On the Structural and Electronic Properties of $[\text{Zn}_2(4,4'-\text{bipyridine})(\text{mes})_4]^{n-} \ (n = 0–2)$, a Homologous Series of Bimetallic Complexes Bridged by Neutral, Anionic, and Dianionic 4,4'-Bipyridine

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Supporting Information

ABSTRACT: Addition of 1 equiv of potassium metal to a tetrahydrofuran (THF) solution of $\text{Zn}_2(4,4'-\text{bipyridine})(\text{mes})_4$ ($\text{mes} = 2,4,6$-Me$_3$C$_6$H$_2)$ in the presence of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) yielded the radical anionic species $[\text{Zn}_2(4,4'-\text{bipyridine})(\text{mes})_4]^{-}$, which was characterized by single crystal X-ray diffraction in $[\text{K}(18\text{-crown-6})(\text{THF})_2][\text{Zn}_2(4,4'-\text{bipyridine})(\text{mes})_4]$ (2). A similar reaction employing 2 equiv of alkali metal afforded the related complex $[\text{K}(18\text{-crown-6})][\text{Zn}_2(4,4'-\text{bipyridine})(\text{mes})_4]$ (3). The $[\text{Zn}_2(4,4'-\text{bipyridine})(\text{mes})_4]^{n-} \ (n = 0–2)$ moieties present in 1–3 are largely isostructural, yet exhibit significant structural variations which arise because of differences in their electronic structure. These species represent a homologous series of complexes in which the ligand exists in three distinct oxidation states. Structural data, spectroscopic measurements, and density functional theory (DFT) calculations are consistent with the assignment of 1, 2, and 3 as complexes of the neutral, radical anionic, and dianionic 4,4'-bipyridyl ligand, respectively. To the best of our knowledge, species 2 and 3 are the first crystallographically characterized transition metal complexes of the 4,4'-bipyridyl radical and dianion.

INTRODUCTION

The redox-active behavior of 4,4'-bipyridine has been well established for over 50 years. Early electron paramagnetic resonance (EPR) studies on organic radicals in solution were the first to identify the 4,4'-bipyridyl anion, ($4,4'-\text{bipy}^-$) as a product of the reduction of pyridine, or 4,4'-bipyridine, with alkali metals. Further studies on the radical anion and dianion were later conducted by several research groups employing a combination of spectroscopic, electrochemical, and computational techniques. The use of 4,4'-bipyridine in molecular squares exhibiting ligand-centered mixed valency (LCMV) has been reported by Hupp and others, who have demonstrated that the electrochemical reduction of neutral supramolecular complexes can give rise to isostructural species where negative charges reside on bridging ligand moieties. However, despite the extensive research in this area, to the best of our knowledge there are no structural data available in the chemical literature for coordination complexes of these highly reductive species.

Our interest in such complexes stems from reports that transition metal complexes of open-shell "non-innocent" ligand systems may exhibit unique reactivity when compared to closely related complexes with ligand systems which are not redox-active. Numerous examples of non-innocent ligands have been reported in the literature and include semiquinone and phenoxyl systems, dithiolates, $\alpha$-dimines, $\alpha$-iminopyridines, $\alpha$-iminoketones, tetrazenes, amminyl radicals, and imino- and thio-phenolates. Similar "non-innocent" behavior has also been established for the 2,2'-isomer of bipyridine.

Herein we report the isolation and electronic characterization of $[\text{Zn}_2(4,4'-\text{bipyridine})(\text{mes})_4]$ (1) as well as of the $[\text{K}(18\text{-crown-6})][\text{Zn}_2(4,4'-\text{bipyridine})(\text{mes})_4]$ (2), and dianionic, $[\text{K}(18\text{-crown-6})][\text{Zn}_2(4,4'-\text{bipyridine})(\text{mes})_4]$ (3), derivatives and apply single-crystal X-ray diffraction, electron paramagnetic resonance (EPR), and NMR spectroscopy and density functional theory (DFT) to characterize their electronic structures. These physicochemical measurements are consistent with the presence of a 4,4'-bipyridyl radical anion in 2, and of the 4,4'-bipyridyl dianion in 3.

EXPERIMENTAL SECTION

General Methods. All reactions and product manipulations were carried out under an inert atmosphere employing standard Schlenk-line techniques.

