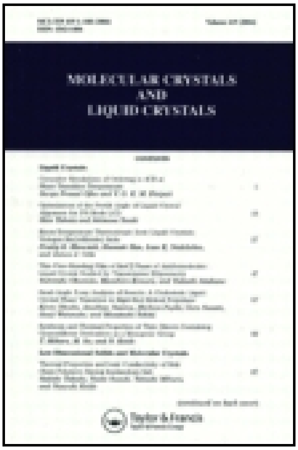


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Preparation and Magnetic Properties of Novel CT Complexes Derived from Organic Stable Radicals

Shin'ichi Nakatsuji [a], Atsushi Takai [a], Masako Mizumoto [a], Hiroyuki Anzai [a], Kazuyoshi Nishikawa [b], Yukio Morimoto [b], Noritake Yasuoka [b], Juergen Boy [c] & Gerd Kaupp [c]

[a] Department of Material Science, Himeji Institute of Technology, Kanaji 1479-1, Kamigori, Hyogo, 678-1297, Japan

[b] Department of Life Science, Faculty of Science, Himeji Institute of Technology, Kanaji 1479-1, Kamigori, Hyogo, 678-1297, Japan

[c] Organic Chemistry I, FB9, University of Oldenburg, P. O. Box 2503, D-26111, Oldenburg, Germany

Version of record first published: 24 Sep 2006

To cite this article: Shin'ichi Nakatsuji, Atsushi Takai, Masako Mizumoto, Hiroyuki Anzai, Kazuyoshi Nishikawa, Yukio Morimoto, Noritake Yasuoka, Juergen Boy & Gerd Kaupp (1999): Preparation and Magnetic Properties of Novel CT Complexes Derived from Organic Stable Radicals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 334:1, 177-184

To link to this article: http://dx.doi.org/10.1080/10587259908023315

Mol. Cryst. and Liq. Cryst., 1999, Vol. 334, pp. 177-184
Reprints available directly from the publisher
Photocopying permitted by license only

Preparation and Magnetic Properties of Novel CT Complexes Derived from Organic Stable Radicals

SHIN'ICHI NAKATSUJI[a], ATSUSHI TAKAI[a],
MASAKO MIZUMOTO[a], HIROYUKI ANZAI[a],
KAZUYOSHI NISHIKAWA[b], YUKIO MORIMOTO[b],
NORITAKE YASUOKA[b], JUERGEN BOY[c] and GERD KAUPP[c]

[a]*Department of Material Science and,* [b]*Life Science, Faculty of Science, Himeji Institute of Technology, Kanaji 1479–1, Kamigori, Hyogo 678–1297, Japan and* [c]*Organic Chemistry I, FB9, University of Oldenburg, P. O. Box 2503, D-26111 Oldenburg, Germany*

Novel charge-transfer complexes have been prepared from organic stable radicals such as 4-dialkylamino-TEMPO or verdazyl radical and electron acceptors. Among them, the CT complexes from 4-dimethylamino- or 4-azetidino-TEMPO and DDQ formed salt-like complexes of protonated 4-dialkylamino-TEMPO and the substituted 1,4-benzoquinone-hydroxylate upon recrystallization from a moist acetone. A series of ternary complexes consisting of organic stable radicals with their corresponding cation salts have been prepared by ball-milling of the solids. The magnetic behavior of the ternary complexes is discussed.

Keywords: TEMPO radical; verdazyl radical; CT complex; magnetic property; X-ray analysis

INTRODUCTION

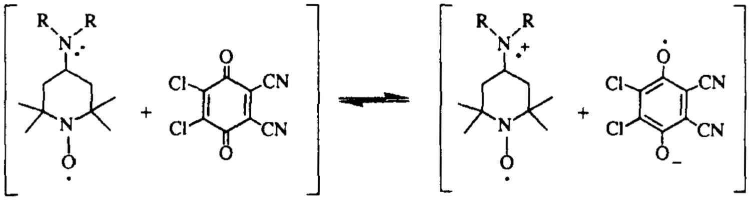
Recently, much attention has been focused on the CT complexes of organic stable radicals and suitable acceptors with the aim to explore new conducting materials.[1] On the other hand, there is continuing current interest in the development of new molecular-based magnetic materials, especially organomagnetic materials. Thus, numerous compounds with organic stable radicals as the key building blocks have been prepared and their magnetic behaviour has been elucidated.[2] In the course of our studies for the development of new organomagnetic materials, we were interested in preparing stable nitroxide radicals (TEMPO-type) with both donor or acceptor properties, for the synthesis of solid charge-transfer complexes.[3] The spins in the solids of these arrange in different ways and the magnetic dipoles may interact in the short-range. We had indeed observed that stable TEMPO radicals[4] or verdazyl radicals[5] did form charge-transfer complexes with appropriate acceptors. The solid CT complexes showed varied magnetic behavior.

