Iridates from the molecular side

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New exotic phenomena have recently been discovered in oxides of paramagnetic Ir⁴⁺ ions, widely known as ‘iridates’. Their remarkable properties originate from concerted effects of the crystal field, magnetic interactions and strong spin-orbit coupling, characteristic of 5d metal ions. Despite numerous experimental reports, the electronic structure of these materials is still challenging to elucidate, and not attainable in the isolated, but chemically inaccessible, [IrO₆]⁸⁻ species (the simplest molecular analogue of the elementary {IrO₆}³⁻ fragment present in all iridates). Here, we introduce an alternative approach to circumvent this problem by substituting the oxide ions in [IrO₆]⁸⁻ by isoelectronic fluorides to form the fluorido-iridate: [IrF₆]²⁻. This molecular species has the same electronic ground state as the {IrO₆}³⁻ fragment, and thus emerges as an ideal model for iridates. These results may open perspectives for using fluorido-iridates as building-blocks for electronic and magnetic quantum materials synthesized by soft chemistry routes.

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The 5d elements of the periodic table possess singular properties including a strong coupling of the electronic spin to its orbit as well as spatially extended valence orbitals leading to a reduced electronic repulsion and large effect on the ligand field. These intrinsic characteristics have been experimentally or theoretically demonstrated to be responsible for new exotic states of matter such as spin-orbit (SO) Mott insulators, topological insulators, super-conductors, spin–liquids and for quantum metal–insulator transitions. The common denominator in these promising materials, collectively referred to as ‘iridates’ (herein named oxido-iridates), is the presence of octahedrally coordinated IrIV ions (Fig. 1a,b) featuring a $t_{2g}^{5}$ electronic configuration.

The half-filled $j_{\text{eff}} = 1/2$ level (Fig. 1c) results from the SO coupling, at the origin of a narrow band gap responsible for the abovementioned phenomena. In all oxido-iridates including Sr$_2$IrO$_4$, the archetypal SO Mott insulator, corner- or edge-sharing $\{\text{IrO}_6\}^{8-}$ distorted octahedra are present (Fig. 1a). While magnetic IrIV–IrIV interactions and their implications for the physical properties have been studied extensively in oxido-iridates, the intrinsic magnetic properties of the elemental iridium are consisently masked by the same long-range interactions. Birol and Haule recently suggested that the design of materials incorporating isolated IrIV octahedra should facilitate smaller bandwidths and promote Mott ground states. If this strategy is developed to its logical end, a discouraging result is obtained as the isolation of the $\{\text{IrO}_6\}^{8-}$ ion (Fig. 1b) is chemically impossible. However for the realization of dimensionally reduced oxido-iridates, the fluoride ion appears as an ideal substitute to oxide being isoelectronic with comparable chemical and physical characteristics, but, importantly, with a reduced charge. Along this idea, we present the synthesis of molecular fluoro-iridates incorporating spatially isolated $\{\text{IrF}_6\}^{2-}$ units. Their local magnetic properties are probed by X-ray magnetic circular dichroism (XMCD) spectroscopy demonstrating that the $\{\text{IrF}_6\}^{2-}$ and $\{\text{IrO}_6\}^{8-}$ units possess virtually identical electronic ground states as suggested by theory. Thus this fluorido-iridate moiety and its intrinsic properties, experimentally determined in this work, can be confidently used to model and emulate the basic $\{\text{IrO}_6\}^{8-}$ unit in oxido-iridates.

