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MAGNETIC INTERACTION IN THE 1:1 SALTS OF NITRONYL NITROXIDE CATIONS WITH THE DICYANOPHTHALOCYANINATOCOBALT(III) ANION

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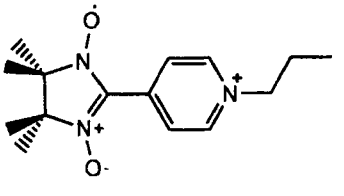
Abstract Two cationic derivatives of α-nitronyl nitroxide (NN), *p*-PPYNN (*p-N-n*-propylpyridinium α-nitronyl nitroxide) and *p*-BPYNN (*p-N-n*-butylpyridinium α-nitronyl nitroxide), have been crystallized with the $[Co(Pc)(CN)_2]^-$ (dicyanophthalocyaninatocobalt(III)) counter anion. Obtained two kinds of 1:1 salt crystals have been found to be isomorphous; monoclinic, $P2_1/c$, a = 15.585(6), b = 11.015(4), c = 26.111(3) Å, β = 89.95(2)°, V = 4482(3) Å^3, Z = 4 for *p*-PPYNN[Co(Pc)$(CN)_2$] and a = 15.830(3), b = 11.201(4), c = 25.709(3) Å, β = 90.29(1)°, V = 4558.4(17) Å^3, Z = 4 for *p*-BPYNN[Co(Pc)$(CN)_2$]. The magnetic interaction between the NN radicals in these two kinds of crystals has been found not to be the same; weak antiferromagnetic interaction operates in *p*-PPYNN[Co(Pc)$(CN)_2$], while only paramagnetic behavior is observed for *p*-BPYNN[Co(Pc)$(CN)_2$].

Keywords: nitronyl nitroxide radical, magnetic interaction, isomorphism

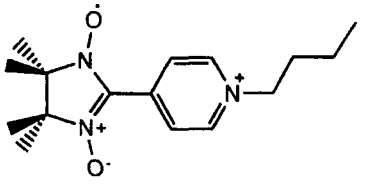
INTRODUCTION

It has been well established that an organic molecular crystal comprising organic radical molecules can be a ferromagnet. The ferromagnetic exchange interaction in molecular crystals is very sensitive to the detailed intermolecular interactions, and there is no clear guideline for designing crystals with the ferromagnetic interaction. We noted that one of α-nitronyl nitroxide (NN) radical derivatives having a ferromagnetic interaction, *p*-pyridyl nitronyl nitroxide,[1] can be transformed to the cationic radical by simple *N*-alkylation.[2] Considering the large negative charge on the oxygen atom in the NO group, short interatomic contacts between the NO group and the positively charged pyridinium ring are expected in the solid state. This arrangement is desirable when the

ferromagnetic coupling is realized through [magnetic orbital]-[non-magnetic orbital]-[magnetic orbital] superexchange pathway. Since this component always needs to crystallize with a counter ion, a wide variety of crystal structures can be derived from varying the anion.[3-5] When the *p*-derivatives are crystallized with I^-, magnetic interaction has been found to change from being antiferromagnetic to ferromagnetic according to the length of the alkyl chain.[6] When the *m*-*N*-methyl-derivative is combined with simple anions, such as I^- or ClO_4^-, the spin-1 *Kagomé* lattice is formed.[7] If the counter anion is much larger, the situation is expected to be very different from those cases. Small anions fill the space between the NN radicals, while large anions rather prescribe the space which can be filled with the NN radicals. This may force the various shaped NN radicals to pack in common circumstances, and the interaction between the NN radicals could finely be controlled. Utilizing such crystals, the correlation between the intermolecular contacts and magnetic interaction can be studied in detail. From this point of view, we have studied crystal structures and magnetic properties of the [Co(Pc)(CN)$_2$] (dicyanophthalocyaninatocobalt(III))[8-11] salts with *p*-PPYNN (*p*-*N*-*n*-propylpyridinium α-nitronyl nitroxide) and *p*-BPYNN (*p*-*N*-*n*-butylpyridinium α-nitronyl nitroxide). They have been found to be isomorphous, but their magnetic properties are different from each other. In this paper, we will describe their crystal structures, magnetic properties, and the details of the intermolecular contacts which are considered to dominate the exchange interaction between the NN radicals.



***p*-PPYNN**



***p*-BPYNN**

EXPERIMENTAL

Both *p*-PPYNN[Co(Pc)(CN)$_2$] and *p*-BPYNN[Co(Pc)(CN)$_2$] were prepared by simple metathesis between *p*-PPYNN·I (or *p*-BPYNN·I) and K[Co(Pc)(CN)$_2$] in acetonitrile. The single crystals were obtained by standing the solution of the metathesis reaction for several days, or by the metathesis with slow diffusion. The static magnetic susceptibility was measured by using a Faraday balance.[12] The temperature dependence of the magnetic susceptibility was measured in the range of 2.6 - 300 K in a field of 1 T.