Received: February 4, 2011
Published: May 03, 2011
or glovebox techniques. Toluene (99.9%, Rathbun Chemicals, Ltd.) and hexanes (99.9%, Rathburn Chemicals, Ltd.) were dried using an MBraun SPS-800 solvent purification system. Tetrahydrofuran (THF; 99.9%, Rathburn Chemicals, Ltd.) was distilled over potassium metal under a dinitrogen atmosphere. All solvents were stored in gastight amules under argon. In addition, toluene and hexanes were stored over activated 3 Å molecular sieves (Acros). Potassium metal (99.95%, Aldrich) was stored under dinitrogen in an MBraun UNILAB glovebox maintained at <0.1 ppm H₂O and <0.1 ppm O₂ and used as received.

IR spectra. See Figures S2 of the Supporting Information for details.12

Zn(4,4'-bipyridine)(mes)₄ (1). Zn (mes)₂ (300 mg, 0.988 mmol) and 4,4'-bipyridine (77 mg, 0.494 mmol) were dissolved in THF (~4 mL) under an inert atmosphere and stirred for 5 h, forming a pale yellow solution. The resulting solution was filtered and layered with hexanes. A powder X-ray diffraction pattern was obtained which matched the simulated diffraction pattern based on the single-crystal X-ray diffraction data (Supporting Information, Figure S1). Anal. Calcld. for C₆₆H₅₀N₂Zn: C 72.34%, H 6.86%, N 3.67%. Found: C 72.25%, H 6.77%, N 3.58%. ¹H NMR (299.9 MHz, δ [THF]) of 1: 1612 (s), 1514 (s), 1352 (s), 1233 (m), 1176 (s), 1019 (m), 944 (w), 770 (w), 687 (w), 578 (w), 438 (m), 322 (m), 298 (w), 277 (w) ppm. IR and Raman data are provided in Supporting Information, Figures S8 and S9.

Synthesis of [K(18-crown-6)][Zn(4,4'-bipyridine)(mes)]₂ (2). A mixture of 1 (100 mg, 0.131 mmol), potassium metal (5 mg, 0.130 mmol), and 18-crown-6 (35 mg, 0.131 mmol) was dissolved in THF (~5 mL) under an inert atmosphere. The reaction mixture initially takes on a deep blue color which, when stirred overnight, gives rise to a dark yellow/brown solution. The reaction mixture was filtered and layered with hexanes. After several days dark brown plate-like crystals of [K(18-crown-6)][Zn(4,4'-bipyridine)(mes)]₂ were obtained in high yields (141 mg, 81.9% crystalline yield). Anal. Calcld. for C₁₀₈H₁₀₀K₂N₄O₂Zn₂: C 61.34%, H 6.75%, N 2.35%. ¹H NMR (299.9 MHz, δ [THF]) of 2: 1612 (s), 1514 (s), 1352 (s), 1233 (m), 1176 (s), 1019 (m), 944 (w), 770 (w), 687 (w), 578 (w), 438 (m), 322 (m), 298 (w), 277 (w) ppm. IR and Raman data are provided in Supporting Information, Figures S8 and S9.

X-ray Diffraction. Single-crystal X-ray diffraction data were collected using an Enraf-Nonius Kappa-CCD diffractometer and a 95 mm
CCD area detector with a graphite-monochromated molybdenum $K_a$
source ($\lambda = 0.71073$ Å). Crystals were selected under Paratone-N oil, mounted on MiTeGen loops and quench-cooled using an open flow $N_2$
cooling device.\textsuperscript{19} Data were processed using the DENZO-SMN package, including unit cell parameter refinement and interfacing scaling (which
was carried out using SCALEPACK within DENZO-SMN).\textsuperscript{20} Structures were subsequently solved using direct methods, and refined on F$^2$
using the SHELXL 97-2 package.\textsuperscript{21}

Transmission powder X-ray patterns were recorded using a Siemens
D5000 diffractometer in modified Debye–Scherrer geometry equipped with an MBrAun position sensitive detector. The instrument produced Cu $K_\alpha_1$
radiation ($\lambda = 1.54056$ Å) using a germanium monochromator and a standard Cu source. Data were recorded on samples in flame-
sealed capillaries under dinitrogen. The capillaries were mounted on a
goniometer head and aligned so that rotation occurred along the long
central axis of the capillary. During a measurement the capillary was
rotated at $\sim$60 rpm to minimize any preferred orientation effects that
might occur.