**Results**

**Syntheses and structures.** Highly water-soluble Na$_3$$\{\text{IrF}_6\}$ was obtained by direct F$_2$ fluorination of Na$_3$$\{\text{IrCl}_6\}$·6H$_2$O at temperature $200^\circ$C and characterized by powder X-ray diffraction. Addition of a solution of PPh$_4$Cl (PPh$_4$ = tetraphenylphosphonium(V) cation) to an aqueous $\{\text{IrF}_6\}^{2-}$ solution yielded (PPh$_4$)$_2$$\{\text{IrF}_6\}$·2H$_2$O (1, Fig. 1a and Supplementary Fig. 1). Electrospray mass spectrometry on 1 indicated complete absence of any hydrolysis products such as $\{\text{IrF}_6\}_2$OH$^-$ (Supplementary Fig. 2). I was subsequently used to synthesize Zn(viz)$_4$$\{\text{IrF}_6\}$ (2, Fig. 2b and Supplementary Fig. 3; viz = 1-vinylimidazole). These compounds incorporate a low symmetry, but close-to-octahedral $\{\text{IrF}_6\}^{2-}$ unit in 1 (P1 space group) and a tetragonally distorted octahedral $\{\text{IrF}_6\}^{2-}$ unit in 2 (P4$_2$/n space group). The axial elongation in both 1 and 2 is ~1%, slightly smaller than, for example, the ~3% found in Sr$_2$IrO$_4$, and the bond angles are all within 1.5 and 0.1% of $90^\circ$, respectively. To elucidate any differences in the IrIV electronic structure when modifying the ligand field, we included in this study the related chloride complex, (PPh$_4$)$_2$$\{\text{IrCl}_6\}$ (3, Fig. 2c and Supplementary Fig. 4), also featuring an approximately octahedral, but axially compressed (~0.7%) $\{\text{IrCl}_6\}^{2-}$ ion. The nearest neighbour Ir–Ir distances (Å) are 10.0 (1), 8.1 (2) and 10.1 (3), which are much longer than in the oxido-iridates (for example, 3.9 Å in Sr$_2$IrO$_4$). Thus the IrIV–IrIV interactions are negligibly small and the $\{\text{IrX}_6\}^{2-}$ (X = F, Cl) unit can be considered as magnetically isolated in 1, 2 and 3.

**Magnetic properties and X-ray spectroscopy.** The susceptibility–temperature product, $\chi T$, of 1–3 (Supplementary Fig. 5) is practically temperature independent (Curie’s law) confirming the lack of significant magnetic interactions between IrIV spins and thus the absence of any magnetic order at least down to 1.8 K. The complete set of magnetization data (M versus $\mu_0 H$–$T$; Supplementary Figs 6–8) could be fitted to the Brillouin function for an effective spin-1/2 (with $g \approx 2$), which corroborates...
the Curie susceptibility and demonstrates the presence of an energetically isolated $I_{\text{eff}} = 1/2$ ground state.

Orbital ($M_{\text{orbital}}$) and spin ($M_{\text{spin}}$) contributions to the total magnetic moments ($M_{\text{total}}$) have been determined experimentally using XMCD, which is defined as the difference between two X-ray absorption spectra (XAS) recorded with either opposite helicity or magnetization direction. XAS spectra were collected on 1–3 at the iridium $L_{2,3}$ edges under an external magnetic field of $\mu_0H = \pm 17$ T and at low temperatures ($T = 2.6–2.9$ K). Since the measurements were performed on powdered samples, the isotropic $L_{2,3}$ XAS spectra could be approximated as $(\sigma^+ + \sigma^-)/2$, where $\sigma^-$ is the absorption cross-section obtained with helicity and magnetization aligned either parallel (+) or antiparallel (−) (Fig. 3). The XAS spectra are dominated by strong resonance peaks (‘white lines’) at both the $L_3$ (2p$_{3/2} \rightarrow$ 5d$_{3/2,5/2}$) and $L_2$ (2p$_{1/2} \rightarrow$ 5d$_{3/2}$) edges with the $L_3$ edge being significantly more intense.

The spectra of 1 and 2 are virtually identical, whereas for 3, a slight shift of the white line peak of ca. 2 eV towards lower energies is observed concomitantly with an additional component at ca. 12 eV higher energy (Supplementary Fig. 9). The latter feature is likely the signature of excitations into delocalized states originating from ligand to metal charge transfer that is not observed in 1 and 2 due to the more ionic Ir–F bond. The effect of SO coupling on the 5d states was quantified through the so-called SO sum rule21. It relates the branching ratio (BR) of the white line integrals at the SO split absorption edges to the expectation value of the angular part of the ground state SO operator per hole. For the $p \rightarrow d$ transitions ($L_2$ and $L_3$ edges), the branching ratio can be expressed as

$$BR = \frac{\mu_{\text{XAS}}^L}{I_{\text{XAS}}^L + \mu_{\text{XAS}}^M} \cdot \frac{2}{3} \cdot \frac{\langle \sum \mathbf{l} \cdot \mathbf{s}_i \rangle}{\langle n_{\text{h}} \rangle}$$

