A new five-coordinated $Cu^{I}P_{2}NO_{2}$ system: XRD structure of 6-acetyl-1,3,7-trimethyl-pteridine-2,4(1*H*,3*H*)-dione and its Cu(I) (N⁵,O⁶¹,O⁴)-tridentate complex with triphenylphosphine. An AIM study of the nature of metal–ligand bonds[†]

Francisco Hueso-Ureña,^a Sonia B. Jiménez-Pulido,^a Maria P. Fernández-Liencres,^b Manuel Fernández-Gómez^b and Miguel N. Moreno-Carretero^{*a}

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The second example of a five-coordinated Cu¹P₂NO₂ system, [Cu(DLMAceM)(PPh₃)₂]ClO₄ (DLMAceM = 6-acetyl-1,3,7-trimethyl-pteridine-2,4(1*H*,3*H*)-dione), is reported. The structural characterization of both the DLMAceM ligand and the Cu(1) compound has been achieved by IR, ¹³C and ¹H NMR and XRD methods. The metal is coordinated to the PPh₃ molecules (Cu–P 2.224(2) and 2.258(2) Å) and the pyrazine N(5) atom (Cu–N(5) 2.058(6) Å) in a trigonal planar arrangement; two additional semi-coordinated atoms (Cu ··· O(4) 2.479(5) and Cu ··· O(61) 2.559(5) Å) can be observed, forming an intermediate SP/TBP polyhedron. To define the nature of the metal–ligand bonds for the Cu(1) compound, especially in regards to the semi-coordinated oxygen atoms, a topological analysis of the electron density ρ_b within the framework provided by the quantum theory of atoms in a molecule (QTAIM) using Hartree–Fock and DFT(B3LYP) levels of theory has been performed. Five bond critical points (BCP) have been found, whose associated bond paths connect the Cu metal with the atoms P(1), P(2), O(4) O(61) and N(5). The type of interaction between the Cu and ligand binding sites has been characterized in terms of the Laplacian of the electron density, $\nabla^2 \rho_b$, the total energy density, H_b , and the delocalization index, δ_{AB} .

Introduction

Lumazines (2,4-dioxo-(1H,3H)-pteridines) are biologically relevant heterocycles that occur as natural products e.g. in the biosynthesis of the flavin co-enzymes.^{1,2} The binding of metal complex fragments to these heterocycles usually occurs through the O(4)–N(5) chelating sites.³ This coordination produces a fivemembered ring containing an unsaturated π -carbonylimino function, which can act as a π -acceptor towards a bound π -electron rich metal center such as rhenium(I). Low-valent metal compounds, including $[Re(CO)_3Cl(DML)]$ (DML = 1,3-dimethyllumazine) have been reported.⁴ Upon trying to extend the coordinative properties of lumazine, the six position of the pyrazine ring has been functionalized with an acetyl group to give the title ligand (DLMAceM), however, there are not any examples where this substituent is involved in the coordination, but it has been reported in the complex [Re(CO)₃Cl(DMLAceM)].⁵ In the present work, we describe the structure of the DLMAceM itself and its fivecoordinated complex with the $Cu(PPh_3)_2^+$ moiety. It should be noted that five-coordinated Cu(I) complexes are very rare,6-8 in contrast with the Cu(II) five-coordinated complexes and, to our knowledge (search of the CCDC database), only one similar $Cu^{I}P_{2}NO_{2}$ coordinating system has been previously reported by Kaim *et al.*⁹ in the Cu^I complex with 2',7',9'-trimethylester of pyrroloquinoline-quinone. As in this example, the geometrical arrangement of the organic ligand DLMAceM in the title complex allows us to suggest the establishment of Cu–O interactions longer than 2.48 Å, cited many times within the literature. This also allows us to describe, in an ambiguous and qualitative fashion, semi-coordination.¹⁰ To know whether the atoms at such long distances are linked by a true chemical bond, the second part of this work has been devoted to the characterization of, by means of theoretical calculations, the nature of these long metal-ligand interactions.

