Crystal Structure of Double Salts with Different Organic Cations Obtained from the Reaction of Tetrabutylammonium Bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(II) and 1-Propyl-1,4-diazabicyclo[2.2.2]octanium Bromide

Kei Onozaki* and **Kazuo Miyamura**

Department of Chemistry, Faculty of Science, Tokyo University of Science,
1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601

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The reaction between $(Bu_4N)_2[Ni(dmit)_2]$ (Bu_4N = tetrabutylammonium, dmit = 2-thioxo-1,3-dithiole-4,5-dithiolato) and the bromide of 1-propyl-1,4-diazabicyclo[2.2.2]octanium (C3DABCO) yielded crystals of the double salt $(Bu_4N)_4(C3DABCO)_2[Ni(dmit)_2]_3$ together with $(C3DABCO)_2[Ni(dmit)_2]$. The structures of the two crystals have been solved and compared. The crystal of the double salt was made up of one $(C3DABCO)_2[Ni(dmit)_2]$ and two $(Bu_4N)_2[Ni(dmit)_2]$ units. In both units, planar $[Ni(dmit)_2]^{2-}$ was sandwiched by two cations. The Ni–N$^+$ distance of the $(C3DABCO)_2[Ni(dmit)_2]$ unit in a single salt was 0.3 Å longer than that in the double salt. The ethyl- and butyl-substituted analogues, abbreviated as C2DABCO and C4DABCO, respectively, were also synthesized by a similar procedure, but did not form a double salt. However, the volume of the C4DABCO single salt was found to be smaller than that of the C3DABCO single salt, although the alkyl chain was elongated.

Since the discovery of the superconducting metal complex 2-thioxo-1,3-dithiole-4,5-dithiolato (dmit) complex in 1986,[1] dmit complexes have been subjects of great interest for studies on molecular conductors and superconductors. Several superconductors based on the metal complex of the dmit ligand have been discovered.[2–7] In the course of exploration for new superconductors, a variety of complexes have been synthesized and examined. Instead of Ni and Pd, which exhibit superconductivity, Cu, Au, Pt, Sn, Sb, V, etc., have been investigated. However, there have been no reports concerning the double salts of the dmit complex to date.

A double salt is a salt constituted of plural cations or anions. A well known example of a double salt is alum $KAl(SO_4)_2 \cdot 12H_2O$. Formation of a double salt occurs by a subtle balance of solubility, which is a consequence of crystal packing. Usually, a single salt pair has the lowest solubility among the possible combinations of a cation(s) and anion(s), and the precipitation of a single salt is preferred. There are a wide variety of double salts that have been reported, but ones with organic cations and a metal complex anion[8–10] are rare.

Here, we report the first example of a double salt of the dmit complex obtained from the reaction of tetrabutylammonium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(II) and 1-propyl-1,4-diazabicyclo[2.2.2]octanium (C3DABCO) bromide. Our aim was to organize organic cations by the self-assembling nature of alkyl ammonium ions with long alkyl groups.[11,12] If it works out effectively, the electrostatic interaction between the cation and dmit complex anion should be weakened and consequently lead to the stacking of dmit complexes, which is crucially important for the electroconductivity. The bulky 1-alkyl-1,4-diazabicyclo[2.2.2]octanium (C*n*DABCO: *n* represents the alkyl chain length) cation has also been chosen to reduce the electrostatic interaction between the cation and anion by the steric effect. We have synthesized a series of C*n*DABCO of different alkyl chain lengths, and when the propyl-substituted analogue C3DABCO was used as a cation, a double salt was obtained unexpectedly.

