Molecular bricklaying: the protonated benzimidazole moiety as a synthon for crystal engineering

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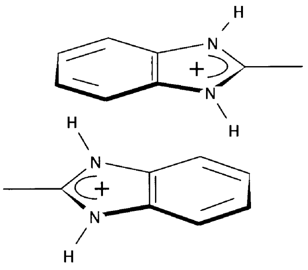
The crystal structures of three salts of diprotonated 1,2-bis(1*H*-benzimidazol-2-yl)ethane, **1**, with tetrahalogenometallates are reported. The crystal lattices are constructed from two types of interactions, the stacking of the protonated benzimidazole groups and N–H···Cl hydrogen bonding between the cations and the complex anions. Depending on the conformation of the cation, two- or three-dimensionally stacked structures are formed. A similar packing motif is found with the related cation formed by 1,3-bis(1*H*-benzimidazol-2-yl)-propane, **2**, and this suggests that the protonated benzimidazole group may be a useful synthon for crystal engineering.

Chemists are becoming increasingly interested in the field of crystal engineering, which has been defined as the understanding of intermolecular attractions in the solid state, and the use of this understanding in the design of new solids.[1–3] To obtain predictable or, more realistically, explicable structures, the interactions between the particles should be sufficiently labile to allow efficient exploration of the potential energy surface to reach thermodynamic minima, and to allow the correction of errors in the packing. Among the approaches adopted in the crystal chemistry of coordination compounds, the use of bridging ligands such as cyanide, oxalates, or 4,4′-bipyridyl, linked by coordination to labile metal ions, has been explored in some detail,[4–7] as has the use of hydrogen bonding to allow well-defined, directed interactions between complex molecules.[8–10] Desiraju has introduced the notion of the supramolecular synthon[1] as a unit that assembles in a crystal in a predictable way, and may thus be used to assemble an extended three-dimensional structure. In this paper we show that protonated benzimidazoles interact in the solid state in such a way as to allow their use as supramolecular synthons.

At first sight the interaction between two cations would be expected to be repulsive and might seem to offer little promise for control of crystal structure, but in their studies of crystal structures containing arylphosphonium counter cations, Dance and Scudder[11] have shown that the interactions between these ions are important, and have drawn attention to the fact that the formally inert counterion may in fact play a major role in the crystal packing.[12] The aryl-aryl interactions that they have identified have also been observed in the crystal packing of complexes of heterocyclic nitrogen ligands such as terpyridyl.[13] For many years such interactions were regarded as simple hydrophobic or dispersion interactions, but the studies of Hunter and Sanders[14] have established the importance of electrostatic forces in these associations. As a consequence, the interaction requires specific orientation of the aryl units to maximise the attraction, and it thereby acquires a definite directional character that allows their use as supramolecular synthons. In parallel with these studies, Stoddart and his co-workers have shown elegantly how the interaction between an electron-poor paraquat moiety and an electron rich para-alkoxy aromatic unit may be used to assemble discrete molecular units as a starting point for template reactions.[15]

The protonated benzimidazole moiety contains an electron-poor region associated with the imidazolonium group, and a relatively electron-rich region associated with the phenylene group. Thus, the interaction between two benzimidazolylium units will be strongest when the imidazolylium group of one unit lies over the phenylene moiety of the other (Scheme 1). Consequently, protonated benzimidazole groups will associate with each other in crystals in a predictable way. A cation containing two protonated benzimidazoles linked by a spacer such as 1,2-bis(benzimidazol-2-ylium)ethane, $\mathbf{1}H_2^{2+}$ (Scheme 2) will organise itself in the solid state so that each cation overlaps



Scheme 1

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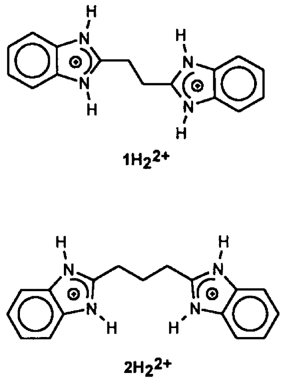


Scheme 2

favourably with other cations and this may be used to build up an extended structure.

