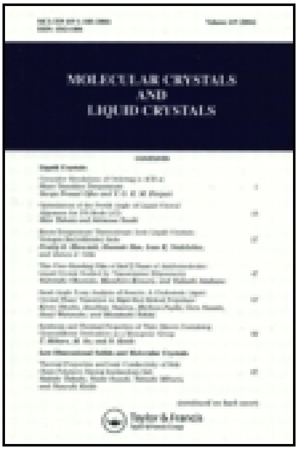


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

New Π-Donor-Acceptor Compounds Derived From a Macrocyclic Metal Complex

P. Cassoux [a] , L. Interrante [b] [a] & J. Kasper [b] [a]
[a] Laboratoire de Chimie de Coordination, C.N.R.S., 205, Route de Narbonne, 31400, Toulouse, France
[b] General Electric CR&D, Schenectady, NY, 12301, U.S.A.

Version of record first published: 14 Oct 2011.

To cite this article: P. Cassoux , L. Interrante & J. Kasper (1982): New Π-Donor-Acceptor Compounds Derived From a Macrocyclic Metal Complex, Molecular Crystals and Liquid Crystals, 81:1, 293-300

To link to this article: http://dx.doi.org/10.1080/00268948208072576

Mol. Cryst. Liq. Cryst., 1982, Vol. 81, pp. 293-300
0026-8941/82/8101-0293$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

NEW π-DONOR-ACCEPTOR COMPOUNDS DERIVED FROM A MACROCYCLIC METAL COMPLEX

P. CASSOUX
Laboratoire de Chimie de Coordination, C.N.R.S.,
205, Route de Narbonne, 31400 Toulouse, France

L. INTERRANTE and J. KASPER
General Electric CR&D, Schenectady, NY 12301, U.S.A.

Received for publication August 17, 1981

The planar, macrocyclic metal complex nickel-1,4,8,11-tetraaza-5,7,12,14-tetramethyl(14)annulene [Ni(TATMA)] has been used as a π-donor to form new π-D·A compounds of the type $[Ni(TATMA)]_2A$ where A=TCNQ and $NiS_4C_4H_4$. Magnetic susceptibility and conductivity measurements have been obtained for both compounds and the structure of the $NiS_4C_4H_4$ derivative has been elucidated by x-ray diffraction methods. Both compounds are semiconductors with $\sigma_{25°}=10^{-4}\rightarrow 10^{-3}\Omega^{-1}cm^{-1}$ and E_a=0.1→0.25eV). The $NiS_4C_4H_4$ derivative contains 1-D stacks of the π-donor which consist of metal-metal bonded $[Ni(TATMA)^+]_2$ dimers separated by uncharged Ni(TATMA) units. The $NiS_4C_4H_4^-$ ions are unstacked and presumably are responsible for the observed Curie-like spin susceptibility. Magnetic susceptibility measurements on the $[Ni(TATMA)]_2$ TCNQ compound show no net spin susceptibility indicating either no net charge transfer in this case or an intermolecular association in the solid state involving <u>both</u> the $Ni(TATMA)^+$ and $TCNQ^-$ units.

INTRODUCTION

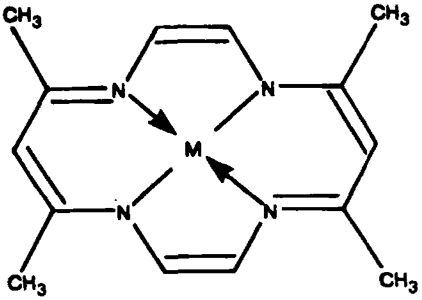
π-donor acceptor compounds (π-D·A) have aroused strong current scientific interest, mainly because of their high conductivity.[1,2] However, other than TTF, TCNQ and their close relatives there are only few π-donor or acceptor systems which seem to meet the required criteria for the formation of these stacked 1-D systems.

Two kinds of criteria may be used to evaluate prospective candidate molecular systems for use in preparing conductive π-D A compounds:

1. - Structural: Overall planar geometry; molecular structure conducive to close 1-D stacking with good π-orbital overlap; relative sizes of donor and acceptor molecules; etc.

2. - Electronic: Extended π-electron systems with π-orbitals of the appropriate symmetry and spatial extent; facile oxidation (for the donor) or reduction (for the acceptor); approximate matching of redox potentials of D and A to provide partial charge transfer and non-integral oxydation states; etc.

