Crystal polymorphism in 2,2′-bipyrimidine-based iridium(III) complexes

Adrián Sanchis-Perucho, Marta Orts-Arroyo, Isabel Castro, Francesc Lloret and José Martínez-Lillo

Instituto de Ciencia Molecular (ICMol)/Departament de Química Inorgànica, Universitat de València, Paterna, València, Spain

ABSTRACT
Mononuclear iridium(III) complexes, NBu₄[IrBr₄(bpym)] (1) and [IrBr₃(bpym)(MeCN)] (2a and 2b) [NBu₄⁺ = tetra(n-butyl)ammonium cation; bpym = 2,2′-bipyrimidine], have been prepared and characterized. Their crystal structures were determined by single-crystal X-ray diffraction. 1 and 2a crystallize in the monoclinic crystal system with space groups P2₁/c and P2₁/n, respectively. The 2b phase crystallizes in the orthorhombic crystal system with space group P2₁2₁2₁. In these complexes, each iridium(III) is six-coordinate and bonded to two (1) or three (2a and 2b) nitrogen atoms from bpym and MeCN (2a and 2b) molecules and three (2a and 2b) or four (1) bromides. In all the cases, they exhibit a distorted octahedral environment. 2a and 2b display a packing polymorphism containing π···Br, C–H···Br and Br···Br intermolecular interactions. Further analyses of their crystal structures were performed through the SHAPE and CrystalExplorer programs. The electrochemical properties of 1 and 2 were investigated through cyclic voltammetry (CV) technique, with 1 showing a reversible iridium(III)–iridium(IV) redox process.

ARTICLE HISTORY
Received 29 June 2022
Accepted 3 August 2022

KEYWORDS
Iridium(III) complexes; X-ray diffraction; polymorphism; Hirshfeld surface; electrochemical properties

CONTACT José Martínez-Lillo f.jose.martinez@uv.es Instituto de Ciencia Molecular (ICMol)/Departament de Química Inorgànica, Universitat de València, c/Catedrático José Beltrán 2, 46980 Paterna, València, Spain

© 2022 Informa UK Limited, trading as Taylor & Francis Group
1. Introduction

Iridium coordination chemistry has undergone a significant growth [1–11]. In particular, Ir$^{\text{III}}$ complexes have been intensively investigated because of their potential technological applications in different areas of current research, such as catalysis, imaging and sensing [12–17].

Regarding the phenomenon of crystal polymorphism (and pseudo-polymorphism) in Ir$^{\text{III}}$ chemistry, only a few works dealing with this topic have been reported [2, 18,19]. Polymorphic species display different packing arrangements of the same constituent molecules and, despite containing identical chemical composition, each phase constitutes a singular crystalline material with its own chemical and physical properties [20,21]. Similar effects can also be observed in pseudo-polymorphic phases [22]. Thus, small changes in the synthesis and crystallization can lead to different polymorphic species, which can provide useful information on the factors that govern the molecular self-assembling process in the crystalline state as well as on structure-property relationships [23,24].

We have conducted a study on different crystalline forms of a family of Ir$^{\text{III}}$ complexes based on the 2,2$^\text{2}$-bipyrimidine (bpym). This heterocyclic N-donor ligand has been the subject of interest in this research because of its coordinating versatility, as it can coordinate to metal centers either as chelating or bis-chelating ligand, being most widely used toward 3d-5d metal ions [25–41]. A recent review of the Cambridge Structural Database (CSD) for mononuclear bpym-based Ir$^{\text{III}}$ complexes revealed that there exist only five crystal structures of this type reported [12, 42–44].

Herein we report the synthesis and crystal structure of three iridium(III) complexes, NBu$_4\{\text{IrBr}_4(\text{bpym})\}$ (1) and [IrBr$_3$(bpym)(MeCN)] (2a and 2b) [NBu$_4^+$ = tetra(n-butyl)ammonium cation; bpym = 2,2$^\text{2}$-bipyrimidine], and the study on their electrochemical properties. Complexes 2a and 2b are polymorphic species.

