Novel Stacking in a Binuclear Iridium Carbonyl Imidazoledicarboxylate

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The crystal structure of $[Bu_4N][Ir_2(mdcbi)(CO)_4]\cdot CH_2Cl_2$ (H_3mdcbi = 2-methylimidazole-4,5-dicarboxylic acid) shows a new type of stacking in which the two iridium atoms of the binuclear complex are both involved in extended metal–metal chains at nearly identical distances.

We report here an *X*-ray crystal structure† with a unique stacking motif based on planar complexes of the dicarboxyimidazolate anion chelating to two metal ions. Binuclear complexes are of special interest from the perspective of catalysis[1] and metal–metal interactions[2] because of the possibilities for multiple electron transfer and the modification in properties due to the concerted effect of the metals. Although proposals for molecular scale 'coaxial conductors' have been made for many years,[3] the synthetic realization of them has proven difficult. Such assemblies should provide the minimum model for certain kinds of extended interactions in the solid state and are of continuing interest for studies of magnetic, optical, and electrical properties.[4]

Heteroaromatic dicarboxylates have been little used for investigations in co-ordination chemistry; most reports are on pyrazines, some of which have been reviewed.[5] We have observed good synthetic characteristics for the imidazoledicarboxylates.[6] These compact, planar, binuclear, anionic complexes resemble the well known mononuclear systems which lead to one-dimensional metals in the case of cyanides and oxalates,[7] but in addition offer intramolecular interactions which are of considerable interest.[8]

The molecular geometry of the complex $[Bu_4N][Ir_2(mdcbi)(CO)_4]\cdot CH_2Cl_2$ (H_3mdcbi = 2-methylimidazole-4,5-dicarboxylic acid) (Figure 1) confirms the binuclear structure. The anion is planar with a maximum deviation of 0.13 Å, except for the hydrogens of the methyl group.

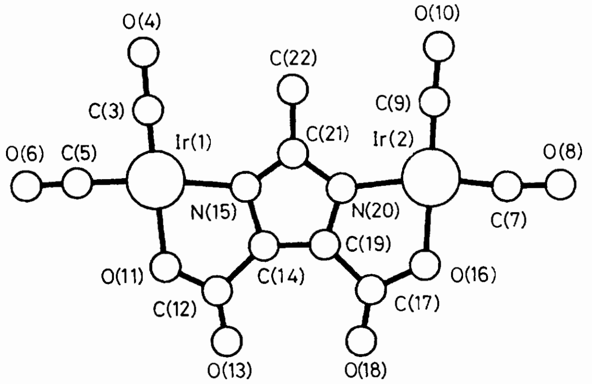

Figure 1. The structure of $[Ir_2(CO)_4(mdcbi)]^-$. Selected bond distances (Å) and angles(°); Ir(1)–N(15) 2.07(2), Ir(2)–N(20) 2.06(2), Ir(1)–O(11) 2.02(2), Ir(2)–O(16) 2.01(2), Ir(1)–C(3) 1.62(4), C(3)–C(4) 1.33(4), Ir(2)–C(9) 1.74(4), C(9)–O(10) 1.27(4), Ir(1)–C(5) 1.80, C(5)–O(6) 1.16(4), Ir(2)–C(7) 1.76(3), C(7)–O(8) 1.23(3), N(15)–Ir–O(11) 79.2(7), N(20)–Ir2–O(16) 79.3(7).

The influence of the π-donor capabilities of the carboxylate ligand is reflected in shorter Ir–C and longer C–O distances *trans* to the ligand, compared to the *cis* carbonyl. Surprisingly this effect is larger for Ir(1) than for Ir(2), thus breaking the nearly ideal two-fold symmetry of the anion. Although the metal atoms are identical in terms of their ligand co-ordination, they differ significantly in their stack relationships. Ir(1) is involved in only one metal–metal interaction whereas Ir(2) is involved in two such interactions (Figure 2). Between inversion related binuclear pairs, the Ir–Ir distance is 3.36 Å, whereas between slip-stacked binuclear pairs it is nearly identical, at 3.30 Å. The iridium distance from the best ligand plane in the latter case is 3.27 Å, so the proximal location of the iridium is nearly ideal. The packing which results from repeating these distances has no tilt relative to the stacking axis and has four iridium atoms in a chain, as a result of slips in the stacking axis by exactly half the length of the ion. The view shown in Figure 2 is (perhaps surprisingly) not perpendicular to any crystallographic axis, but is looking from approximately halfway between axes *b* and *c*.

The dark blue colour of this compound is indicative of these intermolecular interactions (typical Ir^I planar complexes are yellow) and the solubility is typically low.

Perhaps the most unusual feature of the stacking in this crystal is the eclipsed geometry for the anions. Although favourable interactions between iridium atoms may account for this, in most similar cases some kind of 'slip-stacking' is observed, especially prior to partial oxidation. In this instance, the π effects noted above may also be influencing the stacking. The π orbitals of the oxygen bonded to iridium and the π antibonding orbitals of the *trans* CO ligand lying just

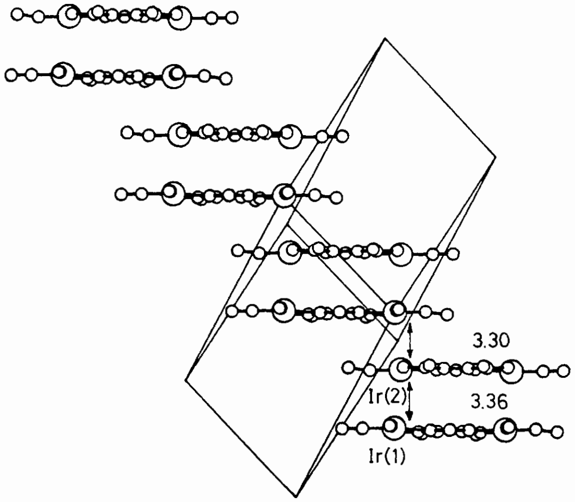

Figure 2. The stacking chains of $[Ir_2(CO)_4(mdcbi)]^-$.

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† $[Bu_4N][Ir_2(mdcbi)(CO)_4]\cdot CH_2Cl_2$ was prepared following the procedure described in ref. 6. Crystals were grown by layering a CH_2Cl_2 solution of the complex with hexane. *Crystal data* for $C_{27}H_{41}N_3O_8Cl_2Ir_2$: $a = 9.212(3)$, $b = 13.635(8)$, $c = 14.933(6)$ Å; $\alpha = 104.21(4)$, $\beta = 107.26(3)$, $\gamma = 81.25(4)$; space group $P\bar{1}$; 4844 reflections collected using Mo-K_α radiation; $2\theta_{max.} = 45°$; 3126 reflections with $I > 3\sigma(I)$ using full-matrix least squares refinement; $R = 7.6\%$, $R_w = 7.5\%$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

above and and/or below can give extra stability to the eclipsed structure. Miller has proposed such an intermolecular HOMO–LUMO interaction to explain the rotation angle of stacked, partially oxidized, bis(oxalato)platinates.[9]

The remarkable packing observed in this crystal will prove very helpful in explaining the interactions found in the partially oxidized iridium compounds, where the metal–metal distances are likely to be even shorter.[10]

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