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H-bonding dependent phosphorescence in a mixed ligand copper(I) complex

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ABSTRACT

The mixed ligand copper(I) derivative [Cu(PPh_3)$_2$(κ^2-O,O″-lact)] (**1**) (lact = L-(+)-lactate) has been prepared and fully characterized. NMR studies indicated the occurrence of a fluxional behavior involving the lactate anion, in solution. The α-hydroxycarboxylate ligand is responsible for the generation of a catemeric O–H···O(CO) H-bonding network that strongly influences the photophysical properties of **1**, in the solid state. Indeed, when irradiated with UV light the title compound shows a bright phosphorescence, which as suggested by DFT calculations is strictly related to the abovementioned H-bonding network.

1. Introduction

Monoanionic α-hydroxycarboxylates possess high versatility in their coordination chemistry due to the presence of two functional groups (OH and COO^-) that can coordinate to one or more metal ions [1]. The most adopted coordination mode for α-hydroxycarboxylates is κ^2-O,O″ (Fig. 1), with both the carboxylate and the hydroxyl group chelating the metal to form a highly stable five-membered ring. The chelation via only the carboxylate group (κ^2-O,O') or through a monodentate carboxylate (κ-O) are less frequent. The κ^2-O,O″ mode is commonly encountered in mixed ligand complexes, either with monodentate ligands (NH_3, H_2O, py, imidazole) [1] or with *N,N'* ancillary ligands like phenanthrolines [2,3], 2,2′-bipyridines [4] or 2,2′-dipyridylamine [5]. One additional significant feature of α-hydroxycarboxylates is the concomitant occurrence of hydrogen bond donor (OH) and acceptor (COO^-) groups, resulting in the possibility to create extended supramolecular arrangements through relatively strong intermolecular H-bonding interactions.

As a directional, site-specific interaction, H-bonding plays a key role in modulating the properties of many molecular and supramolecular systems [6–9]. Concerning transition metal complexes, the photophysical and photochemical behavior can be dramatically influenced both by intra- [10] and intermolecular [11] hydrogen bonds. Indeed, in such hydrogen-bonded systems photoexcitation frequently leads to reorganization of the charge distribution of the different electronic states in the hydrogen donor and acceptor fragments in a process known as excited state H-bonding dynamics (ESHBD) [12,13]. The most relevant examples on the influence of H-bonding on spectral properties of organometallic compounds deal with palladium(II) and platinum(II) complexes. Stang and Han first used density functional theory (DFT) to investigate the ground and excited states of the mixed phosphine-aquo palladium(II) complexes *cis*-[(dppp)Pd(H_2O)(OSO_2CF_3)](OSO_2CF_3) and *cis*-[(dppp)Pd(H_2O)$_2$](OSO_2CF_3)$_2$ [14] and later investigated the effects of intermolecular H-bonding on the fluorescent emission of the bimetallic platinum(II) complex 4,4′-bis(*trans*-Pt(PEt_3)$_2$-OTf)benzophenone [15]. Moriuchi and co-authors [11] demonstrated how the tuning of the emission properties in bio-organometallic platinum(II) compounds could be attained by changing the direction of H-bonding interactions. Then, very recently, Kuwabara et al. made use of intermolecular H-bonding to modulate the emission modes of highly photoluminescent cyclometalated platinum(II) complexes [16].

In recent times we investigated the behavior of luminescent d^{10}-metal compounds, focusing our attention either on zinc(II) derivatives bearing *N,N*-bidentate imidazo-pyridine ligands [17,18] or on trigonal heteroleptic silver(I) complexes [19]. In particular, in the latter case it was possible to modulate the emission

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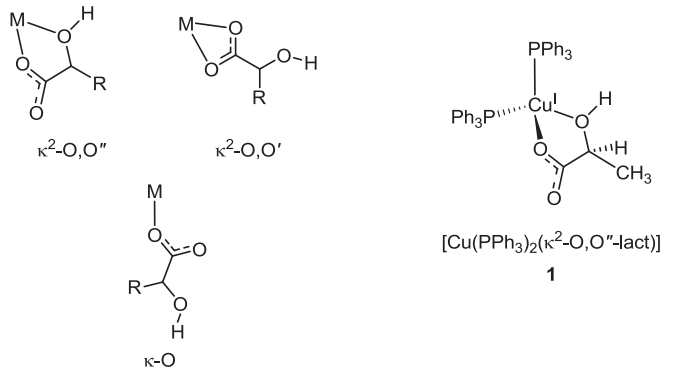

Fig. 1. Left: three possible coordination modes for monoanionic α-hydroxycarboxylates. Right: molecular structure of compound [Cu(PPh_3)$_2$(κ^2-O,O″-lact)] (**1**) (lact = L-(+)-lactate) with the α-hydroxycarboxylate anion coordinated as κ^2-O,O″.

color of the compounds by varying the electronic property of the phosphorous ligand. Continuing on this investigation, in the present work we synthesized a new mixed ligand copper(I) complex, [Cu(PPh_3)$_2$(κ^2-O,O″-lact)] (**1**) (lact = L-(+)-lactate) (Fig. 1) which showed phosphorescence in the solid state. X-ray diffraction analysis revealed how the α-hydroxycarboxylate ligand, coordinated to copper in the κ^2-O,O″ mode, is involved in intermolecular hydrogen bonds whose arrangement (strongly dependent on the solvent used in the crystallization process) affects the emissive properties of **1**.

