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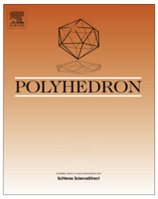

Stabilization of unique valencies of cobalt, nickel and copper by complexation with the tridentate ligand 2-(2′-pyridyl)-8-hydroxyquinoline

Galia Maayan [a,*], Yohai Dayagi [a,1], Rina Arad-Yellin [a,2], Linda J.W. Shimon [b], Abraham Shanzer [a]

[a] *Department of Organic Chemistry, Weizmann Institute of Science, Rehovot 76000, Israel*
[b] *Department of Chemical Research Support, Weizmann Institute of Science, Rehovot 76000, Israel*

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Dedicated to Prof. George Christou, on his 60th birthday, an extraordinary and enthusiastic inorganic chemist, and the most supportive mentor I could ever ask for (GM).

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ABSTRACT

The complexes of cobalt, copper and nickel ions with the known tridentate ligand 2-(2′-pyridyl)-8-hydroxyquinoline (**HQP**) were prepared and characterized. The structures of the complexes with Co(II), Cu(II) and Ni(III) were corroborated by crystal structure analyses. The structures of the complexes with Co(III) and Cu(I) were realized from NMR measurements in solution. It was found that **HQP** stabilizes high oxidation states of the complexed metal ions. The results also suggest that **HQP** binds Cu(II) and Cu(I) in two different modes; Cu(II) forms an octahedral complex with the three elements of the ligand, namely, the 8-hydroxyl the two nitrogens of bipyridine, while Cu(I) binds only to two nitrogens of the bipyridine, yielding a tetra-coordinated complex.

1. Introduction

Metal ions are key elements in both the structure and function of natural biopolymers, being employed in tasks spanning from structure stabilization to catalysis, light-energy conversion and recognition. The structure and catalytic activity of many enzymes, for example, depends upon explicit coordination of metal ions such as copper, cobalt and nickel. Control over the coordination geometry of synthetic metal complexes is therefore an important step towards the ability to mimic the structure and function of biopolymers. It can be achieved via the rational design of unique metal chelators targeted at the binding of specific metal ions with explicit oxidation states in desired coordination geometries.

Ligands based on the pyridine skeleton, i.e., bipyridine and terpyridine, as well as quinoline ligands, especially 8-hydroxyquinoline, are strong metal chelators capable of binding a variety of metal ions yielding different geometries based on the metal ion and its oxidation state [1–3]. The bidentate ligand 8-hydroxyquinoline (HQ), with nitrogen and oxygen atoms for binding, is considered a "medium" ligand, which binds "medium" as well as "hard" metal ions in different coordination modes. Thus, two molecules of HQ form tetra-coordinated planar complexes with Cu(II) ions while coordination to Cu(I) or to Co(II) ions yields tetrahedral complexes [4]. The fact that HQ is a bidentate ligand might prove limiting; Co(III), which is known to form stable six coordinated octahedral complexes, cannot form stable complexes with two HQ ligands and needs an external ligand for this purpose [5]. The chelator terpyridine, a tridentate ligand with three nitrogen atoms for

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Abbreviations: HQ, 8-hydroxyquinoline; HQP, 2-(2′-pyridyl)-8-hydroxy quinoline; ESI-MS, electron spray ionization mass spectrum; NMR, nuclear magnetic resonance spectrum; dd, dt, dq, double doublet, triplet, and quartet, respectively; bs, broad single; UV–Vis, ultraviolet–visible spectrum; IR, infrared; FW, formula weight; MLCT, metal-to-ligand charge transfer.

* Corresponding author. Address: Schulich Faculty of Chemistry, Technion, Israel Institute of Technology, Haifa 32000, Israel.

E-mail address: gm92@techunix.technion.ac.il (G. Maayan).

[1] Current address: Organic Synthesis and Polymerization Laboratory, IKI, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel.

[2] Current address: Semorex Technologies Ltd., Weizmann Scientific Park, Ness Ziona 74140, Israel.

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coordination is a “soft” binding ligand, thus, can bind only a limited range of metal ions. We therefore anticipated that a ligand combining both, pyridine and HQ, in which one Π-accepting pyridine forms a ligand that contains more than one pyridine group coupled to the σ-donating phenol group, will be a good chelator with an ability to bind a variety of metal ions and stabilize high oxidation states of metal ions. Several ligands of this kind were already described in the literature; some of them were found to stabilize high oxidation state of metal ions [6].

In this work, we chose to study the interactions with various 3d transition metal ions of the previously reported tridentate ligand 2-(2′-pyridyl)-8-hydroxyquinoline (**HQP**) [7]. **HQP** combines binding units of the two ligands HQ and 2,2′-bipyridine into one structure (Scheme 1). Its interaction with ruthenium ions was previously described [8]. The structure of **HQP** complexes with biologically relevant metal ions, however, was not realized, and its ability to stabilize high oxidation states as well as to form stable complexes with different oxidation states of the same element (e.g. “soft“ vs. “hard”) was not explored. Herein we demonstrate that **HQP** stabilizes the spontaneous formation of Co(III) and Ni(III) complexes, and suggest that binding of Cu(II) and Cu(I) lead to the formation of two different complexes having two different coordination geometries.