The sample amount was 13.03 mg for *p*-PPYNN[Co(Pc)(CN)$_2$] and 11.02 mg for *p*-BPYNN[Co(Pc)(CN)$_2$], and the estimated error in χT is within 0.005 emu K mol^{-1}, which is mainly due to the large mass contribution from the closed shell anion, [Co(Pc)(CN)$_2$]$^-$.

Table I Data-collection conditions and crystal data.

	p-PPYNN-[Co(Pc)(CN)$_2$]	*p*-BPYNN-[Co(Pc)(CN)$_2$]
Chemical formula	$C_{49}H_{39}O_2N_{13}Co$	$C_{50}H_{41}O_2N_{13}Co$
Molecular weight	900.87	914.90
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	15.585(6)	15.830(3)
b/Å	11.015(4)	11.201(4)
c/Å	26.111(3)	25.709(3)
β/deg	89.95(2)	90.29(1)
V/Å^3	4482(3)	4558.4(17)
Z	4	4
D_{calc}/g cm^{-3}	1.335	1.333
μ(Mo K_α)/cm^{-1}	4.34	4.28
2θ range	$5° < 2\theta < 50°$	$5° < 2\theta < 55°$
Scan width/deg	1.20 + 0.3tanθ	1.20 + 0.3tanθ
Scan mode	ω-2θ	ω-2θ
Scan rate/deg min^{-1}	4	8
No. of reflections measured	6189	11360
No. of independent reflections	2011 ($I_o > 4\sigma(I_o)$)	4324 ($I_o > 3\sigma(I_o)$)
No. of parameters	586	838
R	0.094	0.067
R_w	0.108	0.072

An automated Rigaku AFC-5R diffractometer with graphite monochromatized Mo K_α radiation was used for data collection of X-ray structure analyses. The data-collection conditions and the crystal data are summarized in Table I. Three standard reflections monitored every 150 data measurements showed no significant deviation in intensities. The crystal structures were solved by a direct method and the positions of hydrogen atoms were calculated from the geometry and were not refined for *p*-PPYNN[Co(Pc)(CN)$_2$] and were partly refined for *p*-BPYNN[Co(Pc)(CN)$_2$]. Full-matrix least-squares refinement was carried out with the teXsan program,[13] using anisotropic thermal parameters for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms (temperature factors of hydrogen atoms are fixed in accordance with the bonded carbon atoms for *p*-PPYNN[Co(Pc)(CN)$_2$]). The final R value for *p*-PPYNN[Co(Pc)(CN)$_2$] has not been lowered satisfactorily during the

refinement. Re-examination using the crystals which were more carefully grown has not made any improvement. Defects seem to occur more easily in the crystal of *p*-PPYNN[Co(Pc)$(CN)_2$] than in that of *p*-BPYNN[Co(Pc)$(CN)_2$].

RESULTS AND DISCUSSION

Crystal Structures of *p*-PPYNN[Co(Pc)$(CN)_2$] and *p*-BPYNN-[Co(Pc)$(CN)_2$]

As can be seen from Table I, these two kinds of salt crystals are isomorphous. In general, replacement of a *n*-propyl group by a *n*-butyl group exerts a large influence on molecular packing in the crystal, and in fact, the crystal structure of *p*-PPYNN·I is completely different from that of *p*-BPYNN·I. The difference of alkyl chain length is therefore considerably reduced by combining a large counter anion.

