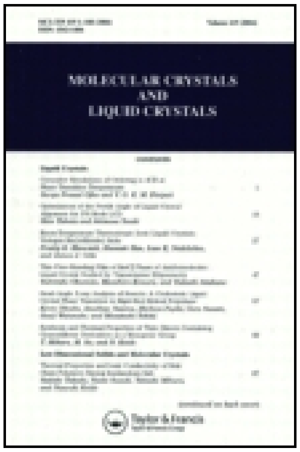
This article was downloaded by: [University of California, San Diego]
On: 21 August 2012, At: 11:44
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Structure and Magnetic Characterization of Binuclear Nickel(Ii) Compound with Bridging 2,2′-Biimidazolate Dianion

Makoto Tadokoro [a] , Kazunobu Sato [a] , Daisuke Shiomi [b] , Takeji Takui [a] & Koichi Itoh [b]

[a] Department of Chemistry Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558, Japan

[b] Department of Material Science, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558, Japan

Version of record first published: 04 Oct 2006

To cite this article: Makoto Tadokoro, Kazunobu Sato, Daisuke Shiomi, Takeji Takui & Koichi Itoh (1997): Structure and Magnetic Characterization of Binuclear Nickel(Ii) Compound with Bridging 2,2′-Biimidazolate Dianion, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 49-56

To link to this article: http://dx.doi.org/10.1080/10587259708044548

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 49–56
Reprints available directly from the publisher
Photocopying permitted by license only

© 1997 OPA (Overseas Publishers Association)
Amsterdam B.V. Published under license
in The Netherlands under the Gordon and Breach
Science Publishers imprint
Printed in India

Downloaded by [University of California, San Diego] at 11:44 21 August 2012

STRUCTURE AND MAGNETIC CHARACTERIZATION OF BINUCLEAR NICKEL(II) COMPOUND WITH BRIDGING 2,2'-BIIMIDAZOLATE DIANION

MAKOTO TADOKORO[1], KAZUNOBU SATO[1], DAISUKE SHIOMI[2], TAKEJI TAKUI[1] AND KOICHI ITOH[2]
Department of Chemistry[1] and Department of Material Science[2], Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

Abstract As novel molecule-based magnetic materials based on metal coordination polymers bridged by bim^{2-}, [(Ni-cyclam)$_2$(bim)](ClO$_4$)$_2$ (**1**) (bim^{2-} = dideprotonated 2,2'-biimidazolate dianion) was synthesized and the crystal structure was characterized by X-ray crystal analysis. (Crystal data: orthorhombic, *P*bca (No. 61), *a* = 16.677(2) Å, *b* = 16.447(5) Å, *c* = 13.212(1) Å, *V* = 3623(1) Å^3, *Z* = 4) The magnetic susceptibility measurements of the dinuclear nickel (II) complex (**1**) in the crystalline state showed the weak antiferromagnetic property (J = - 4.6 cm^{-1}), which was also sujested by the ESR mesurements.

INTRODUCTION

The quest for multifunctionality molecule-based materials has been the focus of current topics in materials science and chemistry. Recently particular attention has been devoted to the development of rational synthetic routes to polymeric coordination complexes of new bridged ligands because they are intriguing complexes in connection with materials science. Their potential properties such as electrical conductivity and molecular magnetism are of particular interest.

In order to investigate new molecule-based materials of electronic multi functionality, we have been exploring novel bridged ligands, which enable us to build up coordination polymers underlying spin-polarized electronic properties. We have investigated transition metal complexes with a bidentate 2,2'-biimidazole ligand with multi-proton donor property as a building block in the solid state. Since 2,2'-biimidazole (H$_2$bim) is a bidentate ligand, it can coordinate to transition metal ions in three forms: neutral (H$_2$bim), mono-deprotonated (Hbim$^-$), and dideprotonated (bim^{2-}) forms.[1] Recently, a coordination polymer of [Fe^{II}(bim)]$_n$ (**2**) has been reported.[2] The polymer reveals magnetic behaviors characteristic of ferromagnetic materials, but the crystal structure has not been known in detail yet. In this paper, we report the synthesis, X-ray structural analysis, and ESR/SQUID magnetic characterization of the Ni(II) dinuclear complex ([(Ni-cyclam)$_2$(bim)](ClO$_4$)$_2$) (1) bridged by 2,2'-biimidazolate dianion, serving as for the understanding of ferromagnetic interactions of the polymer (2). Also the Ni(II) complex can be compared with homobinuclear complexes of Ni(II)[3], Cu(II)[4] and Ti(III)[5], which were already reported by Hendrickson *et al.*