2. Materials and methods

2.1. General remarks

All reactions involving copper(I) species were carried out under purified nitrogen using standard Schlenk techniques. Solvents were dried and distilled according to standard procedures prior to use. NMR spectra were recorded with an AVANCE 400 Bruker spectrometer at 400 MHz for ^{1}H NMR and 162 MHz for ^{31}P{^{1}H} NMR. Chemical shifts are given as δ values in ppm relative to residual solvent peaks as the internal reference (for ^{1}H NMR) and to external H_3PO_4 (85%) (for ^{31}P NMR). *J* values are given in Hz. Elemental analyses were obtained with a Perkin-Elmer CHN Analyzer 2400 Series II. Infrared Spectra were acquired on a Shimadzu Prestige-21 spectrophotometer with a 1 cm^{-1} resolution. Thermogravimetric analyses (TGA) were performed in a N_2 stream on a Netzsch STA 409 PC Luxx (heating rate 10 °C/min). The excitation and emission spectra were measured using a fluorescence spectrometer (Edinburgh Instrument FS5) equipped with a 150 W continuous Xenon lamp as a light source and were corrected for the wavelength response of the instrument; lifetime measurements were performed on the same FS5 Edinburgh Instrument equipped with a LLS-365 Ocean Optics LED Light Source (wavelength 365 nm; FWHM 9 nm; power 1 mW) as the pulsed source. Analysis of the lifetime decay curve was performed using Fluoracle® Software package (Ver. 1.9.1) which runs the FS5 Edinburgh Instrument. Absolute fluorescence quantum yields were determined on a Photon Technologies International QuantaMaster QM-40 spectrometer (equipped with Xe arc lamp, 70 W) using a PhotoMed GmbH K-Sphere Integrating Sphere (3.2 inch. diameter). $Cu(OH)_2$ was prepared according to literature methods [20]; all other chemicals were of reagent grade quality, were purchased commercially (Aldrich, TCI Chemicals) and used as received.

2.2. Synthesis of [Cu(κ^2-O,O″-lact)$_2$(H_2O)$_2$]·0.5H_2O

In a 250 mL flask, 5.0 mL (59.95 mmol) of L-(+)-lactic acid (90% m/m water solution, *d* = 1.20 g/mL) were slowly dropped into a suspension of $Cu(OH)_2$ (2.44 g, 25 mmol) in 100 mL of ethanol. The resulting light blue suspension was stirred at room temperature for 3 days, monitoring the progress of the reaction with a solubility test in water (diversely from $Cu(OH)_2$, the final product is completely soluble in water). After complete neutralization of Cu $(OH)_2$, the suspension was filtered and the solid was washed with ethanol (50 mL) and diethylether (50 mL). Yield: 6.09 g (85%). IR (Nujol, ν/cm^{-1}): 3472 br (OH), 1652 s, 1601 s, 1573 s. *Anal.* Calc. for $C_6H_{15}CuO_{8.5}$ requires: C, 25.13; H, 5.27. Found: C, 25.42; H, 5.06.

2.3. Synthesis of [Cu(PPh_3)$_2$(κ^2-O,O″-lact)] (**1**)

In a two-necked 100 mL flask, 2.9 g (11.06 mmol) of PPh_3 were suspended in 30 mL of deoxygenated ethanol, and the suspension was heated at gentle reflux to favor the complete dissolution of PPh_3. Then, a solution of [Cu(κ^2-O,O″-lact)$_2$(H_2O)$_2$]·0.5H_2O in deoxygenated water (prepared by dissolving 1 g, 3.49 mmol, of Cu(II) precursor in 4 mL of water) was slowly added and the suspension was heated at reflux for 5 h. This led to the formation of a clear, colorless solution, which was evaporated to dryness. The white residue was suspended in deoxygenated diethylether (40 mL), and the solid was filtered, thoroughly washed with diethylether and dried in vacuo. The copper(I) product is highly stable in the solid state, and can be stored under air. Yield: 2.12 g (90%). IR (Nujol, ν/cm^{-1}): 2608br (OH), 1589 s. *Anal.* Calc. for $C_{39}H_{35}CuO_3P_2$ requires: C, 69.17; H, 5.21. Found: C, 68.84; H, 5.30. ^{1}H NMR (400 MHz, CD_2Cl_2/D_2O 25 °C): δ = 1.28 (d, $J_{H,H}$ = 6.8 Hz, 3H, CH_3), 4.02 (q, $J_{H,H}$ = 6.8 Hz, 1H, *CH*), 7.28–7.44 (m, 30H, ArH). ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): 21.11 (CH_3), 67.71 (*CH*), 128.68 (d, J_{PC} = 9.8 Hz, Ar-CH^{meta}), 130.02 (Ar-CH^{para}), 132.45 (d, J_{PC} = 31.5 Hz, Ar-C^{ispo}), 133.74 (d, J_{PC} = 14.9 Hz, Ar-CH^{ortho}) (it was not possible to identify the NMR signal of the two quaternary carbons). ^{31}P NMR (162 MHz, CD_2Cl_2, 25 °C): δ = −2.61.

