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Half-sandwich Ir-based neutral organometallic macrocycles containing pyridine-4-thiolato ligands†

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Neutral organometallic cyclic tri- and tetra-nuclear half-sandwich iridium complexes 1 and 3, connected with pyridine-4-thiolato ligands, were synthesized and characterized by X-ray crystallography.

During the past decade, the metal-directed self-assembly of supramolecular architectures, such as two-dimensional triangles, squares, rectangles and polygons, and three-dimensional cages and polyhedra have attracted interest.[1] In particular, organometallic half-sandwich complexes based on Ir, Rh, Ru fragments are attractive as building blocks, which occupy vertices, because they can be used to build metallamacrocyclic receptors and coordination cages. Many tri-, tetra- and hexa-nuclear metallamacrocycles using the combination of half-sandwich complexes with trifunctional ligands were studied extensively by some groups.[2,3] The 'organometallic boxes' with cyanide-linked cubes that contain octahedral building blocks of rhodium and cobalt derivatives have been investigated extensively by the group of Rauchfuss.[4]

It is well-known that flexible organic molecules can adopt different conformations under different conditions. Thus, the organic molecules in supramolecular architectures are an important factor

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† CCDC reference numbers 698542 (**1**), 698543 (**2**) and 698544 (**3**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b900645c
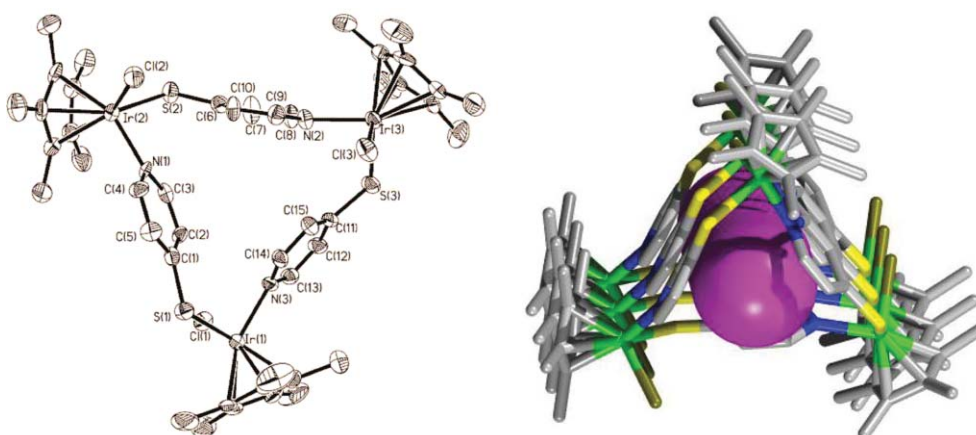
that may be utilized in determining the framework topology by controlling the ligand conformation.[5] To the best of our knowledge, pyridinethiols can display great versatility of coordination chemistry with metal centres through their tautomeric and mesomeric forms; thiol, thione and zwitterionic form.[6] In other words, it can act as a typical anionic thiolato ligand or when in the thione form as a neutral ligand depending on the different reactions.

Following this idea, we choose a flexible pyridine-4-thiolate ligand in which the sulfur atom and nitrogen atom can act as the terminal coordination donors in the same heterocycle. When the ligand coordinated to a metal atom through the sulfur atom, the ligand may coordinate to another metal atom through the nitrogen atom of pyridine and thus form supramolecules. Furthermore, the freedom of rotation around the central C–S–M single bond and angle gives rise to tri- or tetra-conformations, which may be realized through the ligand generate different donor orientations and thus different coordination patterns.