Results

Synthesis

1,2-Bis(benzimidazol-2-ylium)ethane may be synthesised readily by a Phillips[16] reaction between 1,2-diaminobenzene and succinic acid in refluxing 4 M HCl. On cooling the white bis(hydrochloride salt) crystallises out. If the 1,2-diaminobenzene has oxidised the product may be discoloured; this may be rectified by treatment with activated charcoal in ethanol. The tetrahalogenometallate salts were obtained by mixing hot ethanol solutions of $[\mathbf{1}\mathrm{H}_2]\mathrm{Cl}_2$ and of the metal dichloride. The salt $[\mathbf{1}\mathrm{H}_2][\mathrm{MCl}_4]$ crystallises from solution on cooling. Crystals suitable for X-ray diffraction may be obtained by vapour diffusion of diethyl ether into methanol solutions of the salt. 1,3-Bis(benzimidazol-2-ylium)propane and its salts were prepared in an identical way.

Crystal structure of $[\mathbf{1}\mathrm{H}_2][\mathrm{CoCl}_4]$

The crystal structure of $[\mathbf{1}\mathrm{H}_2][\mathrm{CoCl}_4]$ shows the expected ionic structure. Both ions lie on crystallographic twofold symmetry axes passing through the cobalt atom and through the midpoint of the $-\mathrm{CH}_2\mathrm{-CH}_2-$ bond, respectively. The $[\mathrm{CoCl}_4]^{2-}$ anion shows two almost equal Co–Cl bond lengths [average 2.2807(7) Å] and Cl–Co–Cl bond angles in the range 108.58–110.96°, close to the ideal tetrahedral value and in good agreement with previously reported values for bonds between cobalt(II) and hydrogen-bonded chlorides.[17] The cation $[\mathbf{1}\mathrm{H}_2]^{2+}$ is aligned along the c^* axis and shows the expected trans conformation; however, the two benzimidazole planes are not parallel, but inclined at 49.9(9)°. When viewed along its long axis, the cation shows one side open and the other closed (Fig. 1).

All four N–H bonds are involved in hydrogen bonds to the chloride ligands, with N···Cl distances of 3.208(2) and 3.173(3) Å. The hydrogen atoms were located and refined, and the corresponding H···Cl distances are 2.42(2) and 2.33(4) Å, respectively, with N–H···Cl angles of 166(4) and 178(3)°. These values agree with the results of a data base survey by Orpen and collaborators.[18] Fig. 2 shows that each cation effectively acts as a chelating hydrogen bonding ligand to the anion on each side of it. This produces a chain of cations and anions alternating along the crystallographic b axis.

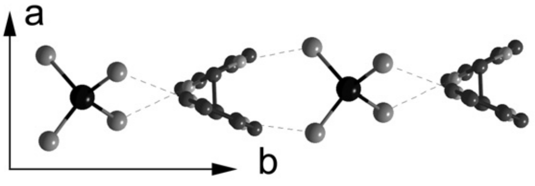


Fig. 1 Crystal structure of $[\mathbf{1}\mathrm{H}_2][\mathrm{CoCl}_4]$, space group $C2/c$. View along the long axis of the cation showing the open and closed sides. The dashed lines indicate hydrogen bonds. A crystallographic twofold symmetry axis along b passes through the cobalt ions.

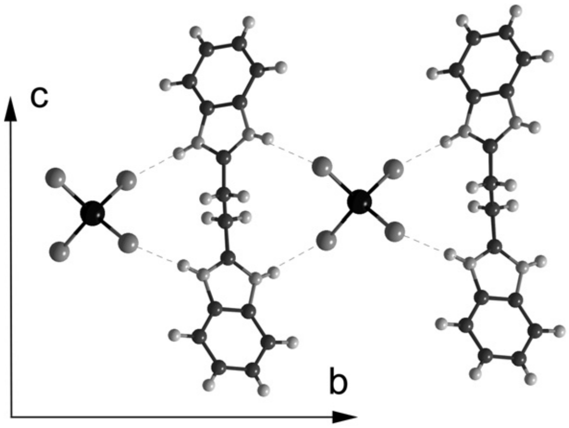


Fig. 2 Crystal structure of $[\mathbf{1}\mathrm{H}_2][\mathrm{CoCl}_4]$: view of the chelate hydrogen bonds between cation and anion. The twofold symmetry axis passes through the cobalt ions.

