The binding mode of the ambidentate ligand dicyanamide to transition metal ions can be tuned by bisimidazoline ligands with H-bonding donor property at the rear side of the ligand†

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The synthesis and crystal structures, as well as the electronic and magnetic properties, of four new compounds containing the ligands 2,2′-biimidazoline (biz) and dicyanamide (dca) with the general formula M(II)(biz)$_x$(dca)$_2$ (where M = Cu(II), Co(II), Ni(II) and x = 1,2) are reported. In the compound Cu(biz)(dca)$_2$(**1**), the equatorial plane around the Cu(II) atom is formed by two nitrogen atoms of one biz ligand and two nitrile atoms of two dca molecules. The dca anions are connected to a neighbouring Cu atom, with the central amide nitrogen acting as the axial atom, forming in this way a 2D polymeric sheet. The compounds Cu(biz)$_2$(dca)$_2$ (**2**) and Co(biz)$_2$(dca)$_2$ (**3**), which are isostructural, contain octahedral metal ions with the basal plane occupied by four nitrogen atoms of two biz ligands and the axial positions formed by two amide nitrogen atoms of monodentate dca ligands. The compound Ni(biz)$_2$(dca)$_2$ (**4**), differs from **2** and **3**, as in this case the axial positions are occupied by the nitrile nitrogen atoms of a monodentate dca ligand. The main difference between the Co and the Cu compounds is the axial M–N bond, which in the case of Cu is elongated to 2.60 Å, due to the Jahn–Teller effect. The coordination of the metal atom *via* the amide nitrogen atoms of dca has so far rarely been observed. All four compounds also show quite different hydrogen bonding systems *via* the N–H groups of the biz ligands and the nitrile nitrogen atoms of the dca molecules, forming interesting 3D and 2D polymeric and sheet-like arrays. The infrared absorptions of the compounds, as well as the electronic and EPR absorptions, are in good agreement with the crystal structures obtained. Magnetic susceptibility measurements revealed that no significant ($J > -1$ cm^{-1}) interactions are present between the metal atoms, as was expected, since no serious overlap of the magnetic metal orbitals takes place *via* the dca ligands.

Introduction

In recent years the dicyanamide anionic ligand has aroused much interest, especially in the form of M(II)(dca)$_2$ [M = Ni, Co, Cu and dca = N(CN)$_2$] compounds, as a new class of molecule-based magnetic materials.[1] Some non-metallic compounds, having fulvalene units (and derivatives) as a cation and dicyanamide as an anion, have been shown to be superconductors[2] at very low temperature. Also in the field of crystal engineering the number of X-ray crystal structures with the dca molecule showing one-, two- and three-dimensional compounds have increased the last few years.[3] Dicyanamide itself is a most interesting anionic bridging ligand and can act as a monodentate, bidentate (2 types of binding), or even as a tridentate ligand.[4] Various coordination modes of the dicyanamide ligand and the metal can occur, from monodentate bonding *via* the nitrile atom, coordination *via* the amide atom or even μ$_4$ coordination where one nitrile atom bridges two metal atoms.[3a]

However, in most cases monodentate or bidentate coordination *via* the nitrile N atom is found. Coordination *via* the amide N atom is observed in a few metal dicyanamide compounds with the general formula M(II)(dca)$_2$ [in which M = Ni(II), Co(II), Cu(II), Mn(II)].[1a,1c,1f] When an auxiliary ligand is introduced into the metal dicyanamide salts, compounds are formed with the general formula M(II)L$_x$(dca)$_2$ (where L = organic ligand). In fact only a few X-ray crystal structures are known showing coordination *via* the amide atom, such as Co(II) and Ni(II) dicyanamide compounds with the ligands 2-aminopyrimidine[3e] and phenazine.[3d] The only Cu(II) X-ray crystal structures with coordination *via* the amide N known at the time of writing are those with bis(2-pyridylcarbonyl)amidate,[3a] with imidazole[3b] and a mixed Cu/Mn anionic compound with ethylenediamine.[3f]

In a search for a better understanding of the role of hydrogen bonds in the crystal lattice of dca compounds, we have undertaken a study with a bifunctional ligand, that is a ligand with at one side a donor and at the other side an H-bond-donating group. The organic ligand selected for this study, 2,2′-biimidazoline (abbreviated as biz, see Fig. 1) differs from the more "flat" molecules, like bisimidazole, bipyridine or bipyrimidine. Due to the two hydrogen atoms present at the rear side of the molecule more steric hindrance then in the above mentioned "flat" molecules is possible. In addition, it

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† Electronic supplementary information (ESI) available: atomic displacement plot of structure **2**. See http://www.rsc.org/suppdata/nj/b2/b212059c/

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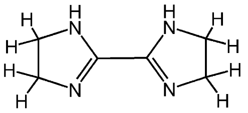


Fig. 1 Chemical structure of 2,2′-biimidazoline (biz).

has two N–H donor groups at the rear side, allowing to form hydrogen bonds, thereby constructing 1D/2D networks.

Already in 1965 some transition metal compounds [Fe(II), Ni(II), Co(II) and Cu(II)] with biz were synthesized, but no structural information was published.[5a] More recently these ligands have been used for iron compounds related to selective dioxygen reactions and oxidations.[5b] So far X-ray structures with biz and transition metals have only been reported for Fe(II) and Fe(III) compounds,[5c] in which neutral biz and mono-deprotonated biz are present.

In this study we present and discuss four new compounds with the general formula M(II)(biz)$_x$(dca)$_2$ [where M = Cu(II), Co(II), Ni(II) and x = 1,2], together with spectroscopic and magnetic measurements, which show that three compounds have the dca anion unusually bonded to the metal *via* the amide nitrogen atom.

