), 290(sh)-311,402
PEDODSDTF(6)	5.5	210	218, 244(sh), 298-314(sh), 410
EDOEDTTTF(7)	14	192	220(sh), 310(sh), 324, 445(sh),490(w,br)
EDOEDSTTF(8)	4.5	187	230(sh), 310(sh), 324, 442(sh),486(w,br)

Preparation of Conducting Salts

Using the compounds of Table I (M=Ni, Pd,Pt) and the compounds (30)-(32), (35), (39) a number of cation deficient metal 1,2-diheterolenes as well as a number of charge transfer complexes and cation radical salts were prepared by chemical (CH) or electrochemical (EL) procedures[1,4,10-12,17,20,22-28, 37-47]. Some of the recently prepared salts are listed in Table IV.

TABLE IV. Some of the recently prepared salts.

Salt	Method	Appearence	Salt	Method	Appearence
$(\underline{1})_x$TCNQ	CH	black μ-crystals	$(\underline{5})_xI_3$	CH	golden bronze needles
$(\underline{1})_xI_3$	CH	golden needles	$(\underline{6})_x$TCNQ	CH	black needles
$(\underline{1})_xI_3$	EL	black needles,plates	$(\underline{6})_xIBr_2$	CH	black plates
$(\underline{1})_xIBr_2$	CH	black needles	$(\underline{6})_xAg(CN)_2$	EL	black μ-crystals
$(\underline{1})_xAuI_2$	EL	black μ-crystals	$(\underline{6})_xAuI_2$	EL	black μ-crystals
$(\underline{2})_x$TCNQ	CH	black needles	$(\underline{6})_1BF_4$	EL	black plates
$(\underline{2})_xI_3$	CH	black needles	$(\underline{7})$TCNQ	CH	black plates
$(\underline{3})_x$TCNQ	CH	black plates	$(\underline{7})_xI_3$	CH	dark bronze needles
$(\underline{4})_x$TCNQ	CH	black plates	$(\underline{7})_xIBr_2$	CH	black needles
$(\underline{4})_xI_3$	CH	dark bronze plates	$(\underline{8})_x$TCNQ	CH	black needles
$(\underline{4})_xBF_4$	EL	black μ-crystals	$(\underline{8})_xI_3$	CH	gray μ-crystals
$(\underline{5})_x$TCNQ	CH	black needles	$(\underline{8})_xIBr_2$	CH	gray plates

RESULTS AND DISCUSSION

Starting from vinylene trithiocarbonate, dichlorodioxane, dichloropyrazine and similar compounds a number of metal 1,2-diheterolenes (I)-(X) and polyheterotetraheterafulvalenes (32),(35),(39), precursors of conducting salts, were prepared by procedures of Schemes 1-10. Salts based on these compounds were found to be in several varying chemical compositions[1,11,12,17,20,23-29,37-47], crystal structures[48-50], and physical properties.[1,4,40-47] X-ray crystal structure solutions showed strong intermolecular interactions due to S---S, S---N, Se---Se, etc contacts, forming sometimes 2-dimensional networks. $(MDTTTF)_2AuI_2$ is a superconductor (Tc=5K), while $(EDTTTF)_2IBr_2$, $(EDTDSDTF)_2IBr_2$, $(EDTTTF)_2AuI_2$, $(EDTTTF)_2AuBr_2$, $(EDTTTF)_2Ag(CN)_2$, $(EDTTF)_2SbF_6$, $(VDTTTF)_2IBr_2$, $(MDSTTF)_2AuI_2$, $(Me_4N)_xPd(dmit)_2$, $(BMDTTTF)_xNi(dcit)_2$, $(PEDTTTF)_3I_3$, etc remain metallic down to low temperatures.

Recently[50], it was found that there are also strong S---O (3.02Å), Se---S (3.6 Å) contacts in some salts (Table IV) based on oxygen-containing tetraheterafulvalens. It is expected that these salts will be good conductors. Details on the crystal structure and physical properties of these new materials will be published in a future paper.

ACKNOWLEDGMENTS

We thank Dr.C.W.Mayer and J.S.Zambounis for recording mass spectra and electrochemical measurements and Dr.A.Terzis for communicating us crystallographic data before the publication.

