ELSEVIER

Synthetic Metals 86 (1997) 1791-1793

SYNTHETIC METALS

New Electrically Conducting Materials Based on the dmit Ligand

A. E. Pullen[a], K. A. Abboud[a], J. R. Reynolds[a*], J. Piotraschke,[b] S. Zeltner[b], R. M. Olk[b], E. Hoyer[b], H. L. Liu[c] and D. B. Tanner[c]

[a]*Department of Chemistry, Center for Macromolecular Science and Engineering, University of Florida, Gainesville, Florida 32611, USA*

[b]*Institut für Anorganische Chemie, Universität Leipzig, Talstraße 35, D-04103 Leipzig, FRG*

[c]*Department of Physics, University of Florida, Gainesville, Florida 32611, USA*

Abstract

The synthesis, X-ray structure analysis and electrochemical characterization of a series of chalcogen-rich, extensively conjugated, and in some cases fully planar tetrathiooxalato bridged dmit-based bimetallic Cu(II) and Ni(II) complexes for molecular conducting materials are reported. Also reported is the synthesis and temperature-dependent electrical conductivity of the new dmit based anion radical salt complex $(CH_3(C_6H_5)_3P)$ $[Ni(dmit)_2]_3$.

Keywords: Electrocrystallization, conductivity, organic conductors, radical anion salt, X-ray diffraction

1. Introduction

Seven $[M(dmit)_2]$ (M = Ni or Pd; dmit = $C_3S_5^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolato) based complexes are known to superconduct, albeit at rather low temperatures [1-10]. The first of these, $TTF[Ni(dmit)_2]_2$, was reported in 1986; it contains the "open-shell" cation TTF and is superconducting at 1.62 K under 7 kbar pressure [1 - 3]. The latest superconducting $M(dmit)_2$-based complex contains the "open-shell" counterion EDT-TTF. The complex α-EDT-$TTF[Ni(dmit)_2]$ is the only $M(dmit)_2$-based complex to show such electrical behavior under ambient pressure (T_c = 1.3 K) [10].

The primary methods used in the search for higher Tc values in the $M(dmit)_2$ salts has been to either change the cation or the metal [11, 12]. Here, we report the electrocrystallization and electrical properties of a new $Ni(dmit)_2$-based salt. We have also designed new complexes combining the dmit-based and tto (tto = $C_2S_4^{2-}$ = tetrathiooxalato) ligands. To extend the delocalization and increase intermolecular interactions in the lattice to potentially improve the electrical properties, we have synthesized and fully characterized a series of bimetallic Cu(II)- and Ni(II)-dmit based complexes. The complexes with the general formula $(Bu_4N)_2\{tto[M(L)]_2\}$ (where M = Cu(II), L = dmit (**1**) [13], mnt (**2**), dsit (**3**), dmid (**4**) [14]; and where M = Ni(II), L = dmit (**5**), dsit (**6**), dmise (**7**)) are chalcogen-rich and extensively conjugated. Some of the complexes are also fully planar. Their synthesis, X-ray structures and electrochemical behavior will be discussed.

2. Results and Discussion

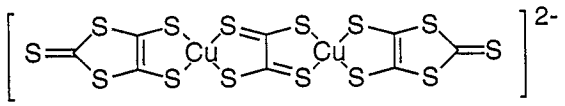
2.1 Synthesis, X-ray structure, electrochemical characterization and conductivity properties of tetrathiooxalate bridged bimetallic Cu(II) complexes

Complexes **1** - **4** (Fig. 1) were synthesized using a unique three-solvent, biphasic method. Reaction of a methanolic solution of $CuCl_2 \cdot 2H_2O$, an aqueous solution of $(Et_4N)_2$tto and a solution of the bis-chelate Zn(II) salt containing the capping ligand in methylene chloride forms the bimetallic Cu(II) complexes in 15 - 25% yield [13, 14].

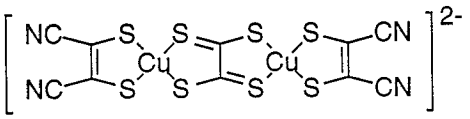
Complex **2** displays perfect planarity while **1**, **3** and **4** have dihedral angles formed between the tto bridging ligand and the capping ligands due to a tetrahedral distortion at the metal center in the range of 18.87(3)° for **1** to 28.3° for **4** [15]. Complexes **1** and **3** form one-dimensional chains from "head-to-tail" thioxo-thiole intermolecular non-bonding interactions.

