Synthesis, Characterisation, Properties and X-ray Structures of Cu^{II} Coordination Compounds with 5,5′-Dimethylbipyridine and Various Anions: Control of Stoichiometry and Structure by the Counterions

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The synthesis, crystal structures, and electronic and magnetic properties of eight new Cu^{II} compounds containing the ligand 5,5-dimethyl-2,2,′-bipyridine (dmbpy) with the general formula $[Cu^{II}(dmbpy)_x(L)_2]$ (where L = BF_4^-, $CF_3SO_3^-$, NO_3^-, Br^-, NCS^-, N_3^-, $HCOO^-$, and x = 1–3) are reported. The geometries of the Cu^{II} ions include a four-coordinate square-planar polymeric compound $[Cu(dmbpy)(N_3)_2]_n$ (**7**), the five-coordinate compounds, $[Cu(dmbpy)_2(C_2H_6O)](CF_3SO_3)_2$ (**2**), $[Cu(dmbpy)_2(NO_3)](NO_3)$ (**3**), $[Cu(dmbpy)_2(Br)]Br$ (**5**), $[Cu(dmbpy)(NCS)_2]_n$ (**6**) and $[Cu(dmbpy)_2(HCOO)](CF_3SO_3)$ (**8**), which have geometries ranging from square pyramidal to trigonal bipyramidal, and the six-coordinate compounds $[Cu(dmbpy)_3](BF_4)_2(C_2H_6O)$ (**1**) and $[Cu(dmbpy)(NO_3)_2]$ (**4**), which adopt an octahedrally based geometry. Except for compounds **3** and **4**, with nitrate as the anion, a variation of the copper/ligand ratios in the synthesis has no influence on the stoichiometry. The compounds have been characterised in detail by infrared, ligand field and EPR spectroscopy; the data are consistent with the single-crystal X-ray structures.

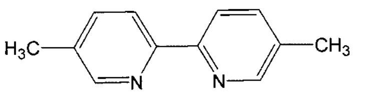
Introduction

The flexible coordination sphere around the copper(II) ion, in combination with steric and packing forces, is one of the effects that give rise to an enormous structural diversity in Cu^{II} coordination chemistry.[1] Copper(II) is one of the most important transition metals, especially due to its relevance as the active-site structure of metalloproteins,[2] but also with respect to its magnetochemistry.[3]

In structural chemistry, hydrogen bonding and π-π stacking forces are known to be important in stabilising the lattice structure. The ligand 2,2′-bipyridine (bpy) is one which has been studied extensively due to its structural aspects[4] and magneto-chemical properties.[3a][3b] Ssubstituted bpy ligands are also known, but their complexes are far less common.

Only a few X-ray crystal structures with Cu^{II} and the ligand 4,4′-dimethyl-2,2′-bipyridine have been reported — two mononuclear structures[5a][5b] and three polynuclear structures with copper(II) halides.[5c−5e] Recently the first X-ray structures of di- tri- and tetranuclear Cu^{II} compounds with this ligand were reported.[5f−5h]

In the present study the ligand 5,5′-dimethyl-2,2′-bipyridine (dmbpy; Scheme 1) has been selected. Quite surprisingly this ligand has hardly been studied and, to the best of our knowledge, only one 3D structure of a Cu^{II} compound has been published.[6] We have now extended this study towards Cu^{II} coordination compounds of general formula $[Cu^{II}(dmbpy)_x(L)_2]$ (where L = BF_4^-, $CF_3SO_3^-$, NO_3^-, Br^-, NCS^-, N_3^-, $HCOO^-$, and x = 1−3). A variety of new structures of different stoichiometry and dimensionality are reported together with their spectroscopic and magnetic properties.



5,5′-dimethyl-2,2′-bipyridine (5,5′-dimethyl-2,2′-dipyridyl)

Scheme 1

Results and Discussion

Eight new Cu^{II} compounds containing the ligand 5,5-dimethyl-2,2′-bipyridine (dmbpy) with the general formula

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Table 1. Cu^{II} compounds with dmbpy

Compound[a]	Geometry Cu atom[b]	Colour	Diffuse reflectance (10^3 cm^{-1}), LF CT	EPR (solid at room temp.)	Elemental Analysis C, H, N obsd. (calcd.)%
1. [Cu(dmbpy)$_3$](EtOH)(BF$_4$)$_2$	oc (6)	blue-green	14.3 7.6 (br) 28.4	$g_\perp = 2.10$, $g_\parallel = 2.26$, $A_\parallel = 11.5$; (77 K: $A_\parallel = 13.3$)	53.7(54.7) 5.2 (5.1) 9.9 (10.1)
2. [Cu(dmbpy)$_2$(EtOH)](CF$_3$SO$_3$)$_2$	tbp (5), $\tau = 0.61$	green	13.5 10.7 (sh) 27.0	$g_1 = 2.03$, $g_2 = 2.12$, $g_3 = 2.28$	43.2 (43.3), 3.5 (3.9), 7.3 (7.2) [8.3(8.3) S]
3. [Cu(dmbpy)$_2$(NO$_3$)](NO$_3$)	sq.pyr. (5), $\tau = 0.34$	blue-green	13.9 10.1 (br) 26.5	$g = 2.14$	51.3 (51.8), 4.5 (4.4), 15.0 (15.1)
4. [Cu(dmbpy)(NO$_3$)$_2$]	oc. (6)	dark-blue	14.6 28.5 (br)	$g_\perp = 2.07$, $g_\parallel = 2.27$	38.6 (38.8), 3.1 (3.3), 15.0 (15.1)
5. [Cu(dmbpy)Br]Br	tbp (5), $\tau = 0.63$	blue	13.8 (br) 10.1 (br) 26.0	$g_x = 2.20$, $g_y = 2.15$, $g_z = 2.01$	48.3 (48.7), 4.2 (4.1), 9.6 (9.5)
6. [Cu(dmbpy)(NCS)$_2$]$_n$	sq.pyr. (5), $\tau = 0.19$	green	15.1 (br) 10.8 (sh) 21.5	$g_x = 2.05$, $g_y = 2.11$, $g_z = 2.23$	45.7 (46.2), 3.2 (3.3), 15.1 (15.4) [17.3 (17.6) S]
7. [Cu(dmbpy)(N$_3$)$_2$]$_n$	sq.pl. (4)	green	15.5 (br) 23.4 (s,br)	$g_\perp = 2.06$, $g_\parallel = 2.23$	42.8 (43.4), 3.5 (3.6), 33.2 (33.8)
8. [Cu(dmbpy)$_2$(HCOO)](CF$_3$SO$_3$)	tbp (5), $\tau = 0.49$	dark-blue	14.1 10.7 (sh) 24.0 (v br)	(77 K) $g_x = 2.24$, $g_y = 2.12$, $g_z = 2.02$	49.7 (49.9), 3.8 (4.0), 9.0 (9.1) [5.1 (5.1) S]

[a] Abbreviations: (v)br = (very)broad, sh = shoulder, s = strong. [b] Coordination number is given in brackets. Abbreviations: oc = octahedral; sq.pyr. = square pyramidal; sq.pl. = square planar; tbp = trigonal bipyramidal.

