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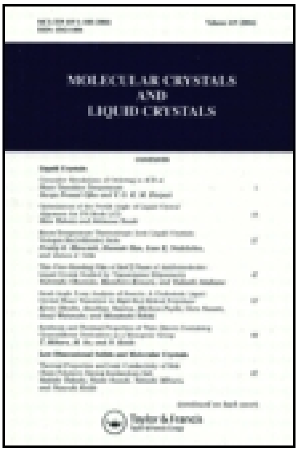

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Structures and Magnetic Properties Of $[Cu(cyclam)(CH_3CN)_2][Ni(dmit)2]2$ and $[Cu(cyclam)]_2[2, 5\text{-DM-DCNQI}]_5$

Hiroki Oshio [a]

[a] Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai, 980, Japan

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STRUCTURES AND MAGNETIC PROPERTIES OF $[Cu(cyclam)(CH_3CN)_2][Ni(dmit)_2]_2$ and $[Cu(cyclam)]_2[2,5\text{-DM-DCNQI}]_5$

HIROKI OSHIO
Department of Chemistry, Faculty of Science, Tohoku University,
Aoba-ku, Sendai 980, Japan

Abstract Organic radical metal complexes $[Cu^{II}(cyclam)(CH_3CN)_2][Ni(dmit)_2]$ (**1**) and $[Cu^{II}(cyclam)]_2[2,5\text{-DM-DCNQI}]_5$ (**2**) (cyclam = 1,4,8,11-tetraazacyclotetradecane, dmit = 1,3-dithiol-2-thion-4,5-dithiolate and 2,5-DM-DCNQI = 2,5-dimethyl-N,N'-dicyanoquinonediimine) have been prepared, and their crystal structures and magnetic properties have been studied. In complex (**1**), the paramagnetic copper atom is magnetically isolated from $[Ni(dmit)_2]^-$, while two $[Ni(dmit)_2]^-$ molecules make an antiferromagnetically coupled dimer ($J = -153(2)$ cm^{-1}). In complex (**2**), there are three kinds of 2,5-DM-DCNQI anions (**A**, **B**, and **C**),where both **A** and **B** coordinate to the crystallographically independent copper complexes, respectively. Two **B**s and **C** form diamagnetic trimer (**BCB**), which constructs quasi-one-dimensional chain (···**BCBBCB**···). Structural data and MNDO calculation suggest that the formal charges of each anion are -1, -2/3, and -2/3, respectively. Magnetic susceptibility measurement for (**2**) suggest that copper complexes are magnetically isolated from the anion radicals and mono-anions **A** forms a strongly coupled ($J < -400$ cm^{-1}) dimer.

Introduction

Considerable effort has been devoted to build a molecular based ferromagnet. Some coordination[1,2,3] and pure organic[4,5] compounds have been revealed to show a spontaneous magnetization at very low temperature. In order to build a molecular based ferromagnet, it is indispensable to have a strong and three dimensional magetic interaction in molecular assemblies. We have been concerned with control of intramolecular and intermolecular magnetic interactions in multi-nuclear and low-dimensional complexes, respectively, to establish the basic technology to build such

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molecular assemblies. That is, a spin polarization mechanism[6] (topological network of dπ spins to the pπ orbitals of a bridging ligand) was applied to have a ferromagnetic interaction ($J = 0.62\ cm^{-1}$) in a binuclear complex $[Fe_2(bpmar)(H_2O)_4](NO_3)_4 \cdot 3H_2O$ (H_2bpmar = 4,6-bis[N,N-bis(2'-pyridylmethyl)aminomethyl]-2-methylresorcinol)[7] and an orthogonal arrangement of adjacent magnetic orbitals allows a intrachain ferromagnetic interaction ($J = 1.22\ cm^{-1}$) in the zig-zag chain complex $[Cu(bpy)(ox)] \cdot 2H_2O$ (bpy = bipyridine).[8] However, the magnitudes of the above ferromagnetic interactions seem not to be strong enough to attain the ferromagnetism even if the magnetic interaction is extended to three dimensional system. Some organic radical systems are known to retain the metallic characteristics down to very low temperature and these solids have a fairly strong electronic interaction through their network system. If a metal complex joins the network, such molecular assemblies are expected to have interesting magnetic and conductive behaviors. In this paper, copper(II) complexes $[Cu(cyclam)]^{2+}$ with organic radicals $[Ni(dmit)]^-$ (cyclam = 1,4,8,11-tetraazacyclotetradecane, dmit = 4,5-dimercapto-1,3-dithiole-2-thione) and $[2,5\text{-}DM\text{-}DCNQI]^{n-}$ (= 2,5-dimethyl-dicyanoquinonediimine), which have been reported to be metallic down to very low temperature,[9,10] were prepared and their crystal structure and magnetic properties were studied.

