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Synthesis, Structural Isomerism, and Magnetism of Extended Framework Compounds of Type $[Cu(dca)_2(pyz)]_n$, Where dca = Dicyanamide ($N(CN)_2^-$) and pyz = Pyrazine

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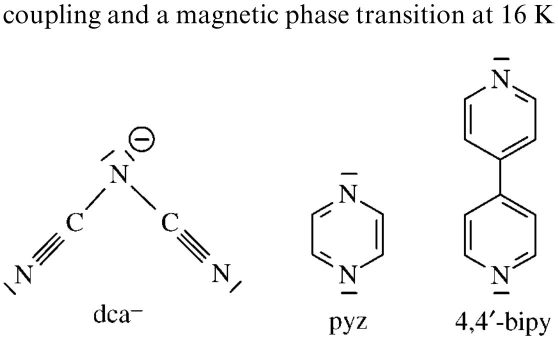
IN HONOUR OF PETER DAY, F.R.S., ON HIS 60TH BIRTHDAY

Two structural isomers of the dicyanamide (dca, $N(CN)_2^-$) complex $[Cu(dca)_2(pyz)]_n$ (pyz = pyrazine) were prepared from aqueous solution and crystals were grown by slow diffusion and gel techniques. Crystal data: α-$[Cu(dca)_2(pyz)]_n$, $CuC_8H_4N_8$, monoclinic, *Pn*, $Z = 16$, $a = 24.2549(7)$ Å, $b = 6.8571(2)$ Å, $c = 24.6445(7)$ Å, $\beta = 91.023(2)$°, $V = 4098.2(2)$ Å^3, $R(F) = 0.0466$ ($F > 4\sigma(F)$), $R_w(F^2) = 0.0939$ (all data); β-$[Cu(dca)_2(pyz)]_n$, $CuC_8H_4N_8$, monoclinic, *C2/m*, $Z = 2$, $a = 9.7659(8)$ Å, $b = 6.8787(7)$ Å, $c = 7.3870(5)$ Å, $\beta = 95.254(7)$°, $V = 494.15(6)$ Å^3, $R(F) = 0.038$, $R_w(F) = 0.074$ ($I > 3\sigma(I)$). The α-isomer consists of two interpenetrating α-Po related networks, while the β-isomer contains sheets composed of $Cu(dca)_2$ chains linked by bridging pyz ligands.

Despite the differences in their network structures, the magnetic properties of these structural isomers are essentially the same. Weak antiferromagnetic coupling of the $S = 1/2$ centers leads to a maximum in susceptibility at 3.5 K. One of the aims of this work is to prepare long-range ordered materials but no magnetic order is observed in the present compounds. The antiferromagnetic coupling is a little stronger than that in the parent $Cu(dca)_2$ but of similar strength to that in chain compounds of type $[Cu(dca)_2(imidazole)_2]_n$. Thus, the pyz linkers enhance the coupling to only a small degree. The networks in the α-isomer behave independently and identically from the magnetic point of view. © 1999 Academic Press

***Key Words*: structure; magnetism; extended framework; copper (II); dicyanamide; pyrazine.**

The considerable interest in extended framework and interpenetrating compounds has, to date, been largely driven by the fascinating structural and topological features of such crystalline materials (1). The metal ion centers used have usually been of the closed shell type, i.e., Cu^I, Ag^I, Cd^{II}, Zn^{II}, thus leading to diamagnetic materials. We (2, 3), and others (4), are developing open-shell *d*-block ion systems which display novel magnetic properties on account of their extended structures and the nature of superexchange coupling which occurs via covalent bridges which connect adjacent metal ions. Most such work has involved $M{-}C\equiv N{-}M$ bridges in Prussian-blue analogues (5) or $M(\mu\text{-}C_2O_4)M$ bridges in metal–oxalate nets (6), both systems usually requiring heterometal or mixed-valence homometallic combinations. Recently, we described the occurrence of long-range ferromagnetic order in binary metal(II)–dicyanamide complexes of type $M(dca)_2$, were M = Co and Ni (3a). These compounds exist as single net rutilelike structures with bridging occurring via both nitrile and amido N atoms. The properties of other $M^{II}(dca)_2$ derivatives are presently being investigated, $Mn(dca)_2$ for instance showing antiferromagnetic coupling and a magnetic phase transition at 16 K (3b).