Experimental

Synthesis

Synthesis of DLMAceM. 6-acetyl-1,3,7-trimethyllumazine was obtained by reacting 6-amino-1,3-dimethyl-5-nitrosouracil with acetylacetone following reported methods.¹¹ The yellow prismatic crystals, suitable for XRD, were isolated by slow evaporation of the filtrate solution. Yield = 90%. Analytical data (%): found C 53.33, H 4.83, N 22.50; calcd for C₁₁H₁₂N₄O₃ C 53.22, H 4.87, N 22.57. IR data/cm⁻¹: v(C–H) 3065 w, 3000 w, 2963 w, v(C=O) 1725 m, (C61=O) 1694 s, (C2=O) 1679 s, (C4=O), v(C=N) 1599 s, 1559 s, v(C=C) + v(C–N) 1494 m, 1455 m, 1288 m. ¹³C NMR data (δ /ppm, TMS): 198.9 (C61), 159.0 (C4), 157.9 (C7),

^aDepartamento Química Inorgánica y Orgánica, Universidad de Jaén, Campus Las Lagunillas B3, 23071 Jaén, Spain. E-mail: mmoreno@ujaen.es; Fax: +34 953 211 876; Tel: +34 953 212 738

^bDepartamento Química Física y Analítica, Universidad de Jaén, Campus Las Lagunillas B3, 23071 Jaén, Spain

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Synthesis of [Cu(DLMAceM)(PPh₃)₂]ClO₄. Yellow-reddish crystals of [Cu(DLMAceM)(PPh₃)₂]ClO₄, suitable for XRD analysis, were isolated after refluxing 0.5 mmol DLMAceM, 0.5 mmol Cu(ClO₄)₂·6H₂O and 0.5 mmol PPh₃ in EtOH (50 mL) for several hours. (CAUTION! Perchlorate salts are explosive and must be handled carefully.) Yield = 31%. Analytical data (%): found C 59.99, H 4.40, N 5.75; calcd for C₄₇H₄₂ClCuN₄O₇P₂ C 60.32, H 4.52, N 5.99. IR data/cm⁻¹: v(C–H) 3054 w, 3004 w, 2955 w, v(C=O) 1717 m (C61=O), 1693 s (C2=O), 1661 s (C4=O), v(C=N) 1574 s, 1547 s, v(C=C) + v(C–N) 1481 m, 1435 m, 1291 m, perchlorate bands 1093 s, 623 m, PPh₃ bands 750 m, 694 s, 520 m. ¹³C and ¹H NMR spectra are virtually coincident with those of the free ligand and also show signals from PPh₃.

Apparatus

C, H and N microanalyses were performed on a Fisons EA1108 apparatus. IR spectra were measured using a Perkin-Elmer FT-IR 1760-X (KBr pellets, 4000–400 cm⁻¹) and a FT-IR Bruker Vector-22 spectrophotometer (polyethylene pellets, 600–220 cm⁻¹). ¹H and ¹³C NMR spectra were recorded using a Bruker DPX-300 apparatus (DMSO-d₆ solutions).

Crystallographic studies

Both structures were solved by direct methods and refined using SHELXL97 program¹² inside the WinGX package¹³ employing full-matrix least-squares methods on F^2 . All non H atoms were refined anisotropically and the hydrogen atoms were placed in calculated ideal positions following riding models. All calculations and graphics were carried out with PLATON.¹⁴

X-Ray crystal structure data for DLMAceM. $C_{11}H_{12}N_4O_3$, $M_r = 248.24 \text{ g mol}^{-1}$, monoclinic, space group $P2_1/c$, unit cell parameters a = 16.030(2), b = 4.4861(6), c = 15.7288(9) Å, $\beta =$ 97.716(8)°, V = 1120.9(2) Å³, T = 293 K, Z = 4; $D_{calcd} = 1.471$ Mg m⁻³, F(000) = 520, yellow prisms ($0.27 \times 0.20 \times 0.13 \text{ mm}^3$), $\mu =$ 0.111 mm^{-1} ; θ range $= 3.0-27.5^\circ$, -20 < h < 20, -5 < k < 5, -20 < l < 20, 25969 measured reflections, 2575 independent, 1802 with $I > 2\sigma(I)$ used in the refinement ($R_{int} = 0.047$). The data were collected using a Bruker-Nonius KappaCCD apparatus with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). Lorentz polarization and multi-scan absorption corrections were applied with SADABS.¹⁵ Weighting scheme w⁻¹ = $\sigma^2(F_o^2) +$ (0.0617P)² + 1.1017P, where $P = 1/3(F_o^2 + 2F_c^2)$. Final R and wR [$I > 2\sigma(I)$] were 0.0548 and 0.1300, data-to-parameter ratio = 15.8, GOF = 1.039, max. and min. $\Delta\rho$ were 0.440 and -0.249 e Å⁻³.

