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Toward new paradigms in mixed-valency: ytterbocene–terpyridine charge-transfer complexes

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$(C_5Me_5)_2Yb\cdot OEt_2$ reacts with terpyridine and tetrapyridinylpyrazine to afford new mixed-valent systems.

The study of mixed valency is a topic central to the search for highly conducting materials, both as a bulk property and in discrete supramolecular systems.[1] Of particular interest and relevance to this paper are discrete assemblies where two metal centres, connected by a bridging ligand, show a pronounced electronic communication. Such interactions allow the possibility of delocalisation of electron density over fairly long distances, and in the emerging field of molecular electronics this represents one of the simplest electronic building blocks: a molecular wire. Moreover, the establishment of a controlling mechanism for this communication could potentially lead to switching states, which is essential for the development of the basic elements of molecular electronic and quantum computing devices.[2]

The present study investigates a novel type of multi-metallic construct that assesses electronic communication between lanthanide metal subunits. Lanthanides have rarely been used for such purposes, and are attractive due to their often-useful photophysical and redox properties. Most importantly, this study brings to bear a paramagnetic ground-state electronic configuration that has recently been reported[3] for various mono- and bidentate N-heterocyclic base adducts of ytterbocene (*e.g.*, Cp*$_2$Yb(bpy) and Cp*$_2$Yb(phen); Cp* = C_5Me_5). The unique energetics in these complexes derive from an apparently spontaneous electron transfer from the f^{14} Yb(II) metal centre to the lowest unoccupied molecular orbital (LUMO) on the ligand. This gives rise to a ground electronic state involving an f^{13} metal centre and a ligand radical anion, which in certain cases leads to an antiferromagnetic exchange interaction for the unpaired spins. We have expanded upon this class of compounds to show that the tridentate tpy ligand (tpy = 2,2′:6′,2″-terpyridine) fits within the ytterbocene wedge. Such a metal–ligand system is appealing since the symmetrical tpy ligand simplifies characterization, due to the metal fragment connection being directed down the main axis of the molecular assembly. A number of dimetallic ytterbocene complexes have been reported.[4] However, systematic structural variations (*i.e.*, progressively increasing metal–metal separation as used to understand communication in Ru(II/III) dimers[5]) have yet to be explored. Here we report our initial findings on the dimetallic complex [Cp*$_2$Yb]$_2$(tpp) (tpp = tetra-2-pyridinylpyrazine), and its structurally homologous monomeric complex.

Complexes **1** and **2** are prepared by reacting one and two equivalents of Cp*$_2$Yb(OEt$_2$)[6] with tpy and tpp in toluene, respectively. Both are purified by recrystallisation from boiling toluene, and crystals for X-ray analysis were obtained from this procedure.† ^{1}H-NMR supports the paramagnetic nature of the complexes. Fig. 1 clearly shows that the tpy ligand is bound in a tridentate manner within the ytterbocene wedge. The central Yb–N bond distance is 2.41(1) and the outer Yb–N distance is 2.42(1) Å. These values are both significantly longer than the mean value of 2.32 Å reported for Cp*$_2$Yb(bpy).[3] This may be due to a significant steric interaction between the exterior pyridyl groups and the Cp* rings. This interaction is also manifested in the Yb–Cp*$_{centroid}$ distances for **1** (2.44 Å) *vs.* 2.32 Å for the bpy complex. However, the Cp*$_{centroid}$–Yb–Cp*$_{centroid}$ angle is essentially the same for both complexes [138.3° for **1** and 139.3° for Cp*$_2$Yb(bpy)].

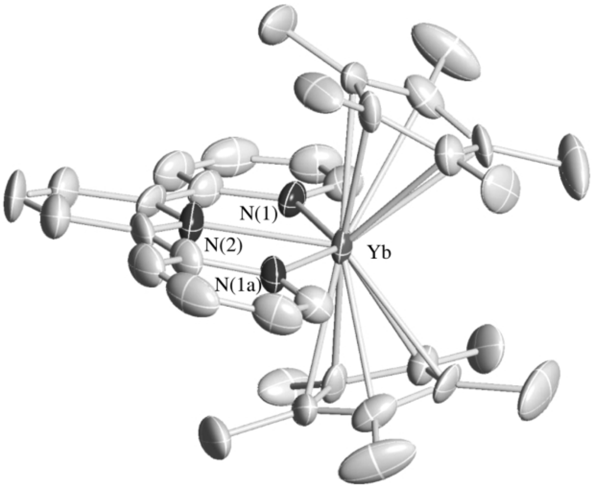

Fig. 1 ORTEP of **1** at 50% probability. H atoms omitted for clarity.