Experimental

Syntheses. All reagents were of reagent grade and used without further purification. $(Bu_4N)_2[Ni(dmit)_2]$ was synthesized by the reported method.[13] The bromide of C3DABCO was synthesized as follows: To 1,4-diazabicyclo[2.2.2]octane (1.12 g, 10 mmol) dissolved in ethanol (40 mL) was added dropwise 1-bromopropane (0.95 mL, 10.5 mmol), followed by stirring for 100 h at room temperature. Ethanol was then evaporated to obtain a crude product. A silica-gel column with the use of the gradient technique of chloroform–methanol was used to purify the product. Yield 1.93 g (80%).

By the inter-diffusion of the acetonitrile solutions of $(Bu_4N)_2[Ni(dmit)_2]$ and (C3DABCO)Br under a nitrogen atmosphere at room temperature, two different types of crystals were obtained after 10 d. The major product was needle-like crystals of $(C3DABCO)_2[Ni(dmit)_2]$; bulky crystals of $(Bu_4N)_4(C3DABCO)_2[Ni(dmit)_2]_3$ were also obtained as a minor product. Since the crystals were obtained always as a mixture, structural analysis was performed without elemental analysis.

The $[Ni(dmit)_2]^{2-}$ salts of C2DABCO and C4DABCO were synthesized by the similar procedures for C3DABCO salt given above using 10.5 mmol of bromoethane and 1-bromobutane, respectively, instead of 1-bromopropane. Yields were ca. 75% and never below 60% in both cases. Elemental Analysis: $(C2DABCO)_2[Ni(dmit)_2]$ found(calcd) C, 35.64(36.01%); H, 4.28(4.67%); N, 7.46(7.63%). $(C4DABCO)_2[Ni(dmit)_2]$ found(calcd) C, 39.00(39.53%); H, 5.00(5.36%); N, 6.79(7.09%).

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Table 1. The Crystallographic Data for Complex Salts

Identification code	$(C2DABCO)_2[Ni(dmit)_2]$	$(C3DABCO)_2[Ni(dmit)_2]$	$(C4DABCO)_2[Ni(dmit)_2]$	$(Bu_4N)_4(C3DABCO)_2[Ni(dmit)_2]_3$	$(Bu_4N)_2[Ni(dmit)_2]$
Empirical formula	$C_{22}H_{34}N_4NiS_{10}$	$C_{24}H_{38}N_4NiS_{10}$	$C_{26}H_{42}N_4NiS_{10}$	$C_{100}H_{182}N_8Ni_3S_{30}$	$C_{38}H_{72}N_2NiS_{10}$
Formula weight	733.84	761.94	789.95	2634.47	936.29
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2(1)/c$	$P\bar{1}$	$P1$	$P\bar{1}$	$P2(1)/c$
Unit cell dimensions	$a = 12.3236(7)$ Å	$a = 8.598(5)$ Å	$a = 8.5040(6)$ Å	$a = 12.4198(6)$ Å	$a = 8.4135(5)$ Å
	$b = 11.0301(6)$ Å	$b = 9.954(6)$ Å	$b = 10.0582(7)$ Å	$b = 13.4264(7)$ Å	$b = 14.7589(9)$ Å
	$c = 12.9758(7)$ Å	$c = 11.307(7)$ Å	$c = 11.3229(8)$ Å	$c = 20.3074(10)$ Å	$c = 19.4437(11)$ Å
	$\alpha = 90°$	$\alpha = 86.742(13)°$	$\alpha = 90.2420(10)°$	$\alpha = 86.1450(10)°$	$\alpha = 90°$
	$\beta = 117.5010(10)°$	$\beta = 70.493(11)°$	$\beta = 110.2460(10)°$	$\beta = 78.8780(10)°$	$\beta = 96.3180(10)°$
	$\gamma = 90°$	$\gamma = 72.907(10)°$	$\gamma = 105.4510(10)°$	$\gamma = 88.7660(10)°$	$\gamma = 90°$
Volume/Å^3	1564.50(15)	871.0(10)	870.83(11)	3315.1(3)	2399.7(2)
Z	2	1	1	1	2
Density (calculated)/Mg m^{-3}	1.558	1.453	1.506	1.320	1.296
Density (observed)/Mg m^{-3}	1.554	1.458	1.508	1.325	
Reflections collected	10588	5565	6055	22039	15733
Independent reflections	3843 [R(int) = 0.0336]	3827 [R(int) = 0.3238]	4947 [R(int) = 0.0269]	14860 [R(int) = 0.0313]	5499 [R(int) = 0.0452]
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0304$	$R1 = 0.0963$	$R1 = 0.0400$	$R1 = 0.0481$	$R1 = 0.0360$
	$wR2 = 0.0805$	$wR2 = 0.2486$	$wR2 = 0.0980$	$wR2 = 0.1251$	$wR2 = 0.0787$