X-Ray crystal structure data for [Cu(DLMAceM)(PPh₃)₂]ClO₄. $C_{47}H_{42}ClCuN_4O_7P_2, M_r = 935.78 \text{ g mol}^{-1}$, monoclinic, space group *Cc*, unit cell parameters a = 10.3034(7), b = 27.145(1), c = 15.387(1) Å, $\beta = 94.071(7)^{\circ}$, V = 4292.9(5) Å³, T = 293 K, Z = 4, $D_{caled} = 1.448$ Mg m⁻³, F(000) = 1936, yellow-reddish prisms (0.56 × 0.32 × 0.19 mm³), $\mu = 0.704$ mm⁻¹, θ range = $3.0-27.5^{\circ}$, -13 < h < 13, -35 < k < 35, -19 < l < 19, 29.259 measured reflections, 9678 independent, 5316 with $I > 2\sigma(I)$ used in the refinement ($R_{int} = 0.076$). The data were collected using a Bruker-Nonius KappaCCD apparatus with graphitemonochromated MoK α radiation ($\lambda = 0.71073$ Å). Lorentz polarization and multi-scan absorption corrections were applied with SADABS.¹⁵ Weighting scheme w⁻¹ = $\sigma^2(F_o^2)$ + (0.1210*P*)², where $P = 1/3(F_o^2 + 2F_c^2)$. Final *R* and w*R* [$I > 2\sigma(I)$] were 0.0717 and 0.1701, data-to-parameter ratio = 17.6, GOF = 1.049, max. and min. $\Delta\rho$ were 0.851 and -0.847 e Å⁻³. Flack parameter = 0.01(2).

Computational details

In order to get the electron wave function to be used in the QTAIM topological analysis of the Cu-ligand bonds, we used the X-ray crystal structure as the initial point to optimize by using Gaussian0316 running on an ia64HP server rx 2600. We performed two optimizations at the DFT/B3LYP17-19 level using the well-known Pople's basis set $6-31 + G^{*20}$ first, and then the SDDall²¹ basis sets, which uses the Dunning-Huzinaga D95V basis set for all atoms up to Ar and applies Stuttgart pseudo potentials on Cu, N, P, C and O atoms. Within the isolated molecule approximation, the optimization arrives at a Cu–O(6) distance noticeably shortened (ca. 0.3 Å) when compared with the initial value, while for the remaining Cu-X distances, the attained final values keep on the same order than the experimental values. This points out that solid-state effects are strong enough to make the isolated molecule approximation invalid. This is the main reason, along with computational limitations, why we decided to obtain the electron wave function from a single point calculation on the experimental X-ray crystal structure. Thus, topological properties were obtained from the electron wave function at DFT/B3LYP with the standard $6-311 + G(2d,2p)^{21}$ and HF/6-311 + G(d,p)^{21} basis sets as levels of calculations from the X-Ray data, using the program AIM2000.²² An integration of the atomic properties over the atomic basins have been performed in natural coordinates, with a tolerance of 10^{-4} per integration step. The radius of the beta sphere used for the integration of the atomic properties was at the default value of 0.5 a.u.

Results and discussion

Crystallographic work

The molecular structure of DLMAceM is displayed in Fig. 1. The free-metal pteridine moiety is almost planar (dihedral angle between pyrimidine and pyrazine mean planes, $1.5(1)^{\circ}$) and is angled with the mean plane of the acetyl substituent (C(6)–C(61)– C(62)–O(61)) by 12.9(1)°. In the crystal structure, the molecules are arranged as columns along the b axis with the pteridine planes parallel to each other and roughly perpendicular to the [311] direction. The columns are built through a partial π -stacking interaction between the pyrimidine and the pyrazine rings of consecutive pteridines (Fig. 2) with the centroids of adjacent rings separated by 3.543(1) Å with α , β , and γ angles, calculated with PLATON, of 1.5, 19.0 and 18.5°, respectively. The slippage between both rings is ca. 1.1 Å and the ring-plane overlap are is ca. 45%.23 Also, the analysis with PLATON indicates the existence of $\sigma \cdots \pi$ -ring interactions (Y–X \cdots Cg) contributing to the stabilization of the crystal structure: $C(2)-O(2)\cdots$ pyrimidine (x, y + 1, z) and C(61)-O(61)...pyrazine (x, y - 1, z), with



