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Article

Bis-qtpy (qtpy = 2,2′:6′,2′′:6′′,2′′′-quaterpyridine) Metal Complexes, [M(qtpy)₂]²⁺

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Reactions of perchlorates of iron(II), nickel(II), and zinc(II) with 2,2′:6′,2′′:6′′,2′′′-quaterpyridine (qtpy) gave the first crystallographically established bis-qtpy metal complexes of formula [M(qtpy)₂][ClO₄]₂ (M = Fe, Ni, Zn). Coordination of two terdentate quaterpyridines to the same center produces a distorted octahedron of six nitrogen atoms around the metal, leaving two pendant pyridyl groups, one for each quaterpyridine. For the diamagnetic zinc system, an NMR investigation has been carried out in order to establish the conditions to obtain the intermediate mono-qtpy complex, of formula [Zn(qtpy)(H₂O)₂][ClO₄]₂, which has also been crystallographically established. The corresponding hexafluorophosphate derivatives [M(qtpy)₂][PF₆]₂ (M = Ni and Zn) were prepared in DMF at room temperature.
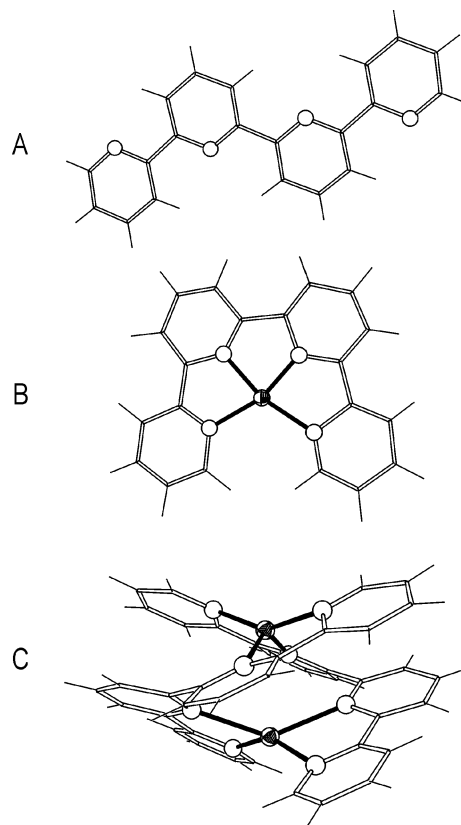
Introduction

A vast literature is available on metal complexes of oligopyridines. The interest for these systems originates from the possibility to control the assembly of helical supramolecular systems.[1] Making specific reference to 2,2′:6′,2′′:6′′,2′′′-quaterpyridine (qtpy), see A in Scheme 1, several 1:1 metal complexes have been reported in the literature.[2] In their large majority, they contain a nearly planar ligand in a quadridentate coordination mode, see B in Scheme 1, especially for metal ions in octahedral or square-planar geometry.[3] For tetrahedral geometries, typically the d^{10} configurations of copper(I) and silver(I), dinuclear double-helical complexes (see C in Scheme 1) may result, where qtpy behaves as a bridging ligand,[4] helication deriving from the twisting about the interannular C–C bond of the coordinated qtpy. Metal complexes are also known where the donor atoms of the ligand, thus identified as hypodentate, are only partially coordinated to the metal center.[5,6]

Hypodentate behavior has a twofold interest: (a) the nitrogen atoms not involved in the first coordination sphere

Scheme 1. Coordination Modes (B and C) of qtpy (A) in 1:1 Metal Complexes

may coordinate other metal cations, thus creating the prerequisite for building polynuclear, homo-, or even het-

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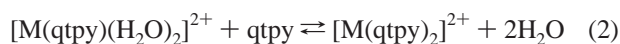
eronuclear complexes; (b) the same metal center can coordinate more than one qtpy ligand, that is, $[M(qtpy)_n]^{m+}$ with $n > 1$. Although multidentate behavior may impose some strain, as first pointed out in model studies[7] that even questioned the ability of qtpy to behave as a planar quaterdentate ligand, the strain in the octahedral coordination geometry of the metal may be released to some extent if the ligand binds to the metal through only three of its nitrogen atoms. For typical octahedral complexes, a second terdentate hypodentate qtpy group may allow the bis-qtpy complex to be formed.

In the case of iron(II), spectroscopically established equilibria had been reported in aqueous solution as early as 1964 pointing to the existence of the $[Fe(qtpy)_2]^{2+}$ cation *in solution*, see eqs 1 and 2.[8]

$$[M(H_2O)_n]^{2+} + qtpy \rightleftharpoons [M(qtpy)(H_2O)_2]^{2+} + (n-2)H_2O \quad (1)$$

$$[M(qtpy)(H_2O)_2]^{2+} + qtpy \rightleftharpoons [M(qtpy)_2]^{2+} + 2H_2O \quad (2)$$

However, only recently was the $[Fe(qtpy)_2]^{2+}$ cation isolated and structurally characterized as the perchlorate derivative $[Fe(qtpy)_2][ClO_4]_2$, as reported in a preliminary communication from these laboratories.[9] We have now established that the isolation of the iron(II) derivative was not unique; as shown in this paper, the nickel(II) and zinc-(II) derivatives also exist. The conditions for their high-yielding preparation have been identified, and their structural data are reported herein. The studies on the diamagnetic

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zinc(II) system, which also led to the crystallographically established 1:1 adduct $[Zn(qtpy)(H_2O)_2][ClO_4]_2$, have allowed the NMR identification of the 1:1 and 2:1 derivatives. As zinc and nickel are involved in the preparation of the ligand itself,[3m] the new findings provide some further hint into the metal-assisted synthetic procedure to qtpy.