2. Experimental

2.1. General

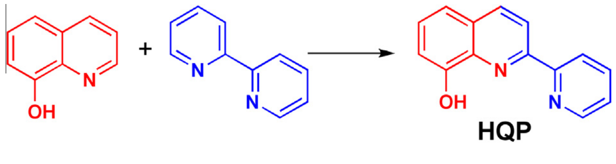
^1H NMR spectra were recorded on Bruker AMX-250 or AMX-400 instruments. Unless otherwise mentioned, $CDCl_3$ was used as solvent. UV–Vis spectra were recorded on a Beckman DU-7500 a diode array spectrophotometer. Mass spectra were recorded on a Platform LCZ 4000 Micromass, Manchester, UK. Ionization Mode was ESI. X-ray diffraction measurements were preformed with Nonius Kappa CCD diffractometer. The crystals were coated with paraffin oil.

UV–Vis experiments were carried out in quartz cuvettes. In a typical measurement, 20 μl of a 10 mM HQP solution (in methanol) or metal complex was placed in a cuvette that contained 3 mL 4:1 methanol:0.1 M aqueous NH_4PF_6 solution and the spectrum was recorded. In case of air-sensitive metal complexes, the solutions were degassed, purged with argon and the experiments were carried out in special Shlank cuvettes under inert atmosphere.

Data collection and treatment of single crystals suitable for X-ray crystallography analysis were done with a Nonius KappaCCD diffractometer with Mo Kα, graphite monochromator (λ = 0.71073 Å). The crystals were coated with paraffin oil. Data were processed with Denzo-Scalepack. The structure was solved by direct methods (SHELXS-97). Full-matrix least-squares refinement was based on F^2 (SHELXL-97). Idealized hydrogen atoms were placed and refined in a riding mode.

2.2. Materials

All solvents and chemicals were of analytical grade. Solvents were freed from stabilizers by passing through activated basic alumina columns. THF was distilled from Na in the presence of benzophenone. Methanol was distilled from magnesium turnings and iodine. Other chemicals and reagents were purchased from commercial sources and were used without further purification.



Scheme 1. Molecular design of **HQP**.

2.3. Synthesis

*Methyl 3-hydroxy 2-nitrobenzoate (**1**):* Dry HCl was bubbled through the refluxing solution of 3-hydroxy 2-nitro benzoic acid (10 g, 0.055 mol) in 150 ml MeOH for 8 h. The solution was concentrated in high vacuum. Addition of H_2O to the concentrated solution precipitated the methyl 3-hydroxy 2-nitro benzoic ester (64% yield, 6.9 g, 0.035 mol). ^1H NMR δ = 7.07 (dd, 1H), 7.26 (m, 1H), 7.58 (d, 1H), 3.94 ($CO_2C\mathbf{H_3}$, s, 3H).

*Methyl 3-(benzyloxy)-2-nitrobenzoate (**2**):* A solution of methyl 3-hydroxy-2-nitrobenzoate (6.9 g, 0.033 mol) in dry DMF (100 ml) was cooled to 0 °C under argon and treated with sodium hydride (0.96 g, 0.04 mol). The reaction mixture was stirred for 10 min and benzyl bromide (6.27 g, 0.036 mol) was added. The reaction mixture was allowed to warm to 25 °C, and stirring was continued for an additional 20 h. A solution of saturated NaCl (30 ml) was added, and the reaction mixture was further diluted with H_2O (100 ml). The aqueous layer was extracted with Et_2O (4 × 150 ml). The combined ether extracts were washed with H_2O (100 ml), washed with saturated NaCl (30 ml), dried over $Na_2SO_4$and the solvent was removed in vacuum. Then $CHCl_3$ was added (30 ml), and the solution was dried over Na_2SO_4 and evaporated in vacuum to yield methyl 3-(benzyloxy)-2-nitrobenzoate as yellow crystals (89% yield, 8.95 g). ^1H NMR δ = 7.58 (dd, 1H, aromatic H), 7.23–7.45 (m, 7H, phenyl and aromatic Hs), 5.19 (s, 2H, $PhC\mathbf{H_2}$), 3.88 ($CO_2C\mathbf{H_3}$, s, 3H).

*3-(Benzyloxy)-2-nitrobenzyl alcohol (**3**):* A solution of methyl 3-(benzyloxy)-2-nitrobenzoate (8.78 g, 0.03 mol) in THF (150 ml) was treated with $LiBH_4$ (2 g, 0.03 mol, 3.0 eq.) at 25 °C under argon atmosphere and stirred for 21 h. Saturated solution of ammonium chloride (70 ml) was added and the reaction mixture was diluted with H_2O (200 ml) and extracted with EtOAc (2 × 150 ml). The organic extract was washed with saturated NaCl, dried (Na_2SO_4), filtered, and the solvent was removed in vacuum. Column chromatography (SiO_2, 30% EtOAc–hexane eluent) afforded 3-(benzyloxy)-2-nitrobenzyl alcohol as a yellow oil (5.11 g, 66% yield). ^1H NMR δ = 7.43–7.26 (m, 6H, phenyl and aromatic Hs), 7.1(d, 1H, aromatic H), 7.0 (d, 1H, Aromatic H), 5.19 (s, 2H, $PhC\mathbf{H_2}OAr$), 4.67 (s, 2H, $C\mathbf{H_2}OH$). IR ($CHCl_3$) v = 1020 cm^{-1} (CH_2OH).