2.4. Synthesis of [Cu(PPh_3)$_2$(κ^2-O,O″-lact-D)] (***1-D***)

Compound [Cu(PPh_3)$_2$(κ^2-O,O″-lact)] (**1**) (0.100 g, 0.148 mmol) was suspended in dry CH_3CN in the presence of D_2O (0.5 mL), and the suspension was stirred at room temperature overnight. Then, the solid was filtered off, dried in vacuo and stored under a constant flow of nitrogen.

2.5. Single-crystal X-ray structure analysis

Crystals of complex **1** were obtained either by slow diffusion of hexane into a saturated dichloromethane solution of **1**, or by slowly cooling to room temperature a hot saturated methanol solution of **1**. The crystals were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo Kα graphite monochromated radiation (λ = 0.71073 Å) with ϕ range 0–200°. The structures were solved by direct methods using the program SHELXS-97, while the refinement and all further calculations were carried out using SHELXL-97 [21]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. In both structures, the solvent molecules were highly disordered and could not be modeled. Nevertheless, the less problematic structure was solved (crystal obtained from the diffusion of

hexane) and the data were sent to the Cambridge structural database. Fig. 3 was drawn with ORTEP [22].

2.6. Computational details

All calculations were carried out at the density functional (DFT) level of theory with the ADF2017.106 program package [23]. C, H, O and P atoms were described through AUG/TZ2P basis sets [triple-ζ Slater-type orbitals (STOs) plus two polarization function and diffuse functions]; the QZ4P basis set (quadruple-ζ STO plus four polarization functions) was used for the Cu atoms. TD-DFT calculations were performed on the [Cu(PPh_3)$_2$(κ^2-O,O″-lact)] complex built up from its X-ray structure employing the dispersion-corrected PBE functional PBE-D [24].

3. Results and discussion

3.1. Syntheses

Compound [Cu(PPh_3)$_2$(κ^2-O,O″-lact)] (lact = L-(+)-lactate) (**1**) was synthesized in a two-steps procedure. First, the copper(II) precursor [Cu(κ^2-O,O″-lact)$_2$(H_2O)$_2$]·0.5H_2O was prepared by an acid-base reaction between Cu(OH)$_2$ and L-(+)-lactic acid (90% m/m water solution). The water content in copper(II) α-hydroxycarboxylate species can vary according to the procedure used [25]. The exact amount of water in our sample was determined both by elemental and thermogravimetric (TGA) analyses: in particular, the TGA plot of [Cu(κ^2-O,O″-lact)$_2$(H_2O)$_2$]·0.5H_2O (Fig. S1) was characterized by a loss of 14.93% weight around 100 °C, to be compared with a theoretical loss of 15.70%. The presence of two coordinated water molecules in the lattice was postulated according to previous studies on Cu(II)-lactate derivatives [20–25,5,3,26,27]. Then, [Cu(κ^2-O,O″-lact)$_2$(H_2O)$_2$]·0.5H_2O was reacted with 3-fold excess of PPh_3, in boiling ethanol, to give the title compound [Cu(PPh_3)$_2$(κ^2-O,O″-lact)] (**1**) as a white, crystalline solid.

The infrared spectrum of **1** (Fig. S2) is characterized by a sharp band at 1097 cm^{-1} due to bound PPh_3 and intense stretching frequencies at 1589 cm^{-1} (ν_{asymm} COO) and 1434 cm^{-1} (ν_{symm} COO) assigned to the lactate. The difference between symmetric and antisymmetric carboxylate stretchings ($\Delta\nu \approx 150$ cm^{-1}) is in accordance with the lactate κ^2-coordinated via COO and OH [2]. The broad, medium band at 2607 cm^{-1} can be related to the presence of OH groups of lactate ions involved in strong O–H···O hydrogen bonds. This feature was confirmed by isotopic substitution: indeed, [Cu(PPh_3)$_2$(κ^2-O,O″-lact)] was treated with D_2O in CD_3CN and converted in the corresponding deuterated compound [Cu(PPh_3)$_2$(κ^2-O,O″-lact-D)] (**1-D**), which as expected showed in its infrared spectrum (Fig. S3) a broad and large band at lower frequencies (2143 cm^{-1}, $\nu_{O\text{-}D}$).