Fig. 1 ORTEP plot with labelling scheme for 6-acetyl-1,3,7-trimethyllumazine (DLMAceM) (ellipsoids at 50% probability).



Fig. 2 View along the [203] direction for the $O(2) \cdots$ pyrimidine \cdots pyrazine $\cdots O(61)$ column-like intermolecular arrangement in the crystal structure of DLMAceM. Hydrogen atoms are omitted for clarity.

 $X \cdots Cg$ distances of 3.260(2) and 3.188(2) Å and $Y-X \cdots Cg$ angles of 100.3(1) and 89.9(1)°, respectively. The unit cell contains no residual solvent-accessible voids.

The structure of $[Cu(DLMAceM)(PPh_3)_2]ClO_4$ consists of isolated $[Cu(DLMAceM)(PPh_3)_2]^+$ cations (Fig. 3) and uncoordinated and disordered perchlorate anions. With the relative arrangement of the acetyl group and the pteridine moiety (N(5)– C(6)–C(61)–O(61) torsion, 166.5(2)°), the free DLMAceM is not able to act as a tridentate ligand through the O(4), N(5) and O(61) atoms; however, the energy difference between the metalfree conformation and the Cu(1)-coordinated conformation (N(5)– C(6)–C(61)–O(61) torsion, 32(1)°), in which the acetyl mean plane is turned off by 128.0° around the C(6)–C(61) bond, is not large



Fig. 3 View of the cationic unit $[Cu(DLMAceM)(PPh_3)_2]^*$, displaying atom numbering (ellipsoids at 50% probability). Bond distances (Å) and angles (°) around the metal: Cu–P(1) = 2.224(2), Cu–P(2) = 2.258(2), Cu–N(5) = 2.058(6), Cu ··· O(4) = 2.479(5), Cu ··· O(61) = 2.559(5), P(1)–Cu–P(2) = 131.38(7), P(2)–Cu–N(5) = 106.7(2), N(5)–Cu–P(1) = 121.9(2), O(4) ··· Cu ··· O(61) = 143.4(2), O(4) ··· Cu–P(1) = 103.4(1), O(4) ··· Cu–P(2) = 91.3(1), O(4) ··· Cu–N(5) = 74.1(2), O(61) ··· Cu–P(1) = 88.0(1), O(61) ··· Cu–P(2) = 107.1(1), O(61) ··· Cu–N(5) = 70.5(2).

enough (43.3 kJ mol⁻¹, RHF-PM3) to avoid the formation of M– L bonds, despite the steric hindrances between the C(62) and C(71) methyl groups. In addition to the rearrangement of the acetyl group, the geometry of coordinated DLMAceM exhibits only minor differences with the metal-free structure one. The most important changes are the opening of the C(7)–C(6)–C(61) angle (4.9°) and the consequent closing of N(5)–C(6)–C(61) (2.1°) and N(5)–C(6)–C(7) (2.9°), due to the above-cited rearrangement of the acetyl substituent.