EXPERIMENTAL

Preparation

The synthetic method of the dinuclear nickel (II) complex [(Ni-cyclam)$_2$(bim)](ClO$_4$)$_2$ (1) was based on the procedure of a 'one-pot' self-assembly in methanol solution. Dinuclear complex (1) was obtained by refluxing the mixture of 2,2'-biimidazole (H$_2$bim) (3 mmol) and cyclam (0.5 mmol) dissolved in MeOH (30 cm^3) and 28 % NaOMe solution (2.0 g) followed by the addition of methanol solution (40 cm^3) of Ni(ClO$_4$)$_2$ · 6H$_2$O (1.5 mmol). The reaction mixture was heated for 30 minutes and filtered. The filtrate was cooled slowly to room temperature and left overnight. The resulting violet crystalline precipitate was filtered and air dried. Single crystals suitable for X-ray diffraction studies were selected from the precipitate. Elemental analysis was made for microcrystalline solids. (Analysis of [(Ni-cyclam)$_2$(bim)](ClO$_4$)$_2$; $C_{26}H_{52}N_{12}Ni_2Cl_2O_8$; Found: C, 36.79%; H, 6.38%; N, 19.75%, Calcd.: C, 36.78%; H, 6.17%; N, 19.80%)

Measurement

Intensity data were collected at 296 K on a Rigaku AFC7R diffractometer with graphite-monochronated Cu-Kα radiation and the ω–2θ scan technique. Accurate cell dimensions and crystal orientation matrices were determined by least-squares fitting procedure.

Crystals Structure

The crystal data of [(Ni-cyclam)$_2$(bim)](ClO$_4$)$_2$ (1) is as follows; formula: $C_{26}H_{52}N_{12}Ni_2Cl_2O_8$, monoclinic, space group *P*bca (No. 61), $FW = 849.08$, $a = 16.677(2)$ Å, $b = 16.447(5)$ Å, $c = 13.212(1)$ Å, $V = 3623(1)$ Å^3, $Z = 4$, $\rho_{calc} = 1.556$ g/cm^{-1}, Cu-Kα radiation, $\lambda = 1.54178$ Å, $6.0 < 2\theta < 120.2°$, 3068 reflections were collected, of which 1188 unique reflections ($I_o > 3\sigma(I_o)$) were used for refinement (226 parameters), converging to $R = 0.058$ and $R_w = 0.060$. The structure of complex (1) was solved by heavy-atom Patterson methods[7] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed in calculation. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.44 and -0.37 eÅ^{-3}. All calculations were performed using the teXsan[8] crystallographic software package.

Downloaded by [University of California, San Diego] at 11:44 21 August 2012

Downloaded by [University of California, San Diego] at 11:44 21 August 2012

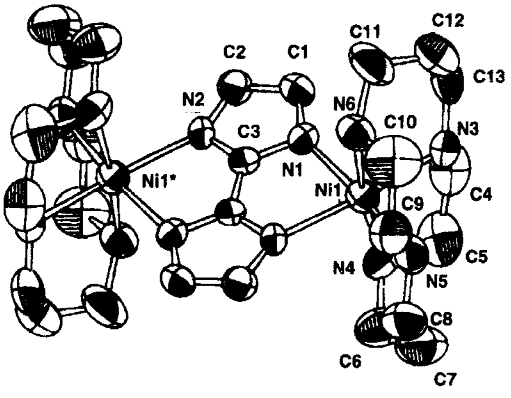


FIGURE 1 ORTEP view of complex (**1**) around nickel atoms.

TABLE I Selected bond lengths (Å) and angles (deg) for compound (**1**)[a].