Experimental

Materials

The ligand 2,2′-bi-imidazoline (biz) was prepared by the method reported in the literature.[5a] The purity was checked by elemental analysis, by IR spectroscopy and ^{1}H NMR. All other chemicals were purchased from commercial sources and used as received.

Syntheses

Cu(biz)(dca)$_2$ (1). An equimolar amount of biz (0.138 g, 1 mmol) and copper(II) perchlorate hexahydrate (0.371 g, 1 mmol) were mixed in ethanol and left to boil for about 5 min. To the green solution, an aqueous solution (5 mL) of sodium dicyanamide (0.180 g, 2 mmol) was added dropwise and the mixture was maintained at a boil for a few more minutes. The green-blue solution was filtered and left to evaporate at room temperature. Light green-blue crystals were obtained within a few days (yield 0.21 g; 45%), m.p. 192 °C dec. Anal. found for $C_{10}H_{10}N_{10}Cu$: C, 35.6; H, 3.2; N, 42.1; Cu, 18.8; calcd: C, 36.0; H, 3.0; N, 42.0; Cu, 19.0%.

M(biz)$_2$(dca)$_2$ (M = Cu, Co and Ni). An ethanolic solution (10 mL) of metal(II) perchlorate hexahydrate (1 mmol) was added with stirring to a boiling ethanolic solution (40 mL) of biz (0.278 g, 2 mmol) [in the case of the copper(II) compound, the small amount of precipitate that formed was redissolved by few drops of water]. To this hot solution, an aqueous solution (5 mL) of sodium dicyanamide (0.180 g, 2 mmol) was added dropwise to prevent any precipitation. The mixture was maintained at a boil for a few minutes. Solutions were filtered and left at room temperature and crystals were obtained within one week.

Cu(biz)$_2$(dca)$_2$ (2). Green-blue crystals (yield 0.37 g; 57%), m.p. 205 °C. Anal. found for $C_{16}H_{20}N_{14}Cu$: C, 40.4; H, 4.6; N, 42.0 Cu, 13.1; calcd: C, 40.7; H, 4.3; N, 41.6; Cu, 13.5%.

Co(biz)$_2$(dca)$_2$ (3). Orange crystals (yield 0.28 g; 43%), m.p. 235 °C dec. Anal. found for $C_{16}H_{20}N_{14}Co$: C, 40.8; H, 4.6; N, 42.3; Co, 12.2; calcd: C, 41.1; H, 4.3; N, 42.0; Co, 12.6%.

Ni(biz)$_2$(dca)$_2$ (4). Grey-green crystals (yield 0.22 g; 35%), m.p. 243 °C dec. Anal. found for $C_{16}H_{20}N_{14}Ni$: C, 40.8; H, 4.7; N, 41.7; Ni, 12.8; calcd: C, 41.1; H, 4.3; N, 42.0; Ni, 12.6%.

Table 1 Selected crystallographic data for compounds **1**–**4**

	1	**2**	**3**	**4**
Compound	$C_{10}H_{10}CuN_{10}$	$C_{16}H_{20}CuN_{14}$	$C_{16}H_{20}CoN_{14}$	$C_{16}H_{20}NiN_{14}$
MW	333.83	472.01	467.39	467.15
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	*P*21/*c* (no.14)	*P*-1 (no.2)	*P*-1 (no.2)	*Pbca* (no.61)
a/Å	7.9536(10)	6.5873(10)	6.7844(10)	16.4081(16)
b/Å	6.7856(10)	8.4512(10)	8.097(2)	6.7991(8)
c/Å	24.295(4)	9.2834(15)	9.462(2)	17.965(2)
α/°	–	67.977(12)	67.890(8)	–
β/°	92.585(12)	81.207(13)	82.440(9)	–
γ/°	–	84.901(15)	86.531(10)	–
U/Å^3	1309.9(3)	473.19(13)	477.34(17)	2004.2(4)
Z	4	1	1	4
μ/cm^{-1}	1.678	1.194	0.939	1.006
Reflect. collect.	27 467	10 285	11 643	42 463
Indep. reflect.	3011	2155	2182	2297
R_{int}	0.0532	0.0415	0.0316	0.0494
Obs. reflect. [$I > 2\sigma(I)$]	2481	1963	2049	1811
$R(F)$ [$I > 2\sigma(I)$]	0.0273	0.0299	0.024	0.0282
wR (F^2)	0.0714	0.0752	0.0581	0.0784

Physical techniques

C,H,N determinations were performed on a Perkin–Elmer 2400 Series II analyzer. Ligand field spectra were obtained on a Perkin–Elmer Lambda900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. FTIR spectra were obtained on a Perkin–Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using the reflectance technique (4000–300 cm^{-1}, resolution of 4 cm^{-1}). X-band EPR spectra were recorded on polycrystalline samples at room temperature and at 77 K and as frozen solutions (DMF–MeOH 1:1) at 77 K with a Jeol RE2X electron spin resonance spectrometer using DPPH (g = 2.0036) as a standard. Magnetic susceptibility measurements (5–300 K) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer (measurements carried out at 0.1 T). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal's constants.