3.2. NMR study

The ^{1}H, ^{13}C and ^{31}P{^{1}H} NMR spectra of complex **1** recorded in CD_2Cl_2 are reported in the Supporting Information (Figs. S4–S8). At room temperature, the ^{1}H NMR spectrum (Fig. S4) shows the signals of lactate to be centered respectively at 1.28 (*CH*$_3$) and 4.02 ppm (*CH*) and to appear as broad, unresolved singlets (Fig. 2a). Such a shape suggests a fluxional behavior for the lactate anion, maybe related to a transitory dissociation of O1, followed by a rotation along the central C–C bond (Fig. 2b). This fluxionality is minimized on lowering the temperature, with the expected doublet (*CH*$_3$, ^3J = 6.8 Hz) and quartet (*CH*, ^3J = 6.8 Hz) appearing at −30 °C (Fig. 2a), while on further lowering the temperature (down to −70 °C) no relevant changes are noticed in the ^{1}H NMR spectrum. Worthy of note, the couplings among aliphatic protons emerge also after addition of D_2O to a CD_2Cl_2 solution of **1**, at room temperature (Fig. 2a). In this case, deuteration leads to the generation of O–D···O interactions (Fig. 2c) which lower the fluxional exchange rate below the NMR time scale, thus allowing the detection of the couplings. The ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) exhibits a singlet resonance at −2.61 ppm (Fig. S7), which does not change at lower temperatures.

3.3. X-ray structural investigation

When hexane is layered on a saturated dichloromethane solution of compound [Cu(PPh_3)$_2$(κ^2-O,O″-lact)] (**1**), the latter crystallizes in the monoclinic space group C_2 (see Table 1 and Fig. 3). Differently from what was observed in the analogous silver(I) derivative [Ag(PPh_3)$_2$(κ^2-O,O′-lact)] [28], where the lactate anion is chelated via the carboxylate group only, here the α-hydroxycarboxylate is coordinated as κ^2-O,O″ via the hydroxyl group and a carboxylate oxygen atom. Consequently, in compound **1** the tetrahedral geometry of copper is composed of two phosphorus atoms from two PPh_3 and two oxygen atoms from lactate. Cu–P and Cu–O bond lengths are in accordance with those reported for tetrahedral Cu(PPh_3)$_2$(O,OH) species [29] (Cu–P1 = 2.244(3), Cu–P2 = 2.228(2), Cu–O1 = 2.051(6) and Cu–O3 = 2.106(6) Å). The

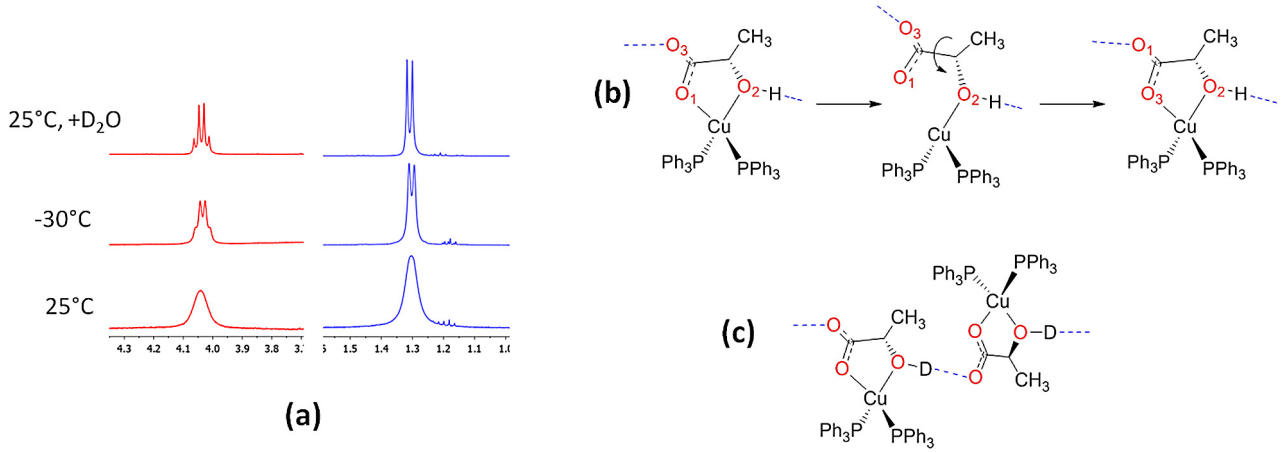

Fig. 2. a) Effect of temperature and D_2O addition on the ^{1}H NMR spectrum of [Cu(PPh_3)$_2$(κ^2-O,O″-lact)] (**1**) recorded in CD_2Cl_2 (25 °C): red, *CH*; blue, *CH*$_3$. b) Proposed fluxional behavior of lactate in compound **1**, in solution. Blue dotted lines designate H-bonding. c) O–D···O interactions in **1-D**. (Colour online.)