*3-(Benzyloxy)-2-nitrobenzaldehyde (**4**):* A solution of 3-(benzyloxy)-2-nitrobenzyl alcohol (200 mg, 0.77 mmol) in CH_2Cl_2 (15 ml) was treated with pyridinium dichromate (436 mg, 1.16 mmol) at 25 °C under Ar. The reaction mixture was stirred at 25 °C for 11 h, filtered through celite, washed with 5% aqueous HCl (1 × 6 ml) and saturated NaCl (1 × 6 ml), dried (Na_2SO_4) and the solvent was removed in vacuum to afford 3-(benzyloxy)-2-nitrobenzaldehyde as a yellow solid (0.1 g, 0.4 mmol, 50% yield). ^1H NMR δ = 9.95 (s, 1H, C**H**O), 7.60–7.48 (m, 2H, aromatic Hs), 7.39–7.32 (m, 6H, phenyl and aromatic Hs), 5.23 (s, 2H, $PhC\mathbf{H_2}OAr$). IR ($CHCl_3$) v = 1709 cm^{-1} (CHO), 1475 cm^{-1} (NO_2).

*2-Amino-3-(benzyloxy)-2–benzaldehyde (**5**):* A solution of 3-(benzyloxy)-2-nitrobenzaldehyde (2.5 g, 10 mmol) in THF (180 ml) was treated with a solution of sodium hydrosulfite (8.47 g, 50 mmol) in H_2O (90 ml). The reaction mixture was warmed at 60 °C for 1 h, poured onto H_2O (150 ml), and extracted with EtOAc (3 × 150 ml). The EtOAc layer was washed with saturated NaCl (100 ml), dried over $Na_2SO_4$and the solvent was removed in vacuum. Column chromatography (SiO_2, 15% EtOAc–hexane eluent) afforded 2-amino-3-(benzyloxy)-2-benzaldehyde as yellow oil (1.5 g, 65% yield). ^1H NMR δ = 9.9 (s, 1H, C**H**O), 7.4 (m, 5H, phenyl Hs), 6.1 (d, 1H), 6.9 (d, 1H), 6.7 (t, 1H), 6.65 (bs, 2H, $N\mathbf{H_2}$), 5.0 (s, 2H, $C\mathbf{H_2}Ph$). IR ($CHCl_3$) v = 1619 cm^{-1} (NH_2CH_2).

8-Benzyloxy-2-(2′-pyridyl)-8-hydroxyquinoline (Ph-HQP): 2-Acetylpyridine (265 mg, 2.18 mmol) was added to a solution of 2-amino-3-benzyloxybenzaldehyde (495 mg, 2.18 mmol) in THF (3 ml) and the solution was cooled tot 0 °C. Triton B (1.46 g, 8.72 mmol) was added, the mixture was stirred for 1 h, the ice bath was removed, and stirring was continued over night. The solvent was evaporated and the residue was washed 4 times with 0.5 N citric acid, extracted with $CHCl_3$, dried over Na_2SO_4 and the solvent was removed. The product was obtained as a slightly yellow solid (600 mg, 88% yield). ^{1}H NMR δ = 8.7 (m, 2H), 8.6 (d, 1H), 8.25 (d, 1H), 7.8 (dt, 1H), 7.45 (dd, 2H), 7.4 (m, 5H, phenyl Hs), 7.34 (m, 1H), 7.1 (dd, 1H), 5.4 (s, 3H).

2-(2′-pyridyl)-8-hydroxyquinoline(HQP): 8-Benzyloxy-2-(2′-pyridyl)-8-hydroxyquinoline (600 mg, 1.9 mmol) was dissolved in formic acid (90 ml) and treated for 3 h with H_2 at atmospheric pressure using 10% Pd/C (300 mg) as catalyst. The reaction mixture was filtered, the solvent was removed, and the residue was purified by column chromatography on silica gel with 9% methanol in chloroform as eluent. The product (385 mg, 90% yield) was obtained as a slightly yellow solid. ^{1}H NMR δ = 8.84 (dd, 1H), 8.74 (dq, 1H), 8.64 (d, 1H), 8.45 (bs, O**H**), 8.39 (d, 1H), 7.9 (dt, 1H), 7.55-7.45 (m, 3H), 7.18 (dd, 1H). ESI-MS *m*/*z* = 222.7.

2.4. Preparation of the metal complexes

[Co(III)(HQP)₂](PF₆): To a solution of **HQP** (20 mg, 0.09 mmol) in methanol (2 ml) was added Co(II) acetate (11.2 mg, 0.045 mmol) and the solution was stirred for 30 minutes. An aqueous solution of NH_4PF_6 (0.56 ml) was added and a red solid precipitated. It was filtered and dried in the air (38.4 mg, 0.076 mmol, 85% yield). ESI-MS: *m*/*z* = 501.77. ^{1}H NMR (CD_3CN) δ = 8.95 (d, 1H), 8.66 (d, 1H), 8.4 (dd, 1H), 8.1 (dt, 1H), 7.55 (t, 1H), 7.30 (d, 1H), 7.22-7.18 (m, 2H), 6.76 (d, 1H).

Co(II)(HQP)₂: A solution of **HQP** (10 mg, 0.045 mmol) in methanol (0.5 ml) was treated with a solution of Co(II) acetate (5.6 mg, 0.0225 mmol) in methanol (0.5 ml) and the mixture was stirred at rt under inert atmosphere (N_2) for 30 min. Removal of the solvent in vacuum afforded a dark red solid (39.7 mg, 0.079 mmol, 88% yield). The complex was crystallized from a methanol solution at room temperature, under inert atmosphere. ESI-MS: *m*/*z* = 501.7.