The chains are linked together into a three-dimensional structure by stacking interactions between benzimidazole units. This is shown clearly in Fig. 3 where the overlapping of the benzimidazole units is seen to be that sketched in Scheme 1. Each cation overlaps with four other cations in a motif similar to bricks in a masonry wall. The stacked benzimidazoles are related by centres of inversion and translation operations and are consequently parallel; there are two crystallographically inequivalent stacking distances of 3.382(9) and 3.434(9) Å. The relative inclination of the benzimidazole units in each cation results in two stacking directions approximately along [2 1 0] and [−2 1 0], and thus the cation-cation interactions alone generate a three-dimensional structure as shown schematically in Scheme 3(c).

Crystal structure of $[\mathbf{1}\mathrm{H}_2][\mathrm{MnCl}_4]$

A first structure determination of $[\mathbf{1}\mathrm{H}_2][\mathrm{MnCl}_4]$ using a four-circle diffractometer showed a triclinic space group $P\bar{1}$ and could be refined satisfactorily to a structure that was very similar to that of $[\mathbf{1}\mathrm{H}_2][\mathrm{CoCl}_4]$. Analysis of the symmetry of the refined structure showed it to be very close to the $C2/c$ structure of the cobalt complex, but transformation of the triclinic space group to $C2/c$ gave a very high R_{int} of 20% for symmetry related reflections. Examination of the crystals using an area

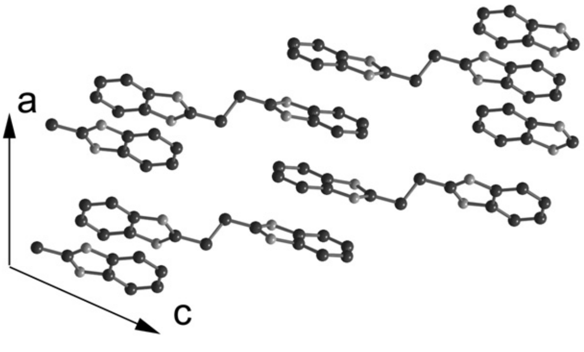
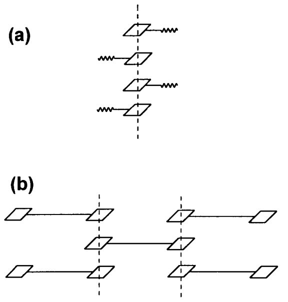


Fig. 3 The stacking interactions between $[\mathbf{1}\mathrm{H}_2]^{2+}$ cations in $[\mathbf{1}\mathrm{H}_2][\mathrm{CoCl}_4]$. The view is at a slight angle to the b axis, and shows the stacks produced by a combination of inversion and translation operations.



Scheme 3

detector at different temperatures showed a splitting of reflection peaks below 240 K. The structure was therefore remeasured at 250 K and found to be isostructural with [**1**H_2][$CoCl_4$]. A DSC scan of the crystals supported the hypothesis of a phase change around 240 K, presumably resulting from a triclinic twinning of the original monoclinic structure.

The Mn–Cl bond lengths average 2.364(1) Å and the Cl–Mn–Cl bond angles are in the range 108.73–109.77°. The two stacking distances are 3.428(6) and 3.476(6) Å, slightly longer than for the cobalt compound, and the angle between the benzimidazole planes of the same cation is virtually the same [50.53(3)°]. The N···Cl hydrogen bonding distances are 3.178(2) and 3.212(2) Å with N–H···Cl bond angles of 177° and 170°, respectively. In some respects the most surprising aspect of this structure is its existence: when Orpen and coworkers endeavoured to crystallise $[MnCl_4]^{2-}$ with diprotonated 4,4′-bipyridyl they observed the formation of [$MnCl_6$] chains with bridging chloride ions.[19] It is possible that the chelation of the tetrahedral unit by the hydrogen bonds prevents this.

