

An intramolecular π - π interaction has no effect on the lifetime of an aryl radical cation

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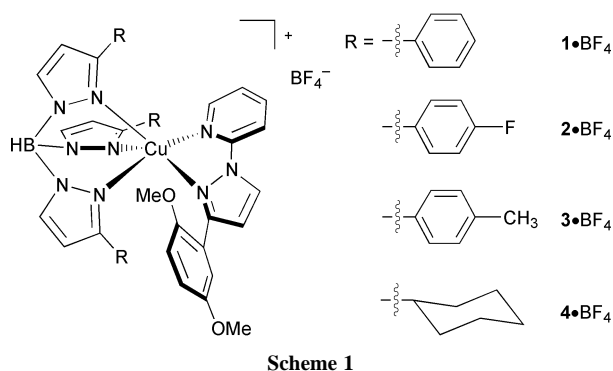
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The lifetimes of electrochemically generated $[\text{Cu}(\text{L}^{1+})(\text{Tp}^{\text{Ph}})]^{2+}$ and $[\text{Cu}(\text{L}^{1+})(\text{Tp}^{\text{Cy}})]^{2+}$ are identical to within experimental error.

We have recently reported that the complexes $[\text{Cu}(\text{L}^1)(\text{Tp}^{\text{R}})]\text{BF}_4$ ($\text{L}^1 = 1$ -[pyrid-2-yl]-3-[2',5'-dimethoxyphenyl]pyrazole; $[\text{Tp}^{\text{R}}]^- = \text{tris}$ -[3-arylpyrazolyl]borate: $\mathbf{1}\cdot\text{BF}_4$ – $\mathbf{3}\cdot\text{BF}_4$, Scheme 1) exhibit an unusual, fully reversible L^1 -based 1-electron oxidation by cyclic voltammetry in $\text{CH}_2\text{Cl}_2/0.5 \text{ M NBu}^n_4\text{PF}_6$ at 298 K.¹ This led us to suggest that an intramolecular π - π stacking interaction observed in $\mathbf{1}\cdot\text{BF}_4$ – $\mathbf{3}\cdot\text{BF}_4$ might be kinetically stabilising the $[\text{L}^1]^+$ -containing oxidation products. This would not be without precedent, in that others have detected unusual reversible voltammetric oxidations of intramolecularly π - π -stacked monocyclic aryl moieties in sesterbenzobicyclo[2.2.2]octane² and *ortho*-cyclophane³ derivatives. In addition, a related $n \rightarrow \pi^*$ charge-transfer interaction leads to a 1000-fold increase in the lifetime of sulfanyl radical cations in aromatic, compound to chlorinated, solvents.⁴ If true, such a result would be of relevance to the properties of proteins such as galactose oxidase (GOase), which contains a tyrosyl radical that is involved in a π - π interaction with a tryptophan indole ring.⁵ This π - π interaction is vital to the function of the enzyme,⁶ although its detailed role in catalysis is unknown. We now report the synthesis of a complex closely related to $\mathbf{1}\cdot\text{BF}_4$ – $\mathbf{3}\cdot\text{BF}_4$ but lacking the π - π interaction, which has allowed us to quantify the effects of π - π stacking on the properties of $[\text{L}^1]^+$. We also describe the spectroelectrochemical characterisation of the aryl radical complex products $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$.



Treatment of hydrated $\text{Cu}(\text{BF}_4)_2$ with one molar equivalent of L^1 and $\text{K}[\text{Tp}^{\text{Cy}}]$ in CH_2Cl_2 affords, following concentration and layering with hexanes, a dark green compound analysing as $[\text{Cu}(\text{L}^1)(\text{Tp}^{\text{Cy}})]\text{BF}_4$ ($\mathbf{4}\cdot\text{BF}_4$) in 55% yield.[†] This complex exhibits a d-d absorption in CH_2Cl_2 at $\nu_{\text{max}} = 15.6 \times 10^3 \text{ cm}^{-1}$ ($\epsilon_{\text{max}} = 104 \text{ M}^{-1} \text{ cm}^{-1}$), which bears a low-energy shoulder. X-band EPR spectroscopy of $\mathbf{4}\cdot\text{BF}_4$ in 10:1 CH_2Cl_2 :toluene shows $\langle g \rangle = 2.13$, $\langle A\{^{63,65}\text{Cu}\} \rangle = 65 \text{ G}$, $\langle A\{^{14}\text{N}\} \rangle = 14$

G at 298 K and $g_{\parallel} = 2.25$, $g_{\perp} = 2.04$, $A_{\parallel}\{^{63,65}\text{Cu}\} = 167 \text{ G}$ at 77 K. The close correspondence of these parameters to those shown by $\mathbf{1}\cdot\text{BF}_4$ – $\mathbf{3}\cdot\text{BF}_4$, which exhibit square pyramidal geometries in the solid state and in solution,¹ strongly suggests that the molecular structure of $\mathbf{4}\cdot\text{BF}_4$ is essentially identical to those of our earlier compounds. A single crystal X-ray analysis[‡] confirmed the proposed molecular connectivity (Fig. 1). Apart from the short apical distance $\text{Cu}(1)$ – $\text{N}(2)$ (Fig. 1), which we have found to be a very plastic parameter in square-pyramidal $\text{Cu}(\text{II})$ /trispyrazolylborate complexes,⁸ the co-ordination geometry at Cu differs insignificantly from that of $\mathbf{1}\cdot\text{BF}_4$.¹