Crystal data: Cell dimensions of the 0.3 × 0.1 × 0.05 mm^3 orange plates $C_{28}H_{18}N_4O_2Co + 3(CH_4O)$: Monoclinic, *P*291/*c* (No. 14), *a* = 13.899(2), *b* = 14.095(2), *c* = 15.907(1) Å, *β* = 114.660(6), from 20° of data, *T* = 120 K, *V* = 2832.1(5) Å^3, Z = 4, Formula weight = 597.52, D_{calc} = 1.401 Mg/m^3, μ = 0.653 mm^{-1}. 5106 reflections collected, $0 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 13$, $-15 \leqslant l \leqslant 13$, frame scan width = 2.0°, scan speed 1°/180 s, typical peak mosaicity = 0.45°, 2525 independent reflections (R_{int} = 0.062). Idealized hydrogen atoms were placed and refined in a riding mode. 376 parameters with 0 restraints, final R_1 = 0.0464 (based on F^2) for data with $I > 2\sigma(I)$ and R_1 = 0.0609 for all data based on 2525 reflections, goodness-of-fit (GOF) on F^2 = 1.068, largest electron density = 0.509 e Å^{-3}.

Cu(II)(HQP)₂(PF₆): A solution of **HQP** (20 mg, 0.09 mmol) in methanol (2 ml) was treated with Cu(II) acetate (9 mg, 0.045 mmol) and was stirred for 30 min under inert atmosphere (N_2). An orange solid precipitated after the addition of NH_4PF_6 (0.56 ml of a 2.6 M aqueous solution). It was filtered, dried and collected (40.9 mg, 90% yield). The complex was crystallized from methylene chloride at room temperature. ESI-MS: *m*/*z* = 504.7.

Crystal data: Cell dimensions of the 0.2 × 0.1 × 0.05 mm^3 orange plates, $2(C_{28}H_{18}N_4O_2Cu) + 2(PF_6) + 2(CH_2Cl_2)$: triclinic, *P*1 (No. 2), *a* = 8.4690(4), *b* = 14.010(6), *c* = 25.9100(8) Å, *α* = 75.180(2), *β* = 84.540(2), *γ* = 80.350(2), from 10° of data, *T* = 120 K, *V* = 2925.5(2) Å^3, Z = 4, formula weight = 735.9, D_{calc} = 1.671 mg/mm^3, μ = 1.059 mm^{-1}. 22,611 reflections collected, $0 \leqslant h \leqslant 8$, $-13 \leqslant k \leqslant 13$, $-25 \leqslant l \leqslant 25$, frame scan width = 1.0°, scan speed 1°/60 s, typical peak mosaicity = 0.7°, 6073 independent reflections (R_{int} = 0.043). 811 Parameters with 0 restraints, final R_1 = 0.0639 (based on F^2) for data with $I > 2\sigma(I)$ and R_1 = 0.0797 for all data based on 6073 reflections, goodness-of-fit (GOF) on F^2 = 1.038, largest electron density = 0.914 e Å^{-3}.

[Cu(I)(HQP)₂](PF₆): A solution of **HQP** (10 mg, 0.045 mmol) in acetonitrile (0.5 ml) was treated with a solution of $Cu(I)(CH_3CN)_4$-PF_6 (8.4 mg, 0.0225 mmol) in acetonitrile (0.5 ml) and the mixture was stirred under inert atmosphere (N_2) for 30 min. Removal of the solvent under vacuum afforded a dark solid (41 mg, 90% yield). ESI-MS: *m*/*z* = 506.7. ^{1}H NMR (CD_3CN) δ = 8.78 (bd, 1H), 8.75 (bd,1H), 8.6 (d, 1H), 8.45 (shoulder + d, O**H** + 1H), 8.2 (bt, 1H), 7.53–7.45 (bm, 3H), 7.2 (bd, 1H).

[Ni(III)(HQP)₂](PF₆): A solution of **HQP** (20 mg, 0.09 mmol) in methanol (2 ml) was treated with Ni(II) acetate (11.2 mg, 0.045 mmol) and was stirred for 30 min at room temperature. An orange solid precipitated after the addition of NH_4PF_6 (0.56 ml of a 2.6 M aqueous solution). It was filtered, dried and collected (43 mg, 86% yield). Crystals were obtained from methanol solution at room temperature. ESI-MS: *m*/*z* = 500.2.

Crystal data: Cell dimensions of the 0.3 × 0.1 × 0.05 mm^3 orange plates, $C_{28}H_{18}N_4O_2Ni + CH_4O + PF_6 + H_2O$: triclinic, $P\bar{1}$ (No. 2), *a* = 8.776(1), *b* = 13.642(2), *c* = 24.911(3) Å, *α* = 75.974(8), *β* = 114.660(6), *γ* = 80.208(2), from 20° of data, *T* = 120 K, *V* = 2843.3(6) Å^3, *Z* = 4, formula weight = 686.19, D_{calc} = 1.603 mg/mm^3, μ = 0.820 mm^{-1} 5616 reflections collected, $0 \leqslant h \leqslant 6$, $-9 \leqslant k \leqslant 10$, $-18 \leqslant l \leqslant 19$, frame scan width = 0.5°, scan speed 1°/120 s, typical peak mosaicity = 0.45°, 2617 independent reflections (R_{int} = 0.071). Idealized hydrogen atoms were placed and refined in a riding mode. 740 parameters with 230 restraints, final R_1 = 0.0957 (based on F^2) for data with $I > 2\sigma(I)$ and R_1 = 0.1076 for all data based on 2617 reflections, goodness-of-fit (GOF) on F^2 = 1.068, largest electron density = 1.388 e Å^{-3}.