Experimental

Syntheses All chemicals used were commercially available and used without further purification. $[Cu(cyclam)](ClO_4)_2$,[11] $[Bu^t_4N][Ni(dmit)_2]$,[12] and Li[2,5-DM-DCNQI][13] were prepared by the literature methods. To a hot acetonitrile solution (200 ml) of $[Bu^t_4N][Ni(dmit)_2]$ or Li[2,5-DM-DCNQI] was added a acetonitrile solution of $[Cu(cyclam)](ClO_4)_2$. After stands for overnight, black crystallines were formed and one of them ($[Cu(cyclam)(CH_3CN)_2][Ni(dmit)_2]_2$ (**1**) and $[Cu(cyclam)]_2[2,5\text{-}DM\text{-}DCNQI]_5$ (**2**)) was subjected to the X-ray analysis. Anal. for (**1**). Calcd for $C_{26}H_{30}CuN_6Ni_2S_{20}$: C, 21.90; H, 2.12; N 5.89 Found: C, 22.20; H, 2.07; N 5.80. Anal. for (**2**). Calcd for $C_{70}H_{88}Cu_2N_8$: C, 58.03; H, 6.12; N 27.07. Found: C, 57.91; H, 6.18; N, 26.83.

Magnetic Measurement

Temperature dependent magnetic susceptibilities of powdered samples were measured by an Oxford Faraday type Magnetic Balance system.

Molecular Orbital Calculation

Semi-empirical molecular orbital calculation MNDO method[14] was done for the DCNQI molecule.

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X-ray Crystallography. Black tabular crystals of (**1**) and (**2**) (dimensions 0.48x0.40x0.04 mm and 0.68x0.50x0.04 mm, respectively) were mounted on a glass fiber and coated with epoxy to retard possible solvent loss. Data were collected at 295 K on a Rigaku AFC5R and an Enraf-Nonius CAD-4 diffractometers using ω - 2θ scan technique to a maximum 2θ = 55 and 60° for (**1**) and (**2**), respectively. Crystal data: $[Cu(cyclam)(CH_3CN)_2][Ni(dmit)_2]_2$ (**1**), triclinic space group P\o(1,¯) with $Z = 2$ in a unit cell of dimensions $a = 11.817(4)$Å, $b = 12.010(4)$Å, $c = 9.561(4)$ Å, $\alpha = 115.59(2)°$, $\beta = 97.72(3)°$, $\gamma = 95.62(3)°$, and $V=1194.1(7)Å^3$ with $R = 0.065$ and $R_w = 0.078$ for 4151 data with $|Fo| > 3\sigma(Fo)$. $[Cu(cyclam)]_2[2,5\text{-}DM\text{-}DCNQI]_5$ (**2**), triclinic space group P\o(1,¯) with $a = 9.518(2)$Å, $b = 14.357(4)$Å, $c = 14.582(2)$ Å, $\alpha = 118.10(2)°$, $\beta = 91.60(2)°$, $\gamma = 90.70(2)°$, $V=1756.4(8)Å^3$, and $Z = 1$ with $R = 0.059$ and $R_w = 0.071$ for 5864 data with $|Fo| > 3\sigma(Fo)$

