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Supramolecular C–H···O, C–H···N and C–H···Cl interactions in metal compounds with multi-topic poly(pyrazolyl)borate ligands

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Abstract

Supramolecular C–H···O and C–H···N hydrogen bonding interactions in metal complexes with dihydrobis(1,2,4-triazolyl)borate (**3**), hydrotris(1,2,4-triazolyl)borate (**4**) and dihydrobis(tetrazolyl)borate ligands (**5**) have been analyzed statistically and with respect to their role in determining the crystal packing arrangement. The additional ring nitrogen atoms in these modified, multi-topic poly(pyrazolyl)borate ligands are the origin of manifold C–H···O and C–H···N hydrogen bonds in this group of compounds. A recurrent example is the orientation of metal-coordinated triazolyl rings from **3** or **4** along the *cisoid* ligand(O/N)–metal-ligand(O/N) bonds because of C–H···O/N bonding. The additional nitrogen atoms play a dual role in enhancing the acidity of the ring hydrogen atoms and serving as hydrogen-bond acceptors. In polynuclear tris(triazolyl)borate copper structures with hydrated chloride anions or chloro ligands C–H···Cl contacts were observed.

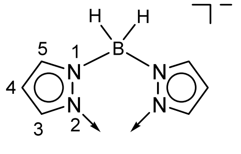
Keywords: Hydrogen bonding; C–H···O bonding; C–H···N bonding; C–H···Cl bonding; Poly(pyrazolyl)borate ligands modified; Supramolecular interactions

1. Introduction

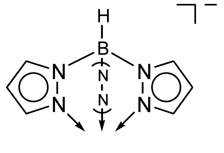
There is a growing interest in the role played by weak supramolecular interactions, such as C–H···O and C–H···N hydrogen bonding, in determining molecular packing and coordination as part of supramolecular crystal engineering [1–8]. Many examples are already known from purely organic structures and there is now little doubt that the weak C–H···O hydrogen bonds are major determinants of crystal packing [9–19] (for theoretical studies on C–H···O bonds, see e.g. Refs. [20–23]). It has also been recognized that C–H···O interactions have a far from negligible role in organometallic crystals where a large number of CO groups are present. It was found that these weak interactions can drive the crystallization process and select a particular molecular structure [24–30]. In contrast, less is known in this context with regard to inorganic coordination complexes [31–33].

A key objective in the field of crystal engineering is the control and manipulation of weak interactions in order to tune the properties of the bulk material. Classical O/N–H···O/N hydrogen bonds are of course the predominant weak interaction [1,24,34–38] (for O/N–H···Cl see Refs. [39–47]). Even weaker control forces are C–H···O/N hydrogen bonds, π···π interactions [48–54], C–H···π [55,56] and even C–H···C interactions [57,58]. Estimates for interaction energies are 16–60 kJ mol^{-1} for O/N–H···O/N hydrogen bonds, $<$16 kJ mol^{-1} for C–H···O hydrogen bonds, $<$2–20 kJ mol^{-1} for π···π interactions and 4–10 kJ mol^{-1} for C–H···π interactions [1,48,55,59,60].

Poly(pyrazolyl)borate ligands (scorpionates) are versatile ligands in physio-chemical, bio-inorganic and structurally oriented coordination chemistry [61–69]. The parent compounds are dihydrobis(pyrazolyl)borate (Bp, **1**) and hydrotris(pyrazolyl)borate (Tp, **2**).



Bp, **1**



Tp, **2**

-(N-N)- denotes the third pyrazolyl ring which is oriented to the rear

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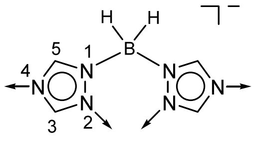

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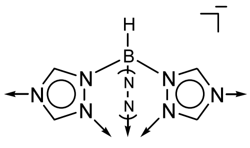

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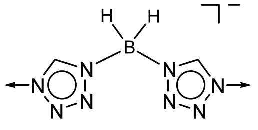

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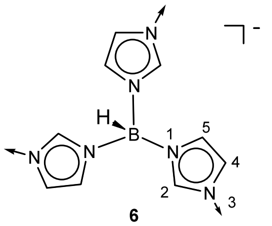

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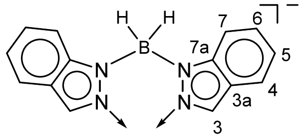

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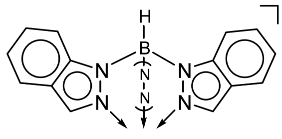

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-(N-N)- denotes the third triazolyl or indazolyl ring which is oriented to the rear

In recent years we, and others, have been interested in metal complexes with modified poly(pyrazolyl)borate ligands and in their supramolecular architecture. These modified scorpionate ligands are bis- and tris(1,2,4-triazolyl)borate (**3** and **4**) [70–85], bis(tetrazolyl)borate (**5**) [70,86,87], bis- and tris(imidazolyl)borate (**6**) [79,88–90] or bis- and tris(indazolyl)borate (**7** and **8**) [79,91–93]. Further examples of functionally modified poly(pyrazolyl)borate ligands are fluorinated tris(pyrazolyl)borate [94] and tris(mercaptoimidazolyl)borate [95–98].

We report here results of an extensive study of inter- and intramolecular C–H···O/N hydrogen bonds in crystal structures with the poly(1,2,4-triazolyl)borate ligands **3** and **4** and the bis(tetrazolyl)borate ligand **5**. Furthermore, evidence for a C–H···Cl contact in polynuclear copper complexes of **4** is given. The coordination chemistry of the ambidentate ligands **3** and **4** is characterized by the formation of both metal chelates as well as coordination polymers [99]. In addition, the nitrogen atoms which are not utilized for metal coordination tend to engage in O–H···N hydrogen bonding with water molecules leading to the formation of solvent stabilized crystal phases with extended water substructures [70,72–74,87,100].

While information on C–H···O bonding is plentiful, documentation of C–H···N bonds is scarce [4,32,101]. A brief discussion of C–H···Cl$^-$ hydrogen bonding was found for $[Pt(C_5H_5N)_4]Cl_2\cdot 3H_2O$ [7] and [Pt(1-O_2N-9{(2-Me_2N-ethyl)amino}acridinato)Cl] [46] (for C–H···F see Refs. [31,102], for C–H···I see Refs. [103]).

