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Synthesis and characterisation of *p*-block complexes of biquinoline at different ligand charge states†

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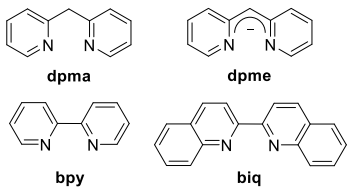
The first examples of *p*-block coordination complexes of biquinoline, namely [(biq)BCl_2]Cl and [(biq)BCl_2]$^{\bullet}$, were synthesized and structurally characterized. The acquired data allowed the estimation of the ligand charge state based on its metrical parameters. The subsequent use of this protocol, augmented with theoretical calculations, revealed ambiguities in the published data for transition metal complexes of biquinoline.

Coordination compounds of redox-active, that is, (redox) non-innocent ligands[1] have received increasing attention in the past decades due to their potential application in many areas such as bond activation and catalysis,[2] and their importance in bioinorganic chemistry and enzymatic transformations in particular.[3] Whilst various classes of redox-active ligands have already been identified and developed, *any* ligand can, in principle, display non-innocent behaviour under the right conditions.[4] However, correctly identifying the charge on the ligand can sometimes be problematic.[5] In a typical scenario, an addition or a removal of an electron causes changes in intraligand bond lengths that can be detected by high-resolution X-ray structure analysis.[6] In some cases, crystallography needs to be augmented with other techniques such as voltammetry, spectroscopy, magnetic measurements, and theoretical calculations to unambiguously determine the ligand charge.

In our previous contribution, we examined the coordination chemistry of 2,2'-dipyridylmethane (dpma) and the possibility of it to display non-innocent behaviour akin to that known for 2,2'-bipyridine (bpy), an omnipresent redox-active bidentate ligand.[7] The results revealed that, due to its methylene bridge, dpma is not only an inferior electron acceptor but also more reactive than bpy. We have already shown that both of these problems can be alleviated by deprotonating dpma to 2,2'-dipyridylmethene (dpme).[8] In a similar fashion, the redox properties of bpy can be affected *via* structural modifications that alter its HOMO-LUMO gap, the simplest being the extension of the conjugated ring system. In this context, it is interesting that, to the best of our knowledge, (biq)$Ti(Cp)_2$ (Cp = cyclopentadienyl) is the only structurally characterized coordination compound of 2,2'-biquinoline (biq) that supposedly contains the ligand as a radical anion.[9] However, the complex was originally described as a Ti(II) species, not Ti(III). Even though the electronic structure of (biq)$Ti(Cp)_2$ has recently been examined theoretically,[10] there is a clear need for structural data on coordination compounds of 2,2'-biquinoline (biq) in which the ligand charge can be unequivocally determined.



Herein, we report the synthesis and characterization of the salt [(biq)BCl_2]Cl (**1**) and the one-electron reduction of its cation to give the paramagnetic complex [(biq)BCl_2]$^{\bullet}$ (**2**). The coordination of biq to boron completely eliminates the possibility for back-bonding and confines all redox processes to the ligand framework, allowing an unambiguous structural characterization of a coordinated anionic biq radical. The acquired results lend further credence to the idea that redox non-innocence is a more common phenomenon in the chemistry of biq than heretofore recognized. A notion we emphasize by theory-aided reinterpretation of the electronic structure of the complex Co(biq)$_2$.

A stoichiometric 1:1 reaction between BCl_3 and biq was carried out in CH_2Cl_2 at −78°C, resulting in slow formation of a yellow precipitate (Scheme 1). The reaction mixture was allowed

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† Electronic Supplementary Information (ESI) available: Complete experimental details for the synthesis and characterization of **1** and **2**, and a full account of the conducted theoretical calculations. CCDC 1518783 and 1518784 contain the crystallographic data for **1** and **2**, respectively See DOI: 10.1039/x0xx00000x

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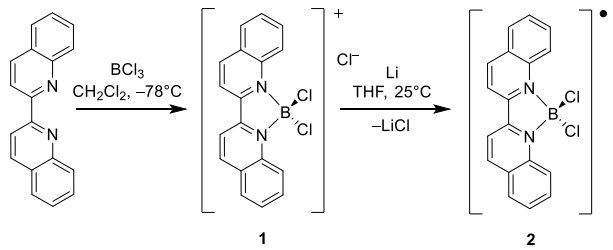

Scheme 1 Synthesis of the salt **1** and its reduction to the neutral radical **2**.

to warm to room temperature and, after an appropriate reaction time, the product was separated from the solution and dried under reduced pressure to afford **1** as a yellow solid in fully quantitative yield. The purity of **1** was confirmed by multinuclear NMR spectroscopy and elemental analysis (see ESI). Once precipitated, **1** has very different solubility properties and it only sparingly redissolves in coordinating solvents such as THF and CH_3CN. Thus, light yellow single crystals of **1** could be grown from a saturated CH_3CN solution kept at −20°C for a few days.