Due to the steric requirements of the Cu(I) complex (Fig. 3), both rings of the pteridine moiety are slightly angled $(7.0(3)^{\circ})$. The two five-membered chelates are also angled to each other by $11.3(3)^{\circ}$. They are not planar and their shape, following the Cremer and Pople's ring puckering analysis,²⁴ can be described as half-chair-twisted on N(5)–Cu (Cu–N(5)–C(4A)–C(4)–O(4), $\phi =$ 165.2 and k = 4.09) and an envelope on C(61) (Cu-N(5)-C(6)-C(61)–O(61), $\phi = 253.5$ and k = 7.04). The metal is trigonalplanar three-coordinated with atoms P(1), P(2) and N(5). The metal center lies only slightly out of the plane defined by the three donor atoms (0.032 Å) and despite bond angles around the metal deviating a little from the ideal value (120°) , their sum is 360°. The lumazine ligand is arranged in a roughly perpendicular fashion (80.6°) to the above mentioned trigonal plane, the metal ion lying 0.455 Å out of this plane. In this plane, there are two additional and very long Cu · · · O(4) and Cu · · · O(61) (2.479(5) and 2.559(5) Å, respectively), which define an intermediate TBP/SP-shaped polyhedron (Fig. 4), whereas the Addison's τ criterion²⁵ describes the polyhedron as a distorted square-pyramid ($\tau = 0.2$, apical atom N(5)), Muetterties and Guggenberger's calculations²⁶ show that the polyhedron is best described as a distorted trigonal-bipyramid $(\Delta = 0.2)$ with an P(1)/P(2)/N(5) equatorial plane and a skewed



Fig. 4 A detailed view of the metallic coordination environment, showing the *quasi*-planar O(4)–P(1)–N(5)–O(61) face (dihedral angle over the P(1)-N(5) edge, 157.5°).

O(61)–Cu–O(4) axis due to the restricted *bite* of the tridentate DLMAceM. The disappointment can be easily explained by the different points of view of both calculation methods. Whereas Addison's τ is based only on the two bigger bond angles over the metal without taking into account the steric array of the donor atoms, Muetterties and Guggenberger's Δ describes the external shape of the polyhedron from the relative position of the donor atoms and, consequently, the dihedral angles between the contiguous faces, without considering the position of the metal inside the polyhedron. A similar contradiction on evaluating the coordination polyhedron shape has been previously reported.⁹

Despite the geometrical data of the previously reported Cu¹P₂NO₂ coordination environment⁹ is very similar to those of the Cu(I) title compound, a closer analysis indicates that the last one shows slightly more unsymmetrical PPh_3 groups with a P(2)atom occupying a somewhat more apical position than P(1), thus, the difference between both Cu-P bond lengths in the title complex (0.034 Å) is higher than those reported by Kaim⁹ (0.014 Å). In addition to this, whereas the exocyclic carbonyl Cu-O distances are similar (2.559(5) and 2.579(4) Å), the endocyclic distances are quite different (2.479(5) and 2.254(4) Å), the very weak O(4)-DLMAceM semi-coordinative behaviour being in accord with previously reported results for analogous lumazine derivatives.^{27,28} On the other hand, a comparison between the structure of the Cu(I) title compound with the previously reported Re(I)-DLMAceM complex,⁵ in which the exocyclic O61 carbonylic oxygen is not coordinated, indicates a great difference in the N(5)-C(6)-C(61)-O(61) torsion (Re(I) complex $106(1)^\circ$, Cu(I) complex $32(1)^\circ$), the steric coupling of the acetyl group with the fac-tricarbonyl ligands over the Re(I) being the main reason of the uncoordination.

The analysis of the short ring interactions in the crystal structure does not indicate the existence of any significant π -stacking interactions. Only the interaction between both pyrimidine and pyrazine rings from DLMAceM and the U phenyl ring from PPh₃ could be cited, but despite distances between the centroids (3.616(4) and 3.867(4) Å), which lie within the range accepted for these interactions (3.4–4.6 Å),²³ the interplanar dihedral angles α (12.2 and 12.6°, respectively) clearly show both rings of each couple are far to be parallel enough to consider the existence of π -stacking.²³ The unit cell contains no residual solvent-accessible voids.

Topological analysis

The structure of Cu(DLMAceM)(PPh₃)₂]⁺ displays values of 2.224(2) and 2.258(2) Å for Cu–P and 2.058(6) Å for Cu–N bonds, respectively, while Cu–O distances are in the range 2.479(5)–2.559(5) Å. Thus, we can formulate doubt about the covalent nature of bonds as long as 2.56 Å. Although the bonding in transition metal complexes is usually rationalized upon an extended molecular orbital scheme, an alternative description that uses local topological analysis of the electron density can be used to get a deeper insight into this matter. The quantum theory of atoms in molecules, developed by Bader,^{29,30} which is widely recognized for its utility in the analysis of chemical bonding, provides such a scheme wherein electron density ρ_b , Laplacian $\nabla^2 \rho_b$, density of the total energy H_b at the bond critical point (BCP) as well as delocalization index δ , are searched for.

