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Orange and Yellow Crystals of Copper(I) Complexes Bearing 8-(Diphenylphosphino)quinoline: A Pair of Distortion Isomers of an Intrinsic Tetrahedral Complex

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Supporting Information

ABSTRACT: The tetrafluoroborate salt of bis{8-(diphenylphosphino)quinoline}copper(I), $[Cu(Ph_2Pqn)_2]BF_4$, afforded orange prismatic (**2O**) or yellow columnar (**2Y**) crystals, dependent on the solvent and concentration of the recrystallization solution used. X-ray analysis revealed that crystals of **2O** and **2Y** had the same composition and exhibited different crystal systems: **2O** was triclinic, with space group $P\overline{1}$ and $Z = 2$, and **2Y** was monoclinic with space group $P2_1/c$ and $Z = 4$. In these crystals, the tetrahedral copper(I) complex exhibited a strong "rocking distortion" toward a trigonal pyramidal coordination geometry (by a slide translation of one of the unsymmetrical bidentate chelating ligands along the tetrahedral edge). In addition, both the **2O** and **2Y** complexes showed a "flattening distortion", meaning that the dihedral angle between the two chelate planes were off-perpendicular and oriented toward opposite directions, which resulted in a pair of distortion isomers: *syn* clinal (*sc*: **2O**) and *anti* clinal (*ac*: **2Y**). ^{31}P CP-MAS NMR spectroscopy indicated that **2O** and **2Y** could be distinguished. Both isomers exhibited inequivalent P atoms, but a larger difference in chemical shift was observed in **2Y**. TD-DFT calculations reproduced the difference in spectra between the orange- and yellow-colored complexes, which originated from metal-to-ligand charge-transfer transitions.

INTRODUCTION

Stereochemical isomerism is the most fundamental and most interesting phenomenon that occurs in coordination chemistry, and a large number of geometrical isomeric pairs of transition-metal complexes have been prepared.[1] The differences in the structure and properties between such isomers have been compared. In the case of four-coordinate square-planar complexes with an unsymmetrical bidentate ligand, (*SP*-4)-[M(A—B)$_2$], a pair of geometrical (*cis* and *trans*) isomers can occur, but both isomers would be achiral (see Scheme 1). In contrast, tetrahedral complexes of (*T*-4)-[M(A—B)$_2$] would be chiral (i.e., *P* and *M* enantiomers would be formed). When (*T*-4)-[M(A—B)$_2$] is distorted toward a planar geometry (i.e., a flattening distortion occurs), there would be two different modes, affording a pair of "distortion isomers". These would be termed *syn* clinal (*sc*) and *anti* clinal (*ac*) isomers, using the nomenclature used for organic compounds[2] (see Scheme 1). This situation is similar to that of square-planar complexes with *cis* (*syn* periplanar, *sp*) or *trans* (*anti* periplanar, *ap*) geometry, where a tetrahedral (skewing) distortion of the coordination plane makes the complex chiral (to give *P* and *M* enantiomers). In previous studies,[3,4] we have prepared and characterized square-planar Ni^{II} and Pd^{II} complexes containing 8-quinolylphosphines (R_2Pqn, where $R_2 = Ph_2$, Me_2, or MePh). At first glance, these complexes should assume a square-planar coordination geometry with a *cis*(*P*,*P*) configuration. However, the coordination plane shows a skewed distortion to some extent, which affords chiral *sp* structures, because of a steric interaction between the *ortho*-H atoms of mutually *cis*-positioned quinolyl groups. In this study, we have investigated the related Cu^{I} complexes with 8-quinolylphosphines, which were envisioned to have an idealized pseudotetrahedral coordination geometry. However, in the case of the Ph_2Pqn complex, we obtained orange- and yellow-colored crystals consisting of one or the other flattened distortion isomers, i.e., the *sc*- or *ac*-isomer. The crystal structure determinations and spectroscopic characterizations of both isomers are reported.

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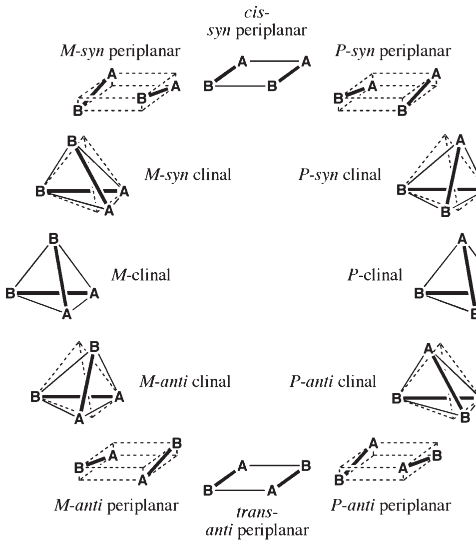
Scheme 1. Nomenclature Used for Distorted Square-Planar and Tetrahedral Complexes