where, $\langle n_{\text{h}} \rangle = \langle n_{\text{h}}^l \rangle = \langle 3/2 \rangle + \langle n_{\text{h}}^s \rangle = \langle 5/2 \rangle$ is the total number of holes in the 5d levels and $\langle \sum \mathbf{l} \cdot \mathbf{s}_i \rangle/\hbar^2 = -3/2 \times \langle n_{\text{h}}^l = \langle 3/2 \rangle + \langle n_{\text{h}}^s \rangle = \langle 5/2 \rangle \rangle$ is the expectation value of the one-electron $\mathbf{l} \cdot \mathbf{s}$ operator summed over all electrons; $\langle n_{\text{h}} \rangle$ being the occupation number of the corresponding levels. The white line integrals are larger in 3 than in 1 or 2, thus more holes in the 5d band should be present for 3 compared with 1 or 2. If one assumes that 1 and 2 are completely ionic, $\langle n_{\text{h}} \rangle = 5$, we obtain $\langle n_{\text{h}} \rangle = 5.26$ for 3. The corresponding results are shown in Table 1. The quantitative analysis of the XMCD spectra was performed by means of the magneto-optical sum rules providing direct access to $M_{\text{orbital}} = -\langle \mathbf{L}_2 \rangle \mu_B$ and $M_{\text{spin,eff}} = -2 \langle \mathbf{S}_\text{eff} \rangle \mu_B$ (the details of this analysis are given in the ‘Methods’ section; Table 1)22,23. The scaling of the field dependence of the XMCD to the bulk magnetization (inset Fig. 3 and Supplementary Fig. 10; see the ‘Methods’ sections) allows the determination of the absolute value of the magnetization at $\mu_0H = \pm 17$ T: $M_{\text{total}} = 1.03, 1.0$ and $0.96 \mu_B$ for 1, 2 and 3 respectively. From these values, the magnetic dipole contribution, $\langle \mathbf{T}_2 \rangle$, and $M_{\text{spin}}$ (given by $M_{\text{spin,eff}} + 7\langle \mathbf{T}_2 \rangle$) can be estimated (Table 1) without the need of any sophisticated theoretical modelling from $M_{\text{total}} = M_{\text{spin}} + M_{\text{orbital}}$ considering $M_{\text{spin,eff}}$ and $M_{\text{orbital}}$ deduced from the sum rules. The magnetic dipole contribution has never been experimentally determined for any iridate systems, but according to these results, $\langle \mathbf{T}_2 \rangle$ cannot be neglected without a significant underestimation of the $M_{\text{orbital}}/M_{\text{spin}}$ ratio, as previously anticipated24.

Theoretical considerations. The molecular nature of 1, 2 and 3 implies that intuitive localized bonding models should be able to disentangle the magnetic moment contributions. The angular overlap model (AOM) allows for a decomposition of the ligand field potential into $\sigma$- and $\pi$-bonding parameters23. As a first approximation, a cubic [IrF$_6$]$^{2-}$ model considering only $\sigma$-bonding (with $\Delta_0 = 27,000$ cm$^{-1}$, Racah interelectronic repulsion parameters $B = 510$ cm$^{-1}$ and $C/B = 4.9$, and the SO coupling constant $\zeta = 3,300$ cm$^{-1}$; Fig. 1c)26 affords ($\sum \mathbf{l} \cdot \mathbf{s}_i \rangle/\hbar^2 = -2.65, M_{\text{orbital}} = 0.74 \mu_B$ and $M_{\text{spin}} = 0.36 \mu_B$, which are close to the ionic values ($M_{\text{orbital}} = 0.67 \mu_B$ and $M_{\text{spin}} = 0.33 \mu_B$) for a pure $I_{\text{eff}} = 1/2$ system22. Whereas the agreement with the experimental results of the fluorido-iridates (Table 1) for ($\sum \mathbf{l} \cdot \mathbf{s}_i \rangle/\hbar^2$ and $M_{\text{orbital}}$ is obtained with a magnetic field of $\mu_0H = \pm 17$ T.

