Supplementary Materials

Recent insights into magneto-structural properties of Co(II) dicyanamide coordination compounds

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Table S1. Magneto-structural data for mononuclear dca-Co(II) compounds.

Compound	Co–N$_{ligand}$ [Å]	Co–N$_{DCA}$ [Å]	Angles [°]		Co···Co [Å]	Magnetism	Ref
			Co-NC$_{(dca)}$	C–N–C$_{(dca)}$			
Monodentate organic ligand							
[Co(bim)$_4$(dca)$_2$]	2.1546(15) 2.1489(15)	2.1575(18)	155.32(18)	122.8(3)	9.686(2)	**dc** $\lambda_M T$ = 3.06 cm^3 mol^{-1} K at room temperature $\lambda_M T$ = 1.76 cm^3 mol^{-1} K at 2.0 K α = 1.18 λ = −132.0 cm^{-1} Δ = −416.3 cm^{-1} TIP = 708.10^{-6} cm^3 mol^{-1} with F = 7.5 · 10^{-6} D – **ac** τ_0 = 0.87 ·10^{-6} s E = 7.74 cm^{-1} at 1000G	[3]
[Co(4bpo)(H$_2$O)$_2$(dca)]H$_2$O	2.189 2.189 2.066 2.066	2.079 2.079	170.0	124.3(3)	9.459	undiscussed	[9]
[Co(NITpPy)$_2$(H$_2$O)$_2$(dca)$_2$]	2.069 2.069 2.167 2.167	2.117 2.117	155.1	122.4(2)	7.187	**dc** μ_{eff} = 5.55 μ_B room temperature μ_{eff} = 1.84 μ_B at 2K J= 4.53 cm^{-1} g = 2.34 θ = 0.1 K R = 6.68·10^{-3}	[10]
Bidentate organic ligand							
[Co(H$_2$biim)$_2$(dca)$_2$]	2.1435(12)	2.1912(13)	118.82(10)	119.27(13)	7.162(1)	**dc**	[1]

	2.1268(12) 2.1435(12) 2.1258(12)	2.1912(13)	120.47(10)			χ_T = 2.55 emuKmol^{-2} room temperature g = 2.33 D = 23.3 cm^{-1}	
[Co(phen)$_2$(dca)$_2$] Crystal 1a	**193K** 2.149(1) 2.147(1) 2.145(1) 2.173(2) **293K** 2.142(2) 2.142(2) 2.141(2) 2.166(2)	**193K** 2.093(2) 2.070(2) **293K** 2.092(2) 2.066(2)	173.8(1) 169.4(2)	121.4(2) 122.4(2)	8.6007(5)	g= 2.657 D = 99.1 cm^{-1}	[7]
[Co(phen)$_2$(dca)$_2$] Crystal 1b	293K 2.139(3) 2.175(3) 2.132(3) 2.157(3)	293K 2.071(3) 2.069(3)	171.3(3) 168.3(3)	124.6(4) 125.8(4)	8.2645(8)	**dc** μ_{eff} = 4.94μ_B room temperature μ_{eff} = 3.86μ_B at 2K g = 2.596 D = 84.8 cm^{-1}	[7]
[Co(hdpa)$_2$(dca)$_2$]	2.128(2) 2.158(2) 2.128(2) 2.158(2)	2.123(2) 2.123(2)	173.5(2)	123.9(3)	8.062	**dc** μ_{eff} = 4.74 μ_B at room temperature μ_{eff} = 4.36 μ_B at 85 K	[5]
[Co(hmpH)$_2$(dca)$_2$]	2.114 2.114 2.165 2.165	2.077 2.077	162.1	120.4(2)	8.5828	undiscussed	[11]
Tridentate organic ligand							
[Co(tppz)$_2$](dca)$_2$]	**125K** N1 1.855(5) N7 1.917(5) N3 1.977(4) N5 2.155(4)	– uncoordinated dca	–	**125K** 120.5(6) **330K** 123.2(7)	**125K** 8.9361(7) **330K** 9.0081(4)	**dc** $\chi_M T$ = 0.42 cm^3 mol^{-1}K in 1.9–170K $\chi_M T$ = 0.675 cm^{3}mol^{-1}K at 400K SCO phenomenon	[4]

	330K N1 1.870(3) N7 1.912(3) N3 2.003(2) N5 2.128(2)				Å		
Tetradentate organic ligand							
[Co(L¹)(dca)₂]	**100K** 2.340(2) 1.920(2) 2.315(2) 1.909(2) **280K** N2 2.002(2) N1 2.351(2) N4 1.999(3) N3 2.324(2)	**100K** 1.927(2) 1.942(2) **280K** 2.003(3) 2.024(3)	**100K** 173.7(2) 166.5(2) **280K** 170.4(3) 164.3(3)	**100K** 117.8(2) 116.2(1) **280K** 121.9(4) 118.0(3)	**100K** 8.9101(6) **280K** 9.0233(8)	χT = 2.55 $cm^3\ mol^{-1}K$ at 400 K χT in a range 0.52–0.49 $cm^3\ mol^{-1}$ K at 80–20 K SCO phenomenon	[2]
[Co(12-TMC)(dca)₂]	2.273(1) 2.176(1) 2.283(1) 2.179(1)	2.076(2) 2.106(1)	160.0(1) 163.2(1)	119.1(2) 123.6(2)	8.174(1)	**dc** χT = 2.61 $cm^3\ mol^{-1}K$ at 400K χT = 1.65 $cm^3\ mol^{-1}K$ at 2 K D = 25.95(9) cm^{-1} E = 0.12(3) cm^{-1} **ac** $\tau_0 = 1.14 \cdot 10^{-8}$ s, U_{eff} = 27.31 cm^{-1} C = 1.54 $s^{-1}\ K^{-4.19}$ n = 4.19	[6]
[Co(LC)₂(dca)₂]	2.1015(19) 2.1075(19) 2.2640(2) 2.2660(2)	2.0590(2) 2.0850(2)	152.2(3) 160.0(3)	121.3(3) 121.1(3)	8.9097(8)	undiscussed	[8]

H_2BiIm = 2,2′-biimidazole; **L[1]**= N,N′-di-tertbutyl-2,11-diaza[3,3](2,6)pyridinophane; **bim** = 1-benzylimidazole; **tppz** = 2,3,5,6-tetrakis(2-pyridyl)pyrazine; **hdpa** = 2,2′-dipirydylamine; **TMC**- 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane; **LC** = lidocaine; **hmpH**= 2-(hydroxymethyl)pyridine; **4-bpo**= 2,5-bis(4-pyridyl)-1,3,4-oxadiazole; **nitppy**= 2-(4′ -pyridyl)-4,4,5,5–tetramethylimidazoline-1-oxyl-3-oxide

Table S2. Shape values for mononuclear Co(II) complexes

Compound	HP-6	PPY-6	OC-6	TPR-6	JPPY-6	Ref.
[Co(bim)$_4$(dca)$_2$]	30.506	29.063	0.122	16.127	32.410	3
[Co(4bpo)$_2$(H_2O)$_2$(dca)$_2$](H_2O)$_2$	32.603	29.787	0.080	16.591	33.122	9
[Co(dca)$_2$(NITpPy)$_2$(H_2O)$_2$]	31.801	29.395	**0.077**	16.316	32.683	10
[Co(H_2biim)$_2$(dca)$_2$]	28.471	28.043	0.659	15.918	31.019	1
[Co(phen)$_2$(dca)$_2$] 1a	31.621	25.065,	0.937	12.946	28.756	7
[Co(phen)$_2$(dca)$_2$] 1b	31.453	25.680	0.808	13.917	29.505	7
[Co(hdpa)$_2$(dca)$_2$]	31.718	27.598	0.357	14.744	31.031	5
[Co(hmpH)$_2$(dca)$_2$]	32.432	25.117	1.092	12.390	29.031	11
[Co(tppz)$_2$](dca)$_2$]	34.295	24.111	2.214	12.736	27.804	4
[Co(L1)(dca)$_2$]	33.208	22.899	2.703	11.181	27.776	2
[Co(12-TMC)(dca)$_2$]	33.728	18.840	**2.966**	7.590	22.627	6
[Co(LC)$_2$(dca)$_2$]	30.898	25.086	1.016	14.126	28.877	8

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Table S3. Magneto-structural data for binuclear dca-Co(II) compounds.