The structure of **2** (Fig. 2) is not of sufficient quality to provide quantitative information but the data are good enough to clearly establish connectivity. The poor data quality is a result of two different orientations of the tpp ligand (and the associated ytterbocene groups) centered around the axis created by the Yb and pyrazine N atoms. Each end of the tpp ligand binds in a tridentate manner. The tpp ligand is significantly distorted about the central pyrazine ring with a C1–C2–C3–C4 torsion angle of *ca.* 55°. This torsion results in a distortion of the N1–C1–C2–N2 torsion angle (*ca.* 24° for **2** vs 1.3° for **1**). The Yb centres are separated by 7.57 Å, which compares to values reported between 6.154–6.891 Å for transition metal tpp complexes.[7]

Voltammetric data (Fig. 3) for **1** are strikingly similar to those obtained for the bpy and phen adducts reported previously.[8] This similarity is *prima facie* evidence for the electron-transfer [(f)^{13}-(Lπ*)^1] ground state rendering **1** a paramagnetic species.

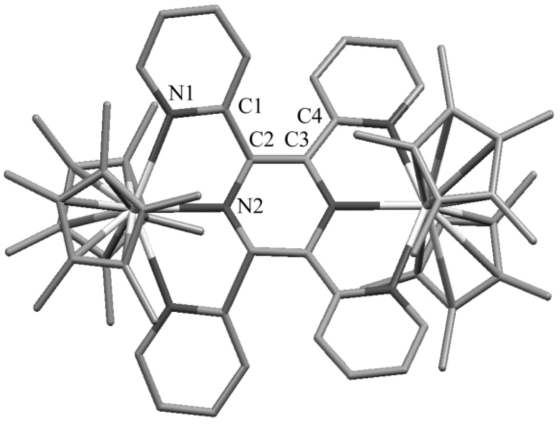

Fig. 2 Molecular structure of **2**. Hydrogen atoms have been omitted for clarity. Only one orientation of the disordered tpp ligand is shown.

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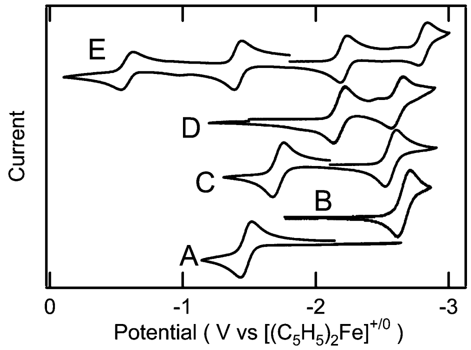

Fig. 3 Cyclic voltammograms of (A) $Cp^*_2Yb(THF)_n$, (B) tpy, (C) **1**, (D) tpp, and (E) **2** in 0.1 M $[(n\text{-}Bu)_4N][B(C_6F_5)_4]$/THF at 200 mV s^{-1}. All solutions are ~5 mM in analyte.

The stabilization of this paramagnetic ground state in **1** relative to the fully oxidized and fully reduced forms (*i.e.*, the comproportionation reaction, K_c[9]) based on these redox data is ~10^{14}. The voltammetric data for **2** reveals two reduction waves and two oxidation waves, all of which are reversible. Free tpp can also be reversibly reduced in two successive 1-electron steps. Based on comparisons to the tpy system and the diimine and bimetallic systems of Andersen *et al.*,[3,4] the redox processes in **2** are assigned to 1-electron reductions of each of the two metal centers and two successive 1-electron oxidation steps of the doubly-reduced tpp ligand. If the two metal centers in **2** were completely non-interacting, the separation between the two metal-based redox waves should approach the theoretical limit of ~ 36 mV (*i.e.*, the separation is determined solely by statistical, entropic factors).[10] The observed separation is ~600 mV indicating significant communication between metal centers. Note also that the separation between the two reduction waves in free tpp (~300 mV) is an approximate measure of the spin-pairing energy for the two electrons in the tpp LUMO. This separation increases to ~830 mV in **2** suggesting that the electronic distribution in the π* orbital(s) of the bridging ligand is significantly different than that in the uncomplexed ligand.