Crystal structure of [1H$_2$][CuCl$_4$] · CH$_3$OH

The $[CuCl_4]^{2-}$ anion is generally distorted from tetrahedral geometry as a result of the d^9 configuration[20] and this is observed here, with a flattening of the tetrahedron to give four small Cl–Cu–Cl angles in the range 97.3–98.9°, and two larger ones [141.37(5)° and 128.86(4)°], similar to previously reported values. There are two crystallographically distinct [**1**H_2]$^{2+}$ cations, aligned roughly along the *b* axis. (Fig. 4) Both lie on centres of symmetry and consequently the benzimidazoles of the same molecule are strictly parallel. The cations stack with other cations related by the glide plane, forming sheets of cations in the *bc* plane with the stacking axis directed along *c* [Scheme 3(b)]. The overlaps between benzimidazole cations are similar to those in Scheme 1 and the interplane distances lie between 3.36 and 3.46 Å with interplane angles of 2.8° and 4.6°. The planes of the crystallographically distinct cations are inclined to each other by 33.8(1)°.

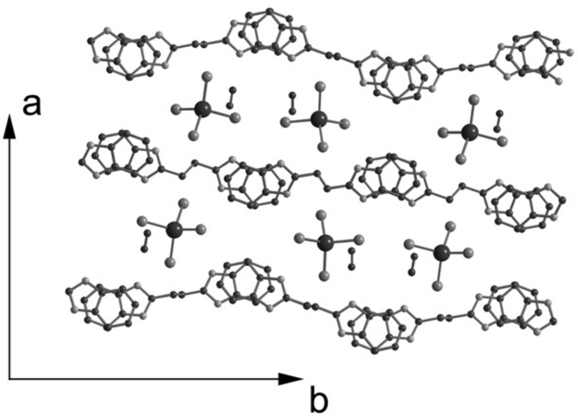


Fig. 4 View of the structure of [**1**H_2][$CuCl_4$]·CH_3OH (spacegroup $P2_1/c$) showing the overlap of the benzimidazole units along the *b* axis.

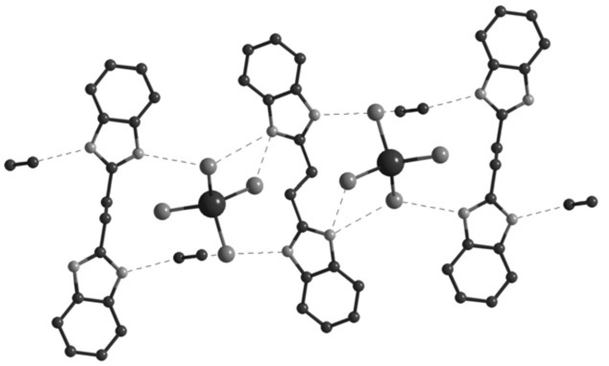


Fig. 5 The hydrogen bonding network of [**1**H_2][$CuCl_4$]·CH_3OH. Hydrogens are omitted for clarity.

The sheets of cations are held together by hydrogen bonds to the $[CuCl_4]^{2-}$ anions and the included methanol as shown in Fig. 5, but the description is more complicated than for the previous salts: one cation acts as a chelating hydrogen bond donor towards the $[CuCl_4]^{2-}$ anion as above [N···Cl distances of 3.197(3) and 3.160(3) Å], but also forms a weaker H-bond to a third chloride [N···Cl distance 3.303(3) Å]. The second cation hydrogen bonds to one of the chlorides that hydrogen bonds to the first cation [N···Cl distance 3.152(4) Å] and to the oxygen atom of the methanol, which in turn acts as a hydrogen bond donor to one of the chlorides that is hydrogen bonded to the first cation. One chloride of the anion forms no hydrogen bonds and this shows the shortest Cu–Cl distance [2.212(1) Å]; the chloride forming one hydrogen bond has a Cu–Cl distance of 2.236(1) Å, and the two forming two hydrogen bonds are longer still [3.284(1) and 3.287(1) Å]

Crystal structure of [2H$_2$][CoCl$_4$]

Addition of an extra carbon to the bridge joining the benzimidazoles in **1** gives **2** and dramatically affects the shape of the cation, since the major axes of the two benzimidazole moieties can no longer be parallel. They are inclined at 17.2° and 51.4°, respectively, to the three carbons of the bridge, and at 59.63(3)° to each other. Each benzimidazole stacks with two others, one crystallographically identical, related by a centre of inversion, with interplane distances of 3.56 and 3.45 Å, and the other related by a glide plane with an interplane angle of 7.6°. The cations are arranged in a zig-zag manner with their long axis roughly along the *c* axis and the mutually inclined stacks in the *ab* plane [Fig. 6, Scheme 3(d)].