[Cu^{II}(dmbpy)$_x$(L)$_2$] (where L = BF$_4^-$, CF$_3$SO$_3^-$, NO$_3^-$, Br$^-$, NCS$^-$, N$_3^-$, HCOO$^-$, and $x = 1-3$) have been synthesised (see Table 1). Except for compounds **3** and **4**, with nitrate as the anion, variation of the copper/ligand ratios in the synthesis has no influence on the stoichiometry. The crystal and molecular structures vary greatly, depending on the counterion, from case to case, as will be described below.

Description of the Crystal Structures

[Cu(dmbpy)$_3$](BF$_4$)$_2$(C$_2$H$_5$OH) (1)

The structure of **1** consists of a [Cu(dmbpy)$_3$]$^{2+}$ cation, two non-coordinating BF$_4^-$ anions and an ethanol lattice molecule. The structure is depicted in Figure 1 together with the numbering scheme. Selected bond lengths and angles are listed in Table 2.

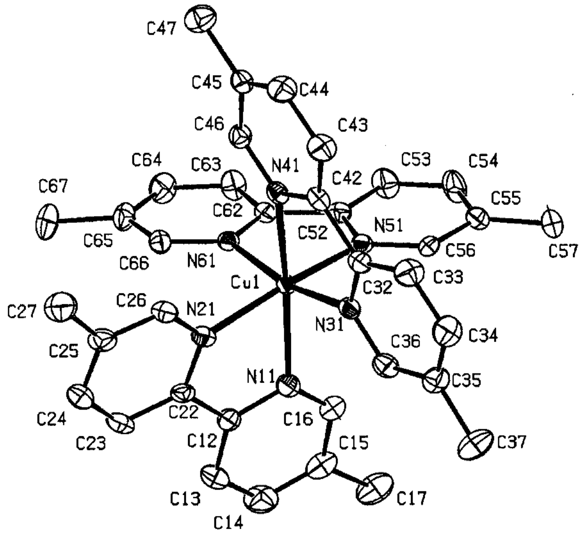

Figure 1. Thermal ellipsoid plot (50% probability) of [Cu(dmbpy)$_3$](BF$_4$)$_2$(C$_2$H$_5$OH) (**1**) with atom-labelling scheme; non-coordinating tetrafluoroborate anions, ethanol molecule and H-atoms are omitted for clarity

Table 2. Selected bond lengths (Å) and angles (°) for [Cu(dmbpy)$_3$](BF$_4$)$_2$(C$_2$H$_6$O) (**1**)

Cu1−N31	2.040(4)	Cu1−N21	2.050(4)
Cu1−N51	2.054(4)	Cu1−N61	2.056(4)
Cu1−N41	2.274(4)	Cu1−N11	2.281(4)
N31−Cu1−N21	95.03(15)	N31−Cu1−N51	94.13(14)
N21−Cu1−N51	166.73(15)	N31−Cu1−N61	168.52(15)
N21−Cu1−N61	92.54(14)	N51−Cu1−N61	79.97(14)
N31−Cu1−N41	76.56(15)	N21−Cu1−N41	96.67(14)
N51−Cu1−N41	94.78(14)	N61−Cu1−N41	94.02(14)
N31−Cu1−N11	99.42(15)	N21−Cu1−N11	76.37(14)
N51−Cu1−N11	92.67(14)	N61−Cu1−N11	90.74(14)
N41−Cu1−N11	171.76(13)		

The Cu atom has a distorted, elongated octahedral coordination with the basal plane comprised of four nitrogens from three chelating dmbpy ligands. The Cu−N distances vary from 2.040(4) to 2.056(4) Å with basal angles of 166.73(15)° and 168.52(15)°. The apical positions are occupied by nitrogen atoms of the two different bis-chelating dmbpy ligands [Cu−N distances of 2.274(4), 2.281(4) Å with an angle of 171.76(13)°].

The lattice structure is stabilised by weak stacking between the pyridine groups (shortest ring-ring distances of 4.29 Å) and by strong hydrogen bonding between the hydroxo group of the ethanol molecule and a fluorine atom of the tetrafluoroborate anion (O1···F12: 2.765 Å).

[Cu(dmbpy)$_2$(C$_2$H$_5$OH)](CF$_3$SO$_3$)$_2$ (2)

The structure of **2** consists of a [Cu(dmbpy)$_2$(C$_2$H$_6$O)]$^{2+}$ cation and two non-coordinating CF$_3$SO$_3^-$ anions. The structure is depicted in Figure 2 together with the numbering scheme. Selected bond lengths and angles are listed in Table 3. The geometry around the copper(II) ion is distorted trigonal bipyramidal with the trigonal plane formed by the two nitrogens of two dmbpy ligands and an oxygen atom of a coordinating ethanol molecule, with a distance of 2.211(2) Å, which is in agreement with the few other structures with a $CuN_4O_{ethanol}$ chromophore.[4a,7]

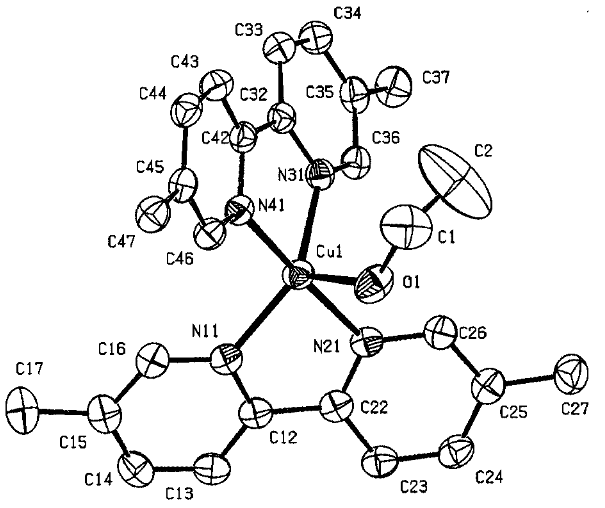

Figure 2. Thermal ellipsoid plot (50% probability) of $[Cu(dmbpy)_2(C_2H_5OH)](CF_3SO_3)_2$ (**2**) with atom-labelling scheme; non-coordinating triflate anions and H-atoms are omitted for clarity

Table 3. Bond lengths (Å) and angles (°) for $[Cu(dmbpy)_2(C_2H_6O)](CF_3SO_3)_2$ (**2**)