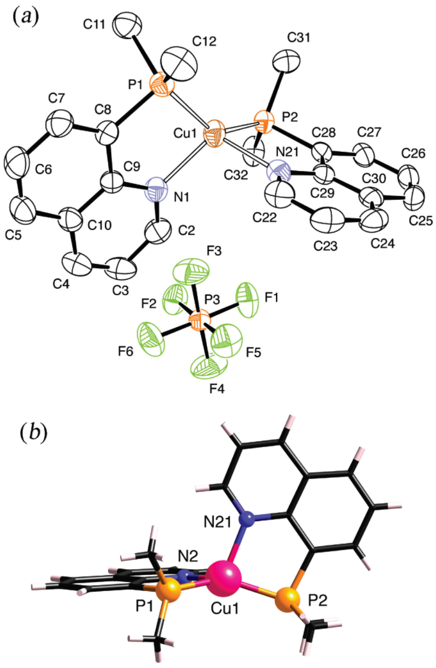


Figure 1. (a) ORTEP view of $[Cu(Me_2Pqn)_2]PF_6$ (**1**); the thermal ellipsoids are drawn at the 50% probability level, and the hydrogen atoms have been omitted for clarity. (b) Schematic drawing of the cation in **1**, emphasizing the rocking distortion of the tetrahedron.

■ RESULTS AND DISCUSSION

Synthesis and Crystal Structure of $[Cu(Me_2Pqn)_2]PF_6$ (1). The reaction of $[Cu(CH_3CN)_4]PF_6$ and 8-(dimethylphosphino)-quinoline in acetonitrile in a molar ratio of 1:2 afforded pale yellow crystals of $[Cu(Me_2Pqn)_2]PF_6$ (**1**) in a near-quantitative yield. Single-crystal X-ray analysis revealed that the molecular structure of **1** is that shown in Figure 1. The ligand, Me_2Pqn, acts as a planar five-membered chelate ligand, with deviations of the Cu1 and P1 atoms from the least-squares plane[qn1] (defined by the N1 and C2−C10 atoms) of only 0.116(4) and 0.038(4) Å, respectively, and those of the Cu1 and P2 atoms from the plane[qn2] (defined by atoms N21 and C22−C30) of 0.095(4) and 0.094(4) Å, respectively. The dihedral angle between the plane [Cu1,P1,N1] (defined by atoms Cu1, P1, and N1) and the plane [qn1] was only 4.77(6)°, and that between the plane [Cu1,P2,N21] and the plane [qn2] was 2.60(7)°. The Cu−P and Cu−N bond lengths are in the range 2.226(2)−2.238(2) and 2.097(3)−2.105(3) Å, respectively, and the P−Cu−N chelate bite angles are 87.3(1)° and 86.9(1)°, which are typically found in other Me_2Pqn complexes.[5] The pseudo-tetrahedral coordination geometry around the Cu atom is not flattened, as the dihedral angle (θ_{Cu}) between plane[Cu1,P1,N1] and plane [Cu1,P2,N21] is 86.29° (the dihedral angle (θ_{qn}) between the two quinoline planes, plane [qn1] vs plane [qn2], is 88.56(9)°), but it exhibits a significant rocking distortion,[6] as emphasized in Figure 1b. The angle between the Cu1−P2 bond and plane[Cu1,P1, N1] (154.3°) is much larger than that between the Cu−N21 bond and plane [Cu1,P1,N1] (119.2°).[7] In addition, the P1−Cu1−P2 bond angle (138.21(6)°) is much larger than the ideal tetrahedral angle, while the N1−Cu1−N21 bond angle (103.4(1)°) is smaller than the ideal tetrahedral angle. This rocking distortion is caused by the intramolecular steric interaction between the $-PMe_2$ groups. In the case of bis(1,10-phenanthroline)-type copper(I) complexes,[6] such a rocking distortion leads to an approximately trigonal pyramidal coordination geometry with an exceptionally long Cu−N(apical) bond. However, in complex **1**, the Cu1−N21(apical) bond length is comparable to that of the Cu1−N1 bond length (see Table S1 in the Supporting Information).

Synthesis and Crystal Structure of $[Cu(Ph_2Pqn)_2]BF_4$ (2). Recently, Tsukuda et al. have reported on the Ph_2Pqn analogue of complex **1**, $[Cu(Ph_2Pqn)_2]PF_6\cdot CH_2Cl_2$ ($\mathbf{2'}\cdot CH_2Cl_2$),[8] independently to our study. They prepared the complex **2′** in a 66% yield from $[Cu(CH_3CN)_4]PF_6$ and Ph_2Pqn and characterized its photophysical properties. They also analyzed the crystal structure of $\mathbf{2'}\cdot CH_2Cl_2$, but did not discuss any distortion of the Cu^I coordination geometry in detail. Similar to complex **1**, no flattening distortion of the idealized pseudo-tetrahedron was observed (θ_{Cu} = 89.46°), but a rocking distortion was shown by the larger angle between the Cu−P(1) bond and plane[Cu,P(2),N(1)] (148.3°) than that between the Cu−N(2) bond and the same plane (124.3°). The P(1)−Cu−P(2) bond angle was 131.12(5)°. These angles indicate that the degree of rocking distortion was smaller in this Ph_2Pqn complex **2′** than that in the corresponding Me_2Pqn complex **1**.