NMR. \textsuperscript{1}$H$ and \textsuperscript{13}$C$ NMR spectra were acquired at 299.9 and 75.4
MHz, respectively, on a Varian Mercury-vx 300 NMR spectrometer. The
\textsuperscript{13}$C$ NMR spectrum of 3 was recorded at 125.8 MHz on a Bruker AVII 500
spectrometer equipped with a $1^3$C cryoprobe. \textsuperscript{1}C and \textsuperscript{1}$H$ spectra
were referenced to $d_4$-THF ($\delta = 25.37$ ppm) and to the most shielded
residual protic solvent resonance (THF $\delta = 1.73$ ppm), respectively.
Diffusion and NOE experiments were performed on a Bruker AVII 500
spectrometer equipped with a TXI inverse probe regulated at 298 K.
Diffusion experiments utilized the BFP-LED stimulated echo sequence
with diffusion times ($\Delta$) of 50 ms, bipolar diffusion-encoding field
gradient pulses of total duration 4 ms ($\phi$) and longitudinal eddy current
delays (LED) of 5 ms.\textsuperscript{22} Additional 0.6 ms purging gradients were
applied whenever magnetization was longitudinal. All gradient pulses
were of half-sine profiles with effective diffusion-encoding gradient
strengths ranging from 0.5 to 20.5 G cm$^{-1}$ (corrected for half-sine
profiles). Data analysis was performed using Bruker TOPSPIN software.
1D NOESY spectra were recorded using a single pulsed field gradient
selective excitation scheme utilizing a 40 ms selective Gaussian inversion
pulse and with a NOE mixing time of 0.8 s.

Computational Methods. All calculations presented in this paper
were carried out with the Gaussian 09 program package at the DFT level
of theory.\textsuperscript{23} Geometries of the complexes 1–3 were fully optimized
without imposing any symmetry constraints ($C_1$ symmetry), employing the
M05–2X hybrid meta-exchange-correlation functional developed by
Truhlar and co-workers.\textsuperscript{24} The M05–2X functional has been recom-
mented for use with Zn compounds and in the present study afforded
slightly better geometries compared to B3LYP. All stationary points
were of half-sine profiles with effective diffusion-encoding gradient
strengths ranging from 0.5 to 20.5 G cm$^{-1}$ (corrected for half-sine
profiles). The NICS(1) values largely reflect the influence of $\pi$-electrons, and are therefore a better indicator of the ring current (aromaticity)
then the values at the center, where $\sigma$-bonding contributions are also of importance.

Additional Characterization Techniques. IR data were recorded
on solid samples in Nujol mulls. The mulls were made up inside an
inert atmosphere glovebox and the KBr plates placed in an airtight
container prior to data collection. Spectra were recorded on a Nicolet
Magna-IR 560 spectrometer in absorbance mode (Happ-Genzel FT
apodization) with a Ge/CsI beam splitter and liquid nitrogen cooled
Mercury Cadmium Telluride (MCT) detector.

Raman spectra were recorded on solid samples under dinitrogen in
flame-sealed Pyrex capillaries using a Dilor Labram 300 spectrometer. The
excitation radiation was produced by a 20 mW helium–neon laser
operating at a wavelength of 632.817 nm. Optical density filters could be
inserted into the beam to reduce photon flux, decreasing the likelihood
that photochemical reactions would take place during the measurement.
Typically measurements were performed at 1% of full intensity with a
counting time of 120 s. Calibration of the spectrometer was performed
before each measurement by referencing to the 520.7 nm line of a silicon
wafer.

CW EPR experiments were performed using an X-band Bruker
BioSpin GmbH EMX spectrometer equipped with a high sensitivity
Bruker probe head. Experiments were conducted with 2–10 mW
microwave power, 0.1 mT modulation amplitude, and a modulation
frequency of 100 kHz. The magnetic field was calibrated at room
temperature with an external 2,2-diphenyl-1-picrylhydrazyl standard
($g = 2.0036$). Solid state spectra were recorded on approximately
2 mg of sample in flame-sealed quartz capillaries. Solution phase spectra
were recorded on 0.1 mM solutions in dry THF.