X-ray Crystallographic Analysis. A single crystal suitable for X-ray diffraction study was mounted on a glass capillary, transferred to a Bruker AXS SMART diffractometer equipped with a CCD area detector and Mo Kα ($\lambda = 0.7103$ Å) radiation, and centered in the beam at 293(2) K. The structures were solved and refined with SHELX-97[14] using the direct method and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The ORTEP diagrams given in the figures were drawn with 50% probability ellipsoids. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-284157 for compound $(C2DABCO)_2[Ni(dmit)_2]$, CCDC-284158 for compound $(C4DABCO)_2[Ni(dmit)_2]$, CCDC-284159 for compound $(C3DABCO)_2[Ni(dmit)_2]$, CCDC-284160 for compound $(Bu_4N)_4(C3DABCO)_2[Ni(dmit)_2]_3$. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

First, in order to make single crystal of $(C3DABCO)_2[Ni(dmit)_2]$ suitable for X-ray crystallographic analysis, the solubility of C3DABCO bromide and $(Bu_4N)_2[Ni(dmit)_2]$ towards various solvents was investigated. When acetonitrile was used, however, two different types of crystals were obtained. The major product was a needle-like crystal, which by X-ray crystallographic analysis was identified as the aimed product $(C3DABCO)_2[Ni(dmit)_2]$. The minor product, also analysed by X-ray crystallography, was a bulky crystal of the double salt $(Bu_4N)_4(C3DABCO)_2[Ni(dmit)_2]_3$. It is quite a rare occasion to obtain a double salt with different organic cations. Similar recrystallization carried out with C2DABCO and C4DABCO did not result in the formation of double salts, but only in single salts. The crystal data of these crystals together with those of already reported $(Bu_4N)_2[Ni(dmit)_2]$ are summarized in Table 1.

Crystal Structure of a Double Salt $(Bu_4N)_4(C3DABCO)_2[Ni(dmit)_2]_3$. The crystal structure of $(Bu_4N)_4(C3DABCO)_2[Ni(dmit)_2]_3$ in Fig. 1 shows that the crystal is comprised

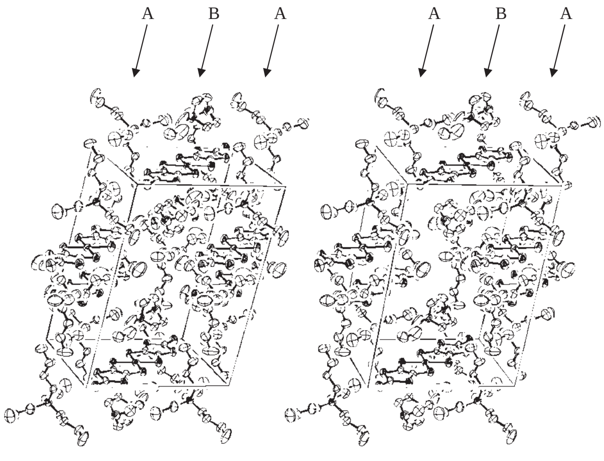

Fig. 1. Crystal structure of double salt $(Bu_4N)_4(C3DABCO)_2[Ni(dmit)_2]_3$ (stereo view). A and B indicate the $(Bu_4N)_2[Ni(dmit)_2]$ and $(C3DABCO)_2[Ni(dmit)_2]$ layers, respectively.