2. Experimental

The structures of the metal complexes of **3**, **4** and **5** which are given in Table 1 have been positively evaluated with respect to C–H···O/N hydrogen bonding. The synthesis and X-ray structural characterization of the compounds has been described earlier; the literature references and Cambridge structural database (CSD)-Refcodes are included in Table 1. Details of the C–H···O/N bonding scheme were calculated by the program PLATON [104]. A CSD search has been performed using the QUEST3D routine on CSD version 5.23 (April 2002) and two updates (257 000 entries). The search fragment was defined as $HB(C_2H_2N_3)_2$ or $H_2B(CHN_4)_2$+O or N with an inter- or intramolecular C–H···O/N contact and H···O/N constrained between 2.0 and 3.0 Å. For an intramolecular H···O/N contact the number of bonds between H and O/N were constrained between 4 (minimum) and 6 (maximum). The results were depicted by the program CSD VISTA. It can be noted that the CSD search may come up with a different number of C–H···O/N contacts than a PLATON calculation. Structural drawings were created with SCHAKAL [105] or PLATON/PLUTON for Windows [104].

3. Results and discussion

In general, the strength and effectiveness of a C–H···O hydrogen bond depends on the C–H carbon acidity [106,107]. For the ligands **3**–**5** it could already be shown by ^{1}H NMR spectroscopy and by AM1 theoretical calculations that the additional nitrogen atom of the poly(triazolyl)borate and the bis(tetrazolyl)borate ligands versus the poly(pyrazolyl)borate systems **1** and **2** leads to an increase in the positive polarization of the triazolyl and tetrazolyl hydrogen atoms [108]. At the same time, the structures of the transition metal complexes of **3**–**5** often contain a considerable number of water molecules both as metal–aqua ligands and as solvent of crystallization. The incorporation of water of crystallization is obviously due to the presence of the additional nitrogen donor atoms and the formation of O–H···N bonds. In view of the large number of oxygen atoms in these poly(azolyl)borate systems, they are good candidates for the study of the possible role of C–H···O bonds in the crystal packing. The water molecules play an important role in the stabilization of the crystal phases. While the stronger O–H···O/N network was immediately obvious and discussed thoroughly in the original publications [70–74,76,77,87,100], the presence and importance of C–H···O/N bonding in the structures of metal complexes of **3**–**5** emerged more slowly during the course of our investigations. Hence, we discuss the possible role of these weak but far from negligible interactions here in a comprehensive paper.

Table 1
Compounds and CSD-Refcodes

Compound [a]	Abbreviation	Reference	CSD-Refcode
${}^{2}_{\infty}\{[\mathrm{Mn}(\eta^{2}\text{-}\mu\text{-}\mathbf{3})_{2}(\mathrm{H_2O})_{2}]\cdot 4\mathrm{H_2O}\}$	Mn-**3**	[74]	YOBROW
$[\mathrm{Ni}(\eta^{2}\text{-}\mathbf{3})_{2}(\mathrm{H_2O})_{2}]\cdot 2\mathrm{H_2O}$	Ni-**3**	[72,74]	ZITKAO
${}^{1}_{\infty}\{[\mathrm{Cu}(\eta^{2}\text{-}\mu\text{-}\mathbf{3})_{2}(\mathrm{H_2O})_{2}]\cdot 6\mathrm{H_2O}\}$	Cu-**3**	[74]	YOBRUC
${}^{1}_{\infty}[\mathrm{K}(\eta^{3}\text{-}\mu\text{-}\mathbf{4})(\mu\text{-}\mathrm{H_2O})_{2}]$	K-**4**	[71]	WIGZUH
$[\mathrm{Ca}(\eta^{3}\text{-}\mathbf{4})_{2}(\mathrm{H_2O})_{2}]\cdot 2\mathrm{H_2O}$	Ca-**4**	[77]	WONZAA
$[\mathrm{Pb}(\eta^{3}\text{-}\mathbf{4})_{2}(\mathrm{H_2O})_{2}]\cdot 2\mathrm{H_2O}$	Pb-**4**	[77]	WONZII
${}^{2}_{\infty}[\mathrm{Pb}(\eta^{5}\text{-}\mu_{3}\text{-}\mathbf{4})(\mathrm{NO_3})\mathrm{H_2O}]$	${}_{\infty}$Pb-**4**	[77]	WONZEE
${}^{1}_{\infty}\{[\mathrm{Mn}(\eta^{2}\text{-}\mu\text{-}\mathbf{4})_{2}(\mathrm{H_2O})_{2}]\cdot 4\mathrm{H_2O}\}$	Mn-**4**	[72]	ZITJUH
$[\mathrm{M}(\eta^{3}\text{-}\mathbf{4})_{2}]\cdot 6\mathrm{H_2O}$ (M = Fe, Co, Ni, Zn)	Fe-**4**	[70]	YEBNUO
	Co-**4**	[70]	YEBPAW
	Ni-**4**	[74]	YOBSAJ (RT)
			YOBSAJ01 (160 K)
	Zn-**4**	[73]	PONKEI
$[\mathrm{Cu}(\eta^{3}\text{-}4)_{2}]\cdot 2\mathrm{CH_3OH}$	Cu-**4**	[70]	WIGZOB
${}^{3}_{\infty}\{[\mathrm{Cu_2}(\eta^{6}\text{-}\mu_{4}\text{-}\mathbf{4})(\mu\text{-}\mathrm{OH})_{2}]\mathrm{Cl}\cdot 6\mathrm{H_2O}\}$	${}^{3}_{\infty}$Cu-**4**	[76]	RAXROX
${}^{2}_{\infty}\{[\mathrm{CuCl}(\eta^{5}\text{-}\mu_{3}\text{-}\mathbf{4})]\cdot \mathrm{H_2O}\}$	${}^{2}_{\infty}$Cu-**4**	[76]	RAXRIR
${}^{3}_{\infty}\{[\mathrm{Zn}(\eta^{3}\text{-}\mu_{3}\text{-}\mathbf{4})_{2}]\cdot 1.5\mathrm{H_2O}\}$	${}_{\infty}$Zn-**4**	[73]	PONKIM
$[\mathrm{Ph_3P{=}N{=}PPh_3}]^{+}[\mathrm{Mo}(\eta^{3}\text{-}\mathbf{4})(\mathrm{CO})_{3}]^{-}$	Mo1-**4**	[82]	LASJIY
$[\mathrm{Mo}(\eta^{3}\text{-}\mathbf{4})(\mathrm{CO})_{2}(\eta^{2}\text{-}\mathrm{S_2CNEt_2})]$	Mo2-**4**	[83]	LATMEY
$[\mathrm{Ru}(\eta^{3}\text{-}\mathbf{4})(\mathrm{CO})_{2}]_{2}(Ru\text{–}Ru)$	Ru-**4**	[83]	WIHCIZ
${}^{2}_{\infty}[\mathrm{Ag}(\eta^{4}\text{-}\mu_{3}\text{-}\mathbf{4})]$	Ag-**4**	[75]	TETPUD
${}^{2}_{\infty}[\mathrm{K}(\eta^{4}\text{-}\mu_{5}\text{-}\mathbf{5})$	K-**5**	[86]	SUHNEO
${}^{2}_{\infty}\{[\mathrm{M}(\eta^{2}\text{-}\mu\text{-}5)_{2}(\mathrm{H_2O})_{2}]\cdot 2\mathrm{H_2O}\}$	Mn-**5**	[87]	YOYZUH
(M = Mn, Fe, Co, Zn, Cd)	Fe-**5**	[87]	YOZBEU
	Co-**5**	[70,87]	YEBPEA (YEBPEA10)
	Zn-**5**	[70,87]	YEBPIE (YEBPIE10)
	Cd-**5**	[70,87]	YEBPOK (YEBPOK10)
${}^{2}_{\infty}[\mathrm{M}(\eta^{2}\text{-}\mu\text{-}5)_{2}(\mathrm{NH3})_{2}]$ (M = Ni, Cu)	Ni-**5**	[72]	ZITKES
	Cu-**5**	[87]	YOZCAR

