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

Aggregation Structure of Quarternary Ammonium Salts of $[Ni(dmit)_2]$ Complex in Crystal

Yuichi Yamamoto [a], Kazuo Miyamura [a] & Yohichi Gohshi [a]

[a] Department of Applied Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo, Tokyo, 113, JAPAN

Version of record first published: 24 Sep 2006.

To cite this article: Yuichi Yamamoto , Kazuo Miyamura & Yohichi Gohshi (1996): Aggregation Structure of Quarternary Ammonium Salts of $[Ni(dmit)_2]$ Complex in Crystal, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 285:1, 137-142

To link to this article: http://dx.doi.org/10.1080/10587259608030791

Mol. Cryst. Liq. Cryst., 1996, Vol. 285, pp. 137–142
Reprints available directly from the publisher
Photocopying permitted by license only

AGGREGATION STRUCTURE OF QUARTERNARY AMMONIUM SALTS OF [Ni(dmit)$_2$] COMPLEX IN CRYSTAL

YUICHI YAMAMOTO, KAZUO MIYAMURA, and YOHICHI GOHSHI
Department of Applied Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo, Tokyo 113, JAPAN

Abstract The aggregation structures of [Ni(dmit)$_2$] complex salts of quarternary ammonium with one or two alkyl ($C_{12}H_{25}$, $C_{18}H_{37}$) groups are analysed by thermal analysis and x-ray crystallographic analysis. The aggregation structure was found to change drastically by the number of alkyl chains.

INTRODUCTION

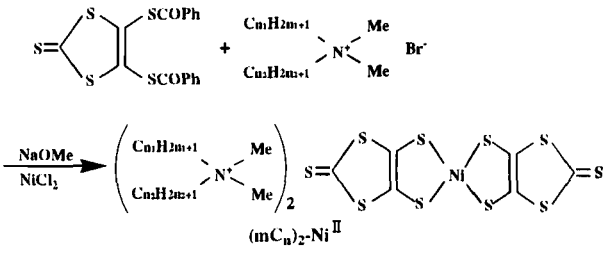
[Ni(dmit)$_2$] (H_2dmit=4,5-dimercapto-1,3-dithiol-2-thion) is known as an acceptor molecule with π-conjugated system. It tends to pile up to form two-dimensional crystals. The first example of a conducting metal complex of the two-dimensional was $(Bu_4N)_{0.29}$[Ni(dmit)$_2$] in which the Ni(dmit)$_2$ columns can be considered as weakly coupled dimers[1,2]. In most cases the complexes were found to be semiconducting, but when (Me_4N)[Ni(dmit)$_2$]$_2$ was compressed to 7kbar it exhibited a transition to the superconducting state at a T_C value of 5K[3]. On the other hand, the introduction of long alkyl chains is effective in increasing the anisotropy of the molecule and also enables the molecules to form Langmuir-Blodgett (LB) monolayer films. Nakamura et al.

investigated the LB film formation from alkyl ammonium salts of [Ni(dmit)$_2$], and found that the bulk conductivities of films changed depending on the length of alkyl chain[4]. Here we report the structural analysis of [Ni(dmit)$_2$] complex salt of quarternary ammonium with one or two alkyl groups.

EXPERIMENTAL

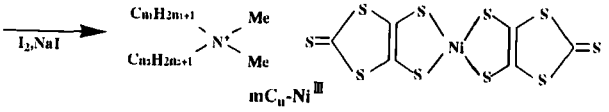
Synthesis

The complexes were prepared following the procedures described by Steimecke et al. (Scheme 1)[5]. First, the Ni(Ⅱ) complex was prepared, and next the Ni(Ⅲ) complexes obtained by oxidation of Ni(Ⅱ) complex. 10 Kinds of complexes synthesized are listed in Scheme 1. They differ each other in charge of [Ni(dmit)$_2$], number and length of alkyl chains. Therefore, they are expressed as $(mC_n)_aNi(b)$, where m, n represent the number and length of alkyl chain of ammonium, respectively and a is for number of cation per complex, and b is for charge of nickel in [Ni(dmit)$_2$]. Since the Ni(Ⅱ) salts have two times as many ammonium cations as the Ni(Ⅲ)