Cu1−N21	1.974(3)	Cu1−N41	1.976(3)
Cu1−N11	2.029(3)	Cu1−N31	2.036(3)
Cu1−O1	2.211(2)		
N21−Cu1−N41	171.08(10)	N21−Cu1−N11	81.53(10)
N41−Cu1−N11	101.63(10)	N21−Cu1−N31	102.34(10)
N41−Cu1−N31	81.37(10)	N11−Cu1−N31	135.43(10)
N21−Cu1−O1	87.21(10)	N41−Cu1−O1	83.94(9)
N11−Cu1−O1	117.99(10)	N31−Cu1−O1	106.57(10)

The Cu−N distances vary from 1.974(3) to 2.036(3) Å. The apical positions are occupied by two nitrogen atoms of the two dmbpy ligands with a *trans* angle of 135.43(10)°. The distortion from square pyramidal can be best described by the structural parameter τ (τ describes the relative amount of trigonality; $\tau = 0$ for square pyramid and $\tau = 1$ for trigonal bipyramidal), which in this case is 0.61. The structure can therefore be best described as distorted trigonal bipyramidal.[8] The lattice is stabilised by stacking of the pyridine rings, with a short ring-ring distance of 3.83 Å and a strong hydrogen bond between the ethanol oxygen hydrogen and the oxygen atom of one of the triflate anions (O1···O21: 2.6967 Å).

$[Cu(dmbpy)_2(NO_3)](NO_3)$ (3)

The mononuclear structure **3** consists of a copper(II) ion, two dmbpy ligands, one monodentate coordinated nitrate anion and one uncoordinated nitrate anion. The structure is depicted in Figure 3 together with the numbering scheme. Selected bond lengths and angles are listed in Table 4.

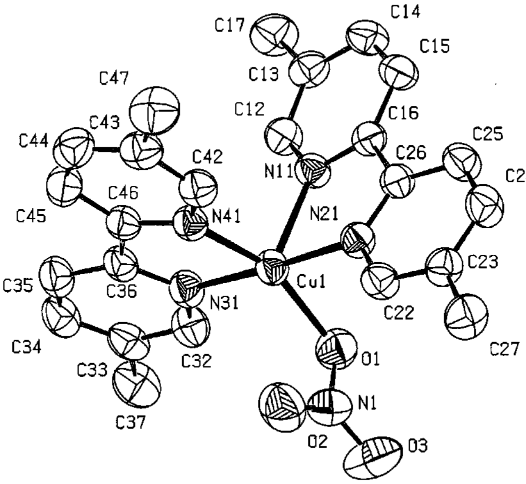

Figure 3. Thermal ellipsoid plot (50% probability) of $[Cu(dmbpy)_2(NO_3)](NO_3)$ (**3**) with atom-labelling scheme; the non-coordinating nitrate anion and H-atoms are omitted for clarity

Table 4. Bond lengths (Å) and angles (°) for $[Cu(dmbpy)_2(NO_3)](NO_3)$ (**3**)

Cu1−N31	1.974(2)	Cu1−N21	2.002(2)
Cu1−N41	2.034(2)	Cu1−O1	2.044(2)
Cu1−N11	2.156(2)	Cu1−O2	2.669(2)
N31−Cu1−N21	177.16(9)	N31−Cu1−N41	81.30(9)
N21−Cu1−N41	97.68(9)	N31−Cu1−O1	93.99(9)
N21−Cu1−O1	87.99(9)	N41−Cu1−O1	156.59(9)
N31−Cu1−N11	98.56(9)	N21−Cu1−N11	79.01(8)
N41−Cu1−N11	101.10(9)	O1−Cu1−N11	102.27(9)
O2−Cu1−N11	153.20(9)		

The geometry around the Cu^{II} atom is distorted square pyramidal with the basal plane formed by three nitrogen atoms of two ligands [distances vary from 1.974(2) to 2.034(2) Å] and one oxygen atom of the coordinated nitrate anion [Cu1−O1: 2.044(2) Å]. The apical position is occupied by a nitrogen atom of one ligand (Cu1−N11: 2.156 Å). A second oxygen atom of the coordinated nitrate anion is at a semi-coordination distance [Cu1−O2: 2.669(2) Å]. The angles of the basal plane are 177.16(9)° and 156.59(9)° and the distortion parameter τ in this case is 0.34. The lattice is stabilised by stacking of the pyridine rings, with a ring-ring distance of 3.74 Å.

$[Cu(dmbpy)(NO_3)_2]$ (4)

The mononuclear structure **4** consists of a copper(II) ion, one dmbpy ligand, and two didentate-coordinated nitrate anions. The structure is depicted in Figure 4 together with the numbering scheme. Selected bond lengths and angles are listed in Table 5.

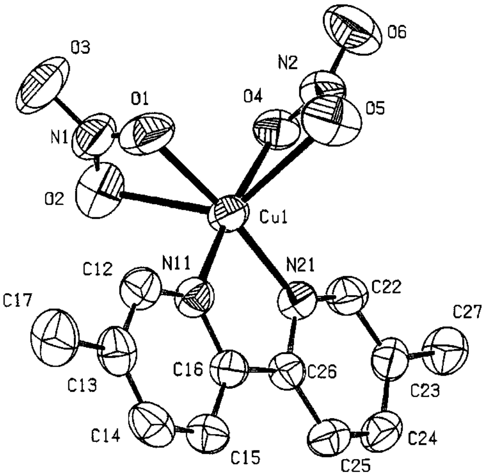

Figure 4. Thermal ellipsoid plot (50% probability) of $[Cu(dmbpy)(NO_3)_2]$ (**4**) with atom-labelling scheme; H-atoms are omitted for clarity

Table 5. Bond lengths (Å) and angles (°) for $[Cu(dmbpy)(NO_3)_2]$ (**4**)

Cu1−N11	1.966(3)	Cu1−N21	1.969(3)
Cu1−O4	1.979(3)	Cu1−O1	1.994(3)
Cu1−O2	2.484(4)	Cu1−O5	2.465(4)
N11−Cu1−N21	82.30(13)	N11−Cu1−O4	172.06(12)
N21−Cu1−O4	95.19(13)	N11−Cu1−O1	95.49(13)
N21−Cu1−O1	172.34(15)	O4−Cu1−O1	87.95(13)
O2- Cu1- O5	131.38(13)		

The geometry around the Cu^{II} atom is elongated octahedral with the basal plane formed by two nitrogen atoms of the dmbpy ligand [Cu−N distances 1.966(3), 1.969(3) Å] and two oxygen atoms of two different coordinated nitrate anions [Cu−O distances 1.979(3), 1.994(3) Å]. The apical positions are occupied by the other two oxygen atoms of two nitrate anions [Cu−O distances 2.484(4), 2.465(4) Å]. The angles of the basal plane deviate by only about 8° from linear [172.06(12)° and 172.34(15)°].