We have been exploring[3,4] the use of metal complex systems as a potential source of π-donors or acceptors which meet these criteria. Among the prospective systems selected as possible π-donors are the metal-1,4,8,11-tetraaza-5,7,12,14-tetramethyl (14)annulenes, M(TATMA):



M = Ni, Cu, Pd,...

Figure 1. M(TATMA)

They can be reversibly oxidized[5] from the 16-electron neutral species and the half-wave potential for the first oxidation of the nickel complex (0.11 V vs. SCE) is very close to the half-wave potential for the reduction of both the nickel ethylene bisdithiolene $NiS_4C_4H_4$ (0.09V) and TCNQ (0.13V),

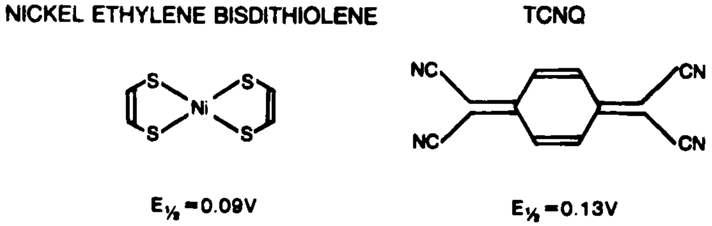


Figure 2. Nickel ethylene bisdithiolene and TCNQ

suggesting that the neutral [Ni(TATMA)] may be an effective π-donor toward both these acceptor species.

EXPERIMENTAL

Ni(TATMA) and [Ni(TATMA)]BF_4 were prepared following a multistep procedure as indicated in Ref. 5.

Reaction under inert atmosphere of hot (60°C) saturated acetonitrile solutions of Ni(TATMA) and A (A = TCNQ or $NiS_4C_4H_4$), yield on cooling, sparingly soluble, black, microcristalline powders. In both cases a compound of stoichiometry $[Ni(TATMA)]_2A$, as determined by elemental analysis, was obtained. The compound with A = $NiS_4C_4H_4$ is of particular interest as apparently the first π-D•A compound which contains metal complexes as both the π-donor and π-acceptor.

Single crystals of both compounds suitable for conductivity measurements and x-ray diffraction studies were obtained by solution diffusion techniques, starting with either neutral components, or, by metathesis, with appropriate salts (i.e., [Ni(TATMA)]BF_4 and Li TCNQ or $NEt_4(NiS_4C_4H_4)$. Four probe conductivity measurements along the neede axis were carried out:

Both compounds are semi-conductors ($\sigma_{300K} = 1.4\ 10^{-3}\Omega^{-1}cm^{-1}$; $Ea = 0.1\ eV$ for $[Ni(TATMA)]_2TCNQ$ and $\sigma_{300K} = 6.10^{-5}\Omega^{-1}cm^{-1}$; $Ea = 0.23\ eV$ for $[Ni(TATMA)]_2NiS_4C_4H_4$).

Magnetic sysceptibility measurements were performed: $[Ni(TATMA)]_2$ TCNQ exhibits no net spin susceptibility; $[NiTATMA)]_2$ $NiS_4C_4H_4$ is paramagnetic with a Curie Law constant appropriate for one electron per formula unit.

The structure was determined from automatic diffractometer data for 1169 reflections with $\sigma > 3.0$. The solution of the structure was made from interpretation of Patterson syntheses. Least squares refinement with anisotropic thermal patterns gives $R = 0.05$ but with large standard deviations for many of the atoms (0.001 to 0.002 in atom coordinates). One of the Ni(TATMA) molecules is disordered and the precise nature of the disorder is still under investigation.

DISCUSSION

Since the $Ni(TATMA)^+$ and $NiS_4C_4H_4^-$, species should each carry a single unpaired electron, the observation of just a single unpaired spin in the case of the $[Ni(TATMA)]_2NiS_4C_4H_4$ compound suggests the existence of magnetically coupled dimers or extended magnetic interactions in the solid state. It should be noted that the $Ni(TATMA)^+$ ion has been observed by Holm and coworkers[6] to occur in the form of a spin-paired cationic dimer.