Compound	Co–N$_{ligand}$ [Å]	Co–N$_{DCA}$ [Å]	Angles [°]		Co···Co [Å] In dimer Between dimers	Magnetism	Ref
			Co-NC$_{(dca)}$	C–N–C$_{(dca)}$			
$[Co(tptz)(H_2O)(dca)]_2\cdot(ClO_4)_2$	2.176(3) 2.087(3) 2.196(3) 2.168	2.108(3) 2.030(3)	145.7(3) 169.7(3)	122.3(4)	7.377(3) 10.577(2)	$\chi_M T$=6.019 cm^{3}K mol^{-1} at 300 K $\chi_M T$= 4.41 cm^{3}K mol^{-1} at 20 K.	[1]
$[Co(bpm)_2(dca)]_2(ClO_4)_2$	2.184(5) 2.197(5) 2.147(5) 2.152(5)	2.150(6) 2.126(5)	158.0(5) 163.7(5)	123.5(6)	7.592(2) 9.266(3)	undiscussed	[2]

Tptz = 2,4,6-tris(2-pyridyl)-1,3,5-triazine; **bpm** = bis[(3,5-di methyl)pyrazolyl]methane

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Table S4. Magneto-structural data for one-dimensional dca-Co(II) coordination polymers.

Compound	**Co–N$_{ligand}$ [Å]**	**Co–N$_{DCA}$ [Å**	**Angles [°]**		**Co···Co in chain or (between chains) [Å]**	**Magnetism**	**Ref**
			Co-NC$_{(dca)}$	**C–N–C$_{(dca)}$**			
Single μ$_{1,5}$- dca bridge							
{[Co(H$_2$BiIm)$_2$(dca)$_2$]Cl}$_n$ helisa	2.1386(18) 2.1593(18) 2.1372(18) 2.1325(18)	2.1900(19), 2.1133(19)	124.4(2) 172.3(2)	120.4(2)	7.2860(5) 7.9690(6)	**dc** χT = 2.34 emu K mol^{-1} D = 40.3 cm^{-1}, zJ/kB = 20.05 cm^{-1}, TIP = 170·10^{-6} emumol^{-1}	[1]
[Co(etpybzam)(dca)$_2$]$_n$	2.154(2) 2.086(2) 2.240(2)	2.164(3) 2.097(3) 2.043(3)	151.4(2) 172.6(2) 160.7(3)	122.3(3) 122.1(3)	8.6068(5) 7.9531(5)	**dc** $\chi_M T$ = 3.35 cm^{3}mol^{-1}K at 300K $\chi_M T$ = 2.25 cm^{3}mol^{-1} K at 2K	[6]
{[Co(imph)$_4$(dca)](ClO$_4$)·(EtOH)$_4$(H$_2$O)}$_n$	2.122 2.122 2.122 2.122	2.066 2.087	180.0	115.14	8.609 11.8073	**dc** $\chi_M T$ = 3.03 cm^3 mol^{-1} K at 300K $\chi_M T$ = 1.47 cm^3 mol^{-1} K at 2 K	[8]
{[Co(L4)(dca)(ClO$_4$)(MeOH)$_2$]}$_n$	Co(A) 2.1619(19) 2.0785(19) 2.1011(18) 2.1323(19) Co(B) 2.141(2) 2.1017(19) 2.097(2)	Co(A) 2.1828(18) 2.0851(19) Co(B) 2.1013(18) 2.089(2)			8.451 Å 8.532 Å	**dc** $\chi_M T$ = 6.0 cm^3 K mol^{-1} at 300K $\chi_M T$ = 3.5 cm^3 Kmol $^{-1}$ at 2K lack of significant magnetic interactions	[9]

	2.1661(19)							
$\{[Co(enbzpy)(dca)](PF_6)\}_n$	2.097(5) 2.038(4) 2.045(4) 2.109(5)	2.128(5) 2.134(5)	172.0(5) 158.5(4)	130.1(7)	8.699(1) 9.183(1)	$\chi_M T$ = 2.67 cm³ mol⁻¹ K $\chi_M T$ = 0.65 cm³ mol⁻¹ K SCO	[16]
$\{[Co(bpm)_2(dca)](ClO_4)\}_n$	2.141 2.141 2.141 2.141	2.102 2.102			8.000 8.551	–	[18]
$[Co(MeOH)_2(3\text{-}PyO)(3\text{-}PyOH)(dca)]_n$	2.138 2.138 2.124 2.124	2.102 2.102	165.54 165.54	121.77	8.665 7.790	$\chi_M T$ = 2.98 cm³ mol⁻¹ K at 300K $\chi_M T$ = 1.5 cm³ mol⁻¹ K at 2K C = 3.123 cm³mol⁻¹K Θ = –16.29K	[21]
$\{[Co(bdpab)(dca)](ClO_4)\}_n$	2.118(6) 2.129(6) 2.183(5) 2.252(6)	2.031(6) 2.109(6)	154.7(6) 168.6(6)	122.2(7)	7.878(1) 8.737(2)	very weak or almost zero interaction due to large Co···Co	[22]
$[Co(pybiu)(dca)]_n$	1.986(3) 1.952(4) 1.966(3)	2.330(4) 1.956(5)	121.3(4) 158.1(4)	120.6(5)	7.2115(8) 7.6779(8)	$\chi_M T$ = 0.399 cm³ mol⁻¹ K at 300 K $\chi_M T$ = 0.102 cm³ mol⁻¹ K at 2K	[23]
$\{[Co(enbzpy)(dca)](ClO_4)\}_n$	**room temperature** 2.102(3) 2.083(3) 2.023(3) 2.028(3) **low temperature** 2.138(8) 2.074(8) 2.089(8)	**room temperature** 2.092(3) 2.136(3) **low temperature** 2.141(9) 2.073(8)	176.3(3) 152.7(3)	121.4(9)	8.569(8) 8.390(6)	$\chi_M T$ = 2.43 cm³ mol⁻¹ K at 300 K $\chi_M T$ = 1. 65 cm³ mol⁻¹ K at 171 K $\chi_M T$ = 1.60 cm³ mol⁻¹ K at 2 K small hysteresis loop SCO DSC	[34]