We report in this paper on the preparation of new CT complexes of 4-dialkylamino-TEMPO radicals with DDQ, their facile hydrolysis to give salt-like CT complexes, and the solid-state preparation of a series of ternary (mixed) complexes of the TEMPO and triphenylverdazyl radicals with their corresponding cation nitrates[6a] and bromides.[6b] The magnetic properties of the solid CT complexes are reported.

RESULTS AND DISCUSSION

Novel Complexes Derived from 4-Dimethylamino-TEMPO or 4-Azetidino-TEMPO and DDQ

The CT complexes **3** and **4** have been formed by mixing dichloromethane solutions of 4-dimethylamino-TEMPO **1** or 4-azetidino-TEMPO **2** and DDQ in the usual way (SCHEME 1). The new complexes **5** and **6** were formed upon recrystallization of the complexes **3** and **4** from acetone including a trace of

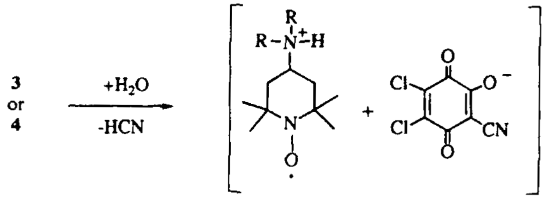


1: R = CH_3 DDQ 3: R = CH_3

2: R, R= $(CH_2)_3$ 4: R, R= $(CH_2)_3$

Scheme 1

water. The structures of the latter are evidenced by the spectroscopic data and the X-ray analysis of **5** as discussed below. No such structural change was observed for the corresponding $TCNQF_4$ complex during similar recrystallization. The electronic absorption spectra of the complexes **3** (λmax 588 and 457 nm in acetonitrile) and **5** (λmax 585 and 410 nm in acetonitrile) showed distinct differences in the longer wavelength region. Furthermore, different peaks were observed in the negative FAB-MS spectra: while the molecular ion peak of m/z = 227 (DDQ) occurred in the complex **3**, the complex **5** gave a peak at m/z = 217 that fits to 2,3-dichloro-5-cyano-6-hydroxy-1,4-benzoquinone. Also a marked difference is observed in the ESR spectra in acetonitrile: **3** exhibits a complicated triplet absorption of the nitroxide radical (g = 2.007) that is possibly overlapped with the spectra of the DDQ radical anion and/or of the trialkylamino radical cation, wheras the spectrum of **5** shows only the typical triplet of a nitroxide radical (g = 2.006) and thus excludes further spins. These facts suggest the structural change as formulated in SCHEME 2.



5: R = CH_3

Scheme 2 6: R, R= $(CH_2)_3$

Further evidence for that interpretation is provided by X-ray structural analysis of complex **5** that also locates the site of the proton (see below).

Similarly, the 4-azetidino-TEMPO/DDQ complex **4** gave the salt-like complex **6** and similar substitutions of cyano groups by hydroxyl groups have been reported in benzamidopyridine/DDQ complexes.[7]

Magnetic Properties of CT Complexes 3-6

The magnetic susceptibility of the complexes **3**-**6** was measured with polycrystalline samples in the temperature range of 2-300 K using a SQUID susceptometer. The data (Curie constant C and Weiss temperature Θ) are summarized in TABLE 1.

TABLE 1 Summary of Magnetic Data of Complexes 3-6

Complex	C (emu·K/mol)[a]	Θ (K)	Magnetic Interaction
3[b]	0.35	-0.4	Antiferromagnetic
4	0.32	-1.1	Antiferromagnetic
5	0.14	-1.3	Antiferromagnetic
6	0.33	-1.6	Antiferromagnetic

[a] Fitting for Curie-Weiss rule. [b] Cf. Ref. [4].

Curie-Weiss behavior was observed for the spins of the complexes **3**-**6** within the large temperature range examined. All complexes showed weak antiferromagnetic interactions between the spins in spite of the difference of their Weiss temperatures. It was also apparent from the values of the Curie-constants of the complexes **3** and **4** that the charge-transfer occurs from the amino-substituent and not from the radical center of the nitroxide to the acceptor molecule, thus retaining the total spin of $S=1/2$. Similarly, in the complex **6** no spin is transmitted to the enolate partner. The low Curie constant in **5** indicates some loss of spins with respect to the original complex **3** that must have a different reason which derives from its crystal structure.