Results and Discussion

Bis-qtpy Metal Complexes. The metal complexes of formula $[M(qtpy)_2]Y_2$ (M = Fe, Y = ClO_4; M = Ni and Zn, Y = ClO_4 or PF_6) are produced in good yields, the product composition being determined essentially, for nickel and zinc, by the qtpy/M molar ratio used in the synthesis. The perchlorate derivatives are best prepared in water through a hydrothermal synthesis that requires heating the metal perchlorate with the ligand at 140 °C in a sealed glass vessel, both qtpy and its metal complexes being scarcely soluble at room temperature. After reaction, by exploiting the temperature gradient down to room temperature, single crystals of the qtpy metal derivatives, suitable for the X-ray diffractometric experiments, were obtained. It is of interest to note that in the case of iron the initial qtpy/Fe molar ratio can be maintained at 1, provided NEt_3 in an equimolar amount with respect to iron is present in the reaction mixture. In the absence of NEt_3, the $[Fe(qtpy)(H_2O)_2]^{2+}$ cation is the predominant species in solution, isolated as the previously reported perchlorate derivative.[9]

The preparations of the nickel(II) and zinc(II) bis-qtpy complexes differ from that of the iron(II) analogue in some important details. In the case of nickel, the use of NEt_3 does not appear to influence the nature of the product; the same results are obtained in the presence or in the absence of the tertiary amine. A color change from green to violet characterizes the coordination of the second qtpy ligand to the metal. On the other hand, the addition of NEt_3 to the zinc system produces a species whose elemental analysis agrees with the analytical formula $[ZnO(qtpy)]$, and which has not been further investigated.

In dimethylformamide (DMF), where qtpy is soluble, fast reactions occur with $Zn(PF_6)_2$ at room temperature, forming 1:1 or 2:1 metal complexes, depending on the qtpy:zinc molar ratio. The mono-qtpy and bis-qtpy complexes are easily distinguished by ^1H and ^{13}C NMR spectra in DMF-d_7. The protonic spectrum of $[Zn(qtpy)(H_2O)_2][ClO_4]_2$, whose qtpy signals are sharp, closely agrees with that reported for the corresponding tetrafluoborate derivative in CD_3CN.[3m] The resonance at 9.4 ppm, assigned to the hydrogen atoms in position 6 of the external rings, is diagnostic of the presence of the mono-qtpy adduct. The ^1H NMR spectrum of $[Zn(qtpy)_2][ClO_4]_2$ shows a lower number of broadened signals, the observed lower complexity, despite the lower symmetry, being reasonably due to the presence of dynamic processes in solution. A similar behavior has been previously encountered with the octahedral complex *fac*-$[ReBr(CO)_3(terpy)]$,[5c] where the hypodentate (bidentate) ligand 2,2′:6′,2″-terpyri-

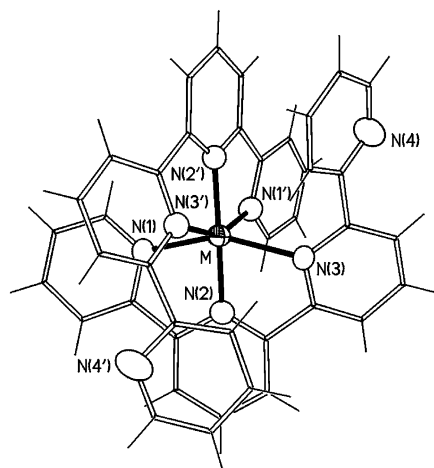(9) Belli Dell'Amico, D.; Calderazzo, F.; Englert, U.; Labella, L.; Marchetti, F. *J. Chem. Soc., Dalton Trans.* **2001**, 357.

Figure 1. View of the molecular structure of cation $[M(qtpy)_2]^{2+}$, M = Ni and Zn. Thermal ellipsoids of M and N are at 30% probability. $' = 1 - x, y, -z + 1/2$.

Table 1. Bond Lengths (Å) and Angles (deg) around the Metal Atom in $[M(qtpy)_2]^{2+}$ Cations, M = Fe, Ni, and Zn[a]

	Fe[b]		Ni	Zn
M−N(1)	2.195(7)	2.331(8)	2.108(7)	2.171(5)
M−N(2)	2.097(6)	2.133(7)	1.994(7)	2.054(5)
M−N(3)	2.198(6)	2.234(7)	2.239(7)	2.364(5)
N(1)−M−N(2)	72.3(3)	73.8(3)	78.5(3)	76.6(2)
N(1)−M−N(3)	144.4(3)	148.0(3)	153.9(3)	151.1(2)
N(1)−M−N(1')	86.5(2)		99.4(2)	105.1(3)
N(1)−M−N(2')	81.7(3)	90.1(3)	100.0(3)	102.5(2)
N(1)−M−N(3')	88.1(2)	103.0(2)	82.9(3)	82.1(2)
N(2)−M−N(3)	73.4(3)	74.2(3)	75.5(3)	74.5(2)
N(2)−M−N(2')	150.2(3)		177.8(5)	178.6(3)
N(2)−M−N(3')	118.2(3)	133.9(3)	105.9(3)	106.5(2)
N(3)−M−N(3')	99.7(2)		106.5(4)	105.2(2)

[a] The apexes in the labels have the same meaning as in Figure 1. [b] As the $[Fe(qtpy)_2]^{2+}$ cation in solid $[Fe(qtpy)_2](ClO_4)_2$ does not possess twofold axial symmetry, both values of bond distances have been reported.

dine (terpy) oscillates between the two possible equivalent positions. IR spectroscopy is not informative about the composition of the metal complex, the spectra of both $[M(qtpy)(H_2O)_2][ClO_4]_2$ and $[M(qtpy)_2][ClO_4]_2\cdot4H_2O$ (M = Ni and Zn), recorded as KBr pellets, being nearly superimposable, as expected.