We are especially interested in preparing and studying crystalline *M*-dca species which contain a linker ligand such as pyrazine (pyz) or 4,4′-bipyridine (4,4′-bipy) as well as dicyanamide bridging frameworks. These ligands are shown

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above. In this way, a number of interesting topologies, including sheet structures and interpenetrating nets, are possible. Chain structures of type $[M(\mathrm{dca})_2(L)_2]_n$ (L = terminal ligand) have been well studied (7). Since the magnetic properties of μ-pyz and μ-4,4′-bipy coordination polymer chains are becoming better understood, the combination of such bridges with those involving dca should provide some unusual magnetic outcomes. We are particularly interested to see under what conditions long-range order occurs. Preliminary studies by ourselves (1a, 1c, 2) and by Miller *et al.* (8) on interpenetrating network materials of a related ligand, tricyanomethanide viz. $M(\mathrm{tcm})_2$, have yielded weak antiferromagnetic coupling without any long-range magnetic order being detected. In this paper we describe new materials of formula $[\mathrm{Cu(dca)}_2(\mu\text{-}L)]_n$, where L = pyz. Structural isomers have been obtained and are labeled α- and β-$[\mathrm{Cu(dca)}_2(\mathrm{pyz})]_n$, the α-form possessing an interpenetrating α-Po 3D-network structure, the β-form a 2D-sheet structure in which $\mathrm{Cu(dca)}_2$ chains are linked by axially coordinated pyz groups.

EXPERIMENTAL

Synthesis

α-[Cu(dca)$_2$(pyz)]$_n$. A hot aqueous solution (5 ml) of $\mathrm{Cu(NO_3)_2 \cdot 3H_2O}$ (147 mg, 0.608 mmol) was added to a hot aqueous solution (10 ml) of Na(dca) (100 mg, 1.12 mmol) and pyz (46 mg, 0.574 mmol). Green/blue needles formed soon after addition and were filtered from solution after cooling. Yield 116 mg, 75%. Selected IR frequencies (cm^{-1}): ν_s (C≡N), 2182; ν_{as} (C≡N), 2250; ν_s(C–N), 919; ν_{as} (C–N), 1379. Analyses: Calculated for $\mathrm{CuC_8H_4N_8}$: C, 34.9; H, 1.5; N, 40.6. Found: C, 34.9; H, 1.2; N, 40.5. Crystals for X-ray crystallography were grown using a slow diffusion technique. Solutions of the reactants were layered in a glass tube and allowed to mix slowly. This led to thin green/blue needles being formed.

β-[Cu(dca)$_2$(pyz)]$_n$. An aqueous solution (25 ml) of $\mathrm{Cu(NO_3)_2 \cdot 3H_2O}$ (700 mg, 2.90 mmol) was added to an aqueous solution (25 ml) of Na(dca) (500 mg, 5.62 mmol) and pyz (225 mg, 2.81 mmol) at room temperature. A pale green/blue powder formed instantly (i.e., α-$[\mathrm{Cu(dca)}_2(\mathrm{pyz})]_n$). Several hours later blue crystals were visible. After four days the green/blue powder had disappeared and only blue crystals remained (yield, 715 mg, 92%). Selected IR frequencies (cm^{-1}): ν_s(C≡N), 2183; ν_{as}(C≡N), 2245; ν_s(C–N), 939; ν_{as}(C–N), 1340. Analyses: Calculated for $\mathrm{CuC_8H_4N_8}$: C, 34.9; H, 1.5; N, 40.6. Found: C, 34.8; H, 1.2; N, 40.5. Crystals for X-ray crystallography were grown using a gel technique. An approximate 1:5 (by volume) mixture of tetramethoxysilane and an aqueous solution of $\mathrm{Cu(NO_3)_2}$ was heated at 50–60°C until a gel formed. An aqueous solution of Na(dca) and pyz was then layered on top of the gel at room temperature. Initially, very fine needles of the green/blue α-phase formed which later disappeared as blue crystals of β-$[\mathrm{Cu(dca)}_2(\mathrm{pyz})]_n$ formed.

X-Ray Structural Analysis

Atomic coordinates and selected bond lengths and angles for both compounds are shown in Tables 1–4.

X-ray structural analysis of α-$[\mathrm{Cu(dca)}_2(\mathrm{pyz})]_n$: crystal dimensions 0.1 × 0.01 × 0.01 mm, green/blue needle, monoclinic, *Pn* (No. 7), $Z = 16$, $a = 24.2549(7)$ Å, $b = 6.8571(2)$ Å, $c = 24.6445(7)$ Å, $\beta = 91.023(2)°$, $V = 4098.2(2)$ Å^3, $\mathrm{C_8H_4CuN_8}$, $M_r = 275.72$, $\rho_{\mathrm{calc}} = 1.788\ \mathrm{g\,cm^{-3}}$, $2\theta_{\max} = 56.5°$, Nonius KappaCCD diffractometer with graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å), data were obtained using ϕ rotations with 1° frames and a detector to crystal distance of 29 mm, integration was carried out by the program DENZO-SMN (9), $T = -100$°C, 31,236 reflections measured, 14,267 unique ($R_{\mathrm{int}} = 0.0718$), data corrected for Lorentz, polarization effects, and absorption, $\mu(\mathrm{Mo}K\alpha) = 2.120\ \mathrm{mm^{-1}}$, solution by direct methods followed by successive difference Fourier Methods, structure refined against F^2, crystal twinned, two nitrogen atoms were disordered equally between two positions (N34/N34A and N37/N37A) and refined isotropically, all other atoms were refined anisotropically, hydrogen atoms were included but not refined, 1222 parameters, $R(F) = 0.0466$ for 10,694 data with $F > 4\sigma(F)$, $R_w(F^2) = 0.0939$ for all data, min/max residual electron density = $-0.470/0.434\ e\,\text{Å}^{-3}$.