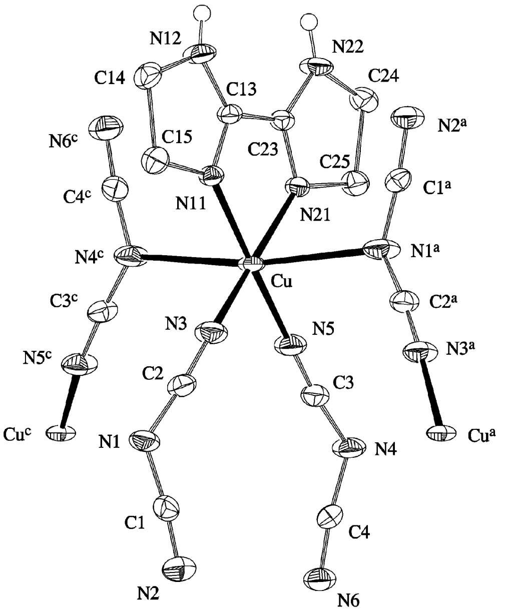


Fig. 2 Atomic displacement plot (50% probability) of compound **1**. Atoms with suffix "a" are generated by symmetry operation $-x$, $1/2+y$, $1/2-z$ and those with suffix "c" by $1-x$, $-1/2+y$, $1/2-z$. Hydrogen atoms attached to a C atom are omitted for clarity.

Crystallography

Crystals suitable for structure determinations were mounted on Lindemann glass capillaries and transferred into the cold nitrogen stream of a Nonius KappaCCD diffractometer on a rotating anode (Mo Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å, $T = 150$ K). Pertinent data for the structure determinations are collected in Table 1. Structures were solved with direct methods using SHELXS97[6b] (compound **4**) or SHELXS86[6a] (other compounds) and refined on F^2 using SHELXL-97-2.[6c] An absorption correction based on a multiple scan algorithm (PLATON/MULABS[6d]) was applied to compounds **1** and **2**; correction range 0.858–0.967 and 0.826–0.909, respectively. All hydrogen atoms were located on difference Fourier maps. To reduce the number of refined parameters the C–H hydrogen atoms of **2**,**3** and **4** were included in the refinement on calculated positions riding on their carrier atoms. The coordinates of the other hydrogen atoms were included as parameters in the refinement. The displacement parameters of all hydrogen atoms were related to the value of the equivalent isotropic displacement parameters of their carrier atoms.

CCDC reference numbers 206278–206281. See http://www.rsc.org/suppdata/nj/b2/b212059c/ for crystallographic files in CIF or other electronic format.

Results and discussion

A. Crystal structures

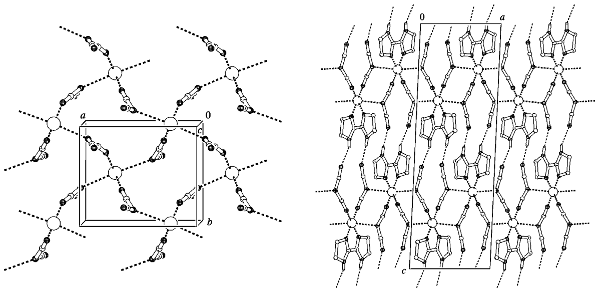
Cu(biz)(dca)$_2$ (1). An atomic displacement plot showing the numbering scheme is given in Fig. 2 and selected bond distances and angles are given in Table 2. The geometry around the copper(II) ion is an axially elongated octahedral. The equatorial plane [with angles of 173.43(7)° and 172.06(7)°] consists of 2 nitrogen atoms of one biz ligand [Cu–N11 = 1.9843(15) Å, Cu–N21 = 1.9807(15) Å], two nitrile nitrogen atoms of the μ-1,3 bridging dca molecule [Cu–N3 = 1.9605(19) Å, Cu–N5 = 1.9643(17) Å]. These dca molecules are connected with the central amide nitrogen to two neighbouring Cu atoms acting as the axial atom and forming in this way a 2D polymeric sheet [Fig. 3(a)]. The axial distances [Cu–N1^a = 2.5698(17) Å, Cu–N4^c = 2.6982(17) Å] are typical for a Cu(II) with a considerable Jahn–Teller distortion. Within the polymeric sheet, each Cu ion is surrounded by 8 nearest neighbour Cu ions in a distorted puckered Cu square network with Cu–Cu distances of 6.0629(10), 6.0712(11), 6.7856(12) and 7.9536(14) Å.

A hydrogen-bonding network is formed by the hydrogen atoms of the secondary amine of the biz ligand to the nitrile nitrogen atoms of the bridging dca molecules of different Cu units, giving a 3D arrangement [see Fig. 3(b); N2···N12 2.974(2) Å, N6···N22 2.923(2) Å]. Further details of the hydrogen bonding are listed in Table 2.

Table 2 Selected bond lengths (Å) and angles (°) for **1**^{a}

Cu–N1^a	2.5698(17)	Cu–N5		1.9643(17)	
Cu–N11	1.9843(15)	Cu–N21		1.9807(15)	
Cu–N3	1.9605(19)	Cu–N4^c		2.6982(17)	
N1^a–Cu–N5	93.35(6)	N5–Cu–N21		93.81(7)	
N1^a–Cu–N21	91.40(6)	N11–Cu–N21		80.72(6)	
N5–Cu–N11	173.43(7)	N3–Cu–N4^c		94.43(6)	
N3–Cu–N5	91.64(8)	N5–Cu–N4^c		90.87(6)	
N3–Cu–N21	172.06(7)	N21–Cu–N4^c		79.74(6)	
N1^a–Cu–N11	83.21(6)	N11–Cu–N4^c		91.71(6)	
N1^a–Cu–N3	94.04(6)	N12–Cu–N4^c		170.42(5)	
Relevant hydrogen bonds		D–H	H···A	D···A	D–H···A
N12–H12···N2 (x, $-1/2-y$, $1/2+z$)		0.80(3)	2.43(3)	2.974(2)	126(2)
N22–H22···N6 (x, $1/2-y$, $1/2+z$)		0.83(2)	2.09(2)	2.923(2)	174(2)

^{a} Suffix "a" denotes symmetry operation $-x$, $1/2-y$, $1/2-z$; suffix "c" denotes symmetry operation $1-x$, $-1/2+y$, $1/2-z$.



