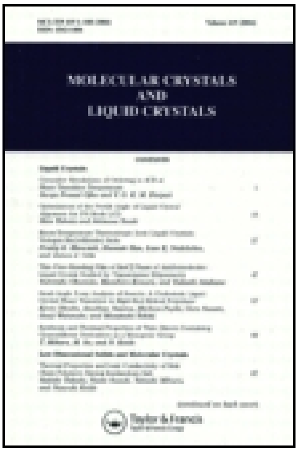

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Intermolecular Arrangements of p-Substituted Aniliniums in the Interlayer of Cupric Chloride

Taketoshi Sekine [a] , Tsunehisa Okuno [a] & Kunio Awaga [a]
[a] Department of Pure and Applied Sciences, The University of Tokyo, Komaba, Meguro, Tokyo, 153, Japan

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INTERMOLECULAR ARRANGEMENTS OF *p*-SUBSTITUTED ANILINIUMS IN THE INTERLAYER OF CUPRIC CHLORIDE

TAKETOSHI SEKINE, TSUNEHISA OKUNO, AND KUNIO AWAGA
Department of Pure and Applied Sciences, The University of Tokyo,
Komaba, Meguro, Tokyo 153, Japan

Abstract Crystal structures and magnetic properties of the layered pervoskite compounds, $(p\text{-X-C}_6H_4NH_3^+)_2CuCl_4^{2-}$ with X=CN (**1**), Cl (**2**), and NO_2 (**3**), were studied. The compound **1** crystallizes in the triclinic $P\bar{1}$ space group. The structure consists of a CuCl layer and an organic bilayer in which the molecular axis of the cyanoanilinium is nearly perpendicular to the inorganic layer. At the middle of the organic bilayer, there is a layer of the CN group, in which the CN groups are arranged to cancel their electric dipoles. The compound **2** has a similar structure to that of **1**. The crystal of **3** belongs to the orthorhombic *Pbca* space group, in which the structure also consists of an inorganic layer and an organic bilayer. The bilayer is formed by short contacts between the NO_2 groups, which appear to incline the molecular axis of the nitroanilinium with respect to the normal to the CuCl layer. AC and DC magnetic susceptibility measurements were carried out on the three salts. Their behavior can be understood with two parameters, ferromagnetic transition temperature T_c and in-plane ferromagnetic coupling constant J. The obtained parameters are T_c=9.5 K and J/k_B=24 K for **1**, T_c=9.1 K and J/k_B=23 K for **2**, and T_c=7.0 K and J/k_B=17 K for **3**. The values of T_c and J of **3** are smaller than those of the other two. The distortion of the molecular arrangement in the organic layer of **3**, is found to result in weakening the magnetic interaction in the CuCl layer.

INTRODUCTION

Physical and chemical properties of nanocomposites made up of organic and inorganic parts are now attracting much interest.[1,2] The compound, $(RNH_3^+)_2CuCl_4^{2-}$ where R is usually an *n*-alkyl chain or an aromatic group, crystallizes in a layered pervoskite structure, consisting of nearly isolated layers of corner-sharing $CuCl_6$ octahedra sandwiched by the organic cations. In the inorganic layer, ferromagnetic couplings operate between the neighboring copper ions, and the material is known to be a 2D ferromagnet whose T_c is ~10 K.[3-5] The $(RNH_3^+)_2CuCl_4^{2-}$ family has extensively been studied so far, and has been revalued as an organic/inorganic hybrid nanocomposite. In this work, we have studied the crystal structures and magnetic properties of $(p\text{-X-}C_6H_4NH_3^+)_2CuCl_4^{2-}$ with X=CN (**1**), Cl (**2**), and NO_2 (**3**). We describe the intermolecular arrangements of the *p*-substituted aniliniums in the interlayer of the cupric chlorides and how the organic layer affects the inorganic layer.

EXPERIMENTAL

Crystals of **1**-**3** were obtained by slow recrystallization from their aqueous-alcoholic mixed solutions, which contained stoichiometrically (*p*-substituted aniline)•HCl and $CuCl_2$.