When [Cp*IrCl$_2$]$_2$ was treated with two equivalents of sodium pyridine-4-thiolate in methanol, the orange complex **1** was obtained in good yield (Scheme 1), which has been characterized by NMR, IR spectroscopy and elemental analysis.‡ A detailed structure was determined by single-crystal X-ray analysis of **1**.†§

As shown in Fig. 1, the crystal structure reveals that complex **1** possesses a triangular macrocyclic structure in which a half-sandwich complex of iridium fragments occupy the corner positions connected by three pyridine-4-thiolate ligands. As expected, the pyridine-4-thiolate ligand acts as a bridging

Fig. 1 (a) Molecular structure of **1** with thermal ellipsoids drawn at the 30% level. (b) Crystal packing diagram of **1** showing the open channels. Hydrogen atoms are omitted for clarity (Ir = green, S = yellow, N = blue, C = grey, Cl = dark yellow). Selected distances (Å) and angles (°): Ir(1)–S(1) 2.357(3), Ir(2)–S(2) 2.349(3), Ir(3)–S(3) 2.366(4), Ir(1)–N(3) 2.120(9), Ir(2)–N(1) 2.114(9), Ir(3)–N(2) 2.133(9), Ir(1)–Cl(1) 2.411(3), Ir(2)–Cl(2) 2.440(4), Ir(3)–Cl(3), 2.437(3), S(1)–C(1) 1.731(13), S(2)–C(6) 1.716(14), S(3)–C(11) 1.758(12), N(3)–Ir(1)–S(1) 91.6(3), N(1)–Ir(2)–S(2) 88.8(3), N(2)–Ir(3)–S(3) 86.3(3), C(1)–S(1)–Ir(1) 118.8(4), C(6)–S(2)–Ir(2) 117.6(4), C(11)–S(3)–Ir(3) 115.9(5).
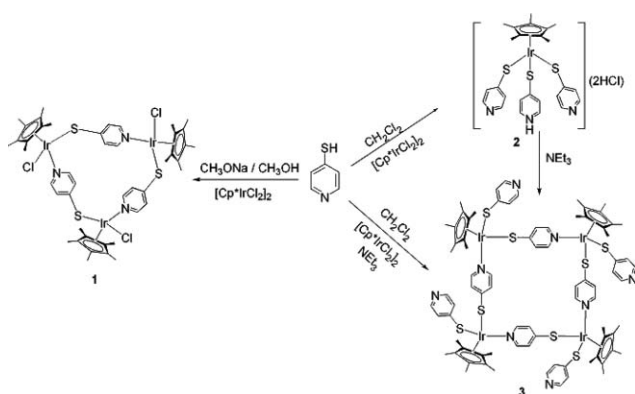
Scheme 1 Synthesis of **1**, **2** and **3**.

ligand through the coordination of sulfur atom and nitrogen atom to two iridium atoms. The coordination sphere of the iridium can be described as a distorted octahedron assuming that the Cp* ligand functions as a three-coordinate ligand. The iridium atoms are 8.16 Å apart from each other resulting a perfectly triangular plane, which is larger than those found for other triangular orangometallic [12] metallacrown-3 complexes (*ca.* 5.5 Å).[2a-c] The average Ir–S and Ir–N bond lengths are 2.357 and 2.122 Å, respectively. The N–Ir–S angles are almost 90°, and the Ir–S–C angles are slightly less than 120°, which appear to be crucial to formation of the molecular triangle. As a result, sulfur atoms are out of the iridium-based triangular plane (1.344 Å, 1.436 Å, 1.209 Å). As shown in Fig. 1(b), the molecular rectangles stack *via* the *a* axis to form triangle channels due to the π–π interactions between the independent molecules.

Treatment of [Cp*IrCl$_2$]$_2$ with pyridine-4-thiol in a 1 : 6 molar ratio in dichloromethane at room temperature, the hydrochloride of mononuclear complex **2** was formed in nearly quantitative yield. Because of its low solubility in dichloromethane, complex **2** was easily isolated by concentrating the reaction mixture. As illustrated in Fig. 2, X-ray crystallographic analysis reveals that