Results and Discussion

Molecular Structure of $[Cu(cyclam)(CH_3CN)_2][Ni(dmit)_2]$ (**1**). Perspective view of the unit cell is shown in Figure 1. The copper atom on the inversion center is bound in distorted octahedral fashion,where four nitrogen atoms from cyclam and two nitrogen atoms from solvent molecule occupy the equatorial and axial sites, respectively. Bond distances between copper and coordinating atoms are 2.028(7) - 2.019(7) Å for equatorial nitrogen and 2.491(6) Å for axial nitrogen atoms. A nickel atom is coordinated by four sulfur atoms and the coordination geometry about nickel atom is square planar. Intermolecular S···S contacts are in the range of 3.026(2) - 3.687(3) Å. As shown in Figure 1 and the short intermolecular S···S contacts, it can be concluded that the two anions ($[Ni(dmit)]^-$) form dimer. Interplanar distances in two $[Ni(dmit)_2]^-$ molecules are in the range of 3.477(2) - 3.655 (2) Å.

Molecular Structure of $[Cu(cyclam)]_2[2,5\text{-}DM\text{-}DCNQI]_5$ (**2**). Ortep drawings of the projection view on bc-plane is depicted in Figure 2. The black crystal consists of two kinds of $[Cu(cyclam)]^{2+}$ and three kinds (**A**, **B**, and **C**) of $[2,5\text{-}DM\text{-}DCNQI]^{n-}$ which are crystallographically independent. Two copper atoms are located on the center of symmetry and their coordination geometries are axially elongated octahedron. The equatorial plane of the copper atom consists of four nitrogen atoms from cyclam, and two axial positions are occupied by nitrogen atoms of nitrile group of 2,5-DM-DCNQI (**A** and **B**). The bond lengths between the copper and equatorial nitrogen atoms (2.017(3) - 2.031(3) Å) are shorter than those for axial bonds (2.410(3) - 2.502(3) Å). The magnetic orbital (ground state) of the copper atoms is a $d_{x^2-y^2}$ orbital which is on the equatorial plane. Two **A**s form dimer and their interplanar distance is 3.71 Å.

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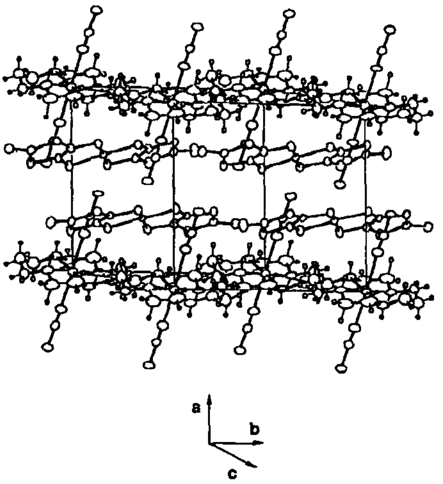


FIGURE 1.
Perspective view of theunict cell of $[Cu(cyclam)(CH_3CN)_2][Ni(dmit)_2]$ (**1**).

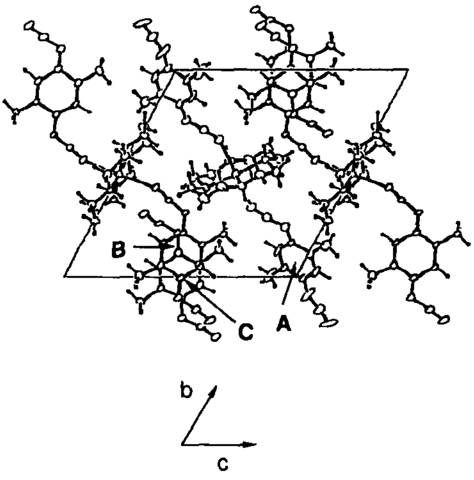
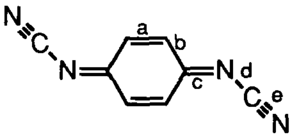


FIGURE 2.
Projection view on bc-plane of $[Cu(cyclam)]_2[2,5\text{-DM-DCNQI}]_5$ (**2**).