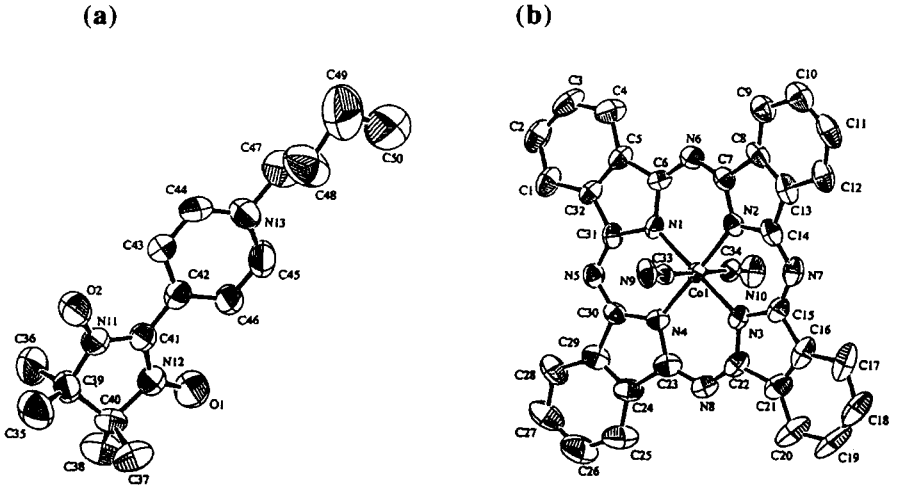


FIGURE 1 ORTEP drawing of *p*-BPYNN (**a**) and [Co(Pc)$(CN)_2$] (**b**) showing the atom numbering scheme.

The molecular structure of *p*-BPYNN$^+$ and [Co(Pc)$(CN)_2$]$^-$ (atom numbering scheme is the same for *p*-PPYNN[Co(Pc)$(CN)_2$] except the terminal methyl carbon) is shown in Fig. 1. The atomic parameters are given in Tables II and III. The crystal structure of *p*-PPYNN[Co(Pc)$(CN)_2$] is shown in Fig. 2(a) and that of *p*-BPYNN[Co(Pc)$(CN)_2$] is shown in Fig. 2(b).

TABLE II Fractional coordinates and equivalent temperature factors for *p*-PPYNN[Co(Pc)$(CN)_2$]

Atom	*x*	*y*	*z*	B_{eq}/Å^2	Atom	*x*	*y*	*z*	B_{eq}/Å^2
Co1	0.7481(2)	0.0959(3)	0.3784(1)	2.82(7)	C18	1.036(2)	0.422(4)	0.258(1)	8(1)
O1	0.870(1)	0.180(2)	0.1957(9)	9.5(9)	C19	0.937(2)	0.469(3)	0.241(1)	8(1)
O2	0.870(1)	-0.035(2)	0.0437(9)	8.2(8)	C20	0.887(2)	0.449(3)	0.251(1)	7(1)
N1	0.673(1)	-0.004(2)	0.4208(8)	3.7(6)	C21	0.877(1)	0.347(3)	0.290(1)	5.3(9)
N2	0.845(1)	0.021(2)	0.4134(7)	3.4(6)	C22	0.798(2)	0.287(3)	0.306(1)	5.0(9)
N3	0.823(1)	0.194(2)	0.3391(7)	3.6(6)	C23	0.652(1)	0.255(3)	0.309(1)	5.4(8)
N4	0.653(1)	0.162(2)	0.3435(7)	3.6(6)	C24	0.568(2)	0.273(3)	0.288(1)	4.8(8)
N5	0.535(1)	0.047(2)	0.3783(10)	4.7(7)	C25	0.537(2)	0.349(3)	0.251(1)	8(1)
N6	0.772(1)	-0.115(2)	0.4723(8)	4.3(6)	C26	0.453(4)	0.355(4)	0.237(2)	13(1)
N7	0.960(1)	0.122(2)	0.367(1)	4.8(7)	C27	0.400(2)	0.267(3)	0.262(1)	6.8(9)
N8	0.720(1)	0.316(2)	0.2892(9)	5.8(7)	C28	0.428(1)	0.192(3)	0.299(1)	6.8(10)
N9	0.761(1)	-0.110(2)	0.3016(8)	5.1(7)	C29	0.510(2)	0.193(3)	0.311(1)	6.6(9)
N10	0.748(1)	0.304(2)	0.4557(8)	5.2(7)	C30	0.565(1)	0.127(2)	0.351(1)	3.5(8)
N11	0.846(1)	0.019(2)	0.083(1)	6.1(8)	C31	0.582(2)	-0.014(3)	0.413(1)	5.4(9)
N12	0.842(2)	0.122(2)	0.160(1)	6(1)	C32	0.554(2)	-0.094(3)	0.453(1)	4.8(8)
N13	1.166(2)	0.116(2)	0.107(1)	8.3(9)	C33	0.756(2)	-0.027(2)	0.327(1)	6.0(9)
C1	0.466(2)	-0.134(2)	0.457(1)	6.6(10)	C34	0.745(2)	0.223(2)	0.429(1)	4.7(8)
C2	0.456(2)	-0.216(3)	0.497(1)	7(1)	C35	0.749(2)	-0.125(2)	0.125(1)	7.3(8)
C3	0.524(2)	-0.262(3)	-0.529(1)	8(1)	C36	0.689(2)	0.022(3)	0.064(1)	6.6(9)
C4	0.608(2)	-0.221(3)	0.520(1)	6.5(9)	C37	0.709(2)	0.077(3)	0.193(1)	11(1)
C5	0.620(1)	-0.139(3)	0.480(1)	5.1(10)	C38	0.721(2)	0.224(2)	0.125(1)	9(1)
C6	0.696(2)	-0.080(2)	0.4572(10)	3.3(8)	C39	0.753(2)	0.003(2)	0.105(1)	4.8(9)
C7	0.840(2)	-0.065(2)	0.448(1)	3.9(9)	C40	0.750(2)	0.107(3)	0.144(1)	4.8(9)
C8	0.929(1)	-0.111(2)	0.4614(10)	3.2(7)	C41	0.895(2)	0.079(2)	0.120(1)	4.3(8)
C9	0.957(2)	-0.198(2)	0.495(1)	5.5(9)	C42	0.989(1)	0.088(3)	0.115(1)	5.2(8)
C10	1.047(2)	-0.215(2)	0.495(1)	5.6(9)	C43	1.035(2)	0.016(2)	0.082(1)	5.9(9)
C11	1.099(2)	-0.152(3)	0.463(1)	5.7(9)	C44	1.126(2)	0.024(3)	0.077(1)	7(1)
C12	1.071(2)	-0.059(2)	0.4297(10)	4.7(8)	C45	1.125(2)	0.178(3)	0.141(1)	6(1)
C13	0.981(2)	-0.045(2)	0.428(1)	4.7(8)	C46	1.036(2)	0.172(2)	0.146(1)	6.1(9)
C14	0.932(1)	0.036(2)	0.3993(10)	3.2(7)	C47	1.264(2)	0.135(3)	0.102(1)	9(1)
C15	0.910(2)	0.196(2)	0.342(1)	4.4(8)	C48	1.313(2)	0.061(3)	0.135(2)	10(1)
C16	0.946(2)	0.291(2)	0.307(1)	5.6(8)	C49	1.406(2)	0.082(4)	0.127(1)	13(1)
C17	1.029(2)	0.320(3)	0.293(1)	9(1)					