The crystal structure of **1** shows the presence of discrete $[(biq)BCl_2]^+$ cations and Cl^- anions. The BCl_2 moiety is symmetrically chelated by the biq ligand, resulting in a tetrahedral geometry around the boron centre (Fig. 1). The structure of the cation is close to, but not quite, C_{2v} symmetry with the backbone of the biq ligand slightly twisted away from planarity. The packing of **1** in the solid state is largely dictated by ion···dipole interactions between the Cl^- anions and the C–H bonds in the biq ligand that collectively organize the $[(biq)BCl_2]^+$ cations to layers along the crystallographic *b*-axis (see ESI). The layer-like packing of **1** is, however, far from perfect as the arrangement of the cations in the solid state is also affected by B–Cl···H–C intermolecular interactions. The individual layers are also connected *via* π-stacking interactions with a stack spacing of *ca.* 3.36 Å, *i.e.* slightly less than the sum of van der Waals radii of two carbon atoms.

Even though the favourable electron accepting properties of biq have been known since the late 1980's,[11] the reduction of **1** was examined by cyclic voltammetry (see ESI) to determine how the coordination of the ligand tunes its redox potential. The results showed that that the $[(biq)BCl_2]^+$ cation undergoes a one electron reduction at −0.82 V (*vs.* SCE) that can be compared with the reduction potential of the free biq ligand, −2.07 V (*vs.* Ag/Ag^+).[11] Although weaker reducing agents would certainly have sufficed, alkali metals were chosen because the expected side products, the salts MCl (M = Li, Na), can easily be separated from the product. Thus, the reduction of **1** was performed by using metallic lithium as the reducing agent.

The reduction was carried out at 25°C by dissolving a small amount of **1** in THF, after which a stoichiometric amount of the metal was added (Scheme 1). The initially yellow-greenish solution slowly tuned dark. After an appropriate reaction time, the solvent was removed under reduced pressure to afford a black solid that was redissolved in CH_2Cl_2 and filtered. Removal of the solvent *in vacuo* yielded **2** as a very dark, almost black, powder in good yield. Dark yellow single crystals of **2** were grown by redissolving the powder in CH_2Cl_2 and carefully layering *n*-hexane on top of the solution before letting it sit at −20°C for a few days. Compound **2** is extremely air sensitive and crystals of it decompose rapidly if removed from the protecting Fomblin® oil and exposed to atmospheric oxygen.

The paramagnetic nature of **2** was confirmed by dissolving a very small amount of the powdery product in CH_2Cl_2 and measuring the EPR spectrum of the resulting orange-yellow solution (Fig. 2). Once in solution, **2** is persistent for hours, showing no signs of decomposition under an inert atmosphere at room temperature. The EPR spectrum consists of a symmetric 60 G wide 16-line pattern at g = 2.0006 with no visible fine structure. Consequently, the simulation of the spectrum was performed using a fitting algorithm and calculated (PBE1PBE/TZVP) hyperfine