3. Results and discussion

3.1. Synthesis of *HQP*–metal complexes and their characterization by ESI-MS and UV–Vis

HQP was used for the preparation of complexes with four metal ions namely Co(II), Cu(II), Cu(I) and Ni(II). In a typical synthetic protocol, an equivalent of the metal salt was added to two equivalents of the ligand in methanol or acetonitrile solution and stirred for half an hour at room temperature in air or under nitrogen. An immediate color change was observed after mixing which signified the formation of the complex. Isolation of the complexes from the colored solution was done in one of the following ways: (i) concentrated aqueous solution of $NH4^+PF_6^-$ was added, yielding the precipitation of the complex, which was filtered and collected, or (ii) the solvent was removed *in vacu* to yield the solid complex.

All complexes were initially characterized by ESI-MS. As depicted in Table 1, the *m*/*z* data clearly indicate that **HQP** forms stable complexes of the type M(**HQP**)₂ with all the metal ions. In addition, data analysis of the complexes [Co(III)(**HQP**)₂](PF₆), Co(II)(**HQP**)₂, Cu(II)(**HQP**)₂(PF₆) and [Ni(III)(**HQP**)₂](PF₆) reflects binding of each ion to two tridentate ligands (four nitrogens and two oxygen atoms). An interesting observation is that the *m*/*z* of the complexes [Cu(I)(**HQP**)₂](PF₆) and Cu(II)(**HQP**)₂(PF₆) differ by two units, which is attributable to two protons on the two hydroxyl group on each of the two ligands. This observation suggests that Cu(I) binds only to four coordinating atoms – the two nitrogen atoms of each ligand [9]. A molecular peak of *m*/*z* = 144, indicative of a PF_6^- anion, was also observed in this spectrum, indicating that the Cu(I) ion is coordinated to four nitrogen atoms and do not interact with the OH groups, and therefore its charge is neutralized by an exterior hexafluorophosphate anion. PF_6^- peaks were also observed in the spectra of all the other metal complexes, excluding the spectrum of Co(II)(**HQP**)₂. These results are discussed below

Table 1
Absorption maxima and ESI-MS data for the metal complexes.

Compound	ESI-MS (*m/z*), calculated[a]	ESI-MS (*m/z*), founded[a]	λ_{max} (nm)[b]	λ_{MLCT} (nm)[b]
HQP	221.23	222.70	265, 285	
Co(III)(**HQP**)$_2$(PF$_6$)	501.40	501.77	303	463
Co(II)(**HQP**)$_2$	501.40	501.70	306	451
Ni(III)(**HQP**)$_2$(PF$_6$)	501.16	500.18	307	466
Cu(II)(**HQP**)$_2$(PF$_6$)	506.01	504.67	307	467
Cu(I)(**HQP**)$_2$(PF$_6$)	508.03	506.72	295, 345	410

[a] *m/z* data for **HQP** and its metal complexes as obtained in the positive mode spectra.

[b] λ_{max} is the wavelength at the maximum absorption. λ_{MLCT} is the wavelength at the maximum metal-to-ligand charge transfer absorption.

(Section 3.2) in the context of ^{1}H NMR and X-ray crystallography characterization of the obtained metal complexes.

The formation of the complexes was followed by UV–Vis spectroscopy. The results are summarized in Table 1. A typical UV–Vis titration curve, illustrating the formation of Co(III)(**HQP**)$_2$(PF$_6$) complex, is depicted in Fig. 1. The UV–Vis spectrum of **HQP** shows two λmax absorption bands at about 265 and 285 nm, attributed to π–π* transitions of **HQP**, which originate from its two chromophores and it is in good agreement with the previous published data [8]. These absorbance bands can be rationalized by comparing the UV–Vis spectrum of **HQP** to the spectra obtained for both the ligands 2,2′-bipyridine and HQ measured in the same solvent system. Our measurements produced a UV–Vis spectrum of the "soft" 2,2′-bipyridine, which shows two λmax absorption bands at about 235 nm and 282 nm, and a UV–Vis spectrum of the "harder" HQ, which shows two λmax absorption bands at about 257 and 384 nm. It is therefore understood that **HQP**, being "harder" then 2,2′-bipyridine and "softer" then HQ undergoes π–π* transitions leading to absorbance bands at longer wavelength then 2,2′-bipyridine and shorter wavelength then HQ.

In the spectra of the complexes, with the exception of [Cu(I)(**HQP**)$_2$](PF$_6$), there is only one λmax absorption band in the 303–345 nm region, implying that the absorption of the two chromophores is coupled. These absorption peaks also are attributed to π–π* transitions of **HQP**. An additional MLCT absorption band, however, in the 410–467 nm region is observed in the spectra of all the metal complexes. Notably, the complex [Cu(I)(**HQP**)$_2$](PF$_6$) is the only one that exhibits two λmax absorption bands, similarly to the λmax bands of the free **HQP**. A possible explanation for this is that Cu(I) is bound to only one part of **HQP** (most likely to the two nitrogen atoms), therefore the absorption is not coupled and the two absorbance bands of the Cu(I) complex with **HQP** show a longer wavelength π–π* absorption at about 295 and 345 nm, then the free **HQP** at about 265 and 285 nm.