2. Experimental

2.1. Materials

All starting chemicals and solvents were purchased from commercial sources [2,2$^\text{2}$-bipyrimidine (bpym, >95%, TCI), glacial acetic acid (CH$_3$COOH, 99.7+%, Alfa Aesar), acetonitrile (MeCN, ≥99.9%, VWR), 2-propanol (2-PrOH, 99.5%, Fisher), dichloromethane (CH$_2$Cl$_2$, 99.8%, Fisher), nitromethane (MeNO$_2$, 98+%, Alfa Aesar), tetra(n-butyl)ammonium hexafluorophosphate (NBu$_4$PF$_6$, 98%, Alfa Aesar), ferrocene (Fc, 98%, Sigma-Aldrich)] and used without purification. The solvents were dried through 3 Å molecular sieves (Fisher). The Ir(IV) precursor (NBu$_4$)$_2$[IrBr$_6$] was prepared following the literature procedure previously reported [45].

2.2. Syntheses

2.2.1. Synthesis and reactivity

Compounds 1, 2a and 2b were synthesized from the iridium salts (NBu$_4$)$_2$[IrBr$_6$] (for 1) and NBu$_4$[IrBr$_4$(bpym)] (for 2a and 2b) in different solvents. 1 was obtained in glacial CH$_3$COOH, whereas 2a and 2b were prepared in MeCN/MeNO$_2$ and MeCN/2-PrOH.
mixtures, respectively. During the synthesis of 1, the reaction mixture in the presence of 2,2'-bipyrimidine is heated at 100 °C under continuous stirring for 1 h, allowing formation of a new Ir(III) complex, NBu₄[IrBr₄(bpym)] (1), which was isolated and characterized as the tetra(n-butyl)ammonium salt. 1 was used as a starting material for the preparation of both 2a and 2b.

In order to explore the chemical reactivity of these new Ir(III) complexes toward their oxidation to Ir(IV), several attempts were made by adding stoichiometric mixtures of different oxidants, such as NH₄[Ce(SO₄)₄]·2H₂O, Br₂, and H₂O₂, in their acidic aqueous solutions. However, no Ir(IV) complex was isolated by means of these oxidizing agents. The subsequent products were the initial Ir(III) complexes, indicating their stability against chemical oxidation. For that reason, electrochemical studies were performed on these Ir(III) complexes.

2.2.2. Synthesis of NBu₄[IrBr₄(bpym)] (1)
A mixture of (NBu₄)₂[IrBr₆] (115.7 mg, 0.10 mmol), 2,2'-bipyrimidine (31.4 mg, 0.20 mmol) and glacial CH₃COOH (20 mL) was heated at 100 °C under continuous stirring for 1 h. The resulting dark red solution was filtered and left to evaporate at room temperature. In 24 h, red crystals of 1 suitable for X-ray diffraction data collection were formed. Yield: ca. 45%. Found: C, 31.4; H, 4.3; N, 7.5%. Calcd. for C₂₄H₄₂N₅Br₄Ir (1): C, 31.6; H, 4.6; N, 7.7%. X-ray microanalysis (SEM-EDX) gave an Ir/Br molar ratio of 1:4. ESI MS (m/z): 674.69 (12.8%), 673.69 (5.7%), 672.69 (50.0%), 671.69 (11.0%), 670.70 (100%), 669.69 (9.0%), 668.69 (93.9%), 666.69 (42.3%), 664.69 (8.3%), 244.29 (1.5%), 243.29 (17.7%), 242.28 (100%) (Figure S1). IR (KBr pellet): 3447 (m), 3063 (m), 2962 (s), 2936 (m), 2873 (m), 1576 (s), 1543 (m), 1469 (m), 1405 (vs), 1383 (w), 1245 (m), 1167 (w), 1071 (w), 1031 (m), 880 (w), 822 (m), 752 (m), 672 (m) cm⁻¹.