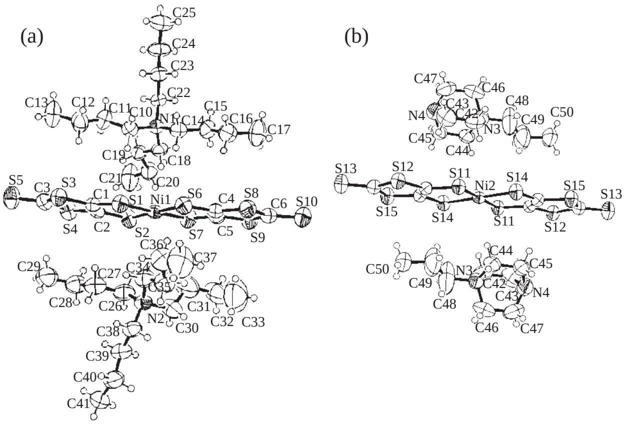

Fig. 2. Molecular structures of (a) $(Bu_4N)_2[Ni(dmit)_2]$ unit and (b) $(C3DABCO)_2[Ni(dmit)_2]$ unit, in $(Bu_4N)_4(C3DABCO)_2[Ni(dmit)_2]_3$ with numbering scheme.

of two $(Bu_4N)_2[Ni(dmit)_2]$ and one $(C3DABCO)_2[Ni(dmit)_2]$ units, as given in Figs. 2a and 2b, respectively, along with the numbering scheme. In all units, the $[Ni(dmit)_2]^{2-}$ anion is sandwiched by two cations placed above and below the molecular plane of the anion. The $[Ni(dmit)_2]^{2-}$ sandwiched by C3DABCO adopted a planar structure, while those sandwiched by Bu_4N were distorted with bending as large as 4.59° present at the coordinating sulfur atoms. In the $(C3DABCO)_2[Ni(dmit)_2]$ unit, the Ni–N^+ distance was 4.42 Å, while in the $(Bu_4N)_2[Ni(dmit)_2]$ units they were 4.66 and 4.41 Å.

The propyl group of C3DABCO adopted an all-*trans* conformation, and were almost parallel to the molecular axis of $[Ni(dmit)_2]$. Seven out of the eight butyl groups of Bu_4N in $(Bu_4N)_2[Ni(dmit)_2]$ units also adopted an all-*trans* conformation, but one butyl group had an end-*gauche* methyl group. The C30–C31–C32–C33 torsion angle in Fig. 2a was 71.42°, while the other torsion angles were within the range of 163–180°. Three butyl groups of Bu_4N, including that with the end-*gauche* methyl group, lied parallel to the molecular plane of $[Ni(dmit)_2]$, and the remaining one butyl group stuck out in the normal direction to the plane. The shortest intermolecular S–S distance of $[Ni(dmit)_2]$ was about 4 Å between the end C=S groups, which was larger than the van der Waals contact S–S distance of 3.7 Å.

In the crystal, $[Ni(dmit)_2]$ complexes were parallel to each other as shown in Fig. 1; however, they were separated by cations so that no apparent S–S contact could be observed. The butyl groups with end-*gauche* conformation are located so as to face their chains to each other. This indicates that the steric repulsion between the butyl chains is the cause of the unstable end-*gauche* conformation. The shortest intermolecular S–S distance was 3.889 Å, too far for electronic interaction.

Comparison with Single Salts. The structural analysis of the single salt $(C3DABCO)_2[Ni(dmit)_2]$ revealed that the $(C3DABCO)_2[Ni(dmit)_2]$ unit was also present as shown in Fig. 3b. The molecular structure was almost the same as that in Fig. 2b, but the Ni–N^+ distance was 4.771 Å, which was about 0.3 Å longer than that in the double salt. $[Ni(dmit)_2]$ also adopted a square-planar geometry. The torsion angle of the propyl group was 178.05°, indicative of the *trans*-conformation. No intermolecular S–S contact was present.