The lengthening of the bridge increases the separation of the benzimidazole groups and the chelating of the anion by hydrogen bonds observed for [**1**H_2][$CoCl_4$] is no longer possible. Each $[CoCl_4]^{2-}$ anion forms four hydrogen bonds (two simple and one bifurcated) to four different benzimidazolonium cations. One chloro ligand forms no hydrogen bonds and shows the shortest Co–Cl distance [2.2579(7) Å], the others range from 2.2659(7) to 2.3028(7) Å. The Cl–Co–Cl angles range from 102.25(2)° to 112.34(2)°, showing a rather larger distortion from pure tetrahedral symmetry than for [**1**H_2][$CoCl_4$].

Discussion

Inspection of the crystal structures suggests two factors control the packing: N–H···Cl hydrogen bonding and the stacking of

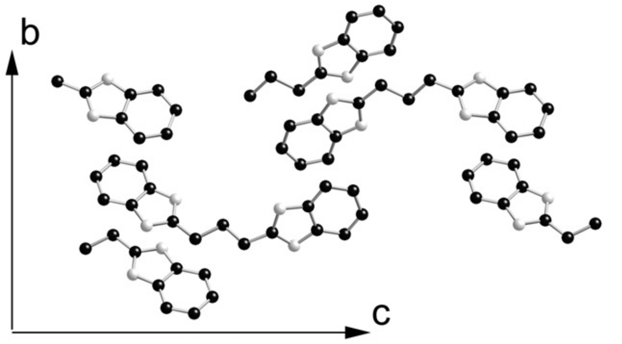


Fig. 6 The stacking interactions between [**2**H$_2$]$^{2+}$ cations in [**2**H$_2$][CoCl$_4$]. In the space group $P2_1/c$ the stacks are generated by inversions and glide planes.

the protonated benzimidazoles. Hydrogen bonding between halogenometallate anions and protonated aromatic nitrogen compounds has been studied in some detail recently,[21–23] particularly by the group of Orpen.[17,19,24–26] The hydrogen bonds observed in our work show no unusual features, although the chelating motif observed in the structures of [**1**H$_2$][CoCl$_4$] and [**1**H$_2$][MnCl$_4$] is to our knowledge novel, and could be used in the design of specific anion receptors. Since the cations carry four potential hydrogen bond donors and the anions four potential hydrogen bond acceptors, there are a numerous ways in which the cations and anions might be arranged to give a satisfactory number of hydrogen bonds. In practice, however, the observed pattern is quite simple and only the hydrogen bonds mentioned in the text were observed.

The stacking interaction is more interesting since it shows a more specific structural requirement, and has not previously been discussed. In the four compounds whose structures are reported here, as in many other structures that will be discussed in future publications, the stacking arrangement shown in Scheme 1 is observed. In all cases the benzimidazole planes are parallel, with a short interplanar distance close to 3.4 Å, and good overlap of the phenylene part of one cation with the imidazole part of the second is observed. This preference leads to the overlapping arrangement given in Scheme 3(a). For a bisbenzimidazolonium cation such as [**1**H$_2$]$^{2+}$ the stacking interactions can build up a lattice in two ways depending on the relative orientation of the two benzimidazoles in the cation. In the simplest case, observed for [**1**H$_2$][CuCl$_4$], the two planes are parallel and this leads to the formation of a sheet structure, with stacking in one dimension only, and the formation of a brickwork-like motif [Scheme 3(b)]. If the two planes are inclined to each other, then two stacking directions are possible [Scheme 3(c)] and the cations can form a three-dimensional network (which will of course require anions to stabilise it). This leads to the interesting possibility that we can switch from a three-dimensional structure to a sheet structure by controlling the conformation of the cation, and thus the relative orientations of the benzimidazoles. The investigation of this hypothesis is currently in progress in our laboratory. If the structure of the cation is modified by the incorporation of an extra carbon in the bridge, the stacking is maintained but now shows a zig-zag motif [Scheme 3(d)] with the inclination of the benzimidazoles again giving rise to a three-dimensional network of cations.