Table 1
Crystallographic and structure refinement parameters for compound **1**·0.5 hexane.

	1·0.5 hexane
Chemical formula	$C_{39}H_{35}CuO_3P_2$·0.5 C_6H_{14}
Formula weight	713.18
Crystal system	monoclinic
Space group	*C* 2 (no. 5)
Crystal color and shape	Blue block
Crystal size	0.23 × 0.19 × 0.18
a (Å)	24.792(2)
b (Å)	9.7840(6)
c (Å)	16.1674(13)
α (°)	90
β (°)	113.252(6)
γ (°)	90
V (Å^3)	3603.2(5)
Z	4
T (K)	173(2)
D_{calc} (g cm^{-3})	1.315
μ (mm^{-1})	0.733
Scan range (°)	1.77 < θ < 29.31
Unique reflections	9721
Observed reflections [I > 2σ(I)]	4958
R_{int}	0.2438
Final *R* indices [$I > 2\sigma(I)$]*	0.1014, wR_2 0.0997
R indices (all data)	0.1971, wR_2 0.1176
Goodness-of-fit (GOF)	1.007
Maximum, minimum $\Delta\rho/e$ (Å^{-3})	1.285, −0.662

*Structures were refined on F_0^2: $wR_2 = [\Sigma[w\ (F_0^2 - F_c^2)^2]/\Sigma w\ (F_0^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$.

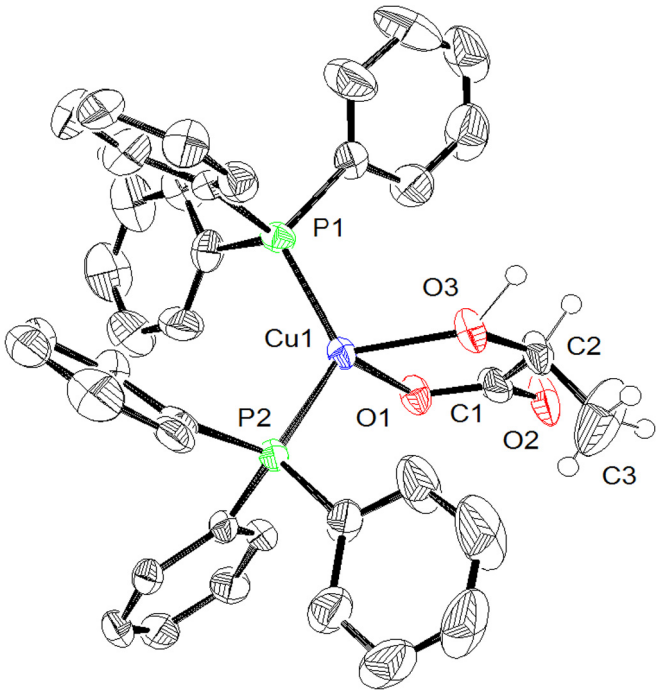

Fig. 3. Molecular structure of [Cu(PPh$_3$)$_2$(κ^2-O,O‘)] (**1**) at 50% probability level. Selected bond lengths (Å) and angles (°): Cu1–P1 2.244(3), Cu1–P2 2.228(2), Cu1–O1 2.051(6), Cu1–O3 = 2.106(6); P1–Cu1–P2 123.89(9), O1–Cu1–O3 79.7(2), P1–Cu1–O1, 109.8(2), P1–Cu1–O3 111.2(2), P2–Cu1–O1 112.9(2), P2–Cu1–O3 110.7(2). Hydrogen atoms of the PPh$_3$ ligands and the hexane molecule were omitted for clarity.

tetrahedral angles around the Cu atom range from 109.84° (O1–Cu–P1) to 123.89° (P1–Cu–P2), with a calculated τ_4 index [30] close to unity (τ_4 = 0.87), as expected for a tetrahedral geometry (the two largest angles α and β used to calculate τ_4 being P1–Cu–P2, 123.9° and P2–Cu–O1, 112.9°). The κ^2-O,O″-coordination of lactate leads to a bite angle of 79.7(2)° (O1–Cu–O3), with the corresponding planar five-membered ring composed by Cu–O1–C1–C2–O3 atoms (root-mean-square deviation of the five atoms from an ideal plane is 0.0285).

One relevant characteristic of the solid state structure of compound **1**·0.5 hexane is the extended network of intermolecular hydrogen bonds generated by the lactate anions (Fig. 4). Indeed, each hydroxyl group acts as H-bonding donor towards the non-bonded (to copper) oxygen atom of the carboxylate moiety of a vicinal molecule, with a O–H···O(CO) distance of 2.56 Å. In the catemeric structure generated by these H-bonding it is possible to identify a dimer, with the two copper atoms pointing towards opposite directions, as a sort of recurring motif (Fig. 4, green circle).