In this study, we investigated the corresponding tetrafluoroborate salt, $[Cu(Ph_2Pqn)_2]BF_4$ (**2**). This compound was similarly obtained from the stoichiometric reaction of Ph_2Pqn and $[Cu(CH_3CN)_4]BF_4$ in a near-quantitative yield. In addition, it could be prepared from the reaction of $Cu(BF_4)_2\cdot 6H_2O$ and Ph_2Pqn in ethanol, albeit with a yield of only ca. 40% after purification by reprecipitation from an ethanol solution after the addition of hexane. Recently, Qin et al. reported on an interesting mixed ligand complex, $[Cu(Ph_2Pqn)(DPEphos)]BF_4$ (where DPEphos = bis[2-(diphenylphosphino)phenyl]ether), which was prepared from a 1:1:1 mixture of $[Cu(CH_3CN)_4]BF_4$, Ph_2Pqn, and DPEphos.[7]

Orange prismatic crystals (**2O**) were deposited when compound **2** was recrystallized from a nitromethane solution or a saturated acetonitrile solution by vapor diffusion of diethyl ether. However, if the concentration of the acetonitrile solution was less than half the saturation value, yellow columnar crystals (**2Y**) were formed (see Figure S1 in the Supporting Information). We could easily separate crystals of **2O** and **2Y** manually under a

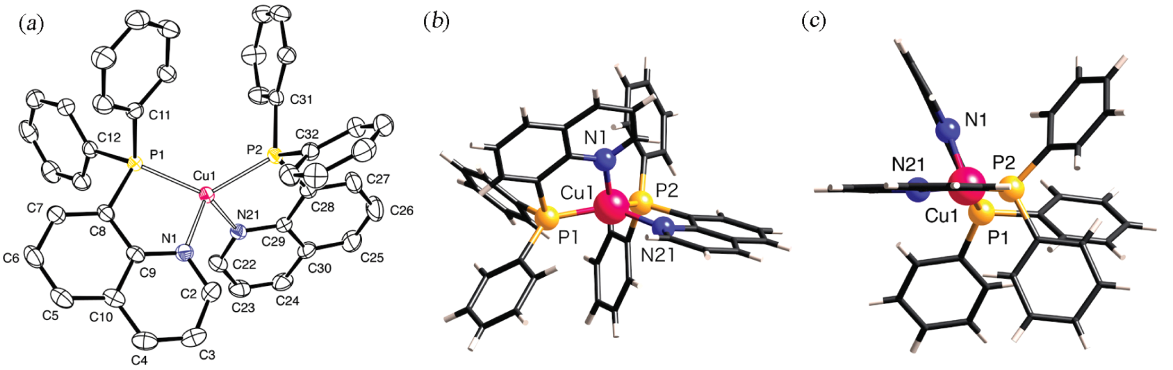


Figure 2. (a) An ORTEP drawing (at the 50% probability level, H atoms omitted) of the cationic complex in the orange prismatic crystals (**2O**) of $[Cu(Ph_2Pqn)_2]BF_4$. (b and c) Schematic views of the cation in **2O**.

microscope. Both crystals had no solvent of crystallization, which was confirmed by elemental analysis, ^{1}H NMR spectroscopy (see Figure S2 in the Supporting Information), and X-ray crystallography (*vide infra*). The UV−vis absorption spectra of acetonitrile solutions of **2O** and **2Y** were identical to each other (see Figure S3 in the Supporting Information). Furthermore, solutions of dissolved **2O** or **2Y** both reproduced crystals of **2O** and **2Y** on recrystallization under suitable conditions (i.e., appropriate solvent and concentration). This observation suggests that crystals of **2O** and **2Y** are polymorphs[9] of $[Cu(Ph_2Pqn)_2]BF_4$, and we succeeded in characterizing both crystal structures using X-ray diffraction.

In the orange crystals of **2O**, the compound crystallizes with a triclinic space group $P\bar{1}$ and $Z = 2$, consisting of a complex cation of $[Cu(Ph_2Pqn)_2]^+$ and a BF_4^- anion in an asymmetric unit. The molecular structure of the complex cation in **2O** is shown in Figure 2. The chelate coordination of Ph_2Pqn is normal, and the P1−Cu1−N1 and P2−Cu1−N21 bite angles are 86.90(5)° and 87.03(5)°, respectively. The five-membered chelate ring is almost planar; the deviations of the Cu1 and P1 atoms from plane[qn1] are 0.256(3) and 0.139(3) Å, respectively; and the deviation of the Cu1 and P2 atoms from plane[qn2] are 0.144(3) and 0.005(3) Å, respectively. Similar to complexes **1** and **2′**, a significant rocking distortion of the pseudo-tetrahedral coordination geometry was observed (see Figure 2b). The angle between the Cu1−P1 bond and plane [Cu,P2,N21] was 154.83°, while the angle between the Co1−N1 bond and the same plane was 125.62°. In addition, the P1−Cu1−P2 bond angle (124.59(2)°) was larger than the ideal tetrahedral angle, while the N1−Cu1−N21 bond angle (97.79(7)°) was much smaller than the tetrahedral angle. The slight elongation of the Cu1−N1 bond, 2.078(2) Å, versus the length of the Cu1−N21 bond, 2.049(2) Å, may be related to this rocking distortion.