X-ray diffraction data of the three crystals were collected on a Rigaku AFC-5 automatic four-circle diffractometer with graphite monochromatized Mo-Kα radiation at room temperature. Their unit cell parameters were derived by least-squares refinements of the setting angles of representative 25 reflections in the range $20<2\theta<25°$. During the data collection, the intensities of three reflections were monitored as a check on crystal stability, and no loss of intensity was found. Lorentz, polarization and absorption effects were corrected. The structures of **1** and **2** were solved by the direct method with SHELXS-86 and by subsequent difference Fourier syntheses. In the analysis of the structure of **3**, the positions of the copper atoms were obtained with the heavy atom method and the other atoms were found *via* subsequent Fourier syntheses. The structure refinements with anisotropic parameters by the block-diagonal least-squares technique using UNICS III,[6] were carried out for all non-hydrogen atoms. Details of the crystallographic parameters are given in Table I. Final positional

TABLE I Crystal data and experimental conditions for **1**-**3**.

	1	**2**	**3**
formula	$C_{14}H_{14}N_4CuCl_4$	$C_{12}H_{14}N_2CuCl_6$	$C_{12}H_{14}N_4O_4CuCl_4$
formula weight	443.65	462.52	483.63
crystal system	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$Pbca$
a / Å	7.361(2)	16.436(4)	7.063(1)
b / Å	17.132(5)	7.397(1)	32.460(6)
c / Å	7.166(1)	7.265(1)	7.925(2)
α / degree	92.90(3)		
β / degree	90.01(2)	101.51(2)	
γ / degree	102.39(3)		
V / Å^3	881.4(3)	865.5(3)	1816.9(6)
Z	2	2	4
D(calc) / g cm^{-3}	1.67	1.78	1.77
μ / cm^{-1}	18.9	22.2	18.6
2θ range / degree	4.0-60	4.0-55	4.0-55
no. collected	5621	2323	2448
no. obsd $(\lvert F_0\rvert>3.0\sigma\lvert F_0\rvert)$	4626	1416	1357
R	0.0586	0.0757	0.0796
R_w	0.0453	0.0733	0.0700

parameters for 1-3 are listed in Tables II-IV, respectively.

AC magnetic susceptibility was measured on a Lake Shore ACS7221 in the temperature range 4-30 K. DC magnetic susceptibility measurements were performed in the temperature range 3-280 K under a magnetic field of 0.5 T, using a Faraday balance.[7]

TABLE II Atomic coordinates (x10000) and equivalent isotropic thermal parameters (100 Å) for 1.

atom	*x*	*y*	*z*	B_{eq}
Cu(A)	5000	5000	5000	1.8
Cu(B)	0	5000	0	1.9
Cl(1A)	4697(1)	3650(0)	5031(1)	2.9
Cl (2A)	-2041(1)	5179(0)	2329(1)	2.6
Cl(1B)	-1047(8)	3652(0)	0032(1)	2.9
Cl(2B)	2779(1)	4820(0)	2669(1)	2.6
C(1A)	8811(3)	2791(1)	4807(3)	2.2
C(2A)	7425(4)	2329(2)	3709(4)	3.2
C(3A)	7090(4)	1507(2)	3790(4)	3.3
C(4A)	8148(4)	1164(1)	4982(4)	2.9
C(5A)	9540(5)	1640(2)	6080(4)	3.6
C(6A)	9887(4)	2468(2)	5982(4)	3.2
C(7A)	7766(5)	300(2)	5070(5)	3.8
C(1B)	3988(3)	2800(1)	9809(3)	2.2
C(2B)	2593(4)	2466(2)	10989(4)	3.2
C(3B)	2099(4)	1637(2)	11077(4)	3.7
C(4B)	3010(4)	1159(1)	9971(4)	2.9
C(5B)	4409(4)	1499(1)	8793(4)	3.2
C(6B)	4893(4)	2321(2)	8690(4)	3.1
C(7B)	2531(5)	303(2)	10068(5)	3.8
N(1A)	9114(3)	3664(1)	4743(3)	2.7
N(2A)	7422(5)	-382(2)	5134(6)	5.6
N(1B)	4558(3)	3667(1)	9742(3)	2.8
N(2B)	2177(5)	-387(2)	10134(5)	5.5

TABLE III Atomic coordinates (x10000) and equivalent isotropic thermal parameters (100 Å) for 2.

atom	*x*	*y*	*z*	B_{eq}
Cu	5000	0	0	1.9
Cl(1)	5175(1)	-2176(2)	-2167(2)	2.9
Cl(2)	3604(1)	-357(2)	-786(3)	3.1
Cl(3)	-34(1)	263(4)	2429(4)	4.7
N	3640(4)	-215(8)	4425(10)	3.1
C(1)	2743(4)	-72(8)	3931(9)	2.3
C(2)	2369(5)	1139(10)	2564(11)	3.3
C(3)	1522(5)	1242(11)	2101(12)	3.8
C(4)	1041(4)	144(10)	3013(10)	2.8
C(5)	1410(4)	-1073(10)	4355(10)	2.9
C(6)	2264(4)	-1172(10)	4812(10)	2.7