Complexes **1** - **4** exhibit similar redox behavior with two separate reversible redox processes (reported vs. Ag/AgCl in 0.1 M Bu_4NClO_4/CH_2Cl_2). Each complex exhibits a first low-potential redox couple with $E_{1/2}$ values in the range of −0.79 to −0.63 V. Complex **2** oxidizes at the highest potential of −0.59 V as expected due to the highly electronegative terminal cyano groups. A second redox process is observed with $E_{1/2}$ values in the range of −0.15 V to 0.00 V. Complex **2** again oxidizes at the highest potential for the second redox process at +0.03 V.

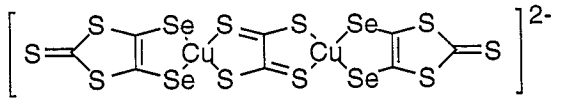
PII S0379-6779(96)04591-2



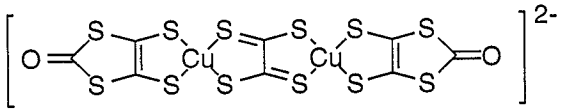
$\{tto[Cu(dmit)]_2\}^{2-}$ (**1**)



$\{tto[Cu(mnt)]_2\}^{2-}$ (**2**)



$\{tto[Cu(dsit)]_2\}^{2-}$ (**3**)



$\{tto[Cu(dmid)]_2\}^{2-}$ (**4**)

Fig. 1. Bimetallic Cu(II) complexes **1 - 4**

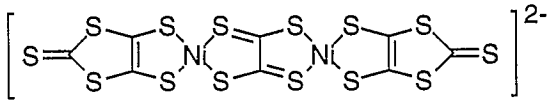
The reaction of **1** with varied amounts of NaI/I_2 in acetone yielded black powders with two-probe pressed-pellet conductivities up to 10^{-2} S/cm [13].

2.2 Synthesis, X-ray structure, electrochemical characterization and conductivity properties of tetrathiooxalate bridged bimetallic Ni(II) complexes

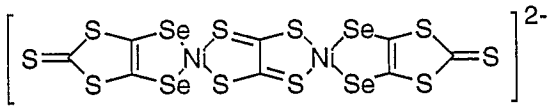
The reaction of tetrabutylammonium bromide, $(Et_4N)_2tto$, the capping ligand in its dianionic form and $NiCl_2{\cdot}6H_2O$ in acetone yields complexes **5 - 7** (Fig. 2) in 30 - 40% yield.

Complex **5** displays perfect planarity while **7** is nearly planar with angles of only 2.3° and 6.1° formed between the tto bridging ligand and the two dmise capping ligands. Complex **6** has angles of 20.5° between the tto and dsit ligands. The crystal packing of **5** and **7** shows extensive S···S interactions due to distances less than the sum of the van der Waals radii from thioxo-thioxo and thioxo-thiole groups in two-dimensional sheet-like arrays separated by tetrabutylammonium cations. The packing of complex **6** is similar to **1** and **3** where "head-to-tail" interactions of thiole and thioxo groups forms one-dimensional chains.

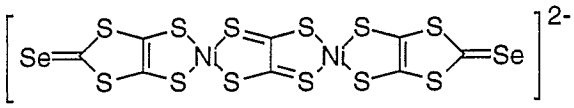
The redox behavior of complexes **5 - 7** is similar (reported vs. Ag/Ag^+ in 0.05 M Me_4NClO_4/CH_3CN). Each complex exhibits a first low-potential reversible redox couple with $E_{1/2}$ values for all complexes approximately at –0.82 V. A second non-reversible redox couple is observed at higher potentials with $E_{p,a}$ values in the range of –0.23 V to –0.15 V.



$\{tto[Ni(dmit)]_2\}^{2-}$ (**5**)



$\{tto[Ni(dsit)]_2\}^{2-}$ (**6**)



$\{tto[Ni(dmise)]_2\}^{2-}$ (**7**)

Fig. 2. Bimetallic Ni(II) complexes **5 - 7**

The reaction of **5** with (TTF)3(BF4)2 [16] in an acetonitrile/acetone mixture yielded a black insoluble precipitate which exhibited a two-probe pressed-pellet conductivity of 0.4 S/cm.