X-ray structural analysis of β-$[\mathrm{Cu(dca)}_2(\mathrm{pyz})]_n$: crystal dimensions 0.20 × 0.16 × 0.12 mm, blue prism, monoclinic, *C*2/*m* (No. 12), $Z = 2$, $a = 9.7659(8)$ Å, $b = 6.8787(7)$ Å, $c = 7.3870(5)$ Å, $\beta = 95.254(7)°$, $V = 494.15(6)$ Å^3, $\mathrm{C_8H_4CuN_8}$, $M_r = 275.72$, $\rho_{\mathrm{calc}} = 1.853\ \mathrm{g\,cm^{-3}}$, $2\theta_{\max} = 120.0°$, Rigaku AFC6R diffractometer with graphite monochromated Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å) and a rotating anode generator, ω–2θ scan mode, $T = 23$°C, 431 reflections measured, 404 unique ($R_{\mathrm{int}} = 0.039$), data corrected for Lorentz and polarization effects and an empirical absorption correction based on azimuthal scans was applied, as well as a correction for secondary extinction, $\mu(\mathrm{Cu}K\alpha) = 3.06\ \mathrm{mm^{-1}}$, solution by direct methods followed by successive difference Fourier methods, structure refined against F, all nonhydrogen atoms made anisotropic, hydrogen atoms included but not refined, 50 parameters, $R(F) = 0.038$, $R_w(F) = 0.074$ for 402 reflections with $I > 3\sigma(I)$, min/max residual electron density = $-0.78/0.55\ e\,\text{Å}^{-3}$.

Magnetic Measurements

Magnetic measurements were made using a Quantum Design MPMS 5 SQUID magnetometer with an applied

TABLE 1
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for α-[Cu(dca)$_2$(pyz)]$_n$