the iridium was surrounded by three pyridine-4-thiolate ligands though monodentate sulfur atoms.§ In addition, one proton bound at nitrogen atom of pyridine, the other two protons located in the middle of nitrogen atom and chloride atom were founded in the structure. We therefore anticipated that the proton bound at the nitrogen atom should be acidic, simultaneously hydrogen chloride was expected to be removed. Taking into account these two characteristics should allow a base-induced transformation of **2**. In fact, if excess of triethylamine was added to the suspension **2** in dichloromethane, the suspension disappeared quickly and the solution color changed to red-orange, and then **3** was obtained in high yield. Alternatively, complex **3** can be prepared directly [Cp*IrCl$_2$]$_2$ and pyridine-4-thiol (molar ratio 1 : 6) in the presence of excess triethylamine.‡ The complex **3** has high solubility in the polar organic solvents such as chloroform, dichloromethane and dichloroethane.
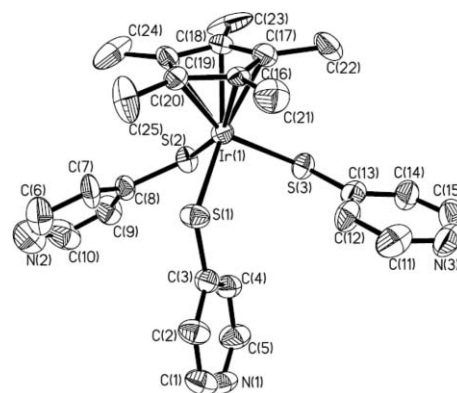

Fig. 2 Cation structure of **2** with thermal ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ir(1)–S(1) 2.353(3), Ir(1)–S(3) 2.365(4), S(1)–C(3) 1.728(13), S(2)–C(8) 1.731(13), S(3)–C(13) 1.738(15), C(3)–S(1)–Ir(1) 119.9(5), C(8)–S(2)–Ir(1) 114.4(6), C(13)–S(3)–Ir(1), 113.4(6). Symmetry transformations used to generate equivalent atoms: $-x$, $1 - y$, $2 - z$.
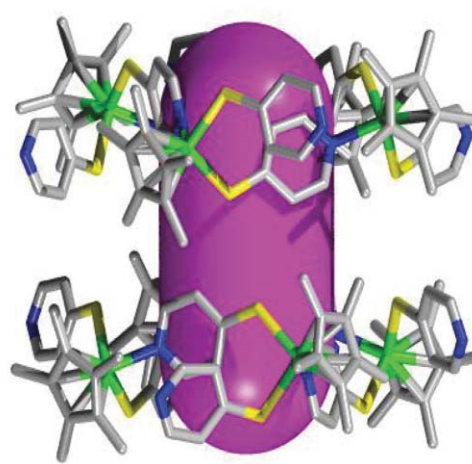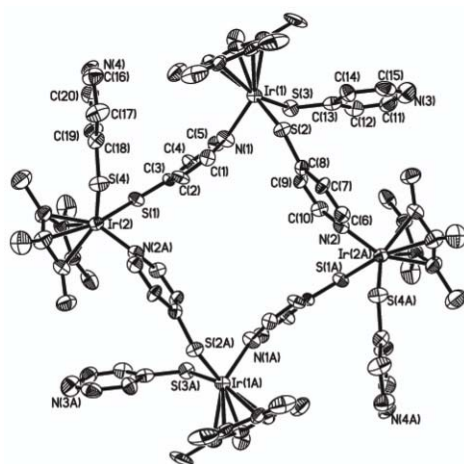

Fig. 3 (a) Molecular structure of **3** with thermal ellipsoids drawn at the 30% level. (b) An image showing how the cavity-forming squares are stacked on top of each other (Ir = green, S = yellow, N = blue, C = grey). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ir(1)–S(2) 2.370(3), Ir(1)–S(3) 2.385(3), Ir(2)–S(1) 2.361(3), Ir(2)–S(4) 2.392(3), Ir(1)–N(1) 2.107(9), Ir(2)–N(2A) 2.120(10), S(1)–C(3) 1.676(11), S(2)–C(8), 1.707(11), S(3)–C(13) 1.722(14), S(4)–C(18) 1.728(12), N(1)–Ir(1)–S(2) 89.3(3), N(1)–Ir(1)–S(3) 88.5(3), S(2)–Ir(1)–S(3) 99.78(11), N(2A)–Ir(2)–S(1) 88.9(3), N(2A)–Ir(2)–S(4) 88.4(3), S(1)–Ir(2)–S(4) 99.49(11), C(3)–S(1)–Ir(2) 116.6(4), C(8)–S(2)–Ir(1) 117.6(4), C(13)–S(3)–Ir(1) 112.5(5), C(18)–S(4)–Ir(2) 114.4(5). Symmetry transformations used to generate equivalent atoms: $3/2 - x$, $1/2 - y$, z.

