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The first binuclear $Ir^{I}-Cd^{II}$ complex to be structurally characterised, $I(CO)_{2}Ir(\mu-Ph_{2}Ppy)_{2}CdI_{2}$ [Ph₂Ppy = 2-(diphenyl-phosphino)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 ³MLCT 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(µ-dpm)₂][PF₆],^{3a} [AuIr(CNMe)₂(µ-dpm)₂][PF₆]₂^{3c} and [AuIr(CNMe)₃(µ-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 $CdIr(CO)_2Cl_2(\eta^5-C_5Me_5)$, 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(µ-Ph₂Ppy)₂CdI₂ $[Ph_2Ppy = 2-(diphenylphosphino)pyridine]$, which features an unusual distorted octahedral co-ordination geometry about the Ir^I centre.

In the presence of CO, reaction of CdI_2 with $Ir(CO)-Cl(Ph_2Ppy-P)_2$ **1**, prepared from $[Ir(cod)Cl]_2$ (cod = cycloocta-1,5-diene) and Ph_2Ppy, afforded $I(CO)_2Ir(\mu-Ph_2Ppy)_2CdI_2$ **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 v(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 v(CO) bands of **3** shift to higher values (2001.7, 2066.0 cm⁻¹), indicating that the Ir^L-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 Fe⁰-M complexes bearing the N,P-bridging ligand Ph₂Ppy.⁷

The molecular structure of $I(CO)_2 Ir(\mu-Ph_2Ppy)_2 CdI_2$ **3** has been determined by single-crystal X-ray analysis (Fig. 1).§ The

iridium and cadmium atoms are supported by a pair of bidentate μ -Ph₂Ppy 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(II) 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 Cl₂Hg(μ -Cl)₂HgIr(CO)Cl(dpm)(μ -dpmAuCl)^{4b} and 2.587(1) Å in [(η^5 -C₅Me₃)(CO)₂IrHgCl][HgCl₃].^{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-(μ -EtPhPpy)₂Cd(NCS)₂ [EtPhPpy = 2-(ethylphenylphosphino)pyridine].¹¹ The P–Ir–P and N–Cd–N fragments are each

 \ddagger Preparation of complex **3**. Carbon monoxide was passed through a CH₂Cl₂ solution containing [Ir(cod)Cl]₂ (0.10 g, 0.15 mmol) and Ph₂Ppy (0.16 g, 0.60 mmol) for 1 h.⁶ Solid CdI₂ (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 C₃₈H₂₈CdI₃IrN₂O₂P₂: C, 34.10; H, 2.23; N, 2.21%). IR (CH₂Cl₂): 2001.7, 2066.0 cm⁻¹. ³¹P-{¹H} NMR (CDCl₃, 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 diodearray spectrophotometer. The ³¹P-{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(μ-Ph₂Ppy)₂CdI₂ **3.** $C_{36}H_{28}$ CdI₃IrN₂O₂P₂, M=1267.8, monoclinic, space group $P2_1/c$ (no. 14), a=15.333(3), b=13.573(3), c=18.197(4) Å, $\beta=95.85(3)^\circ$, U=3767(2) Å³, Z=4, $D_c=2.235$ Mg m⁻³, F(000)=2352, orange prism with dimensions $0.15 \times 0.20 \times 0.18$ mm, μ (Mo-Ka) = 6.67 mm⁻¹. Intensity data were collected on a MSC/Rigaku RAXIS IIC imaging-plate diffractometer at 294 K using graphite-monochromatized Mo-Ka radiation ($\lambda = 0.710$ 73 Å) from a rotating-anode X-ray generator operating at 50 kV and 90 mA (crystal to plate distance 69.5 mm, $2\theta_{max} = 55.2^\circ$, 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 $[|F_0| > 6\sigma(F_0)$ out of 7102 unique reflections] converged to $R_F \equiv \Sigma(|F_0| - |F_c|)/\Sigma|F_0| = 0.062$ and $R_{wF}^2 \equiv [\{\Sigma w(|F_0| - |F_c|)^2\}/\{\Sigma w|F_0|^2\}]^2 = 0.073$ with $w^{-1} = \sigma^2(|F_0|) + 0.000$ 05 $|F_0|^2$. CCDC reference number 186/687.

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Scheme 1

Ph

OC,

OC,

Ph[●] _ Ph

2

Cdl₂

CO

OC

Ph Ph

3

CI

+CO

-co



Fig. 1 An ORTEP⁵ drawing (35% thermal ellipsoids) showing the molecular structure of $I(CO)_2Ir(\mu-Ph_2Ppy)_2CdI_2$ 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 $Ir(\mu$ -Ph₂Ppy)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 Ph₂Ppy 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

 $\epsilon_{max}>2000, \ they \ are \ assigned \ to \ metal-to-ligand \ charge-transfer (MLCT) \ bands \ of \ the type \ Ir^I \longrightarrow phosphine \ or \ CO.$

Complex **1** is weakly emissive and shows an emission at 650 nm with a lifetime of 87 μ s measured in a frozen CH₂Cl₂ solution at 77 K. Under the same conditions, complex **3** shows an emission at 666 nm with a lifetime of 249 μ s. The emission from a CH₂Cl₂ 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 μ s at 298 K. We tentatively assign this luminescence to emission from a ³MLCT 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[PF₆]₂), the excited-state electron-transfer reaction shown in equation (1) was observed.

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

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

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