(a) (b)

Fig. 3 Crystal packing of **1**. (a) 2D network of Cu(dca)$_2$. The biz ligand has been omitted for clarity. (b) Hydrogen bonds between subsequent layers of Cu(dca)$_2$(biz), projection down the b axis.

M(biz)$_2$(dca)$_2$[M = Cu (2) and Co (3)]. The compounds **2** and **3** are isostructural and will be discussed together. An atomic displacement plot with the numbering scheme for the cobalt compound **3** is given in Fig. 4 and in Fig. S1 (Electronic supplementary information, ESI) for compound **2**. Selected bond distances and angles for compounds **2** and **3** are listed in Table 3. The metal atom is located at a crystallographic centre of symmetry. The equatorial plane of the octahedral compound consists of four nitrogen atoms of two biz ligands, while the axial positions are occupied by two N$_{\text{amido}}$ atoms of monodentate dca ligands. The equatorial bonds lengths in the cobalt compound **3** are slightly longer than in the copper complex **2** [Cu1–N11 = 1.9983(15) Å, Cu1–N21 = 2.0023(15) Å, while Co1–N11 = 2.1022(12) Å, Co1–N21 = 2.1063(12) Å]; this is what one would expect from the ionic radii. Martin and co-workers[7] observed the same phenomena in M$_n$(dca)$_{2n}$bipym compounds (bipym = bipyrimidine). As expected, the coordination polyhedron of the Co(II) compound **3** is more regular [Co–N$_{\text{amido}}$ 2.2307(14) Å] than that of the corresponding Cu(II) compound **2**, which shows an elongation due to the Jahn–Teller distortion [Cu–N$_{\text{amido}}$ = 2.6050(19) Å]. These distances are in harmony with the few crystals structures known to contain an M–N$_{\text{amido}}$ bond, like the Co–N$_{\text{amido}}$ bond of 2.213(2) Å in the compound [Co(dca)$_2$(H$_2$O)(phenazine)][3d] and the different values obtained for Cu–N$_{\text{amido}}$ distances, like 2.799,[3a] 2.610[3f] and *ca.* 2.6 Å[3g] in the literature. Only in the

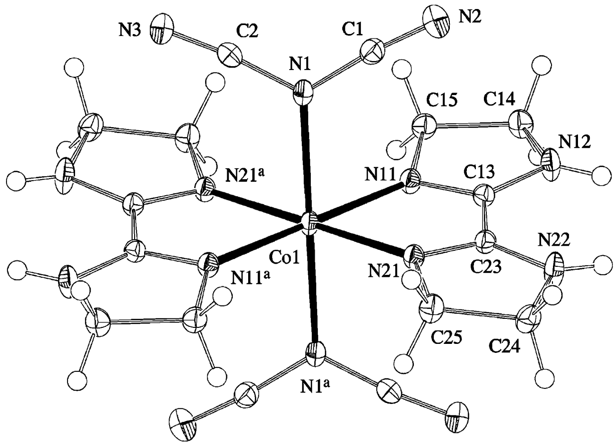


Fig. 4 Atomic displacement plot (50% probability) of structure **3**. Atoms with suffix "a" are generated by symmetry operation $-x$, $1-y$, $-z$.

Table 3 Selected bond lengths (Å) and angles (°) for **2**, **3** and **4** (M = Cu, Co, Ni).[a]

	2	**3**		**4**	
M1–N_{dca}	2.6050(19)	2.2307(14)		2.0947(14)	
M1–N11	1.9983(15)	2.1022(12)		2.0621(13)	
M1–N21	2.0023(15)	2.1063(12)		2.1062(11)	
N_{dca}–M1–N11	83.50(6)	86.85(5)		88.07(5)	
N_{dca}–M1–N11^{a}	96.50(6)	93.15(5)		91.93(5)	
N_{dca}–M1–N21	96.76(6)	93.83(5)		91.89(5)	
N_{dca}–M1–N21^{a}	83.24(6)	86.17(5)		88.11(5)	
N11–M1–N21	81.28(6)	78.07(4)		79.09(5)	
N11–M1–N21^{a}	98.72(6)	101.93(4)		100.91(5)	
		D–H	H···A	D···A	D–H···A
Relevant hydrogen bonds for **2**					
N12–H12···N3 (x, y, $1+z$)		0.76(3)	2.36(3)	3.074(2)	157(3)
N22–H22···N3 (x, y, $1+z$)		0.77(3)	2.12(3)	2.869(2)	167(3)
Relevant hydrogen bonds for **3**					
N12–H12···N3 (x, y, $1+z$)		0.854(18)	2.345(19)	3.159(2)	159.3(16)
N22–H22···N3 (x, y, $1+z$)		0.825(17)	2.103(18)	2.9171(19)	169.0(19)
Relevant hydrogen bonds for **4**					
N12–H12···N3 ($1/2-x$, $-y$, $1/2+z$)		0.86(2)	2.08(2)	2.908(2)	161.8(19)
N22–H22···N3 ($1/2-x$, $-y$, $1/2+z$)		0.87(2)	2.13(2)	2.949(2)	158.2(19)