{[Co(H_3daps)(dca)](MeOH)$_2$(MeCN)}$_n$	2.203(3) 2.141(3) 2.215(3) 2.231(2) 2.190(2)	2.083(3) 2.081(3) mostek	169.1(3) 172.1(3)	118.2(3)	7.9803(7) 10.6741(6)	**dc** $\chi_M T$ = 2.76 cm^3 mol^{-1} K at 300 K $\chi_M T$ = 1.61 cm^3 mol^{-1} K at 2 K D = 41.3(5) cm^{-1} E = 0.81(3) cm^{-1} J= 0.004 cm^{-1} **Ac** U_{eff} = 9.9 K (6.88 cm^{-1}) τ =5.3·10 $^{-6}$ s	[37]
{[Co(pypz)(dca)(H_2O]·dca}$_n$	2.1082(18) 2.1891(19) 2.1685(18)	2.057(2) 2.096(2)	155.6(2) 165.03(19)	121.7(2)	7.447(6) 8.4287(7)	**dc** μ_{eff} = 5.17μB **ac** U_{eff} = 103 K τ =1.2·10^{-11}s	[39]
{[Co_2(tppz)(dca)$_4$]$_n$·CH_3CN}$_n$	2.078(2) 2.213(2) 2.220(2) 2.005(2)	2.096(2) 2.104(2)	170.4(2) 172.4(2)	124.6(2)	8.465(3) 8.559(3)	$\chi_M T$ = 2.99 cm^3 mol^{-1} K at 2 K θ = −9.78 K C = 4.92 cm^3·K·mol^{-1}	[40]
Double $\mu_{1,5}$- dca bridge							
{[Co(azpyph)(dca)](BF$_4$)·MeOH}$_n$	2.309(2) 2.041(2) 2.346(3) 2.045(2)	2.070(3) 2.100(3)	156.3(2) 177.2(2)	125.3(3)	8.3790(9) 9.276(1)	$\chi_M T$ = 3.14 cm^3 mol^{-1} K at 300 K D = −72.3 cm^{-1} E/D =0.00 zj = −0.273 cm^{-1}	[2]
{[Co(nic)$_2$(dca)$_2$]$_n$·2nCH_3OH}$_n$	2.157 2.157	2.114 2.127 2.114 2.127	162.3 156.7	119.3(3)	7.353 6.827	$\chi_M T$ = 3.36 cm^3 mol^{-1} K at 300 K $\chi_M T$ = 1.842 cm^3 mol^{-1} K at 300 K C = 3.58 cm^3·mol^{-1}·K, θ = −17.8 K	[3]
{[Co(dca)$_2$(H_2O)$_2$]·(hmt)}$_n$	2.082	2.123	162.0	118.2(2)	7.3617	**dc**	[5]

	2.082	2.118 2.123 2.118	162.6	118.2(2)	7.1243	$\chi_M T$ = 2.95 cm^3 mol^{-1} K at 300 K $\chi_M T$ = 2.1 cm^3 mol^{-1} K at 15 K	
[Co(1-Pytz)$_2$(dca)$_2$]$_n$	2.159 2.159	2.107 2.107 2.113 2.113	148.3 163.5	118.8(1)	7.259 7.817	**dc** C= 3.55K cm^3/mol Θ= –27.6 K	[7]
{[Co(H$_2$O)$_2$(dca)$_2$](2,6-lut-NO)}$_n$	2.073(2) 2.077(2)	2.125(3) 2.132(3) 2.131(3) 2.145(3)	147.1(3) 162.8(3)	119.4(3)	7.4471(8) 7.4471(8)	**dc** C = 3.39 cm^{3}Kmol^{-1} θ= –15.2 K J= 16.6±0.3 K	[10]
[Co(2-ampy)$_2$(dca)$_2$]$_n$	2.193(3) 2.193(3)	2.126(2) 2.126(2) 2.128(2) 2.128(2)	157.7 165.8	121.05(2)	7.3934 7.4488	undiscussed	[11]
[Co(dmf)$_2$(dca)$_2$]$_n$	2.109 2.109	2.102 2.122 2.102 2.122	159.7 151.7	120.4(3)	7.3787 6.4415	undiscussed	[13]
[Co(im)$_2$(dca)$_2$]$_n$	2.095 2.095	2.152 2.152 2.157 2.157	155.7 161.7	117.9(2)	7.3585 6.5665	**dc** $\chi_M T$ = 1.97 cm^3 mol^{-1} K at 300 K θ= – 39.8 K J = –24.8 K predominant antiferromagnetic coupling	[14]
[Co(im)$_2$(dca)$_2$]$_n$	2.101 2.101	2.164 2.164 2.161 2.161	155.4 162.1	118.6(2)	7.395 6.580	**dc** $\chi_M T$ = 3.26 cm^3 mol^{-1} K at 300 K $\chi_M T$ = 1.795 cm^3 mol^{-1} K at 2 K C = 2.8–3.4 cm^{3}Kmol^{-1} J = –0.7cm^{-1}	[15]
[Co(4-MOP-NO)$_2$(dca)$_2$]$_n$	Co-O	2.127	160.6	117.7(1)	7.3603	**dc**	[17]

	2.0572 2.0572	2.127 2.132 2.132	145.9		6.6096	$\chi_M T$ = 3.24 cm^3 mol^{-1} K at 300 K $\chi_M T$ = 2.20 cm^3 mol^{-1} K at 2 K C = 3.58 $cm^3 Kmol^{-1}$ θ= – 15.5 K	
$[Co(dmf)_2(dca)_2]_n$	2.101 2.101 Co-O	2.124 2.124 2.124 2.124	152.81	119.34(1)	7.393 7.722	undiscussed	[18]
$[Co(4\text{-}OMP)_2(dca)_2]_n$	2.125 2.125	2.116 2.116 2.124 2.124	163.26 158.50	114.75(5)	7.213 7.076	**dc** $\chi_M T$ = 3.24 cm^3 mol^{-1} K at 300 K $\chi_M T$ = 2.20 cm^3 mol^{-1} K at 2 K C = 3.58 $cm^3 mol^{-1}$ Θ = –15.5 K	[20]
$\{(PPh_4)[Co(dca)_4]\}_n$	2.091 2.091	2.176 2.176 2.165 2.165	157.73 157.73	120.8(3)	7.589 12.314	**dc** C = 1.394 cm^3 $Kmol^{-1}$ Θ = +0.1 K	[24]
$\{[Co(phen)(H_2O)(dca)_2]\cdot MeOH\}_n$	2.210(2) 2.127(2)	2.112(2) 2.103(2) 2.106(2) 2.126(2)	152.6(2) 149.2(2) 160.1(2) 166.5(2)	117.4(2) 117.4(2)	7.3244(5) 6.7451(6)	undiscussed	[26]
$[Co(pyr)_2(dca)_2]_n$	2.097(2) 2.072(3)	2.084(3) 2.084(3) 2.099(2) 2.099(2)	159.3 159.3 159.5 159.5	117.8 115.5	7.220 8.513	**dc** $\chi_M T$ = 3.0 cm^3 mol^{-1} K at 300 K $\chi_M T$ = 1.5 cm^3 mol^{-1} K at 2 K	[28]
$[Co(py\text{-}NH_2)_2(dca)_2]_n$	2.147 2.147	2.097 2.097 2.154 2.154	173.8 144.2	117.9(3)	7.2934 7.6977	**dc** $\chi_M T$ = 3.2 cm^3 mol^{-1} K at 300 K $\chi_M T$ = 2.01 cm^3 mol^{-1} K at 2 K C = 3.64 $cm^3 mol^{-1}$	[30]