[a] ${}^{n}_{\infty}$ Describes an extended coordination polymeric network of dimension n; η^{m} refers to the number m of nitrogen donor atoms which coordinate to metal atoms; μ_k indicates the number k of metal atoms which are bridged by the ligand ($\mu = \mu_2$); for Cu compounds two of the metal-ligand contacts are elongated due to the Jahn–Teller distortion.

Our studies of hydrogen bonding rely primarily on X-ray crystal structures which suffer from the known deficiencies that the position of the hydrogen atom is determined with the least accuracy and that the C–H distances are systematically shortened by 0.05–0.10 Å [28]. The technique of structure determination by neutron diffraction, where the H-atom positions are determined with great accuracy [5,7], is, however, not as routinely available, especially if for statistical purposes a large number of non-bonded contacts needs to be investigated, and necessitates the growing of large enough crystals. Neutron diffraction data is only available for the nickel compound of **4** [100].

Geometrical criteria to assess the significance of a particular C–H···O entity are still a matter of discussion [8,28]. The C–H···O bond is primarily electrostatic

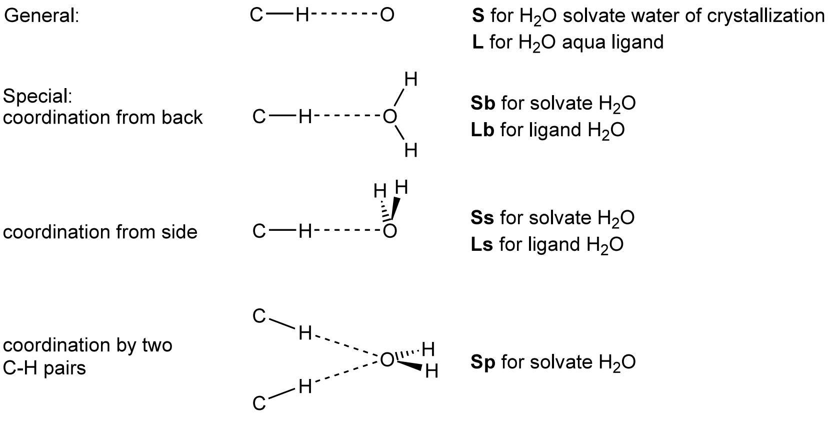

Fig. 1. Schematic presentation of C–H···O bonding types in compounds of **3**–**5**; the C–H···O angle can vary and is not meant to be 180°.

Table 2
Selected geometrical parameters for C–H···O hydrogen bonds in selected metal compounds of **3** and **4**[a]

Compound, Refcode [b]	Contact [c]	H···O [Å]	C–H···O (°)	Type [d]	Figure
Mn-**3**, YOBROW	C1–H1···O1	2.79(5)	116(3)	Ls	Fig. 5(a)
	C2–H2···O1	2.77(4)	116(3)	Ls	
	C2–H2···O2	2.63(5)	144(4)	Sb	
Pb-**4**, WONZII (isostructural with Ca-**4**, WONZAA)	C3–H3···O1	2.84(4)	118(4)	Ls	Fig. 6(a)
	C9–H9···O2	2.80(5)	129(4)	Ls	
	C6–H6···O3	2.47(5)	159(5)	Sb	
	C8–H8···O3	2.53(6)	153(5)	Ss	
Mn-**4**, ZITJUH	C1–H1···O1	2.85(5)	113(3)	Ls	Fig. 5(b)
	C1–H1···O3	2.71(4)	129(3)	Sb	
	C2–H2···O1	2.88(5)	110(3)	Ls	
Ni-**4**, YOBSAJ01 (isostructural with Zn-**4**, PONKEI)	C1–H1···O5	2.45(5)	163(4)	Sp	
	C4–H4···O4	2.53(4)	162(4)	Sp	
	C5–H5···O2	2.58(6)	163(5)	Sb	
	C8–H8···O4	2.35(5)	167(4)	Sp	
	C4–H4···O4	2.89(5)	110(4)	Sb	
Cu-**4**, WIGZOB	C2–H3···O1	2.52(5)	167(4)	Sb to MeOH	Fig. 8
	C5–H6···O2	2.52(5)	162(4)	Sb to MeOH	
	C6–H7···O2	2.61(5)	124(4)	Sb to MeOH	

[a] Calculated with PLATON, cutoff for H···O distances is < 3.0 Å.
[b] CSD-Refcodes are defined and referenced in Table 1.
[c] Symmetry relations omitted; see respective figure for a pictorial representation.
[d] Types are sketched in Fig. 1.