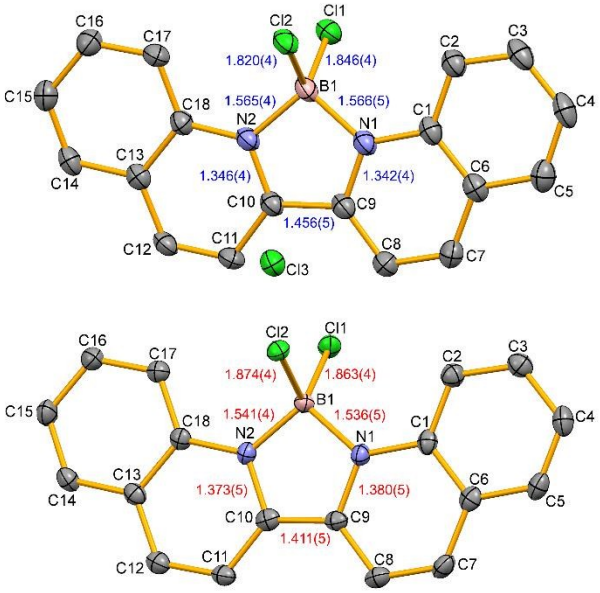

Fig. 1 Thermal ellipsoid plots (50% probability, hydrogen atoms omitted for clarity) of **1** (top) and **2** (bottom). Selected bond lengths (Å) are shown in the figure. Selected bond angles (°): (**1**) N1-B1–N2 98.7(3), B1-N1-C9 110.9(3), N1-C9-C10 109.6(3), B1-N2-C10 110.3(3), N2-C10-C9 110.4(3), Cl1-B1–Cl2 112.8(2); (**2**) N1-B1–N2 99.9(3), B1-N1-C9 109.9(3), N1-C9-C10 110.0(3), B1-N2-C10 110.0(3), N2-C10-C9 110.1(3), Cl1-B1–Cl2 109.9(2).

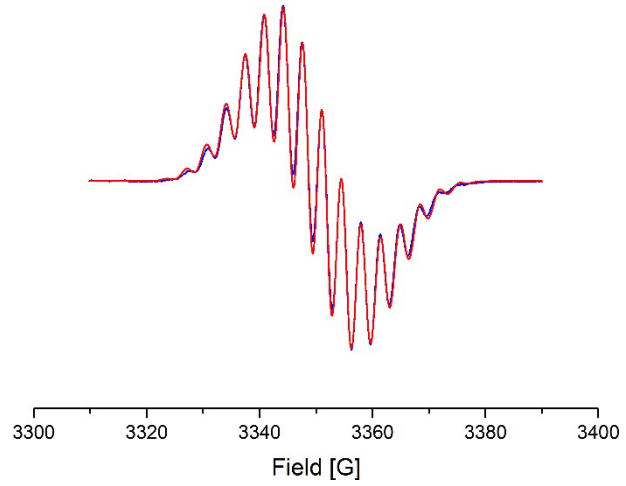

Fig. 2 Experimental (blue) and simulated (red) X-band EPR spectra of a CH_2Cl_2 solution of **2** at room temperature.

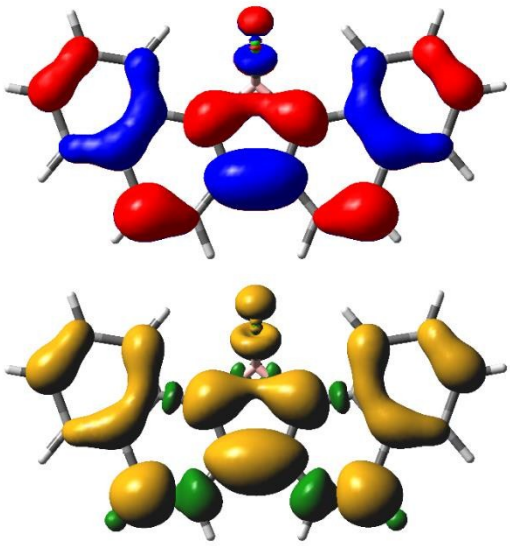

Fig. 3 Isosurface plots of the SOMO (± 0.03, top) and spin density (± 0.0008, bottom) of **2**.

coupling constants (hfccs) as initial estimates of the true couplings (see ESI).

The calculations showed that the singly occupied molecular orbital (SOMO) of **2** (Fig. 3) is, as anticipated, almost exclusively confined to the ligand framework with major contributions from nitrogen and carbon along with significantly smaller contributions from the *p*-type orbitals on the two chlorine atoms. The calculated α-spin density of **2** mirrors the topology of the SOMO, while spin polarization effects lead to concentration of β-spin density on boron and hydrogen atoms (Fig. 3). Consequently, the calculated hfccs indicate coupling of the unpaired electron primarily to one ^{10,11}B and two equivalent ^{14}N and ^{35,37}Cl nuclei as well as to four unique pairs of ^{1}H centres (Table 1). The hfccs calculated for the other ^{1}H nuclei in **2** are significantly smaller (absolute values less than 0.50 G) and were, therefore, excluded from the simulation and treated indirectly by adjusting line shape.