						Θ = –17.9 K	
$[Co(pyo)_2(dca)_2]_n$	2.075 2.075	2.121 2.121 2.121 2.121	153.2 153.2	117.7	7.318 9.405	**dc** $\chi_M T$ = 2.7 $cm^3\ mol^{-1}$ K at 300 K $\chi_M T$ = 1.4 $cm^3\ mol^{-1}$ K at 2 K small amount of ferromagnetic or canted antiferromagnetic-ordered impurities →[α- or ß-$[Co(dca)_2]_n$] C = 2.8–3.4 $cm^3 mol^{-1}$ J = –1.54 K	[33]
$[Co(5,6\text{-}(Me)_2\text{-}bzim)_2(dca)_2]_n$	2.1165(19) 2.1165(19)	2.1981(14) 2.1981(14) 2.1981(14) 2.1981(14)	161.49(12)	120.20(18)	7.734(1) 9.428(1)	**dc** D=63(19) cm^{-1} **ac**	[36]
$[Co(5\text{-}Mebzim)_2(dca)_2]_n$	2.122(3) 2.122(3)	2.141(2) 2.141(2) 2.141(2) 2.141(2)	160.41(19)	117.8(3)°	7.322(3) 8.966(1)	**dc** D=60(8) cm^{-1} **ac**	[36]
$[Co(bpym)_2(dca)_2]_n{\cdot}H_2O$	2.151 2.151	2.092 2.092	161.8 150.8	125.0(9)	8.649 6.735	**dc** Θ = –42 K $\chi_M T$ = 3.33 emu K mol^{-1}	[38]
$\{[Ph_4P]_2\{Co(dca)_2]_4\}_n$	2.083 2.083	2.166 2.166 2.160 2.160	158.0 153.8	120.7(2)	7.5684 12.2867	No peaks in ac measurements	[41]
$[Co(dmf)_2(dca)_2]_n$	2.097 2.097	2.124 2.124 2.134 2.134	151.4 155.1	119.3(7)	7.403 7.728	undiscussed	[42]
$[Co(apym)(dca)_2]_n$	2.159	2.112 2.112	$\mu_{1,5}$ 162.4	117.8 117.8	6.1182	undiscussed	[6]

		2.085 2.085	161.2 **μ3** Co-NC 120.7 120.7				
$[Co(pydz)_2(dca)_2]_n$ monoclinic	2.166 2.166	2.110 2.110 2.110 2.110	158.2 158.2	119.4	7.3409 9.3107	**dc** μ_{eff} = 5.26 μ_B C = 3.46 cm^3mol^{-1} Θ = –20.46 K	[19]
$\mu_{1,3,5}$- dca bridge							
$[Co(pydz)_2(dca)_2]_n$ orthorhombic	2.140	Single $\mu_{1,5}$ 2.088 $\mu_{1,3,5}$ 2.122 2.122 2.231	Single $\mu_{1,5}$ 162.93 162.93 $\mu_{1,3,5}$ 160.12 160.12	117.72 117.09	7.3474 (via $\mu_{1,5}$) and 6.0490 (via $\mu_{1,3,5}$) 9.4155	**dc** μ_{eff} = 5.29 μ_B C = 3.50 cm^3mol^{-1} Θ = –18.11 K	[19]
double Bridges (ligand + dca)							
$[Co(bpds)(dca)_2]_n$	2.180 2.180	2.136 2.144 2.136 2.144	152.2 159.5	121.5(5)	7.302 8.092	χ_MT = 3.1 cm^3 mol^{-1} K at 300 K χ_MT = 1.65 cm^3 mol^{-1} K at 2 K	[5]
$[Co(bpp)(dca)_2]_n$	2.143 2.143	2.119 2.119 2.130 2.130	152.78 156.46	118.9(3)	7.0497 8.1720	χ_MT = 1.88 emu mol^{-1} K at 300 K χ_MT = 1.59 cm^3 mol^{-1} K at 2 K	[35]
$\{[Co_3(nic)_4(H_2O)_8(dca)_2]\cdot(H_2O)_2\}_n$	Co1 and Co3 2.057(3) 2.115(3) 2.145(3) 2.161(3)	Co1 and Co3 2.087(3)– 2.142(3)	-	-	-	short-range antiferromagnetic coupling	[32]

	Co2 2.093(2) 2.094(2)						
$[Co_2(tppz)(dca)_4]_n$	2.156(2) 2.156(2) 2.114(2) 2.114(2) 2.140(2) 2.140(2)	2.044(2) 2.044(2) 2.141(2) 2.141(2)	168.9(2) 152.3(2)	119.1(2)	7.377 A 5.9262(5)	**dc** $\chi_M T$ = 4.12 cm^3 mol^{-1} K at 300 K $\chi_M T$ = 0.20 cm^3 mol^{-1} K at 2K J= –1.10 cm^{-1} J′ = – 0.05 cm^{-1}	[27]
dca as a co-ligand							
$[Co(bimb)_2(dca)_2]_n$	2.168 2.154 2.168 2.154	2.139 2.139	169.9 169.9	124.1(2) 124.1(2)	10.146 7.583	undiscussed	[4]
$[Co(HFlu)_2(dca)_2]_n$	2.082 2.082	2.140 2.172	147.96 162.33	123.2(5)	10.132 9.073	undiscussed	[12]
$[Co(bte)_2(dca)_2]_n$	2.165 2.165 2.124 2.124	2.132 2.132	157.0	119.4(3)	8.345 9.597	**dc** $\chi_M T$ = 3.2 cm^3 mol^{-1} K at 300K $\chi_M T$ = 1.32 cm^3 mol^{-1} K at 2K θ = –0.57 K C = 2.80 $cm^3 mol^{-1}$K	[29]
$[Co(4\text{-}bpmp)_2(H_2O)_2(dca)_2]_n$	2.110 2.110 2.149	2.104 2.104	160.9	123.9(2)	16.652 8.2570	undiscussed	[31]
Two different dca bridges							
$\{(Ph_4As)_2[Co_2(dca)_6(H_2O)]\cdot H_2O\cdot xCH_3OH\}_n$	2.108(4) 2.100(4)	2.133(4) 2.096(4) 2.116(4) 2.119(5)	157.4(4) 161.7(4) 154.1(3) 164.3(4)	118.6(5) 117.4(4)	7.3703(8) In the ladder 8.6502(8)	μ_{eff} = 4.8μ_B at 300 K μ_{eff} = 3.94μ_B at 4.5 K	[25]

					10.1883(9)		

H_2BiIm = 2,2′-biimidazole; **L(azpyph)**= N,N′-di-tert-butyl-2,11 diaza[3,3](2,6)pyridinophane; **nic** = isonicotinamide; **bimb** = 1,4-bis(im idazol-1-yl)-butane; **hmt** = hexamethylenetetramine; **bpds** = 4,4′-bipyridyl disulfide; **etpybzam** = (N,N-diethyl,N′-(pyridin-2-yl)benzylidene)ethane-1,2-diamine; **1-Pytz** =1-(pyrid-2-yl)-1H-tetrazole; **imph**= 4-(imidazol 1-yl)phenol; **L^4** = N^4-Schiff base ligand; **2ampy**= 2-aminopyridine; 2**,6-lut-NO** = 2,6-lutidine-N-oxide; **HFlu** = fluconazole; **dmf** = dimethylformamide; **im** = imidazole; **enbzpy** = N,N′-(bis(pyridine-2-yl)benzylidene)ethane-1,2 diamine; **MOP-NO**= 4-methoxypyridine-N-oxide; **bpm** = bis[(3,5-dimethyl)pyrazolyl]methane; **pydz** = pyridazine; **4-OMP**= 4-hydroxymethylpyridine; **3-pyOH** = 3-hydroxypyridine; **bdpap** = pyrazolyl containing tetradentate N4- coordinate ligand; **pybiu** =N-(picolinoyl)-biurate; **phen**= 4,7-phenanthroline, **tppz**= tetra-2-pyridylpyrazine; **pyr** = 2-pyrrolidone; **bte** = 1,2-bis(1,2,4-triazol-1-yl)ethane; **py-NH2**-2-aminopyridine; **4-bpmp** = bis(4-pyridylmethyl)piperazine); **pyo**=pyridine-N-oxide; **enbzpy** = N,N′-bis(2-pyridinylben zylidene)ethane-1,2-diamine; **5,6-(Me)$_2$-bzim** = 5,6-dimethylbenzimidazole, **5-Mebzim** = 5-methyl benzimidazole, **H_4daps** = 2,6-bis(1-salicyloylhydrazonoethyl) pyridine; **bpym** = 2,2′-bipyrimidine; **apym** = 2-aminopyrimidine; **pypz** = 2,6- bis(pyrazol-1-yl)pyridine; **bpp**=1,3-bis(4′-pyridyl)propane; **H_3daps** = 2,6-bis(1-salicyloylhydrazonoethyl) pyridine