Table III Fractional coordinates and equivalent temperature factors for *p*-BPYNN[Co(Pc)$(CN)_2$].

Atom	*x*	*y*	*z*	B_{eq}/Å^2	Atom	*x*	*y*	*z*	B_{eq}/Å^2
Co1	0.74885(6)	0.09420(9)	0.37761(4)	2.67(2)	C18	1.0363(6)	0.4104(9)	0.2608(4)	6.9(3)
O1	0.8646(4)	0.1785(8)	0.1940(3)	9.6(3)	C19	0.9689(7)	0.4704(9)	0.2408(4)	8.1(3)
O2	0.8741(4)	-0.0360(7)	0.0422(3)	7.7(2)	C20	0.8880(7)	0.4370(8)	0.2517(4)	6.6(3)
N1	0.6725(3)	-0.0015(5)	0.4185(2)	3.1(1)	C21	0.8759(6)	0.3442(8)	0.2861(3)	4.7(2)
N2	0.8433(3)	0.0201(5)	0.4127(2)	3.1(1)	C22	0.8009(5)	0.2822(7)	0.3042(3)	3.9(2)
N3	0.8242(4)	0.1919(5)	0.3385(2)	3.3(1)	C23	0.6578(5)	0.2535(7)	0.3056(3)	4.1(2)
N4	0.6536(3)	0.1648(5)	0.3417(2)	3.1(1)	C24	0.5715(5)	0.2771(7)	0.2858(3)	4.5(2)
N5	0.5396(4)	0.0489(6)	0.3773(2)	3.6(1)	C25	0.5404(6)	0.3561(9)	0.2486(4)	6.7(3)
N6	0.7712(4)	-0.1097(6)	0.4725(2)	3.8(1)	C26	0.4551(7)	0.355(1)	0.2386(4)	7.7(3)
N7	0.9583(3)	0.1180(6)	0.3676(2)	4.0(2)	C27	0.4025(6)	0.276(1)	0.2645(4)	7.1(3)
N8	0.7245(4)	0.3119(6)	0.2889(2)	4.4(2)	C28	0.4322(5)	0.1967(9)	0.3003(4)	5.5(2)
N9	0.7626(4)	-0.1105(6)	0.2993(3)	4.5(2)	C29	0.5184(5)	0.1987(8)	0.3111(3)	4.2(2)
N10	0.7488(4)	0.3009(7)	0.4565(3)	5.3(2)	C30	0.5706(4)	0.1292(6)	0.3467(3)	3.3(2)
N11	0.8473(4)	0.0128(7)	0.0837(3)	5.2(2)	C31	0.5865(4)	-0.0085(7)	0.4116(3)	3.5(2)
N12	0.8419(4)	0.1201(7)	0.1543(3)	5.5(2)	C32	0.5521(4)	-0.0913(7)	0.4494(3)	3.7(2)
N13	1.1586(4)	0.1206(7)	0.1119(3)	6.4(2)	C33	0.7557(4)	-0.0319(6)	0.3267(3)	2.8(1)
C1	0.4695(5)	-0.1308(8)	0.4585(4)	5.0(2)	C34	0.7461(4)	0.2210(7)	0.4283(3)	3.2(2)
C2	0.4575(5)	-0.2110(9)	0.4991(4)	5.8(3)	C35	0.7542(7)	-0.1248(8)	0.1250(4)	6.7(3)
C3	0.5237(6)	-0.2462(9)	0.5289(4)	6.4(3)	C36	0.6981(7)	0.005(1)	0.0559(4)	7.1(3)
C4	0.6062(6)	-0.2103(9)	0.5208(4)	5.7(2)	C37	0.7027(7)	0.074(1)	0.1891(4)	8.4(4)
C5	0.6194(5)	-0.1328(7)	0.4786(3)	3.9(2)	C38	0.7215(7)	0.218(1)	0.1184(5)	8.3(4)
C6	0.6949(5)	-0.0776(6)	0.4576(3)	3.5(2)	C39	0.7575(5)	-0.0015(8)	0.1018(3)	4.7(2)