[a] Suffix "a" denotes symmetry operation $-x$, $1-y$, $1-z$ for **2**; $-x$, $1-y$, $-z$ for **3** and $-x$, $-y$, $-z$ for **4**. N_{dca} is N1 for compounds **2** and **3** and N2 for compound **4**.

compounds without any additional ligands, like Cu(dca)$_2$, are these axial distances shorter [2.478(2) Å].[1a]

An interesting hydrogen-bonding system is formed by one of the two $N_{nitrile}$ atoms with the two amine hydrogen atoms of a biz ligand of a neighbouring unit [N3···N12 3.074(2) Å and N3···N22 2.869(2) Å for **2**; N3···N12 3.159(2) Å and N3···N22 2.9171(19) Å for **3**], giving in this way an unusual one-dimensional polymeric array with hydrogen bonds (see Fig. 5), parallel to the *c* direction. Further details of the hydrogen bonding are given in Table 3.

Ni(biz)$_2$(dca)$_2$ (4). A plot showing the numbering scheme is shown in Fig. 6 and selected bond distances and angles are listed in Table 3. The Ni ion is located at a crystallographic centre of symmetry. The equatorial positions of the octahedrally coordinated nickel atom are formed by four imine nitrogen atoms of the two biz ligands [Ni–N11 = 2.0621(13) Å, Ni–N21 = 2.1062(11) Å], while the axial positions are occupied by two nitrile nitrogen atoms of two monodentate dca ligands [Ni–$N_{nitrile}$ = 2.0947(14) Å]. The hydrogen-bonding system is formed by the second $N_{nitrile}$ from a dca ligand to two amine nitrogen atoms of a neighbouring biz ligand [N3···N12 2.908(2) Å and N3···N22 2.949(2) Å], giving a sheet-like 2D array. The bulky nodes of the 2D array fit in the open spaces of the next layer (see Fig. 7). Further details of the hydrogen bonding are included in Table 3.

All C–C and C–N distances are in agreement with the literature values of the crystal structure of the pure biz ligand.[5d]

B. The role of hydrogen bonding in the packing

Comparing the packing of these four new structures, a number of quite exciting features can be observed. First of all, it appears that the dicyanamide anion is not very critical with respect to its donor site to metal ions, and subtle differences in the packing or the ionic radius seem to co-determine how it binds. The fact that the bisimidazoline ligand offers hydrogen bonding at the rear end of a nonplanar ligand (so that stacking interactions are excluded), allows significant stabilization on the backside of the co-ordinating dicyanamide anion. This indeed results in new chains and sheets, whereby the lone pairs of the dicyanamide have interactions with a metal (or two, in case of compound **1**) and simultaneously with one or two hydrogen-bond donor groups.

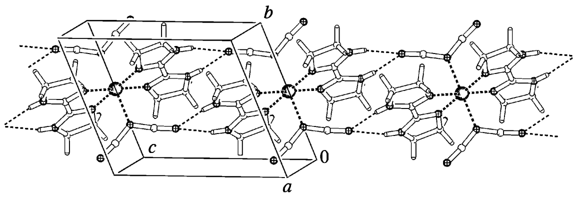


Fig. 5 Extended interactions in **3**, showing the H-bonding contacts.

C. Infrared and electronic spectra

IR spectra. A summary of the most important IR bands corresponding to compounds **1** to **4**, together with their assignments, is displayed in Table 4. As observed, these

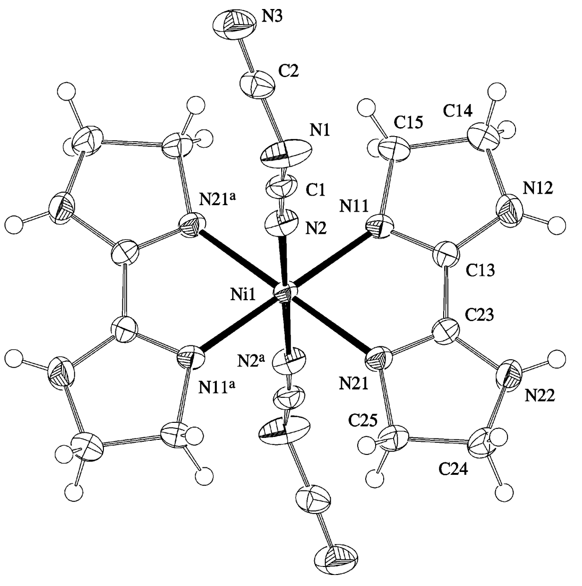


Fig. 6 Atomic displacement plot (50% probability) of structure **4**. Atoms with suffix "a" are generated by symmetry operation $-x$, $-y$, $-z$.

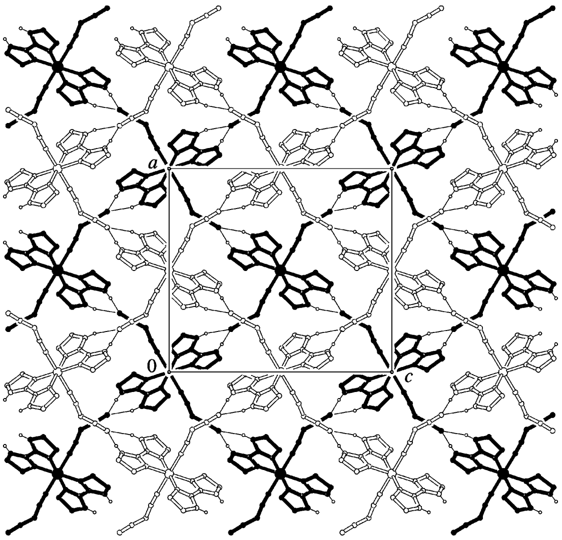


Fig. 7 Packing diagram of **4**, showing the layered structure and the H-bonding contacts.