which is evidenced by the orientation of the H atom towards the lone pairs of the O atom. Hence, it falls off much more slowly with distance than van der Waals contacts and normal C–H···O bonds can lie somewhere between H···O = 2.00 and 2.80 Å, accompanied by C–H···O bending angles which cluster in the range 150–180° (corresponding to C···O contacts of 3.0–4.0 Å) [8,28,109]. However, longer C–H···O bonds have been

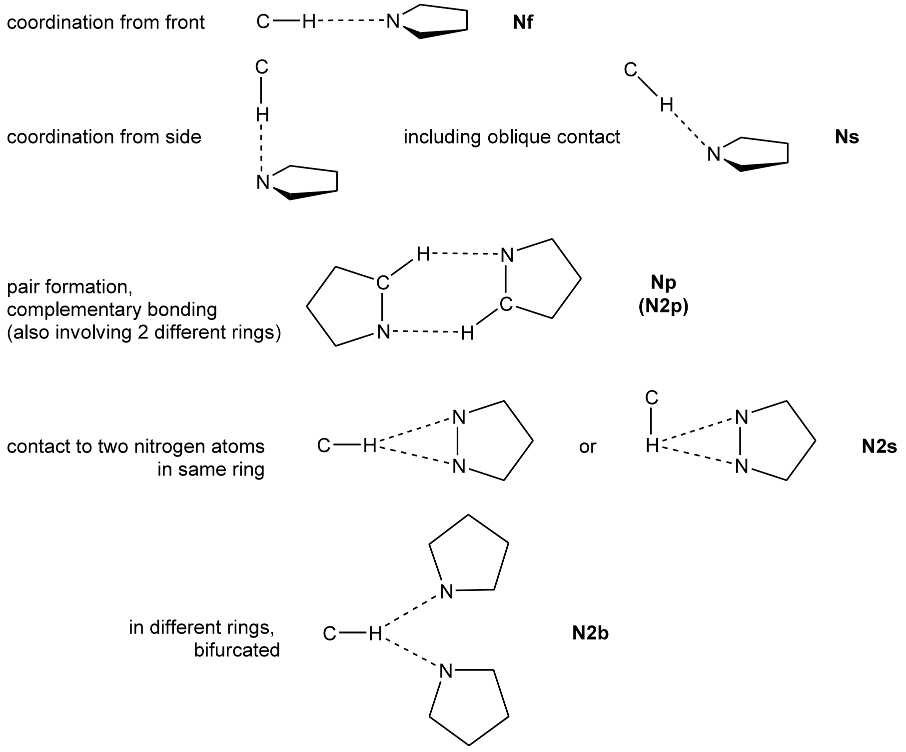

Fig. 2. Schematic presentation of C–H···N bonding types in compounds of **3**–**5**; the C–H···N angle can vary and is not meant to be 180°.

also justified and short C···O contacts can be observed with small bending angles [1,110].

Structural parameters for the C–H···O/N bonding interactions in some of the metal compounds of **3**–**5**, below a cutoff criterion of 3.0 Å, are collected in Tables 2 and 3, respectively. Table 4 summarizes the parameters for the C–H···Cl bonding in $^{3}_{\infty}$Cu-**4** and $^{2}_{\infty}$Cu-**4**. Different types of C–H···O/N bonding (cf. [5,7]) can

Table 3
Selected geometrical parameters for C–H···N hydrogen bonds in selected metal compounds of **3**–**5**[a]

Compound, refcode [b]	Contact [c]	H···N (Å)	C–H···N (°)	Type [d]	Figure
Mn-**3**, YOBROW	C3–H3···N3	2.96(5)	108(3)	Ns	Fig. 5(a)
	C4–H4···N3	2.85(4)	108(2)	Ns	
Pb-**4**, WONZII (isostructural with Ca-**4**, WONZAA)	C1–H1···N6	2.95(5)	142(4)	Ns	Fig. 6(b)
	C2–H2···N10	2.96(5)	132(4)	Ns, N2b	
	C2–H2···N13	2.86(5)	127(4)	N2s, N2b	
	C2–H2···N14	2.98(5)	143(4)	N2s, N2b	
	C4–H4···N12	2.92(5)	122(4)	Ns	
	C4–H4···N9	2.69(5)	135(4)	Ns–Nf	
	C11–H11···N15	2.95(6)	114(4)	Ns, N2p	
	C12–H12···N5	2.90(3)	150(5)	Ns	
Mn-**4**, ZITJUH	C2–H2···N7	2.74(5)	96(4)	N2s	Fig. 5(b)
	C2–H2···N8	2.69(5)	115(4)	N2s	
	C3–H3···N3	2.84(5)	114(3)	Ns	
	C3–H3···N2	2.56(4)	134(3)	Ns	
	C4–H4···N1	2.68(5)	98(3)	N2s	
	C4–H4···N2	2.91(5)	103(3)	N2s	
	C4–H4···N3	2.86(5)	108(4)	Ns	
	C5–H5···N5	2.60(4)	142(3)	Ns	
Ni-**4**, YOBSAJ01 (isostructural with Zn-**4**, PONKEI; also Fe-**4**, Co-**4** and Ni-**4** at RT)	C2–H2···N9	2.71(6)	122(4)	Nf, Np	Fig. 7
	C3–H3···N3	2.72(5)	132(4)	Ns, N2p	
	C6–H6···N3	2.65(6)	127(4)	Nf, Np	
	C7–H7···N9	2.67(5)	125(4)	Ns, N2p	
$_{\infty}$Zn-**4**, PONKIM	C1–H2···N5	2.55(5)	148(4)	Ns	Fig. 9
	C1–H2···N6	2.80(5)	109(4)	Ns	
	C2–H3···N6	2.72(5)	109(4)	Ns	
	C3–H4···N9	2.77(5)	114(3)	Ns	
	C4–H5···N9	2.77(5)	110(4)	Ns	
	C5–H6···N2	2.81(6)	145(4)	Ns	
	C5–H6···N6	2.84(5)	117(4)	Ns	
	C6–H7···N3	2.73(5)	111(4)	Ns	
Cu-**4**, WIGZOB	C4–H5···N9	2.42(5)	163(4)	Nf	Fig. 8
	C6–H7···N6	2.93(5)	107(4)	Ns	
Ag-**4**, TETPUD	C1–H1···N2	2.91(2)	169(2)	Ns, Np	Fig. 10
	C2–H2···N6	2.56(2)	163(2)	Ns, N2b	
	C2–H2···N7	2.73(2)	94(2)	N2s, N2b	
	C2–H2···N8	2.92(2)	102(2)	N2s, N2b	
	C3–H3···N4	2.84(2)	158(2)	N2s	
	C3–H3···N5	2.74(2)	173(2)	N2s	
	C4–H4···N9	2.62(2)	125(2)	Ns	
	C5–H5···N2	2.62(2)	148(2)	Ns	
	C6–H6···N2	2.67(2)	146(2)	Ns, N2b	
	C6–H6···N5	2.66(2)	116(2)	Ns, N2b	
Mn-**5**, YOYZUH isostructural with	C–H2···N2	2.60(3)	165(2)	Ns–Nf	Fig. 11
Fe-**5**, YOZBEU	C–H2···N2	2.63(3)	158(2)	Ns–Nf	
Co-**5**, YEBPEA	C–H2···N2	2.67(3)	154(2)	Ns–Nf	
Zn-**5**, YEBPIE	C–H2···N2	2.78(3)	158(2)	Ns–Nf	
Cd-**5**, YEBPOK	C–H2···N2	2.63(3)	164(2)	Ns–Nf	