C7	0.8385(4)	-0.0664(6)	0.4496(3)	3.3(2)	C40	0.7511(5)	0.1015(9)	0.1409(3)	5.0(2)
C8	0.9251(5)	-0.1107(7)	0.4608(3)	4.0(2)	C41	0.8947(5)	0.0752(8)	0.1181(3)	4.5(2)
C9	0.9544(5)	-0.1985(8)	0.4943(4)	4.6(2)	C42	0.9857(5)	0.0907(8)	0.1168(3)	4.2(2)
C10	1.0403(5)	-0.2178(2)	0.4963(4)	5.3(2)	C43	1.0350(5)	0.0193(9)	0.0850(3)	5.4(2)
C11	1.0950(5)	-0.1507(9)	0.4646(4)	5.6(2)	C44	1.1208(6)	0.0354(10)	0.0826(4)	6.7(3)
C12	1.0652(5)	-0.0656(8)	0.4311(3)	4.7(2)	C45	1.1116(6)	0.1880(8)	0.1438(4)	5.9(3)
C13	0.978(5)	-0.0452(7)	0.4293(3)	4.0(2)	C46	1.0270(5)	0.1751(8)	0.1473(4)	5.2(2)
C14	0.9274(4)	0.0365(7)	0.3998(3)	3.7(2)	C47	1.2531(7)	0.142(1)	0.1051(5)	8.2(4)
C15	0.9106(5)	0.1906(6)	0.3409(3)	3.5(2)	C48	1.2986(8)	0.074(1)	0.1407(6)	11.5(5)
C16	0.9437(5)	0.2848(8)	0.3072(3)	4.7(2)	C49	1.401(1)	0.109(2)	0.1360(7)	15.3(7)
C17	1.0277(6)	0.3182(9)	0.2964(4)	6.1(3)	C50	1.431(1)	0.033(2)	0.1016(8)	16.5(7)

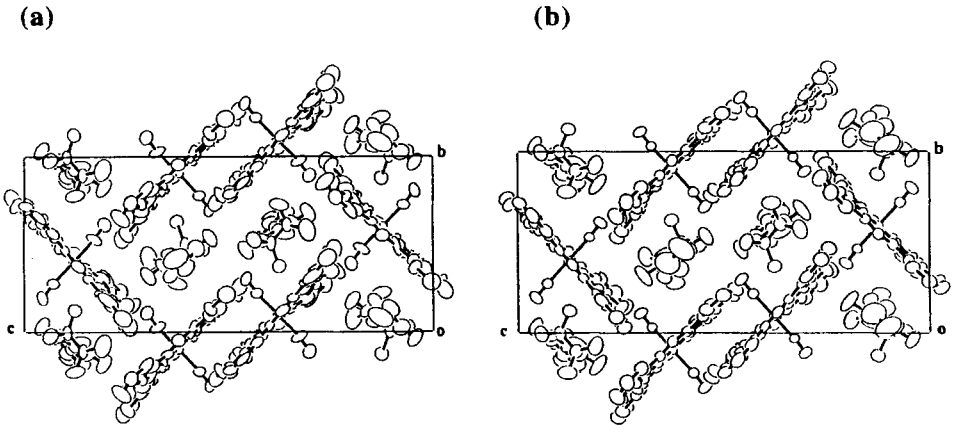


FIGURE 2 Crystal structures of *p*-PPYNN[Co(Pc)$(CN)_2$] (**a**) and *p*-BPYNN[Co(Pc)$(CN)_2$] (**b**).