compounds exhibit a strong absorption in the 2310–2150 cm^{-1} region corresponding to the combination modes of vibration of the dca anion. These bands are characteristic of the $\nu_{s(C–N)} + \nu_{as(C–N)}$ and $\nu_{(C\equiv N)}$ vibrations, for which the first band is diagnostic of the binding mode.[7] In compound **1**, the first band possesses an additional satellite band at 2285 cm^{-1}. These features appear to be indicative of two different binding modes of dca anions around the Cu^{2+} ion, and are consistent with the X-ray structure in which dca was found to coordinate to copper through its cyano nitrogen atoms and also the amide nitrogen. The frequencies of these vibrations are in good agreement with those reported in the literature.[1d,1e,8]

The spectra of these complexes also feature an intense band around 1560 cm^{-1} characteristic of the $\nu_{(C=N)}$ vibration of the coordinated imine nitrogen atoms of biz. Furthermore, a broad absorption around 3200 cm^{-1} is attributed to $\nu_{N–H}$ vibrations and the sharp band apparent at 3346, 3275, 3278 and 3232 cm^{-1} for complexes **1**, **2**, **3** and **4**, respectively, is assigned to hydrogen-bonding interactions between cyano nitrogen atoms of dca and H–N amide of biz, as revealed by the X-ray structure determinations.

Electronic spectra. The absorption spectra for these four compounds exhibit essentially similar patterns in the 200–400 nm region, with a strong band having a shoulder at around 330 and 280 nm, respectively, due to intraligand and charge-transfer transitions.

The two copper(II) complexes exhibit a broad ligand field band, asymmetric on the side of the lower wave numbers at 632 and 618 nm for compounds **1** and **2**, respectively. The positions as well as shapes of these bands agree with pseudooctahedral configuration.[9]

The ligand field spectrum of the cobalt(II) complex exhibits three spin-allowed absorptions: one asymmetric near-IR band at 930 nm and two shoulders at 499 and 427 nm. The third shoulder at 612 nm may be due to a spin-forbidden absorption.[10] The positions of the visible bands as well as the asymmetric near-IR band provide evidence for the octahedral stereochemistry.[10b,10c] The three spin-allowed d–d transitions are assigned in decreasing energy order to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions.

The electronic spectrum of the nickel(II) compound exhibits two spin-allowed bands at 572 and 1043 nm; it is noted that the third band at higher energy is completely obscured by the metal → ligand charge-transfer band. These observed d–d bands are characteristic of octahedral structures and arise from $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(^3P)$ transitions. These observations are consistent with an octahedral geometry around Ni^{2+} ion with NiN_6 chromophores[11] and a ligand field splitting 10*D*q value of 960 cm^{-1}.

Table 4 IR bands (cm^{-1}) and assignments for compounds **1–4**

	1	2	3	4
dca: $\nu_{s(C–N)} + \nu_{as(C–N)}$	2302, 2285	2253	2243	2288
dca: $\nu_{as(C\equiv N)} + \nu_{s(C\equiv N)}$	2232, 2158	2201, 2148	2213, 2157	2235, 2157
biz: $\nu_{(C=N)}$	1576	1564	1549	1545
biz: $\nu_{(N–H)}$	3346, 3172	3275, 3137	3278, 3156	3232, 3207

D. Magnetic properties

The EPR spectra of compounds **1** and **2**, measured as polycrystalline powders at 77 K, show an axial $S = 1/2$ spectrum with a $g_\perp$ of 2.09 and a (very weak, broad) $g_{//}$ of 2.22 for compound **1**, while compound **2** shows one broad absorption with a maximum at $g = 2.06$.

Frozen solution spectra in DMF–MeOH (1:1) recorded at 77 K show a $g_\perp$ of 2.06, a $g_{//}$ of 2.23 with $A_{//} = 18.06 \pm 0.2$ mT and $A_{\perp N} = 1.6 \pm 0.1$ mT for **1** and a $g_\perp$ of 2.06, a $g_{//}$ of 2.23 with $A_{//} = 18.5 \pm 0.2$ mT and $A_{\perp N} = 1.6 \pm 0.1$ mT for **2**. These values are in agreement with a $d_{x^2-y^2}$ ground state[1b,9] and in good agreement with the elongated octahedral topology of the $CuN_4(N_2)$ chromophore.[10a] Similar values have been reported for other dissolved copper(II) dicyanamide polymeric compounds.[8,12] As observed, the band at high field is well-resolved and shows five superhyperfine lines ($A_{\perp N} = 1.5$ mT) due to the interaction of the Cu(II) atom with nitrogen donor atoms.