The 3-D structure determination of the $[Ni(TATMA)]_2$ $NiS_4C_4H_4$ provides quite satisfactory interpretation of the unusual magnetic properties of this compound. The arrangement of the molecules shows 1-D chains of Ni(TATMA) units stacked along the z axis and comprised of $[Ni(TATMA)^+]_2$ dimers separated by uncharged Ni(TATMA) molecules.

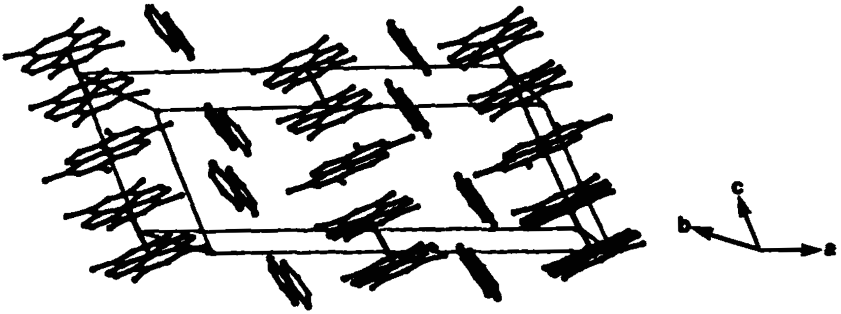


Figure 3. (a) Unit cell of Ni(TATMA) $_2NiS_4C_4H_4$ showing the stacked arrangement of alternating Ni(TATMA) dimers and monomers and also the non-stacked distribution of $NiS_4C_4H_4$ molecules. The molecule sandwiched by the dimers is actually disordered with respect to rotation around 001 . Only one orientation is shown here.

The $NiS_4C_4H_4^-$ species are unstacked and lie in 2-D sheets parallel to the (100) face. The remaining neutral Ni(TATMA) units are found alongside the $[Ni(TATMA)]^{0,1+}$ chains with their molecular plane oriented perpendicular to the y axis, i.e. to both the other $[Ni(TATMA)]^{0,1+}$ and $NiS_4C_4H_4^-$ units.

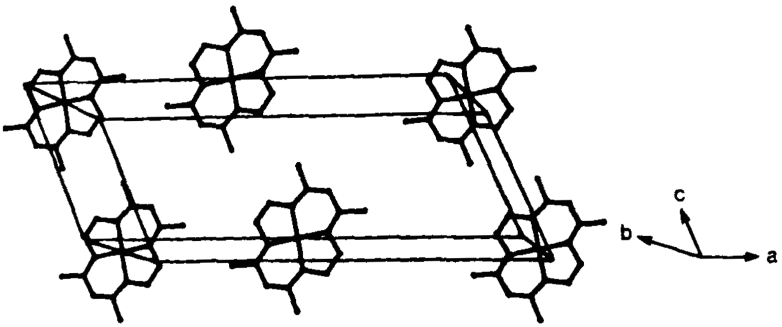


Figure 4. The arrangement of the non-stacked Ni(TATMA) molecules in the unit cell, whose centers are displaced by 0 1/2 0 from the centers of the dimers in a.

The single paramagnetic unpaired and magnetically uncoupled electron per $[Ni(TATMA)]_2NiS_4C_4H_4$ formula unit is then probably on the unstacked $NiS_4C_4H_4^-$ ion whereas in the $[Ni(TATMA)^+]_2$ dimers the $Ni(TATMA)^+$ electrons are paired in a bonding molecular orbital. A similar situation has been encountered previously for the compound TTF_2 $NiS_4C_4H_4$ where the arrangement of the D (TTF) and A ($NiS_4C_4H_4$) units is quite similar to that found for $[Ni(TATMA)]_2$ $NiS_4C_4H_4$

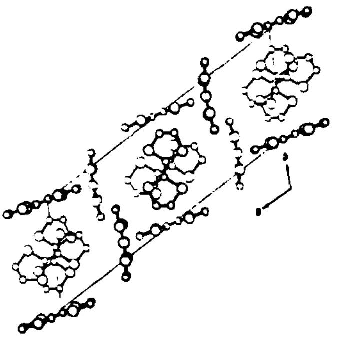


Figure 5a - Projection of the $2TTF{\cdot}NiS_4C_4H_4$ structure on the ac plane. (ref. 7)