TABLE IV Atomic coordinates (x10000) and equivalent isotropic thermal parameters (100 Å) for 3.

atom	*x*	*y*	*z*	B_{eq}
Cu	0	0	5000	2.2
Cl(1)	2673(2)	118(1)	1976(2)	2.7
Cl(2)	223(3)	687(1)	5520(3)	2.7
C(1)	5163(9)	1107(2)	5017(9)	2.5
C(2)	4531(13)	1404(2)	6130(11)	3.3
C(3)	4791(13)	1816(3)	5758(11)	3.5
C(4)	5716(11)	1909(2)	4257(11)	2.9
C(5)	6319(12)	1619(3)	3137(11)	3.7
C(6)	6019(12)	1202(2)	3531(10)	3.0
N(1)	6057(10)	2344(2)	3833(9)	3.4
N(2)	4897(8)	0670(2)	5443(9)	2.9
O(1)	5189(10)	2609(2)	4611(9)	5.1
O(2)	7151(10)	2424(2)	2688(9)	4.9

RESULTS AND DISCUSSION

Crystal Structures

The compound 1 crystallizes in the triclinic $P\bar{1}$ space group.[8] The structure consists of an inorganic CuCl layer and an organic cyanoanilinium bilayer. Figures 1(a) and (b) show a top (a view of the inorganic layer and a half of the organic bilayer) and a side view of the layered structure, respectively. The NH_3^+ group of the cyanoanilinium is located at the center of the square of the chloride atoms which exist out of the CuCl plane. In the organic layer, the cyanoanilinium ion stands nearly perpendicular to the CuCl layer and the nearest-neighbor phenyl rings are arranged to be perpendicular to each other. There is a layer of the CN groups at the middle of the organic bilayer, whose top view is shown in Figure 2(a). The CN groups make a square lattice, in which each one is surrounded by four which belong to the opposite side of the organic bilayer and are arranged to cancel the electric dipole of the central one. The distances between the nearest-neighbor CN groups are about a half of the length of the *a* or *c* axis, *i.e.* ~3.6 Å. This is an attractive space, from the view point of controlling the arrangement of organic guest molecules to create fascinating physical properties. For instance, if larger atoms, *e.g.* sulfur, tellurium, *etc.*, can be inserted into this space, orbital overlaps between them may give rise to electrical conduction. On the other hand, the CuCl plane includes two kinds of Cu-Cl bonds; longer and shorter, because of the Jahn-Teller effect. Table V shows the lengths of the two Cu-Cl bonds, and their difference. The in-plane Cu-Cl-Cu angle and the Cu-Cu distance are also listed. It is notable that the distortion in 1 is one of the smallest in the $(RNH_3^+)_2CuCl_4^{2-}$ materials.[9]

The compound **2** crystallizes into the monoclinic $P2_1/c$ space group. The structure (not shown) is quite similar to that in **1**. The chloroanilinium cations form a bilayer, in which the Cl atoms are arranged to make a planner square lattice.

The crystal **3** belongs to the orthorhombic *Pbca* space group. Figures 3(a) and (b) show a top and a side view of the layered structure, respectively. The nitroanilinium ions form a bilayer, as well as the others. There is an NO_2 layer at the middle of it, whose view is shown in Figure 2(b). There are two intermolecular distances between O•••N; 3.02(1) Å (solid line, see Figure 2(b)) and 3.17(1) Å (broken line), which would be caused by the Coulombic attraction between the polarized charges on the NO_2 groups. The contacts form a one-dimensional array of the NO_2 groups along the *a* axis,