The magnetic susceptibility of the powdered samples **1** to **4** were measured from 5 to 300 K. The inverse susceptibility *vs.* temperature plot shows that the curve follows the Curie–Weiss law. For Cu(II) compounds **1** and **2** the μ_{eff} *vs.* temperature plot shows hardly any changes at lower temperatures and remains constant at a value of 1.76–1.66 BM down to 5 K, which is close to the spin-only value for copper(II) (1.73 BM). Such values have also been found in other copper(II) dicyanamide compounds.[3o,8c,8d,12a,12c,12d] Given the fact that the magnetic ($d_{x^2-y^2}$) orbitals of copper(II) ions within the sheet are mutually orthogonal (the 4 short Cu–N bonds are within the same planes) and that the other Cu···Cu distances are fairly large, one would not expect any significant interactions.[4b,13]

The μ_{eff} *vs.* temperature behaviour of the Ni(II) compound **4** remains constant within a value of 3.00–3.11 BM (spin-only value is 2.83 BM) and decreases slightly at about 12 K to 2.83 BM, while the μ_{eff} *vs.* temperature plot of the Co(II) compound **3** remains constant within a value of 4.30–4.48 BM (spin-only value of 3.88 BM) and slowly decreases at about 50 K towards 3.60 BM. Such values are typical for high-spin Co(II) and have also been observed earlier for $Co(dca)_2^{2+}$ compounds.[3u] The feature for **3** is most probably due to the zero-field splitting (ZFS) effect.[13] So for these types of compounds, at best, a very weak antiferromagnetism ($J > -1$ cm^{-1}) can be present, as down to 5 K no maximum in χ is observed.

Conclusions

The results described in this paper have clearly shown that the proper choice of (bifunctional) ligands, in combination with the asymmetric multidentate dicyanamide ion, can lead to a great variety of new crystal structures. Three of the crystal structures decribed here have an uncommon $M–N_{amide}$ mode of bonding. The hydrogen bonding between the uncoordinated imine N atom of the ligand and the nitrile N atom of the dca molecules gives interesting 1D and 2D polymeric structures. As expected from their lattice structures, no magnetic interaction was found in the four new compounds. Further work with biz and other bridging anionic and neutral ligands is ongoing.

Note added in revision: Just recently a structure was published with a Co–N(amide) binding mode, which resembles our Co(II) structure **3**, but with a different ligand.[14]

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References

1 (*a*) S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray and R. Robson, *Chem. Commun.*, 1998, 439; (*b*) J. L. Manson, D. W. Lee, A. L. Rheingold and J. S. Miller, *Inorg. Chem.*, 1998, **37**, 5966; (*c*) P. Jensen, S. R. Batten, G. D. Fallon, B. Moubaraki, K. S. Murray and D. J. Price, *Chem. Commun.*, 1999, 177; (*d*) J. L. Manson, C. R. Kmety, Q.-Z. Huang, J. W. Lynn, G. M. Bendele, S. Pagola, P. W. Stephens, L. M. Liable-Sands, A. L. Rheingold, A. J. Epstein and J. S. Miller, *Chem. Mater.*, 1998, **10**, 2552; (*e*) J. L. Manson, C. D. Incarvito, A. M. Arif, A. L. Rheingold and J. S. Miller, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A*, 1999, **334**, 605 and references cited therein; (*f*) M. Kurmoo and C. J. Kepert, *New J. Chem.*, 1998, **22**, 1515; (*g*) S. R. Batten and K. S. Murray, *Aust. J. Chem.*, 2001, **54**, 605; (*h*) C. R. Kmety, J. L. Manson, S. McCall, J. E. Crow, K. L. Stevenson and A. J. Epstein, *J. Magn. Magn. Mat.*, 2002, **248**, 52.

2 (*a*) U. Geiser, A. M. Kini, H. H. Wang, M. A. Beno and J. M. Williams, *Acta Crystallogr., Sect. C*, 1991, **47**, 190; (*b*) H. Yamochi, T. Nakamura, T. Komatsu, N. Matsukawa, T. Inoue, G. Saito, T. Mori, M. Kusunoki and K. Sakaguchi, *Solid State Commun.*, 1992, **82**, 101.

3 (*a*) B. Vangdal, J. Carranza, F. Lloret, M. Julve and J. Sletten, *J. Chem. Soc., Dalton Trans.*, 2002, **566** and references cited therein (which covers all dca references till mid 2001); (*b*) J. Luo, M. Hong, Y. Liang and R. Cao, *Acta Crystallogr., Sect. E*, 2001, **57**, m359 (in view of the displacement ellipsoids and crystal packing the element types of C4 and N5 should be interchanged); (*c*) I. Potočňák, M. Burčák, C. Wagner and L. Jäger, *Acta Crystallogr., Sect. C*, 2002, **58**, m327; (*d*) A. M. Kutasi, S. R. Batten, B. Moubaraki and K. S. Murray, *J. Chem. Soc., Dalton Trans.*, 2002, 819; (*e*) P. Jensen, D. J. Price, S. R. Batten, B. Moubaraki and K. S. Murray, *Chem.-Eur. J.*, 2002, **6**, 3186; (*f*) Z.-M. Wang, B.-W. Sun, J. Luo, S. Gao, C.-S. Liao, C.-H. Yan and Y. Li, *Inorg. Chim. Acta*, 2002, **332**, 127; (*g*) J. Luo, M. Hong, J. Weng, Y. Zhao and R. Cao, *Inorg. Chim. Acta*, 2002, **329**, 59; (*h*) J. Cho, U. Lee and J. C. Kim, *Transition Met. Chem.*, 2002, **27**, 429; (*i*) W.-F. Yeung, S. Gao, W.-T. Wong and T.-C. Lau, *New J. Chem.*, 2002, **26**, 523; (*j*) G. A. van Albada, I. Mutikainen, U. Turpeinen and J. Reedijk, *Acta Crystallogr., Sect. E*, 2001, **57**, m421; (*k*) H. Kooijman, A. L. Spek, G. A. van Albada and J. Reedijk, *Acta Crystallogr., Sect. C*, 2002, **58**, m124; (*l*) T. Kusaka, T. Ishida, D. Hashizume, F. Iwasaki and T. Nogami, *Mol. Cryst. Liq. Cryst.*, 2002, **376**, 463; (*m*) S. R. Marshall, A. L. Rheingold, L. N. Dawe, W. W. Shum, C. Kitamura and J. S. Miller, *Inorg, Chem.*, 2002, **41**, 3599; (*n*) A. M. Kutasi, S. R. Batten, A. R. Harris, B. Moubaraki and K. S. Murray, *Aust. J. Chem.*, 2002, **55**, 311; (*o*) J. Carranza, C. Brennan, J. Sletten, F. Lloret and M. Julve, *J. Chem. Soc., Dalton Trans.*, 2002, 3164; (*p*) B. Li, J. Ding, J. Lang, Z. Xu and J. Chen, *J. Mol. Struct.*, 2002, **616**, 175; (*q*) I. Potočňák, M. Burčák, W. Massa and L. Jäger, *Acta Crystallogr, Sect. C*, 2002, **58**, m523; (*r*) E.-Q. Gao, Z.-M. Wang, C.-S. Liao and C.-H. Yan, *New J. Chem.*, 2002, **26**, 1096; (*s*) S. Dalai, P. S. Mukherjee, E. Zangrando and N. R. Chaudhuri, *New J. Chem.*, 2002, **26**, 1185; (*t*) Q. Shi, R. Cao, X. Li, J. Luo, M. Hong and Z. Chen, *New J. Chem.*, 2002, **26**, 1397; (*u*) P. Jensen, S. R. Batten, B. Moubaraki and K. S. Murray, *J. Chem. Soc., Dalton Trans.*, 2002, 3712.