[a] Calculated with PLATON, cutoff for H···N distances is < 3.0 Å.
[b] CSD-Refcodes are defined and referenced in Table 1.
[c] Symmetry relations omitted; see respective Figure for a pictorial representation.
[d] Types are sketched in Fig. 2.

Table 4
Geometrical parameters for C–H···Cl hydrogen bonds in the copper coordination polymers of **4**[a]

Compound, Refcode[b]	Contact [c]	H···Cl (Å)	C–H···Cl (°)	Figure
$^{3}_{\infty}$Cu-**4**, RAXROX		2.6(1)	161(8)	
$^{2}_{\infty}$Cu-**4**, RAXRIR	C1–H1···Cl2	2.95(2)	98(1)	Fig. 12
	C6–H6···Cl2	2.74(2)	126(1)	
	C7–H7···Cl2	3.09(2)	98(1)	
	C7–H7···Cl1	2.91(2)	161(1)	
	C8–H8···Cl2	3.01(2)	115(1)	
	C9–H9···Cl1	3.04(2)	104(1)	
	C12–H12···Cl1	2.78(2)	120(1)	

[a] Calculated with PLATON, cutoff for H···Cl distances is <3.1 Å.

[b] CSD-Refcodes are defined and referenced in Table 1.

[c] Symmetry relations omitted; see respective Figure for a pictorial representation.

be discerned as shown in Figs. 1 and 2 and those classifications have been included in Tables 2 and 3.

Figs. 3 and 4 show distributions of C–H···O and C–H···N angles versus the H···O/N distance, respectively, for the hydrogen bonds in the metal complexes of **3**–**5**. The C–H···O and C–H···N distance distributions generally are broad due to the inherent weakness of these interactions; H···N contacts are observed at relatively longer distances than H···O contacts.

The scattergram in Fig. 3 illustrates that the shorter the H···O separations the larger the C–H···O angle. With H···O bonds below 2.4 Å the C–H···O angle focuses around 170°. With longer H···O contacts towards 3.0 Å the C–H···O angle narrows to 100°. The narrowing of the C–H···O distribution around an angle of 160°–170° as the H···O separation decreases is similar to what has been observed for C–H···O bonding in other compounds [1,2,5,6,8]. For the weaker C–H···N bonds (scattergram in Fig. 4), there is already a large angular distribution from 130° to 170° for H···N contacts, which start above 2.4 Å. This angular distribution widens with longer H···N distance down to C–H···N angles of 100°. The larger distance/smaller angle correlation is less pronounced for C–H···N than for C–H···O contacts.

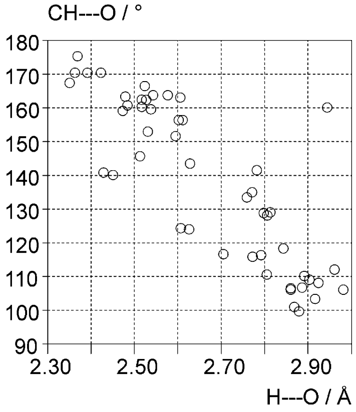

Fig. 3. Plot of C–H···O angle versus H···O distance for C–H···O hydrogen bonds in metal complexes of **3**–**5** from a CSD search (the H···O cutoff was set to 3.0 Å).

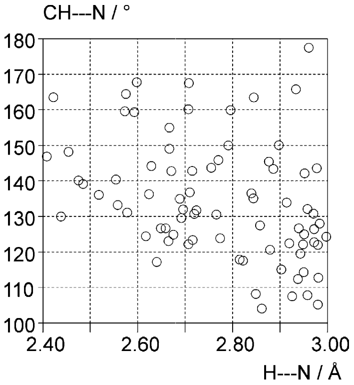

Fig. 4. Plot of C–H···N angle versus H···N distance for C–H···N hydrogen bonds in metal complexes of **3**–**5** from a CSD search (the H···N cutoff was set to 3.0 Å).

The C–H···O/N bonding in metal compounds of **3**–**5** is, however, better illustrated through the presentation of selected examples in addition to a statistical analysis.

Fig. 5 details the C–H···O/N bonding in the polymeric manganese complexes Mn-**3** and Mn-**4**. Weak hydrogen bonds are formed from each triazolyl ring to the nitrogen or oxygen donor atoms of *cis*-coordinated triazolyl or aqua ligands. The planes of the triazolyl rings are arranged along the *cisoid* O/N–M–O/N bonds with only little deviation of about 2°–20° between the plane and the *cisoid* O/N–M–O/N bond axis. It is suggested that these close to coplanar/colinear arrangements are due to the hydrogen bonding contributions. Packing considerations would otherwise prefer a stronger tilted arrangement.

The structure of Pb-**4** (isostructural with Ca-**4**) together with part of the C–H···O/N bonding scheme is depicted in Fig. 6. From Fig. 6(a) it is evident that the relative orientation of the two tris(triazolyl)borato ligands **4** around the metal deviates considerably from what could be considered an ideal staggered arrangement with respect to each other and also with respect to the two aqua ligands. One of the triazolyl rings from each ligand is clearly oriented towards one of the aqua ligands—apparently through the C–H···O interaction. The triazolyl ring containing C1–H1 and C2–H2 (unlabelled ring in Fig. 6(a)) is strongly tilted from the B···Pb vector (Fig. 6(b)). The basis for this tilting may be a series of C–H···N interactions which are pointing in the tilt direction.