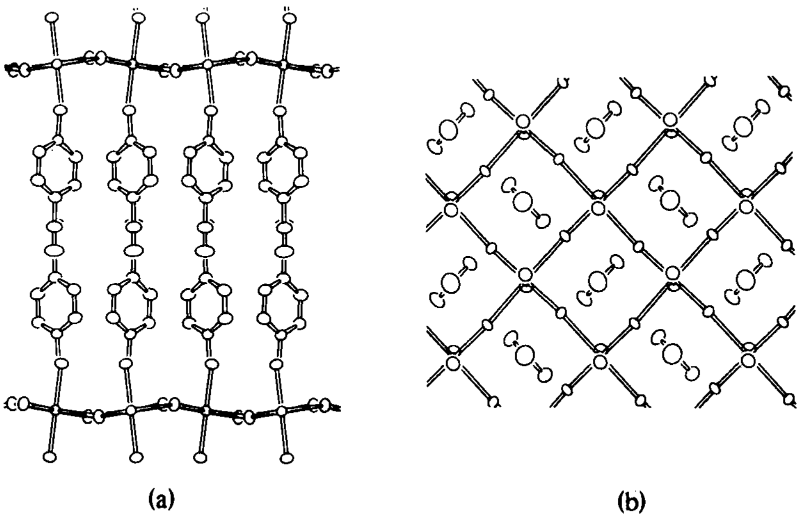
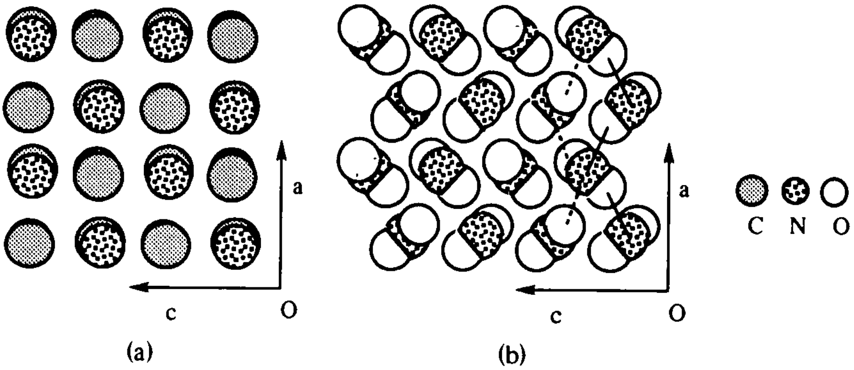

(a) (b)

FIGURE 1 A top (a) and a side (b) view of the layered structure in **1**.



(a) (b)

FIGURE 2 Intermolecular arrangements of the *p*-substituents; (a) the CN groups in **1**, (b) the NO_2 groups in **3**.

TABLE V Structural parameters in the CuCl plane.

	1[a)]		2	3
	site A	site B		
longer Cu-Cl / Å	2.875(1)	2.877(1)	2.906(2)	3.075(2)
shorter Cu-Cl / Å	2.298(1)	2.300(1)	2.309(2)	2.303(2)
Δ(Cu-Cl) / Å	0.577	0.577	0.597	0.772
∠Cu-Cl-Cu / degree	165.85(3) 165.94(3)		167.4(1)	161.3(1)
Cu-Cu / Å	5.135		5.184	5.308

a) This involves two crystallographically-independent copper atoms.

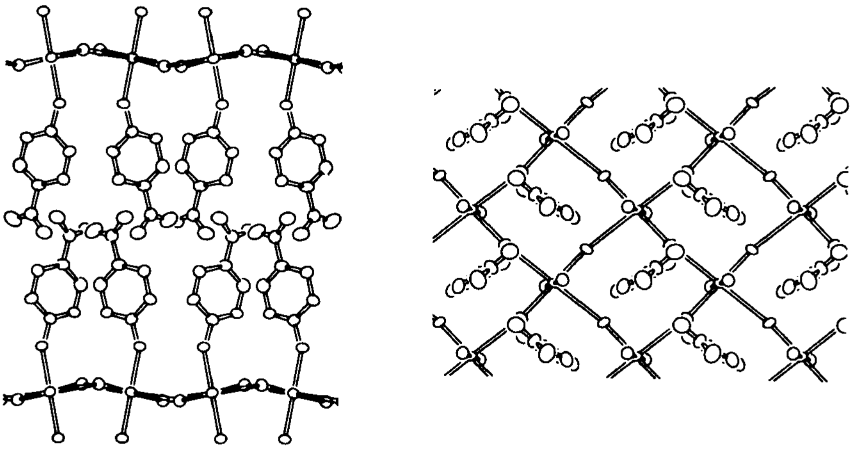

(a) (b)

FIGURE 3 A top (a) and a side (b) view of the layered structure in **3**.

in contrast that the CN groups and the Cl atoms are connected by the isotropic interactions in the crystals of **1** and **2** , respectively. The anisotropic feature in **3** clearly results in the large difference between the lengths of the *a* and the *c* axis. Further, the contacts between the NO_2 groups appear to incline the molecular axis of the nitroanilinium with respect to the normal to the CuCl layer. The two in-plane Cu-Cl distances in **3** are also listed in Table V. The Jahn-Teller distortion in **3** is found to be enhanced, compared with those in **1** and **2**. In addition, the distance between the copper ions in **3** is longer than the others.