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Table S5. Magneto-structural data for two-dimensional dca-Co(II) coordination polymer

<table>
<tr><th rowspan="2">Compound</th><th rowspan="2">Co–N_{Ligand} [Å]</th><th rowspan="2">Co-N_{DCA} [Å]</th><th colspan="2">Kąty [°]</th><th rowspan="2">Co···Co [Å]</th><th rowspan="2">Magnetyzm</th><th rowspan="2">Ref</th></tr>
<tr><th>Co–NC_{dca}</th><th>C–N–C_(dca)</th></tr>
<tr><td colspan="7">μ3 + μ1,5</td><td></td></tr>
<tr><td>[Co(pzdo)(dca)2]n</td><td>Co1
2.138
2.138
Co(2)-</td><td>Co1
μ1,5
2.099
2.099
2.099
2.099

Co(2)
μ1,5
2.089
2.089
2.089
2.089

μ3
2.179
2.179</td><td>μ1,5
149.5
149.5
μ3
160.5
160.5</td><td>119.9
120.8</td><td>Co1···Co1
7.4313
Co2···Co2
7.4313
Co1···Co2
6.0188</td><td>dc
χT = 3.08 cm3·K·mol−1 at 300 K
χT =3.07 cm3·K·mol−1 at 8 K
χT =3.15 cm3·K·mol−1 at 2 K
Θ = –9.4 K
C = 3.17 cm3 mol-1 K
FCM and ZFCM curves measured in a low field of 100 Oe show two abrupt increases in M at ca. 8.5 and 2 K, indicating the occurrence of two long-range ferromagnetic transitions</td><td>[4]</td></tr>
<tr><td>[Co(mpdo)(dca)2]n</td><td>Co(1)
7.499
7.499
Co(2)</td><td>Co(1)
2.136
2.136
2.154
2.154
Co(2)
2.096</td><td>μ1,5
148.1
148.1
155.3
155.3
μ3
161.7</td><td>148.1
148.1
119.3</td><td>Co1···Co1
7.5001
Co2···Co2
7.5001
Co1···Co2
6.078</td><td>dc
χT = 3.06 cm3·K·mol−1 at 4.75 K
Θ = –13.7 K
C = 3.34 cm3 mol-1 K
ZFCM and FCM data show phase transitions
ac</td><td>[4]</td></tr>
</table>

		2.096 2.100 2.100	161.7			nonzero values of χ′ and χ′′ signals at about 8.2 and 2.5 K hysteresis loop measured at 1.78 K	
$[Co_2(2,5\text{-dmpdo})_2(dca)_4]_n$	2.122 2.122	**μ1,5** 2.065 2.104 **μ3** 2.177 2.089	**μ1,5** 172.1 153.2 **μ3** 118.9 166.7	120.4(2) 174.6(3)	via μ1,5-dca 7.8770 via μ3-dca 5.8034	**dc** χT = 6.03 cm³·K·mol⁻¹ at 300 K C = 6.61 cm³ mol⁻¹ K Θ= –33.5 K T_N = 10.8 K	[23]
μ3 + μ1,3,5							
$[Co(H_2O)(dca)_2\cdot phz]_n$	2.049	μ1,5 2.080 2.086 μ1,3,5 2.213 2.121 2.163	**μ1,5** 159.4 160.4 **μ1,3,5** 164.4 163.0 120.9 122.5	119.5(2) 116.4(2)	7.4110	**dc** FCM and ZFCM suggested lack of long-range order weak intra network ferromagnetic coupling	[31]
Single μ1,5 + double μ1,5							
$[Co(phen)(dca)_2]_n$	2.134(1) 2.121(1)	2.211(2) 2.108(2) 2.085(2) 2.135(2)	134.0(1) 173.6(1) 145.1(1) 160.9(2)	120.1(2) 122.1(2)	7.6455(6) 7.3282(5)	**dc** χT = 2.80 cm³·K·mol⁻¹ at 300 K μ_{eff} = 4.77 μ_B χT =1.82 cm³·K·mol⁻¹ at 2 K	[1]
$[Co(2,9\text{-dmphen})(dca)_2]_n$	2.188(2) 2.171(2)	2.149(2) 2.127(2) 2.087(2)	168.9(2) 146.9(2) 171.4(2)	119.2(2) 120.5(2)	7.4301(4) 7.7722(4)	**dc** χT = 2.85 cm³·K·mol⁻¹ at 300 K μ_{eff} = 4.73 μ_B	[1]

		2.110(2)	160.2(2)			χT =1.57 cm^3·K·mol^{-1} at 2 K	
[Co(4,5-dmphen)(dca)$_2$]$_n$	2.127(1) 2.136(1)	2.099(2) 2.097(2) 2.263(2) 2.096(2)	150.9(2) 167.1(2) 165.4(2) 136.1(2)	124.6(2) 120.0(2)	7.9399(4) 7.3024(4)	**dc** χT = 2.63 cm^3·K·mol^{-1} at 300 K μ_{eff} = 4.59 μ_B χT =1.55 cm^3·K·mol^{-1} at 2 K	[1]
[Co(biq)(dca)$_2$]$_n$	2.156(1) 2.173(1)	2.091(1) 2.105(1) 2.117(1) 2.121(1)	174.5(1) 151.1(1) 146.4(1) 167.7(1)	117.6(1) 120.9(1)	7.3764(4) 8.0434(5)	**dc** μ_{eff} = 4.98 μ_B at 300 K μ_{eff} = 3.1 μ_B at 2 K D = 66.4 cm^{-1} E/D = 0.14 zJ = 0.88 cm^{-1} **ac** U_{eff} = 2.77 cm^{-1}	[5]
{[Co$_2$(bpm)(dca)$_4$]$_n$·H$_2$O}$_n$	2.165(2) 2.165(2)	**Double** 2.098(3) 2.079(3) **Single** 2.103(3) 2.103(3)	**Double** 158.3(3) 160.1(3) **Single** 160.2(3) 163.8(3)	117.3 114.1	**Double** 7.201(1) **Single** 8.299(1)	antiferromagnetic interactions	[10]
[Co$_2$(4bpym)(dca)$_2$]$_n$·H$_2$O	2.165(3) 2.167(3)	**Double** 2.075(3) 2.096(3) **Single** 2.114(4) 2.102(4)	**Double** 158.6(3) 161.2(3) **Single** 164.5(3) 158.8(3)	117.9 120.9(4)	**Double** 7.220(2) **Single** 8.288(2) **Ligand** (5.766(2))	**dc** Θ = –42 K μ_{eff} = 5.16 μ_B	[29]
{[Ph$_4$P]{Co[dca]$_3$}	–	**Single** 2.155 2.155	**Double** 161.8 159.6	118.8(2) 126.5(6)	**Double** 7.4426	No magnetic ordering	[11]

