Conducting and Superconducting Salts Based on MDTTTF, EDTTTF, VDTTTF, EDTDSDTF, MDSTTF, BMDTTTF, $Pd(dmit)_2$, and $Ni(dcit)_2$

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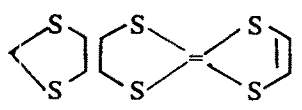
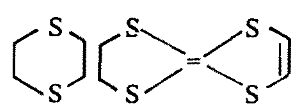
Abstract. Conducting and superconducting salts based on methylenedithiotetrathiafulvalene (MDTTTF), ethylenedithiotetrathiafulvalene (EDTTTF), vinylenedithiotetrathiafulvalene (VDTTTF), ethylenedithiodiselenadithiafulvalene(EDTDSDTF), methylenediselenotetrathiafulvalene(MDSTTF), bis(methylenedithio)tetrathiafulvalene(BMDTTTF), bis(4,5-dimercapto-1,3-dithiole-2- thione) palladate(Pd[dmit]$_2$), and bis(3,4-dimercapto-5-cyanoisothiazole) nickelate (Ni[dcit]$_2$) have been prepared and studied.

Introduction

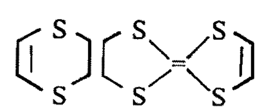
Recently, a number of conducting and superconducting salts based on unsymmetrical donor molecules as well as on metal 1,2-dithiolenes have been prepared and studied (see [1-12], and refs.therein). In this paper the preparations, crystal structures and physical properties of some salts based on the compounds (1)-(8) (: π-donors or π-acceptors) are described



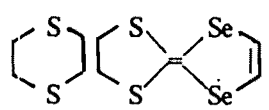
(1): (MDTTTF)



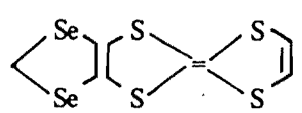
(2): (EDTTTF)



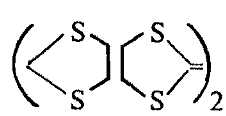
(3): (VDTTTF)



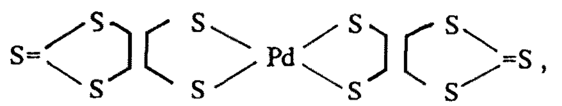
(4):(EDTDSDTF)



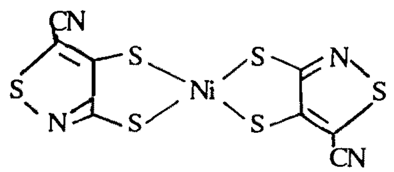
(5):(MDSTTF)



(6):(BMDTTF)



(7): $Pd(dmit)_2$



(8): $Ni(dcit)_2$

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Experimental

Compounds (1)-(5) have been prepared from the corresponding 2-oxo-1,3-dithioles or selenium analogs and 4,5-bis(methylcarboxy)-1,3-dithiole-2-thione or selenium analog by a two-step sequence:coupling via triethylphosphite and demethoxycarboxylation with LiBr in hexamethylphosphoramide[1,2,6]. Compound (6) has been prepared by coupling of 4,5-methylenedithio-1,3-dithiole-2-one via triethyl phosphite [6]. The half-wave oxidation potentials ($E^1_{1/2}, E^2_{1/2}$) [13] of (1), (2),(5), (6) have values 535, 915; 545, 970; 490, 870; 595, 880 mV, respectively. These values are intermediate between those of TTF(470, 940 mV) and BEDTTTF (600, 980 MV) [13].Similar results are expected for the compounds (3), (4), etc. [4], [6]. $(Me_4N)_2Pd(dmit)_2$ and $(Bu_4N)_2Ni(dcit)_2$ have been prepared from the corresponding disodium salts of the ligands (dmit, dcit) after treatment with $Pd(NH_3)_4(NO_3)_2$ and $NiCl_2$ in presence of Me_4NBr and Bu_4NBr, respectively. From the compounds (1)-(8) a number of conducting salts have been prepared mainly by electrooxidation methods.$(Me_4N)_xPd(dmit)_2$ has been prepared by oxidation of aceton solutions of $(Me_4N)_2Pd(dmit)_2$ as follows:

$$(Me_4N)_2Pd(dmit)_2 \xrightarrow{I} (Me_4N)_1Pd(dmit)_2 \xrightarrow{air} (Me_4N)_xPd(dmit)_2 \text{ (needles)}$$