X-ray Analysis on the Complex 5

To see the magneto-structural relationship in the complexes, an X-ray structural analysis of **5** was carried out with a single crystal as grown from a moist acetone solution of the 4-dimethylamino-TEMPO/DDQ complex **3**. Clearly, the analysis reveals that one of the cyano groups in the DDQ molecule of the original **3** was replaced by hydroxylate. The C-O bond length (1.25 Å) at that site is found shorter than the one that is typical for C-CN. The other C-O bond that is adjacent to the remaining CN group is almost of equal length (1.23 Å), whereas the third is shorter (1.21 Å). Furthermore, similar bond length (1.40 Å and 1.43 Å) of the two C-C bonds in the conjugated enolate moiety indicate the expected delocalization. In the TEMPO part of the complex, the N-O bond length (1.29 Å) of the nitroxide radical is retained at the normal length. Clearly, no electron is transferred from the nitroxide radical. Thus, a cyano group of the DDQ moiety in **3** has been substituted by water to form 2,3-dichloro-5-cyano-6-hydroxy-benzoquinone and the proton of the latter compound was transferred to the amino-group of the dialkylamino-TEMPO part to form the salt **5**.

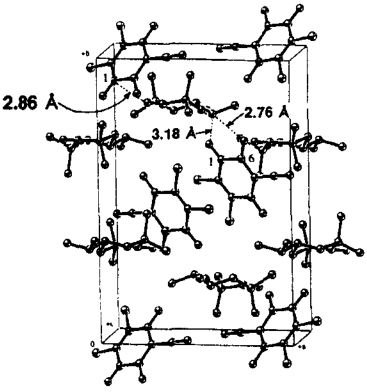
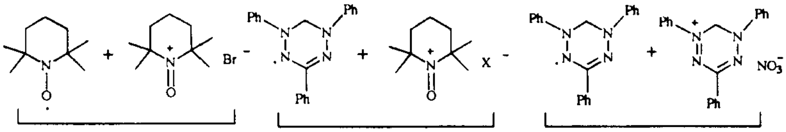


FIGURE Crystal structure of 5 viewed almost along c-axis

The crystal packing of the complex exhibits head-to-tail dimer pairs of the enolate that are surrounded by sheets of the radical molecules. Two kinds of short contacts are found between the nitrogen atom of the protonated dimethylamino group in the radical component and the two oxygen atoms attached to C1 and C6 in the enolate (3.18 Å and 2.76 Å, see FIGURE). Another short contact (2.86 Å) is found between the oxygen atom of the nitroxide group in the radical component and the C1 atom in the enolate component. It might be responsible for the totally different structure as compared to the structures in related complexes such as TEMPO/TCNQF$_4$ which exhibit segregated columnar alignments of both donor and acceptor molecules.[4] Although the distances between the NO groups of the radicals are not short enough for direct spin-spin interactions, the interactions between the spins are probably transmitted by the short contacts (FIGURE) with the enolate acting as transmitter for the spins. The partial loss of the spins in the complex **5** (low Curie constant) is probably caused by the short contacts between the two components.

Novel Ternary Complexes Derived from Stable Radicals

It is now well known and established that CT complexes can be prepared in the solid-state, preferably by the ball-milling method.[6] We have prepared several



7: 1:1 complex
8: 2:1 complex

9 ($X=NO_3$): 1:1 complex
10 (X=Br): 1:1 complex

11: 1:1 complex
12: 2:1 complex

ternary (mixed) complexes **7-12** from the stable radicals TEMPO or 1,3,5-triphenyl verdazyl and TEMPO-nitrosonium-bromide (m.p. 87 °C), -nitrate (m.p. 115 °C, dec.), and 1,3,5-triphenylverdazylium-nitrate (m. p. 85 °C, dec.) in the absence of solvents. The donor (radical) to acceptor (cation salt) ratio can be freely selected and thus complexes with different stoichiometries could be prepared by ball-milling of the appropriate mixtures in a teflon beaker with agate balls for 30 min at room temperature. We studied the complexes **7**, **9**, **10** and **11** with a donor-to-acceptor ratio of 1:1 and **8** and **12** with a 2:1 ratio Any charge-transfer is resonant in **7**, **8**, **11**, **12**, and nearly so in **9** and **10**.

Magnetic Properties of CT Complexes 7-12

The magnetic susceptibility data of the complexes **7-12** have been measured in the solid-state using a SQUID susceptometer. The derived magnetic data are summarized in TABLE 2 and compared to the data of the solid parent radicals.