Salts of $[Ni^{Ⅱ}(dmit)_2]^{2-}$

2×2 chains	①n_1=18, n_2=18	$(2C_{18})_2$-Ni(Ⅱ)
〃	②n_1=12, n_2=12	$(2C_{12})_2$-Ni(Ⅱ)
2×1 chains	③n_1=18, n_2=1	$(C_{18})_2$-Ni(Ⅱ)
〃	④n_1=12, n_2=1	$(C_{12})_2$-Ni(Ⅱ)
no chain	⑤n_1=1, n_2=1	$(C_1)_2$-Ni(Ⅱ)



Salts of $[Ni^{Ⅲ}(dmit)_2]^{-}$

2 chains	⑥n_1=18, n_2=18	$2C_{18}$-Ni(Ⅲ)
〃	⑦n_1=12, n_2=12	$2C_{12}$-Ni(Ⅲ)
1 chain	⑧n_1=18, n_2=1	C_{18}-Ni(Ⅲ)
〃	⑨n_1=12, n_2=1	C_{12}-Ni(Ⅲ)
no chain	⑩n_1=1, n_2=1	C_1-Ni(Ⅲ)

SCHEME 1

salts, the number of alkyl chains is expressed as 4(2×2), etc. All samples were recrystallized by slowly cooling in air after heating in the solvent of Acetonitrile and benzene (1:1). Single crystals suitable for X-ray crystallographic analysis were obtained for ⑥ and ⑨ by the same procedures.

Measurements

Thermal analysis (DSC,TG,DTA) were performed using TG/DTA320, DSC320 of Seiko Instruments Inc. X-ray crystallographic analysis were performed by Rigaku AFC7R using Patterson methods.

RESULTS AND DISCUSSION

Figure 1 shows the results of calorimetric analysis (DSC) for salts (a) with no alkyl chain ($(C_1)_2$-Ni(Ⅱ)) and (b) with alkyl chains ($(C_{18})_2$-Ni(Ⅱ)). In the sample with alkyl chains, an endothermic peak was always observed, while it was absent for the sample without alkyl chain. The transition temperatures and heats of the endothermic peaks are give in Table 1. Since this phase transition was observed only for the complexes with alkyl chains, this phase transition was assigned to the melting induced by the movement of alkyl side chains.

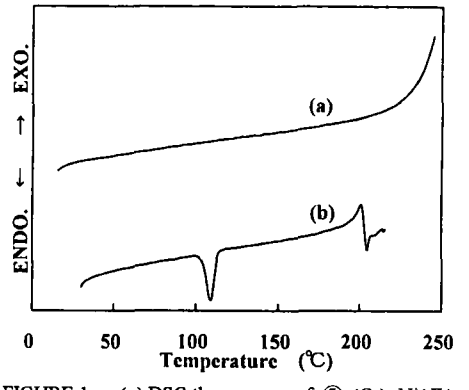


FIGURE 1 (a) DSC thermogram of ⑤ $(C_1)_2$-Ni(Ⅱ)
(b) DSC thermogram of ③ $(C_{18})_2$-Ni(Ⅱ)

TABLE 1 Transition temperature and heat of endothermonic peak (℃(mJ/mol))

	Ni(Ⅱ)		Ni(Ⅲ)	
	2×2	2×1	2	1
C_{18}	171 (19) ①	109 (91) ③	111 (83) ⑥	161 (134) ⑧
C_{12}	162 (40) ②	147 (103) ④	112 (104) ⑦	161 (155) ⑨
C_1	no peak ⑤		no peak ⑩	

