Crystal engineering through charge transfer interactions; assisted formation of a layered coordination polymer (4-cyanopyridine)cadmium(II) iodide·diiodine

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Formation of a layered coordination polymer (4-cyanopyridine)cadmium(II) iodide is assisted by n–σ* donor–acceptor interactions between coordinated iodine atoms of the layers and iodine molecules which bridge adjacent layers.

We are very interested in the role that (n–σ*) charge transfer interactions might play in the design of functional solids. We have utilized this interaction to prepare a variety of diazine·I_2 complexes in which N···I charge-transfer interactions at either end of both the donor and acceptor molecules result in the formation of extended chains.[1] More recently we have reported on the utility of N···I based charge transfer complexes for the interconversion of polymorphic forms of a donor molecule, tetrapyridylpyrazine,[2,3] and have begun a systematic investigation of complexes of iodine with a variety of nitrogen-based donors.[4]

We are also interested in the role that coordination polymers might play in structure design. Group 12 (IIB) metal halides are particularly promising, owing to the variety of coordination numbers and geometries provided by the d^{10} configuration of the metal center. This structural diversity is closely dependent on factors such as the dimensions of the metal ions and halides, nature of other ligands, and the availability of other structure controlling interactions, such as hydrogen-bonding and charge transfer.[5–7] If this diversity can be controlled, group 12 metal halides offer an ideal system for structural engineering and design.

We have found that pyrazine forms 1 : 1 complexes with cadmium(II) halides, CdX_2·pyrazine (X = Cl **1**, Br **2**, I **3**).[8] All of the complexes crystallize as infinite CdX_2 chains in which cadmium atoms are doubly bridged by pairs of halide atoms; pyrazine ligands complete the pseudo-octahedral coordination of the cadmium atoms and link the CdX_2 chains to form extended two-dimensional layers. Numerous attempts to form a similar architecture with the bridging ligand, 4-cyanopyridine, were unsuccessful; however, an interesting bis-pyridyl complex, bis(4-cyanopyridine)cadmium(II) iodide **4**, was formed.[9] This complex crystallizes as infinite CdI_2 chains, in which cadmium atoms are doubly bridged by pairs of iodine atoms; 4-cyanopyridine ligands coordinated through the pyridyl nitrogen atom occupy *trans* positions to complete an octahedral coordination about the cadmium. The chains are associated into layers through self-association of the cyano groups. When co-crystallized with mercury(II) iodide (1 : 2 ratio) bis(4-cyanopyridine)cadmium(II) iodide·$2HgI_2$ **5** is formed. The layer structure of **4** is essentially unchanged in **5**, as the mercury(II) iodide molecules are intercalated between the layers.

Based on the donor–acceptor interactions between coordinated iodine atoms and the mercury center observed in **5**, it was anticipated that a similar interaction might occur with molecular iodine serving as the acceptor. Here, we report the construction‡ of a layered structure, (4-cyanopyridine)cadmium(II) iodide which was the unattainable target of our previous efforts. It is particularly significant that the formation of this structure is made possible by the assistance of n ⟶ σ* charge transfer interactions between the coordinated iodides and a complexed neutral iodine molecule.

Similar to the (pyrazine)CdX_2 complexes, 4-(cyanopyridine)cadmium(II) iodide I_2 **6** (Fig. 1) crystallizes as infinite CdI_2 chains in which cadmium atoms are doubly bridged by pairs of iodide atoms; adjacent cadmium atoms in the chain are related by mirror symmetry perpendicular to the ***a***-axis at (0 *y z*).§ The 4-cyanopyridine ligand is bonded through both the pyridyl and nitrile groups to complete a pseudo-octahedral coordination of the cadmium atoms and acts as a bridging ligand to link the CdI_2 chains related by a 2_1 operation parallel to ***b*** at (1/4 *y* 1/4), to form extended two-dimensional layers (Fig. 2). The layers are bisected by a mirror plane perpendicular to the ***c***-axis at (*x y* 1/4). The layers are joined in the stacking direction (the ***c***-axis) through an n ⟶ σ* charge transfer interaction from the