Atom	x	y	z	U(eq)
Cu(1)	9982	10276(1)	9984	12(1)
Cu(2)	12491(1)	9994(2)	7500(1)	11(1)
Cu(3)	10395(1)	9531(1)	4574(1)	13(1)
Cu(4)	7866(1)	9642(1)	7107(1)	12(1)
Cu(5)	10263(1)	5148(1)	6996(1)	12(1)
Cu(6)	12377(1)	5439(1)	9871(1)	12(1)
Cu(7)	9800(1)	5205(1)	12312(1)	11(1)
Cu(8)	7691(1)	5120(1)	9433(1)	13(1)
N(1)	10795(3)	10298(10)	9426(3)	31(2)
N(2)	10994(3)	9715(15)	8468(3)	57(3)
N(3)	11855(3)	9981(10)	7988(3)	19(2)
N(4)	9503(3)	10298(9)	9334(2)	20(1)
N(5)	9274(4)	10828(13)	8373(3)	54(3)
N(6)	8576(3)	9606(10)	7760(3)	26(2)
N(7)	9196(3)	10314(11)	10545(3)	26(2)
N(8)	8321(3)	9874(12)	10996(3)	45(2)
N(9)	8071(3)	10005(9)	11947(3)	22(2)
N(10)	10464(3)	10294(9)	10632(3)	21(2)
N(11)	11029(3)	10254(12)	11457(3)	36(2)
N(12)	12042(3)	10362(8)	11517(2)	20(1)
N(13)	13131(3)	9939(10)	8208(3)	26(2)
N(14)	13689(3)	10909(11)	8997(3)	30(2)
N(15)	14679(3)	10483(8)	9159(2)	17(1)
N(16)	11794(3)	10017(9)	6724(3)	32(2)
N(17)	11745(2)	8966(9)	5768(2)	23(1)
N(18)	11054(3)	9518(9)	5067(3)	21(2)
N(19)	9775(3)	9565(10)	5371(2)	24(2)
N(20)	8803(3)	9397(14)	5604(3)	50(2)
N(21)	8381(3)	9651(9)	6489(3)	19(2)
N(22)	7295(3)	9599(9)	7674(3)	21(2)
N(23)	6358(3)	9102(10)	8000(3)	32(2)
N(24)	5909(3)	10500(10)	8790(3)	24(2)
N(25)	9990(3)	7311(8)	9970(3)	14(1)
N(26)	9995(3)	3245(8)	9972(3)	15(1)
N(27)	12488(3)	7004(9)	7479(3)	13(2)
N(28)	12489(3)	2974(9)	7478(3)	16(2)
N(29)	10386(3)	6561(8)	4584(3)	12(1)
N(30)	10397(3)	2508(9)	4578(3)	15(2)
N(31)	7861(3)	6646(9)	7089(3)	14(2)
N(32)	7867(3)	2629(8)	7096(3)	12(2)
N(33)	11012(3)	5206(10)	6409(3)	24(2)
N(34)	11604(6)	3680(2)	5738(6)	36(3)
N(34A)	11353(6)	3980(2)	5571(6)	40(4)
N(35)	12070(3)	4879(9)	4931(3)	20(2)
N(36)	10740(3)	5121(8)	7663(3)	18(2)
N(37)	10871(5)	5140(2)	8655(6)	29(3)
N(37A)	11005(7)	4270(3)	8579(7)	46(4)
N(38)	11734(3)	5446(10)	9181(3)	27(2)
N(39)	9532(3)	5095(9)	7664(3)	17(2)
N(40)	9264(3)	5717(11)	8603(3)	31(2)
N(41)	8364(3)	5124(9)	8994(3)	21(2)
N(42)	9725(3)	5146(8)	6380(3)	19(2)
N(43)	9055(3)	4365(14)	5677(3)	46(2)
N(44)	8051(3)	4543(10)	5659(3)	29(2)
N(45)	13007(3)	5474(9)	9360(3)	22(2)
N(46)	13911(3)	5970(11)	8971(3)	33(2)
N(47)	14297(3)	4773(10)	8126(3)	21(2)
N(48)	11818(3)	5443(10)	10447(3)	18(2)
N(49)	11302(3)	5237(14)	11281(3)	44(2)
N(50)	10307(3)	5243(9)	11452(3)	28(2)
N(51)	9116(3)	5209(8)	11868(3)	19(2)
N(52)	8298(3)	4832(12)	11286(3)	46(2)
N(53)	8237(3)	5125(9)	10295(3)	22(2)
N(54)	7097(3)	5134(10)	8668(3)	22(2)
N(55)	6480(3)	4139(9)	7917(3)	23(2)
N(56)	5512(3)	4753(8)	7713(2)	18(1)
N(57)	10257(3)	8125(8)	7001(3)	12(1)
N(58)	10266(3)	12150(8)	6990(3)	16(1)
N(59)	12403(3)	8420(8)	9879(3)	13(2)
N(60)	12395(3)	12445(8)	9875(3)	16(2)
N(61)	9807(3)	8195(9)	12303(3)	13(2)
N(62)	9820(3)	12224(8)	12312(3)	12(2)
N(63)	7703(3)	8122(9)	9439(3)	14(2)
N(64)	7700(3)	12141(8)	9427(3)	13(2)
C(1)	10765(3)	10266(11)	11007(3)	20(2)
C(2)	11572(3)	10282(10)	11462(3)	22(2)
C(3)	10933(3)	10045(13)	8984(4)	27(2)
C(4)	11464(4)	9900(13)	8241(3)	27(2)
C(5)	9369(3)	10482(11)	8887(3)	23(2)
C(6)	8884(3)	10109(10)	8075(3)	17(2)
C(7)	8802(3)	10138(11)	10783(3)	19(2)
C(8)	8215(3)	9945(11)	11504(3)	23(2)
C(9)	13419(3)	10343(11)	8556(3)	15(2)
C(10)	14218(3)	10619(10)	9064(3)	18(2)
C(11)	11741(3)	9589(11)	6265(3)	24(2)
C(12)	11356(3)	9308(10)	5418(3)	17(2)
C(13)	9336(4)	9526(12)	5507(3)	18(2)
C(14)	8605(3)	9578(14)	6084(4)	25(2)
C(15)	6865(3)	9478(10)	7844(3)	13(2)
C(16)	6146(3)	9920(10)	8437(3)	18(2)
C(17)	9520(3)	6285(9)	9967(3)	18(2)
C(18)	9522(3)	4266(9)	9959(3)	15(2)
C(19)	10458(3)	4255(9)	9960(3)	15(1)
C(20)	10463(3)	6279(9)	9965(3)	16(2)
C(21)	12040(3)	6008(9)	7348(3)	17(2)
C(22)	12039(3)	3977(9)	7345(3)	17(2)
C(23)	12946(3)	3999(9)	7595(3)	17(2)
C(24)	12944(3)	6015(9)	7595(3)	17(2)
C(25)	9951(3)	5521(9)	4736(3)	14(1)
C(26)	9958(3)	3536(9)	4727(3)	17(2)
C(27)	10839(3)	3546(9)	4422(3)	20(2)
C(28)	10830(3)	5542(10)	4421(3)	17(1)
C(29)	7396(3)	5651(10)	7053(3)	16(2)
C(30)	7398(3)	3621(10)	7058(3)	16(2)
C(31)	8341(3)	3656(9)	7121(3)	15(2)
C(32)	8328(3)	5645(10)	7113(3)	16(1)
C(33)	11247(3)	4683(12)	6066(3)	24(2)
C(34)	11809(3)	4487(11)	5297(3)	24(2)
C(35)	10860(3)	4986(12)	8106(3)	29(2)
C(36)	11380(4)	5182(13)	8896(3)	28(2)
C(37)	9386(3)	5342(11)	8086(4)	19(2)
C(38)	8779(3)	5374(11)	8785(3)	15(2)
C(39)	9388(3)	4832(12)	6064(3)	19(2)
C(40)	8521(3)	4510(11)	5691(3)	24(2)
C(41)	13423(3)	5648(11)	9157(3)	19(2)
C(42)	14088(3)	5270(12)	8518(3)	18(2)
C(43)	11544(3)	5403(11)	10818(3)	16(2)
C(44)	10766(4)	5251(12)	11337(3)	24(2)
C(45)	8746(3)	5042(10)	11570(3)	16(2)
C(46)	8296(3)	5030(11)	10752(3)	23(2)
C(47)	6779(3)	4737(11)	8325(3)	17(2)
C(48)	5967(3)	4539(10)	7844(3)	18(2)
C(49)	10190(3)	9154(9)	7455(3)	15(1)
C(50)	10195(3)	11144(9)	7446(3)	15(2)
C(51)	10337(3)	11124(9)	6533(3)	14(2)
C(52)	10332(3)	9102(10)	6540(3)	18(2)
C(53)	12439(3)	9433(9)	10332(3)	16(1)
C(54)	12440(3)	11465(9)	10334(3)	15(2)
C(55)	12363(3)	11426(9)	9406(3)	18(2)
C(56)	12363(3)	9462(10)	9413(3)	15(1)
C(57)	9891(3)	9191(9)	12758(3)	16(2)
C(58)	9895(3)	11210(10)	12766(3)	18(2)
C(59)	9742(3)	11217(9)	11847(3)	15(2)
C(60)	9744(2)	9193(9)	11844(3)	12(1)
C(61)	7670(3)	9118(9)	9895(3)	17(2)
C(62)	7670(3)	11135(9)	9884(3)	16(2)
C(63)	7735(3)	11131(9)	8965(3)	17(2)
C(64)	7735(3)	9109(9)	8968(3)	15(1)