The lattice is stabilised by stacking of the pyridine rings, with a ring-ring distance of 3.70 Å. The nitrate anion is known to be a versatile anion, which in many cases gives rise to different coordinations. Also with the ligand bpy, a number of Cu^{II} compounds exists with different variations in the coordination of the nitrate anion.[6b,9]

$[Cu(dmbpy)_2(Br)]Br$ (5)

The structure of **5** consists of a Cu^{II} ion, two dmbpy ligands, one coordinated bromide atom and one uncoordinated bromide atom. The structure is depicted in Figure 5 together with the numbering scheme. Selected bond lengths and angles are listed in Table 6. The geometry around the copper(II) ion is distorted trigonal bipyramidal with the trigonal plane formed by three nitrogens of the two dmbpy ligands. The apical positions are occupied by an N-atom and a bromide atom, with a *trans* angle of 135.32(8)°. The Cu−N distances vary from 1.979(3) to 2.113(3) Å, while the Cu−Br distance is 2.4256(6) Å.

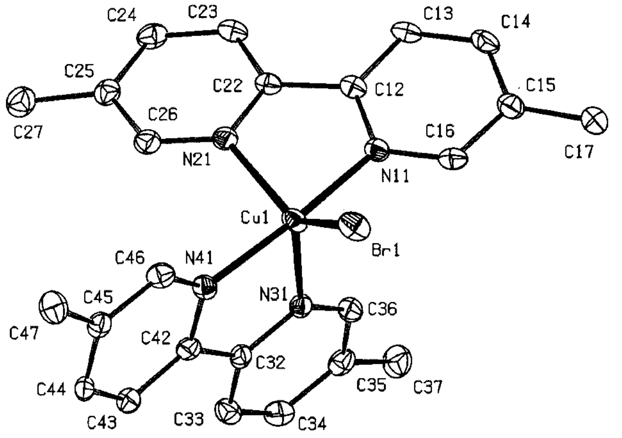

Figure 5. Thermal ellipsoid plot (50% probability) of $[Cu(dmbpy)_2(Br)]Br$ (**5**) with atom-labelling scheme; the non-coordinating bromide anion and H-atoms are omitted for clarity

Table 6. Bond lengths (Å) and angles (°) for $[Cu(dmbpy)_2(Br)]Br$ (**5**)

Cu1−N41	1.979(3)	Cu1−N11	1.985(3)
Cu1−N21	2.106(3)	Cu1−N31	2.113(3)
Cu1−Br1	2.4256(6)		
N41−Cu1−N11	173.31(11)	N41−Cu1−N21	94.79(11)
N11−Cu1−N21	79.40(11)	N41−Cu1−N31	80.29(11)
N11−Cu1−N31	97.07(11)	N21−Cu1−N31	97.65(10)
N41−Cu1−Br1	93.32(8)	N11−Cu1−Br1	93.17(8)
N21−Cu1−Br1	135.32(8)	N31−Cu1−Br1	127.03(8)

The distortion parameter τ in this case is 0.63. The lattice is stabilised by stacking of the pyridine rings, with a ring-ring distance of 3.60 Å. The parameters are in agreement with related structures with a $[Cu(N_4)Br]Br$ chromophore;[10] the parameters of $[Cu(bpy)_2(Br)]Br$[10c] are closest to those of compound **5**, with only a slight difference in the N11−Cu1−N31 bite angle of the bpy rings [106.7°; 97.07(11)° in **5**].

$[Cu(dmbpy)(NCS)_2]_n$ (6)

The structure of **6** is polymeric and consists of a Cu^{II} ion, one dmbpy ligand, one bridging and one monodentate coordinating thiocyanate anion. The structure is depicted in Figure 6 together with the numbering scheme. Selected bond lengths and angles are listed in Table 7. The geometry around the copper(II) ion is distorted square pyramidal with the basal plane formed by the two nitrogen atoms of the dmbpy ligand and two nitrogen atoms of two thiocyanate anions. The Cu−N distances vary from 1.950(3) to 2.014(3) Å. The apical position is occupied by a sulfur atom of the bridging thiocyanate anion with a Cu−S distance of 2.6335(12) Å, forming in this way a polynuclear compound in which the NCS^- anion forms a zigzag chain with the Cu

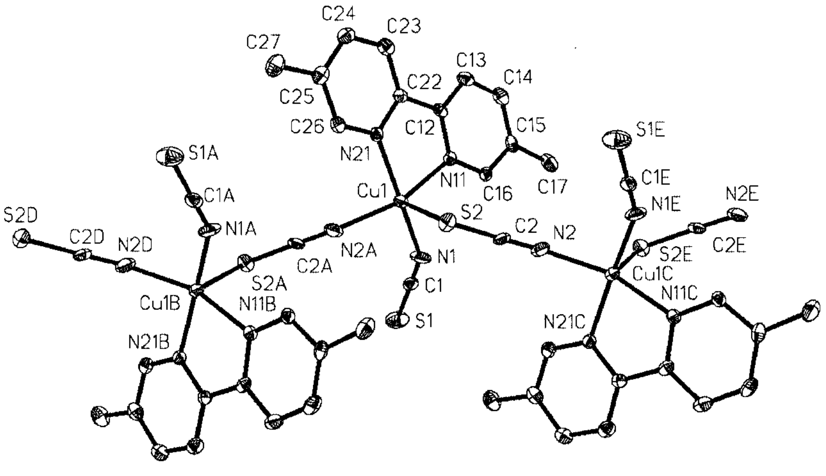

Figure 6. Thermal ellipsoid plot (50% probability) of $[Cu(dmbpy)(NCS)_2]_n$ (**6**) with atom-labelling scheme; H-atoms are omitted for clarity

Table 7. Bond lengths (Å) and angles (°) for $[Cu(dmbpy)(NCS)_2]_n$ (**6**)

Cu1−N11	950(3)	Cu1−N2a	1.989(4)
Cu1−N21	2.005(3)	Cu1−N11	2.014(3)
Cu1−S2	2.6335(12)		
N1−Cu1−N2a[a]	90.70(15)	N1−Cu1−N21	166.03(14)
N2a−Cu1−N21	91.10(14)	N1−Cu1−N11	91.76(14)
N2a−Cu1−N11	154.57(15)	N21−Cu1−N11	80.78(13)
N1−Cu1−S2	99.98(12)	N2A−Cu1−S2	103.22(12)
N21−Cu1−S2	93.09(9)	N11−Cu1−S2	101.27(9)
N1−C1−S1	179.0(4)	N2−C2−S2	178.4(4)

[a] a = $-x + 1$, $y + 1/2$, $-z + 1/2$.

ions. The angles of the square plane are 166.03(14)° and 154.57(15)°. The distortion parameter τ in this case is 0.19, and the two thiocyanate anions are almost linear (178.43° and 179.01°). The lattice is stabilised by stacking of the pyridine rings, with a ring-ring distance of 3.70 Å. The distances and angles are similar to the related compound $[Cu(bpy)(NCS)_2]_n$.[11a]

$[Cu(dmbpy)(N_3)_2]_n$ (7)

The structure of **7** is also polymeric and consists of a Cu^{II} ion coordinated by one dmbpy ligand and two bridging azide anions. The structure is depicted in Figure 7 together with the numbering scheme. Selected bond lengths and angles are listed in Table 8.