	Distances		
Ni(1) - N(1)	2.191(7)	Ni(1) - N(2)	2.149(8)
Ni(1) - N(3)	2.102(8)	Ni(1) - N(4)	2.095(9)
Ni(1) - N(5)	2.138(7)	Ni(1) - N(6)	2.125(9)
	Angles		
N(1) - Ni(1) - N(2)	81.1(3)	N(1) - Ni(1) - N(3)	90.8(3)
N(1) - Ni(1) - N(4)	91.7(3)	N(1) - Ni(1) - N(5)	172.9(3)
N(1) - Ni(1) - N(6)	95.1(3)	N(2) - Ni(1) - N(3)	171.2(3)
N(2) - Ni(1) - N(4)	92.7(3)	N(2) - Ni(1) - N(5)	92.1(3)
N(2) - Ni(1) - N(6)	92.4(3)	N(3) - Ni(1) - N(4)	84.0(4)
N(3) - Ni(1) - N(5)	96.0(3)	N(3) - Ni(1) - N(6)	91.8(3)
N(4) - Ni(1) - N(5)	90.8(4)	N(4) - Ni(1) - N(6)	172.1(3)
N(5) - Ni(1) - N(6)	82.9(4)		

[a] Estimated standard deviations are given in parentheses.

RESULTS AND DISCUSSION

Molecular Structure of $[(\text{Ni-cyclam})_2(\text{bim})](\text{ClO}_4)_2$ (**1**)

The single crystal structure of $[(\text{Ni-cyclam})_2(\text{bim})](\text{ClO}_4)_2$ (**1**) was solved using standard heavy-atom techniques. The final positional and anisotropic thermal parameters are presented in Table I while the bond distances and angles are given in Table II. The structure consists of discrete binuclear cations, $[(\text{Ni-cyclam})_2(\text{bim})]^{2+}$, and ClO_4^- anions. The binuclear cation is located about a crystallographic center of inversion. In Figure 1 is shown an ORTEP view of the inner coordination around each nickel (II) ion and the bridging biimidazolate dianion with the numbering scheme indicated. The central C-C distance of the dinuclear complex (**1**) (*i.e.*, C(3)-C(3)* = 1.32(2) Å) is smaller than

TABLE II Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2).

atom	x	y	z	B_{eq}
Ni(1)	0.40630(10)	0.9351(1)	0.1541(1)	4.02(3)
Cl(1)	0.7012(2)	0.8311(2)	0.1024(2)	5.87(8)
O(1)	0.6633(6)	0.8621(8)	0.1833(7)	14.7(4)
O(2)	0.7528(8)	0.7743(8)	0.1367(7)	15.1(4)
O(3)	0.7522(9)	0.8875(9)	0.0625(8)	17.3(5)
O(4)	0.6488(5)	0.8052(7)	0.0287(6)	11.0(3)
N(1)	0.4171(5)	0.9300(5)	-0.0111(5)	4.0(2)
N(2)	0.4919(4)	0.9861(5)	-0.1358(5)	3.7(2)
N(3)	0.3025(5)	0.8627(5)	0.1489(6)	4.8(2)
N(4)	0.3250(5)	1.0319(6)	0.1456(6)	5.1(2)
N(5)	0.4106(6)	0.9455(6)	0.3153(5)	5.8(2)
N(6)	0.4802(5)	0.8321(6)	0.1811(6)	4.9(2)
C(1)	0.3901(6)	0.9017(6)	-0.1021(7)	4.1(2)
C(2)	0.4364(6)	0.9364(7)	-0.1771(6)	4.3(2)
C(3)	0.4788(6)	0.9784(6)	-0.0366(6)	3.5(2)
C(4)	0.2409(8)	0.9138(9)	0.0966(8)	6.8(4)
C(5)	0.2439(8)	0.997(1)	0.1428(9)	7.9(4)
C(6)	0.3362(8)	1.0992(8)	0.2165(9)	7.3(4)
C(7)	0.3400(9)	1.0740(9)	0.3259(9)	8.6(4)
C(8)	0.4098(8)	1.0242(8)	0.3592(8)	7.0(4)
C(9)	0.4838(7)	0.9006(8)	0.3487(9)	6.5(3)
C(10)	0.4851(8)	0.8207(9)	0.2920(10)	8.3(4)
C(11)	0.4588(8)	0.7581(8)	0.1234(10)	8.0(4)
C(12)	0.3735(7)	0.7317(7)	0.1416(8)	6.5(3)
C(13)	0.3081(7)	0.7849(8)	0.0991(8)	6.9(3)