The electronic-absorption spectra of **1** and **2** (Fig. 4) are characterized by four band systems between 3500 and 32 000 cm^{-1} (labeled I–IV) that are tentatively assigned to imine-localized (I–III) or π*(imine) → f charge-transfer (IV) transitions. The electrochemical data for **1** and **2** suggest that these ytterbocene–imine adducts form the spontaneous Yb→imine charge-transfer ground state characteristic of ytterbocene adducts of this type (*vide supra*). It is anticipated on this basis that the electronic spectra of **1** and **2** will exhibit imine-localized π→π* and/or π*→π* absorption bands that resemble those of uncoordinated $(tpy)^-$ and $(tpp)^{2-}$, respectively. (Similar spectral assignments were made for $Cp^*_2Yb(bpy)$ and $Cp^*_2Yb(phen)$.[3]) The strong intensities of bands I, II, and III are consistent with their assignment to imine-localized π→π* and/or π*→π* bands. Further spectroscopic evidence for the presence of Yb→imine charge-transfer ground states for **1** and **2** is provided by the observation of absorption bands (IV) attributable to optically promoted π*(imine)→f transitions, which are the converse of the spontaneous process responsible for creating the charge-transfer ground state of these molecules. The energies of these π*(imine)→f transitions for **1** and **2** are expected to roughly correlate with the separations between the $(tpy)^{-1/0}/Yb^{3+/2+}$ or $(tpp)^{-2/-1}/Yb^{3+/2+}$ pairs of redox waves, respectively; notably, the separation between these imine- and metal-based redox processes (~ 0.8 V or 6400 cm^{-1}) gives a reasonable approximation to the energies of their respective π*(imine)→f LMCT band (ΔE ~ 4300–6500 cm^{-1}).

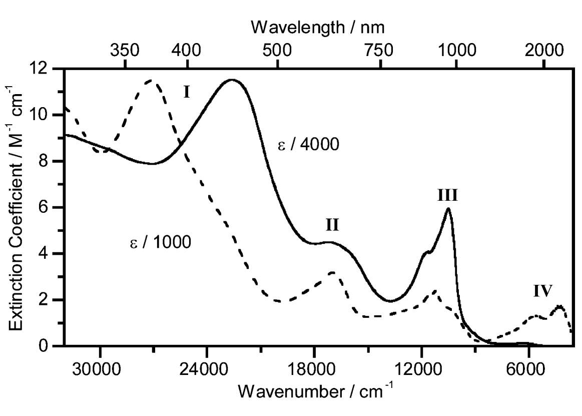

Fig. 4 Electronic spectra of **1** (---) and **2** (—) in toluene at 300 K.

In summary, the tridentate ligand tpy has been found to bind symmetrically within the wedge of ytterbocene. Based on eletrochemical and spectroscopic data, and comparisons with known adducts of ytterbocene, this complex is deduced to have an $[(f)^{13}((tpy)\pi^*)^1]$ electronic ground state configuration. In a similar manner, the dimetallic system based on tpp was prepared and assigned an $[(f)^{13}(tpp)^2(f)^{13}]$ electronic configuration. The rather large K_c values (~10^{14}) associated with the monomeric complex and the bridged dimer are direct measures of the marked stabilisation of the various mixed valent forms of the complexes. These data (reversibility of couples and separation between waves) clearly suggest that each discrete redox state in both **1** and **2** can be achieved by chemical or bulk electrolytic means. In particular, one-electron reduction of **2** would achieve a mixed valence form (Yb^{II}–Yb^{III}) analogous to the Creutz–Taube[11] system, but instead where an electron hole is delocalised through a doubly-reduced bridging ligand. Future studies will focus on the detailed characterization of these various ligand-localised mixed-valent forms and on the effects of incorporating systematically longer bridging ligands, as well as various other lanthanide complexes. These studies are anticipated to be of practical importance for the design of new mixed-valent systems.

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Notes and references

† Crystallographic data for **1**: $C_{35}H_{41}N_3Yb$, M = 676.7, orthorhombic, *Pbna*, a = 14.214(9), b = 14.214(9), c = 14.68(1), V = 2966(3), Z = 4, T = 203 K, $R1$ $[I > 2\sigma(I)]$ = 0.0795, $wR2[I > 2\sigma(I)]$ = 0.1966. **2**: $C_{64}H_{76}N_6Yb_2$, M = 1275.4, orthorhombic, $P2(1)/m$, a = 15.591(4), b = 11.252(3), c = 17.228(5), V = 2989(1), Z = 2, T = 203 K, $R1$ $[I > 2\sigma(I)]$ = 0.1394, $wR2[I > 2\sigma(I)]$ = 0.2704. CCDC 212458. See http://www.rsc.org/suppdata/cc/b3/b306484k/ for crystallographic data in .cif or other electronic format.

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