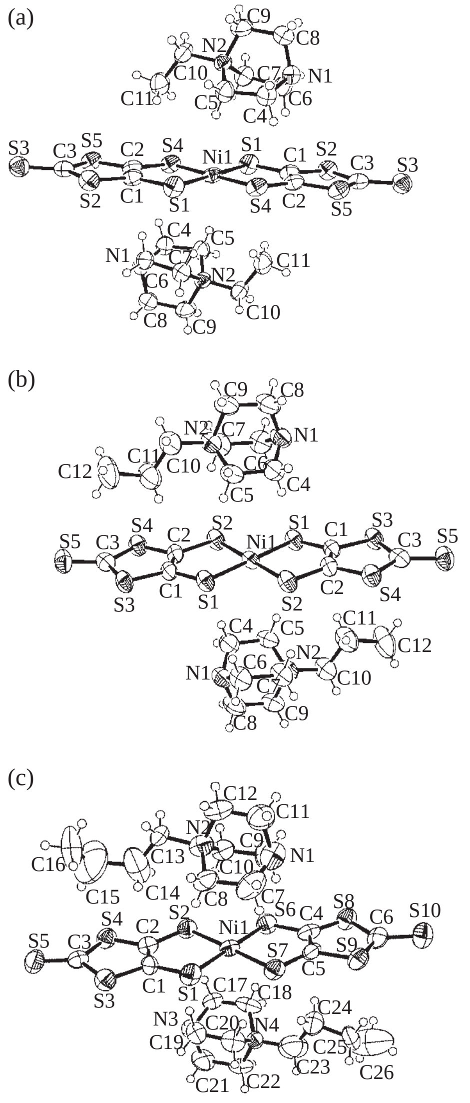

Fig. 3. Molecular structures of (a) $(C2DABCO)_2[Ni(dmit)_2]$ unit, (b) $(C3DABCO)_2[Ni(dmit)_2]$ unit, and $(C4DABCO)_2[Ni(dmit)_2]$ unit, in the single salt.

In order to compare the crystal structure of the $(Bu_4N)_2[Ni(dmit)_2]$ obtained from the same conditions, recrystallization of $(Bu_4N)_2[Ni(dmit)_2]$ from an acetonitrile solution was attempted, but the solubility was too high to obtain crystals of sufficient quality. Hence, the addition of a small amount of ethanol was needed to crystallize $(Bu_4N)_2[Ni(dmit)_2]$. The obtained crystallographic data given in Table 1 are in accord with the reported data.[15] The crystal was composed of $(Bu_4N)_2[Ni(dmit)_2]$ units similar to that in the double salt. However, two out of the four butyl groups in Bu_4N were all-*trans*, while the other two contained the end-*gauche* conformation. This conformation has also been reported for $(Bu_4N)_2[Pd(dmit)_2]$[16–18] and $(Bu_4N)_2[Cu(dmit)_2]$.[19] Furthermore, a similar conformation was also reported for the Bu_4N salts of nonplanar complexes $[Cd(dmit)_2]$[20] and $[Zn(dmit)_2]$.[21] However, in $(Bu_4N)_2[Pt(dmit)_2]$,[1] all butyl groups were reported to adopt an all-*trans* conformation. Thus, it can be said that the conformation of Bu_4N in the double salt is rather unusual. Since the *gauche* conformation is energetically, the structure of the dou-