Fig. 7 should emphasize the pairwise C–H···N Ns–N2p- and Nf–Np-type bonding interaction (see Fig. 2) between neighboring metal-ligand octahedra in Ni-**4** and isostructural Zn-**4** together with the related room temperature structures of M-**4** (M = Fe, Co, Ni, see

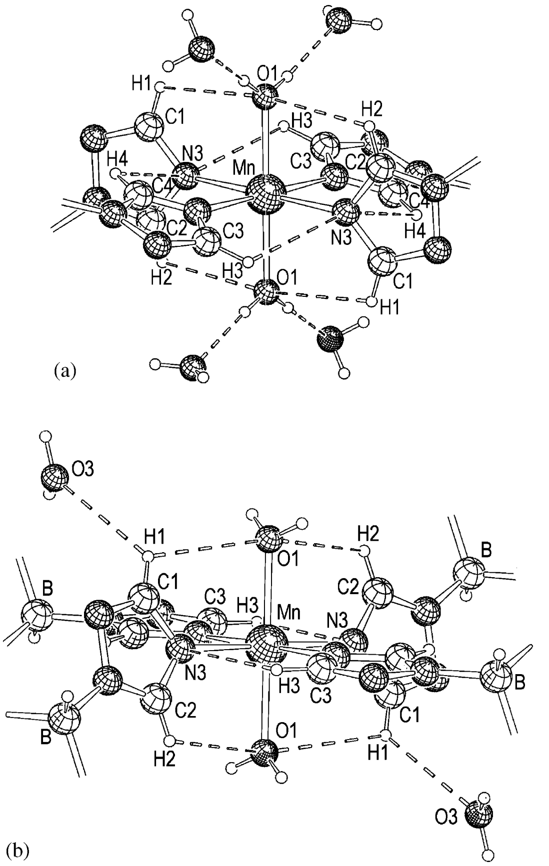

Fig. 5. C–H···O/N hydrogen bonding networks around the manganese centers in the coordination polymers (a) Mn-**3**, YOBROW and (b) Mn-**4**, ZITJUH showing the triazolyl ring-plane orientation along the *cisoid* ligand–metal–ligand bond axis; see Table 1 for definition of CSD-Refcode and Tables 2 and 3 for individual distances and angles. In (a) Mn-**3** the acute angle between Mn–O1 and ring(C1,C2) is 2°, between Mn–N3 and ring(C3,C4) 19°. In (b) Mn-**4** the acute angle between Mn–O1 and ring(C1,C2) is 13°, between Mn–N3 and ring(C3) 4°.

Table 1). The pairwise C–H···N interaction surely helps in the ordered layer arrangement of the complex molecules in the *bc*-plane. Neighboring layers of complex molecules are then separated by layers of water molecules of crystallization [70,73,74,100]. The pairwise interaction can either involve two different triazolyl rings on neighboring complexes as seen in Fig. 7(a) or does consist of a complementary C–H···N bonding as shown in Fig. 7(b). The former pairwise C–H···N interaction involving H7···N9 and H3···N3 extends in the *b*-direction. The latter complementary C–H···N interaction involving H2···N9 and H6···N3 continues along the *c*-direction. The metal complex substructure can be described as being formed by 2D-grids of molecules linked via C–H···N interactions.

The combined C–H···O/N network around a complex molecule of Cu-**4** is shown in Fig. 8. Here, methanol solvate molecules act as acceptors for the C–H···O bonds. The Jahn–Teller distortion of the centrosymmetric copper ion is perpendicular to the plane of projection in Fig. 8, that is, the long Cu···N bonds are to the triazolyl ring containing C2–H3.

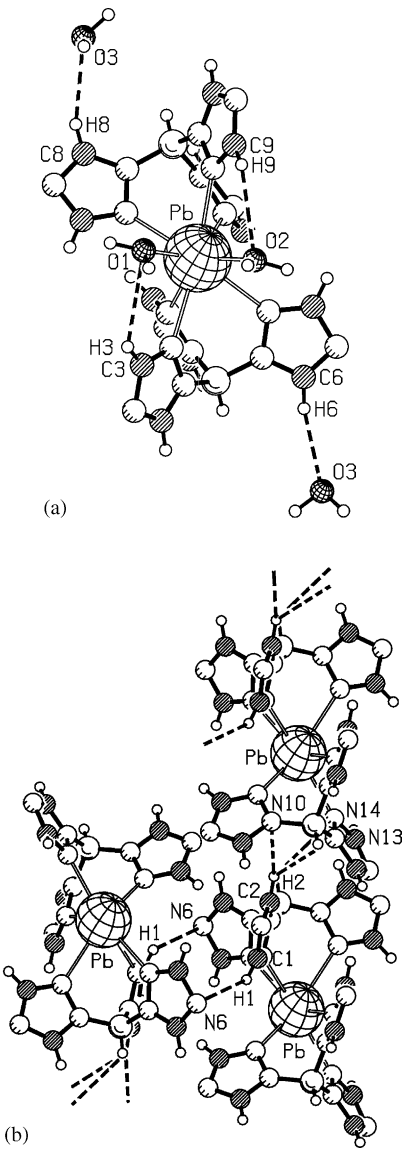

Fig. 6. (a) C–H···O and (b) part of the C–H···N hydrogen bonding in Pb-**4**, WONZII and isostructural Ca-**4**, WONZAA; see Table 1 for definition of CSD-Refcode. In (b) the aqua ligands have been omitted for clarity; see Tables 2 and 3 for individual distances and angles.

In the structure of 3D-polymeric $_{\infty}$Zn-**4** the planes of the triazolyl rings are arranged along the *cisoid* N–M–N bonds much like seen before in Mn-**3** and Mn-**4** (cf. Fig. 5). There is only little deviation of about 4–10° between the plane and the *cisoid* N–M–N bond axis. It is again suggested that these close to coplanar/colinear arrangements are due to the hydrogen bonding contribution (Fig. 9).