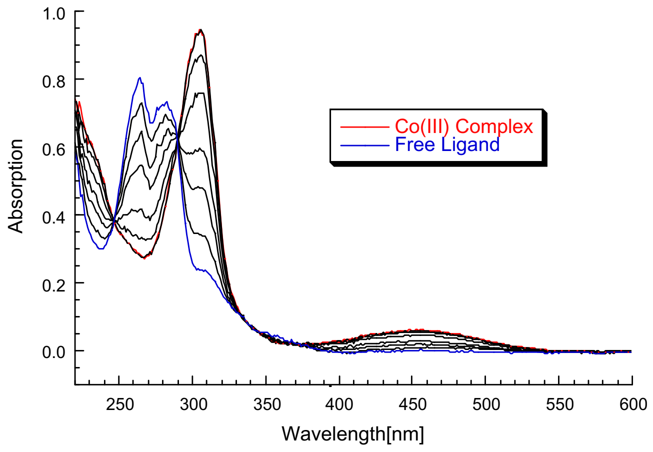


Fig. 1. Formation of Co(III) complex followed by UV spectroscopy. A 5 mM solution of **HQP** in MeOH was titrated with 10 mM solution of Co(III) ion in MeOH. 0.1 equivalents of the metal ion were added in each step. Saturation of all binding sites was obtained after 0.5 equivalents of the metal ions were added.

Similar absorbance bands at about 296 and 343 nm were previously observed for a Cu(I) complex of 6,6′-diphenyl-2,2′-bipyridine-4,4′-dicarboxylic acid ([Cu(H$_2$**6**)$_2$]Cl) [10]. In this complex, Cu(I) is bound to the two nitrogen atoms of the 2,2′-bipyridine part of the ligand in a tetrahedral coordination geometry. Overall, these data provide another indication for unique tetra-coordination of Cu(I) to **HQP**, as implied by the MS data of this complex. Based on the distinct difference between the absorbance bands and the MS data of the complexes [Cu(I)(**HQP**)$_2$](PF$_6$) and Cu(II)(**HQP**)$_2$(PF$_6$) we can propose that two different coordination compounds are being formed; Cu(II) with a hexa-coordination geometry and Cu(I) with a tetra-coordination geometry.

3.2. Characterization by solution ^{1}H NMR and X-ray crystallography

In order to provide a final conformation for our conclusion, we made attempts to crystallize the two copper complexes for further characterization of their structure and coordination geometry by X-ray analysis. The complex Cu(II)(**HQP**)$_2$(PF$_6$) was crystallized from dichloromethane solution at room temperature. Full crystallographic data are described in the Section 2. Its crystal structure is depicted in Fig. 2. This complex exhibits a non-perfect octahedral geometry. The unit cell contains two molecules related to each other by mirror-plane symmetry. It is apparent that Cu(II) ions

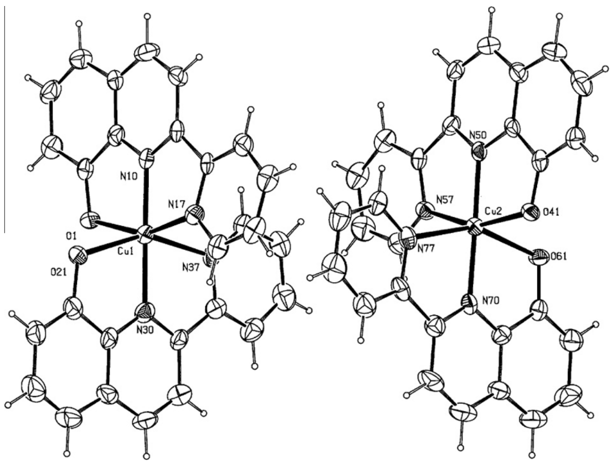


Fig. 2. Perspective view of the Cu(II)(**HQP**)$_2$(PF$_6$) complex. Selected bond distances (Å) and angles (°, errors in digits in parentheses): Cu1–N2 = 1.947(4), Cu1–N4 = 2.004(4), Cu1–O = 2.122(4), Cu1–N1 = 2.142(4), Cu1–N3 = 2.223(5), Cu1–O2 = 2.334 (4); N2–Cu1–N4 = 178.95(19), N2–Cu1–O1 = 79.23(16), N4–Cu1–O1 = 100.78(16), N2–Cu1–N1 = 77.41(17), N4–Cu1–N1 = 102.69(17), O1–Cu1–N1 = 155.84(15), N–Cu1–N3 = 102.16(17), N4–Cu1–N3 = 76.80(17), O1–Cu1–N3 = 97.02(15), N1–Cu1–N3 = 93.83(16), N2–Cu1–O2 = 105.77(15), N4–Cu1–O2 = 75.28(16), O1–Cu1–O2 = 89.94(14), N1–Cu1–O2 = 90.52(15), N3–Cu1–O2 = 152.02(14).