		Double 2.118 2.118 2.114 2.114	**Single** 161.8 149.5		**Single** 8.7948		
$[Co(ptzda)_2(dca)]_n$	2.131(3) 2.142(2)	2.150(3) 2.138(3) 2.107(3) 2.104(3)	167.6(3) 163.0(2) 163.8(3) 158.9(2)	123.5(3) 118.3(3)	7.343(4) 8.498(5)	undiscussed	[13]
$\{(Ph_4As)[Co(dca)_3]\}_n$	–	**Double** 2.121 2.121 2.111 2.111 **Single** 2.140 2.140	**Double** 162.0 157.0 **Single** 168.9 157.5	118.6(2) 124.0(3)	**Double** 7.4416 **Single** 8.7500	**dc** μ_{eff} = 3.80μ_B at 4.2 K small negative Θ no long-range magnetic order	[25]
$[Co(dmpzm)(dca)_2]_n$	2.180(2) 2.164(2)	2.102(2) 2.133(2) 2.126(2) 2.127(2)	175.6(2) 159.5(2) 158.6(2) 153.4(2)	123.7(3) 120.3(3)	7.4900(8) 8.5727(8)	**dc** χT = 3.44 $cm^3 \cdot K \cdot mol^{-1}$ at 300 K χT = 2.35 $cm^3 \cdot K \cdot mol^{-1}$ at 2 K C = 3.67 $cm^3 \cdot mol^{-1}$K θ = –18.8 K	[27]
Single $\mu_{1,5}$							
$\{[Co(dca)_2(Mepyz)_2]_n \cdot H_2O\}_n$	2.155 2.155	2.121 2.121 2.101 2.101	157.0 168.3 157.0 168.3	125.9(2) 125.9(2)	8.3186 8.3186	**dc** μ_{eff} = 4.95μ_B at 300K μ_{eff} = 3.58μ_B at 2 K	[2]
$[Co(4NOpy)_2(dca)_2(CH_3CN)_2]_n$	2.149(3)	2.106(3)	166.36	119.24	8.125(1)	–	[3]

	2.162(3)	2.111(3) 2.107(2) 2.110(3)	162.72 164.03 167.09	121.85	8.156(1)		
$[Co(4NOpy)_2(dca)_2]_n$	2.156(5) 2.167(5)	2.107(5) 2.100(6) 2.102(5) 2.097(6)	162.2(7) 161.4(6) 164.7(6) 159.9(5)	119.0(8) 119.4(9)	7.822(1) 7.840(1)	**dc** $\chi T = 3.4$ cm^3·K·mol^{-1} at 300 K $\chi T = 2.5$ cm^3·K·mol^{-1} at ca. 30 K $J_{Co-NOpy}/k_B = -0.8$ K $\lvert D \rvert /k_B = 185$ K zero-field-cooled magnetization (ZFCM); field-cooled magnetization (FCM); remnant magnetization (RM) suggested the formation of 2-D (or 3-D) canted antiferromagnets below $T_N = 6$ K	[3]
$\{[Co(NH_2pyz)_2(dca)_2]·H_2O\}_n$	2.171 2.171	2.110 2.110 2.119 2.119	173.7 169.8	122.31(2) 122.31(2)	8.2107(3)	**dc** $\chi T = 3.32$ cm^3 mol^{-1}K at 300 K $\chi T = 1.98$ cm^3 mol^{-1} K at 2 K D = +95.4 cm^{-1} E/D = 0.025 **ac** U_{eff} =24.5–28.2 cm^{-1} $\tau_0 = 1.19–2.5 \cdot 10^{-7}$ s	[6]
$[Co_3(HOpyz)_5(dca)_6(H_2O)_2]_n$	Co1 2.203(2) 2.221(2)	Co(1) 2.071(2) 2.056(2) 2.078(2)	167.2(2) 174.0(2) 159.4 166.4	123.9(3) 126.8(3)	8.4746(4)	**dc** $\chi T = 10.46$ cm^3 mol^{-1}K at 300 K $\chi T = 5.08$ cm^3 mol^{-1} K at 2 K D = +76.5 cm^{-1}	[6]

	Co(2) 2.187 2.187	**2.165(2) h20** Co(2) 2.114 2.114 2.073 2.073				**ac** U_{eff} = 1 cm^{-1}	
$[Co(atz)_2(dca)_2]_n$	2.168 2.168	2.097 2.097 2.089 2.089			8.0415	**dc** χT = 2.77 cm^3 $mol^{-1}K$ at 300 K χT = 1.78 cm^3 mol^{-1} K at 2 K **ac** U_{eff} = 5.1 cm^{-1} $\tau_0 = 1.7 \cdot 10^{-6}$ s	[7]
$[Co(bim)_2(dca)_2]_n$	2.128(3) 2.134(3)	2.190(3) 2.220(3) 2.209(3) 2.219(3)	169.5(3) 158.3(3)	125.1(4) 123.8(4)	8.927(2) 8.968(2)	**dc** χT = 3.04 (2) cm^3 mol^{-1} K at 300K χT = 1.71 cm^3 mol^{-1} K at 2K $\lvert D \rvert$ = 74.3 cm^{-1} **ac** $\tau_0 = 1.54 \cdot 10^{-6}$ s U_{eff} = 5.33 cm^{-1}	[8]
$[Co(bmim)_2(dca)_2]_n$	2.156(3) 2.163(3)	2.127(3) 2.153(3) 2.152(3) 2.145(3)	169.7(3) 160.2(3)	124.3(4) 124.3(4)	8.7110(5) 8.7158(5)	**dc** χT = 3.28 cm^3 $mol^{-1}K$ at 300K χT = 1.31 cm^3 $mol^{-1}K$ at 2K **ac** $\tau_0 = 0.63 \cdot 10^{-6}$ s U_{eff} = 13.81 cm^{-1} $\lvert D \rvert$ = 75.8 cm^{-1}	[8]
$[Co(H_2O)_2(dca)_2]_n$	2.054 2.054	2.122 2.122 2.125	157.6 173.1	119.8(8)	7.895	**dc** χT = 2.86 cm^3 $mol^{-1}K$ at 300K	[9]

		2.125					
$[Co(NH_3)_2(dca)_2]_n$	2.137 2.137	2.120 2.120 2.135 2.135	173.6 167.0	120.6(2)	8.362	**dc** χT = 2.89 $cm^3 \cdot K \cdot mol^{-1}$ at 300K (μ_{eff} = 4.81μ_B) χT = 1.60 $cm^3 \cdot K \cdot mol^{-1}$ at 2K	[12]
$[Co(bzim)_2(dca)_2]_n$	2.149 2.149	2.115 2.115 2.143 2.143	157.1 147.3	118.6(2)	7.623	**dc** χT = 3.01 $cm^3 \cdot K \cdot mol^{-1}$ at 300K χT = 1.21 $cm^3 \cdot K \cdot mol^{-1}$ at 2K Θ = 17.14 K C = 3.17 cm^3 K mol^{-1}	[18]
$[Co(dat)_2(dca)_2]_n$	2.122 2.122	2.135 2.135 2.129 2.129	142.4 142.2	119.9(5)	7.2744	undiscussed	[20]
$\{[Co(2\text{-}abim)_2(dca)_4]\}_n$	2.117 2.117 Pojedynczy mostek	2.160 2.160 2.152 2.152	143.4 159.2	119.4(1)	8.1858	undiscussed	[21]
$[Co(dmdpy)(dca)_2]_n$	2.142 2.142	2.095 2.095 2.114 2.114	163.8 166.7	124.1(5)	8.1016	**dc** χT = 3.34 $cm^3 \cdot K \cdot mol^{-1}$ at 300K χT = 2.03 $cm^3 \cdot K \cdot mol^{-1}$ at 2K C = 4.33 emumol^{-1} Θ= –4.62K D = 95.37cm^{-1}	[22]
$\{[Co(H_2O)_2(dca)_2](2,3,5,6\text{-}tmpdo)\}_n$	2.097 2.097	2.097 2.100	176.1 177.3	120.9(4)	8.3363	**dc** χT = 2.89 $cm^3 \cdot K \cdot mol^{-1}$ at 300K χT = 2.00 $cm^3 \cdot K \cdot mol^{-1}$ at 2K Θ= –11.5 K C = 3.01 cm^3 mol^{-1}	[23]
$[Co(DMSO)_2(dca)_2]_n$	2.0868	2.1151	162.12	117.84(9)	7.6640	**dc**	[26]