REFERENCES

1. G.C.Papavassiliou in Proc.NATO-ASI on Lower Dim.Systems and Mol.Electronics, Spetses Island, Greece, June 1989, edited by R.M.Metzger (Plenum 1990) in press.
2. D.O.Cowan, Proc. 4th Int.Conf. on New Aspects of Org.Chem., Kyoto, Nov. 1988, edited by Z.Yoshida, T.Shiba, Y.Oshiro (Kobansha Ltd, Tokyo and Verlaysgesllschaft, FRG) 1989.
3. J.M.Williams, H.H.Wang, A.M.Kini, M.A.Beno, UrsGeiser, A.J.Schultz, K.Douglas Carlson, J.R.Ferraro, and M.-H.Whangbo, in Proc.of NATO-ASI on Lower Dim.Systems and Molecular Electronics, Spetses Island, Greece, June 1989, edited by R.M.Metzger (Plenum, 1990), in press; G.Saito, ibid.; P.Delhaes, ibid. ; D.Schweitzer; ibid., K.Kikuchi, ibid.; refs. 1-12 cited in ref.1 herein.
4. G.C.Papavassiliou, Proc.1st Int.Symp.Organic Superconductors, Tokyo, August 1989, edited by G.Saito, Springer (1990), in press.
5. M.Narita and C.H.Pittmann, Synthesis, 489 (1976) or commercial available.
6. H.Poleschner, Z.Chem., 26, 138 (1986).
7. M.V.Lakshikantham and M.P.Cava, J.Org.Chem. 45, 2632 (1980).
8. A.Mayer and B.Gebhardt, Chem.Ber. 47, 1298 (1964); W.Schroth and J.Peschel, Chimia, 18 , 171(1964) and refs. therein.
9. H.Poleschner and E.Faghanel, J.Prakt.Chem., 324, 691(1982); H.Poleschner, R.Radeglia, and H.Mayer, Org.Magn.Res., 22, 480(1984).
10. G.C.Papavassiliou, V.C.Kakoussis, G.A.Mousdis, and J.S.Zambounis, Chem.Scripta, in press (1989) and unpublished work.
11. G.C.Papavassiliou, J.S.Zambounis and S.Y.Yiannopoulos, Chem.Scripta, 27, 261(1987).
12. G.C.Papavassiliou, Z.Naturforsch., 36b, 1200(1981) and refs. 62-65 cited in ref.1 herein.
13. R.-M.Olk, W.Dietzsch, R.Kirmse, J.Stach, E.Hoyer and L.Golio, Inorg.Chim.Acta, 128, 251(1987) and refs.therein.
14. R.M.Olk, W.dietzsch, J.Mattusch, J.Stach, C.Nieke, E.Hoyer, W.Meiler, and W.Robien, Z.anorg.allg.Chem., 544, 199 (1987).
15. H.Poleschner, W.Hohn, G.Kampe and E.Hoyer, Z.Chem., 18, 345(1978)and refs.therein; R.-M. Olk, W.Dietzsch, K.Kohler, R.Kirmse, J.Reinhold and H.Hoyer, Z.anorg.allg.Chem., 567, 131 (1988).
16. See for example ref.10, 11 herein.
17. G.C.Papavassiliou, J.S.Zambounis, and S.Y.Yiannopoulos, Physica, 143b, 307(1986).
18. C.T.Vance, R.D.Beremann, J.Bordmer, W.E.Haffield and J.H.Helms, Inorg.Chem. 24, 2905 (1985); J.H.Welch, R.D.Bermann, and D.Sinch, Inorg.Chim.Acta, 163, 93(1989) and refs.therein.
19. T.Nakamura, T.Nogami, and Y.Shirota, Bull.Chem.Soc.Jpn., 60, 3447(1987).
20. G.C.Papavassiliou, J.Physique, 63 1257 (1983) and unpublished work.
21. T.Suzuki, H.Yamochi, G.Srdanov, K.Hinkelmann and F.Wudl, J.Am.Chem.Soc., 111, 3108 (1989) and unpublished work.
22. A.Rosenbaum, H.Kibchberg and E.Leibnitz, J.Prakt.Chem. 19, 1(1963); Moradpour, V.Peurussan, I.Johansen, and K.Bechgaard, J.Org.Chem. 48, 388(1983). G.C.Papavassiliou, D.J.Lagouvardos, V.C.Kakoussis and G.A.Mousdis, work in progress: $Bu_4NSeC(=Se)NMe_2$ (mp=109^{o}C); (21) (X=Se, mp=209^{o}C); (21') (X=Se, mp=226^{o}C).
23. G.C.Papavassiliou, V.Gionis, S.Y.Yiannopoulos, J.S.Zambounis, G.A.Mousdis, K.Kobayashi and K.Umemoto, Mol.Cryst.Liq.Cryst., 156, 277(1988) and refs. 61-65 cited therein.
24. G.C.Papavassiliou, Pure Appl.Chem., in press; G.C.Papavassiliou, G.A.Mousdis,

S.Y.Yiannopoulos, V.C.Kakoussis, and J.S.Zambounis, Synth.Metals, 27 B373(1988).