CHN elemental analyses were performed on 5 mg samples submitted
under vacuum in flame-sealed Pyrex ampoules.

\section*{RESULTS AND DISCUSSION}

\textbf{Synthesis.} The complex \textsuperscript{2}$Zn_2(4,4'-bipyridine)\{mes\}_4$ (1) was
synthesized by direct reaction of 4,4'-bipyridine (4,4'-bipy) with
Zn(mes)$_2$ (mes = $2,4,6$-Me$_3$C$_6$H$_2$) in a 1:2 ratio in anhydrous
tetrahydrofuran (THF). A compositionally pure white crystalline
solid can be isolated in high yields (>60%) by layering a THF
solution of 1 with hexanes. The purity of 1 was confirmed by
multielement NMR spectroscopy, powder X-ray diffraction (see
Supporting Information), and elemental analysis. No other
products were observed for this reaction. Single-crystal X-ray
diffraction measurements reveal two dimerization moieties that are
bridged by a 4,4'-bipy ligand (Figure 1a). Crystallographic data and experimental parameters for the structure are presented
in Table 1. There are numerous Zn/4,4'-bipyridine complexes in the
field of coordination polymer/metal—organic framework
chemistry;\textsuperscript{32} however, discrete two-to-one species in which two
zinc nuclei are bridged by a single 4,4'-bipyridine ligand are much
rarer.\textsuperscript{33} Rarer still are 4,4'-bipyridine-bridged homoleptic organ-
ometallic zinc complexes, none of which have been structurally
classified to date.\textsuperscript{34}\

Reduction of 1 with 1 equiv of potassium metal in THF in the
presence of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane)
was found to yield a dark blue solution from which [K(18-crown-6)\-
(THF)$_2$][Zn$_2$(4,4'-bipy)\{mes\}_4] (2) was isolated. The compositional
NMR spectrum with a chemical shift of 2.42 and 2.32 ppm for complexes
1 and 3, respectively. Nuclear-Independent Chemical Shifts (NICS)
values were calculated at the same level using the GIAO method as
recommended by Schleyer et al.\textsuperscript{31} The NICS probes (ghost atoms) were
placed 1 Å above the centers of the rings (defined as the average of the
Cartesian coordinates of the ring atoms). The NICS(1) values largely
reflect the influence of $\pi$-electrons, and are therefore a better indicator of the ring current (aromaticity) than the values at the center, where $\sigma$-bonding contributions are also of importance.
Figure 1. Thermal ellipsoid plots of (a) one of the two crystallographically unique \(\text{Zn}_2(4,4\text{-bipy})(\text{mes})_4\) units present in the asymmetric unit of 1; (b) one of the \([\text{Zn}_2(4,4\text{-bipy})(\text{mes})_4]^{2-}\) radical anions present in 2a; (c) the \([\text{Zn}_2(4,4\text{-bipy})(\text{mes})_4]^{2-}\) dianion present in 3 (a crystallographic center of inversion sits between C13 and C13'). All hydrogen atoms have been omitted for clarity. Anisotropic displacement ellipsoids are pictured at the 50% probability level.