Magnetic Properties

Figure 4 shows the temperature dependence of the AC magnetic susceptibilities, χ' and χ'', of **1**-**3**. The salts, **1** and **2**, show ferromagnetic transitions at T_C=9.5 and 9.1 K, respectively, accompanied with the abrupt increases in both χ' and χ''. Since, in the

$(\text{alkylammonium}^+)_2CuCl_4^{2-}$ system, the transition temperature determined by heat capacity measurements corresponds to the onset of the increase in χ'',[10] we adopted it as T_C. Below T_C their magnetic behaviors appear to be different. This would be caused by the demagnetization effect through their different crystal shapes. The salt **3** also shows a ferromagnetic transition at T_C=7.0 K which is clearly lower than those of **1** and **2**.

The temperature dependence of the DC magnetic susceptibilities of **1**-**3** were also measured (not shown). Their behavior above 50 K can be understood in terms of two-dimensional ferromagnetic Heisenberg spins,[11] with in-plane ferromagnetic coupling constants of J/k_B=24 K for **1**, J/k_B=23 K for **2**, and J/k_B=17 K for **3**. The lower T_C of **3** would be attributable to the decrease in J.

The Jahn-Teller distortion in **3** is larger than those in the other two. Further the in-plane Cu-Cl-Cu angle in **3** shows the largest deviation from 180°. The angle of 180° means an exactly-orthogonal relation between the two neighboring $d_{x^2-y^2}$ orbitals, and should bring about an intense ferromagnetic coupling.[12] Therefore it is expected that larger the deviation of the angle from 180°, weaker the ferromagnetic interaction. The ferromagnetic coupling in **3** would be weakened owing to this factor, in addition to the

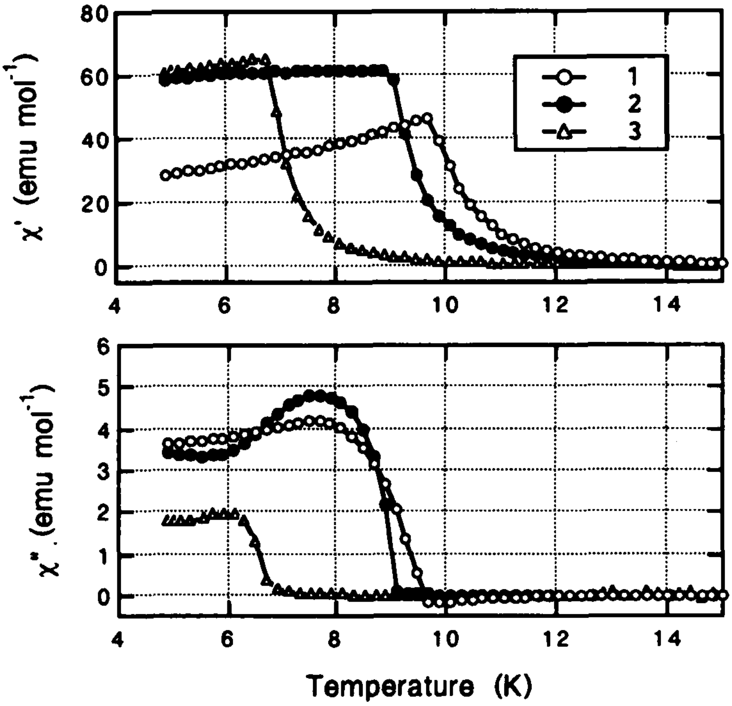


FIGURE 4 Temperature dependence of the AC magnetic susceptibilities of 1-3.

longer Cu-Cu distance. The molecular-arrangement distortion in the organic layer in **3**, is concluded to weaken the ferromagnetic interaction in the CuCl layer.

SUMMARY

The intermolecular arrangements of the three *p*-substituted aniliniums intercalated ih the $CuCl_4^{2-}$ layer, have been examined. We found an interesting space at the middle of the organic bilayer, where the *p*-substituents interact with each other. The crystals of **1** and **2** have the two-dimensional arrays of the CN groups and the Cl atoms, respectively, while **3** has the one-dimensional one of the NO_2 groups. The difference in the interaction dimensionality is reflected in their lattice constants. The ferromagnetic interaction in **3** is weaker than those in **1** and **2**, because of the distortion in the inorganic CuCl layer which is caused by the intermolecular contact between the NO_2 groups in the organic layer.

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