The compounds $[M(qtpy)_2][ClO_4]_2\cdot4H_2O$ (M = Ni and Zn) are isotypical. They contain mononuclear hexacoordinated cations with two terdentate qtpy ligands, each having one pendant pyridyl group, see Figure 1. Although similar to the iron(II) complex,[9] they display some important differences. The structurally characterized iron derivative does not contain lattice water and the iron atom has a distorted octahedral geometry, with a contribution to the stability of the system possibly originating from the weak interaction of the pendant ring nitrogen with iron (the Fe···N nonbonding distance is 2.819 Å, i.e., 0.6 Å longer than the average Fe−N bond distance). Thus, the iron atom approaches heptacoordination. On the contrary, in the nickel and zinc derivatives, both pendant pyridyl groups look outward with respect to the metal. Thus, nickel and zinc are hexacoordinated with four short and two long M−N bonds. Zinc−nitrogen bond distances, see Table 1, are slightly longer than the nickel− nitrogen ones, consistent with the larger radius of the zinc
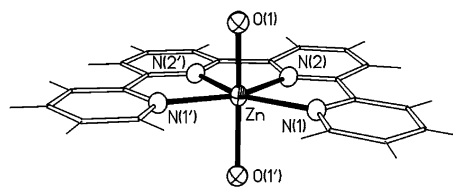

Figure 2. View of the structure of the $[Zn(qtpy)(H_2O)_2]^{2+}$ cation in $[Zn(qtpy)(H_2O)_2][ClO_4]_2$. Thermal ellipsoids of Zn, O, and N are at 30% probability. $' = 1 - x, y, z + 1/2$.

cation.[10] The lengthening of the metal nitrogen bonds M−N(3) is possibly due, as noted elsewhere,[5e] to steric repulsions with the non coordinated ring.

Both complexes of nickel and zinc are stabilized by π-stacking between the ring containing N(4) and the coordinated ring containing N(2') of the other qtpy ligand, duplicated by the symmetry operator. Such interaction was present also in the iron system, although it was limited to only one of the two pendant pyridyl rings. Stacking interactions are reported to be a key feature in the assembly of a double-helix[11] derivative. It is to be further noted that in both the nickel and zinc structures, the nitrogen of the pendant pyridyl group is hydrogen-bonded to two lattice water molecules.

Mono-qtpy Complexes. The mono-qtpy $[M(qtpy)L_2]^{2+}$ cations, M = Ni and Zn, have been reported in the literature and the crystal structures of $[Ni(qtpy)(MeCN)_2][PF_6]_2$,[12] and $[Ni(qtpy)(H_2O)_2][BF_4]_2$, have been established.[3m] The coordination around the metal is distorted octahedral with the essentially planar quaterpyridine in the equatorial positions, the monodentate ligands occupying the axial sites. Changing the axial ligand and the anion does not involve major differences of the cation structure, as shown in several derivatives containing the $[M(qtpy)LL']^{n+}$ cations and displaying a similar arrangement around the metal center. Even the introduction of substituents in the 4' and 4'' positions of qtpy (qtpy''') did not lead to any[13] significant change of bond distances and angles.

According to literature, $[Zn(qtpy)(H_2O)_2][BF_4]_2$[3m] has been obtained by refluxing a hydro-alcoholic solution containing $[Zn(H_2O)_6][BF_4]_2$ and qtpy. However, since no X-ray data were available, we decided to solve the crystal structure of $[Zn(qtpy)(H_2O)_2][ClO_4]_2$, see Figure 2 (bond lengths and angles around the Zn atom are shown in Table 2). In the cation, qtpy is substantially planar and the zinc atom shows a distorted octahedral geometry with the two H_2O ligands in axial positions. The distortion of qtpy in this mode of coordination has already been noted;[12] similarly (i) the metal-nitrogen bond distance (2.183 Å) involving the terminal rings are significantly longer than that to the internal ones (2.119

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Table 2. Bond Lengths [Å] and Angles [deg] around the Zn Atom in the [Zn(qtpy)(H$_2$O)$_2$]$^{2+}$ Cation of [Zn(qtpy)(H$_2$O)$_2$][ClO$_4$]$_2$, See Figure 2 for Labels

Zn−N(1)	2.183(3)	Zn−O(1)	2.148(3)
Zn−N(2)	2.119(3)		
O(1)−Zn−N(1)	86.9(1)	N(1)−Zn−N(1′)	135.7(2)
O(1)−Zn−N(2)	99.4(1)	N(1)−Zn−N(2′)	149.3(1)
O(1)−Zn−O(1′)	157.7(2)	N(2)−Zn−O(2′)	74.2(2)
N(1)−Zn−N(2)	75.1(1)		