Critical points (CP) of the charge distribution are classified by their rank and sign analyzing the Hessian matrix of ρ_b . Accordingly, four kinds of CP can be characterized. Those with three non-zero eigenvalues λ_i , two of them negative $(\lambda_1, y, \lambda_2)$ and the remaining positive (λ_3) are named bond critical points (3, -1). The first two eigenvalues λ_i , (i = 1, 2) measure the curvature of ρ_b along the interatomic surface and the latter eigenvalue provides curvature along the atomic interaction line. Thus, a covalent bond is characterized by the charge density exhibiting two large negative curvature along the bond at the position of the (3,-1) critical point. At the BCP, the gradient of the density vanished, $\nabla \rho_b = 0$ and the sum of the three λ_i yields the Laplacian, $\nabla^2 \rho_b$.

The type of pairwise atomic interactions is characterized by the sign of the Laplacian of the electron density at the BCP. If electrons are locally concentrated in the BCP ($\nabla^2 \rho_b < 0$), the electron density is shared then by both nuclei (pure covalent shared-shared interaction). Otherwise, the electrons are concentrated in each of the atomic basins separately ($abla^2
ho_{
m b} > 0$) and the interaction belongs to the closed-shell type (partially covalent shared-closed interaction; the closed-closed one is of a van der Waals or ionic nature).³¹ In this latter case, the difference between them is the sign of $H_{\rm b}$, which is positive for the closed-closed interaction and negative for the other. Several studies³²⁻³⁴ have shown that bonds involving metals present characteristics associated with closedshell type interactions: $\rho_{\rm b}$ is small, λ_3 dominates and $\nabla^2 \rho_{\rm b}$ is positive, while $H_{\rm b}$ is negative and close to zero, showing, therefore, features typical of ionic (ρ_b and $\nabla^2 \rho_b$) and covalent (H_b) bonds. Bianchi et al.³⁴ have proposed a set of indicators, related to the mentioned topological parameters, enabling an assignment in terms of the different subclasses of the shared and closed-shell interactions, thus the metal-ligand interactions can be classified as intermediate between ionic and covalent bonds and they are included as belonging to closed-shell type interactions.

Although the presence of a bond path provides a universal indicator of bonding, the criteria based solely on electron density, however, look too restrictive for the large variety of bonds found in transition metal compounds.³⁵ Thus, the delocalization index $\delta(A \cdots B)$ seems to be a more sensitive probe at this aim. According to Fradera *et al.*,³⁶ the delocalization index, defined as

	11,1711	p_b/c_A	V pre A	U _{AB}	G _b / hartiee A	V _b / hartice A	H_b / flattiee A
HF/6–311 + G(p,d)							
$Cu \cdots O(4)$	2.480	0.0259	0.1059	0.131	0.0294	-0.0323	-0.0029
$Cu \cdots O(61)$	2.559	0.0217	0.0878	0.106	0.0236	-0.0252	-0.0016
$Cu \cdots P(1)$	2.257	0.0821	0.1994	0.616	0.0766	-0.1033	-0.0267
$Cu \cdots P(2)$	2.244	0.0872	0.2154	0.582	0.0830	-0.1121	-0.0291
$Cu \cdots N(5)$	2.058	0.0718	0.3879	0.346	0.1066	-0.1163	-0.0097
B3LYP/6-311 + G(20	d,2p)						
$\overline{\mathrm{Cu}\cdots\mathrm{O}(4)}$	2.480	0.0286	0.0979	0.174	0.0279	-0.0313	-0.0034
$Cu \cdots O(61)$	2.559	0.0243	0.0822	0.145	0.0224	-0.0243	-0.0019
$Cu \cdots P(1)$	2.257	0.0838	0.1425	0.690	0.0667	-0.0978	-0.0311
$Cu \cdots P(2)$	2.244	0.0890	0.1546	0.733	0.0723	-0.1059	-0.0336
$Cu \cdots N(5)$	2.058	0.0762	0.3276	0.444	0.0980	-0.1141	-0.0161

 $\label{eq:constraint} \textbf{Table 1} \quad \textbf{Bond lengths and topological properties of the electron density at the critical points of Cu-ligand bonds in the cation [Cu(DLMAceM)(PPh_3)_2]^+ (Cu(DLMAceM)(PPh_3)_2)^+ (Cu(DLMACeM)(PPh_3)_3)^+ (Cu(DLMACeM)(PPh_3)_3)^+ (Cu(DLMACeM$



Fig. 5 Molecular graph determined by the topology of the electron density in the planes containing Cu centers and the donor atoms. Positions of the bond CPs are denoted by the cross.