Experimental

Syntheses

1,2-Bis(benzimidazol-2-yl)ethane dihydrochloride, (1H$_2$)Cl$_2$. To *o*-phenylenediamine (10.81 g, 100 mmol) and succinic acid (5.90 g, 50 mmol) was added 4 M hydrochloric acid (120 cm^3). The mixture was refluxed for 17 h at 120 °C and gradually cooled to room temperature, at which point the hydrochloride separated as a crystalline solid. The solid was filtered, washed with acetone and dried under vacuum at 60 °C. Yield (11.29 g, 69%). Anal. found: C, 57.3; H, 4.8; N, 16.7; calcd for $C_{16}H_{14}N_4\cdot 2HCl$: C, 57.3; H, 4.8; N, 16.7%. IR (KBr): 3426m (br), 3019–2612s (br), 1623s, 1573s, 1511s, 1481w, 1461s, 1435m, 1380s, 1299m, 1264m, 1229s, 1184w, 1107w, 1020w, 924m, 898m, 817s, 763w, 732s, 620s, 510m, 433m cm^{-1}. ^{1}H NMR (300 MHz, D$_2$O) δ: 7.68 (m, 4H, arom H$^{4/7}$), 7.53 (m, 4H, arom H$^{5/6}$), 3.80 (s, 4H, CH_2); ^{13}C NMR (75 MHz, D$_2$O) δ: 149.8 (C^2), 130.6 (C$^{8/9}$), 126.5 (C$^{5/6}$), 113.8 (C$^{4/7}$), 24.0 (CH$_2$).

1,3-Bis(benzimidazol-2-yl)propane dihydrochloride, (2H$_2$)Cl$_2$. This compound was synthesised in a similar manner, yield 64%. Anal. found: C, 52.7; H, 5.7; N, 14.5; calcd for $C_{17}H_{16}N_4\cdot 2HCl\cdot 2H_2O$: C, 53.0; H, 5.8; N, 14.5%. IR (KBr): 3369s, 3051m, 1631s, 1568s, 1508m, 1463s, 1422s, 1230s, 1154w, 1011w, 768s, 619s, 481s cm^{-1}. ^{1}H NMR (300 MHz, CD$_3$OH) δ: 7.72 (m, 4H, arom H$^{4/7}$), 7.56 (m, 4H, arom H$^{5/6}$), 3.39 (m, 4H, CH_2), 2.55 (m, 2H, CH_2).

1,2-Bis(2-benzimidazolonium)ethane tetrachloromanganate(II), [1H$_2$][MnCl$_4$]. A solution of manganese(II) dichloride tetrahydrate (0.311 g, 1.6 mmol) in ethanol (20 cm^3) was added to 1,2-bis(benzimidazol-2-yl)ethane dihydrochloride (0.524 g, 1.6 mmol) in hot ethanol (130 cm^3). The resulting white precipitate was filtered, washed with diethyl ether and air dried. The product was recrystallised by vapour diffusion of diethyl ether into a saturated methanolic solution of the complex to yield clear needle-like crystals. The crystals were dried under vacuum at 60 °C. Yield (0.558 g, 76%). Anal. found: C, 41.6; H, 3.5; N, 12.1; calcd for $C_{16}H_{16}N_4\cdot MnCl_4$: C, 41.7; H, 3.5; N, 12.2%. IR (KBr): 3442m (br), 3069–2620s (br), 1623s, 1570s, 1516w, 1487m, 1452s, 1385m, 1301m, 1260w, 1217s, 1179w, 1145w, 1111w, 1028m, 941w, 893w, 756s, 670m, 621m, 434m cm^{-1}

The other salts were synthesised in a similar way.

1,2-Bis(2-benzimidazolonium)ethane tetrachlorocobaltate(II), [1H$_2$][CoCl$_4$]. Yield 90%. IR (KBr): 3068s (br), 1625s, 1574s, 1453s, 1217s, 1146m, 1029m, 892m, 757s, 620s, 436m, 293s cm^{-1}.

1,2-Bis(2-benzimidazolonium)ethane tetrachlorocuprate(II), methanol solvate [1H$_2$][CuCl$_4$]·CH$_3$OH. Yield 76%. IR (KBr): 3112s (br), 1625s, 1570s, 1456s, 1299m, 1220s, 1150m, 1028m, 894m, 760s, 671m, 620s, 496w, 434m, 301s cm^{-1}.