2.2.3. Synthesis of [IrBr₃(bpym)(MeCN)] (2a and 2b)
Compound 2a was prepared by dissolving 1 (91.3 mg, 0.10 mmol) in 10 mL of a MeCN/MeNO₂ (2:1, v/v) mixture under continuous stirring for 1 h. The resulting solution was left to evaporate and orange crystals suitable for X-ray diffraction studies were
obtained in a week and a half. Yield: ca. 5%. Compound 2b was prepared as 2a but using a MeCN/2-PrOH (2:1, v/v) solution instead of the indicated solvents mixture of 2a. Yield: ca. 20%. Found: C, 18.8; H, 1.3; N, 11.0. Calcd. for C_{10}H_9N_5Br_3Ir (2a/2b): C, 19.0; H, 1.4; N, 11.1%. In both cases, X-ray microanalysis (SEM-EDX) gave an Ir/Br molar ratio of 1:3. ESI MS (m/z): 624.74 (27.4%), 623.80 (9.0%), 622.79 (74.1%), 621.79 (12.7%), 620.79 (100%), 619.80 (7.0%), 618.79 (62.5%), 617.80 (1.8%), 616.79 (14.0%) (Figure S2). IR (KBr pellet): 3442 (m), 3070 (s), 3025 (w), 2987 (w), 2920 (w), 2335 (w), 1582 (vs), 1553 (m), 1451 (m), 1409 (vs), 1335 (w), 1246 (w), 1211 (w), 1141 (w), 1029 (m), 817 (m), 743 (s), 693 (w), 673 (m), 463 (w) cm⁻¹.

2.3. Physical measurements

Elemental analyses (C, H, N) were performed on a CE Instruments EA 1110 CHNS analyzer. Infrared spectra were recorded on a Thermo-Nicolet 6700 FT-IR spectrophotometer from 4000 to 400 cm⁻¹. Ir/Br molar ratios were analyzed through a Hitachi S-4800 field emission scanning electron microscope (SEM-EDX) equipped with a system of X-ray microanalysis. Electrospray Ionization Mass Spectrometry (ESI-MS) spectra of 1 and 2 were performed on a SCIEX TripleTOF 6600+ mass spectrometer by using a direct infusion electrospray ionization source (ESI). 1 was dissolved in CHCl₃ and its scans were realized over positive and negative ions (Figure S1), whereas 2 was dissolved in MeCN and recorded for negative ions (Figure S2). All these measurements were performed in the Central Service for the Support to Experimental Research (SCSIE) at the University of Valencia. Cyclic voltammetry (CV) measurements were carried out with an Autolab/PGSTAT204 and a three-electrode measuring cell with Metrohm electrodes, a 3 mm diameter Pt disc as working electrode, a glassy carbon rod as auxiliary electrode and Ag/AgCl (3 M KCl) as reference electrode. CV curves were obtained with a 1 mM solution of 1 and 2 in dry CH₂Cl₂, and the conductivity of the system was improved with a 0.25 M NBu₄[PF₆] solution as supporting electrolyte. Argon gas was
directly bubbled through the solution in the cell and stirred before each CV experiment. All the CV curves were recorded at 20°C. The studied potential range was from -1.0 to +1.7 V vs. Ag/AgCl at a scan rate between 10 and 500 mV·s⁻¹. Ferrocene (Fc) was added at the end of the experiment as an internal standard.

2.4. Crystallographic data collection and structure determination

X-ray diffraction data of single crystals of 1, 2a and 2b [with dimensions 0.69 × 0.31 × 0.17 (1), 0.43 × 0.11 × 0.09 (2a) and 0.30 × 0.13 × 0.09 mm³ (2b)] were collected on a Bruker D8 Venture diffractometer with PHOTON II detector using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by standard direct methods and subsequently completed by Fourier recycling using SHELXTL [46]. The final full-matrix least-squares refinements on F², minimizing the function Σw[(F₀² - |Fₑ|²)²] / [w(F₀²)]¹/², reached convergence with values of the discrepancy indices given in Table 1. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms of the bpym and MeCN molecules were set in calculated positions and refined as riding atoms. Graphical manipulations were performed using DIAMOND [47]. CCDC 2178030 (1), 2178031 (2a) and 2178032 (2b).

3. Results and discussion

3.1. Crystal structures of 1, 2a and 2b

Crystal structures and exact chemical compositions of 1, 2a and 2b were established by single-crystal X-ray diffraction. While 1 and 2a crystallize in the monoclinic crystal system with space groups P2₁/c (1) and P2₁/n (2a), 2b crystallizes in the orthorhombic crystal system with space group P2₁2₁2₁ (Table 1). The crystal structure of 1 is made