Compared with the molecular structure of the complex cation in **2′**, there was a marked additional flattening distortion of the Cu^I coordination geometry in **2O**. The dihedral angle of θ_{Cu} (plane[Cu1,P1,N1] vs plane [Cu1,P2,N21]) was 69.88°, and the angle of θ_{qn} (plane [qn1] vs plane [qn2]) was 63.31(6)°. According to the notation shown in Scheme 1, this complex was assigned as the *sc*-isomer, which is well recognizable when the complex is viewed from the direction parallel to the two quinoline planes (see Figure 2c).

Note that the compound in **2O** is isomorphous with $[Ni(Ph_2Pqn)_2]BF_4$.[3] The Ni^I complex was also assigned as the *sc*-isomer, because the dihedral angle of θ_{Ni} was 57.43° (the dihedral angle of θ_{qn} was 61.06(9)°). In a previous study, we have also characterized the crystal structure of the corresponding Ni^{II} complex, *cis*(*P*,*P*)-$[Ni(Ph_2Pqn)_2](BF_4)_2$, where the dihedral angle of θ_{Ni} was 19.7° (the dihedral angle of θ_{qn} was 35.0(2)°).[3] Therefore, the Ni^{II} complex was assigned as the *sp* (*syn* periplanar) isomer (see Scheme 1).

In the yellow crystals of **2Y**, the compound crystallizes with monoclinic space group $P2_1/c$ and $Z = 4$. Similar to **2O**, crystals of **2Y** also consisted of a complex cation of $[Cu(Ph_2Pqn)_2]^+$ and a BF_4^- anion in an asymmetric unit. The molecular structure of the complex cation in **2Y** is shown in Figure 3. Similar to the complex in **2O** discussed above, a rocking distortion of the pseudo-tetrahedron of Cu^I coordination geometry was observed (see Figure 3b). The angle between the Cu1−P2 bond and plane[Cu, P1,N1] was 150.57°, and the angle between the Co−N21 bond and the same plane was 126.35°. This observation indicates that a rocking distortion is common for Cu^I complexes with 8-quinolylphosphines (**1**, **2′**, **2O**, and **2Y**). Presumably, this arises from the large intramolecular steric interaction between the methyl or phenyl substituents on the P atoms.

The P1−Cu1−P2 bond angle was 137.60(2)°, which is comparable to that observed in complex **1**. However, unlike the other complexes of **1**, **2′**, and **2O**, the N1−Cu1−N21 bond angle was markedly large, at 120.72(6)°. A flattening distortion was observed, but the direction of the distortion was opposite to that observed in **2O**. In **2Y**, the two phosphino donor groups were twisted away from each other (see Figure 3c). The dihedral angle of θ_{Cu} was 101.99° and the dihedral angle of θ_{qn} was 105.23(4)° (the angles of θ_{Cu} and θ_{qn} were defined as 0° and 180° for the *cis* (*sp*) and *trans* (*ap*) isomers, respectively). Thus, the complex cation in **2Y** was assigned as the *ac*-isomer (see Scheme 1), which is the counterpart of the complex observed in **2O** as the pair of "flattening distortion isomers" of the intrinsic tetrahedral complex. The Cu−P bond length in **2Y** was comparable to that in **2O**, while the Cu−N bond lengths, Cu1−N1 (2.064(2) Å) and Cu1−N21 (2.101(2) Å), are slightly longer than those observed in **2O** (by 0.02 Å).

The Cu^I complexes in **2O** and **2Y** are a pair of distortion isomers, but the degrees of their flattening distortion (from an idealized tetrahedron with $\theta = 90°$) are not similar. The distortion of the *sc*-isomer in **2O** ($\theta_{Cu} = 69.88°$) is almost twice that observed for the *ac*-isomer in **2Y** ($\theta_{Cu} = 101.99°$). This fact may be a key factor for understanding the optical properties of these crystals, which will be discussed later on. Moreover, in the crystals of **2Y**, the chelate coordination of one of the Ph_2Pqn ligands is unusual. The Cu1 atom is displaced out of the plane [qn2] by 0.413(2) Å, while the deviation of the P2 atom is only

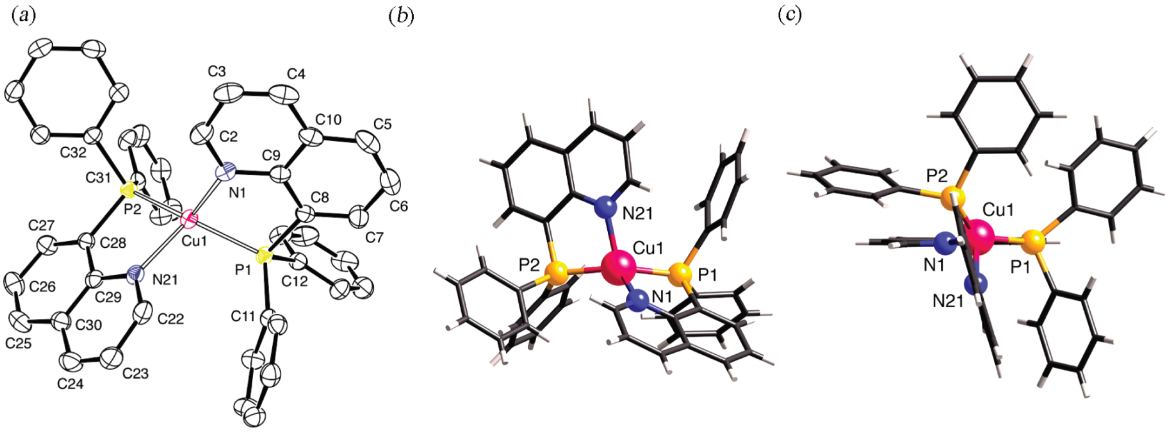


Figure 3. (a) ORTEP drawing (at the 50% probability level, H atoms omitted) of the cationic complex in the yellow columnar crystals (**2Y**) of $[Cu(Ph_2Pqn)_2]BF_4$. (b and c) Schematic views of the cation in **2Y**.