TABLE I. List of Bond Lengths of DCNQI series with a Different Formal Charge

compound	a	b	c	d	e	formal charge
DCNQI	1.336(2)	1.450(2)	1.303(2)	1.334(2)	1.150(2)	neutral[a]
		1.446(2)				
$Cu[2,5\text{-DM-DCNQI}]_2$	1.350(6)	1.433(6)	1.342(6)	1.312(6)	1.159(6)	-1/2[b]
		1.442(6)				
$Li[2,5\text{-DM-DCNQI}]_2$	___	___	1.323(3)	1.328(3)	1.145(3)	-1/2[c]
Conformer **B**	1.356(5)	1.431(4)	1.350(4)	1.306(4)	1.152(4)	-2/3
	1.354(5)	1.412(6)	1.334(4)	1.330(4)	1.145(4)	
Conformer **C**	1.356(4)	1.444(4)	1.341(4)	1.326(4)	1.155(5)	-2/3
		1.423(6)				
Conformer **A**	1.376(7)	1.361(5)	1.374(6)	1.282(6)	1.109(7)	-1
	1.372(5)	1.385(6)	1.405(5)	1.313(5)	1.149(5)	

[a] refrerence 15(a). [b] Reference 10(c). [c] Reference 15(b)



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C on the inversion center forms trimer with two **B**s and the trimers (**BCB**) make a quasi-one dimensional structure (···**BCBBCB**···). The overlap of the 2,5-DM-DCNQI molecules within the trimer (**BCB**) is of usual "double bond ring" type and the interplanar distances within the trimer and between trimers are in the range of 3.03 - 3.18 Å and 3.13 - 3.14 Å, respectively. Interatomic distances of the [DCNQI] molecule can suggest the formal oxidation number of the molecule. Principal bond lengths of the anions are listed in Table I together with those of other DCNQIs.[15] Interatomic bond lengths of **B** and **C** are identical with each other. Comparison of the bond lengths of **B** or **C** with **A** clearly reveals the bonds **a** and **c** to be longer for **A**, and bonds **b** and **d** to be shorter for **A** (see Table I) . The different bond lengths can be interpreted by the virtue of molecular orbital calculation. MNDO molecular orbital calculation for DCNQI$^-$ was done and its SOMO (singly occupied molecular orbital) was depicted in Figure 3. Bonds like **a** and **c** with an anti-bonding character should be lengthen as the negative charge of the molecule increases, while a bond like **b** with a bonding character should be reverse, and a bond like **e** with a small orbital coefficient should be insensitive. It should be concluded that the formal charge of **A** should be more negative than those for **B** and **C**. Tendency of the change in bond lengths with different negative charges is in good accord with other DCNQIs (Table I). The formal charges for **B** and **C**, whose intramolecular bond lengths are similar are expected to be identical with each other and they should be smaller than that for **A**. Total number of charges (spins) for the anions is four, so the four charges can be divided into two each for the trimer (two **B**s and **C**) and dimer (two **A**s). Hense, the formal charges for **B**, **C**, and **A** are concluded to be -2/3, -2/3, and -1, respectively.

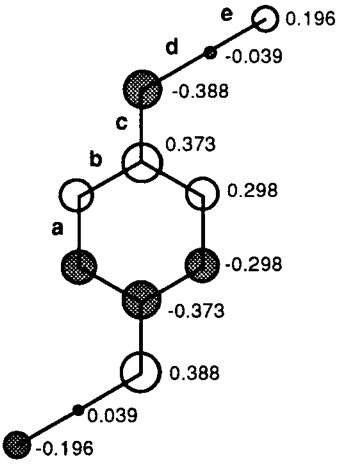

FIGURE 3. MNDO diagram (SOMO) of [DCNQI]$^-$

Magnetic Properties. Variable temperature magnetic susceptibility data for (**1**) and (**2**) were collected down to 2.5 K and $\chi_m T$ vs. temperature plots were depicted in Figure 4, where χ_m is the molar magnetic susceptibility. Small humps appearing in the