Note. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 2
Selected Bond Lengths (Å) for α-$[Cu(dca)_2(pyz)]_n$

Cu(1)-N(10)	1.961(6)	Cu(1)-N(4)	1.963(6)
Cu(1)-N(25)	2.033(5)	Cu(1)-N(26)^{i}	2.036(6)
Cu(1)-N(7)	2.373(7)	Cu(1)-N(1)	2.426(7)
Cu(2)-N(3)	1.971(7)	Cu(2)-N(9)^{ii}	1.976(7)
Cu(2)-N(28)^{i}	2.044(6)	Cu(2)-N(27)	2.051(6)
Cu(2)-N(13)	2.316(7)	Cu(2)-N(16)	2.529(7)
Cu(3)-N(18)	1.989(7)	Cu(3)-N(15)^{iii}	2.001(6)
Cu(3)-N(29)	2.036(6)	Cu(3)-N(30)^{i}	2.041(6)
Cu(3)-N(24)^{ii}	2.318(7)	Cu(3)-N(19)	2.492(7)
Cu(4)-N(22)	1.984(7)	Cu(4)-N(21)	1.986(7)
Cu(4)-N(32)^{i}	2.048(6)	Cu(4)-N(31)	2.055(6)
Cu(4)-N(6)	2.336(7)	Cu(4)-N(12)^{iii}	2.451(6)
Cu(5)-N(42)	1.984(7)	Cu(5)-N(36)	1.993(6)
Cu(5)-N(57)	2.042(5)	Cu(5)-N(58)^{iv}	2.056(6)
Cu(5)-N(33)	2.344(7)	Cu(5)-N(39)	2.439(6)
Cu(6)-N(48)	1.981(6)	Cu(6)-N(45)	1.997(7)
Cu(6)-N(59)	2.045(6)	Cu(6)-N(60)^{iv}	2.053(6)
Cu(6)-N(38)	2.288(7)	Cu(6)-N(44)^{v}	2.515(7)
Cu(7)-N(51)	1.971(6)	Cu(7)-N(56)^{v}	1.975(6)
Cu(7)-N(62)^{iv}	2.045(6)	Cu(7)-N(61)	2.050(6)
Cu(7)-N(47)^{vi}	2.366(7)	Cu(7)-N(50)	2.468(6)
Cu(8)-N(35)^{vi}	1.958(7)	Cu(8)-N(41)	1.975(7)
Cu(8)-N(64)^{iv}	2.042(6)	Cu(8)-N(63)	2.058(6)
Cu(8)-N(54)	2.351(7)	Cu(8)-N(53)	2.484(7)