Table 1 | Summary of the X-ray spectroscopy results.

|   | 1   | 2   | 3   |
|---|-----|-----|-----|
| Branching ratio       | 0.85 | 0.85 | 0.82 |
| ($\sum \mathbf{l} \cdot \mathbf{s}_i \rangle/\hbar^2$)       | $-2.8$ | $-2.7$ | $-2.5$ |
| ($\langle n_{\text{h}}^l = 5/2 \rangle/\langle n_{\text{h}}^s = 3/2 \rangle$)       | 4.7 | 4.4 | 3.8 |
| $M_{\text{total}}$ ($\mu_B$)       | 1.03 | 1.00 | 0.96 |
| $M_{\text{spin}}$ ($\mu_B$)       | 0.24 | 0.23 | 0.31 |
| $M_{\text{orbital}}$ ($\mu_B$)       | 0.79 | 0.77 | 0.65 |
| ($\langle \mathbf{T}_2 \rangle$ ($\mu_B$)       | $-0.11$ | $-0.10$ | $-0.081$ |
Electron paramagnetic resonance spectroscopy. For an ideal $J_{\text{eff}} = 1/2$ state, magnetic anisotropy is absent, but minuscule deviations from cubic symmetry may result in strong $g$-factor anisotropy that can be probed experimentally by electron paramagnetic resonance (EPR) spectroscopy. The X-band ($\nu = 9.634$ GHz) EPR spectrum of an $[\text{IrF}_6]^{2-}$ doped Zn(viz)$_4[\text{ZrF}_6]$ single crystal (\~{}1\% Ir) was measured at 5 K (Supplementary Figs 12–16; Table 2). The experimental eigenvalues of the $g$-tensor are indeed remarkably anisotropic with $g_z = 1.37$ and $g_{\text{xy}} = 2.11$ in good agreement with the CASSCF calculations leading to $g_z = 1.30$ and $g_{\text{xy}} = 2.24$ (Supplementary Table 2).

These combined experimental and theoretical results establish that the electronic ground state of the molecular $[\text{IrF}_6]^{2-}$ species is $J_{\text{eff}} = 1/2$ as suggested for the $[\text{IrO}_6]^{8-}$ unit, present in all oxido-iridates.

Dynamic magnetic properties. The magnetization dynamics of the molecular fluoro-iridates was studied by a.c. susceptibility (Fig. 4 and Supplementary Figs. 17–22 for 1, 2 and 3). The presence of peaks in the a.c. frequency ($\nu$) dependence of the imaginary component, $\chi''(T)$ (Fig. 4b), which shift with temperature, clearly indicates the slow relaxation of the magnetization, while the vanishing of the real component, $\chi'(T)$, in the adiabatic limit ($\nu \to \infty$) reveals a blocking of the magnetization that concerns the whole volume of the material. Note that for the three compounds, the slow dynamics of the magnetization is observed only on the application of a small static magnetic field that likely serves to decouple the Ir$^{IV}$ $J_{\text{eff}} = 1/2$ from nuclear spins as justified by a comparable magnitude of the applied field (75 mT) to the width of the EPR spectra (Supplementary Fig. 15).

The real and imaginary components of the a.c. susceptibility could be well-fitted to a generalized Debye model$^{27}$ with small values of the distribution parameter (Supplementary Fig. 23) reflecting a single characteristic relaxation time. The temperature dependence of the extracted relaxation time is shown for 2 in Fig. 4 (and also Supplementary Fig. 24 for 1–3). In these molecular iridates, the spin-lattice relaxation rates $\tau^{-1}$ were modelled considering Raman and phonon-bottlenecked direct processes, described as a sum of power laws, $\tau^{-1} = CT^\alpha + DT^\beta$, and leading to $C = 46 \times 10^{-3}$ s$^{-1}$ K$^{-\alpha}$, $D = 17$ s$^{-1}$ K$^{-\beta}$ for 2 (ref. 28). The magnetization dynamics appears to be similar in 1, 2 and 3 (Supplementary Fig. 24), suggesting that this property is an intrinsic characteristic of the Ir$^{IV}$ electronic structure. The slow relaxation of the magnetization in 2 was confirmed by muon spin relaxation ($\mu^+\text{SR}$) measurements at low temperatures (above 1.9 K; Supplementary Figs 25 and 26), where the implanted muons probe the local dynamics of magnetic fields, thereby ruling out any long-range order. This conclusion is further supported by magnetization measurements on an oriented single crystal of 1 and 2 below 2 K (Supplementary Figs 27–30). The magnetic susceptibility ($\chi = d\mathcal{M}/dH$) estimated from these experiments in the zero-field limit follows a Curie–Weiss law, $\chi = C/(T - \theta)$, down to lowest accessible temperature of 0.03 K, confirming the absence of magnetic order (Supplementary Fig. 31). For 2, the magnetization reaches saturation faster when the d.c. field is applied perpendicular to the $C_3$ axis rather than along this axis (Supplementary Figs 29 and 30), confirming the easy-plane magnetic anisotropy in agreement with the extracted $g$-factors (vide supra). The temperature and magnetic field sweep rate dependence of the magnetization revealed the existence of a weak hysteretic behaviour. At the lowest temperatures (<0.4 K) and in agreement with the a.c. susceptibility data (Fig. 4), butterfly-shaped $M$ versus $\mu^0H$ hysteresis loops for both 1 and 2 (Supplementary Figs 27–30) confirm the presence of phonon-bottlenecked direct processes that dominate the magnetization relaxation$^{29}$.