Single crystals of **3** suitable for X-ray analysis were obtained by the diffusion diethyl ether into a solution of **3** in dichloromethane.§ To our surprise, as shown in Fig. 3 (a), the structure of **3** possesses a somewhat distorted "neutral tetranuclear square" structure with the dimension of 8.0×8.0 Å. It does indeed contain four pseudo-octahedral iridium centers, four bridging pyridine-4-thiolate ligands as typical anionic thiolato ligand. The Ir–N bonds are all about 2.11 Å, and each N–Ir–S bond angle falls in the range of 88–89°. In addition, every iridium center is coordinated with one pyridine-4-thiolate ligand though monodentate sulfur atom. The stacking patterns of macrocycle **3** in the solid-state showed that the neutral squares are stacked along the *c* axis, resulting in long channel-like cavities (Fig. 3 (b)).

In conclusion, we have synthesized mono-, tri- and tetra-iridium complexes **1–3** containing pyridine-4-thiolato ligand and revealed their novel skeletal transformations from mono-iridium complex **2** to square **3** *via* using base. Although further investigation to elucidate the reaction mechanisms for these conversions is required, the present study has demonstrated that the pyridine-4-thiolato ligand works as a versatile and potential bridging unit to construct new polymetallic systems. Work is in progress to study the physicochemical properties of these complexes.

Acknowledgements

Notes and references

‡ All manipulations were performed under an atmosphere of argon using standard Schlenk techniques. Solvents were dried and deoxygenated by MBraun Solvent Purification System (4464) and collected just before use. [Cp*IrCl₂]₂[7] was prepared according to literature methods. IR spectra were recorded on a Nicolet AVATAR-360 IR spectrometer, Elemental analyses were carried out by Elementar III Vario EI Analyzer. ¹H-NMR spectra were obtained on Bruker DMX-500 or Bruker DMX-400 spectrometer in CDCl₃ solution. **1**: Pyridine-4-thiol (22 mg, 0.2 mmol) was added to a solution of CH₃ONa (11 mg, 0.2 mmol) in methanol (20 mL) at room temperature and stirred for 1 h. [Cp*IrCl₂]₂ (80 mg, 0.1 mmol) was added to the resulting solution and the mixture was stirred for 6 h. After removal of the solvent *in vacuo* the product was extracted with dichloromethane. Subsequent addition of diethyl ether and evaporation of the solvent under reduced pressure gave an orange powder, which was dried *in vacuo*. Yield: 76%. ¹H-NMR (400 MHz, CDCl₃, 298 K): δ 7.82 (d, 3H, Py–H), 7.80 (d, 3H, Py–H), 7.24 (d, 3H, Py–H), 7.22 (d, 3H, Py–H), 1.42 (s, 15H, Cp*), 1.41 (s, 15H, Cp*), 1.39 (s, 15H, Cp*) ppm. Elemental analysis (%) calcd for C₄₅H₅₇Cl₃Ir₃N₃S₃: C 38.08, H 4.05, N 2.96, S 6.78; found (%): C 38.31, H 2.84, N 2.65; S 6.72. **2**: Pyridine-4-thiol (66 mg, 0.6 mmol) was added to a solution of [Cp*IrCl₂]₂ (80 mg, 0.1 mmol) in dichloromethane (20 mL) at room temperature, the pale yellow solution turned to red suspension, and the suspension was stirred for another 3 h at room temperature. the solvent was removed, and the residue was washed with dichloromethane and diethyl ether, giving red crystals of **2** (yield: 98%). Elemental analysis (%) calcd for C₂₅H₂₈IrN₃S₃·2HCl: C 41.03, H 4.13, N 5.74, S 13.14; found (%): C 41.22, H 4.06, N 5.65; S 13.52. **3**: Triethylamine (10 mL) was added to the suspension **2** (0.1 mmol) in dichloromethane (10 mL), the suspension disappeared quickly and the solution color turned the red-orange, the solution was washed with water and dried over MgSO₄. After evaporation of the solvent and dried under vacuum to give an red powder **3** (yield: 92%). ¹H-NMR (400 MHz, CDCl₃, 298 K): δ 8.51–7.21 (m, 32H, Py–H), 1.49–1.35 (m, 60H, Cp*) ppm. Elemental analysis (%) calcd for C₈₀H₉₂Ir₄N₄S₄: C 47.88, H 4.62, N 2.79, S 6.39; found (%): C 47.65, H 4.46, N 2.54, S 6.28.