Excellent simulation of the EPR spectrum of **2** (Fig. 2) was obtained by using the hfccs given in Table 1. In general, there is a good agreement between the hfccs obtained by spectral fitting and those given by theory, especially for the heavier nuclei. It needs to be emphasized that the small hfccs (less than 1.00 G) to

Table 1 Experimental and calculated hyperfine coupling constants [G] of **2**[a]

Nucleus	Equivalent nuclei	Exptl.	Calc.
^{10}B / ^{11}B	1	1.13 / 3.37	−1.54 / −4.59
^{14}N	2	2.75	2.41
^{35}Cl / ^{37}Cl	2	3.77 / 3.14	2.46 / 2.05
^{1}H	2	4.00	−3.83
^{1}H	2	0.91	−1.04
^{1}H	2	0.50	1.00
^{1}H	2	0.44	−0.85

[a] Experimental parameters were determined from a simulation optimized to match the recorded spectrum. The simulation used a Voigtian line shape with Gaussian and Lorenzian peak-to-peak line widths of 0.90 and 0.15 G, respectively.

^{1}H nuclei remain ambiguous as the broad spectral line width allows for multiple equally acceptable fits to the experimental data. The smaller ^{1}H couplings can also be treated indirectly by increasing the line width, which shows that the other hfccs change very little from one fit to the other and collectively give rise to the dominant 16-line pattern in the experimental spectrum. Furthermore, all attempts to simulate the experimental EPR spectrum with fewer hfccs than those to one ^{10,11}B and two equivalent ^{14}N, ^{35,37}Cl, and ^{1}H nuclei were unsuccessful. Thus, we are confident that the data corresponds to the $[(biq)BCl_2]^{\bullet}$ radical, which indicates that the ligand has undergone a one electron reduction.

The identity of **2** was subsequently confirmed *via* full crystallographic analysis. The molecular structure of the radical has C_{2v} symmetry with a fully planar ligand backbone (Fig. 1). The crystallographic data for **2** (and $[(biq)BCl_2]^{+}$) allow for interesting relationships to be drawn between the electronic structure of the biq ligand and its metrical parameters. Specifically, the unpaired electron leads to lengthening of the N–C bonds (from 1.342(4) and 1.346(4) Å to 1.373(5) and 1.380(5) Å) and shortening of the C–C bond connecting the two quinoline units (from 1.456(5) to 1.411(5) Å), which is fully consistent with the topology of the SOMO of **2** as well as trends established for the bpy ligand at different charge states.[10] In the latter context, the metrical parameters of **1** and **2** can be compared to that of the analogous bpy complexes $[(bpy)BCl_2]^{+}$ and $[(bpy)BCl_2]^{\bullet}$,[12] which shows that the annulation of the ligand has virtually no effect on key intraligand bond lengths and changes in them upon reduction. Furthermore, while $[(bpy)BCl_2]^{\bullet}$ has been called a persistent radical, it is in fact isolable and essentially indefinitely stable in the solid state under anaerobic conditions.[12]

The metrical parameters of **1** and **2** can be compared with crystallographic data reported for transition metal complexes of biq for any apparent ambiguities in their characterization.[13] It has already been discussed in the literature that, according to theoretical evidence, the complex $(biq)Ti(Cp)_2$ contains a Ti(III) centre and a biq anion radical though it is not certain if the two unpaired electrons couple ferromagnetically or antiferromagnetically.[10] The structural trends established herein corroborate the above interpretation and also suggest that the complex $Co(biq)_2$, originally described as a Co(0) species,[14] should instead be viewed as a Co(II) complex incorporating two anionic biq radicals. The strongest structural evidence supporting this view is the length of the intraligand C–C bond that connects the two quinoline units: the two biq ligands in $Co(biq)_2$ are inequivalent with short C–C distances of 1.427(6) and 1431(5) Å. Consequently, the electronic structure of $Co(biq)_2$ was subjected to a comprehensive theoretical analysis using multireference methods (NEVPT2/SA-CASSCF(13,9)) to correctly identify the ligand charge state (see ESI).