	2.0868	2.1151 2.1108 2.1108	162.34			χT = 2.30 $cm^3 \cdot K \cdot mol^{-1}$ at 300K Θ= –10.80 K C = 2.29 cm^3 mol^{-1}	
$[Co(2\text{-}Mebzim)(dca)_2]_n$	2.1513(18) 2.1513(18)	2.1445(19) 2.1445(19) 2.1405(19) 2.1405(19)	151.16(18) 160.73(19)	119.7(2)	8.273(9)	**dc** D = 65(20) cm^{-1} **ac** and **FIRMS** measurements	[28]
single $\mu_{1,5}$ + ligand							
$\{[Co(btrm)_2(dca)]ClO_4\}_n$	Co1 2.140(6) 2.146(6) 2.142(6) 2.150(6) Co2 2.136 2.157	Co1 single 2.072(5) 2.082(5) Co2 single 2.085 2.085	160.3(6) 164.4	122.6(9)	Co1···Co1 8.894(4) Co2···Co2 8.526	**dc** μ_{eff} = 4.27μ_B at 300K μ_{eff} = 2.01μ_B at 2 K	[16]
$\{[Co(DPNDI)(dca)]_n \cdot 2nDMF \cdot nH_2O\}_n$	2.143 2.143	2.116 2.116 2.125 2.125	160.8 159.7	119.2(1)	7.3769	**dc** χT = 4.21 $cm^3 \cdot K \cdot mol^{-1}$ at 300K χT = 2.73 $cm^3 \cdot K \cdot mol^{-1}$ at 2K θ = −20.09 K C = 4.47 cm^3 K mol^{-1}	[19]
$[Co(bnzd)(dca)_2]_n$	2.190 2.190	2.099 2.099 2.117 2.117	153.7 161.4	118.2(2)	7.2931	**dc** χT = 3.3 $cm^3 \cdot K \cdot mol^{-1}$ at 300K χT = 1.0 $cm^3 \cdot K \cdot mol^{-1}$ at 2K J = –3.38K (–4.86 cm^{-1})	[24]
Three types of bridges							
$[Co(3\text{-}bpo)(dca)_2]_n$	2.175(5)	2.091(5)	154.3(4)	121.8(5)	7.383(3)	**dc**	[15]

	2.160(5)	2.136(5) 2.103(4) 2.114(4)	164.1(4) 161.6(4) 156.4(4)	119.1(4)	7.587(2)	$\chi T = 3.5\ cm^3 \cdot K \cdot mol^{-1}$ at 300K $\chi T = 2.1\ cm^3 \cdot K \cdot mol^{-1}$ at 12K in 12-2K region presence of a small amount of ferromagnetic or canted antiferromagnetic-ordered impurities, likely, α- or β-[Co(dca)$_2$] with T_c at 9-10 K.	
Dca as a co-ligand							
{[Co(pypypz)$_2$(dca)](OH)(gly)$_2$}$_n$	2.182 2.163	2.163 2.182 2.175 2.175	166.3 171.1 173.6 171.1	129.0(5) 129.0(5)	14.537	undiscussed	[14]
[Co(pypypz)$_2$(dca)$_2$]$_n$	2.158 2.171 Polimer przez ligand	2.158 2.171 2.088 2.088 Dca nie jest łącznikiem	160.7	125.3(7)	16.465	undiscussed	[14]
{[Co(pypypz)$_2$(dca)$_2$](H$_2$O)}$_n$	2.129 2.129 Polimer przez ligand	2.057 2.057 2.127 2.127 Dca nie jest łącznikiem	168.2	121.9(5)	17.535	undiscussed	[14]
different							
{BeTriMe[Co(dca)$_3$(H$_2$O)]}$_n$	2.086(4)	single 2.082(3) 2.118(3) 2.103(3) 2.091(3)	single 162.4(4) 156.4(3) 167.5(3) 155.8(4)	118.5(9) 118.2(4)	8.5297(6)	**dc** C = 1.55(1) emu mol^{-1} K Θ = –15.0(4) K $\mu_{eff} = 3.52(1)\mu_B$ weak ferromagnetism	[17]

		μ_3 2.225(4)	120.9(8) μ_3 Co-NC 122.4(3) 119.3(3)				

phen = 1,10-phenanthroline; **2,9-dmphen** = 2,9-dimethylphenanthroline; **4,7-dmphen** = 4,7-dimethylphenanthroline; **Mepyz** = methylpyrazine; **4NOpy** = 4(N-tert-butyloxylamino)pyridine; **pzdo** = pyrazinedioxide; **mpdo** = 2-methyl pyrazine dioxide; **biq** = 2,2′-biquinoline; **NH_2pyz** = 2-aminopyrazine; **HOpyz** = 2-hydroxypyrazine; **atz**= 2-amino 1,3,5-triazine; **bim** = 1-benzylimidazole; **bmim** = 1-benzyl-2-methylimidazole; **L** = pyridinium-4-olate; **bpm** = 2,2-bipyrimidine; **NH_3** = ammonia; **pzda**= 2,4-diamino-6-pyridyl-1,3,5-triazine; **3-bpo** = 2,5-bis(3-pyridyl)-1,3,4-oxadiazole; **btrm** = 1,2-bis(1,2,4-triazole-1-yl)methane, **bzim** = benzimidazole; **dpndi** = N,N′-di(3-pyridyl)−1,4,5,8-naphthalenetetracarboxydiimide; **dat**= 1,5-diaminotetrazole; **2-abim** = 2-aminobenzimidazole; **dmdpy** =5,5′-dimethyl-2,2′-dipyridine; **2,5-dmpdo** = 2,5-dimethylpyrazine-dioxide; **2,3,5,6-tmpdo**=2,3,5,6-tetramethylpyrazine dioxide; **bnzd** = benzidine; **dmpzm** = bis(3,5-dimethylpyrazolyl)methane**;** **phz** = phenazine; **pypypz** = bis[3,5- dimethyl-4-(49-pyridyl)pyrazol-1-yl]methane; **ptzda** = 2,4-diamino-6-pyridyl-1,3,5-triazine

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Table S6. Magneto-structural data for three-dimensional dca-Co(II) coordination polymer

Compound	Co–N$_{ligand}$ [Å]	Co–N$_{DCA}$ [Å]	Angles [°]		Co⋯Co through dca or (ligand) [Å]	Magnetism	Ref
			Co-NC$_{(dca)}$	C–N–C$_{(dca)}$			
No co-ligand							
[TPrA][Co(dca)$_3$]$_n$ 4 polymorphs	–	2.106(3) 2.116(3) 2.119(4) 2.130(3) 2.145(3) 2.153(3)	Co-NC 160.5(4) 163.4(4) 164.6(3) 170.6(4) 172.7(4) 176.6(5)	122(2) 122.1(4) 123.2(6)	8.1262(7)	undiscussed	[1]
α-[Co(dca)$_2$]$_n$	–	μ$_{1,5}$ 2.092 2.092 μ$_3$ 2.150	μ$_{1,5}$ Co-NC 159.9 159.9 μ$_3$ 120.6 120.6	117.1 117.1	5.9187	Θ = 24.5 K hysteresis in magnetisation with a coercive field of 538 Oe. spin-canted antiferromagnet	[5]
[Co(dca)$_2$]$_n$	–	μ$_{1,5}$ 2.096 2.096 μ$_3$ 2.153	159.9	117.3	5.9231	C = 2.82 cm^{3}mol^{-1}K θ = 9.7(6) K Tc= 9.7(2) K mean-field magnets	[8]
{bzBuNH$_3$[Co(dca)$_3$]}$_n$	–	2.159 2.185	174.9 179.6	126.3 127.9(4)	8.806	C = 3.27 cm^{3}mol^{-1}K Θ= – 30.8 K	[16]