Results and Discussion

The results of conductivity measurements in a number of salts (1)-(12) are summarized in Fig.1 and Fig.2. (1): $(MDTTTF)_2AuI_2$ (orth., Pbmn [3,7]) is metallic (σ_{RT}=12-36 S/cm) and becomes a superconductor at low temperature (Tc=5K under 1bar, Tc=3K under 1.5 kbar) [3,8,14]. (2):$(EDTTTF)_2IBr_2$ (tricl., P$\bar{1}$ [7]) remains metallic down to 1.35 K σ_{RT}=150-550 S/cm) [3,12]. Same results have been obtained for (3): $(EDTDSDTF)_2IBr_2$ (tricl., P$\bar{1}$); (σ_{RT}=1050-1660 S/cm). (4):$(EDTTTF)_2AuI_2$ (orth. F222 [7]) is metallic (σ_{RT}=500 S/cm) down to low temperature MIT ≈ 200 K under 1 bar [5]; MIT ≈ 20 K under 4.8 kbar). (5): $(EDTTTF)_2AuBr_2$ (monoch., C 2/m [7]) is metallic (σ_{RT}=230-330

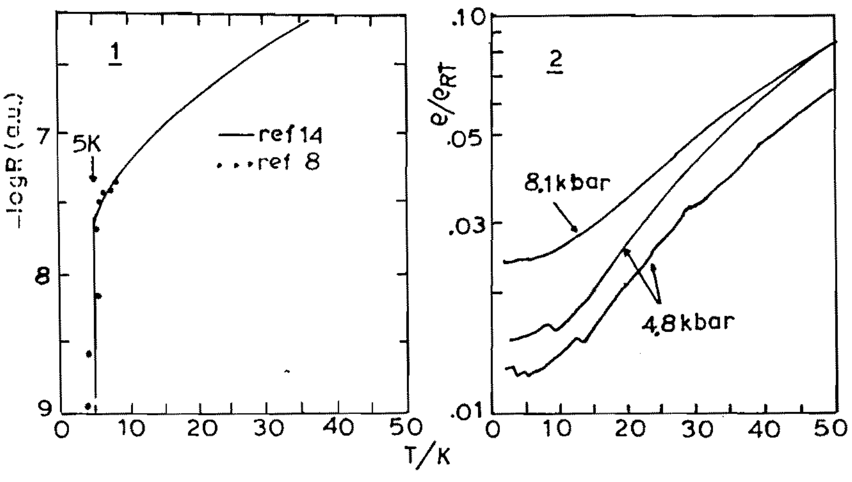

Fig.1. Temperature dependence of resistance and normalized resistivity of (1) and (2) respectively.