§ Crystals of **1**, **2** and **3** suitable for X-ray diffraction study were obtained by slow diffusion of diethyl ether into a concentrated solution of the complexes in dichloromethane. Crystal data for **1**: C₄₅H₅₇Cl₃Ir₃N₃S₃, $M_r = 1419.07$, triclinic, space group $P\bar{1}$, $a = 8.838(3)$, $b = 17.675(7)$, $c = 18.572(7)$ Å, $\alpha = 68.877(5)$, $\beta = 85.029(6)$, $\gamma = 88.798(5)°$, $V = 2695.9(18)$ Å³, $Z = 2$, $\rho_{calcd} = 1.748$ g cm⁻³, $F(000) = 1356$, $\mu(MoK\alpha) = 7.682$ mm⁻¹, A total of 11 192 of which 9285 reflections were independent ($R_{int} = 0.0674$). The structure was refined to final $R_1 = 0.0531$ [$I > 2\sigma(I)$], w$R_2 = 0.1231$ for all data, GOF = 0.854, and residual electron density max./min. = 1.948 and −1.358 e Å⁻³. Crystal data for **2**: C₂₅H₂₈IrN₃S₃·3CH₂Cl₂·2HCl, $M_r = 986.58$, monoclinic space group $P2_1/c$, $a = 15.650(4)$, $b = 8.128(2)$, $c = 30.788(8)$ Å, $\beta = 92.797(5)°$, $V = 3911.8(17)$ Å³, $Z = 4$, $\rho_{calcd} = 1.675$ g cm⁻³, $F(000) = 1944$, $\mu(MoK\alpha) = 4.144$ mm⁻¹, A total of 13 549 of which 6845 reflections were independent ($R_{int} = 0.0915$). The structure was refined to final $R_1 = 0.0744$ [$I > 2\sigma(I)$], w$R_2 = 0.1605$ for all data, GOF = 0.985, and residual electron density max./min. = 1.567 and −0.680 e Å⁻³. Crystal data for **3**: C₈₀H₉₂Ir₄N₄S₄, $M_r = 2190.90$, orthorhombic, space group $Pccn$, $a = 22.221(7)$, $b = 29.634(9)$, $c = 14.913(4)$ Å, $V = 9820(5)$ Å³, $Z = 4$, $\rho_{calcd} = 1.482$ g cm⁻³, $F(000) = 4256$, $\mu(MoK\alpha) = 5.613$ mm⁻¹, A total of 39 019 of which 8652 reflections were independent ($R_{int} = 0.1245$). The structure was refined to final $R_1 = 0.0483$ [$I > 2\sigma(I)$], w$R_2 = 0.1078$ for all data, GOF = 0.777, and residual electron density max./min. = 1.315 and −1.026 e Å⁻³. All single crystals were immersed in mother solution and sealed in thin-walled glass. Data were collected on a CCD-Bruker SMART APEX system at room temperature (293 K). All the determinations of unit cell and intensity data were performed with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). All the data were collected at room temperature using the ω scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. All the calculations were carried out with the SHELXTL program.[8–10] In complexes **1**, **2** and **3**, all non-hydrogen atoms were refined anisotropically. In all complexes, hydrogen atoms (except three protons that bound nitrogen and chloride atoms in complex **2**) were placed in the geometrically calculated positions with fixed isotropic thermal parameters. There are disordered solvent molecules in complex **3** and the SQUEEZE algorithm was used to omit them. Therefore, new data sets corresponding to omission of the disordered anions and solvents were generated and the structures were refined to convergence.

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