| Compound | 1  | 2a | 2b |
|----------|----|----|----|
| Formula  | C₂₄H₄₂N₅Br₁Ir | C₁₀H₉N₅Br₃Ir | C₁₀H₉N₅Br₃Ir |
| Mr (g mol⁻¹) | 912.45 | 631.15 | 631.15 |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic |
| Space group | P2₁/c | P2₁/n | P2₁2₁2₁ |
| a (Å) | 11.982(1) | 8.407(1) | 9.891(1) |
| b (Å) | 17.424(1) | 18.457(1) | 11.035(1) |
| c (Å) | 14.664(1) | 10.204(1) | 14.160(1) |
| α (°) | 90.0 | 90.0 | 90.0 |
| β (°) | 100.12(1) | 106.97(1) | 90.0 |
| γ (°) | 90.0 | 90.0 | 90.0 |
| V (Å³) | 3013.8(2) | 1514.2(1) | 1545.5(1) |
| Z | 4 | 4 | 4 |
| Dc (g cm⁻³) | 2.011 | 2.769 | 2.713 |
| μ (Mo-Kα) (mm⁻¹) | 9.755 | 16.727 | 16.388 |
| F(000) | 1752 | 1114 | 1144 |
| Goodness-of-fit on F² | 1.067 | 1.213 | 1.123 |
| R₁/ wR₂ [I > 2σ(I)] | 0.0309/0.0704 | 0.0356/0.0690 | 0.0148/0.0343 |
| Abs. structure (Flack parameter) | -0.014(6) | -0.014(6) | -0.014(6) |

Table 1. Crystal data and structure refinement for 1, 2a and 2b.
up of (NBu$_4$)$^+$ cations and [IrBr$_4$(bpym)]$^-$ anions (Figure 1). The crystal structures of 2a and 2b are made up of neutral [IrBr$_3$(bpym)(MeCN)] complexes (Figures 2 and S3).

The six-coordinate Ir(III) in 1 is bonded to four bromides and two nitrogen atoms from one bpm molecule in a distorted octahedral environment. The N(1)–Ir(1)–N(2) bite angle in 1 is $80.2(1)^\circ$ and the average values of the Ir–N and Ir–Br bond lengths are 2.028(1) and 2.488(1) Å, respectively. The two rings of the bpm molecule are planar and show a dihedral angle between them of $5.1(1)^\circ$. In 2a and 2b, the Ir(III) is six-coordinate and bonded to three bromides and three nitrogen atoms from the bpm and MeCN molecules, generating a distorted octahedral geometry of this fac-isomer. The N(1)–Ir(1)–N(2) bite angles for 2a and 2b are $79.4(1)$ and $79.8(1)^\circ$, respectively. The average values of the Ir–N and Ir–Br bond lengths are 2.029(1) and 2.487(1) Å for 2a and 2.029(1) and 2.487(1) Å for 2b, respectively. As in 1, the rings of the bpm molecules in 2a and 2b are planar, but they exhibit dihedral angle values somewhat lower than that of 1 [approximately $2.7(1)$ and $3.9(1)^\circ$ for 2a and 2b, respectively]. In the three compounds, the C–C and C–N bond lengths of the bpm ligand are as expected for this molecule when coordinated to a metal center [33, 34, 37, 41].

The coordination environment and geometry of the Ir(III) ions of this family of mononuclear complexes were further analyzed through the SHAPE program [48,49]. In all the cases, the Ir(III) ions display a coordination number equal to six (Figures 1, 2 and S3). The lower SHAPE values computed for these Ir(III) ions were 1.086, 1.135, 1.168 for 1, 2a and 2b, respectively. 0 being the perfect match for the ideal polyhedron (Table 2). As expected, these calculated values can be assigned to an octahedral geometry, hence indicating the same geometry for the Ir(III) ions in 1, 2a, and 2b. The most regular octahedron in this family would be that of 1. In any case, this is an approximation, because the Ir(III) ions exhibit a slightly distorted octahedral geometry generated mainly by the short bite angle of the bpm ligand (see above).

In the crystal packing of 1, adjacent [Ir$_{III}$Br$_4$(bpym)]$^-$ anions are connected through bifurcated C–H⋯N interactions between bpm ligands, which generate dimeric units.
of anions [C⋯N distances covering the range ca. 3.24(1)–3.55(1) Å; \( a = -x + 1, -y + 1, -z + 1 \)] (Figure 3). These dimeric units are linked by weak C–H⋯Br interactions [C–Br distance of ca. 3.62(1) Å; \( b = x, -y + 1/2, z + 1/2 \)], forming a 2D network that grows in the crystallographic bc plane (Figure 3). Additional C–H⋯Br interactions between (NBu₄)⁺ cations and \([\text{IrIIIBr}_4(\text{bpym})]\)⁻ anions stabilize the 3D supramolecular structure in 1 (Figure S4).