In the absence of 4,4′-bipyridine in the field of metal organic framework chemistry it is also worth highlighting that reduction of the ligand character to the \(\text{Zn}^{2+}\) bond and has the effect of moderately weakening the bonds between the \(\text{Zn}(II)\) centers and the strongly \(\sigma\)-donating mesityl substituents (manifested in a lengthening of the \(\text{Zn}--\text{C}\) bonds). A similar effect, albeit less pronounced, has been reported by our research group for the \(\text{Fe}/2,2\text{-bipyrindyl systems }[\text{Fe}(2,2\text{-bipy})(\text{mes})_2]^{n+} (n = 0, 1, 2)\). The second most pronounced structural change, and the most meaningful, is to bond distances between pyridyl rings of the 4,4′-bipyridine moieties. These distances are significantly shortened on going from the neutral complex (1.482(\text{av}) Å) to the radical (1.420(\text{av}) Å) and dianionic (1.373(4) Å) analogues. The degree of contraction of this \(\text{C}--\text{C}\) bond is very similar to that observed in recent studies on the reduction of the 2,2′- and 4,4′-isomers of bipyridine to the corresponding anions and dianions. The lowest unoccupied molecular orbital (LUMO) of 4,4′-bipyridine, which becomes occupied upon reduction, is a \(\pi^*\) antibonding orbital with an in-phase relationship between the \(p\) orbitals on the carbon atoms linking the two rings (as pictured in Figure 3b). This in-phase relationship implies a greater degree of double bond character in the reduced species. Because of the ubiquitous use of 4,4′-bipyridine in the field of metal organic framework chemistry it is also worth highlighting that reduction of the ligand has a cumulative effect on the \(\text{Zn}--\text{Zn}\) distances in these systems which shorten from 11.435(\text{av}) Å in 1, to 11.232(\text{av}) Å for 2, and finally to 11.187(1) Å in 3.
We have optimized the geometries of complexes 1DFT (S = 0), 2DFT (S = 1/2), and 3DFT (S = 0) in the indicated electronic states. For complex 3DFT we have also located an excited triplet state, which has not been considered further, because of the high energy separation (+43 kcal mol⁻¹) from the ground state. In all cases, the optimized geometries obtained using DFT were found to be in line with the crystallographically determined data (see Table 2). The C–C and C–N bond distances are within ±0.01 Å of their experimental counterparts, while the Zn–N and Zn–C interactions are typically overestimated by 0.02–0.06 Å. Upon reduction of the neutral species to the anionic and dianionic forms, the Zn–N distances contract from 2.24 to 2.07 and 1.97 Å (for complexes 1DFT, 2DFT and 3DFT, respectively) compared to 2.18, 2.04, and 1.98 Å for 1, 2 and 3, respectively. At the same time the Zn–C interactions are weakened (2.01, 2.03, and 2.06 Å). The C–C bridge between the two pyridyl rings of the 4,4’-bipyridine ligand also contracts considerably upon reduction from 1.48 Å to 1.43 Å and 1.38 Å, as a result of successive double bond in the dianionic species. The same trend is apparent for bond 2 (according to the numbering scheme employed in Figure 3), although the contraction is less pronounced compared

| Table 1. Selected X-ray Data Collection and Refinement Parameters for [Zn₂(4,4’-bipyridine)(mes)₄] (1), [K(18-crown-6)(THF)]₂[Zn₂(4,4’-bipyridine)(mes)₄] (2a and 2b), [K(18-crown-6)]₂[Zn₃(4,4’-bipyridine)(mes)₄] (3), and [K(18-crown-6)(THF)][Zn(mes)₃] (4) |
|-----------------|----------------|----------------|----------------|----------------|----------------|
| compound | 1 | 2a | 2b | 3 | 4 |
| formula | CₓHᵧN₂Zn₂ | CₓHᵧN₂KₓOᵧZn₂ | CₓHᵧN₂KₓOᵧZn₂ | CₓHᵧN₂KₓOᵧZn₂ | CₓHᵧKₒZn |
| Fw | 763.64 | 1211.26 | 1211.26 | 1370.46 | 798.42 |
| space group, Z | 1, 4 | 1, 4 | 1, 4 | 1, 4 | 1, 4 |
| a (Å) | 11.3857(1) | 19.7748(3) | 20.6578(3) | 20.8215(1) | 13.8582(2) |
| b (Å) | 19.2169(2) | 20.6378(3) | 20.8215(1) | 20.8215(1) | 13.8582(2) |
| c (Å) | 19.5817(2) | 21.1360(3) | 27.0298(1) | 22.4989(4) | 24.2059(1) |
| α (deg) | 83.461(1) | 118.439(1) | 76.111(1) | 90.0 | 90.0 |
| β (deg) | 80.452(1) | 109.127(1) | 81.897(1) | 92.474(1) | 90.0 |
| γ (deg) | 73.809(1) | 98.547(1) | 61.729(1) | 90.0 | 90.0 |
| V (Å³) | 4047.15(7) | 6666.9(2) | 9953.6(1) | 3652.6(1) | 8770.7(1) |
| ρcalc (g cm⁻³) | 1.253 | 1.207 | 1.212 | 1.246 | 1.209 |
| radiation, λ (Å), temp (K) | Mo Kα, 0.71073, 150(2) | | | | |
| μ (mm⁻¹) | 1.218 | 0.833 | 0.837 | 0.828 | 0.700 |
| reflections collected | 35531 | 41137 | 89021 | 15136 | 19056 |
| independent reflections | 18473 | 23111 | 45306 | 8264 | 9975 |
| R(int) | 0.0286 | 0.0403 | 0.0261 | 0.0329 | 0.0250 |
| R1/wR2, l ≥ 2σl (%) | 3.88/9.62 | 4.78/12.41 | 4.71/11.66 | 4.54/9.98 | 4.07/10.37 |
| R1/wR2 all data (%) | 5.11/10.45 | 7.04/16.61 | 7.08/13.09 | 7.85/11.25 | 6.45/11.37 |