$B_{eq} = 8/3\{p^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)\}$

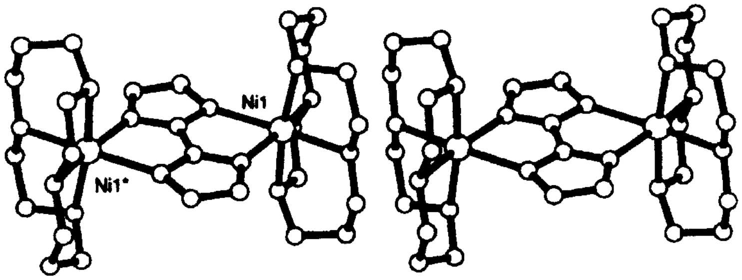


FIGURE 2 Stereoscopic plot of complex (1).

Downloaded by [University of California, San Diego] at 11:44 21 August 2012

Downloaded by [University of California, San Diego] at 11:44 21 August 2012

that observed (1.449(4) Å) for the dinuclear copper complex $[(CuMe_5dien)_2(bim)](BPh_4)_2$[3], and the same distance as that (1.405(12) Å) for the dinuclear rhodium complex $[Rh(COD)]_2(bim)$[6]. The stereoscopic plot of complex (1) illustrated in Figure 2 can give the best view of the coordination geometry around the nickel(II) ion. It is possible to view the coordination geometry as being distorted from octahedral symmetry, where the square plane consists of the atoms N(1), N(2), N(3) and N(5). The deviation of a nickel atom from the least-squares-fit plane (N(1), N(2), N(3) and N(5)) is given in 0.0043 Å. The bond distance around nickel atoms is in the range of 2.10-2.19 Å. The deformation from perfect octahedral coordination is due to the structure restriction with the cyclam ligand. The intramolecular distance between the nickel atoms is 5.56 Å, and the closest intermolecular Ni-Ni distance is 6.41 Å.

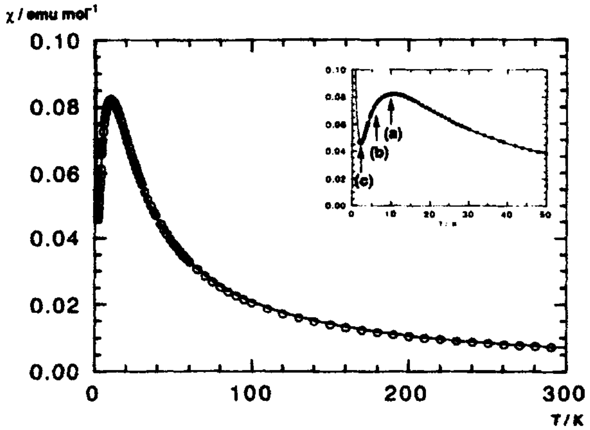


FIGURE 3 Temperature dependence of magnetic susceptibility of complex (1).

Magnetic susceptibility measurements

Temperature dependence of magnetic susceptibility data was obtained for the complex (1), as shown in Figure 3. As can be seen in Figure 3, the susceptibility of (1) is characteristic of dominant antiferromagnetic exchange interaction in the crystal state. It shows a maximum in the corrected molar paramagnetic susceputibility, χ_p, at ca. 10 K. The exchange interaction between the two nickel(II) ions bridged by the bim^{2-} ligand is simply expressed as a Heisenberg Hamiltonian,

$$H = -2JS_1 \cdot S_2 \qquad (1)$$

where J denotes the exchange interaction parameter and S_1 and S_2 are the spin operators. The eigenenergies of equation (1), E(S), for a spin quantum numbers S (S=0, 1 , 2) are,

$$E(0) = +4J,\ E(1) = +2J,\ E(2) = -2J. \qquad (2)$$

The Boltzmann distribution over these states gives the paramagnetic susceptibility χ_p,

$$\chi_p = A / T\,(6e^{-2J/k_BT} + 30e^{2J/k_BT}) / (e^{-4J/k_BT} + 3e^{-2J/k_BT} + 5e^{2J/k_BT})$$
$$A = N_A g^2\beta^2/3k_B, \qquad (3)$$

as a function of temperature T. The symbols N_A, β, k_B have their usual meanings and g stands for the averaged g-factor. The observed temperature dependence of magnetic susceptibility for complex (1) was fit to equations (4a) and (4b),