2.3 Synthesis, X-ray structure and conductivity properties of $(CH_3(C_6H_5)_3P)[Ni(dmit)_2]_3$

The non-integer oxidation state complex $(CH_3(C_6H_5)_3P)[Ni(dmit)_2]_3$ was obtained via constant current electrocrystallization. The complex $(Bu_4N)[Ni(dmit)_2]$ [17] was oxidized in the presence of an electrolyte containing the cation $CH_3(C_6H_5)_3P^+$ in an acetonitrile/acetone mixture in a two-compartment glass H-cell with Pt wire electrodes. Black chunk-like and platelet crystals were harvested.

X-ray structure analysis of the platelets shows extensive S···S interactions between $Ni(dmit)_2$ units in a two-dimensional array. The $Ni(dmit)_2$ units form dimers which interacts with six other surrounding dimers. The dimers form columns separated by columns of $CH_3(C_6H_5)_3P^+$ counterions.

The room-temperature four-probe conductivities of two single crystals of platelet form are 0.07 - 0.1 S/cm.

Temperature-dependent measurements show a semiconducting behavior with a thermal activation energy of 0.22 eV.

3. Conclusions

A series of bimetallic Cu(II) and Ni(II) chalcogen-rich dmit-based complexes have been synthesized. The extensive conjugation and planarity along with chalcogen atoms in the periphery of the complexes make them excellent precursors to highly electrically conducting materials. The compounds are currently being investigated with a variety of counterions in diffusion and electrocrystallization experiments. The complex $(CH_3(C_6H_5)_3P)[Ni(dmit)_2]_3$ has been electrocrystallized and displays semiconducting electrical properties.

4. Acknowledgments

This work was funded by grants from the Air Force Office of Scientific Research (F49620-96-1-0067 and F49620-93-1-0322), the IAESTE program at the University of Leipzig, Leipzig, Germany (ref #951405-R) and the National Science Foundation (DMR-9403894). KAA wishes to acknowledge the National Science Foundation for funding of the purchase of the X-ray equipment.

References

[1] M. Bousseau, L. Valade, J. P. Legros, P. Cassoux, M. Garbauskas and L. V. Interrante, *J. Am. Chem. Soc., 108* (1986) 1908.
[2] L. Brossard, M. Ribault, M. Bousseau, L. Valade and P. Cassoux, *C. R. Acad. Sci. (Paris), Série II, 302* (1986) 205.
[3] L. Brossard, M. Ribault, L. Valade and P. Cassoux, *Physica B & C (Amsterdam), 143* (1986) 378.
[4] A. Kobayashi, A. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita and W. Sasaki, *Chem. Lett.*, (1987) 1819.
[5] K. Kajita, Y. Nishio, S. Moriyama, R. Kato, H. Kobayashi and W. Sasaki, *Solid State Commun., 65* (1988) 361.
[6] L. Brossard, H. Hurdequint, M. Ribault, L. Valade, J. P. Legros and P. Cassoux, *Synth. Met., 27* (1988) B157.
[7] L. Brossard, M. Ribault, L. Valade and P. Cassoux, *J. Phys. (Paris), 50* (1989) 1521.
[8] A. Kobayashi, H. Kobayashi, A. Miyamoto, R. Kato, R. A. Clark and A. E. Underhill, *Chem. Lett.*, (1991) 2163.
[9] H. Kobayashi, K. Bun. T. Naito, R. Kato and A. Kobayashi, *Chem. Lett.*, (1992) 1909.
[10] H. Tajima, M. Inokuchi, A. Kobayashi, T. Ohta, R. Kato, H. Kobayashi and H. Kuroda, *Chem. Lett.*, (1993) 1235.
[11] P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark and A. E. Underhill, *Coord. Chem. Rev., 110* (1991) 115.
[12] P. Cassoux, L. Brossard, M. Takumoto, H. Kobayashi, A. Moradpour, D. Zhu, M. Mizuno and E. Yagubskii, *Synth. Met., 71* (1995) 1845.
[13] J. Piotraschke, A. E. Pullen, K. A. Abboud and J. R. Reynolds, *Inorg. Chem., 34* (1995) 4011.
[14] A. E. Pullen, S. Zeltner, R. M. Olk, E. Hoyer, K. A. Abboud and J. R. Reynolds, *Inorg. Chem., 35* (1996) 4420.
[15] R. Vicente, J. Ribas, S. Alvarez, A. Segui, X. Solans and M. Verdaguer, *Inorg. Chem., 26* (1987) 4004.
[16] F. Wudl, *J. Am. Chem. Soc., 97* (1975) 1962.
[17] T. K. Hansen, J. Becher, T. Jorgensen, K. S. Varma, R. Khedekar and M. P. Cava, *Org. Synth., 73* (1995) 270.