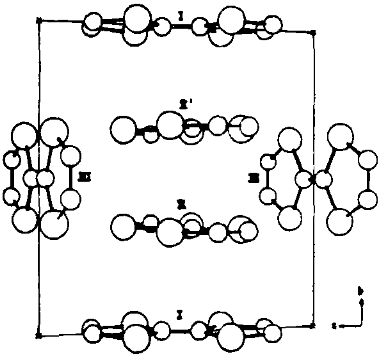


Figure 5b - A view of the $2TTF{\cdot}NiS_4C_4C_4$ structure normal to the bc plane. (ref. 7)

and where again the $NiS_4C_4H_4^-$ electrons are magnetically noninteracting and the spins on the TTF^+ ions are paired in a singlet ground state due to the formation of $(TTF^+)_2$ dimers.

As concluded in the case of the $(TTF)_2NiS_4C_4H_4$ system[8] the thermally activated conductivity observed for the $[Ni(TATMA)]_2NiS_4C_4H_4$ compound probably arises from excitation of electrons from the bound electron pair associated with the $[Ni(TATMA)^+]_2$ intermolecular "bond" into conduction band states associated with the 1-D stacks of the $[Ni(TATMA)]^{0,1^+}$.

In the case of the $[Ni(TATMA)]_2$ TCNQ compound only x-ray powder diffraction data is available, at present, and these data indicate that the structure of this compound is different from that of either $[Ni(TATMA)]NiS_4C_4H_4$ or $TTF_2NiS_4C_4H_4$. On the basis of redox potentials of $NiS_4C_4H_4$ (0.09 V) and TCNQ (0.13 V), charge transfer between the Ni(TATMA) and TCNQ units in this compound would appear at least as likely as in the $NiS_4C_4H_4$ case. Therefore the diamagnetic character of this compound suggests, again, the existence of some sort of magnetic coupling process in the solid state, in this case presumably involving both the $Ni(TATMA)^+$ and $TCNQ^-$ species.

REFERENCES

1. "Molecular Metals", W.E. Hatfield, ed., NATO Conference Series, Vol. 1, Series VI, Plenum Press, New York (1979); A.J. Epstein and J.S. Miller, Scientific American, October, p. 52 (1979).
2. Anon., Chemistry and Engrg. News, Nov. 12, p. 26 (1979); J.B. Torrance, et al., J. Amer. Chem. Soc., 101, 4747 (1979); "Synthesis and Properties of Low-Dimensional Materials", J.S. Miller and A.J. Epstein, eds., Anals. N.Y. Acad. Sci., Vol. 313 (1978).
3. L.V. Interrante (IUPAC) Coordination Chemistry, 21, Proc. XXI Int'l. Conf. on Coordn. Chem., Toulouse, France; J.P. Laurent, ed., Pergamon Press, Oxford (1981) p. 87 ff; L.V. Interrante, et al., Proc. Int'l. Conf. on Quasi One-Dimensional Conductors, Lecture Notes in Physics, 96, Vol. II, Springer Verlag Publ., pp. 56-58 (1979).
4. P. Cassoux and A. Gleizes, Inorg. Chem., 19, 665 (1980); P. Cassoux, L. Interrante and J. Kasper, C.R. Acad. Sc. Paris, p. 291, Serie C, p. 25 (1980).
5. T.J. Truex and R.H. Holm, J. Amer. Chem. Soc., 94, 4529 (1972).
6. S.M. Peng, J.A. Ibers, M. Millar and R.H. Holm, J. Amer. Chem. Soc., 98, 8037 (1976).

7. L.V. Interrante, K.W. Browall, H.R. Hart, Jr., I.S. Jacobs, G.D. Watkins and S.H. Wee, J. Amer. Chem. Soc., 97, 889 (1975); J.S. Kasper, L.V. Interrante and C.A. Secaur, ibid, 97, 890 (1975).
8. L.V. Interrante, Advan. Chem. Series, 150, 1 (1976).

ACKNOWLEDGMENTS

We thank Drs. Howard R. Hart, Jr., and Israel S. Jacobs of General Electric CR&D for magnetic susceptibility measurements on the $[Ni(TATMA)]_2A$ compounds. Research at G.E. CR&D was sponsored, in part, by the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract F49620-79-C-0051. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon.