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A novel luminescent iridium(I)–cadmium(II) binuclear complex displaying a long-lived metal-to-ligand charge-transfer excited state. Synthesis and structural characterisation of $I(CO)_2Ir(\mu\text{-}Ph_2Ppy)_2CdI_2$ [Ph_2Ppy = 2-(diphenylphosphino)pyridine]

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The first binuclear Ir^I–Cd^{II} complex to be structurally characterised, $I(CO)_2Ir(\mu\text{-}Ph_2Ppy)_2CdI_2$ [Ph_2Ppy = 2-(diphenylphosphino)pyridine], has a donor–acceptor metal–metal bond of length 2.784(1) Å; at room temperature, excitation of a solid sample of the complex with UV light led to a red emission at 739 nm with a lifetime of 6.48 μs that presumably originates from a ^{3}MLCT excited state.

There has been considerable interest in the metal–metal interaction, electronic absorption spectra, and luminescence properties of binuclear complexes with d^8–d^8,[1] d^{10}–d^{10} [2] and d^8–d^{10} [3] electronic configurations. Several years ago, Balch and coworkers reported a number of luminescent binuclear iridium–Group 11 complexes such as $[AuIr(CO)Cl(\mu\text{-dpm})_2][PF_6]$,[3a] $[AuIr(CNMe)_2(\mu\text{-dpm})_2][PF_6]_2$ [3c] and $[AuIr(CNMe)_3(\mu\text{-dpm})_2][PF_6]_2$ [3c] [dpm = bis(diphenylphosphino)methane]. However, related studies on iridium–Group 12 binuclear complexes which exhibit a significant donor–acceptor metal–metal interaction are very scarce.[4] To our knowledge, only one Ir^I–Cd^{II} complex, namely $CdIr(CO)_2Cl_2(\eta^5\text{-}C_5Me_5)$, has been reported in the literature, but its crystal structure is unknown.[4d] Herein we describe the synthesis, spectroscopic properties and crystal structure of a new binuclear Ir^I–Cd^{II} complex, $I(CO)_2Ir(\mu\text{-}Ph_2Ppy)_2CdI_2$ [Ph_2Ppy = 2-(diphenylphosphino)pyridine], which features an unusual distorted octahedral co-ordination geometry about the Ir^I centre.

In the presence of CO, reaction of CdI_2 with $Ir(CO)Cl(Ph_2Ppy\text{-}P)_2$ **1**, prepared from $[Ir(cod)Cl]_2$ (cod = cycloocta-1,5-diene) and Ph_2Ppy, afforded $I(CO)_2Ir(\mu\text{-}Ph_2Ppy)_2CdI_2$ **3**,‡ in which a halide exchange has occurred (Scheme 1).

The equilibrium between complex **1** and intermediate **2** is substantiated by IR spectral data recorded in dichloromethane solution at room temperature, which show that complex **1** has only one ν(CO) absorption band at 1969.7 cm^{-1}, whereas **2** exhibits two bands at 1970.3 and 1935.1 cm^{-1}. Complex **2** is not stable enough to be isolated in the solid state. Compared with **2**, the ν(CO) bands of **3** shift to higher values (2001.7, 2066.0 cm^{-1}), indicating that the Ir^I–Cd^{II} bond is donor–acceptor in nature with a reduction of electron density at the iridium centre. This observation is in accord with previous studies in the formation of hetero-binuclear Fe^0–M complexes bearing the N,P-bridging ligand Ph_2Ppy.[7]

The molecular structure of $I(CO)_2Ir(\mu\text{-}Ph_2Ppy)_2CdI_2$ **3** has been determined by single-crystal X-ray analysis (Fig. 1).§ The iridium and cadmium atoms are supported by a pair of bidentate $\mu\text{-}Ph_2Ppy$ ligands. The co-ordination geometry at the Ir(1) atom is distorted octahedral, which is seldom found for iridium(I) although it is quite common for iridium(III) and higher oxidation states. The co-ordination geometry at Cd(1) is trigonal bipyrimidal. The measured Ir(1)–Cd(1) distance of 2.784(1) Å is much longer than the related Ir^I–Hg^{II} distances of 2.618(3) Å in $Cl_2Hg(\mu\text{-}Cl)_2HgIr(CO)Cl(dpm)(\mu\text{-dpmAuCl})$ [4b] and 2.587(1) Å in $[(\eta^5\text{-}C_5Me_5)(CO)_2IrHgCl][HgCl_3]$.[4d] The Cd(1)–N bond distances, both 2.51(1) Å are slightly longer than those [2.397(5) and 2.412(5) Å] found in $(CO)_3Fe(\mu\text{-EtPhPpy})_2Cd(NCS)_2$ [EtPhPpy = 2-(ethylphenylphosphino)pyridine].[11] The P–Ir–P and N–Cd–N fragments are each

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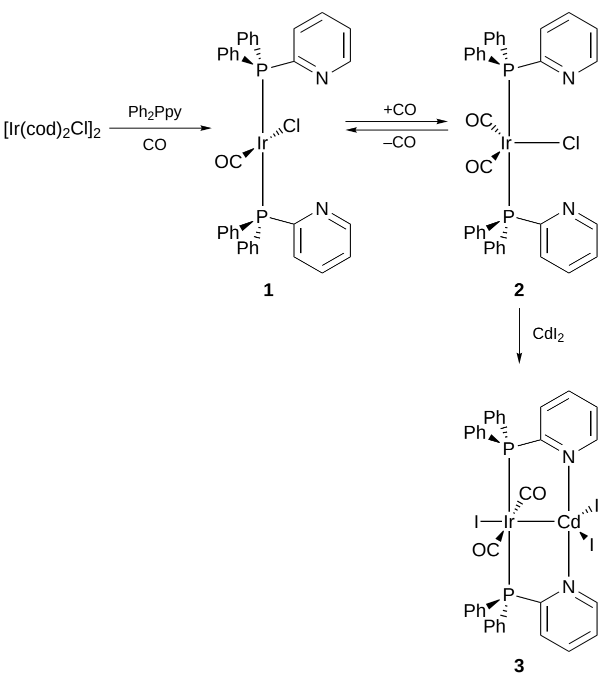
‡ Preparation of complex **3**. Carbon monoxide was passed through a CH_2Cl_2 solution containing $[Ir(cod)Cl]_2$ (0.10 g, 0.15 mmol) and Ph_2Ppy (0.16 g, 0.60 mmol) for 1 h.[6] Solid CdI_2 (0.28 g, 0.60 mmol) was then added. The mixture was stirred for 24 h at room temperature, after which the solvent was reduced to about 5 ml and diethyl ether (15 ml) added to the solution to give orange microcrystals. Yield: 0.12 g (57%) (Found: C, 34.62; H, 2.34; N, 2.20. Calc. for $C_{36}H_{28}CdI_3IrN_2O_2P_2$: C, 34.10; H, 2.23; N, 2.21%). IR (CH_2Cl_2): 2001.7, 2066.0 cm^{-1}. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$, 300 MHz, 298 K): δ 10.45.

Infrared spectra were recorded on a Shimadzu 435 spectrometer, and UV/VIS spectra were obtained on a Milton Roy Spectronic 3000 diode-array spectrophotometer. The $^{31}P\text{-}\{^1H\}$ NMR data were measured on a AC-P200 spectrometer. Steady-state emission spectra were recorded on a Spex Fluorolog-2111 spectrofluorimeter equipped with a Hamamatsu R928 photomultiplier, and transient difference absorption spectroscopy was performed by using the 355 nm output of a Quanta-Ray GCR-150 pulsed Nd-YAG laser as the excitation source of the flash-photolysis set-up.

§ Crystal data for $I(CO)_2Ir(\mu\text{-}Ph_2Ppy)_2CdI_2$ **3**. $C_{36}H_{28}CdI_3IrN_2O_2P_2$, $M = 1267.8$, monoclinic, space group $P2_1/c$ (no. 14), $a = 15.333(3)$, $b = 13.573(3)$, $c = 18.197(4)$ Å, $\beta = 95.85(3)°$, $U = 3767(2)$ Å^3, $Z = 4$, $D_c = 2.235$ Mg m^{-3}, $F(000) = 2352$, orange prism with dimensions 0.15 × 0.20 × 0.18 mm, μ(Mo-Kα) = 6.67 mm^{-1}. Intensity data were collected on a MSC/Rigaku RAXIS IIC imaging-plate diffractometer at 294 K using graphite-monochromatized Mo-Kα radiation (λ = 0.710 73 Å) from a rotating-anode X-ray generator operating at 50 kV and 90 mA (crystal to plate distance 69.5 mm, $2\theta_{max} = 55.2°$, 36 5° oscillation frames in the range 0–180°, exposure 8 min per frame).[8] A self-consistent semiempirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied using ABSCOR.[9] The structure was determined by direct methods and refined by full-matrix least squares using the SHELXTL-PC program package.[10] Hydrogen atoms were placed in their calculated positions with C–H = 0.96 Å, assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent C atoms. Refinement of 425 parameters for 47 non-hydrogen atoms and 5382 observed data $[|F_o| > 6\sigma(F_o)$ out of 7102 unique reflections] converged to $R_F \equiv \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.062$ and $R_{wF}{}^2 \equiv [\{\Sigma w(|F_o| - |F_c|)^2\}/\{\Sigma w|F_o|^2\}]^{\frac{1}{2}} = 0.073$ with $w^{-1} = \sigma^2(|F_o|) + 0.000\,05\ |F_o|^2$. CCDC reference number 186/687.