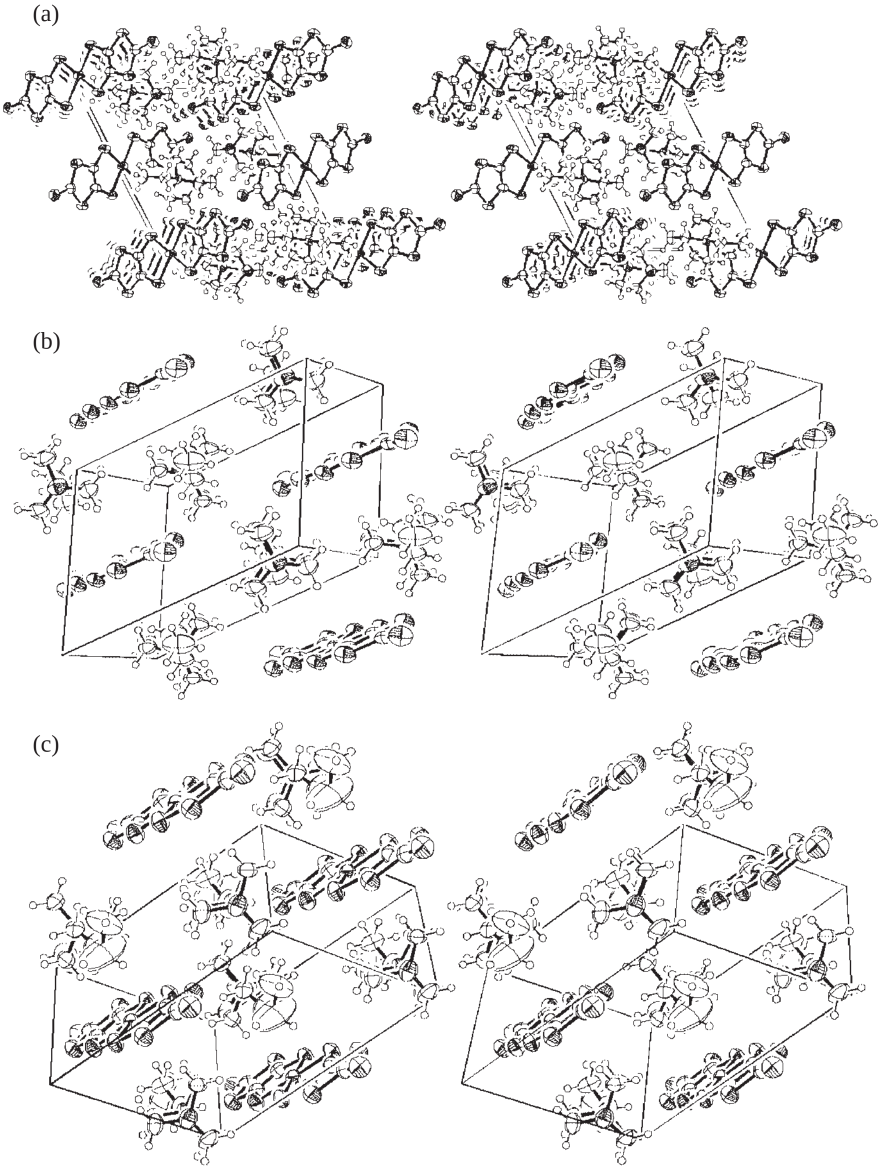

Fig. 4. Crystal structures of (a) $(C2DABCO)_2[Ni(dmit)_2]$, (b) $(C3DABCO)_2[Ni(dmit)_2]$, and (c) $(C4DABCO)_2[Ni(dmit)_2]$ (stereo views).

ble salt is energetically in regards to the conformation of Bu_4N.

We could calculate the theoretical density of the double salt from the observed densities of the single salts. The calculated value, however, was 1.348 Mg m^{-3}, which was slightly larger than the observed value of 1.320 Mg m^{-3}. This fact suggests that the crystal packing of the double salt is slightly light.