The 2D-polymeric network of Ag-**4** exhibits a large number of C–H···N hydrogen bonds which are illustrated in Fig. 10. The compound Ag-**4** crystallizes in the non-centrosymmetric space group $Pna2_1$ with a polar *c*-

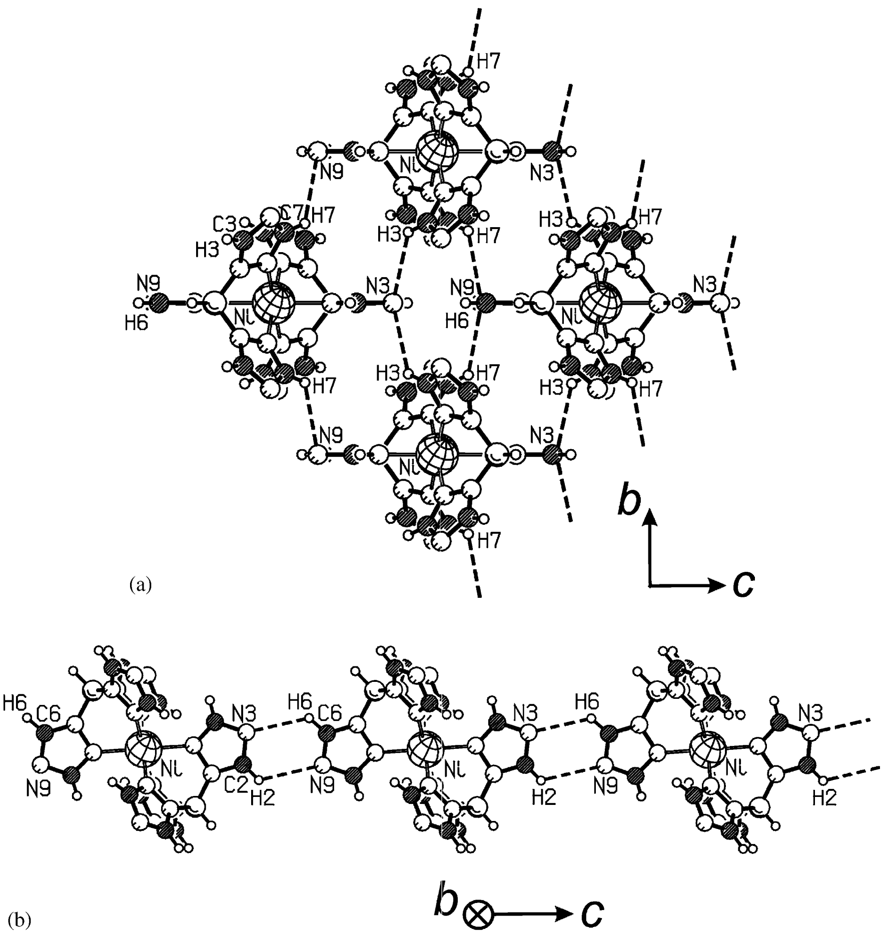

Fig. 7. The C–H···N hydrogen bonding network around the octahedral metal complexes of Ni-**4**, YOBSAJ01 and also the isostructural M-**4** compounds with M = Fe, Co, Ni (room temperature), and Zn; see Table 1 for definition of CSD-Refcode and Table 3 for individual distances and angles. Part (a) shows the C–H···N network from the pairwise interaction involving two different rings along the *b*-direction. Part (b) illustrates the complementary C–H···N bonding along the *c*-direction which would not have shown well in (a) because of the perpendicular orientation of the involved triazolyl rings. In (a) these triazolyl rings with N9 or N3, respectively, are lying exactly perpendicular to the front and rear of the paper plane, thus nitrogen atoms N9 or N3 can be superimposed by C6 or C2, respectively. Water molecules of crystallization together with the C–H···O contacts are not shown for clarity.

axis. The material was proven to possess non-linear optical properties [75]. For the polar arrangement of the building blocks in the crystal the weak C–H···N interactions together with other weak Ag···π(triazolyl) contacts surely must play a role for the homopolar orientation of neighboring layers.

Neighboring layers in the isostructural 2D-coordination polymers M-**5** (M = Mn, Fe, Co, Zn, Cd) are connected through C–H···N bonding as shown in Fig. 11. Besides, there is of course classical hydrogen bonding between the aqua ligands on the metal and water of crystallization [87].

A summary of the C–H···Cl contacts in the coordination polymers $^{3}_{\infty}$Cu–**4** and $^{2}_{\infty}$Cu-**4** is provided in Table 4. Fig. 12 provides a pictorial representation of the two shortest C–H···Cl contacts in $^{2}_{\infty}$Cu-**4**. Weak hydrogen bonds are formed from triazolyl rings to the *cis*-coordinated chloro ligands, similar as seen before in the structures of the polymeric manganese complexes Mn-**3** and Mn-**4** to the *cis*-coordinated triazolyl or aqua ligands (cf. Fig. 5). The planes of the triazolyl rings are

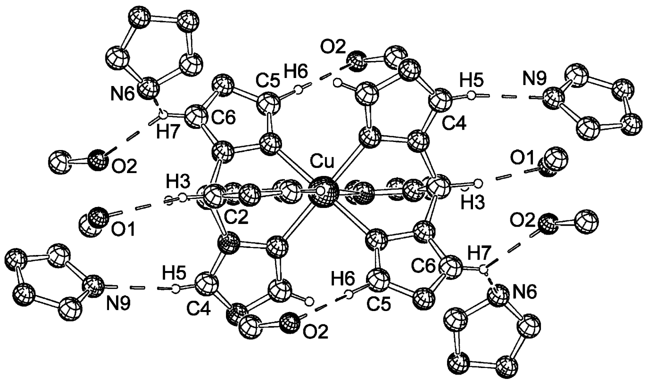

Fig. 8. Combined C–H···O/N network around a complex molecule of Cu-**4**, WIGZOB; see Table 1 for definition of CSD-Refcode. C–H···O binding is to methanol solvate molecules (only CO shown for clarity); see Tables 2 and 3 for individual distances and angles.