In the crystal packing of 2a, intermolecular π⋯Br interactions direct chains of \([\text{IrBr}_3(\text{bpym})(\text{MeCN})]\) complexes that grow along the crystallographic [111] direction, the shortest π⋯Br distance being ca. 3.43(1) Å; \( b = x + 1, y, z \), which are formed by neighboring bpym ligands and bromides, resulting in a layered structure. Additional C–H⋯Br interactions [C(10)⋯Br(3c) distance of ca. 3.88(1) Å; \( c = -x + 3/2, y - 1/2, -z + 1/2 \)] occur between metal groups of coordinated MeCN molecules and bromides and, along with Br⋯Br interactions of ca. 4.50(1) Å [50,51], lead to a 3D supramolecular framework in 2a (Figure 4). As in 2a, intermolecular π⋯Br interactions generating chains of \([\text{IrBr}_3(\text{bpym})(\text{MeCN})]\) complexes are also observed in 2b, but the shortest π⋯Br distance in 2b is somewhat longer than that of 2a [ca. 3.38(1) Å; \( a = -x + 1, y + 1/2, -z + 3/2 \)]. These chains are connected by C–H⋯Br interactions between \([\text{IrBr}_3(\text{bpym})(\text{MeCN})]\) complexes forming a helical motif [C(8b)⋯Br(3) distance of ca. 3.62(1) Å; \( b = -x + 2, y - 1/2, -z + 3/2 \)], which is not observed in the 2a phase (Figure 5). Further C–H⋯Br interactions of approximately 3.76(1) Å [C(7c)⋯Br(2); \( c = -x + 3/2, -y + 1, z - 1/2 \)] contribute to stabilizing the 3D supramolecular framework in 2b.

### 3.2. Analysis of the Hirshfeld Surfaces

Hirshfeld surfaces of \([\text{IrBr}_4(\text{bpym})]^-\) (1) and neutral \([\text{IrBr}_3(\text{bpym})(\text{MeCN})]\) (2a and 2b) complexes were calculated and their close intermolecular interactions were analyzed through the CrystalExplorer program [52–57]. These surfaces were mapped taking into account the distance from a point on the surface to the nearest atom outside (\( d_e \)) and inside (\( d_i \)) their surface. To overcome limitations related to the size of atoms, a normalized contact distance (\( d_{\text{norm}} \)) was also considered [52–57]. Hirshfeld surfaces for 1, 2a, and 2b are shown in Figures 6–8, respectively. In general, the shorter contacts are displayed by using red color, whereas white indicates contacts around the van der Waals separation, and blue is for longer contacts [52]. In 1, the most important contacts are the C–H⋯Br interactions, which mainly involve (NBu₄)⁺ cations and bromides of the
[IrBr₄(bpym)]⁻ complexes and represent approximately 51% of the complete fingerprint plot (Figure 6). Moreover, intermolecular C–H···N interactions generated by bpm ligands are highlighted from the full fingerprint as ca. 22% of the plot (figure 6). In 2a, intermolecular C–H···Br contacts between bromides and bpm and MeCN molecules of the [IrBr₃(bpym)(MeCN)] complexes are the main interactions detected on the Hirshfeld surface, and they cover approximately 34% of the fingerprint plot (Figure 7). Additional intermolecular interactions have been highlighted from the full fingerprint (11%) as intermolecular C–H···N (Figure 7). In 2b, very similar interactions and values to those of 2a were found. Intermolecular C–H···Br interactions between [IrBr₃(bpym)(MeCN)] complexes gave ca. 30% of the fingerprint plot, whereas intermolecular C–H···N contacts cover approximately 10% of the fingerprint plot of 2b (Figure 8).
Figure 6. Hirshfeld surface mapped with $d_{\text{norm}}$ function (left) and fingerprint plot (right) for 1.

Figure 7. Hirshfeld surface mapped with $d_{\text{norm}}$ function (left) and fingerprint plot (right) for 2a.