It can easily be seen that their crystal structures are practically identical. Slipped stacked Pc units are arranged so that a one-dimensional tunnel formed by these units is running parallel to the *a*-axis. As shown in Fig. 2, the size of the cross section of this tunnel is suitable for two *p*-PPYNN (or *p*-BPYNN) when the molecular long axis is parallel to the one-dimensional tunnel. Due to the electrostatic interaction, these two radicals prefer to arrange in an anti-parallel way, i. e., head-to-tail arrangement. These two radicals can be regarded as a dimer unit. No direct intermolecular contacts exist between the one-dimensional arrays of these dimer units, since the tunnel formed by the [Co(Pc)$(CN)_2$] anions completely interrupt it. Interaction between the dimer units along the *a*-axis is considered to be weak, since contacts occur only between the aliphatic groups. Consequently, the dimer unit is rather isolated from the other radicals.

The [Co(Pc)$(CN)_2$] unit has been utilized for the construction of multi-dimensional electronic systems.[8-11] Due to the steric interaction between the axial cyano groups, the molecule cannot stack directly above another molecule. Hence, the molecule needs to slip a large distance to make contacts between the planar parts. Highly

conducting crystals which have two-dimensional sheets or three-dimensional $\pi-\pi$ overlaps of $[Co(Pc)(CN)_2]$ have been obtained by electrochemical oxidation of the salts.[8,9] On the other hand, in the case of the simple salts, the $[Co(Pc)(CN)_2]$ units have been found to prefer to form isolated dimer units or one-dimensional chains in the crystal.[10]

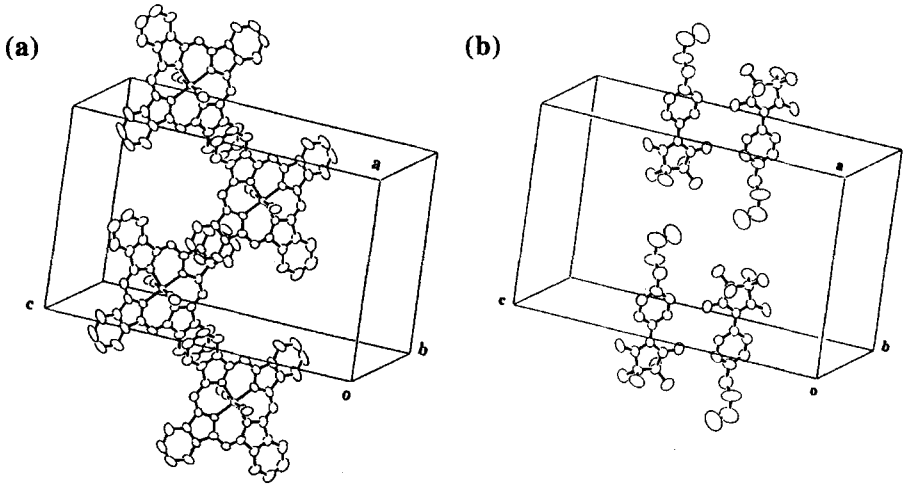


FIGURE 3 Arrangement of the $[Co(Pc)(CN)_2]$ units (**a**) and the NN radicals (**b**) in *p*-BPYNN$[Co(Pc)(CN)_2]$.

The crystals studied here are simple salts, and the $\pi-\pi$ overlap is restricted only in the zig-zag one-dimensional chain, as shown in Fig. 3. This is due to that the charge-transfer interaction between the $[Co(Pc)(CN)_2]$ units is quite weak because of its closed-shell electronic system. However, the rigid framework is found to be advantageous to prescribing the lattice in which the counter parts are packed.