Curie-Weiss behavior was observed for the spins of all complexes **7** - **12** within the large temperature range examined. The complexes **7**, **9**, **10** and **11** exhibit only weak antiferromagnetic interactions between the spins, whereas short-range order is evident in the spins of the complexes **8** and **12**. Such short-range order is also found in each of the parent radicals.[9] The large decrease of the magnetic susceptibility (estimated also from the listed Curie constants) in all complexes with the donor-to-acceptor ratio of 1:1 suggests an

TABLE 2 Summary of Magnetic Data of Mixed Complexes **7**-**12**

Mixed Complex	m.p. (°C)	C (emu·K/mol)[a,b]	Θ (K)[b]	Magnetic Interaction
7	115/161[c]	0.0034	-0.21	Antiferromagnetic
8	114/150[c]	0.60	-5.7[e]	Antiferromagnetic
9	146/150[d]	0.071	-0.09	Antiferromagnetic
10	158	0.0079	-0.25	Antiferromagnetic
11	174	0.094	-0.12	Antiferromagnetic
12	139	0.20	-3.3[e]	Antiferromagnetic

[a] Fitting for Curie-Weiss rule. [b] The data of parent radicals are as follows; TEMPO (m.p. 36-38 °C): C = 0.38 emu·K/mol, Θ = -5.9 K; 1,3,5-Triphenylverdazyl (m.p. 142-143 °C, Ref. [9]): C = 0.38 emu·K/mol, Θ = -9.9 K. [c] DSC endotherms without melting. [d] DSC endotherms with melting and decomposition. [e] Short-range order is suggested.

almost complete resonant or near-resonant charge-transfer from stable radical to cation with equal distribution of the spin over both partners that become chemically identical if the anion is symmetrically located. On the other hand, no large decrease of the Curie constants and no large difference in the Weiss temperatures occurs with the spins of the complexes **8** and **12** where the donor-to-acceptor ratio is 2:1, if compared with the values for the pure solid radicals. We conclude that the interactions of the resonant complexes with the remaining radicals do not prevent short-range spin alignment. Crystal structural data are required for a better understanding of the magneto-structural relationships and further studies along these lines are now in progress together with conductivity measurements of the solid complexes.

Acknowledgments

Financial support of this work by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (No. 09640644) and by the Fonds der Chemischen Industrie, Germany is gratefully acknowledged.

References

[1.] Cf. C. D. Bryan, A. W. Cordes, R. M. Fleming, N. A. George, S. H. Glarum, R. C. Haddon, R. T. Oakley, T. T. M. Palstra, A. S. Perel, L. F. Schneemeyer, and J. V. Waszczak, *Nature*, **365**, 821 (1993); K. A. Huchison, G. Srdanov, R. Menon, J-C. P. Gabriel, B. Knight, and F. Wudl, *J. Am.*

References

[1] Cf. C.D. Bryan, A.W. Cordes, R.M. Fleming, N.A. George, S.H. Glarum, R.C. Haddon, R.T. Oakley, T.T.M. Palstra, A.S. Perel, L.F. Schneemeyer, and J.V. Waszczak, *Nature,* **365,** 821 (1993); K.A. Huchison, G. Srdanov, R. Menon, J-C.P. Gabriel, B. Knight, and F. Wudl, *J. Am. Chem. Soc.,* **118,** 13081 (1996)..

[2] Cf. H. Iwamura, *Adv. **Phys. Org. Chem.,*** **26,** 179 (1990); O. Kahn, *Molecular magnetism* (VCH, Weinheim, 1993); J.S. Miller and A.J. Epstein, *Angew. Chem. Int. Ed. Engl.,* **33,** 385 (1994).

[3] S. Nakatsuji and H. Anzai, *J. Mater. Chem.,* **1997,** 2161.

[4] S. Nakatsuji, A. Takai, K. Nishikawa, Y. Morimoto, N. Yasuoka, K. Suzuki, T. Enoki, and H. Anzai, *J. Chem. Soc., Chem. Commun.,* **1997,**275; S. Nakatsuji, A. Takai, K.

Nishikawa, Y. Morimoto, N. Yasuoka, and H. Anzai, *Mol. Cryst. Liq. Crst.*, **313,** 229 (1998).

[5] S. Nakatsuji, A. Kitamura, K. Nishikawa, Y. Morimoto, N. Yasuoka, H. Kawamura, and H. Anzai, *Mot Cryst. Liq. Crst.*, **313,** 235 (1998); S. Nakatsuji, A. Kitamura, A. Takai, K. Nishikawa, Y. Morimoto, N. Yasuoka, and H. Anzai, *Z. Naturforsch.*, **53b,** 495 (1998).

[6] a) G. Kaupp and J. Schmeyers, *J. Org. Chem.*, **60,** 5494 (1995); b) G. Kaupp, J. Boy, and J. Schmeyers, *J. Prakt. Chem./Chem.-Ztg.*, **340,** 346 (1998).

[7] Cf. P. Bruni, G. Tosi, and G. Valle, *J. Chem. Soc., Chem. Commun.*, **1988,** 1022.

[8] The crystallographic data will be deposited with Cambridge Structural Data Base.

[9] Cf. E. Dormann, H. Winter, W. Dyakonow, B. Gotschy, A. Lang, H.N. Naarmann, and N. Walter, *Ber. Bunsenges. Phys. Chem.*, **96,** 922 (1992).