Scheme 2. Synthesis of the qtpy Ligand

$$2\ 6\text{-Cl-dipy} \xrightarrow[\text{Zn excess}]{\text{NiCl}_2(\text{PPh}_3)_2 + \text{PPh}_3} \text{"qtpy"}$$
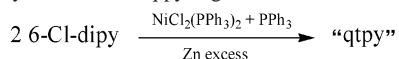
Å), (ii) the slight twisting of the pyridyl rings is larger for the two internal rings, the dihedral angles being 5.1° and 3.8°, respectively, and (iii) the O−Zn−O angle (157.7°), is lower than 180°, the H$_2$O ligands bending toward the less crowded area of the equatorial plane.
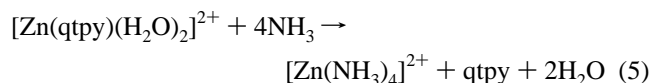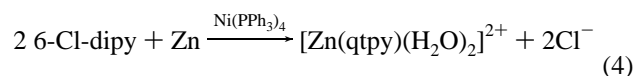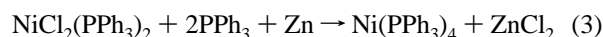
Moreover, the reactivity of the zinc adducts towards HClO$_4$ has been studied in a DMF/H$_2$O mixture. The bis-qtpy complex [Zn(qtpy)$_2$][ClO$_4$]$_2$ reacts quantitatively (acid/Zn molar ratio = 2) producing both [Zn(qtpy)(H$_2$O)$_2$][ClO$_4$]$_2$, which is soluble in the reaction mixture, and [qtpyH$_2$][ClO$_4$]$_2$, which precipitates out. Although the presence of the uncoordinated nitrogen sites in [M(qtpy)$_2$]$^{2+}$ could bring protonated complexes, such as [Zn(qtpy)(qtpyH)]$^{3+}$ or [Zn(qtpyH)$_2$]$^{4+}$, no evidence concerning the formation of these species was collected. The reaction of [Zn(qtpy)(H$_2$O)$_2$][ClO$_4$]$_2$ with excess HClO$_4$ leads to complete removal of coordinated qtpy. On the other hand, when an acid/Zn molar ratio of 2 is used, the displacement of qtpy from [Zn(qtpy)(H$_2$O)$_2$][ClO$_4$]$_2$ is not complete, part of the complex remaining unchanged, as evidenced by the ^{1}H NMR spectrum.

We have also observed that the displacement of the zinc- and nickel-coordinated quaterpyridine can be easily achieved with ammonia. Treatment of [M(qtpy)(H$_2$O)$_2$][ClO$_4$]$_2$, M = Ni and Zn, with an excess of ammonia in a DMF/H$_2$O mixture causes the precipitation of free quaterpyridine, which is recovered in high yields. The complexes [Zn(NH$_3$)$_4$]$^{2+}$ or [Ni(NH$_3$)$_6$]$^{2+}$ can be precipitated from the filtrate of the reaction mixture as the hexafluorophosphate salts. This behavior allows qtpy to be obtained from its metal complexes, as an alternative to qtpy displacement by cyanide (vide infra).

Synthesis of qtpy. In the course of the present study, the synthesis of qtpy has constituted an important point. According to literature,[3m] an excess of zinc is used to reduce both the nickel complex NiCl$_2$(PPh$_3$)$_2$ and 6-Cl-dipy (Scheme 2), nickel being used in an equimolar amount with respect to 6-Cl-dipy, and PPh$_3$ complexing nickel as Ni(PPh$_3$)$_4$. At the end of the reaction, an aqueous solution of ammonia is reported to be finally added in order to complex the zinc ion; the supposedly nickel(II)-complexed qtpy is set free by treatment with cyanide. We have also carried out the synthesis of qtpy with the conventional molar amounts of the reagents, but with the probably important difference that we operated under a dinitrogen atmosphere throughout. We found that treatment of the final reaction mixture with

aqueous ammonia is sufficient to set qtpy free, which was extracted with CHCl$_3$, together with PPh$_3$ and, probably, Ni-(PPh$_3$)$_4$.

Separate experiments showed that (a) Zn is able to reduce [Ni(qtpy)(H$_2$O)$_2$]$^{2+}$ in DMF solution with formation of [Zn(qtpy)(H$_2$O)$_2$]$^{2+}$ and (b) qtpy can be successfully displaced from the coordination sphere of either Zn^{2+} or Ni^{2+} with an excess of aqueous ammonia. This procedure finds an explanation in eqs 3−5 and allows pure qtpy to be obtained, thus avoiding the use of cyanide. It is interesting to note that the synthesis carried out with a 6-Cl-dipy:Ni molar ratio of about 10 gave only a slightly lower yield of qtpy, 40%, to be compared with the 63% yield of sublimed product obtained by using the stoichiometric amount of nickel under otherwise comparable reaction conditions. This shows that nickel acts as a catalyst in this system, being reduced to the zerovalent state during the synthetic procedure and undergoing oxidative addition by 6-Cl-dipy. The qtpy ligand must therefore be preferentially coordinated to zinc(II) at the end of the reaction.