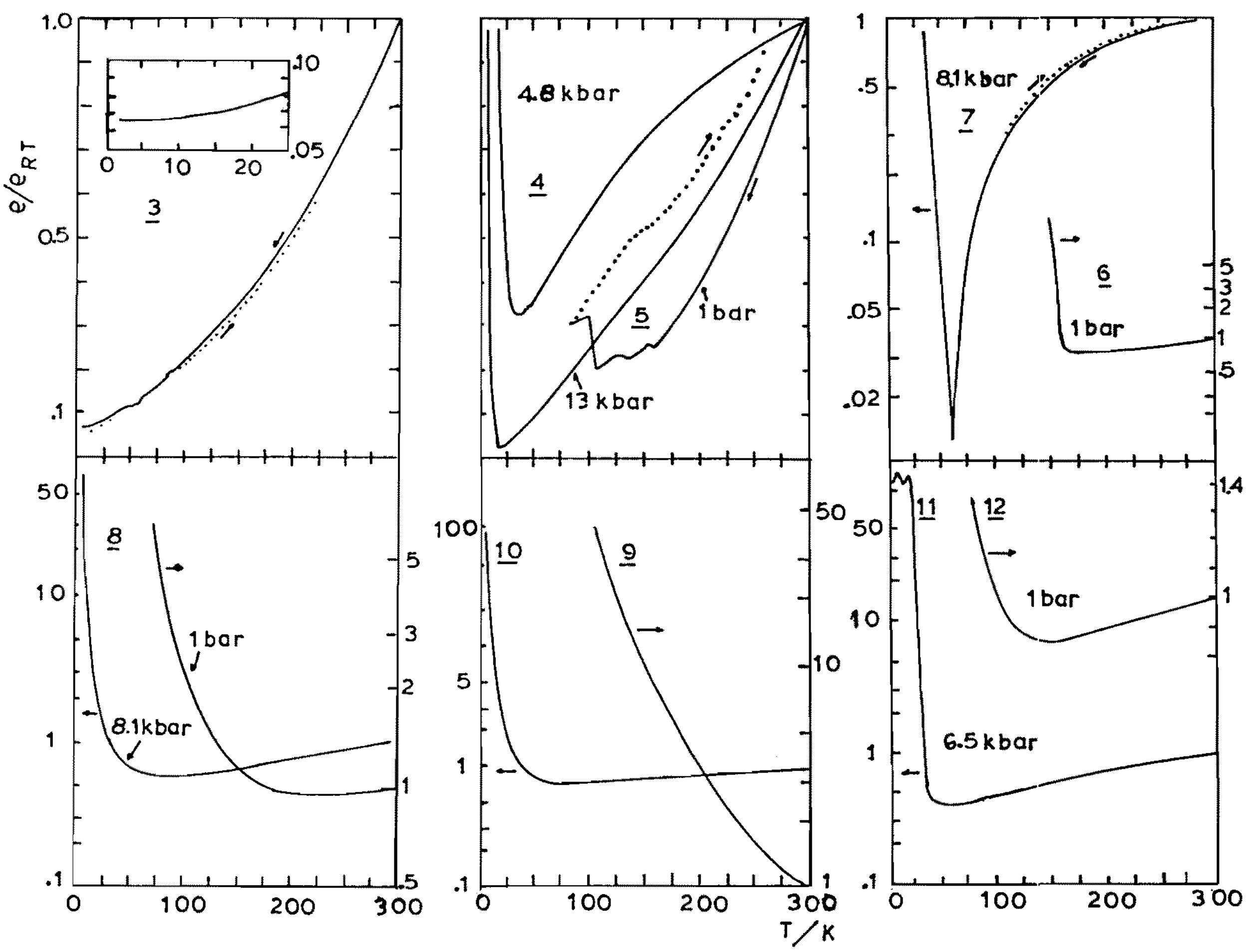

Fig.2. Temperature dependence of normalized resistivity of (3)-(12).

S/cm; MIT ≈ 140 K under 1 bar; MIT ≈ 15 K under 13 kbar) (see also [9]). (6): $(EDTTTF)_2Ag(CN)_2$ is metallic (σ_{RT}= 2-50 S/cm; MIT ≈ 150 K under 1bar). (7) : $(EDTTTF)_2SbF_6$ is metallic (σ_{RT}= 20-120 S/cm; MIT ≈ 200 K under 1 bar, MIT ≈ 70 K under 8.1 kbar). (8):$(VDTTTF)_2IBr_2$ is metallic (σ_{RT}=50-714 S/cm; MIT ≈ 200 K under 1 bar, MIT ≈ 50 K under 8.1 kbar). (9): $(MDTTTF)_2AuBr_2$ (triecl., $P\bar{1}$) is semiconducting (σ_{RT}=205S/cm). (10): $(MDSTTF)_2AuI_2$ is metallic (σ_{RT}=305 S/cm; MIT ≈ 50K under 1 bar). (11):$(Me_4N)_xPd(dmit)_2$ (needles) is metallic (σ_{RT}= 28 S/cm; MIT ≈ room temp. under 1bar, MIT ≈ 20 K under 6.5 kbar) (see also [15]). (12): $(BMDTTTF)_xNi(dcit)_2$ (plates) is metallic (σ_{RT}= 20-40 S/cm; MIT ≈ 120K under 1 bar).