As the number of alkyl chains increases, the transition temperature of Ni(Ⅱ) complexes increase while that of the Ni(Ⅲ)

complexes decreases. Heats of transition tend to decrease as the length of alkyl chains increases, and are smaller in the salts of ammonium cation with two alkyl chains than in that with single chain. As a whole, the heat of transition tends to increase as the number of alkyl chains decreases. The molecular and the crystal structures obtained by X-ray crystallographic analysis of both ⑥ ($2C_{18}$-Ni(Ⅲ)) and ⑨ (C_{12}-Ni(Ⅲ)) are shown in Figure 2. The crystallographic parameters and experimental conditions are given in Table 2. The planar [Ni(dmit)$_2$] molecules, in both structures of ⑥ and ⑨, are arranged in the side by side and face to face fashion along b and c axis, respectively. In the structure of ⑥ ($2C_{18}$-Ni(Ⅲ)), the [Ni(dmit)$_2$] molecules form dimers as shown in Figure 2(a-3).

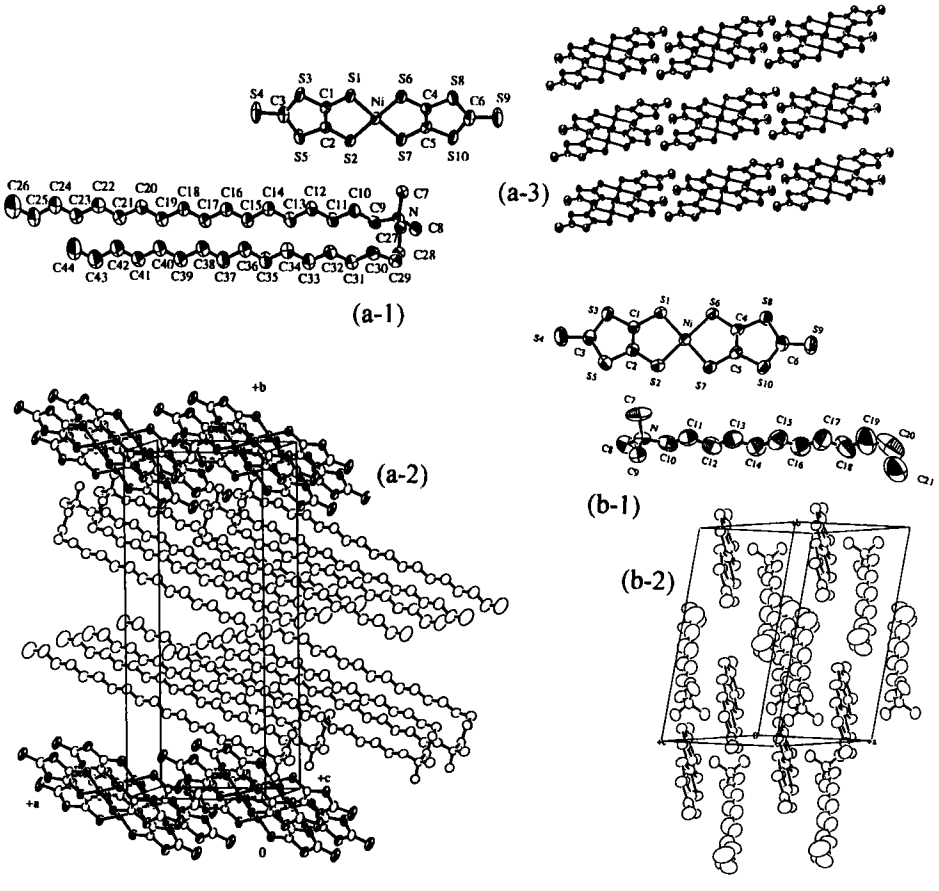


FIGURE 2 Molecular and crystal structures of (a) ⑥ $2C_{18}$-Ni(Ⅲ), (b) ⑨ C_{12}-Ni(Ⅲ)