$$\text{NiCl}_2(\text{PPh}_3)_2 + 2\text{PPh}_3 + \text{Zn} \rightarrow \text{Ni(PPh}_3)_4 + \text{ZnCl}_2 \quad (3)$$

$$2\ 6\text{-Cl-dipy} + \text{Zn} \xrightarrow{\text{Ni(PPh}_3)_4} [\text{Zn(qtpy)(H}_2\text{O})_2]^{2+} + 2\text{Cl}^- \quad (4)$$

$$[\text{Zn(qtpy)(H}_2\text{O})_2]^{2+} + 4\text{NH}_3 \rightarrow$$
$$[\text{Zn(NH}_3)_4]^{2+} + \text{qtpy} + 2\text{H}_2\text{O} \quad (5)$$

Summary

Metal bis-qtpy complexes, [M(qtpy)$_2$]$^{2+}$, M = Fe(II), Ni-(II), and Zn(II), have been prepared by working with the appropriate stoichiometry, thus considerably enlarging this class of complexes, previously limited to iron(II). The qtpy ligand in these complexes is terdendate, with a pendant pyridyl group possibly available to coordinate another metal center; the nickel(II) and zinc(II) derivatives [M(qtpy)$_2$]-(ClO$_4$)$_2$ are isostructural, the corresponding iron(II) complex possessing slightly different crystallographic and structural details. A simplified synthesis of the ligand has been identified.

Experimental Section

General Procedure. All preparations were carried out in standard Schlenk tubes. All reactions were carried out under dinitrogen, unless otherwise stated. The compounds Ni(ClO$_4$)$_2$·6H$_2$O, and Zn-(ClO$_4$)$_2$·6H$_2$O were purchased (Aldrich) and used as received. The preparations of 6-chloro-dipyridine[14] and [qtpyH$_2$][PF$_6$]$_2$[3m] were according to literature. Elemental analyses (C, H, N) were performed by Laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa, using a C. Erba model 1106 elemental analyzer. IR spectra were measured with a Perkin-Elmer FT-IR model 1725X spectrophotometer. NMR spectra were recorded using a Varian Gemini 200 MHz instrument, the data being expressed in ppm from TMS for ^{1}H and ^{13}C.

CAUTION: Some of the qtpy complexes were prepared in aqueous media at about 140 °C. The heating was carried out by

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suspending the glass vials in an oil bath, and leaving a large part of the vial, not occupied by the solution, outside the heated region. This operation was carried out inside a hood, behind a protecting screen. No explosion ever occurred. Small amounts (~0.2 g or lower) of the dry perchlorate derivatives reported in this paper were handled.

Synthesis of $[M(qtpy)_2]Y_2$, $Y = ClO_4$ and PF_6; $M = Ni$ and Zn. Similar procedures have been used for the preparation of the two complexes. The preparation of the zinc complex is described in detail.

A solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.13 g, 0.35 mmol) in H_2O (20 mL) was introduced under dinitrogen into a glass vessel (800 mL) containing qtpy (0.22 g, 0.71 mmol), which was then flame sealed. The initial suspension was heated to 140 °C for 3 h, resulting in a colorless solution. Large colorless crystals of the title compound (0.19 g, 61% yield) were obtained on cooling slowly (over 24 h) down to room temperature. Elemental analyses were performed after drying the crystals under vacuum. Anal. Calcd for $[Zn(qtpy)_2]$-$[ClO_4]_2$, $C_{40}H_{28}Cl_2N_8O_8Zn$: C 54.3, H 3.2, N 12.7. Found: C 53.4, H 3.1, N 12.2. ^1H NMR (DMF-d_7, ppm): δ 8.4 (d, 1H), 8.6–8.4 (m, 4H), 8.1 (t, 1H), 7.5 (td, 1H). ^{13}C NMR (DMF-d_7, ppm): δ 149.6; 142.5; 139.6; 126.6; 124.7; 123.7; 123.1. IR (KBr, Nujol, $1700–600$ cm^{-1}): 1599s, 1579s, 1566s, 1494w, 1450s, 1436m, 1400w, 1318w, 1300w, 1252m, 1195w, 1166w, 1156w, 1144w, 1099ms, 1083ms, 1029m, 1012m, 995m, 779ms, 748w, 676w, 663w, 651w, 640m, 623s.

$[Zn(qtpy)_2](PF_6)_2$ was prepared by treating a DMF (1 mL) solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.03 g, 0.08 mmol) and qtpy (0.046 g, 0.15 mmol) with an aqueous solution (8 mL) of $NaPF_6$ (0.05 g, 0.30 mmol). The colorless product, which immediately precipitated out, was filtered, washed with H_2O (3 × 1 mL) and diethyl ether (3 × 1 mL), and dried under vacuum (0.06 g, 82% yield). Anal. Calcd for $[Zn(qtpy)_2][PF_6]_2$, $C_{40}H_{28}F_{12}N_8P_2Zn$: C 49.2, H 2.9, N 11.5. Found: C 47.4, H 4.0, N 11.8. ^1H NMR (DMF-d_7, ppm): δ 8.8 (d, 1H); 8.7–8.4 (m, 4H); 8.1 (t, 1H); 7.6 (t, 1H). IR (KBr, Nujol, $1700–600$, cm^{-1}): 1646m, 1630m, 1599s, 1580s, 1579s, 1567s, 1532w, 1493m, 1446s, 1318w, 1303w, 1249m, 1192m, 1162w, 1102m, 1091m, 1052w, 1029m, 1014m, 898w, 841s, 783s, 775s, 754m, 664w, 651w, 643m, 621w, 558s.