| Table 2. Mean Bond Distances [Å] and Angles [deg] for the [Zn₂(4,4’-bipyridine)(mes)₄] Moieties Crystallographically Characterized in 1–3 and the Optimized Computed Geometries |
|-----------------|----------------|----------------|----------------|----------------|
| bond | 4,4’-bipyridine | neutral | radical | dianion |
| bond | 1DFT | 2DFT | 3DFT | 1DFT | 2DFT | 3DFT |
| Zn–N–N | 2.183 | 2.24 | 2.043 | 2.043 | 2.07 | 1.977 |
| Zn–mes-N | 1.975 | 2.01 | 1.987 | 1.992 | 2.03 | 2.004 |
| torsion | 17.23 | 35.25 | 38.2 | 2.83 | 2.40 | 0.0 |
| N–Zn–C | 103.32 | 100.1 | 111.12 | 114.44 | 109.6 | 114.33 |
| C–Zn–C | 153.26 | 159.8 | 137.69 | 137.05 | 140.9 | 131.33(10) |

| Figure 2. Thermal ellipsoid plot of the atoms present in the asymmetric unit of 4. All hydrogen atoms and minor component arising from some crystallographic disorder of the THF molecule have been omitted for clarity. Anisotropically displacement ellipsoids are pictured at the 50% probability level. |
to the interpyridyl bond. Conversely, bonds 1 and 3 follow the opposite trend, lengthening upon reduction. The higher degree of overlap in the central bond also enforces coplanarity of the two pyridyl moieties, the optimum torsion angle being reduced from 38.2° in 1DFT to 0° in both 2DFF and 3DFF. A spin density plot for the radical anionic complex 2DFF is provided in the Supporting Information, Figure S20.

■ MAGNETIC RESONANCE STUDIES (NMR AND EPR)

EPR spectra were recorded for samples 2 and 3. The EPR spectrum of a solid sample of 2 reveals a strong resonance at room temperature with a g value of 2.0039 (Figure 4). This resonance is relatively sharp as would be expected for an organic radical anion and is very similar to that observed for solid samples of the alkali metal salts of the 4,4'-bipyridyl radical anion such as Na(4,4'-bipy)(en) (g = 2.0043 in the solid state).7 The spectrum of a solid sample of 3 reveals a much weaker resonance at a similar g value which we attribute to trace amounts of the 4,4'-bipyridyl anion present in the sample. 3 is extremely air- and moisture-sensitive, and we believe that in recording the EPR spectrum some sample decomposes to give rise to the radical anion.

The solution phase EPR spectrum of a THF solution of 2 reveals a complex asymmetric resonance exhibiting extensive hyperfine coupling (Supporting Information, Figure S21). All of our attempts to model this resonance have thus far proven unsuccessful. We believe that the observed spectrum is a composite of two resonances arising from two distinct paramagnetic species. The most significant component of such a resonance is the [Zn2-(4,4'-bipy)(mes)4]1− radical anion present in the crystal structure of 2. Diffusion NMR data for the neutral analogue 1 (vide infra) indicate that the bipyridyl-bridged structure observed in the solid state is largely intact in solution; however, a minor amount of ligand dissociation is also likely to be present. At the high dilution limits required for solution phase EPR spectrometry the degree of dissociation of [Zn2(4,4'-bipy)(mes)4] to Zn(mes)2 and 4,4'-bipyridine is expected to be more pronounced (an increased effective concentration of THF is likely to favor heavily solvated Zn(mes)2). Such dissociation is also likely to be present for sample 2 and 3. In the case of a THF solution of 2, this would give rise to an additional contribution to the EPR spectrum arising from the free 4,4'-bipyridyl radical anion. The spectrum of the 4,4'-bipyridyl radical anion has previously been reported by us and others and found to have a g value of 2.00439.1,2,7 The overlap of both such resonances gives rise to the asymmetric spectrum we have recorded. Because of the extensive hyperfine coupling which is expected for both contributing species, deconvolution and modeling of the observed spectrum has proved univiable. These results were reproducible and observed on each occasion a solution phase sample of 2 was studied.