Discussion

The principle of dimensional reduction in solid-state structures is based on the formation of a derived compound, $A_{\text{nat}}\text{MX}_n\text{C}_m$ from a parent $\text{MX}_n$ precursor and an $A_n\text{X}$ salt, thereby forcing termination of M–X–M polymerization$^{30}$. If A is voluminous, for instance an organic cation, child compounds with structurally and magnetically isolated molecular units can be formed. For many oxides, the ultimate dimensional reduction to molecular $[\text{MO}_6]^{8-}$ is impeded by the progressive development of large localized negative charges (for example, for $[\text{IrO}_6]^{8-}$). Thus, truly single-metal ion analogues of most oxides are difficult, if not impossible, to isolate. In the case of octahedral species, no example has been reported so far. As discussed herein for Ir$^{IV}$, the exchange of oxide with a less negatively charged fluoride results
in dimensional reduction of the iridate as compared with the ternary iridium oxide parents. Although their local structures are obviously comparable, the electronic resemblance between these compounds should be discussed here. The branching ratios extracted from XAS (0.85; Table 1) are identical for 1 and 2, and very close to the values found for oxido-iridates, for example, 0.87 for Sr2IrO4 and 0.85 for Y2IrO7 (ref. 31,32). In addition, the L2/L3 XMCD intensity ratio of 4.7% for 2 is almost identical to the value determined for Sr2IrO4 (~5%) (ref. 33). This striking agreement demonstrates the resemblance of the electronic structure of the [IrO6]2– moieties in oxido-iridates and the molecular [IrF6]2– unit. A M/orbital/M/spin = ⟨Lz⟩/2⟨S2⟩ ratio of ~2.5 in Sr2IrO4 was recently obtained by non-resonant magnetic X-ray scattering that circumscribes the need for the estimation of ⟨Tz⟩ (ref. 34). For comparison, M/orbital/M/spin ratios of 3.3, 3.3 and 2.1 are obtained for 1, 2 and 3, respectively. The slightly larger ratio for 1 and 2 as compared with Sr2IrO4 and 3 is attributed to the weaker covalency of the Ir–X bond for X = F than for X = O, Cl, as reflected in the nephelauxetic series (ref. 35). It is worth emphasizing that the fluoride ion is the least nephelauxetic of all known halides, and thus the [IrF6]2– moiety has the closest proximity to a perfectly ionic nature. As a less-pronounced covalency would induce a larger M/orbital/M/spin ratio, a larger orbital magnetic moment is found in [IrF6]2– over [IrO6]8– and [IrCl6]2–, as expected.

In oxido-iridates, the purity of the Ioff = 1/2 state depends crucially on the structural deviation from the octahedral symmetry, rendering oxido-iridate systems with weakly distorted [IrO6]8– octahedra highly interesting. Remarkably, the [IrF6]2– moiety in 2 is structurally closer to cubic than any reported oxido-iridate system. Therefore fluorido-iridates are promising materials for stabilizing an ideal Ioff = 1/2 Mott ground state as was already concluded from the experimentally determined values of M/orbital and M/spin. Paramagnetic relaxation in oxido-iridates has been reported for diamagnetically doped honeycomb systems where the imperfect stoichiometry resulted in the blocking of the magnetization at low temperature (ref. 36,37). Our low-temperature experiments reveal that the slow dynamics of the magnetization is indeed intrinsic to the IrIV centre, that might have implications for quantum magnetism.

Herein, we have established that a molecular [IrF6]2– species and the [IrO6]8– unit, present in all oxido-iridates, possess the same electronic Ioff = 1/2 ground state. The dominating role of the SO coupling on the peculiar magnetism intrinsic to IrIV was elucidated by studying spatially isolated, magnetically decoupled, [IrF6]2– complexes in the IrIV centre, that might have implications for quantum magnetism.