Magnetic Properties of *p*-PPYNN$[Co(Pc)(CN)_2]$ and *p*-BPYNN-$[Co(Pc)(CN)_2]$

The temperature dependence of the paramagnetic susceptibility, χ_p, is obtained after compensating the diamagnetic contribution from the observed magnetic susceptibility. χ_pT vs T plots of *p*-PPYNN$[Co(Pc)(CN)_2]$ and *p*-BPYNN$[Co(Pc)(CN)_2]$ are shown in Fig. 4. χ_pT of *p*-PPYNN$[Co(Pc)(CN)_2]$ clearly decreases with decreasing temperature, indicating that the antiferromagnetic exchange interaction operates in this crystal. The Weiss temperature is obtained from the fitting curve in Fig. 4 as about -0.4 K. On the

other hand, χ_pT of *p*-BPYNN[Co(Pc)(CN)$_2$] is virtually constant in the wide temperature range. Since χ_pT is approximately equal to the Curie constant (slight deviation from 0.375 emu K mol^{-1} is due to the experimental error owing to the large mass contribution from [Co(Pc)(CN)$_2$]$^-$), the exchange interaction must be very weak, though a slight increase at low temperatures may suggest the existence of the ferromagnetic exchange interaction. It is quite interesting that the magnetic exchange interactions in *p*-PPYNN[Co(Pc)(CN)$_2$] and *p*-BPYNN[Co(Pc)(CN)$_2$] are different from each other, since both *p*-PPYNN and *p*-BPYNN must be situated in very similar circumstances.

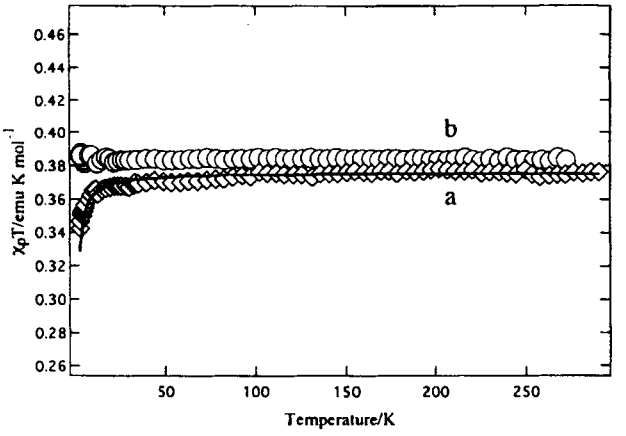


FIGURE 4 Temperature dependence of the paramagnetic susceptibility of *p*-PPYNN[Co(Pc)(CN)$_2$] (**a**) and *p*-BPYNN[Co(Pc)(CN)$_2$] (**b**).

Intermolecular Contacts between the *p*-PPYNN radicals and between the *p*-BPYNN radicals

As mentioned in their crystal structures, intermolecular contacts between the radicals are predominantly restricted within the dimer unit. The geometrical relation between the radical cations within the dimer unit is shown in Fig. 5. The intermolecular interatomic distances including those much larger than the sum of the van der Waals radii are listed in Table IV. Since the radical cations are arranged in an anti-parallel way, as expected from the electrostatic interaction between the negatively charged NO groups and the positively charged pyridinium ring, the magnetic orbital localized at the O1-N12-C41-N11-O2 group can contact only with the non-magnetic orbital at the pyridinium ring. Actually, the O2···O2 distance is so long (4.70(4) Å for *p*-PPYNN[Co(Pc)(CN)$_2$] and 4.62(1) Å for *p*-BPYNN[Co(Pc)(CN)$_2$] vs. 3.04 Å for the twice of the van der Waals

radius of oxygen) that direct exchange interaction between them can be assumed to be unimportant.

TABLE IV Intermolecular interatomic distance (Å) between the NN radicals in the dimer unit

	p-PPYNN[Co(Pc)(CN)$_2$]	*p*-BPYNN[Co(Pc)(CN)$_2$]
O2···O2	4.70(4)	4.62(1)
O2···C42	4.73(4)	4.70(1)
O2···C43	3.59(4)	3.58(1)
O2···C44	3.16(4)	3.21(1)
O2···C47	4.48(4)	4.44(2)
O2···N13	4.07(4)	4.10(1)
C43···C43	4.41(6)	4.52(2)
C43···C44	4.86(4)	4.99(2)
C43···N11	4.69(4)	4.74(1)
C44···C36	4.70(4)	4.61(2)
C44···N11	4.22(5)	4.34(1)
C36···C47	4.72(4)	4.52(2)