25. G.C.Papavassiliou, G.A.Mousdis, J.S.Zambounis, and S.Y.Yiannopoulos in Org.Inorg.Low Dim.Cryst.Materials Ed. P.Delhaes and M.Drilon, Plenum, 168, 301 (1987) and refs.therein.
26. P.J.Nigrey, Synth.Metals 27, B365 (1988) and refs. therein.
27. G.C.Papavassiliou, A.M.Cotsilios, and C.S.Jacobsen, J.Mol.Structure, 115, 41(1984).
28. G.C.Papavassiliou and G.A.Mousdis unpublished work.
29. R.Vicente, J.Ribas, C.Faulmann, J.-P.Legros, and P.Cassoux, C.R.Acad.Sci.Paris, II, 305 1055 (1987).
30. J.D.Wallis, A.Kerrer, and J.D.Dunitz, Helv.Chim.Acta, 69, 69(1986).
31. K.S.Varma and A.E.Underhill, Physica 143 B, 321(1986).
32. G.A.Mousdis, V.C.Kakoussis, and G.C.Papavassiliou in Proc.NATO-ASI on Lower Dim.Systems and Mol.Electronics, Spetses Island, Greece, June 1989 edited by R.M.Metzger (Plenum, 1990) in press.
33. V.Y.Lee, E.M.Engler, R.R.Schumaker and S.S.P.Parkin, J.Chem.Soc.Chem.Commun. 236(1983).
34. A.M.Clifford and J.G.Lichty, J.Am.Chem.Soc., 54, 1163(1932) or commercial available .
35. R.K.Summerbell and H.E.Lunk, J.Am.Chem.Soc., 79, 4802(1957).
36. K.Hiratani, H.Shiono, and M.Okawara, Chem.Lett., 867(1973).
37. G.C.Papavassiliou, J.S.Zambounis, G.A.Mousdis, V.Gionis and S.Y.Yiannopoulos, Mol.Cryst.Liq.Cryst. 156, 269 (1988).
38. G.C.Papavassiliou, S.Y.Yiannopoulos, J.S.Zambounis, K.Kobayashi, and K.Umemoto, Chem.Lett. 1279 (1987).
39. G.C.Papavassiliou, S.Y.Yiannopoulos, J.S.Zambounis, Chem.Scripta 27, 265(1987); Physica, 143B, 310 (1986); J.Chem.Soc.Chem.Commun. 820(1986).
40. G.C.Papavassiliou, G.A.Mousdis, V.Gionis, J.S.Zambounis and S.Y.Yiannopoulos, Z.Naturforsch, 42b, 1050 (1987).
41. A.Terzis, A.Hountas, A.E.Underhill, A.Clark, B.Kaye, B.Hilti, C.Mayer, J.Pfeiffer, S.Y.Yiannopoulos, G.Mousdis, and G.C.Papavassiliou, Synth.Metals 27, B97 (1988).
42. 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).
43. K.Kikuchi, H.Kamio, K.Saito, S.Y.Yiannopoulos, G.C.Papavassiliou, K.Kobayashi and I.Ikemoto, Bull.Chem.Soc.Jpn. 61, 741 (1988).
44. G.C.Papavassiliou, A.E.Underhill, B.Kaye and H.P.Geserich, Material Science, 13, 185(1987).
45. G.C.Papavassiliou, A.Terzis, A.E.Underhill, H.P.Geserich, B.Kaye, A.Hountas and S.Y.Yiannopoulos Synth.Metals, 19 703(1987).
46. G.C.Papavassiliou, J.S.Zambounis, A.E.Underhill, B.Kaye and H.P.Geserich, Mol.Cryst.Liq.Cryst. 134, 53(1986).
47. G.C.Papavassiliou, Z.Naturforsch. 37b, 825(1982); Mol.Cryst.Liq.Cryst. 86, 159 (1982).
48. A.Hountas, A.Terzis, G.C.Papavassiliou, B.Hilti, M.Burkle, C.W.Mayer, J.S.Zambounis, Acta Cryst., in press; A.Terzis, A.Hountas, G.C.Papavassiliou, B.Hilti, and J.Pfeiffer, ibid.; A.Hountas, A.Terzis, G.C.Papavassiliou, B.Hilti, and J.Pfeiffer, ibid; A.Terzis, A.Hountas, and G.C.Papavassiliou, Sol.St.Commun., 66, 1161(1988).
49. A.Terzis, G.C.Papavassiliou, H.Kobayashi, and A.Kobayashi, Acta Cryst. C45, 683(1989); A.Terzis, V.Psycharis, A.Hountas and G.C.Papavassiliou, ibid, 44, 128(1988); V.Psycharis, A.Hountas, A.Terzis and G.C.Papavassiliou, ibid, 44, 125 (1988).
50. A.Terzis, A.Hountas, G.C.Papavassiliou, unpublished work.