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temperature range from 30 to 50 K in both complexes are due to the absorbed oxygen. Complex (**1**) has $\chi_m T$ values steadily decrease from 0.90 emu mol^{-1} K at 260 K down to 0.50 emu mol^{-1} K at 80 K, whereupon the values do not change down to 14 K. X-ray structural analysis showed that the copper ion is magnetically isolated from [Ni(dmit)2]$^-$ ions whereas two [Ni(dmit)2]$^-$ molecules form dimer. The magnetic susceptibility data for (**1**) were fit to the sum of Curie (for copper complex) and Bleaney-Bauweres[16] (for [Ni(dmit)2]$^-$ dimer) equations, as shown in equation (1),

$$\chi_m = \frac{Ng_{Cu}^2\beta^2}{4kT} + \frac{Ng^2\beta^2}{kT}\left[\frac{2}{3+\exp(\;2J/kT)}\right] + N\alpha \qquad (1)$$

where N, g_{Cu}, g, β, k and J represent Avogadro's number, g value for copper, g value for [Ni(dmit)2]$^-$, Bohr magneton, Boltzmann, and exchange coupling constant, respectively. The temperature independent paramagnetism, Nα, was taken as 60x10^{-6} emu/Cu. The best fit of equation (1) was obtained with J = -153(2) cm^{-1}, g_{Cu} = 2.253(6), and g = 2.08(2).

$\chi_m T$ value of (**2**) gradually decreases from 1.10 emu mol^{-1} K at 269.0 K to 1.05 emu mol^{-1} K at 100 K, and then $\chi_m T$ value does not change down to 10 K followed by sudden decrease. As stated in the structural study of (**2**), there are two kinds of copper complexes and three kinds of DCNQI molecules (**A**, **B**, and **C**). Although **A** and **B** coordinate to the copper atoms, the magnetic interaction between the copper atoms and **A** or **B** must be negligible because of the long bond lengths (2.410(3) and 2.502(3) Å) between the copper and the coordinating nitrogen atoms of **A** or **B**. Interplanar distances within trimer (**BCB**) are in the range of 3.030 - 3.179 Å. Some anion radical salts of

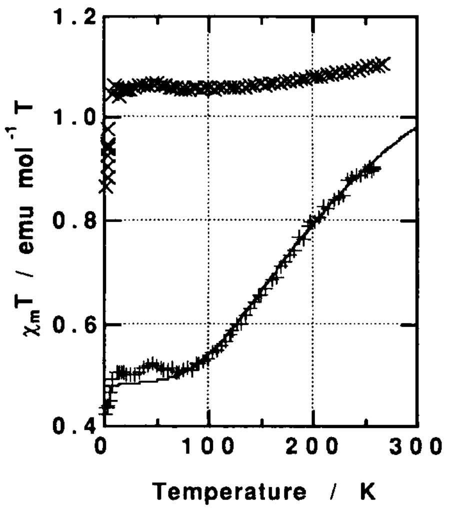

FIGURE 4. $\chi_m T$ vs. T plot of (+) [Cu(cyclam)(CH$_3$CN)$_2$][Ni(dmit)$_2$]$_2$ and (x) [Cu(cyclam)]$_2$[2,5-DM-DCNQI]$_5$

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DCNQI series has been reported to be metallic down to very low temperature. Stacking mode of such conductors is "ring-double bond" type which is same type as (**2**) and their interplanar distances are in the range 3.13 - 3.27 Å. It can be expected that two spins on the trimer (**BCB**) are strongly coupled to be diamagnetic. Gradual increase of χ_mT value as the temperature raised is thought to be due to the DCNQI dimer (two **A**s) and this magnetic behavior allows an estimate of $J < -400$ cm^{-1} for the dimer.

Conclusion

Organic radicals ([Ni(dmit)$_2$] and [2,5-DM-DCNQI]), which are known as an organic conductor in the mixed valence state, were used to build a metal radical complex network. In [Cu(cyclam)(CH$_3$CN)$_2$][Ni(dmit)$_2$]$_2$, the cations are magnetically isolated, while the anions form dimer with antiferromagnetic interaction (J = -153(2) cm^{-1}). In [Cu(cyclam)]$_2$[2,5-DM-DCNQI]$_5$ (**2**), the copper complexes join the quasi-one dimensional network which consists of 2,5-DM-DCNQI molecules. The magnetic interaction of copper complexes with paramagnetic 2,5-DM-DCNQI are negligible because the Jahn-Teller distortion of the copper atoms (d^9 configuration) makes the metal-nitrile bonds weak. The paramagnetic metal complexes, of which magnetic orbital directs at the coordinating atom of the organic radicals, should be introduced in order to have the magnetic interaction between metal sites and network components.

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