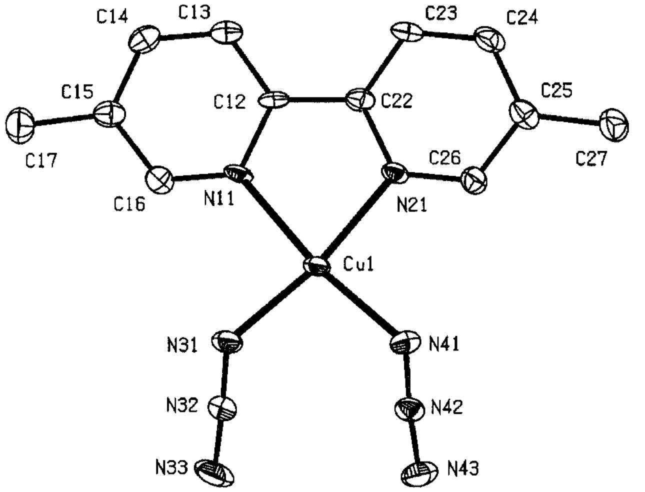

Figure 7. Thermal ellipsoid plot (50% probability) of $[Cu(dmbpy)(N_3)_2]_n$ (**7**) with atom-labelling scheme; H-atoms are omitted for clarity

Table 8. Bond lengths (Å) and angles (°) for $Cu(dmbpy)(N_3)_2$ (**7**)

Cu1−N31	1.980(5)	Cu1−N41	1.981(6)
Cu1−N11	2.039(5)	Cu1−N21	2.047(5)
Cu 1−N31a[a]	2.652(6)	Cu1−N43b[b]	2.708(7)
N31−Cu1−N41	98.2(2)	N31−Cu1−N11	90.5(2)
N41−Cu1−N11	171.1(2)	N31−Cu1−N21	170.2(2)
N41−Cu1−N21	90.9(2)	N11−Cu1−N21	80.3(2)
N33−N32−N31	176.4(7)	N43−N42−N41	174.9(7)

[a] a = $1 - x$, $-y$, $1 - z$. [b] b = $-x$, $-y$, $1 - z$.

The geometry around the copper(II) ion is square-planar based with the basal plane formed by the two nitrogen atoms of the dmbpy ligand and two nitrogen atoms of two azide anions [Cu−N distances vary from 1.980(5) to 2.047(5) Å]. The basal planes are 171.1(2)° and 170.2(2)°. The two azide anions are almost linear [176.4° and 174.9(7)°]. The apical positions are occupied by nitrogen atoms of neighbouring azide anions at semi-coordination distances of 2.652(6) Å (Cu1−N31a, 1,1-azide bond) and 2.708(7) Å (Cu1−N43b, 1,3-azide bond), forming in this way a polymeric array (Figure 8). This array (--Cu--[(1,1-$N_3)_2$]--Cu--[(1,3-$N_3)_2$]--Cu--) is rather rare. So far, to the best of our knowledge, only one Cu^{II} compound, $[Cu(3\text{-picoline})(N_3)_2]_n$,[12a] has been published with this alternating azide array. The lattice of the compound is further stabilised by stacking of the pyridine rings, with a ring−ring distance of 3.72 Å.

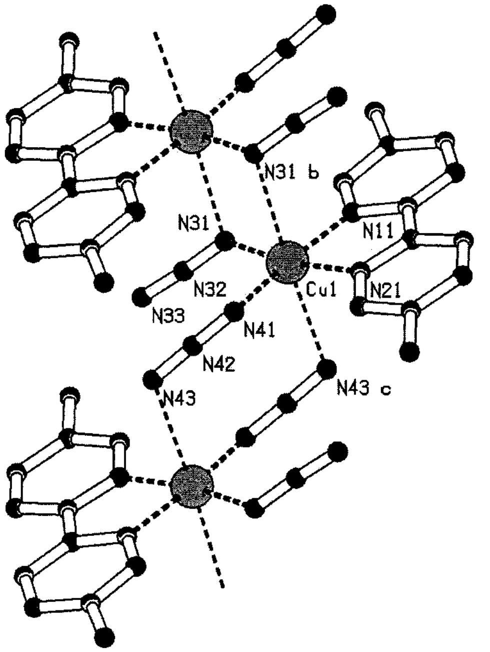

Figure 8. The polymeric structure of compound **7** with a bridging azide ligand

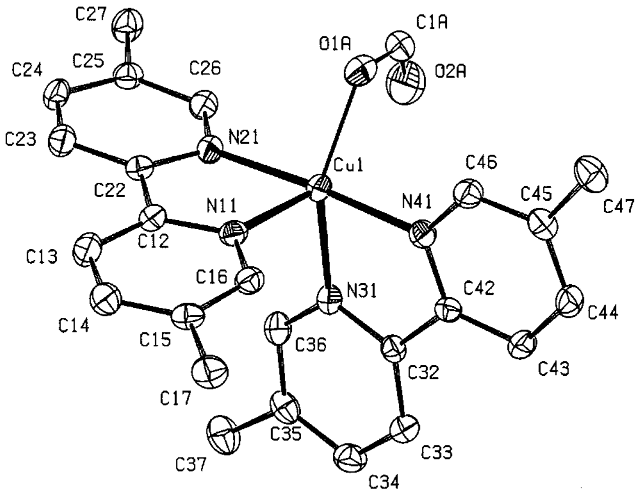

Figure 9. Thermal ellipsoid plot (50% probability) of [Cu(dmbpy)$_2$(HCOO)](CF$_3$SO$_3$) (**8**) with atom-labelling scheme; the noncoordinating triflate anion and H-atoms are omitted for clarity; the formato anion shows only the major component (see text)

[Cu(dmbpy)$_2$(HCOO)](CF$_3$SO$_3$) (8)

The structure of **8** consists of a [Cu(dmbpy)$_2$(HCOO$^-$)]$^+$ cation and one non-coordinating CF$_3$SO$_3$$^-$ anion. The structure is depicted in Figure 9 together with the numbering scheme. Selected bond lengths and angles are listed in Table 9.