Crystal Structures of C2DABCO and C4DABCO Salts. We have also synthesized and examined a series of C*n*DABCO salts with different alkyl chain lengths. In the course of the study, we found that the crystal packing of C3DABCO salt is unusually loose. All crystals were constituted of the $(CnDABCO)_2[Ni(dmit)_2]$ unit, as given in Figs. 3a–3c. The molecular structures of these units were so similar that no apparent difference could be noticed except for the alkyl chain length. However, the data of the volume per $(CnDABCO)_2[Ni(dmit)_2]$ unit calculated from the lattice volume given in Table 1 show that the $(C3DABCO)_2[Ni(dmit)_2]$ unit (871.01 Å^3) occupies a larger space than the $(C4DABCO)_2[Ni(dmit)_2]$ unit (870.83 Å^3). This is unusual since the latter unit has two more methylene groups. The crystal structures of $(CnDABCO)_2[Ni(dmit)_2]$ ($n = 2$–4) given in Figs. 4a–4c show that the crystal structures of $(C3DABCO)_2[Ni(dmit)_2]$ and $(C4DABCO)_2[Ni(dmit)_2]$ are alike, but that of $(C2DABCO)_2[Ni(dmit)_2]$ is different from the two. Figures 4b and 4c are the stereo views from the molecular axis of C*n*DABCO. The difference between $(C3DABCO)_2[Ni(dmit)_2]$ and $(C4DABCO)_2[Ni(dmit)_2]$ is that the end-methylene groups in the $(C4DABCO)_2[Ni(dmit)_2]$ unit stick out to the vacant space present in the crystal packing of $(C3DABCO)_2[Ni(dmit)_2]$ by adopting the end-*gauche* conformation shown in Fig. 5c.

Figures 5a–5c show the conformation of C*n*DABCO in the crystals of corresponding single salts. There were two independent structures for C4DABCO, but both structures adopted the end-*gauche* structure, although the orientation of the end-methyl groups were different (Fig. 5c). It is noteworthy that if the end-methyl group adopts the *trans* conformation, the mo-

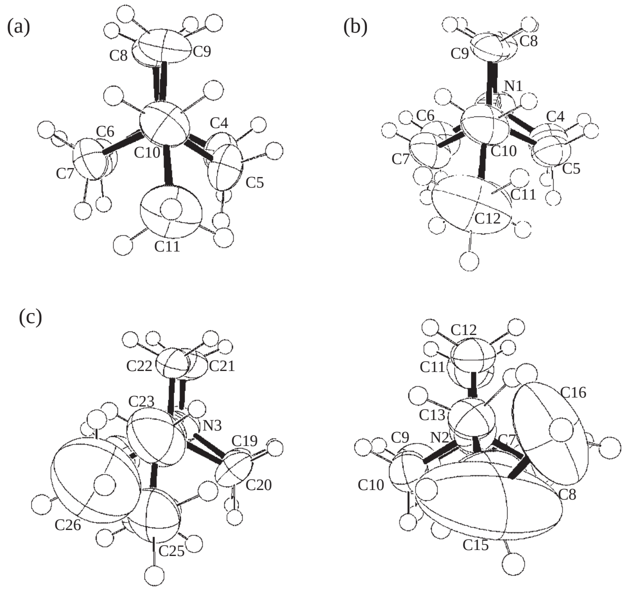

Fig. 5. Conformation of (a) C2DABCO, (b) C3DABCO, and (c) two independent C4DABCO. Notice that the end-methyl groups of C4DABCO are sticking out in different directions.

lecular shape of C4DABCO loses its compactness, and the crystal structure is altered totally. In the crystal structure of $(C3DABCO)_2[Ni(dmit)_2]$, there is a large vacant space ahead of the propyl group. By adopting the end-*gauche* structure in Fig. 5c, the end-methyl group of C4DABCO filled the vacant space so that the volume did not increase but rather decreased, probably due to the van der Waals attractive interaction. This unusually loose packing of the $(C3DABCO)_2[Ni(dmit)_2]$ single salt may be the reason for the double salt formation.

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