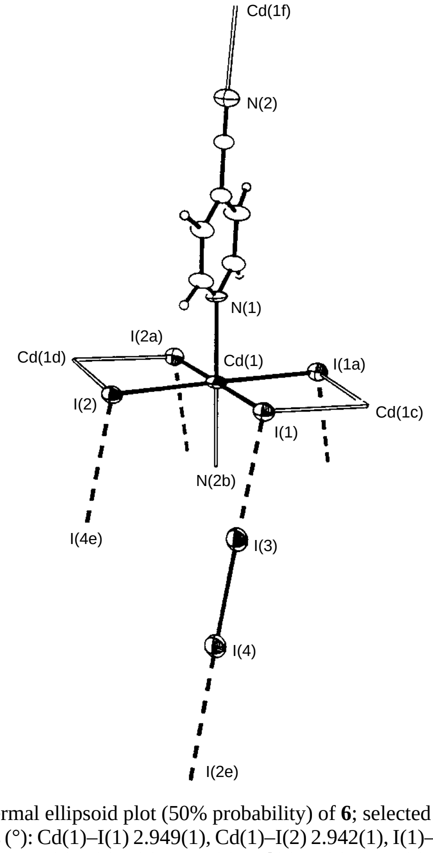

Fig. 1 Thermal ellipsoid plot (50% probability) of **6**; selected distances (Å) and angles (°): Cd(1)–I(1) 2.949(1), Cd(1)–I(2) 2.942(1), I(1)–I(3) 3.367(1), I(2)–I(4e) 3.436(1), I(3)–I(4) 2.757(1), Cd(1)–N(1) 2.391(9), Cd(1)–N(2b) 2.403(10); I(1)–Cd(1)–I(2) 91.2(1), I(1)–Cd(1)–N(1) 90.2()2, I(2)–Cd(1)–N(1) 90.6(2), I(1)–Cd(1)–I(1a) 88.1(1), I(2)–Cd(1)–I(1a) 179.0(1), I(2)–Cd(1)–I(2a) 89.4(1), I(1)–Cd(1)–N(2b) 89.6(2), I(2)–Cd(1)–N(2b) 89.7(2), N(1)–Cd(1)–N(2b) 179.7(4), Cd(1)–I(1)–Cd(1c) 91.9(1), Cd(1)–I(2)–Cd(1d) 90.4(1), Cd(1)–I(1)–I(3) 105.9(1), Cd(1)–I(2)–I(4e) 107.6(1), I(1)–I(3)–I(4) 178.8(1), I(3)–I(4)–I(2e) 177.8(1). (Atoms labelled with a lower-case character were generated by the following symmetry operation: a *x*, *y*, 1/2 − *z*; b 1/2 − *x*, −1/2 + *y*, 1/2 − *z*; c 1 − *x*, *y*, *z*; d − *x*, *y*, *z*; e 1/2 − *x*, 1/2 − *y*, 1 − *z*; f 1/2 − *x*, 1/2 − *y*, −z.)

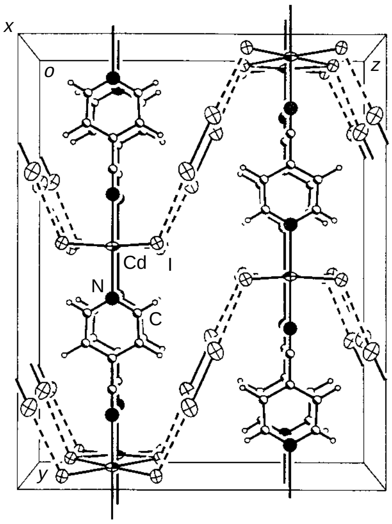

Fig. 2 Crystal packing of **6**, viewed down the ***a***-axis, parallel to the CdI_2 chains

coordinated iodine atoms as donors to either end of a bridging I_2 molecule.

The Cd–I···I_2 donor–acceptor (n → σ* charge transfer) interactions are present at either end of the I_2 molecule and involve both of the coordinated iodine atoms. The interactions occur at approximately tetrahedral angles at the coordinated iodide and are oriented in a linear fashion to the I–I σ-bond. The I···I distances are well within the sum of van der Waals radii for iodine (1.98 Å),[10] and are similar to those seen in the related compounds, $Cd(NH_3)_4I_2{\cdot}I_2$ [3.386(2) Å] and $Cd(NH_3)_4(I{\cdot}I_2)_2$ [3.3780(9) Å].[11]