Figure 8. Hirshfeld surface mapped with $d_{\text{norm}}$ function (left) and fingerprint plot (right) for 2b.
3.3. Electrochemical properties

The electrochemical properties of 1 and 2 were studied employing cyclic voltammetry (CV) technique (Figure 9). For 1, only a redox couple was detected and assigned to the Ir(III)/Ir(IV) pair (Figures S5 and S6), whereas no reversible peaks were observed for 2. Figure 9 shows the reversibility of this system, which was tested from 10 to 500 mV s\(^{-1}\). It also shows a position of the anodic (\(E_{pa}\)) and cathodic peaks (\(E_{pc}\)) which is independent from the scanning rate, as expected for a reversible redox process. The value of the half-wave potential, defined by the half sum of the cathodic and anodic peaks, \[E_{1/2} = \frac{E_{pa} + E_{pc}}{2}\], was \(+0.758(3)\) V versus Fc/Fc\(^{+}\) for the Ir(III)/Ir(IV) couple in 1. This value is in agreement with those reported for similar compounds of general formula \([\text{IrBr}_4(L)_2]^-\) (L = solvent), which have been reported in MeCN and within the range from \(+0.53\) to \(+1.14\) V versus Fc/Fc\(^{+}\) [58]. In addition, the peak-to-peak separation stands for the absolute value of the potential difference between cathodic and anodic peaks, \((\Delta E_p = |E_{pa} - E_{pc}|)\), which supports the reversibility of the process, having in mind a value of \(ca. 56\) mV for the ideal one-electron exchange reversible process at 20°C. In the studied scan rate, the values obtained for 1 are from 72 to 90 mV. Although these results are somewhat greater than those expected for the one-electron exchange of the Ir(III)/Ir(IV) pair, this deviation is mainly caused by the Ohmic drop of the non-aqueous solvent, that confers a high resistivity medium, which is only partially compensated by the supporting electrolyte [59–62].

The one-electron exchange assigned to the Ir(III)/Ir(IV) pair in 1 is also supported by the fact that the value of \(\Delta E_p\) found for the Fc/Fc\(^{+}\) system under the same conditions was \(ca. 102\) mV at 10 and 100 mV s\(^{-1}\). On the other hand, the intensity of the anodic (\(I_{pa}\)) and cathodic peaks (\(I_{pc}\)) show a good linear relationship with the square root of the scan rate, indicating that both processes are controlled by diffusion mechanisms in the studied scan rate range (Figure S7). The reversibility of a redox couple can also
be proved through the absolute value of the ratio between peak currents when these are steady and equal to one ($|I_{pa}/I_{pc}| = 1$), as observed for 1 (Table S1).

4. Conclusion

A family of mononuclear iridium(III) complexes, NBu$_4$[IrBr$_4$(bpym)] (1) and [IrBr$_3$(bpym)(MeCN)] (2a and 2b) [NBu$_4^+$ = tetra(n-butyl)ammonium cation; bpym = 2,2'-bipyrimidine], have been synthesized and characterized. The study of their crystal structure through single-crystal X-ray diffraction revealed that 2a and 2b are polymorphic species containing π···Br, C−H···Br and Br···Br intermolecular interactions with different crystallographic values in their packings. A further analysis of their crystal structure was performed through the SHAPE and CrystalExplorer programs. In addition, the electrochemical properties of 1 and 2 were investigated by cyclic voltammetry (CV). 1 exhibits a reversible one-electron exchange process, assigned to the Ir(III)/Ir(IV) pair, with a half-wave potential of ca. +0.758(3) V. Complex 2 displays different electrochemical behavior, with no detected reversible process. The results of this study could be very useful for obtaining paramagnetic bpym-based Ir(IV) species that allow us to investigate their magnetic properties. Finally, these complexes are new members of the short list of mononuclear bpym-based Ir(III) systems.

Acknowledgements

The authors wish to thank Prof. Giovanni De Munno for his friendship and continuous support, and also for his superb guidance and valuable encouragement when hosting Spanish young researchers during their graduate/postgraduate studies and postdoctoral stays.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This research was funded by the Spanish Ministry of Science and Innovation (Grant number PID2019-109735GB-I00). A.S.P. and M.O.A. thank the Spanish Ministry of Science and Innovation for predoctoral FPU and FPI fellowships, respectively.