Interestingly, we could demonstrate that the O–H···O(CO) network is altered when [Cu(PPh$_3$)$_2$(κ^2-O,O″)] (**1**) is crystallized in the presence of polar, protic solvents such as methanol. Indeed, by slowly cooling to room temperature a hot, saturated solution of **1** in methanol, the title compound crystallizes in the space group $P2_1$ as a disordered CH_3OH/H_2O solvate. Again, the lactate anion is κ^2-O,O″ bound to the metal center, which then shows a similar P_2O_2 tetrahedral environment (Fig. S8). Bond distances and angles around the copper atoms are almost identical to those found in **1**·0.5 hexane.

The replacement of hexane by methanol/water in the crystal packing of **1** modifies the H-bonding network. Besides the O–H···O(CO) interaction encountered in [Cu(PPh$_3$)$_2$(κ^2-O,O″)]·0.5 hexane (Fig. 4), a second network involving methanol and water molecules is observed, leading to the formation of a new arrangement of intermolecular hydrogen bonds, where dimers of [Cu(PPh$_3$)$_2$(κ^2-O,O″)] units linked by O–H···OC(O) interactions (green dotted circle in Fig. 5) are connected through a methanol/water system where the two solvents act both as H-bonding donor and acceptor moieties. As will be discussed later (Section 3.4), we believe that the generation of different H-bonding networks is responsible for the phosphorescent emission behavior of complex **1** in the solid state.

3.4. Phosphorescent behavior

Compound [Cu(PPh$_3$)$_2$(κ^2-O,O″-lact)] (**1**) shows interesting luminescent properties which strongly depend on the H-bonding network built-up by the lactate anion. Fig. 6 reports the excitation and emission spectra of **1** in the solid state: complex **1** is characterized by a broad and unstructured emission in the blue region when irradiated with UV light, with λ_{max} centered at 468 nm when λ_{exc} = 370 nm. A moderate absolute quantum yield of 0.14 was measured for **1** in the solid state. Notably, these features are identical when measurements are performed either on bulk **1** or on grinded crystals of the hexane solvate.

The time-resolved luminescence behavior of the copper complex is described by a mono-exponential decay with τ = 1.6 μs (Fig. S9), thus suggesting a phosphorescent emission from a triplet excited state. TD-DFT calculations were used to get insight on the nature of the main electronic transitions involved. The calculated UV spectrum of compound **1** is in good accordance with the experimental trace recorded in the solid state (Fig. S10). Analysis of the main electronic transitions (with oscillator strength >0.1) shows that the dominant electronic transfer (>98% transition density) in compound **1** arises from a filled Natural Transition Orbital (NTO) localized on copper and the lactate anion to an empty NTO orbital which has a complete PPh$_3$ contribution (Fig. 7). Hence, the main transition has a mixed metal-ligand to ligand charge transfer (MMLLCT) character, as known for other mixed ligand metal complexes [31–33].

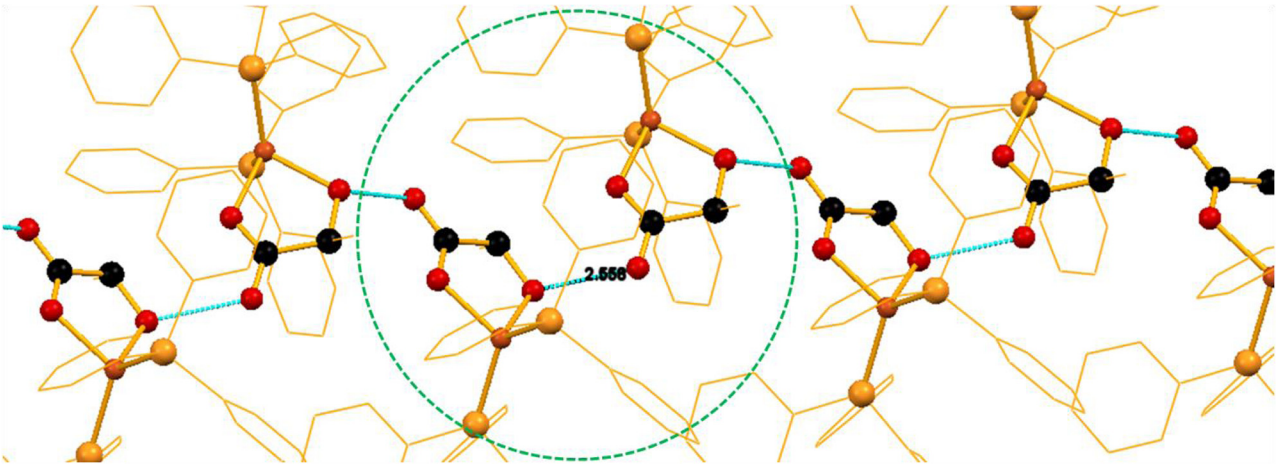

Fig. 4. Catemeric network of intermolecular hydrogen bonds in the molecular structure of **1**·0.5 hexane. The green dotted line highlights dimer of [Cu(PPh_3)$_2$(κ^2-O,O“-lact)] units linked by a O–H···OC(O) interaction (light blue dotted line). Color code: red, oxygen; light brown, copper; grey, carbon; orange, phosphorus. (Colour online.)