Table 9. Bond lengths (Å) and angles (°) for [Cu(dmbpy)$_2$(HCOO)](CF$_3$SO$_3$) (**8**)[a]

Cu1−O1A	2.005(2)	Cu1−N41	1.9890(19)
Cu1−N21	1.9955(19)	Cu1−N11	2.1585(19)
Cu1−N31	2.084(2)	Cu1−O1B	1.923(9)
N41−Cu1−N21	175.56(8)	N41−Cu1−O1A	91.92(8)
N21−Cu1−O1A	92.08(8)	O1A−Cu1−N31	145.59(8)
N41−Cu1−N31	79.48(8)	N21−Cu1−N31	98.22(8)
N41−Cu1−N11	97.09(7)	N21−Cu1−N11	79.33(7)
O1A−Cu1−N11	117.68(8)	N31−Cu1−N11	96.53(7)
O1B−Cu1−N41	89.4(2)	O1B−Cu1−N21	94.8(2)
O1B−Cu1−N31	102.9(2)	O1B−Cu1−N11	160.3(2)

[a] O1A, O1B are the major and minor disordered components of the formato anion which were refined in two positions with ratio 0.8:0.2.

The geometry around the copper(II) ion is distorted trigonal bipyramidal with the trigonal plane formed by three nitrogens of the two dmbpy ligands [Cu-N distances vary from 1.9955(19) to 2.1585(19) Å]. The apical positions are occupied by an N-atom and an oxygen atom of the formato anion with a *trans* angle of 145.59(8)° (the *trans* angle of the major component of the disordered formato anion is chosen here). The second oxygen of the formato anion (O2A) is at a very long distance [2.912(2) Å]. All distances are in agreement with the few other known structures with the formato anion.[13] The distortion parameter τ for this compound is 0.49 (angle taken from the major component), and is therefore intermediate between trigonal pyramidal and square pyramidal. The lattice is stabilised by stacking of the pyridine rings, with a ring-ring distance of 3.672 Å.

Infrared Spectroscopy

In the infrared spectra the most important bands for characterisation of the compounds are those of the anions. In compound **1** the vibration of the tetrafluoroborate anion is observed at 1030 cm^{-1} as a single strong band. The most sensitive characteristic vibrations of the triflate anion is the ν_{as}S−O, which is observed in compound **2** at 1245 cm^{-1} as a broad band with a weak, but sharp, peak at 1273 cm^{-1} and in compound **8** at 1263 cm^{-1}, in agreement with the literature for mononuclear or H-bonded triflate anions.[14]

The two related compounds **3** and **4** differ in composition (1:1 and 1:2, respectively). In compound **3** one nitrate anion is coordinating and one is non-coordinating, while in compound **4** both nitrate anions are coordinated. Most of the regions that are characteristic of nitrate vibrations[11b,15] are overlapped by strong ligand vibrations. However, in the region 1200−1300 cm^{-1} a clear difference in the infrared spectra is observed. In both compounds a broad strong band is observed at about 1270 cm^{-1}, which originates from the chelating nitrate anion.[11b,16] In addition, in compound **3**, which has two different types of nitrate coordination, a strong vibration is observed at about 1333 cm^{-1}. Although this value is slightly higher than expected for a free nitrate bond,[11b,15] this vibration must originate from the non-coordinated nitrate anion.

In compound **6** the vibrations of the thiocyanate anion are observed as a strong split band at 2084 and 2047 cm^{-1} in agreement with the two types of thiocyanate (bridging and monodentate) present in the structure,[11] while in compound **7** the vibration of the azide anion is found as a split strong band at 2027 and 2070 cm^{-1}, in agreement with the two different types of bonding of the azide anions.[12]

The C=O stretching vibration of the formato anion in compound **8** is observed at 1597 cm^{-1} as a clear, strong, sharp band, in accordance with the literature[11b] and also with the fact that this band is absent in compounds **1**−**7**.

Electronic Spectroscopy

The diffuse-reflectance spectra of all compounds measured as solids are tabulated in Table 1. Compounds **1**, **4** and **7**, which have a square-planar based geometry exhibit bands at around 14.3−15.5 × 10^3 cm^{-1}, which is normal for planar-based (octahedral) geometries.[17] Compound **1** also displays a very broad shoulder at 7.6 × 10^{3}cm^{-1}, which is rather rare for distorted octahedral geometries and must originate from a small Jahn−Teller distortion.[17a]

The five-coordinate compounds **2**, **3**, **5**, **6** and **8**, which have trigonal bipyramidal or square-pyramidal geometries, all show bands at around 13.5−15.1 × 10^{3}cm^{-1} and 10.1−10.8 × 10^{3}cm^{-1}, which are considered normal transitions for these geometries.[17]

All compounds have charge-transfer bands at around 26−28 × 10^{3}cm^{-1}, except the thiocyanate compound **6**, which has a band at 21.5 × 10^3 cm^{-1} of medium intensity that originates from a Cu^{II}−NCS charge transfer.[11] The azide compound **7** displays a very strong band at 23.4 × 10^{3}cm^{-1}, which originates from the strong Cu^{II}-azide charge transfer.[18]

Magnetic Properties

EPR Spectroscopy

The powder EPR spectrum of compound **1** at room temperature reveals an axial signal with $g_\perp = 2.10$ and $g_\parallel = 2.26$. A weak hyperfine splitting is observed with $A_\parallel = 11.5$ mT. At 77 K the hyperfine splitting $A_\parallel$ becomes 13.3 mT, an indication that the geometry is changing at low temperature. The EPR values are in agreement with the distorted octahedral structure of this compound.

The spectrum of compound **2** at room temperature and at 77 K displays a rhombic signal with $g_1 = 2.03$, $g_2 = 2.12$ and $g_3 = 2.28$. This last value (g_3) is observed as a weak band. This spectrum agrees with the square-pyramidal geometry of the Cu^{II} atom.[17]

The EPR spectra of the nitrate compounds show a different pattern according to their different Cu^{II} geometry. Compound **3** at room temperature and at 77 K reveals an isotropic signal with $g = 2.14$, while compound **4** at room temperature and at 77 K shows the same axial signal with a $g_\perp$ of 2.07 and an unresolved $g_\parallel$ of 2.27.