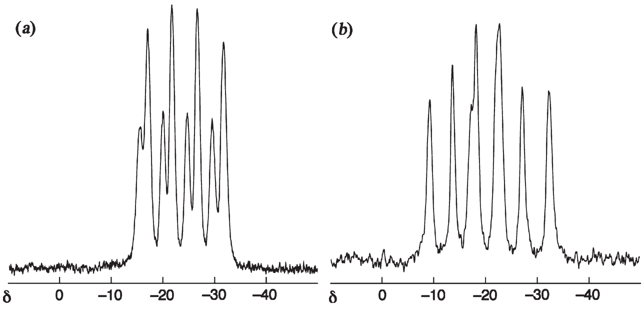


Figure 4. ^{31}P CP-MAS NMR spectra (242.64 MHz, spinning frequency of 25 kHz, 30 °C) of (a) **2O** and (b) **2Y**.

0.006(2) Å, forming an envelope-type five-membered chelate ring. The other Ph_2Pqn chelate in **2Y** is more planar. The deviation of the Cu1 and P1 atoms from the plane[qn1] is 0.247(2) and 0.047(2) Å, respectively. The dihedral angle between plane[Cu1,P2,N21] and plane[qn2] is 15.26(4)°, while the dihedral angle between plane[Cu1,P1,N1] and plane[qn1] is 8.40(4)°. This nonplanarity of one of the Ph_2Pqn chelates may have a significant effect on the inequivalency of the two P nuclei observed using ^{31}P CP-MAS NMR spectroscopy (*vide infra*).

^{31}P CP-MAS NMR Spectra of $[Cu(Ph_2Pqn)_2]BF_4$ (2). The ^{31}P CP-MAS NMR spectra of solid samples of **2O** and **2Y** were measured. In Figure 4, it can be clearly seen (and in Figure S4 in the Supporting Information) that the spectra of **2O** and **2Y** are different from each other. We measured several spectra for each sample, using crystals from different batches, and the results were the same as those shown in Figure 4. In addition to the coupling to a ^{63}Cu or ^{65}Cu nucleus ($I = 3/2$), both spectra showed inequivalency of the two P atoms, which was confirmed using two different spectrometers with different magnetic fields (see Figure S4 in the Supporting Information). Sample **2O** exhibited two quartet resonances at $\delta = -24.3$ ($J_{Cu-P} = 1190$ Hz) and -22.5 ($J_{Cu-P} = 1120$ Hz), while **2Y** exhibited two quartet resonances at $\delta = -25.2$ ($J_{Cu-P} = 1250$ Hz) and -16.2 ($J_{Cu-P} = 1100$ Hz). Our X-ray crystal structure analysis indicated that the Cu^I complexes in **2O** and **2Y** were the flattening distortion isomers. However, the flattening distortion itself cannot cause the two P nuclei in each complex to be inequivalent. For the chemical inequivalency of the two P nuclei, it is necessary to have either a rocking distortion of the Cu^I coordination geometry, or different bonding environments for the two Ph_2Pqn ligands. Our X-ray analysis showed that the degree of rocking distortion in **2O** and **2Y** was similar (*vide supra*). In contrast, one of the two Ph_2Pqn chelates in **2Y** showed a remarkable deviation from planarity. In other words, the inequivalency between the two Ph_2Pqn chelate coordination modes is more pronounced in **2Y**. Thus, the observed inequivalency in the ^{31}P NMR chemical shift can be taken into account by the different crystal structures of **2O** and **2Y**.

Diffuse Reflectance Spectra and TD-DFT Calculations of $[Cu(Ph_2Pqn)_2]BF_4$ (2). The colorimetric difference between **2O** and **2Y** is obvious (see Figure S1 in the Supporting Information), and the diffuse reflectance spectra of powdered samples are compared in Figure 5. The spectrum of **2Y** exhibited an absorption shoulder occurring at ∼360 nm, while the spectrum of **2O** exhibited a stronger skirt on the absorption band, occurring ∼470 nm. We carried out time-dependent density functional theory (TD-DFT) calculations to characterize the differences in the spectra of **2O** and **2Y**. The energy levels of the molecular orbitals used for the complex cations found in **2O** and **2Y** were calculated using the X-ray structures at the density functional theory (DFT) level. The absorption spectra of the complexes were simulated (up to 350 nm, for simplicity), using the excitation energies and oscillator strengths calculated at the TD-DFT level. The absorption bands were assumed to have a Gaussian line-shape function having a full width at half-maximum of 5000 cm^{-1}. The calculated difference in the spectra agreed well with the observed difference (see Figure 5).