TABLE 2 Crystallographic Parameters and Experimental Conditions

Compound	⑥ $2C_{18}$-Ni(Ⅲ)	⑨ C_{12}-Ni(Ⅲ)
Colour	dark green	dark green
Formula	$C_{44}H_{80}NNiS_{10}$	$C_{21}H_{34}NNiS_{10}$
M	1002.42	679.81
Crystal system	triclinic	triclinic
Space group	P1(#2)	P1(#2)
a/Å	12.211(1)	10.1754(8)
b/Å	28.516(6)	16.919(2)
c/Å	7.720(2)	9.7208(9)
β/°	91.89(2)	90.465(9)
U/Å^3	92.78(1)	107.210(7)
Z	91.66(1)	75.991(7)
D/g cm^{-3}	1.241	1.459
F(000)	1078.00	710.00
μ (Mo Kα)/cm^{-1}	7.80	13.15
Crystal size(mm)	0.15×0.65×0.30	0.5×0.5×0.15
No. of reflections obsd	9923	5777
No. of unique reflections	9438	5440
R[a)]	0.043	0.042
Rw[b)]	0.027	0.028

a) $R=\Sigma(||Fo|-|Fc||)/\Sigma|Fo|$ b) $Rw=[\Sigma w(|Fo|-|Fc|)^2/\Sigma w|Fo|^2]^{1/2}$

In this dimer structure, the [Ni(dmit)$_2$] molecules are stacked with the presence of inter-molecular Ni···Ni contacts (3.558 Å). Between the dimers of ⑥ in the crystal, the S···S contacts (3.322 Å) is present to form layer of two-dimensional network of [Ni(dmit)$_2$] ions. This layer of dimers is piled alternatively with the possibly insulating layers of alkyl groups in the crystal. It is interesting to notice that the layer of alkyl ammonium ions form a sort of bimolecular membrane. It is well known that the quarternary ammonium ions with two long alkyl chains tend to form bimolecular membranes in aqueous solution. On the other hand, [Ni(dmit)$_2$] of ⑨ (C_{12}-Ni(Ⅲ)) is in inter-molecular S···S contacts (3.535 Å) and Ni···Ni contacts (>3.60 Å) with the neighbouring [Ni(dmit)$_2$], which are much longer than those of ⑥. Therefore, the inter-molecular interaction between [Ni(dmit)$_2$] in ⑥ should be much larger than that in ⑨. In this crystal structure no distinct layers of alkyl groups can be observed. It can be said that the tendency to form bimolecular membrane of alkyl ammonium ions with two long alkyl chains, enforces the [Ni(dmit)$_2$] ions to stack and to form two-dimensional network. From the thermal analysis, it was shown that the transition temperature of ⑨ was much larger than that of ⑥. The formation of bimolecular structure of bis alkyl ammonium

ions seems to decrease the transition temperature. The heat of transition, on the other hand, is large in ⑨. This means that the phase transition of ⑨ requires larger energy than that of ⑥. Therefore, the breakage of bonds between alkyl groups in ⑥ requires only a little energy.

ACKNOWLEDGEMENT

This work was partly supported by Asahi Glass Foundation.

REFERENCES

1. R.Kato, T.Mori, A.Kobayashi, Y.Sasaki and H.Kobayashi, Chem Lett., 1(1984).
2. L.Valede, J.P.Legros, M.Bousseau, P.Cassoux, M.Garbauskas and L.V.Interrante, J.Chem.Soc., Dalton Trans., 783(1985).
3. A.Kobayashi, H.Kim, Y.Sasaki, R.Kato, H.Kobayashi, S.Moriyama, Y.Nishio, K.Kajita and W.Sasaki, Chem Lett., 1819(1987).
4. T.Nakamura, H.Tanaka, M.Matsumoto, H.Tachibana, E.Manada and Y.Kawabata, Chem Lett., 1667(1988).
5. G.Steimecke, H.J.Sieler, R.Kirmse and E.Hoyer, Phosphorus and Sulfur, 7, 49(1979).