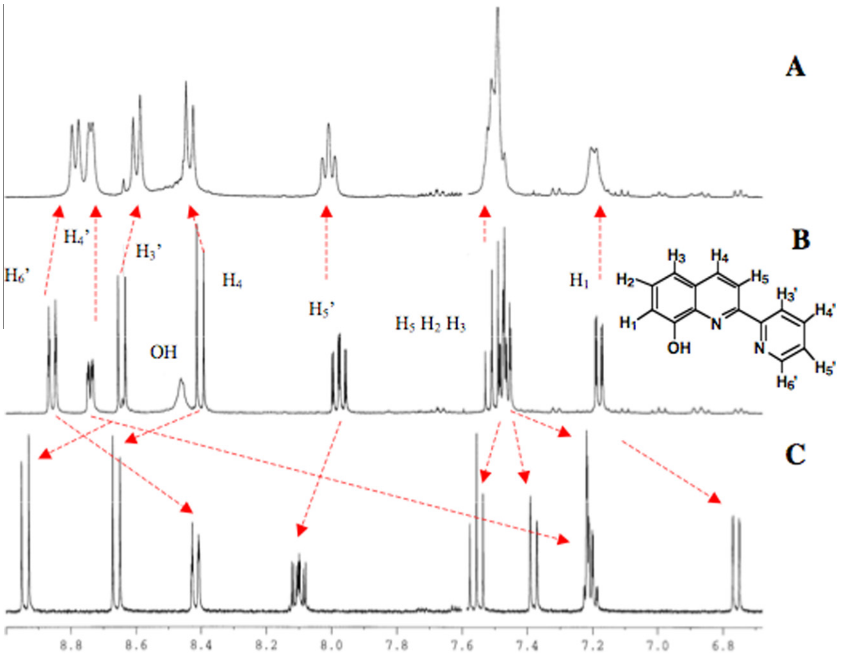


Fig. 3. ^{1}H NMR spectra of **HQP** (B) and its complexes with Cu(I) (A) and Co(III) (C). The structure of **HQP** and the numbering system is also depicted.

interact differently with the two oxygen atoms. The bond distance between Cu(1)–O(1) is shorter than that of Cu(1)–O(21). This observation and the presence of a PF_6^- anion in the unit cell for neutralization of the charge, suggests that the bond Cu(1)–O(21) is an ionic whereas Cu(1)–O(1) is a coordinative bond.

Attempts to obtain high quality crystals of Cu(I)(**HQP**)$_2$(PF$_6$) for X-ray analysis were not successful. However, taking into account that Cu(I)(**HQP**)$_2$(PF$_6$) is diamagnetic, we sought to gain structural information of this complex by performing ^{1}H NMR experiment in solution. The results are shown in Fig. 3A and this spectrum is compared to the spectrum of the free **HQP** ligand (Fig. 3B) and to the spectrum of the Co(III) complex [Co(III)(**HQP**)$_2$](PF$_6$), which is also diamagnetic. The chemical shift of the proton at position 7 of the quinoline ring (H_1) in the ^{1}H NMR spectrum of the Cu(I) complex is the same as that of the free ligand and is highly shifted in the spectrum of the Co(III) complex. The broad peak of the OH at $\delta = 8.45$ ppm (Fig. 1B) is absent in the spectrum of the Co(III) complex and present in the spectrum of the Cu(I) complex (broad shoulder by the dublet of H_4, Fig. 3A). These observations suggest that the OH group of the quinoline ring is taking part in the complexation of Co(III) but it is not involved in the binding of Cu(I) ions, and support the ESI-MS and UV–Vis data obtained for the Cu(I) complex.

The clear ^{1}H NMR spectrum depicted on Fig. 3C indicates that the complex is diamagnetic. Therefore we assumed that when the formation of the cobalt complex was carried out in the air, by mixing a solution of **HQP** with half an equivalent of Co(II) acetate in methanol, the Co(II) ions were spontaneously oxidized to Co(III) and the complex [Co(III)(**HQP**)$_2$](PF$_6$) was obtained. In fact, the observation that phenolate ions stabilize the Co(III) oxidation state by about 1 V relative to that of Co(II) complexed to 2,2′,6′,2″-terpyridine was already described [6]. The peaks in the ^{1}H spectrum of this complex are shifted relative to those of the free ligand (Fig. 3B and Fig. 3C) and the broad peak at $\delta = 8.45$ ppm, which corresponds to the OH group, is absent. This observation, together with the ESI-MS data confirms the participation of O^- in the structure of the complex and supports hexa-coordinated geometry. ESI-MS and NMR spectra were recorded on the same sample for both Cu(I)(**HQP**)$_2$(PF$_6$) and [Co(III)(**HQP**)$_2$](PF$_6$) complexes.

Although the NMR spectra of both these complexes support our assumption regarding their binding coordination, they do not provide a clear proof for these suggested coordination geometries. The broad peaks observed in the NMR spectrum of the Cu(I) complex, for example, could result from a small amount of Cu(II) present in solution. However, the combination between the NMR, ESI-MS and UV data can provide a good basis for our assumption that (i) Cu(I) is only bound to the bipyridine part of **HQP** in a tetra coordination geometry and is not bound to **HQP** in an octahedral geometry as the other metal ions are, and (ii) that Co(III) is bound to all N, N and O atoms of **HQP** in an hexa-coordinated geometry.