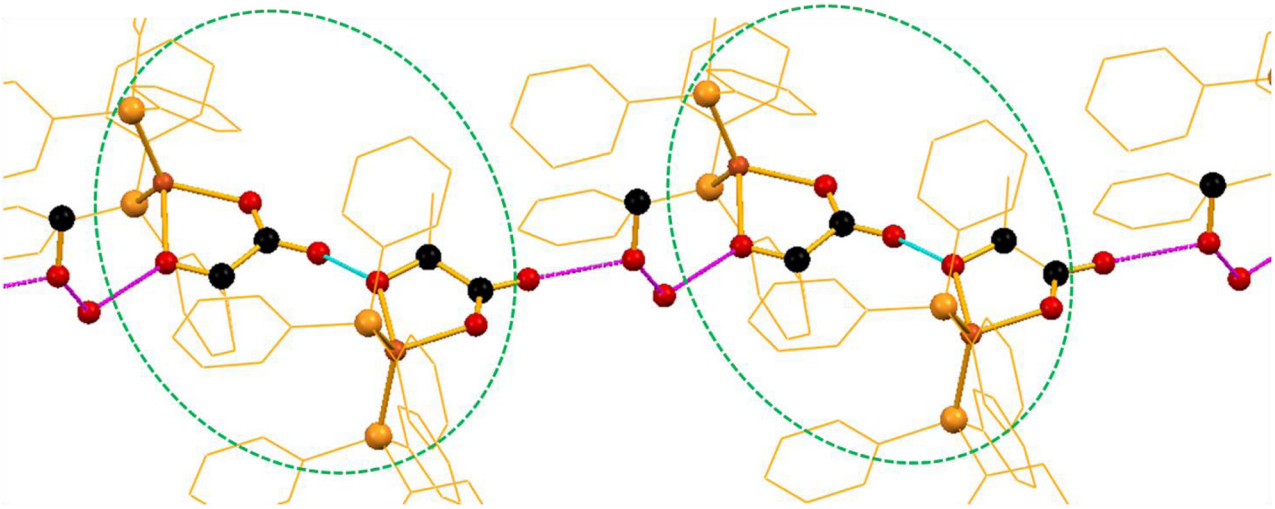

Fig. 5. Network of intermolecular hydrogen bonds in the molecular structure of **1**·CH_3OH·H_2O. The green dotted line highlights dimer of [Cu(PPh_3)$_2$(κ^2-O,O“-lact)] units linked by O–H···OC(O) interactions (light blue dotted line), connected through a second H-bonding network (magenta dotted lines) generated by methanol and water. Color code: red, oxygen; light brown, copper; grey, carbon; orange, phosphorus. (Colour online.)

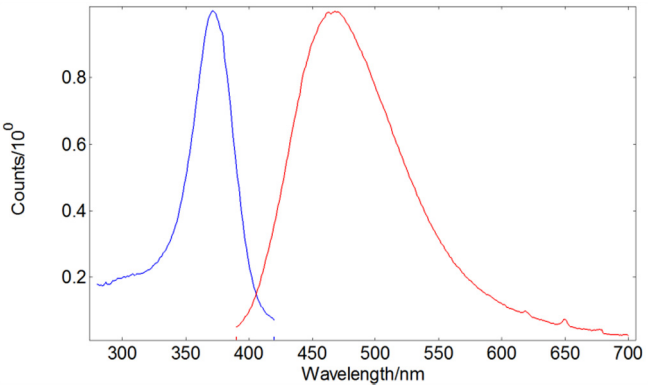

Fig. 6. Normalized excitation (blue line) and emission (red line) spectra of compound [Cu(PPh_3)$_2$(κ^2-O,O“-lact)] (**1**) in the solid state. (Colour online.)