1H and 13C{1H} NMR spectroscopic studies of a d6-THF solution of 1 indicate that the two-to-one structure which is observed in the solid-state remains intact in solution with little evidence of ligand dissociation. The 1H NMR spectrum of 1 reveals five resonances at 8.57, 7.71, 6.73, 2.42, and 2.21 ppm. The two resonances at 8.57 and 7.71 ppm correspond to the ortho- and meta- 4,4'-bipyridyl protons, respectively. These resonances are shifted with respect to free 4,4'-bipyridine (8.69 and 7.67 ppm). As would be expected, the resonances arising from the mesityl moieties occur at very similar chemical shifts to the Zn(mes)2 precursor (6.71, 2.45, 2.20 ppm). To confirm that the structure of 1 remains intact in solution and that there is no significant ligand dissociation, a one-dimensional NOESY spectrum on a d6-THF solution of 1 was conducted. The resonance arising because of the mesityl ortho-methyl groups (2.42 ppm) was selectively inverted which resulted in the enhancement of the signal intensities for the mesityl meta-protons and the 4,4'-bipyridyl ortho-protons, consistent with the bridged structure remaining intact in solution. The resonance arising from the 4,4'-bipyridyl meta-protons was enhanced to a much lesser degree than those in the ortho-positions indicating that they are more distant from the ortho-methyl groups of the mesityl functionalities. Additional room-temperature (298 K) diffusion experiments on Zn(mes)2, 4,4'-bipyridine and 1 were also conducted to establish the structure of 1 in solution (Supporting Information, Figure S7). The diffusion coefficient values (D) determined for 1 show that those arising from 4,4'-bipyridine resonances (1.132 x 10−9 and 1.133 x 10−9 m²/s for the ortho- and meta-protons, respectively) are very close in magnitude to those arising from the Zn(mes)2 moieties (1.027 x 10−9, 1.021 x 10−9, and 1.031 x 10−9 m²/s for the meta-protons, the ortho-methyl, and para-methyl substituents, respectively). The small discrepancy in the values obtained for the diffusion coefficients indicates that if there is any dissociation of 1 to give 2 equiv of Zn(mes)2 and 4,4'-bipyridine in solution, the equilibrium lies strongly shifted toward species 1. This assumption is further supported by the observation that the observed D values are significantly different to those obtained for a solution of 4,4'-bipyridine of the same molarity (1.911 and 1.913 x 10−9 m²/s for the ortho- and meta-protons, respectively).

The 1H NMR spectrum of sample 3 (which is contaminated by a small amount of 4) reveals a significant shift of the 4,4'-bipyridyl resonances with respect to the values observed for the neutral parent compound 1 from 8.57 and 7.71 ppm to 5.92 and 4.51 ppm for 1 and 3, respectively. A comparison of the 1H NMR spectra of 1 and 3 is provided in the Supporting Information, Figure S16. The chemical shift values observed for 3 are consistent with those previously reported for the only known...
example of a complex of the 2,2’-bipyridyl dianion, [\(\{\text{Yb}(\mu^2-N_2C_2H_2)(\text{THF})_2\}_2\}]^3-\text{N}\), which were reported at 6.54, 5.28, 5.02, and 4.01 ppm.99 The lower chemical shift values of the bipyridyl resonances observed in the $^1H$ NMR spectrum of 3 are consistent with a significant reduction in the aromatic character of the bipyridyl ring system and a greater degree of localized alkenelike character to the bond between the carbon atoms to which the protons are bonded. No paramagnetic resonances were observed in the $^1H$ NMR spectrum of a $d_0$-THF solution of 2. They are presumably broadened and lost in the baseline of the spectrum.