ORCID

José Martínez-Lillo http://orcid.org/0000-0003-1107-2344

References

[1] R. Crabtree. Acc. Chem. Res., 12, 331 (1979).
[2] C.H. Shin, J.O. Huh, M.H. Lee, Y. Do. Dalton Trans., 6476 (2009).
[3] H. Yersin, A.F. Rausch, R. Czerwieniec, T. Hofbeck, T. Fischer. Coord. Chem. Rev., 255, 2622 (2011).
[40] D. Armentano, A. Sanchis-Perucho, C. Rojas-Dotti, J. Martínez-Lillo. *CrystEngComm*, **20**, 4575 (2018).

[41] M. Orts-Arroyo, I. Castro, F. Lloret, J. Martínez-Lillo. *Cryst. Growth Des.*, **20**, 2044 (2020).

[42] S.-Y. Yao, Y.-L. Ou, B.-H. Ye. *Inorg. Chem.*, **55**, 6018 (2016).

[43] F.-F. Cheng, Z.-Q. Bian, C.-H. Huang. *Chin. J. Chem.*, **24**, 1219 (2006).

[44] Y. Shiba, A. Inagaki, M. Akita. *Organometallics*, **34**, 4844 (2015).

[45] W.P. Carbery, A. Verma, D.B. Turner. *J. Phys. Chem. Lett.*, **8**, 1315 (2017).

[46] SHELXTL-2017/1, Bruker Analytical X-ray Instruments; Bruker: Madison, WI, USA 2017

[47] DIAMOND 4.5.0. Crystal Impact GbR, CRYSTAL IMPACT, K. Brandenberg and HPutz GbR, Bonn, Germany (2018).

[48] M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez. *Shape 2.1*, Universitat de Barcelona: Barcelona, Spain (2013).

[49] S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llunell, D. Avnir. *Coord. Chem. Rev.*, **249**, 1693 (2005).

[50] J. Martínez-Lillo, J. Kong, M. Julve, E.K. Brechin. *Cryst. Growth Des.*, **14**, 5985 (2014).

[51] J. Martínez-Lillo, A.H. Pedersen, J. Faus, M. Julve, E.K. Brechin. *Cryst. Growth Des.*, **15**, 2598 (2015).

[52] J.J. McKinnon, D. Jayatilaka, M.A. Spackman. *Chem. Commun.*, 3814 (2007).

[53] M.A. Spackman, D. Jayatilaka. *CrystEngComm*, **11**, 19 (2009).

[54] M.J.; Turner, J.J.; McKinnon, S.K.; Wolff, D.J.; Grimwood, P.R.; Spackman, D.; Jayatilaka, M.A.; Spackman. CrystalExplorer 17, University of Western Australia (2017).

[55] A. Sanchis-Perucho, M. Orts-Arroyo, J. Camús-Hernández, C. Rojas-Dotti, E. Escrivà, F. Lloret, J. Martínez-Lillo. *CrystEngComm*, **23**, 8579 (2021).

[56] M. Orts-Arroyo, A. Ten-Esteve, S. Ginés-Cárdenas, I. Castro, L. Martí-Bonmatí, J. Martínez-Lillo. *IJMS*, **22**, 4586 (2021).

[57] M. Orts-Arroyo, A. Silvestre-Llora, I. Castro, J. Martínez-Lillo. *Crystals*, **12**, 448 (2022).

[58] R.A. Cipriano, W. Levason, D. Pletcher, N.A. Powell, M. Webster. *J. Chem. Soc., Dalton Trans.*, (1901).

[59] N. Elgrishi, K.J. Rountree, B.D. McCarthy, E.S. Rountree, T.T. Eisenhart, J.L. Dempsey. *J. Chem. Educ.*, **95**, 197 (2018).

[60] N.G. Tsierkezos. *J. Solution Chem.*, **36**, 289 (2007).

[61] A.M. Bond, E.A. McLennan, R.S. Stojanovic, F.G. Thomas. *Anal. Chem.*, **59**, 2853 (1987).

[62] D. Ranchet, J.B. Tommasino, O. Vittori, P.L. Fabre. *J. Solution Chem.*, **27**, 979 (1998).