The powder EPR spectra of compounds **5** and **6** (Figures 10 and 11) each display a rhombic pattern with three distinct g values. Compound **5** shows an inverted EPR signal with $g_x = 2.20$, $g_y = 2.15$ and $g_z = 2.01$. This pattern (with the lowest g value < 2.03) agrees with the fact that this compound has a compressed rhombic site and a predominant d_{z^2} ground state.[3b,17,19a] This value agrees with a trigonal bipyramidal geometry with an unpaired electron situated along the N11−N41 axis. For compound **6** the lowest g value is greater than 2.03, with $g_x = 2.05$, $g_y = 2.11$ and $g_z = 2.23$, which indicates a $d_{x^2-y^2}$ ground state.[3b,17,19b,19c]

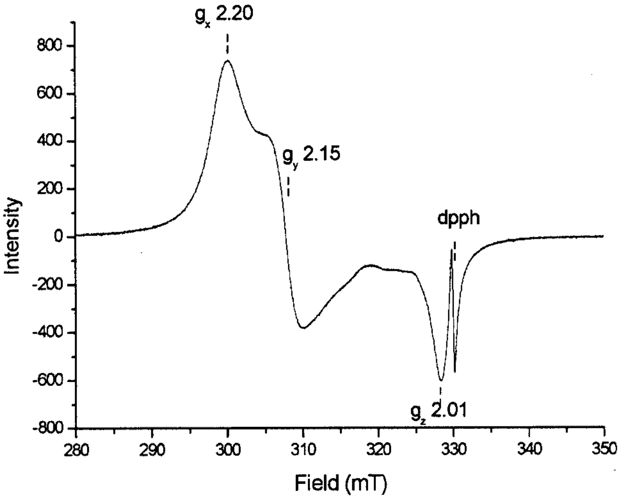

Figure 10. EPR spectrum (solid) of compound (**5**), see text

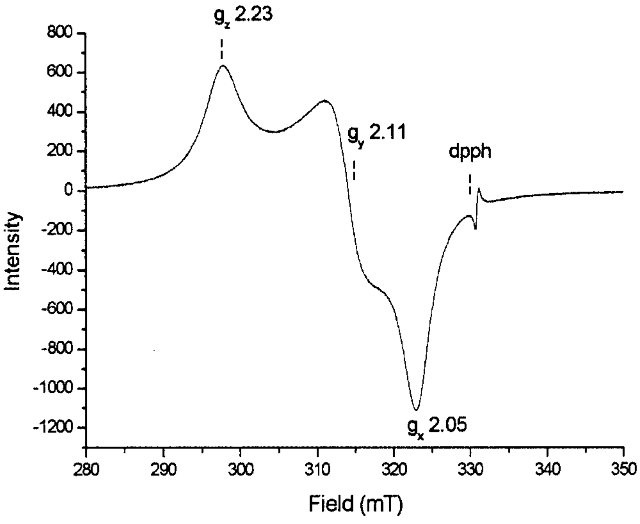

Figure 11. EPR spectrum (solid) of compound (**6**), see text

The EPR spectrum of compound **7** at room temperature and at 77 K reveals the same axial signal with a $g_\perp$ of 2.06 and an unresolved $g_\parallel$ of 2.23, which confirms the square-planar based structure of the compound.

The EPR spectrum of compound **8** at 77 K shows, like compound **5**, an inverted EPR signal with $g_x \approx 2.22$, $g_y =$

2.12 and $g_z = 2.02$. The g_x appears as a broad band. This pattern (with lowest g value < 2.03) indicates a predominantly d_{z^2} ground state,[3b,17,19a] which is in agreement with the five-coordinate geometry.

For assigning the ground state in rhombic spectra the parameter $R = (g_2 - g_1)/(g_3 - g_2)$, with $g_3 > g_2 > g_1$, has been introduced.[3b,17c] This parameter is greater or smaller than 1 if the ground state is d_{z^2} or $d_{x^2-y^2}$, respectively. For the rhombic compounds **2**, **5**, **6** and **8** the R values are 0.56, 2.80, 0.50 and about 1.0, respectively, which confirms our conclusions.

Magnetic Susceptibility

For a few of the new compounds with potential magnetic exchange as a result of their structure and bridging anions, detailed variable-temperature magnetic susceptibility studies were performed. In the literature a number of Cu^{II} thiocyanate compounds exist which display a weak magnetic interaction even though the Cu−Cu distance is large (about 6 Å) and the magnetic orbitals are not co-planar. Examples are the compounds $[Cu(bpy)(NCS)_2]_n$ and $[Cu(pyrazine)(NCS)_2]_n$, with a weak antiferromagnetic interaction,[11a,11f] and two mixed-metal (Cu^{II}-Co^{II}) thiocyanide compounds,[11e] which give rise to a weak ferromagnetic interaction. In light of these results the magnetic susceptibility of a powdered sample of **6** was measured from 5 to 300 K. The spectrum of μ_{eff} versus T does not change significantly and stays within a range of 1.65−1.75 BM, which is close to the spin-only value of Cu (1.77 BM), so no significant interaction could be observed between neighbouring Cu atoms.

Similar results were obtained for compound **7**, which also gives no significant change between 5 and 300 K (μ_{eff} between 1.76−1.82 BM), so no magnetic interaction could be detected between neighbouring Cu atoms. This behaviour can be understood on the basis of the magnetic orbital orientation.[3a]

Conclusions

In this study eight new mononuclear Cu^{II} compounds with the ligand dmbpy have been synthesized and characterised. Depending on the selected anions, a great variety of geometries have been observed with Cu^{II}. In all cases the dmbpy ligand appears to be rather rigid, irrespective of whether one, two or three ligands bind to Cu^{II}. Five-coordinate structures, varying from square pyramidal to trigonal bipyramidal, are observed with triflate, nitrate, bromide, thiocyanate and formate as the anion. With tetrafluoroborate, nitrate and azide square-planar based (square planar to octahedron) complexes are obtained.

Comparing our results to Cu^{II} compounds with bpy as a ligand, we observe quite important differences: with bpy a very large number of mononuclear and anion-bridged dinuclear compounds has been reported with a similar set of anions,[4b] while the method of synthesis is similar to ours. Apparently the steric hindrance of the methyl groups of dmbpy prevents crystallisation of such dinuclear compounds.

In summary: the effect of the two methyl groups has resulted in a great variety of new compounds, which have no counterparts in bipyridine-containing complexes. Such dramatic differences resulting from apparently small ligand changes are as yet not fully understood.

Experimental Section

All chemicals were purchased from commercial sources and used as received.

General Synthesis of the Compounds: An equimolar amount of dmbpy and the copper(II) salt were dissolved separately in ethanol and were then slowly mixed together (Cu solution added to the ligand solution) and heated to about 40 °C. The solution was filtered to remove any solid particles and left to evaporate at room temperature. Crystals were obtained in a few days to a few weeks. Yields 43 to 72%. A difference in the ligand:copper ratio had no influence on the compounds, except for the nitrate compounds **3** and **4**, which are very sensitive to the exact ratio (1:1 and 1:2, respectively). The products were characterised by IR spectroscopy and elemental analysis (see Table 1).

Compounds **6** and **7** were prepared in the same way as above (using Cu^{II} triflate as the copper salt), but an equimolar amount of sodium thiocyanate or sodium azide, respectively, dissolved in a very small amount of water, was added slowly to the total solution. The solution was then filtered and left standing in the open air.