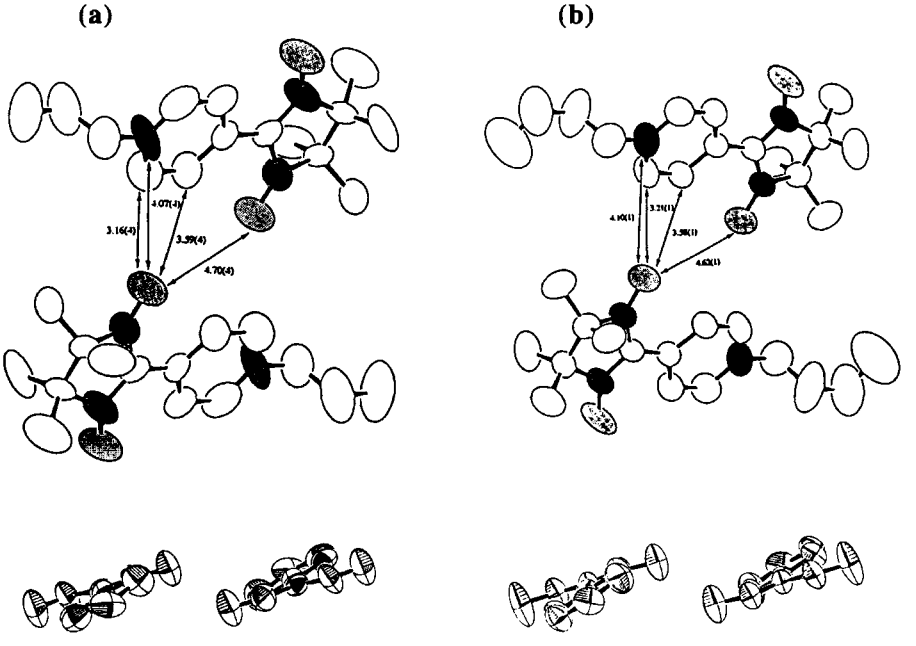


FIGURE 5 Relative arrangement of the NN radicals in the dimer unit with interatomic distance (Å); in *p*-PPYNN[Co(Pc)(CN)$_2$] (**a**) and in *p*-BPYNN[Co(Pc)(CN)$_2$] (**b**). Each bottom shows the π-conjugated parts in the dimer viewed along the molecular long axis.

In both cases, the nearest contact is O2···C44 (3.16(4) and 3.21(1) Å for *p*-PPYNN[Co(Pc)$(CN)_2$] and *p*-BPYNN[Co(Pc)$(CN)_2$], respectively) and the next shortest is O2···C43 (3.59(4) and 3.58(1) Å for *p*-PPYNN[Co(Pc)$(CN)_2$] and *p*-BPYNN[Co(Pc)$(CN)_2$], respectively). The dihedral angle between the two π-orbital planes, the O-N-C-N-O plane and the pyridinium ring in the neighboring molecule, is practically the same for both salts as shown in Fig. 5, 14.88° in *p*-PPYNN[Co(Pc)$(CN)_2$] and 15.41° in *p*-BPYNN[Co(Pc)$(CN)_2$]. Simply considering the spin polarization, C43 and C44 have polarized spins of which polarity is opposite to each other. The O2···C44 distance is slightly shorter in *p*-PPYNN[Co(Pc)$(CN)_2$] than in *p*-BPYNN[Co(Pc)$(CN)_2$]. On the other hand, the O2···C43 distance is almost the same. If the O2···C44 contact induces the antiferromagnetic coupling and the O2···C43 contact induces ferromagnetic coupling, the larger antiferromagnetic contribution in *p*-PPYNN[Co(Pc)$(CN)_2$] than in *p*-BPYNN[Co(Pc)$(CN)_2$] seems to be consistent with the observed magnetic behavior. However, it is hard to conclude it, since the exchange interaction energy is so small and the standard deviations of the distances are rather large. Also it is not sure how the distances will change by temperature change, especially at which temperature the magnetic exchange interaction becomes important.

The contribution from superexchange interaction through the π-system of [Co(Pc)$(CN)_2$] may also not be ruled out completely. The shortest intermolecular contact between the NN radicals and [Co(Pc)$(CN)_2$] is O1···C21 for both cases; the distance is 3.06(3) Å for *p*-PPYNN[Co(Pc)$(CN)_2$] and is 3.01(1) Å for *p*-BPYNN[Co(Pc)$(CN)_2$]. Similarly, short contacts exist between O1 and C20 and between O1 and C22 in both crystals. The interaction through these contacts may generate a three-dimensional network.

In conclusion, we have found that two kinds of simple salt crystals of *p*-PPYNN[Co(Pc)$(CN)_2$] and *p*-BPYNN[Co(Pc)$(CN)_2$] are isomorphous. Antiferromagnetic exchange interaction has been found to operate between the NN radicals in *p*-PPYNN[Co(Pc)$(CN)_2$], while simple paramagnetic behavior has been observed for *p*-BPYNN[Co(Pc)$(CN)_2$]. The energy of the interaction is, however, too small to elucidate the difference merely from the room temperature structure analyses. This study clearly reveals that the magnetic interaction is very sensitive to the relative geometric arrangement of the molecules carrying the spin.

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were members of his group at IMS and even after moving to the present positions. It is a great pleasure to dedicate this work to Prof. Y. Maruyama.

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