To verify the link between aromaticity and the changes in $^1$H NMR chemical shifts, we have computed these parameters using DFT, along with the Nucleus Independent Chemical Shifts (NICS) 1 Å above the center of the bipyridyl rings. The calculations reproduce the significant shielding of the aromatic 4,4’-bipy resonances: $\delta_{\text{calc}} = 8.51$ and 7.40 ppm in $^1$DFT and 6.20 and 4.66 ppm in $^3$DFT. A full list of computed and measured chemical shifts is given in the Supporting Information, Table S1. The NICS methodology has emerged as a sensitive probe of aromaticity because the electronic environment of the NICS probe ghost atom (see Experimental Section for details) is highly sensitive to the ring currents characteristic of aromatic systems. For $^1$DFT, the strongly negative values calculated for the pyridyl rings, $-9.98$ ppm, are indicative of substantial aromatic character, and are in fact identical to the values computed for the free ligand at the same level of theory (NICS(1) = $-9.82$ ppm). The aromaticity as measured by NICS is diminished by the addition of one ($^2$DFT, NICS(1) = $-1.88$ ppm) and two ($^3$DFT, NICS(1) = $-4.08$ ppm) electrons to the $\pi$-system of the ligand. The value for 3 is in fact close to that for the free dianionic bipyridine (+4.94 ppm), and clearly reflects the antiaromatic character of the rings of the dianion.

The topology of the electron density in $^1$DFT, $^2$DFT, and $^3$DFT, analyzed using the atoms in molecules (AIM) methodology, provides an alternative perspective on the changes in the bonding of the rings. Full details of the analysis are presented in Supporting Information, Table S2. The ellipticity at the central C=C bond critical points is a sensitive measure of $\pi$-character: values close to zero indicate a cylindrical symmetric (i.e., $\sigma$) bond, while deviations away from zero indicate increasing $\pi$-character (values in the range 0.18–0.22 are found for aromatic C=C double bonds with partial $\pi$-character). The $\epsilon$ value for the bridging bond increases dramatically from 0.04 in $^1$DFT to 0.34 in $^3$DFT, again strongly supporting the formulation of the central C=C bridge as double bond. Similarly, the ellipticity of bond 2 within the pyridyl rings increases from 0.22 to 0.37 upon two-electron reduction.

All attempts to measure the standard potentials for the reduction of the neutral complex 1 to the radical anion, $[\text{Zn}_2(4,4’-\text{bipy})(\text{mes})_4]^{2-}$, and dianion, $[\text{Zn}_2(4,4’-\text{bipy})(\text{mes})_4]^{3-}$, were severely hindered by the extreme air- and moisture-sensitivity of all three species. Such data would have strongly complemented our experimental observations and provide an interesting comparison with respect to the electrochemical data available for 4,4’-bipyridine.83 Despite numerous attempts at recording cyclic voltammograms for 1 we were unable to observe any meaningful signals because of sample decomposition. Despite extensive purging of predried solvents with dinitrogen and the transfer of solutions under an inert atmosphere, we invariably found that samples decomposed prior to the application of an electrical potential. The 0.1 mM solutions required for such measurements are presumably too dilute to allow for the manipulation of the samples on the bench, even under an inert atmosphere.

### CONCLUSIONS

We have isolated and characterized a homologous series of isostructural bipyridyl-bridged dimers, $[\text{Zn}_n(4,4’-\text{pyridine})_n(\text{mes})_4]^{n-}$ ($n = 0 \ (1), \ 1 \ (2), \ 2 \ (3)$), containing neutral, radical anionic and dianionic forms of the 4,4’-bipyridyl ligand, respectively. Species 2 and 3 represent the first crystallographically authenticated examples of complexes containing the chemically reduced forms of the 4,4’-bipyridyl ligand. The rich redox chemistry of this common ligand may be exploited in coordination polymers and metal organic frameworks giving rise to “switchable” materials where the redox chemistry of ligands and metals are finely matched to facilitate electron transfer between them.

### ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic files in CIF format for 1–4. Full experimental and computational details as well as NMR, IR and Raman spectra, powder X-ray diffraction data. This material is available free of charge via the Internet at http://pubs.acs.org.

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### ACKNOWLEDGMENT

We thank the EPSRC and the University of Oxford (studentships to M.I. and T.K.) for financial support of this research. We also thank Dr. Tim Claridge for assistance with NMR spectroscopy, Dr. Jeffrey Harmer for help with EPR spectroscopy, Ragnar Björnsson for helpful comments on NMR calculations, Stephen Boyer (London Metropolitan University) for the elemental analyses, and the University of Oxford for access to OSC, CAESR, and Chemical Crystallography facilities.

### REFERENCES