Methods

Synthetic methods. Na2[IrCl6]: 0.69 g was heated to 150 ºC in vacuo for 6 h, cooled to room temperature (exp. (calc. for Na2[IrCl6] weight loss = 19% (19%)) and subsequently heated to 200 ºC in a flow reactor under F2 gas (10% diluted in Ar) and kept for 6 h. The last step was repeated to improve the crystallinity of the white product (exp. (calc. for Na2[IrCl6] weight loss = 23% (22%)) that was identified as Na2[Em] by powder X-ray diffraction (Supplementary Fig. 32). A solution of Na2[Em] (68 mg, 0.19 mmol) in water (1 ml) was added a solution of PPh3Cl (200 mg, 0.53 mmol) in water (3 ml). The resulting solution was left undisturbed for 1 h to produce crystalline 1 (114 mg, 59%). Anal. calcld. (found) for Ca2H3F4Ir2O2Cl2: C: 56.46% (56.58%), H: 4.34% (4.19%). I1 can reversibly be oxidized to IrCl3 (E1/2 = 0.8 V versus F−/F2−/Supplementary Fig. 33). The addition of 1-vinylimidazole (0.80 g, 8.5 mmol) to a methanol solution (40 ml) of 1 (100 mg, 0.098 mmol) and Zn(NO3)2·6H2O (100 mg, 0.34 mmol) afforded crystals of 1 after 2 days. Yield: 60% (82%). Anal. calcld. (found) for Cu2H2F6Ir2Cl2Zn: C: 31.11% (31.26%), H: 3.23% (3.26%), N: 14.98% (14.67%). Complex 3 was obtained from (NH4)2[IrCl6] (203 mg, 0.46 mmol) and trimethyl phosphine (0.1 M, 100 ml). The solution was heated to 50 ºC and filtered hot. To this solution, a solution of PPh3Cl (360 mg, 0.963 mmol) in aqueous HCl (0.1 M, 70 ml) was added slowly, inducing an immediate precipitation of orange-brown crystals. On the next day, the reaction mixture was cooled to room temperature and stirred for 30 min leaving only a slightly coloured solution. The product was filtered off and washed three times with water and dried in a dynamic vacuum. Yield: 453 mg (91%). Anal. calcld. (found) for Ca2H2Cl2Ir2P2: C: 53.20% (53.24%), H: 3.72% (3.67%).
respectively). The same normalization procedure was applied to the corresponding XMCD integrals. The precise sample temperature of 2.6–2.9 K and the absolute magnitude of the magnetic moment at \( \mu_H = \pm 17 \) T was determined by scaling the field and temperature dependent XMCD signal intensity to coincide with the \( \mu_H \) versus \( \mu_H \) master curve obtained from bulk magnetometry. The normalized spectra were analysed using the magneto-optical sum rules given by equation 2 for \( L_2 \) and \( L_3 \) absorption edges6,22:

\[
(h\nu) = \frac{2}{3} \left( \frac{\Delta_{\text{XMC}}}{\Delta_{\text{XAS}}} + \frac{\Delta_{\text{XMCD}}}{\Delta_{\text{XMCD}}} \right)
\]

\[
(h\nu) = \left( \frac{\Delta_{\text{XMC}}}{\Delta_{\text{XAS}}} + \frac{\Delta_{\text{XMCD}}}{\Delta_{\text{XMCD}}} \right)
\]

Ligand field and ab initio calculations. The AOM calculations were performed using the Ligfield programme on the full d5 configuration44,45. All matrices were calculated in the weak-field basis and subsequently transformed to the eigen-basis corresponding to the parameter vectors given below. The octahedral component of the ligand field, \( \Delta_B \), was taken to be equal to 0.016 T. The authors on request.

EPR spectroscopy. The spectra were acquired at \( T = 5 \) K on a Bruker Elexys E500 spectrometer equipped with a Bruker ER 4116 DM dual mode cavity, an EIP 538B frequency counter and an ER3035M NMR Guass-meter, and with a microwave frequency counter and an ER035M NMR Gauss-meter, and with a microwave

| \( A^1\text{Ir} \) | \( A^{193}\text{Ir} \) | \( A_{xy}^{193}\text{Ir} \) | \( A_{xy}^{193}\text{Ir} \) | \( A^2 \) | \( A^{2}_{xy} \) | \( A_{xy} \) | \( A^{XY} \) |
|---|---|---|---|---|---|---|---|
| 28.6 (12) | 31.04 (6) | 27.98 (11) | 30.68 (7) | 66.36 (6) | 3.1 (2.5) | 98.58 (5) | 3.5 (2.7) |
| 10.58 (6) |

Parameter values are in units of \( 10^{-4} \) cm\(^{-1} \).