The salts (2) and (3) are isostructural with the β-$(BEDTTTF)_2X$ superconductors [7,16] and have a residual conductivity $\sigma_{1.35}$>10000 S/cm. According to the treatment reported in [17] these crystals could be candidates for superconductivity at lower temperature. The temperature dependence of the resistivity of (4)-(8) and (10-(12) indicate that these salts could be superconductors under pressure-values higher than those reported above.

References

1. G.C.Papavassiliou,,in Proc. NATO-ASI on Lower-Dim. Systems and Mol.Electronics, Spetses Island, Greece, 12-23 June, 1989, Ed.R.M.Metzger, Plenum, in press.
2. G.C.Papavassiliou, Pure, Appl.Chem., in press.
3. 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).
4. G.C.Papavassiliou, G.A.Mousdis, S.Y.Yiannopoulos, V.C.Kakoussis and J.S.Zambounis, Synth.Metals 27, B373 (1988).
5. A.Terzis, A.Hountas, A.E.Underhill, A.Clark, B.Kaye, B.Hilti, C.Mayer, J.Pheiffer, S.Y.Yiannopoulos, G.Mousdis and G.C.Papavassiliou, Synth.Metals 27, B97 (1988).
6. G.C.Papavassiliou, V.C.Kakoussis, G.A.Mousdis and J.S.Zambounis, Chem.Scripta, in press (1989).
7. A.Hountas, A.Terzis, G.C.Papavassiliou, B.Hilti, M.Burkle, C.W.Mayer and J.S.Zambounis, Acta Cryst. in press (1989) and refs. [2,11] cited therein.
8. A.M.Kini, M.A.Beno, D.Son, H.H.Wang, K.D.Carlson, L.C.Porter, U.Welp, B.A.Vogt, J.M.Williams, D.Jung, M.Evain, M.-H.Whangbo, O.L.Overmyer, and J.E.Schirber, Sol.St.Commun. **69**, 503(1989).
9. T.Mori and H.Inochuchi, Sol.St.Commun. **70**, 823 (1989).
10. R.Kato, H.Kobajashi and A.Kobajashi, Chem.Lett. 781(1989), and in press.
11. H.Nakano, K.Miyawaki, Y.Shirota, S.Harada, and N.Kasai, Bull.Chem.Soc.Jpn 62, 2604 (1969); Y.Honda, K.Murata, K.Kikuchi, K.Saito, I.Ikemoto, and K.Kobayashi, Sol.St.Commun., in press.
12. See refs. [37-41, 49-51, 61-99] cited in ref.1 here.
13. Donor :$7x10^{-4}$, M, Bu_4NPF_6:0.025 M in benzonitril at 23^oC vs.SCE at a Pt-disc electrode (anode); scam rate 100 mV/s; see also H.Tatemitsu , J.Chem.Soc. Chem. Commun. 106 (1985).
14. M.Freund, J.L.Olsen, B.Hilti, C.W.Mayer and J.S.Zambounis, presented at EPS meeting, Nice, France March 1989; B.Hilti, A.Terzis, G.C .Papavassiliou to be published.
15. A.Kobayashi, H.Kim, Y.Sasaki, Synth.Metals 27, B339 (1988).
16. T.Ishiguro, Physica C 153-155, 1055(1988).
17. M.Tokamoto, H.Anzai, K.Murata, K.Kajimura and T.Ishiguro, Synth.Metals 27, A251 (1988).