Compound **8** was initially obtained by using Cu^{II} triflate and the ligand dmbpy in methanol and adding a few drops of sodium hydroxide dissolved in water to the total solution. Within a few weeks dark-blue blocks of crystals appeared, which turned out to contain the formato anion. Apparently, the formato anion was formed in situ, a phenomenon observed earlier by using triethyl orthoformate.[13a,20] Subsequently, this compound was also synthesized in higher yield by adding sodium formate (dissolved in water) to the Cu/ligand solution in methanol.

Physical Techniques: C,H,N determinations were performed on a Perkin−Elmer 2400 Series II analyser. Ligand-field spectra were obtained on a Perkin−Elmer Lambda900 spectrophotometer using the diffuse-reflectance technique, with MgO as a reference. FT-IR spectra were obtained on a Perkin−Elmer Paragon 1000 FT-IR spectrophotometer equipped with a Golden Gate ATR device, using the reflectance technique (4000−300 cm^{-1}, resolution 4 cm^{-1}). X-band EPR spectra were recorded on polycrystalline samples at room temp. and 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 1000 Gauss). Data were corrected for magnetisation of the sample holder and for diamagnetic contributions, which were estimated from Pascal constants.

X-ray Crystallography. Compounds 1−4: A crystal was selected and mounted onto a glass fiber using the oil-drop method. Data were collected on a Rigaku AFC-7S diffractometer (graphite-monochromated Mo-K_α radiation, ω-2θ scans). The intensity data were corrected for Lorentz and polarisation effects, for absorption (psi-scan absorption correction) and extinction. The structures were solved by direct methods. The programs teXsan,[21a] SHELXS-97,[21b] and SHELXL-97[21c] were used for data reduction, structure solution

Table 10. Crystallographic data

Crystal data	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Formula	$C_{38}H_{42}B_2CuF_8N_6O$	$C_{28}H_{30}CuF_6N_4O_7S_2$	$C_{24}H_{24}CuN_8O_6$	$C_{12}H_{12}CuN_4O_6$	$C_{24}H_{24}Br_2CuN_4$	$C_{14}H_{12}CuN_4S_2$	$C_{12}H_{12}CuN_8$	$C_{26}H_{25}CuF_3N_4O_5S$
Molecular mass	835.94	776.22	556.03	371.79	591.83	363.94	331.84	626.10
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	*Pbca* (no. 61)	$P2_1/n$ (no.14)	$P\bar{1}$ (no.2)	$P2_1/n$ (no.14)	$P2_1/c$ (no.14)	$P2_1/c$ (no.14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no.2)
a (Å)	14.162(2)	12.634(3)	8.1350(10	11.274(2)	7.9980(10)	9.0470(9)	7.6800	8.2240(6)
b (Å)	18.098(4)	17.073(4)	10.572(2)	10.349(2)	28.542(3)	10.9230(12)	17.620(4)	10.6900(9)
c (Å)	30.786(6)	15.252(3)	15.740(2)	12.849(3)	11.1440(10)	17.0520(16)	10.462(2)	15.3270(15)
α (°)	–	–	96.69(2)	–	–	–	–	92.024(8)
β (°)	–	100.03(3)	104.47(2)	100.61(3)	116.730(10)	118.985(8)	110.72(3)	99.527(7)
γ (°)	–	–	105.88(2)	–	–	–	–	90.056(7)
V (Å^3)	7891(3)	3239.6(13)	1235.6(3)	1473.5(5)	2272.1(4)	1474.0(3)	1324.2(5)	1328.0(2)
Z	8	4	2	2	4	4	4	2
$D_{calcd.}$ (g·cm^{-3})	1.407	1.591	1.494	1.676	1.730	1.640	1.665	1.566
F(000)	3448	1588	574	756	1180	740	676	642
μ (cm^{-1})	14.52	29.33	17.00	24.63	44.98	17.61	16.56	9.67
Crystal size (mm)	0.24 × 0.09 × 0.07	0.50 × 0.22 × 0.09	0.30 × 0.20 × 0.10	0.30 × 0.30 × 0.30	0.20 × 0.19 × 0.18	0.18 × 0.08 × 0.03	0.10 × 0.02 × 0.02	0.25 × 0.25 × 0.17
Colour	blue-green	green	blue-green	dark blue	blue	green	green	dark blue
Temperature (K)	193(2)	193(2)	293(2)	293(2)	173(2)	173(2)	173(2)	173(2)
θmin, θmax (°)	2.87–67.01	3.92–66.93	2.96–67.93	4.80–67.98	5.04–27.52	5.01–27.49	5.08–26.97	3.03–27.50
Total data	7024	5746	4821	2831	20518	16347	20508	20687
Total uniq. data (Rint)	7024 (0.0000)	5744 (0.0917)	4479 (0.0563)	2691 (0.0255)	5200 (0.500)	3356 (0.1133)	2737 (0.1019)	6034 (0.0374)
Observed data [$I > 2\sigma(I)$]	4694	4950	4051	1956	3730	2131	1989	4680
No. of ref. parameters	505	433	334	208	280	190	190	372
$wR2$ (all data)[a]	0.1672	0.1357	0.1443	0.1248	0.0859	0.1226	0.1935	0.0951
R[b]	0.0667	0.0511	0.0489	0.0476	0.0395	0.0528	0.0751	0.0386
S	1.029	1.068	1.023	1.032	1.022	1.029	1.073	1.025
Max. and min. Resd. dens. (e/Å^3)	0.0999;-0.037	0.840;-0.580	0.596; −0.347	0.415; −0.39	0.451; −0.530	0.695; −0.575	1.769; −1.067	0.458; −0.354

[a] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

and structure refinement, respectively. All non-hydrogen atoms were refined anisotropically. All H atoms, except the hydroxo atom of the ethanol molecule in compound **2**, were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms.

Compounds 5–8: Crystals suitable for structure determination were mounted in Lindemann-glass capillaries and transferred into the cold nitrogen stream of a Nonius KappaCCD diffractometer on a rotating anode (Mo-K_α radiation, graphite monochromator, λ = 0.71073). The intensity data were corrected for Lorentz and polarisation effects, and for absorption and extinction. The structures were solved by direct methods. The programs COLLECT,[21d] SHELXS-97,[21b] and SHELXL-97[21c] were used for data reduction, structure solution and structure refinement, respectively. All non-hydrogen atoms were refined anisotropically. All H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. For compound **8** the formato anion was found to be disordered and was refined in two positions with ratio 0.8/0.2. Plots were obtained using the PLATON package.[21e] Crystallographic data of all compounds are listed in Table 10.

CCDC-228793–228800 (for compounds **1–8**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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