For nickel, large violet crystals of the title compound (0.21 g, 72% yield) were obtained by slowly cooling the aqueous reaction mixture (for 24 h) to room temperature. Elemental analyses were performed after drying the crystals under vacuum. Anal. Calcd for $[Ni(qtpy)_2][ClO_4]_2$, $C_{40}H_{28}Cl_2N_8NiO_8$: C 54.7, H 3.2, N 12.7. Found: C 54.6, H 3.4, N 12.6. IR (KBr, Nujol, $4000–600$ cm^{-1}): 1601m, 1578m, 1565m, 1496w, 1419m, 1397w, 1321w, 1301w, 1247m, 1193w, 1166w, 1155w, 1096ms, 1076ms, 1035s, 1012m, 993m, 779s, 748m, 676m, 666m, 650m, 622s, 601m.

$[Ni(qtpy)_2][PF_6]_2$ has been prepared by treating a DMF (1 mL) solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.027 g, 0.074 mmol) and qtpy (0.046 g, 0.15 mmol) with an aqueous solution (8 mL) of $NaPF_6$ (0.050 g, 0.30 mmol). The violet precipitate was filtered, washed with H_2O (3 × 1 mL) and diethyl ether (3 × 1 mL), and dried under vacuum (0.050 g, 70% yield). Anal. Calcd for $[Ni(qtpy)_2][PF_6]_2$, $C_{40}H_{28}F_{12}N_8NiP_2$: C 49.6, H 2.9, N 11.6. Found: C 48.2, H 2.9, N 11.2. IR (KBr, Nujol, $1700–600$ cm^{-1}): 1650w, 1631w, 1602m, 1583m, 1576m, 1565m, 1532w, 1494w, 1486w, 1448s, 1320w, 1303w, 1244m, 1189m, 1162w, 1102m, 1070w, 1034m, 1015w, 899m, 843s, 782s, 773s, 754m, 666w, 643m, 620w, 558s.

Synthesis of $[M(qtpy)(H_2O)_2][ClO_4]_2$, $M = Fe$, Ni, and Zn. Similar procedures have been used for the preparation of the three complexes. The preparation of the zinc derivative is reported.

A solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.16 g, 0.43 mmol) in H_2O (20 mL) was introduced under dinitrogen in a glass vessel (800 mL) containing qtpy (0.13 g, 0.42 mmol). The container, after being flame sealed, was heated to 140 °C for 3 h, the initial suspension being thus converted to a colorless solution. Heating was interrupted and the vial was cooled to room temperature (about 24 h). Large ivory crystals of the title compound (0.18 g, 70% yield) were obtained. Anal. Calcd for $[Zn(qtpy)(H_2O)_2][ClO_4]_2$, $C_{20}H_{18}Cl_2N_4O_{10}$-Zn: 39.3, H 3.0, N 9.2. Found: C 39.5, H 3.1, N 9.5. ^1H NMR (DMF-d_7, ppm): δ 9.4 (d, 1H), 9.0–8. 7 (m, 3H), 8.7 (t, 1H), 8.5 (td, 1H), 8.0 (t, 1H). ^1H NMR (CD$_3$CN, ppm): δ 9.1 (d, 1H), 8.6–8.5 (m, 4H), 8.3 (td, 1H), 7. 9 (td, 1H). ^{13}C NMR (DMF-d_7, ppm): δ 150.7, 149.9, 148.7, 148.3, 144.1, 141.3, 127.9, 124.0, 123.9, 123.6. IR (KBr, Nujol, $1700–600$ cm^{-1}): 1645m, 1600s, 1580s, 1568m, 1492m, 1444s, 1405w, 1322w, 1270w, 1253w, 1194w, 1099ms, 1085ms, 1021s, 975m, 916w, 777ms, 739w, 656m, 623s.

If the synthesis is carried out in the presence of NEt_3, a solid analyzing as $ZnO(qtpy)$ is obtained. Anal. Calcd for $Zn(qtpy)O$, $C_{20}H_{14}N_4OZn$: C 61.3, H 3.6, N 14.3. Found: C 62.4, H 4.1, N 14.4.

Large green crystals of $[Ni(qtpy)(H_2O)_2][ClO_4]_2$ were obtained for nickel (0.22 g, 67% yield) on slowly cooling the reaction solution (for 24 h to get back to room temperature). Anal. Calcd for $[Ni(qtpy)(H_2O)_2](ClO_4)_2$, $C_{20}H_{18}Cl_2N_4NiO_{10}$: C 39.8, H 3.0, N 9.3. Found: C 40.2, H 3.0, N 9.4. IR (KBr, Nujol, $4000–600$ cm^{-1}): 3387(br), 2925ms, 2855ms, 1652w, 1600m, 1577m, 1566m, 1489m, 1395m, 1320w, 1267w, 1253w, 1098s, 1085s, 1026s, 973m, 775s, 623s. In the case of nickel, the synthesis had an identical outcome when carried out in the presence of triethylamine.