Note. Symmetry operations: (i) x, $y + 1$, z; (ii) $x + 1/2$, $2 - y$, $z - 1/2$; (iii) $x - 1/2$, $2 - y$, $z - 1/2$; (iv) x, $y - 1$, z; (v) $x + 1/2$, $1 - y$, $z + 1/2$; (vi) $x - 1/2$, $1 - y$, $z + 1/2$.

field of 1 T. The samples were contained as powders in a gelatin capsule which was held in the center of a drinking straw and fixed to the end of the sample rod. Tests for the presence of long-range magnetic order were made by measuring the magnetization, with field cooling (FCM) and zero-field cooling (ZFCM), in an applied field of 5 Oe. Values were found to be identical, which indicated no long-range order.

TABLE 3
Atomic Coordinates ($\times 10^4$) and B(iso)/B(eq) (Å^2) for β-$[Cu(dca)_2(pyz)]_n$

Atom	x	y	z	B(iso)/B(eq)
Cu(1)	0	5000	5000	0.89(4)
N(1)	0	2018(7)	5000	0.91(8)
N(2)	1224(4)	5000	7267(6)	1.17(9)
N(3)	2757(4)	5000	10093(6)	2.4(1)
N(4)	1896(4)	5000	13107(5)	1.3(1)
C(1)	299(4)	1000(6)	3545(5)	0.98(7)
C(2)	1905(5)	5000	8635(7)	1.3(1)
C(3)	2251(5)	5000	11685(7)	1.3(1)
H(1)	516	1674	2487	1.17

Note. $B(\mathrm{eq}) = 8\pi^2/3(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

TABLE 4
Selected Bond Lengths (Å) and Angles (°) for β-$[Cu(dca)_2(pyz)]_n$

Cu(1)–N(1)	2.051(5)	Cu(1)–N(2)	1.966(5)
Cu(1)–N(4)	2.420(5)	N(1)–C(1)	1.337(4)
N(2)–C(2)	1.158(7)	N(3)–C(2)	1.299(7)
N(3)–C(3)	1.317(8)	N(4)–C(3)	1.135(7)
C(1)–C(1)	1.376(8)		
Cu(1)–N(1)–C(1)	121.6(2)	Cu(1)–N(2)–C(2)	177.7(4)
Cu(1)–N(4)–C(3)	148.1(4)	C(1)–N(1)–C(1)	116.9(4)
N(1)–C(1)–C(1)	121.6(2)	C(2)–N(3)–C(3)	118.5(4)
N(2)–C(2)–N(3)	175.3(5)	N(3)–C(3)–N(4)	175.8(5)

RESULTS AND DISCUSSION

Synthesis and Characterization

Reaction of sodium dicyanamide, copper(II) nitrate and pyz in water in 2:1:1 mole ratio leads to instant precipitation of the α-isomer $[Cu(dca)_2(pyz)]_n$ as a pale green/blue powder. It can be filtered off and used in powder form. Needle-shaped crystals are obtained by layering the reagents together in a glass tube and allowing slow diffusion to occur. If the powder of the α-form is not removed but allowed to remain in solution, it transforms into blue crystals of the β-isomer. This isomer is obtained as single crystals by layering an aqueous solution of sodium dicyanamide and pyz onto a tetramethoxysilane gel containing copper(II) nitrate. The α-needles form first and then disappear as crystals of the β-form grow. The structural isomers both

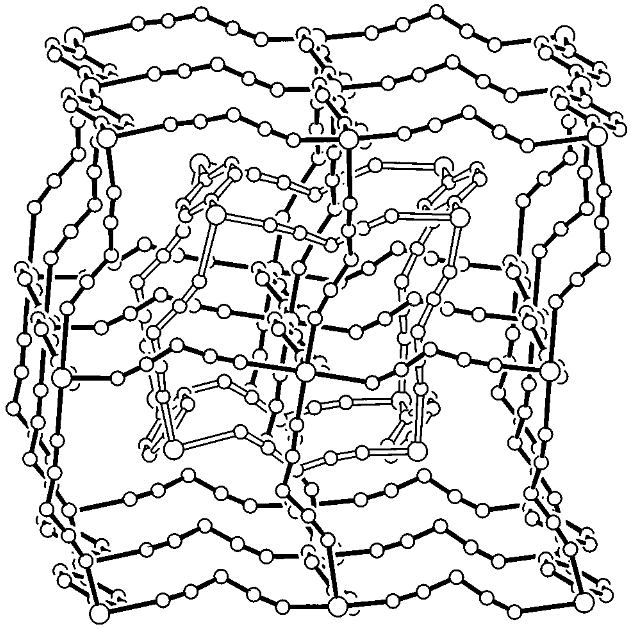

FIG. 1. The two interpenetrating α-Po related networks of α-$[Cu(dca)_2(pyz)]_n$.

give well-resolved IR and Raman spectra, characteristic IR bands of the coordinated dca moiety being listed under Experimental.

