Supporting Information for:

Unexpected structural homologies involving hydrogen-bonded and halogen-bonded networks in halopyridinium halometallate salts

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Crystal structure of compound 1: description of C–H···Cl(Pd) hydrogen bonding and π-stacking

Adjacent ribbons interact via weak bifurcated hydrogen bond on the same anion [(C)H···Cl(Pd) 2.644 Å, C–H···Cl 160.67 °, Pd–Cl···H 94.30 ° and (C)H···Cl(Pd) 2.894 Å, C–H···Cl 116.95 °, Pd–Cl···H 88.10 °] and via weak bifurcated hydrogen bond on neighbour anions [(C)H···Cl(Pd) 2.760 Å, C–H···Cl 122.29 °, Pd–Cl···H 131.12 ° and (C)H···Cl(Pd) 2.781 Å, C–H···Cl 116.36 °, Pd–Cl···H 131.99 °] the last contact also supporting the strong hydrogen bond interaction (Fig. 2a). Weak hydrogen bond interactions [(C)H···Cl(Pd) 2.840 Å, C–H…Cl 111.70 °, Pd–Cl…H 90.31 °] further pack the ribbons in the final 3D structure, where each ribbon is surrounded by six others (Fig. 3a). The inter ribbon distance is d = 5.060 Å (distance between mean plane of an anion and metal center in nearest ribbon). The ribbons pack via offset stacked antiparallel π···π interactions ($d_{cent\text{-}cent}$ = 4.233 Å; $d_{cent\text{-}plane}$ = 3.358 Å).

Crystal structure of compound 2: description of C–H···Cl(Cu) hydrogen bonding and π-stacking

Adjacent ribbons interact via C–H···Cl(Pd) hydrogen bonds [(C)H···Cl(Cu) 2.644 Å, C–H···Cl 127.82 °, Cu–Cl···H 111.12 ° and (C)H···Cl(Cu) 2.559 Å, C–H···Cl 140.39 °, Cu–Cl···H 142.79 °] and via weak bifurcated hydrogen bond on neighbor anions [(C)H···Cl(Cu) 2.900 Å, C–H···Cl 117.53 °, 163.16 ° and (C)H···Cl(Cu) 2.734 Å, C–H···Cl 115.54 °, Cu–Cl···H

143.14 °] the last contact also supporting the strong hydrogen bond interaction (Fig. 2b). Weak hydrogen bond interactions [**(**C)H···Cl(Cu) 2.865 Å, C–H···Cl 113.48 °, Cu–Cl···H 89.99 ° and 103.87 °] further pack the ribbons in the final 3D structure, where each ribbon is surrounded by six others (Fig. 3b). Weak interactions between the metal centers and the bridging chlorines lead to an offset stacked arrangement of the anions [(Cu)Cl···Cu 3.011 Å, Cu–Cl···Cu 93.84 °; (Cu)Cl···Cu 3.109 Å, Cu–Cl···Cu 90.03 and 93.68 ° and (Cu)Cl···Cu 2.987 Å, Cu–Cl···Cu 95.66 and 93.97 °]. The length of the terminal Cu–Cl bonds is 2.251 and 2.253 Å; the length of the bridging Cu–Cl bonds is between 2.276 and 2.351 Å. The inter ribbon distance is d = 2.989 - 3.085 Å (distance between mean plane of an anion and metal center in nearest ribbon - see Figure 5). The ribbons pack via offset stacked parallel π···π interactions ($d_{cent\text{-}cent}$ = 3.878 Å; $d_{cent\text{-}plane}$ = 3.409 Å).

Crystal structure of compound 3: description of C–H···Cl(Pt) hydrogen bonding

C–H···Cl(Pt) hydrogen bonds connect the two interpenetrated nets [(C)H···Cl(Pt) 2.629 Å, C–H···Cl 151.5 °, Pt–Cl···H 101.1 °; **(**C)H···Cl(Pt) 2.900 Å, C–H···Cl 126.3 °, Pt–Cl···H 93.8 °; **(**C)H···Cl(Pt) 2.787 Å, C–H···Cl 120.9 ° Pt–Cl···H 128.6 °; **(**C)H···Cl(Pt) 2.896 Å, C–H···Cl 131.6 ° Pt–Cl···H 85.7 °; **(**C)H···Cl(Pt) 2.831 Å, C–H···Cl 156.0 °, Pt–Cl···H 86.7 °].