Reactions of the qtpy-zinc Complexes with $HClO_4$ in DMF. After dissolving $Zn(ClO_4)_2 \cdot 6H_2O$ (0.024 g, 0.064 mmol) and qtpy (0.040 g, 0.129 mmol) in DMF (1 mL), the formation of the complex $[Zn(qtpy)_2]^{2+}$ was verified by ^{13}C NMR spectrometry. An aqueous solution of $HClO_4$ (1.1 mL, 0.12 N; 0.132 mmol) was then added. The resulting colorless precipitate, $[qtpyH_2][ClO_4]_2$, was filtered, washed with H_2O (3 × 1 mL) and with diethyl ether (3 × 1 mL), and dried. ^1H NMR (DMF-d_7, ppm): δ 9.1–9.0 (m, 6H), 8.7–8.6 (m, 4H), 8.4 (t, 2H), 8.1 (td, 2H).[3m]

After dissolving $Zn(ClO_4)_2 \cdot 6H_2O$ (0.023 g, 0.062 mmol) and qtpy (0.019 g, 0.061 mmol) in DMF (1 mL), the formation of $[Zn(qtpy)$-$(H_2O)_2]^{2+}$ was verified by ^{13}C NMR spectrometry. An aqueous solution of $HClO_4$ (1.1 mL, 0.12 N; 0.132 mmol) was then added. A suspension was obtained. The colorless precipitate, $[qtpyH_2]$-$[ClO_4]_2$, was filtered, washed with H_2O (3 × 1 mL) and with diethyl ether (3 × 1 mL), and dried (0.017 g, 54% yield). The product was characterized by ^1H NMR spectrometry (see above). The ^{13}C NMR spectrum of the filtrate still showed the signals due to $[Zn$-$(qtpy)(H_2O)_2]^{2+}$; the addition of an excess of $HClO_4$ produced precipitation of further $[(qtpyH_2)][ClO_4]_2$ and disappearance of the zinc-coordinated qtpy resonances in the NMR spectrum of the aqueous phase.

Reaction of $[Zn(qtpy)(H_2O)_2](ClO_4)_2$ with Aqueous NH_3 in DMF. To a solution of $[Zn(qtpy)(H_2O)_2](ClO_4)_2$ (0.035 g, 0.057 mmol) in DMF-d_7 (0.5 mL), NH_3 (0.13 mL of a 30% aqueous solution) was added. The colorless precipitate (qtpy) was filtered, washed with H_2O (3 × 1 mL), and dried (15.1 mg, 85% yield). ^1H NMR (CDCl$_3$, ppm): δ 8.7–8.6 (m, 3H), 8.4 (d, 1H), 7.8 (td, 1H), 8.0 (t, 1H), 7.3 (td, 1H). A ^1H NMR spectrum of the filtrate showed that the qtpy complex of zinc was absent. The zinc-amine complex was then precipitated with $NaPF_6$ (0.032 g, 0.19 mmol), yielding $[Zn(NH_3)_4](PF_6)_2$ (0.02 g).

Table 3. Crystal Data and Structure Refinement for the qtpy Complexes of Nickel(II) and Zinc(II)

compound	$[Ni(qtpy)_2](ClO_4)_2 \cdot 4H_2O$	$[Zn(qtpy)_2](ClO_4)_2 \cdot 4H_2O$	$[Zn(qtpy)(H_2O)_2](ClO_4)_2$
empirical formula	$C_{40}H_{36}Cl_2N_8O_{12}Ni$	$C_{40}H_{36}Cl_2N_8O_{12}Zn$	$C_{20}H_{14}Cl_2N_4O_{10}Zn$
formula weight	950.38	957.04	606.62
crystal system	monoclinic	monoclinic	monoclinic
space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$C2/c$ (No. 15)
a/Å	24.353(8)	24.233(6)	14.581(5)
b/Å	8.100(2)	8.0247(3)	11.191(3)
c/Å	22.624(6)	22.856(4)	15.101(3)
β/deg	108.49(3)	107.54(2)	99.27(2)
U/Å^3	4232(2)	4238 (1)	2432(1)
Z	4	4	4
D_{calc}/Mg·m^{-3}	1.491	1.500	1.657
μ/mm^{-1}	0.657	0.778	1.292
no. measured	2465	3357	2686
no. unique [R_{int}]	1795 [0.0221]	2513 [0.0105]	2136 [0.0147]
no. parameters	265	273	203
R_1, wR_2 (all data)	0.091, 0.279	0.072, 0.207	0.043, 0.125
goodness of fit on F^2	1.430	1.056	1.082

Similar results were obtained with nickel, the violet $[Ni(NH_3)_6]$-$[PF_6]_2$ (0.07 g) and qtpy (81% yield) being formed.

Reaction of $[Ni(qtpy)(H_2O)_2](ClO_4)_2$ with Zn in DMF. [Ni-(qtpy)(H_2O)_2](ClO_4)_2 (0.026 g, 0.043 mmol) was dissolved under N$_2$ in DMF (1 mL). Zinc powder (0.056 g, 0.86 mmol) was added and the suspension was stirred for 30 min. The suspension was then decanted and the ^{13}C NMR spectrum of the solution was registered. The spectrum showed the signals of the complex [Zn-(qtpy)(H_2O)_2]$^{2+}$.