As said, the blue emission of [Cu(PPh_3)$_2$(κ^2-O,O″-lact)] is not maintained in solution: indeed, a dichloromethane solution of **1** does not show any luminescent emission. A possible dissociation of a PPh_3 molecule, leading to a different non-emissive species, is reasonably excluded on the basis of the $^{31}P\{^1H\}$ NMR investigation (see text), since the shape and position of the single ^{31}P resonance observed does not change at low temperatures. Furthermore, also the addition of PPh_3 (one equivalent) to solution of **1** in CH_2Cl_2 (in order to repress a potential dissociation equilibrium) does not cause significant variations. Then, the lack of emission in solution noticed for **1** can be attributed to the above mentioned fluxional behavior of the lactate anion in [Cu(PPh_3)$_2$(κ^2-O,O″-lact)] (see NMR discussion), which weakens the O–H···O(CO) hydrogen bonds network, thus somehow extinguishing the phosphorescent emission of **1** in solution. Additionally, when the solvent is removed from the dichloromethane solution of **1**, and solid [Cu(PPh_3)$_2$(κ^2-O,O″-lact)] is recovered, the original phosphorescence is restored. A further proof of our hypothesis is represented by the absence of any luminescent emission in compounds [Cu(PPh_3)$_2$(κ^2-O,O″-lact-D)] (**1-D**) and [Cu(PPh_3)$_2$(κ^2-O,O″-lact)]·CH_3OH·H_2O (**1**·CH_3OH·H_2O), at the solid state. In these cases, either the isotopic substitution in **1-D** or the presence of methanol and water in the crystal lattice of **1**·CH_3OH·H_2O, alters the original O–H···O(CO) H-bonding network of **1** and again the phosphorescent emission is lost.

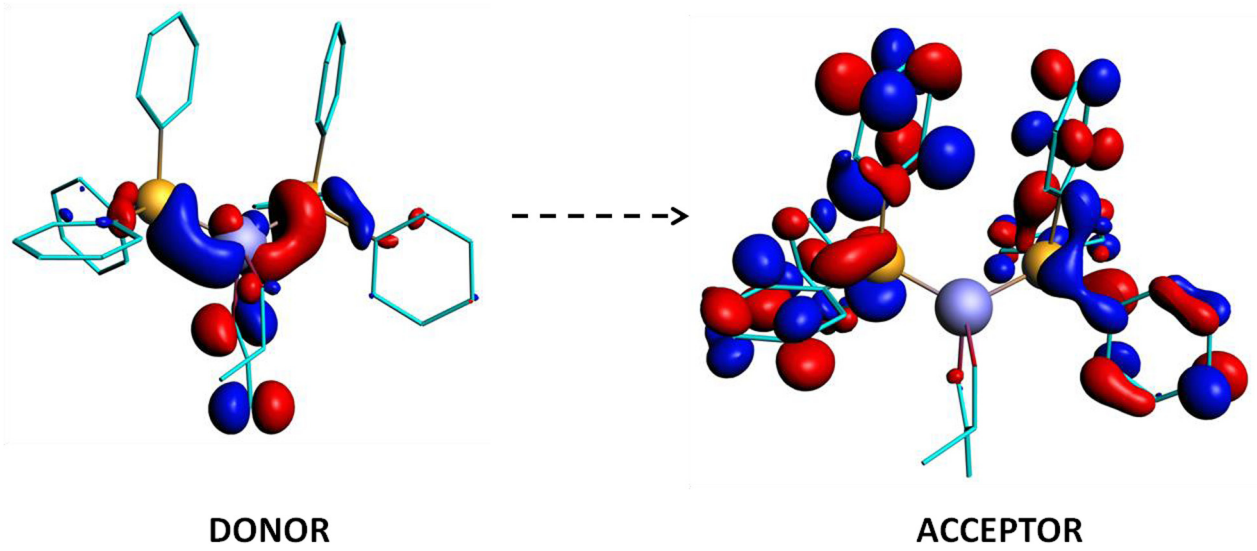

Fig. 7. Dominant Natural Transition Orbitals pair of the principal electronic transition in complex **1**, which accounts for about >98% of the transition density. Left: donor orbital primarily localized on the copper center and the lactate group. Right: acceptor orbital localized on PPh_3 ligands.

4. Conclusions

In this work, we presented the synthesis of a mixed ligand phosphorescent copper(I) complex, where both the α-hydroxycarboxylate anion and the ancillary phosphines play a role in determining the photophysical properties of the title compound. X-ray crystal structure analysis revealed that the hydroxyl and the carboxylate groups of the κ^2-O,O″-bound lactate build up a O–H···O (CO) hydrogen bonds network. Interestingly, when the compound is crystallized in the presence of methanol, the protic solvent (together with a water molecule) enters the lattice and alters the O–H···O(CO) network, increasing the probability of non-radiative processes and thus quenching the phosphorescence. TD-DFT calculations identified the principal electronic transition responsible for the emission of our compound as a MMLLCT, originating from a donor orbital localized on the copper center and the lactate group to an acceptor orbital localized on PPh_3 ligands. These results enlarge the scenario of luminescent metal complexes whose emissive properties are tuned by intermolecular hydrogen bonds generated in the solid state.

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Appendix A. Supplementary data

CCDC 1575333 contains the supplementary crystallographic data for **1**·0.5 hexane. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.poly.2017.10.025.

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