		2.194	176.5	127.9(4)		μ_{eff} = 4.85μ_B at 300 K μ_{eff} = 3.38μ_B at 2.0 K single-ion behavior of high-spin Co(II) ions antiferromagnetic exchange between the Co centers	
{[Cp·$_2$Co][Co(dca)$_3$]}$_n$	No structure data available from *cif* file					C = 3.45 cm^{3}mol^{-1}K Θ = −30.1 K.	[17]
{(MePh$_3$P)[Co(dca)$_3$]}$_n$	–	2.185(1) 2.127(2) 2.128(2) 2.096(2) 2.088(2) 2.130(2)	157.5(2) 167.1(1) 168.2(2) 153.4(2) 169.1(2) 157.9(2)	121.2(2) 116.7(2) 123.9(2) 118.7(2) 123.6(2)	7.3778(3)	μ_{eff}= 4.9 μ_B at 300 K μ_{eff}= 3.5μ_B at 4 K no ferromagnetic ordering	[18]
{(EtPh$_3$P)[Co(dca)$_3$]}$_n$	–	2.101(2) 2.111(2) 2.116(2) 2.125(2) 2.132(2) 2.137(2)	159.4(2) 155.6(2) 147.0(2) 155.1(2) 161.0(2)	117.0(3) 119.1(2) 121.5(2) 122.3(3) 122.3(3) 122.6(3)	7.4377(5)	μ_{eff}= 4.9 μ_B at 300 K μ_{eff}= 3.5μ_B at 4 K no ferromagnetic ordering	[18]
{(MV)[Co$_3$(dca)$_8$]}$_n$	–	$\mu_{1,5}$ 2.085 2.092 2.097(2) 2.122(2) $\mu_{1,3,5}$ 2.163 2.110(2) 2.114(2)	$\mu_{1,5}$ 159.9(2) 164.0(2) 172.0(2) $\mu_{1,3,5}$ 118.6 121.4		5.863	χ_MT= 8.38 cm^{3}mol^{-1}K at 300 K χ_MT= 5.63 cm^{3}mol^{-1}K at 5 K χ_MT= 2.79 cm^{3}mol^{-1}K at 2 K C = 8.54(4) cm^{3}mol^{-1}K θ = −7.3(8) K	[19]
two types of bridge: organic ligand + dca							

{[Co(bipim)(dca)](dca)}$_n$	2.187(2) 2.187(2) 2.137(2) 2.137(2)	2.074(3) 2.056(3)	152.8(2) 171.3(2)	171.3(2)	8.2321(4) (5.7345(4))	χ_MT= 2.64 cm^{3}mol^{-1}K at 300 K χ_MT= 0.03 cm^{3}mol^{-1}K at 2 K J = –7.22 cm^{-1} zJ = –0.15 cm^{-1}	[2]
{[Co(bipim)(dca)]$_2$·(ClO$_4$)$_2$·(CH$_3$OH)$_2$·H$_2$O}$_n$	2.139(3) 2.145(5) 2.163(3) 2.184(4)	2.044(4) 2.077(5)	162.9(5) 170.8(4)	123.1(5)	7.8407(8) (5.7372(9))	χ_MT= 2.75 cm^{3}mol^{-1}K at 300 K χ_MT= 0.03 cm^{3}mol^{-1}K at 2 K J = –7.11 cm^{-1} zJ = –0.11 cm^{-1}	[2]
{[Co(bpe)$_2$(dca)](dca)$_2$·4H$_2$O}$_n$	2.149 2.149 2.189 2.189	2.113 2.113	167.6 167.6	125(1)	8.7093 (13.6302)	undiscussed	[4]
[Co(dbtp)(dca)$_2$]$_n$	Co1 2.136 2.136 Co2 2.195 2.195	Co1 2.154 2.154 Co2 2.110 2.087	134.8 134.8 163.5 162.7	123.7(8) 115.2(8) 164.3	7.6751 (9.845(1))	μ_{eff}= 4.62 μ_B at 300K μ_{eff}= 3.16μ_B at 4K weak antiferromagnetic coupling no long range ordering	[7]
{[Co(bte)(dca)$_2$]·H$_2$O}$_n$	2.139(2) 2.125(2)	2.091(2) 2.128(2) 2.128(2) 2.142(2)	163.0(2) 146.2(2)	122.9(3)	7.858(2) (6.809(1))	χ_MT= 3.05–3.11 at 100-300 K χ_MT= 1.39 at 2 K weak antiferromagnetic coupling no long range ordering	[10]
[Co(bpeado)(dca)$_2$]$_n$	2.082 2.082	2.119 2.119 2.134 2.134	172.6 170.4		8.1489 (14.0137)	antiferromagnetic interaction transported by dca or bpeado χ_MT= 3.26 cm^{3}mol^{-1}K at 300 K Θ = –13.4K C = 3.34 cm^{3}mol^{-1}K	[14]
[Co(bpy)(dca)$_2$]$_n$	2.158 2.158	2.144 2.113	158.85 151.30	116.24 113.87	8.556 (11.4251)	undiscussed	[15]

		2.112 2.122	178.52 173.29				
$[Co(bipy)(dca)_2{\cdot}0.5H_2O{\cdot}0.5MeOH]_n$	2.138 2.138	2.111 2.111 2.118 2.118	158.7 142.4	118.5(2) 118.5(2)	7.3249	very weak antiferromagnetic coupling $\Theta = -13$ K C = 3.32 $cm^3mol^{-1}K$	[30]
Single dca as a linker							
$[Co(phpyk)(dca)_2]_n$	2.128(2) 2.207(1)	2.059(2) 2.079(2) 2.081(2) 2.138(2)	173.9(2) 175.2(2) 164.0(2) 150.3(2)	123.0(2) 122.1(2)	8.1236(3)	undiscussed	[3]
$[Co(tmeda)(dca)_2]_n$	2.225 2.225	2.099 2.112	165.5 175.2	122.1	7.463	antiferromagnetic coupling	[12]
$\{[Co(deen)(dca)_2]\}_n$	2.190(2) 2.250(2)	2.122(2) 2.062(2) 2.155(1) 2.145(2)	168.9(2) 177.7(2) 161.7(2)	119.8(2) 121.4(2)	7.9457(3)	χ_MT= 1.63 $cm^3mol^{-1}K$ at 300 K $\Theta = -4.755$ K C = 3.988 $cm^3mol^{-1}K$	[13]
Cubane-like structure							
$[Co_4(CH_3O)_4(CH_3OH)_4(dca)_4]_n$	–	2.100(5) 2.134(4)	154.3(4) 166.0(5)	117.7(5)	7.2780(9)	**ac** no λ_M'' signal in external field	[11]

TPrA = tetrapropylammonium cation; **bipim** = 2,2-bipyrimidine; **phpyk** =2-benzoylpyridine; **dbtp** = 1,3-di(benzotriazol-1 yl)propane; **tmeda** = tetramethylethylenediamine; **deen** = N,N-diethyl-ethylenediamine; **bpeado** = 1,2-bis(4-pyridyl)ethane-N,N′-dioxide; **bzBuNH**$_3$ = benzyltributylammonium; **MV**$^{2+}$ = methylviologen dication; **bipy** = 4,4′-bipyridine

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