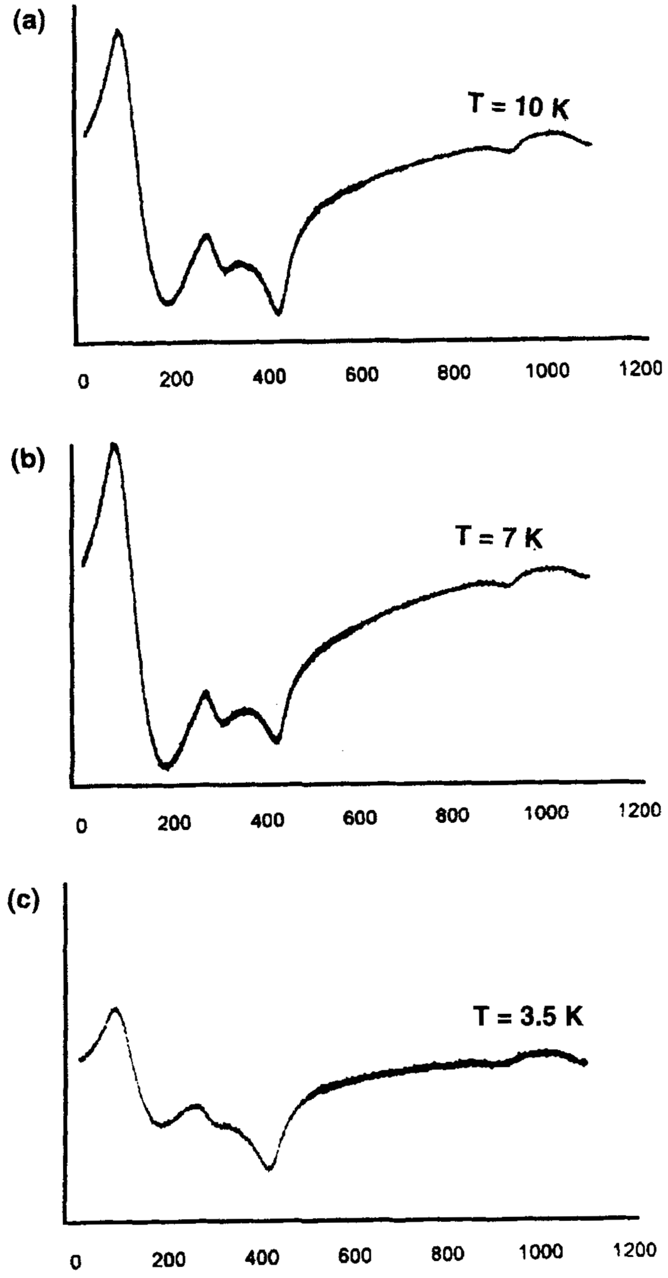
$$\chi = (1-p)\chi_p + p\chi' + \chi_{dia}, \qquad (4a)$$
$$\chi' = 2N_A g^2\beta^2/3k_BT, \qquad (4b)$$