Scheme 1

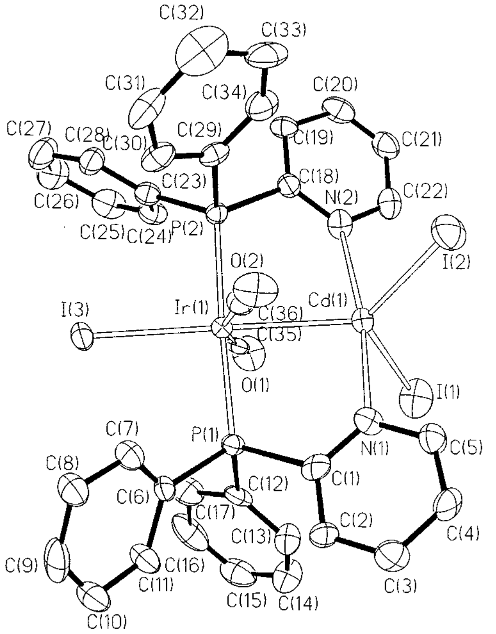


Fig. 1 An ORTEP[5] drawing (35% thermal ellipsoids) showing the molecular structure of $I(CO)_2Ir(\mu\text{-}Ph_2Ppy)_2CdI_2$ **3**. Pertinent bond lengths (Å) and angles (°): Ir(1)–Cd(1) 2.784(1), Ir(1)–P(1) 2.357(4), Ir(1)–P(2) 2.359(4), Cd(1)–N(1) 2.51(1), Cd(1)–N(2) 2.51(1); Cd(1)–Ir(1)–P(2) 89.0(1), P(1)–Ir(1)–P(2) 177.5(1), Ir(1)–Cd(1)–N(1) 85.5(3), Ir(1)–Cd(1)–N(2) 86.2(3), N(1)–Cd(1)–N(2) 171.0(4). Torsion angles (°): P(1)–Ir(1)–Cd(1)–N(1) 26.0, P(2)–Ir(1)–Cd(1)–N(2) 22.8

almost linear with bond angles P(1)–Ir(1)–P(2) 177.5(1)° and N(1)–Cd(1)–N(2) 171.0(4)°, respectively. The $Ir(\mu\text{-}Ph_2Ppy)_2Cd$ core is distorted from planarity, the relevant torsion angles being P(1)–Ir(1)–Cd(1)–N(1) 26.0° and P(2)–Ir(1)–Cd(1)–N(2) 22.8°. This twisting of the chelate rings allows the iridium and cadmium atoms to approach closer to each other despite the rigidity of the bridging Ph_2Ppy ligand.

The UV/VIS spectrum of complex **1** in dichloromethane solution shows absorption bands at 338, 386 and 440 nm with the last having the lowest ε_{max} value. On the other hand, complex **3** shows broad absorptions ranging from 300 to 390 nm. Since the absorptions of **1** and **3** at 300–400 nm have $\varepsilon_{max} > 2000$, they are assigned to metal-to-ligand charge-transfer (MLCT) bands of the type $Ir^I \longrightarrow$ phosphine or CO.

Complex **1** is weakly emissive and shows an emission at 650 nm with a lifetime of 87 µs measured in a frozen CH_2Cl_2 solution at 77 K. Under the same conditions, complex **3** shows an emission at 666 nm with a lifetime of 249 µs. The emission from a CH_2Cl_2 solution of **3** is hardly observable at room temperature, but a solid sample shows a red emission at 739 nm with a lifetime of 6.48 µs at 298 K. We tentatively assign this luminescence to emission from a ^{3}MLCT excited state.

The long excited life-time of complex **3** suggests that it may possess rich photochemical properties. Upon flashing a degassed acetonitrile solution of **3** and *N*,*N*′-dimethyl-4,4′-bipyridinium dihexafluorophosphate ($Mv[PF_6]_2$), the excited-state electron-transfer reaction shown in equation (1) was observed.

$$\mathrm{Ir^{I}{-}Cd^{II} + Mv^{2+} \longrightarrow Ir^{II}{-}Cd^{II} + Mv^{\bullet +}} \qquad (1)$$

Formation of the $Mv^{\bullet +}$ radical cation was substantiated by recording the different absorption spectrum 10 µs after the 355 nm laser flash. The bands at 400 and 630 nm are characteristic of the $Mv^{\bullet +}$ radical cation.

Acknowledgements

This work is supported by Hong Kong Research Grants Council Earmarked Grant CUHK 311/94P.

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Received 28*th July* 1997; *Communication* 7/05431I