That these interactions occur only to the cyano-coordinated side of the CdI_2 plane is a result of the smaller size of the cyano-group; unfavorable steric interactions involving the pyridine rings prevent interaction on the other side of the CdI_2 plane.¶ When 4-cyanopyridine and cadmium(II) iodide are combined in a variety of stoichiometric ratios (1 : 1, 1 : 2, 2 : 1) in the absence of I_2, compound **4** is the only product formed. The considerably weaker donor strength of the nitrile group relative to the pyridyl group is presumably the reason for preferred formation of **4**. When I_2 is present, however, combination of cadmium(II) iodide and 4-cyanopyridine in the same stoichiometric ratios yields **6** as the only product. Formation of **6** and the fact that 4-cyanopyridine does serve as a bridge in this compound appears to be a result of the structural support provided by the charge transfer complexed iodine molecules which link adjacent groups in a zigzag fashion to form a reinforced three-dimensional network.

Thermal analysis of **6** by TGA‖ showed an initial mass loss of *ca.* 42% with an onset temperature of 83 °C. A second mass loss of 11% occurred at 163 °C, and the remainder of the mass was lost at 408 °C. These data suggest that **6** thermally decomposes by initial loss of the bridging I_2 molecule (35% by mass) coupled with a small amount of the ligand, the remainder of the ligand is lost in the second event, followed by sublimation of cadmium iodide at high temperature. The initial process is probably more complicated than simple diffusion of I_2 out of the solid. Powder diffraction on a sample of **6** heated to 120 °C for approximately 20 h revealed CdI_2 as the only crystalline product. This result coupled with our observation that recrystallization of **6** from ethanol gives **4** and CdI_2, and that leaching of **6** with boiling hexane leaves behind only solid CdI_2 suggests that the layered structure of **6** is tenuous. Removal of the supporting I_2 molecules leads to total collapse of the two-dimensional architecture and of the compound itself.

Continuing efforts to find gentler methods to remove or perhaps to exchange the I_2 supports through a diffusion process are underway. The stabilization of **6** by charge transfer interactions suggests the utility of these highly directional and attractive forces for isolating other metastable structures, and we are actively pursuing additional examples of this interesting phenomenon.

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Notes and References

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‡ *Synthesis* of $(C_6H_4N_2)CdI_2{\cdot}I_2$ **6**: 4-Cyanopyridine (0.0618 g, 0.594 mmol) was dissolved in a solution of cadmium(II) iodide (0.224 g, 0.613 mmol) and iodine (0.195 g, 0.770 mmol) in 95% ethanol. Slow evaporation of solvent yielded 0.279 g of red crystals of **6** (65% yield based on the ligand); mp 154–155 °C. IR(Nujol) (cm^{-1}): 2280, 1617, 1413, 1225, 826, 557, 207, 188. Elemental analyses calc. (obs.): C 9.95 (10.31), H 0.56 (0.58), N 3.87 (3.80)%.

§ *Crystal data* for $(C_6H_4N_2)CdI_2{\cdot}I_2$ **6**: orthorhombic, space group *Cmcm* (no. 63); a = 8.411(2), b = 20.277(4), c = 15.986(3) Å, U = 2726(1) $Å^3$ (based on 25 reflections; $20.35 < 2\theta < 39.48°$), Z = 8 [atoms Cd(1), N(1), C(3), C(4) and N(2) lie on mirror perpendicular to ***c*** (z = 1/4); atoms I(1) and I(2) lie on mirrors perpendicular to ***a*** (x = 0) and 1/2, respectively)], D_c = 3.53 g cm^{-3}, μ(Mo-Kα) = 10.63 mm^{-1}, empirical absorption correction, transmission coefficients: 0.77–1.00, 1370 unique data measured, 973 observed [$I > 2\sigma(I)$], $R(F)$ = 0.028, $R_w(F)$ = 0.035. Data were collected on a reddish-brown platelet (0.02 × 0.15 × 0.15 mm) at −110 ± 1 °C by using a Rigaku AFC7R (18 kW) diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) to $2\theta_{max}$ of 50.0°. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. CCDC 182/863.

¶ All attempts to prepare similar compounds with ligands possessing only larger pyridyl donors (such as pyrazine and 4,4′-bipyridine) have been unsuccessful, presumably due to steric protection of the metal halide donor sites.

‖ Thermal gravimetric analysis of **6** was performed on a Perkin-Elmer Series 7 analyzer with the TGA7 software package (version 2.20). For onset calculations, the samples were heated at a constant rate of 5 °C min^{-1} from 25 °C until all of the material had evaporated.

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