 $\delta_{ij} = 2(N_j N_k - N_{jk})$ (N_i being the numbers of electrons in a particular atomic basin and N_{ij} being the number of the electron pairs involved in two atomic basins), turns out to be the covalent bond order when a single-determined wave function is used, as is the case.³⁷ Large values of $\delta(A \cdots B)$ are indicative of electron shared interactions while low $\delta(A \cdots B)$ values characterize closed-shell interactions.

The molecular graph for the Cu complex reproduces the bond path corresponding to the Cu–P(1), Cu–P(2), Cu–O(4), Cu–O(61) and Cu–N(5) bonds (see Fig. 5). The results of the topological analysis are given in Table 1. The bond critical points along Cu–X (X = N, O, P) bonds are characterized by a low ρ_b and a positive Laplacian, which indicates a weakly closed-shell interactions, while the energy density, H_b , which is the sum of the kinetic and potential energies at the critical point, is slightly negative, indicating a bond that is weakly covalent. All this, as well as small values for the delocalization index, point out that the bonding involving Cu is more of a partially covalent shared–closed interaction type, regardless of the atom that Cu is linked to. The delocalization indices computed from the HF wave function are slightly smaller than those obtained from B3LYP as Poater *et al.*³⁸ already pointed out, indicating a slightly enhanced covalency of DFT as compared to HE.³⁹ As can be seen, the magnitude of $H_{\rm b}$ parallels the increase in the values of $\rho_{\rm b}$ and $\nabla^2 \rho_{\rm b}$. The delocalization index for bonded interactions also increases along with the values of $\rho_{\rm b}$.

The charge densities at the Cu–P BCPs, as for those in other cases,⁴⁰ have a reverse trend with respect to the corresponding bond distance, are close to zero (0.085 e Å⁻³ average) and their Laplacian are small and positive (0.2 and 0.15 e Å⁻³ average with HF and B3LYP methods, respectively). The charge densities at the Cu–O BCPs are also small, although lower than those calculated for Cu–P, and their Laplacian values are positive and even smaller (*ca.* 50% average) than those for Cu–P bonds, indicating that they are dative bonds.³⁴ Thus, in other words, it could be stated that the Cu–O bond is weaker and more polarized than the Cu–P bond. By virtue of the *G*_b and $|V_b|$ values of the Cu–P bonds, which are almost comparable, $|V_b|$ prevailing, the resulting energy densities *H*_b have small negative values. On the other hand, the

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 δ (Cu–O) indices are lower than the δ (Cu–P) values and this is related to the higher covalent character of the Cu–P bonds *versus* the Cu–O interactions, with the Cu–N interaction being intermediate between both.

Conclusions

The structure of the second example of a five-coordinated $Cu^{I}P_2NO_2$ system, [Cu(DLMAceM)(PPh_3)_2]ClO_4 (DLMAceM = 6-acetyl-1,3,7-trimethyl-pteridine-2,4(1*H*,3*H*)-dione), is reported. The metal is coordinated to the PPh₃ molecules and the pyrazine N(5) atom in a trigonal planar arrangement and long-distanced interactions (> 2.48 Å) with two semi-coordinated oxygen atoms can be observed, designing an intermediate SP/TBP polyhedron.

The nature of the metal-ligand bonds, especially in regards to the semi-coordinated oxygen atoms, has been defined using topological analysis of the electron density ρ_b within the framework provided by the quantum theory of atoms in molecules (QTAIM). The results point out that the Cu–X (X = N, O, P) bonds are characterized by a low ρ_b and a positive Laplacian, which indicates a weakly closed-shell interaction, while H_b is slightly negative, indicating a bond that is weakly covalent. All this, as well as small delocalization index values, point out that bonding involving copper is more of a partially covalent shared–closed interaction type, regardless of the atom to which Cu is linked.

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