Structures

The structure of α-$[Cu(dca)_2(pyz)]_n$ contains two interpenetrating α-Po-like networks (Fig. 1) (1a). Each Cu is coordinated to four dca ligands (via the nitrile nitrogens) and two *trans* pyz ligands. The two-connecting dca bridges connect the Cu atoms into square-grid-like $Cu(dca)_2$ sheets, and these sheets are connected to each other in the *b* direction by the bridging pyz ligands to give the α-Po-like nets. All the Cu atoms show Jahn–Teller distortion, with the two long Cu–N bonds involving the dca ligands.

The structure of β-$[Cu(dca)_2(pyz)]_n$ consists of square-grid-like sheets (Fig. 2). Each Cu atom is coordinated to four dca anions through the nitrile nitrogens and two *trans* pyz ligands. The two-connecting dca ligands now connect each copper to only *two* neighboring Cu atoms (cf. *four* Cu neighbors in the α isomer) via two $Cu(dca)_2Cu$ "double" bridges. This results in linear $Cu(dca)_2$ chains which are then cross-linked by the bridging pyz ligands to give a sheet-like topology. The sheets stack in the *a* direction and are interdigitated (Fig. 3). The Cu atoms show Jahn–Teller distortion, with the two long Cu–N bonds again involving the dca ligands.

Unlike the $M(dca)_2$ structures (3), which contain three-connecting dca ligands, the amido nitrogens of the dca ligands in both isomers do not participate in any bonding interactions.

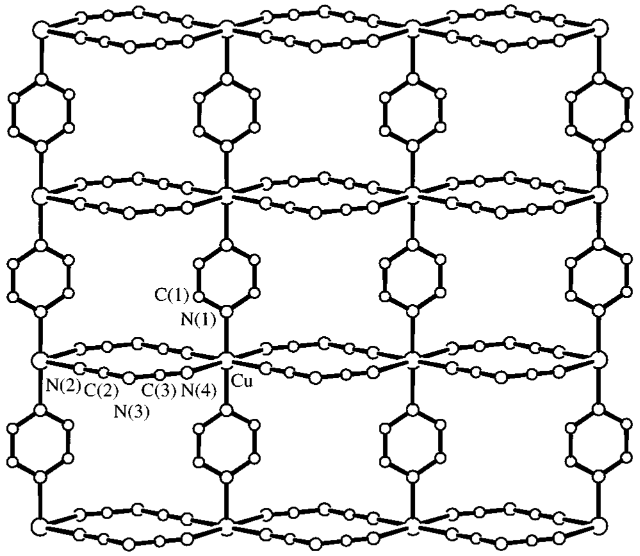

FIG. 2. The sheet topology of β-$[Cu(dca)_2(pyz)]_n$. $Cu(dca)_2$ chains are linked by bridging pyz ligands.

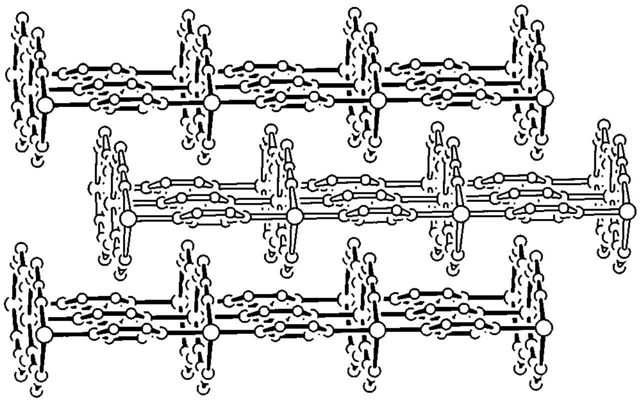

FIG. 3. Three interdigitated sheets in the structure of β-$[Cu(dca)_2(pyz)]_n$.