4 (*a*) J. Mroziński, J. Kohout and M. Hvastijová, *Pol. J. Chem.*, 1997, **71**, 883; (*b*) A. Escuer, F. A. Mautner, N. Sanz and R. Vincente, *Inorg. Chem.*, 2000, **39**, 1668.

5 (*a*) J. C. Wang and J. E. Bauman Jr., *Inorg. Chem.*, 1965, **4**, 1613; (*b*) M. G. Burnett, V. McKee and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 1492; (*c*) J. P. Roth, S. Lovell and J. M. Mayer, *J. Am. Chem. Soc.*, 2000, **122**, 5486; (*d*) C. J. Brennan and V. McKee, *Acta Crystallogr, Sect. C*, 1999, **55**, 1492.

6 (*a*) G. M. Sheldrick, SHELXS86 Program for Crystal Structure Determination, University of Göttingen, Germany, 1986; (*b*) G. M. Sheldrick, SHELXS97 Program for Crystal Structure Determination, University of Göttingen, Germany, 1997; (*c*) G. M. Sheldrick, SHELXL-97-2 Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997; (*d*) A. L. Spek, PLATON. A Multi-purpose Crystallographic Tool, Utrecht University, The Netherlands, 2002, http://www.cryst.chem.uu.nl/platon.

7 (*a*) S. Martín, M. G. Barandika, J. I. Ruiz de Larramendi, R. Cortés, M. Font-Bardia, L. Lezama, Z. E. Serna, X. Solans and T. Rojo, *Inorg. Chem.*, 2001, **40**, 3687; (*b*) H. Köhler, A. Kolbe and G. Lux, *Anorg. Allg. Chem.*, 1977, **428**, 103.

8 (*a*) M. Hvastijová, J. Kohout, M. Okruhlica, J. Mroziński and L. Jäger, *Transition Met. Chem.*, 1993, **18**, 579; (*b*) M. Hvastijová, J. Kožíšek, J. Kohout, J. Mroziński, L. Jäger and I. Svoboda, *Polyhedron*, 1997, **16**, 463; (*c*) J. Mroziński, J. Kohout and M. Hvastijová, *Polyhedron*, 1989, **8**, 157; (*d*) J. Mroziński, J. Kohout, M. Hvastijová and H. Köhler, *Transition Met. Chem.*, 1986, **11**, 481.

9 (*a*) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5**, 143; (*b*) B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1972, 1196; (*c*) J. Reedijk, *Transition Met. Chem.*, 1981, **6**, 195; (*d*) D. E. Billing and A. E. Underhill, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2147; (*e*) B. J. Hathaway, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, UK, 1987, vol. 5, ch. 53.

10 (*a*) J. A. Weil, J. R. Bolton and E. Wertz, *Electron Spin Resonance, Elementry Theory and Practical Applications*, John Wiley & Sons, New York, 2nd edn., 1994; (*b*) A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1987; (*c*) A. B. P. Lever, *Coord. Chem. Rev.*, 1982, **43**, 63.

11 C. Jubert, A. Mohamadou, C. Gérard, S. Brandes, A. Tabard and J. P. Barbier, *J. Chem. Soc., Dalton Trans.*, 2002, 2660.

12 (*a*) J. Mroziński, M. Hvastijová and J. Kohout, *Polyhedron*, 1992, **22**, 2867; (*b*) J. Kohout, J. Mroziński and M. Hvastijová, *Z. Phys. Chem. (Leipzig)*, 1989, **270**, 975; (*c*) G. A. van Albada, M. E. Quiroz-Castro, I. Mutikainen, U. Turpeinen and J. Reedijk, *Inorg. Chim. Acta*, 2000, **298**, 221; (*d*) I. Riggio, G. A. van Albada, D. D. Ellis, A. L. Spek and J. Reedijk, *Inorg. Chim. Acta*, 2001, **313**, 120.

13 O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, 1993.

14 S. R. Marshall, C. D. Incarvito, W. W. Shum, A. L. Rheingold and J. S. Miller, *Chem. Commun.*, 2002, 3006.