where χ' is the susceptibility of non-dimeric, S= 1 impurities with the portion of p. The diamagnetic susceptibility, χ_{dia} contains the contribution from the orbital paramagnetism (temperature independent paramagnetism) of the nickel(II) ion. The data for complex (1) was least-squares fit to equation (4a). This left three parameters J, g, and p for each least-squares fitting. In the case of complex (1), the fitting to equation (3) can be seen reasonably well, giving $J = -4.6$ cm^{-1}, $g = 2.18$, and the percentage of paramagnetic impurities = 7 %. The calculated curve fitting is illustrated by the solid lines in Figure 3. The susceptibility data for the biimidazolate bridged complex (1) clearly demonstrate that weak antiferromagnetic interactions between the two Ni(II) ions take place via extended organic bridges. The antiferromagnetic interactions are considerably weak as expected from the similarity observed for the binuclear Ti(III), Ni(II) and Cu(II) complexs, $[(\mathrm{Ni\text{-}tren})_2(\mathrm{bim})]^{2+}$ ($J = -2.9$ cm^{-1})[3], $[(\mathrm{Cu\text{-}tren})_2(\mathrm{bim})]^{2+}$ ($J < 0.5$ cm^{-1})[4] and $[(\mathrm{Cp_2Ti})_2(\mathrm{bim})]$ ($J = -25.2$ cm^{-1})[5].

ESR measurements

Electron spin resonance spectra of complex (1) were observed at three temperatures, (a) 10K, (b) 7 K and (c) 3.5 K. Upon cooling the powder sample to 10 K fine-structure spectra due to high-spin mixture appeared as illustrated in Figures 4. On futher cooling to 3.5 K, the intensity of the ESR signal decreased, indicating the low-spin ground state. Detailed analysis is in progress in order to extract spin Hamiltonian parameters for dipolar interactions related to the local molecular structure.

Downloaded by [University of California, San Diego] at 11:44 21 August 2012



FIGURES 4 ESR spectra were obtained for the three temperature, (a) 10K, (b) 7 K and (c) 3.5 K.

Downloaded by [University of California, San Diego] at 11:44 21 August 2012

Downloaded by [University of California, San Diego] at 11:44 21 August 2012

CONCLUSION

In view of the close resemblance between the dinuclear homometal Cu(II), Ti(III) and Ni(II), the ferromagnetic behavior of the $[\mathrm{Fe^{II}(bim)}]_n$ polymeric compound (2) is possibly due to antiferromagnetic interaction between Fe(II) and oxidized Fe(III) ions. This possibility is also supported by the fact the Fe(II) compound is unstable and easily oxidized.

ACKNOWLEDGMENTS

This work was supported by Grant-sin-Aid for Scientific Research on Priority Areas "Molecular Magnetism"(Area No. 228/04 242 103 and 04 242 105) from the Ministry of Education, Science and Culture, Japan and also by the Ministry of International Trade and Industries (NEDO Project "Organic Magnets"). The authors thank the Analytical Center, Faculty of Science, Osaka City University, for the use of a 4-Circle Single Crystal X-ray Diffractometer (Rigaku AFC-5R).

REFERENCES

1. (a) M. Tadokoro, K. Isobe, A. Miyazaki, T. Enoki and K. Nakasuji, Mol. Cryst. Liq. Cryst., 278, 199 (1996). (b) M. Tadokoro, K. Isobe and K. Nakasuji, Mol. Cryst. Liq. Cryst., 278, 209 (1996). (c) M. Tadokoro, K. Isobe and K. Nakasuji, Mol. Cryst. Liq. Cryst., 278, 213 (1996). (d) M. Tadokoro, K. Isobe and K. Nakasuji, Mol. Cryst. Liq. Cryst., 278, 217 (1996). (e) M. Tadokoro, K. Isobe, H. Uekusa, Y. Ohashi and K. Nakasuji, Mol. Cryst. Liq. Cryst., 278, 221 (1996).
2. M. A. M. Lorente, F. Dahan, Y. Sanakis, V. Petrouleas, A. Bousseksou and J. -P. Tuchagues, Inorg. Chem., 34, 5346 (1995)
3. M. S. Haddad and D. N. Hendrickson, Inorg. Chem., 17, 2622 (1978)
4. B. F. Fieselmann, D. N. Hendrickson and G. D. Stucky, Inorg. Chem., 17, 2078 (1978)
5. M. S. Haddad, E. N. Duesler and D. N. Hendrickson, Inorg. Chem., 18, 141 (1979)
6. S. W. Kaiser, R. B. Saillat, W. M. Butler and P. G. Rusmussen, Inorg. Chem., 15, 2681 (1976)