Magnetic Properties

The magnetic susceptibility versus temperature plots of the α- and β-forms are very similar in shape and magnitude. The data for the β-form, measured in a field of 1 T, are shown in Fig. 4. A maximum in χ occurs at 3.5 K, indicative of very weak antiferromagnetic coupling. Above this temperature the χ values follow a Curie–Weiss dependence with $\theta = -6.2$ K. The corresponding χT (and μ_{eff}) values decrease only a small degree from $0.480\,cm^3\,mol^{-1}\,K$ ($1.96\,\mu_B$) at 300 K to $0.438\,cm^3\,mol^{-1}\,K$ ($1.87\,\mu_B$) at 50 K before decreasing more rapidly to reach $0.085\,cm^3\,mol^{-1}\,K$ ($0.82\,\mu_B$) at 2 K. We are presently developing models to try and fit the data and deduce an exchange constant. Simple pairwise or linear chain $S = 1/2$ models cannot replicate the shape of the curve in the χ_{max} region. (See Note Added in Proof.)

Measurements of magnetization made in very small applied fields such as 5 Oe show no evidence for long-range magnetic order. Thus, the use of pyz to link polymeric $Cu(dca)_2$ sheets or chains only enhances the strength of antiferromagnetic coupling a little. It does not lead to the occurrence of a magnetic phase transition. The weak antiferromagnetism is similar to that observed in two structurally uncharacterized chainlike isomers of $[Cu(dca)_2(imidazole)_2]_n$, although no maximum in χ was observed. Long-range order was postulated to occur at low temperatures in the imidazole systems but no proof was given and it is unlikely to be correct (7a).

Other $[M(dca)_2(pyz)]_n$ species, where $M =$ Mn, Fe, Co, Ni have recently been isolated and found to generally form the present kind of α-structure (10). Their properties will be described elsewhere. They likewise all tend to be weakly antiferromagnetically coupled without any bulk ordering of spins noted. This contrasts markedly with the magnetically ordered parent rutilelike $M(dca)_2$ phases. We are presently

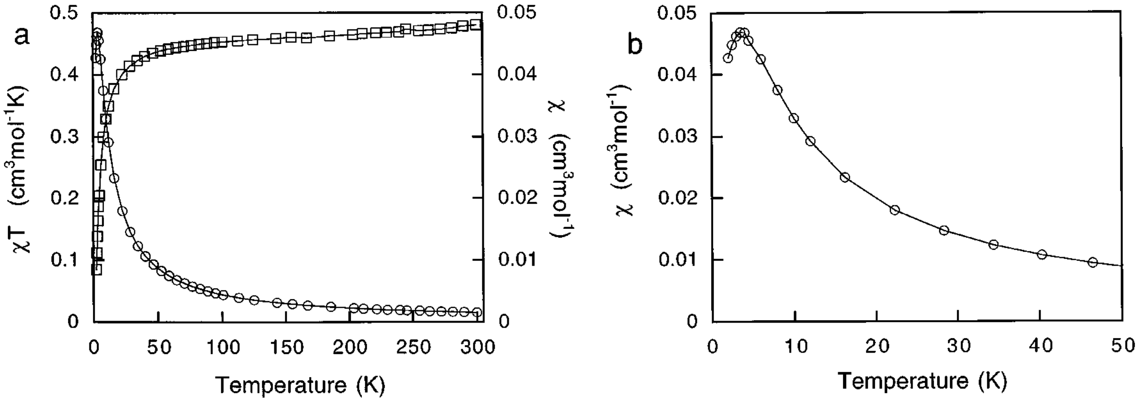

FIG. 4. (a) Temperature dependence of magnetic susceptibility, χ(○), and of χT(□) for β-[Cu(dca)$_2$(pyz)]$_n$. (b) Expansion of the low temperature susceptibility region. The solid lines simply connect the experimental points.

using other linear ligands such as 4,4′-bipyridine and smaller anions such as CN^- or N_3^-; such anions are known to be capable of transmitting ferromagnetic coupling which, in some cases, leads to long-range order (11). The "ground rules" for designing molecular-based magnets in the present kind of "linked" network structures still need to be developed. The coordinating mode of linker ligands such as azide may well be important in view of a lack of order noted, for instance, in "end-to-end" bridging between Mn^{II} centers, found in a 3D-scaffold example [Mn(4,4′-bipy)(N$_3$)$_2$]$_n$ (12), while magnetic order was observed in a mixed end-on/end-to-end example [Mn(4-CN-pyridine)$_2$(N$_3$)$_2$]$_n$ (13).

Finally, we note that the two interpenetrating networks in the α-isomer each behave the same way magnetically, with no interactions evident between the nets. It remains to be seen whether this is a general phenomenon.

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Note Added in Proof. Use of the Lines model (14) for 2D systems with $S = 1/2$, based on that of Rushbrooke and Wood (15), gave a very good fit of the data at all temperatures including the region of maximum susceptibility. The best fit parameters are $g = 2.25$, $J = -2.6\ \text{cm}^{-1}$ (for Hamiltonian $JS_1.S_2$) and temperature independent susceptibility $= 0.00006\ \text{cm}^3\ \text{mol}^{-1}$. This single J model is approximate for systems of the present kind which possess two different bridging pathways.

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