In the calculations on both distortion isomers in **2O** and **2Y** (Figure 6), the LUMO (164) and LUMO+1 (165) orbitals were the localized π^* orbital of the quinoline moiety of the Ph_2Pqn ligands, which are, in principle, independent of the distortion of the tetrahedral coordination geometry of Cu^I. In contrast, the HOMO (163), HOMO−1 (162), and HOMO−2 (161) orbitals, which are three M−L σ antibonding orbitals and have their main contribution from the Cu^I d orbitals (the t_2 set in an idealized tetrahedral system), showed a considerable dependence on the flattening distortion. Figure 6b illustrates the exchange of HOMO and HOMO−1 orbitals between the *sc*- and *ac*-isomers (in **2O** and **2Y**, respectively). More importantly, the difference in energy between the HOMO and HOMO−1 orbitals of the *sc*-isomer in **2O** is markedly larger than the difference in energy of the *ac*-isomer in **2Y**. The larger flattening distortion in the *sc* isomer in **2O** would lead to a larger difference in energy between these orbitals. Thus, the HOMO-to-LUMO

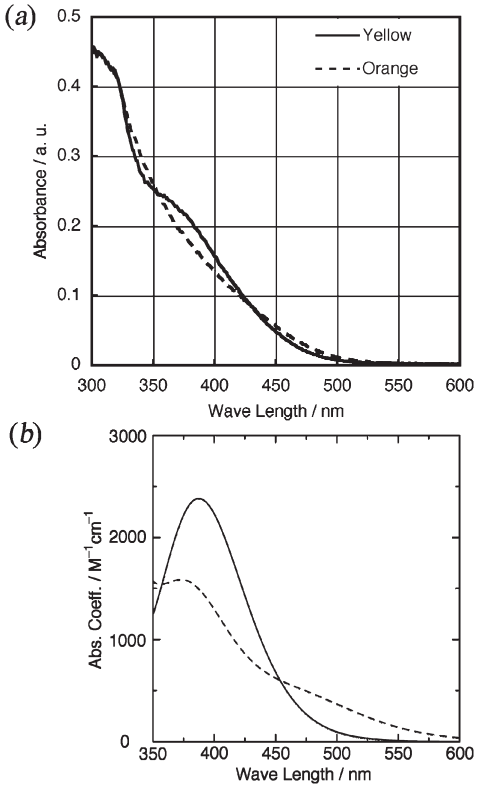


Figure 5. (a) Observed diffuse reflectance spectra in the solid state, and (b) TD-DFT-derived absorption spectra of the orange crystals (**2O**: dashed line) and the yellow crystals (**2Y**: solid line) of $[Cu(Ph_2Pqn)_2]BF_4$.

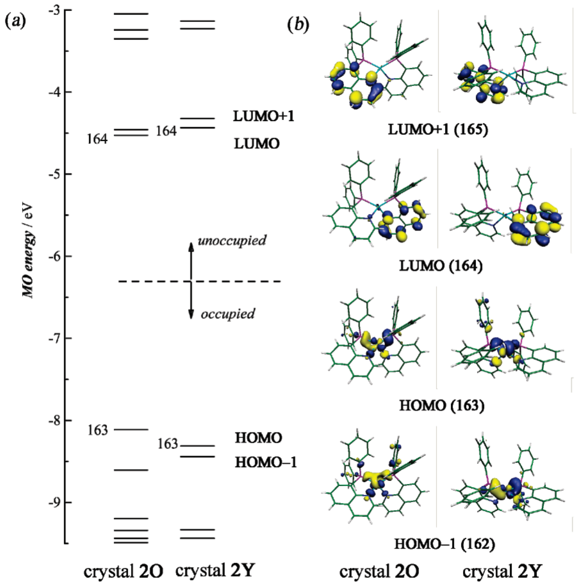


Figure 6. (a) Time-dependent density functional theory (TD-DFT)-derived molecular orbital energy, and (b) illustration of the HOMO−1, HOMO, LUMO, and LUMO+1 orbitals of the cationic complexes in **2O** and **2Y**.

(or LUMO+1) and (HOMO−1)-to-LUMO (or LUMO+1) transitions (and therefore, the metal-to-ligand charge-transfer transitions) of **2O** would occur at ~470 and ~380 nm, while the same transitions in **2Y** were observed to be almost degenerate at ~390 nm (see Figure 5b).

Distortion Isomers and Polymorphs of $[Cu(Ph_2Pqn)_2]BF_4$ (2). The Cu^I complexes in the crystals of **2O** and **2Y** form a pair of distortion isomers, and no interconversion between these isomers was observed in the solid state (at least at ambient temperature). However, as mentioned in the above section, acetonitrile solutions of **2O** and **2Y** exhibited identical UV−vis absorption spectra (see Figure S3 in the Supporting Information), showing two distinct absorption peaks occurring at ~450 nm and ~360 nm. Our ^1H NMR measurements on CD_3CN solutions of **2O** and **2Y** also exhibited identical spectra, corresponding to a single species, which also exhibited an equivalency of the two Ph_2Pqn ligands in solution. These observations can be taken into account by a rapid equilibrium that occurs between the distorted isomers, relative to the NMR time scale. This fact may indicate that crystals of **2O** and **2Y** are *conformational polymorphs*[9] of complex **2**.