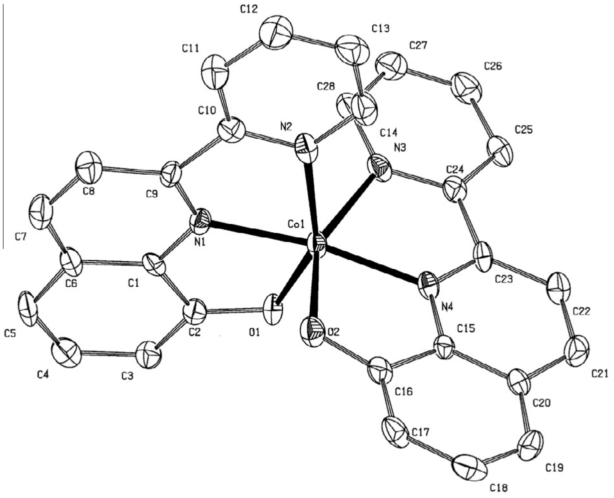


Fig. 4. Perspective view of the [Co(III)(**HQP**)$_2$](PF$_6$) complex. Selected bond distances (Å) and angles (°, errors in digits in parentheses): Co1–N4 = 2.019(4), Co1–N1 = 2.024(4), Co1–O2 = 2.124(3), Co1–O1 = 2.134(3), Co1–N3 = 2.175(4), Co1–N2 = 2.180(4); N4–Co1–N1 = 170.64(16), N4–Co1–O2 = 78.59(14), N1–Co1–O2 = 93.68(13), N4–Co1–O1 = 97.82(14), N1–Co1–O1 = 78.17(15), O2–Co–O1 = 100.02(13), N4–Co1–N3 = 75.02(16), N1–Co1–N3 = 113.22(15), O2–Co1–N3 = 152.71(14), O1–Co1–N3 = 90.39(14), N4–Co1–N2 = 110.79(16), N1–Co1–N2 = 74.71(17), O2–Co1–N2 = 93.95(14), O1–Co1–N2 = 150.15(14), N3–Co1–N2 = 89.02(15).

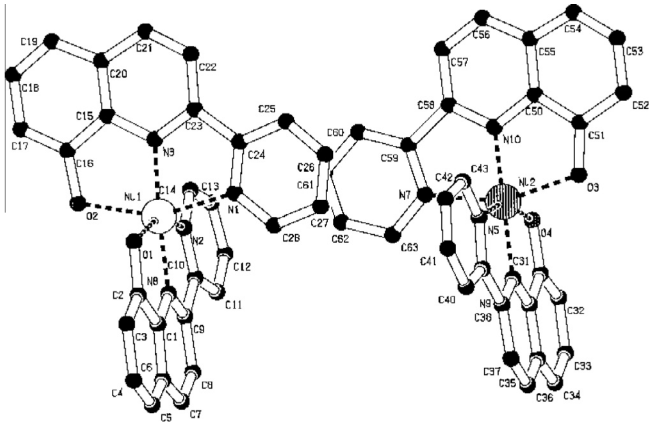


Fig. 5. Perspective view of the [Ni(III)(**HQP**)$_2$](PF$_6$) complex. Selected bond distances (Å) and angles (°, errors in digits in parentheses): Ni1–N3 = 1.967(11), Ni1–N8 = 1.979(10), Ni1–O1 = 2.184(8), Ni1–N2 = 2.092(11), Ni1–N1 = 2.118(9), Ni1–O2 = 2.164(7); N3–Ni1–N8 = 176.2(4), N3–Ni1–N2 = 102.4(4), N8–Ni1–N2 = 77.9(4), N3–Ni1–N1 = 75.5(4), N8–Ni1–N1 = 100.7(4), N2–Ni1–N1 = 94.9(4), N3–Ni1–O = 79.2(4), N8–Ni1–O2 = 104.6(3), N2–Ni1–O2 = 92.3(3), N1–Ni1–O2 = 154.7(4), N3–Ni–O1 = 102.9(3), N8–Ni1–O1 = 76.9(4), N2–Ni1–O1 = 154.7(4), N1–Ni1–O1 = 92.2(3).

Mixing **HQP** with half an equivalent of Co(II) in methanol under inert atmosphere has yielded the complex Co(II)(**HQP**)$_2$. The structure of this complex was corroborated by X-ray structure analysis (Fig. 4). The crystallographic data is summarized in the Experimental section. From Fig. 4 it is clear that each cobalt(II) ion is bound to two molecules of **HQP** forming a complex with an octahedral geometry.

Another evidence for the ability of **HQP** to stabilize high oxidation states was the spontaneous formation of the Ni(III) complex [Ni(III)(**HQP**)$_2$](PF$_6$) from a Ni(II) salt in air. Thus, mixing **HQP** with half an equivalent of Ni(II) acetate in methanol yields a light orange solution. The orange precipitation obtained after the addition of concentrated aqueous solution of $NH_4^+PF_6^-$ was crystallized from methanol. The X-ray structure of the complex is depicted in Fig. 5 and the crystallographic data is summarized in Experimental section. The [Ni(III)(**HQP**)$_2$](PF$_6$) complex has an octahedral geometry, with two unrelated molecules in the unit cell. The PF_6^- ion, found in the unit cell, indicates that the oxidation state of the nickel ion is Ni(III).

4. Conclusions

The tridentate ligand **HQP**, which is a hybrid of the two bidentate ligands 2,2′-bipyrine and 8-hydroxyquinoline, was synthesized, and its complexes with several metal ions were prepared. This system is highly interesting because of its ability to yield complexes with various coordination geometries; metal ions that prefer to bind to O and N atoms of the HQ form octahedral geometry while metal ions with preference to the N, N atoms of the bipyridine system form complexes with tetra-coordinated geometry. We describe complexes of the two geometries – Cu(II)(**HQP**)$_2$ (PF$_6$) having a octahedral geometry and [Cu(I)(**HQP**)$_2$](PF$_6$) having a tetra-coordinated geometry. We have also demonstrated the ability of this N, N, O tridentate ligand to stabilize high oxidation states of metal ions, i.e., cobalt(III) and nickel(III) by the spontaneous formation of the complexes [Co(III)(**HQP**)$_2$](PF$_6$) and [Ni(III) (**HQP**)$_2$](PF$_6$) from the salts of Co(II) and Ni(II), respectively, in air.

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Appendix A. Supplementary data

CCDC 941955–941957 contain the supplementary crystallographic data for the complexes described in this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.06.038.

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