The theoretical results show that the ground state of $Co(biq)_2$ is a spin-doublet that is separated from the first excited state by 1437 cm^{-1}. Decomposition of the ground state wave function into contributions from various electronic configurations shows that roughly 60% of them contain a high-spin Co(II) ion and two anionic radical ligands; the remaining 40% includes different ligand-to-metal and metal-to-ligand charge transfer

configurations. Thus, rather than invoking extensive metal-to-ligand backbonding to explain the observed structural features,[14] the ground state of $Co(biq)_2$ should instead be viewed in terms of an antiferromagnetically coupled high-spin Co(II) centre and two biq radicals, stabilized by strong kinetic exchange.

There are other examples of complexes incorporating the biq ligand that potentially deserve a second look. For example, the intraligand metrical parameters in $[(biq)Ru([9]aneS_3)Cl][PF_6]$ ([9]aneS$_3$ = 1,4,7-trithiacyclononane),[15] and the short C–C bond connecting the two quinoline units in particular (1.39(2) Å), hint of the possibility of an anionic radical and Ru(III) but this interpretation has not been discussed. Further evidence supporting the presence of an anionic biq radical is seen in the solid state packing of $[(biq)Ru([9]aneS_3)Cl][PF_6]$ in which the cations form distinctive dimers *via* π-stacking interactions between the biq ligands (shortest C···C distance *ca.* 3.31 Å). Interestingly, the same kind of packing is not observed for analogous complexes employing related polypyridine ligands,[15] which suggests that the dimeric arrangement in $[(biq)Ru([9]aneS_3)Cl][PF_6]$ might result from weak antiferromagnetic interactions between two biq anion radicals. Further experimental and theoretical data are clearly needed to test the validity of this hypothesis.

We conclude our work with a discussion of the packing of **2** in the solid state. In this instance, the radicals form well-arranged layers along the crystallographic *c*-axis with the BCl_2 moieties facing in alternate directions in neighbouring layers (see ESI). The packing is again dictated by B–Cl···H–C hydrogen bonding along with π-stacking interactions that connect the individual layers. Interestingly, the layers in **2** are essentially uniformly spaced (stack spacing *ca.* 3.40 Å), which is surprising considering that planar organic radicals typically interact antiferromagnetically to form π-dimers,[16] generally leading to something else than even spaced stacking in the solid state. A classic example is the solid state structure of the 2,5,8-tri-tert-butylphenalenyl radical in which the radicals form π-dimers (C···C distances *ca.* 3.29 Å) that are strongly antiferromagnetically coupled.[17]

The even spacing of layers in the crystal structure of **2** can be explained by considering the topology of the SOMO that leads to accidental orthogonality of adjacent magnetic orbitals in the observed structure (see ESI). Consequently, radical···radical dimerization is not energetically preferred and the molecules of **2** remain essentially isolated in the solid state. This interpretation is supported by theoretical calculations (PBE1PBE/TZVP) that show the singlet and triplet states of a pair of adjacent radicals in the crystal structure geometry of **2** to be separated by 0.5 kJ mol^{-1}.

In summary, we have synthesized two related coordination compounds of biquinoline, $[(biq)BCl_2]Cl$ and $[(biq)BCl_2]^{\bullet}$, in which the ligand adopts different charge states. The compounds are the first structurally characterized *p*-block complexes of biquinoline and, by confining all redox processes to the ligand framework, allow the structural consequences of ligand reduction to be unambiguously determined. The acquired data were subsequently used to establish a reinterpretation of the electronic structure of $Co(biq)_2$ which was shown to contain the metal in the +II (not 0) oxidation state by help of theoretical calculations. The estimation of ligand charge state by means of its metrical parameters is already a well-established practice for metal complexes of bipyridine and, with the data reported herein, this practice can, and in fact should, be extended to complexes incorporating the redox non-innocent biquinoline ligand.

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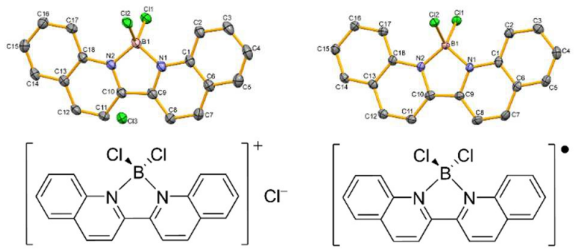

Compounds $[(biq)BCl_2]Cl$ and $[(biq)BCl_2]^{\bullet}$ are the first crystallographically characterized *p*-block complexes of biquinoline that allow the structural consequences of ligand reduction to be determined.