1,3-Bis(2-benzimidazolonium)propane tetrachlorocobaltate(II), [2H$_2$][CoCl$_4$]. Yield 87%. IR (KBr): 3059s (br), 1625s, 1567s, 1485m, 1459s, 1382m, 1223s, 1031m, 757s, 621s, 431m, 290s cm^{-1}.

Crystal structure determinations

Crystals suitable for X-ray diffraction were obtained by vapour diffusion of diethyl ether into the methanol solution, mounted in inert oil and measured on a Stoe IPDS diffractometer with Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Structures were solved by direct methods and refined by full matrix least squares. Numerical absorption corrections were applied. All calculations other than the structure solution and absorption[27] were carried out using the XTAL system.[28]

Crystal data for C$_{16}$H$_{16}$Cl$_4$CoN$_4$, (1H$_2$)[CoCl$_4$]. $M = 465.1$, monoclinic, space group $C2/c$, $a = 10.5048(8)$, $b = 10.1302(6)$, $c = 18.3692(13)$ Å, $\beta = 104.724(9)°$, $U = 1890.6(2)$ Å^3, $T = 200$ K, $Z = 4$, $\mu = 1.48$ mm^{-1}, 11 725 reflections measured, 1765 unique ($R_{\text{int}} = 0.031$), of which 1415 were classed as observed [$|F_o| > 4\sigma(F_o)$]. The structure was solved with Multan87.[29] All hydrogen atoms were observed and refined with fixed isotropic displacement parameters (0.05 Å^2). The final $wR(F)$ was 0.039.

Crystal data for $C_{16}H_{16}Cl_4MnN_4$, (1H$_2$)[MnCl$_4$]. $M = 461.08$, monoclinic, space group $C2/c$, $a = 10.6142(6)$ $b = 10.2541(9)$, $c = 18.4091(11)$ Å, $\beta = 105.005(7)°$, $U = 1935.3(2)$ Å^3, $T = 250$ K, $Z = 4$, $\mu = 1.24$ mm^{-1}, 8412 reflections measured, 1821 unique ($R_{int} = 0.032$), of which 1326 were classed as observed [$|F_o| > 4\sigma(F_o)$]. The structure is isostructural to [1H$_2$][CoCl$_4$] All hydrogen atoms were observed and refined with isotropic displacement parameters. The final $wR(F)$ was 0.032.

Crystal data for $C_{17}H_{20}Cl_4CuN_4O$, (1H$_2$)[CuCl$_4$]MeOH. $M = 501.8$, monoclinic, space group $P2_1/c$, $a = 17.1984(13)$, $b = 17.9232(9)$, $c = 7.1133(5)$ Å, $\beta = 101.599(8)°$, $U = 2147.9(3)$ Å^3, $T = 200$ K, $Z = 4$, $\mu = 1.55$ mm^{-1}, 23 280 reflections measured, 3974 unique ($R_{int} = 0.048$), of which 2500 were classed as observed [$|F_o| > 4\sigma(F_o)$]. The structure was solved with SIR97.[30] All hydrogen atoms were observed and refined with fixed isotropic displacement parameters (0.04 Å^2). The final $wR(F)$ was 0.036.

Crystal data for $C_{17}H_{18}Cl_4CoN_4$, (2H$_2$)[CoCl$_4$]. $M = 479.1$, monoclinic, space group $P2_1/c$, $a = 7.6181(5)$, $b = 14.6719(7)$, $c = 18.3996(13)$ Å, $\beta = 93.294(8)°$, $U = 2053.2(2)$ Å^3, $T = 200$ K, $Z = 4$, $\mu = 1.37$ mm^{-1}, 21 739 reflections measured, 4671 unique ($R_{int} = 0.043$), of which 3138 were classed as observed [$|F_o| > 4\sigma(F_o)$]. The structure was solved with SIR97.[30] All hydrogen atoms were observed and refined with fixed isotropic thermal displacement parameters (0.04 Å^2). The final $wR(F)$ was 0.026.

CCDC reference numbers 199045–199048. See http://www.rsc.org/suppdata/nj/b2/b207073a/ for crystallographic data in CIF format.

Acknowledgements

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