Polymorphism, or pseudo-polymorphism, associated with color changes is often observed in transition-metal complexes.[9,10] Polymorphism is found in almost every substance, and it is typically based on the packing forms of the constituent molecules or ions, where weak intermolecular interactions, such as hydrogen bonds, $\pi-\pi$ stacks, and $C-H/\pi$ interactions often play an important role. In typical polymorphs of transition-metal complexes, differences in color between polymorphs are not commonly observed, because the constituent metal complexes have the same geometrical structure.[11] When crystals contain different types and/or numbers of solvent molecules of crystallization, then they are categorized as pseudo-polymorphs, and often exhibit different colors, because the solvent molecules may have an interaction with the metal center or the ligands, inducing a change in the coordination geometry.[4] In the case of a compound having the same composition, but with different constituent units (exhibiting another type of pseudo-polymorphism), the crystals of metal complexes often show a distinct change in color. For example, Reedijk et al. reported that dichlorocopper(II) complexes with long-chain bidentate N−N ligands afforded red crystals consisting of a monomeric $[CuCl_2(N-N)]$ complex and green crystals consisting of a polymeric $[CuCl_2(\mu\text{-}N-N)]_n$ one-dimensional chain-type compound.[12] Green and orange crystals of monomeric and polymeric oxovanadium(IV) complexes containing a tetradentate Schiff base ligand represent another example.[13] Supramolecular isomerism in network solids[14] is also categorized as pseudo-polymorphism.

A notable precedent for conformational polymorphism in transition-metal complexes is a sulfimide copper(II) complex, $[CuCl_2(NHSPh_2)_2]$, exhibiting blue and green crystals.[15] In the blue crystals, the Cu^{II} ion exhibits a perfect square-planar geometry, while a pseudo-tetrahedral coordination geometry is observed in the green crystals. The (trifluoroacetato)(tripyrrinato)palladium(II) complex also shows two different molecular structures in polymorphic crystals, i.e., a helical distortion of the tripyrrin ligand or a pronounced tetrahedral deviation of the Pd^{II} coordination plane (although the colors of these polymorphic crystals are indistinguishable).[16] The present case is another example of a conformational polymorph that consists of a pair of flattening distortion isomers of the intrinsic tetrahedral complex.

In summary, we have isolated a pair of *sc*- and *ac*-isomers of $[Cu^I(A-B)_2]^+$-type complexes, $[Cu(Ph_2Pqn)_2]BF_4$, and their crystal structures have been confirmed from X-ray analyses. Distinguishable properties between the solid-state isomers have been observed in diffuse reflectance and ^{31}P CP-MAS NMR spectra. In solution, these complexes immediately reach equilibrium. However, if a suitable molecular design is provided by the ligand, then each isomer can be produced selectively.

Table 1. Crystallographic Data

abbreviation	1	2O	2Y
compound	$[Cu(Me_2Pqn)_2]PF_6$	$[Cu(Ph_2Pqn)_2]BF_4$	$[Cu(Ph_2Pqn)_2]BF_4$
formula	$C_{22}H_{24}CuF_6N_2P_3$	$C_{42}H_{32}BCuF_4N_2P_2$	$C_{42}H_{32}BCuF_4N_2P_2$
formula weight, FW	586.88	776.99	776.99
temperature, T (K)	200(2)	200(2)	200(2)
color, shape	pale yellow, block	orange, prism	yellow, column
crystal size (mm)	0.20 × 0.20 × 0.12	0.40 × 0.30 × 0.22	0.30 × 0.12 × 0.1
crystal system	monoclinic	triclinic	monoclinic
space group, Z	$P2_1/c$, 4	$P\bar{1}$, 2	$P2_1/c$, 4
a (Å)	9.762(7)	8.6882(5)	10.8254(11)
b (Å)	27.08(2)	12.2070(6)	14.8647(17)
c (Å)	9.651(8)	17.3712(9)	22.025(3)
α (deg)	90	88.981(1)	90
β (deg)	92.42(7)	80.862(2)	99.646(6)
γ (deg)	90	79.761(1)	90
V (Å^3)	2548(4)	1789.9(2)	3494.1(7)
D_x (Mg m^{-3})	1.530	1.442	1.477
F(000)	1192	796	1592
μ(Mo Kα) (mm^{-1})	1.103	0.755	0.773
T_{min}, T_{max}	0.810, 0.898	0.752, 0.851	0.647, 0.927
Refln/param ratio	5855/308	8156/470	8050/469
$R1$ [$F_0^2 > 2\sigma(F_0^2)$]	0.059	0.039	0.035
$wR2$ (all refln)	0.118	0.160	0.062
goodness of fit, GoF	1.001	1.113	0.998

EXPERIMENTAL SECTION

The ligands Me_2Pqn[5b] and Ph_2Pqn[17] were prepared according to literature methods. The phosphines were handled under an atmosphere of nitrogen using the standard Schlenk technique until such time that the air-stable copper(I) complexes were formed. The copper(I) acetonitrile complexes, $[Cu(CH_3CN)_4]BF_4$ and $[Cu(CH_3CN)_4]PF_6$, were synthesized using literature methods.[18]

Preparation of the Complexes. *[Cu(Me$_2$Pqn)$_2$]PF$_6$ (**1**).* To an acetonitrile solution of $[Cu(CH_3CN)_4]PF_6$ (0.52 g, 1.4 mmol), 8-(dimethylphosphino)quinoline (0.56 g, 3.0 mmol) was added dropwise with stirring. After stirring the mixture at room temperature for ca. 1 h, the solvent was removed to dryness under reduced pressure. The resulting yellow residue was recrystallized from an acetonitrile solution by diffusion of diethyl ether vapor, affording pale yellow crystals of **1**. Yield: 0.68 g (83%). Anal. Found: C 44.5, H 4.23, N 4.58%. Calcd. for $C_{22}H_{24}CuF_6N_2P_3$: C 45.0, H 4.12, N 4.77%.