Synthesis of qtpy. A synthetic procedure is described, slightly modified with respect to the literature.[3m] By operating under dinitrogen, DMF (100 mL) was added to PPh$_3$ (10.1 g, 38 mmol), NiCl$_2$(PPh$_3$)$_2$ (11.7 g, 18 mmol), and zinc dust (3.59 g, 55 mmol). The resulting brick-red suspension was stirred for 1 h at room temperature before introducing 6-chloro-dipyridine (3.4 g, 18 mmol). The mixture was heated at 50 °C for 24 h and, after cooling, was treated with a deaerated aqueous solution of ammonia (50 mL, 30%). After 1 h of stirring, extraction with deaerated CHCl$_3$ (3 × 100 mL) was carried out. The volatiles were removed from the organic layer in vacuum. A fractional sublimation ($\sim 10^{-2}$ mmHg) afforded PPh$_3$ at 120 °C and pure qtpy at 160 °C (1.75 g, 63% yield). The use of a catalytic amount of NiCl$_2$(PPh$_3$)$_2$ (10−15%) with respect to 6-chloro-dipyridine over similar reaction times lowered the yield to 40%. ^1H NMR (CDCl$_3$, ppm): δ 8.8−8.7 (m, 3H), 8.5 (d, 1H), 8.0 (t, 1H), 7.9 (td, 1H), 7.4 (td, 1H). ^1H NMR (DMF-d_7, ppm): δ 8.8−8.7 (m, 3H), 8.5 (dd, 1H), 8.2 (td, 1H), 8.1 (tdd, 1H), 7.5 (dt, 1H). ^{13}C NMR (DMF-d_7, ppm): d 156.7, 156.6, 156.5, 150.1, 139.1, 137.9, 125.0, 121.3, 121.2, 121.0. IR (KBr windows, Nujol, 1600−500 cm^{-1}): 1583w, 1580s, 1563s, 1562s, 1447m, 1378m, 1268w, 1191w, 1121m, 1111w, 1093w, 1076m, 1039w, 991w, 820w, 767ms, 737m, 723m, 697m, 635m, 542m.

X-ray Diffraction Experiments. The X-ray diffraction experiments were carried out at room temperature ($T = 293$ K) by means of a Bruker P4 diffractometer equipped with graphite-monochromated Mo-K_α radiation. The samples were sealed in glass capillaries under an atmosphere of dinitrogen. The intensity data collection was carried out with the $\omega/2\theta$ scan mode, collecting a redundant set of data. Three standard reflections were measured every 97 measurements to check sample decay. The intensities were corrected for Lorentz and polarization effects and for absorption by the Ψ-scan method[15] for the bis-qtpy complexes of nickel and zinc

and by an integration method based on the crystal shape[16] for [Zn-(qtpy)(H_2O)_2][ClO_4]_2. The structure solutions were obtained by means of the automatic direct methods contained in SHELXS97.[17] The refinements, based on full-matrix least-squares on F^2, were done by means of the SHELXL97 [17] program. Some other utilities contained in the WINGX suite[18] were also used. The more relevant crystal parameters for the samples analyzed are listed in Table 3.

The systematic absences in the diffraction intensity data of [Zn-(qtpy)_2][ClO_4]_2 \cdot 4H_2O indicated the Cc or $C2/c$ space group. Taking into account the multiplicity of the group and the expected molecular volume, the structure solution was found in the centrosymmetric $C2/c$ space group. The asymmetric unit contains one-half cation, one anion and two molecules of lattice water, the metal lying on a twofold axis. The abnormally high thermal parameters of the perchlorate and water oxygens, obtained in the first cycles of refinement, suggested the presence of disorder. The last refinement cycles were done with the anion with fixed geometry distributed in two different orientations, while the oxygens of the lattice water were treated as ordered atoms leaving their anisotropic thermal parameters to simulate an abnormally high thermal motion. In the last cycle, anisotropic thermal parameters were used for the heavy atoms of the cation, for the chlorine atoms of the anion, and for the oxygens of the lattice water. The hydrogen atoms of one lattice water were not introduced in the calculations; all the others were let ride on the connected heavy atoms. The final reliability factors are listed in Table 3.

The structure refinement of [Ni(qtpy)_2][ClO_4]_2 \cdot 4H_2O, which was shown to be isotypical with [Zn(qtpy)_2][ClO_4]_2 \cdot 4H_2O, was done by starting from the atomic parameters obtained for the zinc derivative. Similar disorder problems were encountered for the anion and the lattice water molecules. The anion was refined, as in the preceding case, as distributed in two different orientations, but in this case the oxygen atoms of water were also refined as distributed in two different positions. The water hydrogen atoms were not introduced in the model. The final refinement cycle was done by using anisotropic thermal parameters for all the heavy atoms of the cation and for chlorine atoms, while the hydrogen atoms were left to 'ride' on the connected carbon atoms. The resulting reliability factors are listed in Table 3.

The structure solution of [Zn(qtpy)(H_2O)_2][ClO_4]_2 was found in the $C2/c$ space group. The asymmetric unit that resulted was made

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(17) Sheldrick, G. M.; *SHELX97, Programs for Crystal Structure Analysis (Release 97−2)*; University of Göttingen: Göttingen, Germany, 1998.

(18) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

by one-half cation with the zinc atom on a twofold axis and by a ClO_4^- anion. Disorder was present in the orientation of the anion. The latter was then refined with a fixed geometry as distributed in two different orientations. The final refinement cycle was done by using anisotropic thermal parameters for all the heavy atoms, letting the hydrogen atoms 'ride' on the connected carbon atoms and disregarding the hydrogens of the water groups. The resulting reliability factors are listed in Table 3.

Supporting Information Available: Crystallographic data in CIF format for $[Zn(qtpy)_2][ClO_4]_2 \cdot 4H_2O$, $[Ni(qtpy)_2][ClO_4]_2 \cdot 4H_2O$, and $[Zn(qtpy)(H_2O)_2][ClO_4]_2$ have been deposited with the Cambridge Crystallographic Data Centre, Cambridge, United Kingdom (CCDC$-$No. 233815, 233814 and 233813). This material is available free of charge via the Internet at http://pubs.acs.org.

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