For example, fluctuating magnetic moments in the vicinity of a muon would produce a fluctuating dipolar magnetic field, and therefore, a polarization relaxation from its initial value to zero. The time scale of the relaxation can be extracted from the field dependence of the muon spin-lattice relaxation, \( \lambda \), considering the following equation53:

\[
\lambda = \frac{\Delta^2}{1 + \gamma^2\mu H^2}
\]

where, \( \Delta \) is the magnitude of the local magnetic field, \( \gamma \) is the gyromagnetic ratio of the muon, \( \mu \) is the applied magnetic field and \( t \) is the fluctuation time scale. The equation above assumes that \( \Delta \) and \( t \) are field-independent. From the fit of \( \lambda \) as a function of \( \mu H \) (Supplementary Fig. 26) \( \tau \approx 0.016 \mu s \) is obtained. The small value of \( \tau \) compared with that obtained from a.c. susceptibility measurements is due to the fact that \( \mu \)SR reflects the integrated contribution over \( q \)-space as a local, point-like probe, while a.c. susceptibility measures the response for \( q = 0 \) (ref. 52).

Data Availability. The X-ray crystallographic coordinates for structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 1431835–1431837. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request cif. All other relevant data are available from the authors on request.

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Muon-spin relaxation. The \( \mu \)SR measurements were performed on the Dolly spectrometer at the Paul Scherrer Institut (Villigen, Switzerland). Fully spin-polarized muons were implanted into the sample and acted as a local probe of the internal magnetic fields. The time evolution of the polarization, which was monitored via the anisotropic \( \beta \)-decay of the implanted muons (lifetime 2.2 \( \mu s \)), is determined by the temporal and spatial properties of the local magnetic field49.
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Acknowledgements

We thank E. Lebrad and P. Voisin for technical and experimental assistance on powder X-ray diffraction and on XAS/XMCD experiments, respectively. The μ+SR and X-ray spectroscopy experiments were performed at the Paul Scherrer Institute (Swiss Muon Source (SμS)), Villigen, Switzerland and at the European Synchrotron Radiation Facility (ESRF, Grenoble, France), respectively. Y.L. and W.W. thank the EU for financial support within the FP7 FET-Proof project MoQuSuS No610449 and the Agence Nationale de la Recherche (ANR) project MolQuSpin, ANR-13-BST6. K.S.P. and R.C. thank the Danish Research Council for Independent Research for a DFF-Sapere Aude Research Talent grant (4090-00201), the University of Bordeaux, the Région Aquitaine, the ANR, the CNRS and the GdR MCM-2: Magnetisme et Commutation Moléculaires.

Author contributions

K.S.P., J.B. and R.C designed the research project. K.S.P., A.T., E.D. and J.B. synthesized the compounds and developed the fluorination technologies. K.S.P. and D.N.W. performed the structural analysis. R.C., W.W., Y.L. and K.S.P. acquired and analysed the magnetic data. K.S.P., A.R., K.O., F.W., C.M., S.P. and R.C. acquired and analysed the X-ray spectroscopic data. H.W. and K.S.P. performed the EPR experiments and analysed the data. J.B., T.J.M., S.I.K. and S.O. performed the ligand field and quantum chemical calculations. Z.S. and K.S.P. obtained and analysed the μ+SR data.

Additional information

Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing financial interests: The authors declare no competing financial interests.

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How to cite this article: Pedersen, K. S. et al. Iridates from the molecular side. Nat. Commun. 7:12195 doi: 10.1038/ncomms12195 (2016).

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Erratum: Iridates from the molecular side

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Nature Communications 7:12195 doi: 10.1038/ncomms12195 (2016); Published 20 Jul 2016; Updated 31 Aug 2016

The original version of this Article contained an error in which the first affiliation was incorrectly given as ‘CNRS, ICMCB, UPR 9048, Pessac 33600, France’. This has now been corrected in both the PDF and HTML versions of the Article.

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