*[Cu(Ph$_2$Pqn)$_2$]BF$_4$ (**2**).* To a refluxing solution of Ph_2Pqn (0.51 g, 1.6 mmol) in ethanol (20 cm^3), an ethanol solution (5 cm^3) of $Cu(BF_4)_2\cdot 6H_2O$ (0.276 g, 0.80 mmol) was added. The color of the mixture immediately turned dark green and then gradually changed to a yellow-orange color upon refluxing for 2 h. After cooling the mixture to ambient temperature, the solution was concentrated (to ca. 5 cm^3) under reduced pressure. The resulting pale yellow precipitate was collected by filtration and recrystallized from a mixture of ethanol and hexane. Yield: 0.229 g (37%). Anal. Found: C 64.5, H 4.06, N 3.57%. Calcd. for $C_{42}H_{32}BCuF_4N_2P_2$: C 64.9, H 4.15, N 3.61%.

*Crystallization of **2O** and **2Y**.* When the above product (**2**) was recrystallized from a saturated acetonitrile solution by vapor diffusion of Et_2O, orange prismatic crystals (**2O**) were deposited. Recrystallization from nitromethane by vapor diffusion of Et_2O also gave orange crystals of **2O**. Yellow columnar crystals (**2Y**) were afforded, together with **2O**, when Et_2O vapor was diffused into an acetonitrile solution of **2** with a concentration less than half that of saturation. Recrystallization from dichloromethane by vapor diffusion of Et_2O gave only yellow needles of **2Y**. Anal. Found for **2O**: C 64.8, H 3.95, N 3.59%. Found for **2Y**: C 63.9, H 4.00, N 3.63%. Calc. for $C_{42}H_{32}BCuF_4N_2P_2$: C 64.9, H 4.15, N 3.61%.

Measurements. The diffuse reflection spectra of solid samples were recorded at room temperature, using a Jasco Model V-550 spectrophotometer using a Jasco Model ISN-470 integration sphere. The solution ^{1}H NMR spectra were measured using a JEOL Model EX-270 spectrometer at 30 °C. The chemical shifts were referenced to the residual signal of CD_3CN, and are reported vs TMS. The ^{31}P CP-MAS NMR spectra were acquired using two spectrometers: (1) a Chemagnetics Model CMX 300 system (121.64 MHz for ^{31}P) at 25 °C with a spinning frequency of 9 kHz, and (2) a Varian Model VNS 600 system (242.64 MHz for ^{31}P) at 30 °C with a spinning frequency of 25 kHz. Ammonium monohydrogenphosphate, $(NH_4)_2HPO_4$, was used as the external standard for the ^{31}P chemical shifts.

Crystallography. The X-ray diffraction data were obtained at −73(2) °C using a Rigaku R-axis rapid imaging plate detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A suitable crystal was mounted with a cryoloop and flash-cooled using a cold nitrogen gas stream. The data were processed using the Process-Auto software package,[19] and the absorption corrections were applied using the empirical method.[20] The structures were solved using the direct method employing the SIR92 software package[21] and refined on F^2 (with all independent reflections) using the SHELXL97 software package.[22] All the nonhydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced at the positions calculated theoretically and treated with riding models. All the calculations were performed using the CrystalStructure software package.[23] The crystal data are shown in Table 1.

DFT Calculations. The energy levels of the molecular orbitals of the copper(I) complexes were calculated using the X-ray structures at the DFT level. The basis functions used in the computations were the Dunning−Hay split-valence double-ζ functions for the C, H, and N atoms (D95) and the Hay−Wadt double-ζ functions with the Los Alamos relativistic effective core potential for heavy atoms (LANL2DZ).[24] The hybrid functional of Perdew, Burke, and Ernzerhof (PBE1PBE) was employed.[25] The absorption spectra of the complexes were simulated using the excitation energies and oscillator strengths calculated at the TD-DFT level. The absorption bands were assumed to have a Gaussian line-shape function, having a full width at half-maximum of 5000 cm^{-1}. All the DFT calculations were performed using the Gaussian 03.D suite.[26] Drawings of the molecular orbitals were made using the Molekel software package.[27]

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** X-ray crystallographic information for all the compounds analyzed in this study (CIF format); tables of selected bond lengths and angles of the complexes, a photograph of crystals **2O** and **2Y**, UV−vis and ^{1}H NMR spectra of complex **2** in solution, and the ^{31}P CP-MAS NMR spectra of **2O** and **2Y** taken using the other spectrometer (PDF) are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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