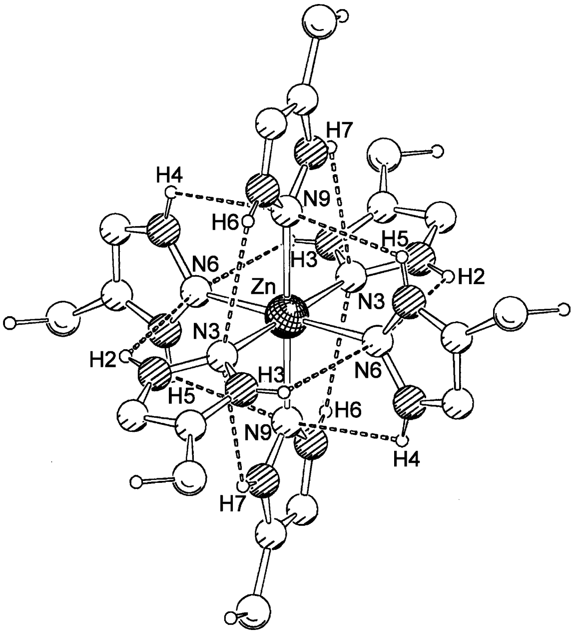

Fig. 9. C–H···N hydrogen bonding network around the zinc center in the 3D-coordination polymer $_{\infty}$Zn-**4**, PONKIM showing the triazolyl ring-plane orientation along the *cisoid* ligand–metal–ligand bond axis; see Table 1 for definition of CSD-Refcode and Table 3 for individual distances and angles. The acute angle between Zn–N3 and ring(N9) is 9°, between Zn–N6 and ring(N3) 4°, between Zn–N9 and ring(N6) 6°.

arranged along the *cisoid* Cl–M(–N) bonds with only little deviation of about 4°–5.5° between the plane and the *cisoid* Cl–M(–N) bond axis.

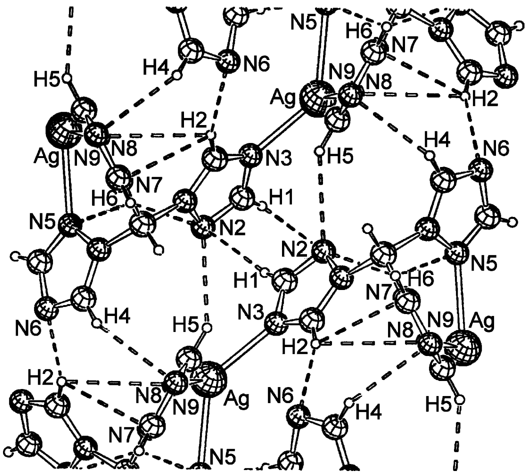

Fig. 10. Part of the C–H···N hydrogen bonding network in the 3D-coordination polymer Ag-**4**, TETPUD; see Table 1 for definition of CSD-Refcode and Table 3 for individual distances and angles. Contacts C3–H3···N4 and C3–H3···N5 are outside of the chosen drawing and not shown here. Nitrogen atoms N8 and N9 are superimposed with N9 lying on top of N8.

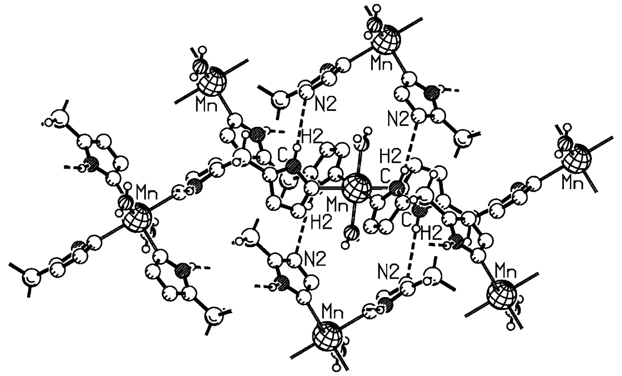

Fig. 11. The C–H···N hydrogen bonding network between neighboring layers in the 2D-coordination polymer of Mn-**5**, YOYZUH and the isostructural nets M-**5** (M = Fe, Co, Zn, Cd); see Table 1 for definition of CSD-Refcode and Table 3 for individual distances and angles.

4. Conclusions

Weak C–H···O/N hydrogen bonding interactions in transition metal coordination compounds still have to be investigated in a systematic manner compared to the thoroughly explored organic and organometallic solids. We have studied here the effect of C–H···O and C–H···N hydrogen bonds on the crystal structures of metal compounds containing the poly(azolyl)borate ligands dihydrobis(triazolyl)borate **3**, hydrotris(triazolyl)borate **4** and dihydrobis(tetrazolyl)borate **5** (triazolyl refers to 1,2,4-triazolyl).

Intramolecular ligand arrangements as well as the intermolecular orientations between metal complexes or complexes and solvent molecules of crystallization can

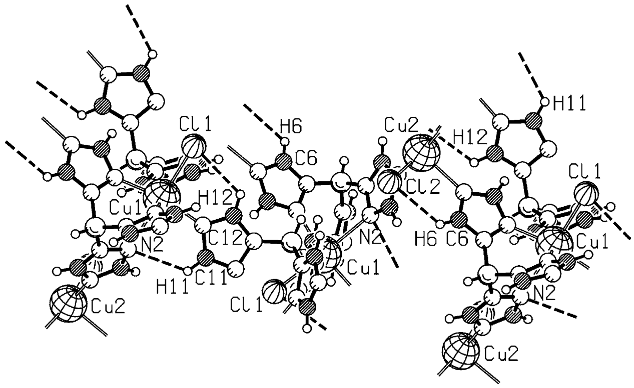

Fig. 12. The two shortest C–H···Cl hydrogen bonding contacts in the 2D coordination polymer $^{2}_{\infty}$Cu-**4**, RAXRIR showing the triazolyl ring-plane orientation along the *cisoid* chloro-metal-ligand bond axis; see Table 1 for definition of CSD-Refcode and Table 4 for individual distances and angles. The acute angle between Cu1–Cl1 and ring(C11,C12) is 4°, between Cu2–Cl2 and ring(C6) 5.5°. Also, one of the C–H···N bonds is shown which complements the triazolyl ring(C11,C12) contacts along the *cisoid* Cl1–Cu1–N2 bond axis; H11 ···N2 2.61(2) Å, C11···N2 3.207(8) Å, C11–H11···N2 123(1)°. Water molecules of crystallization in $^{2}_{\infty}$Cu-**4** are not shown for clarity.

be traced to C–H···O and C–H···N hydrogen bonds. In particular the orientation of metal-coordinated triazolyl rings from **3** or **4** along *cisoid* ligand(O/N)–metal–ligand(O/N) bonds can be traced to C–H···O/N bonding. Concerning water or methanol of crystallization, the azolyl C–H donors can participate in the coordination of water molecules in the same way and with the same functionality, albeit weaker, as OH from aqua ligands. The formation of C–H···N hydrogen bonds may be responsible for the homopolar oriented cystal packing of the building blocks in non-centrosymmetric space groups.

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For a caveat on C–H contacts to $X=O^+–H$