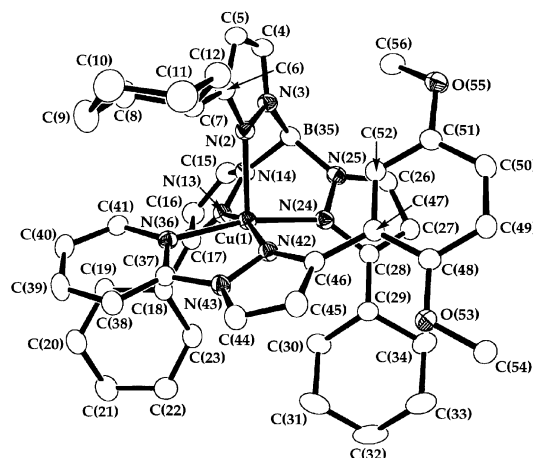


Fig. 1 View of the complex cation in the crystal of $\mathbf{4}\cdot\text{BF}_4\cdot 2\text{CHCl}_3$ with 35% probability ellipsoids, showing the atom numbering scheme employed. For clarity, all H atoms have been omitted. Selected distances (Å) and angles ($^\circ$): $\text{Cu}(1)$ – $\text{N}(2)$ 2.153(2), $\text{Cu}(1)$ – $\text{N}(13)$ 2.024(2), $\text{Cu}(1)$ – $\text{N}(24)$ 1.984(2), $\text{Cu}(1)$ – $\text{N}(36)$ 2.029(2), $\text{Cu}(1)$ – $\text{N}(42)$ 2.0596(19), $\text{N}(2)$ – $\text{Cu}(1)$ – $\text{N}(13)$ 92.41(8), $\text{N}(2)$ – $\text{Cu}(1)$ – $\text{N}(24)$ 93.80(8), $\text{N}(2)$ – $\text{Cu}(1)$ – $\text{N}(36)$ 98.86(8), $\text{N}(2)$ – $\text{Cu}(1)$ – $\text{N}(42)$ 102.66(8), $\text{N}(13)$ – $\text{Cu}(1)$ – $\text{N}(24)$ 85.70(8), $\text{N}(13)$ – $\text{Cu}(1)$ – $\text{N}(36)$ 94.34(8), $\text{N}(13)$ – $\text{Cu}(1)$ – $\text{N}(42)$ 164.25(8), $\text{N}(24)$ – $\text{Cu}(1)$ – $\text{N}(36)$ 167.32(8), $\text{N}(24)$ – $\text{Cu}(1)$ – $\text{N}(42)$ 97.69(8), $\text{N}(36)$ – $\text{Cu}(1)$ – $\text{N}(42)$ 78.99(8).

The cyclic voltammogram of $\mathbf{4}\cdot\text{BF}_4$ in $\text{CH}_2\text{Cl}_2/0.5 \text{ M NBu}^n_4\text{BF}_4$ at 298 K exhibits all the processes shown by $\mathbf{1}\cdot\text{BF}_4$ – $\mathbf{3}\cdot\text{BF}_4$ in this solvent.¹ Hence, a chemically reversible L^1 -based 1-electron oxidation is observed at $E_{\frac{1}{2}} = +1.06 \text{ V vs. ferrocene/ferrocenium}$ ($\Delta E_p = 96 \text{ mV}$),[§] which is 60–90 mV more positive than the values we have recorded for $\mathbf{1}\cdot\text{BF}_4$ – $\mathbf{3}\cdot\text{BF}_4$. In order to quantify any kinetic stabilisation of $\mathbf{1}^{2+}$ – $\mathbf{3}^{2+}$ afforded by intramolecular π - π stacking, we have measured the half-lives of $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$ and $\mathbf{4}^{2+}$ at 298 K in the electrochemical cell using convolution methods.⁹ The values obtained are almost identical within experimental error: $\mathbf{1}^{2+}$, $t_{\frac{1}{2}} = 1.7(2) \text{ s}$; $\mathbf{2}^{2+}$, $t_{\frac{1}{2}} = 1.39(17) \text{ s}$; and $\mathbf{4}^{2+}$, $t_{\frac{1}{2}} = 0.98(11) \text{ s}$. Although it is unclear whether the assumption of first-order decomposition kinetics employed by the convolution procedure is valid in our system, it is clear that

the kinetic stabilities of 1^{2+} , 2^{2+} and 4^{2+} are essentially identical.

Attempts to electrogenerate bulk samples of 1^{2+} and 2^{2+} for EPR measurements were unsuccessful, resulting in appreciable decomposition of the sample over the timescale of the experiment. *In situ* spectroelectrochemical characterisation of the oxidised species 1^{2+} and 2^{2+} was therefore undertaken. Electrooxidation of $1 \cdot \text{BF}_4$ in $\text{CH}_2\text{Cl}_2/0.5 \text{ M NBU}_4\text{BF}_4$ at 243 K at a potential corresponding to the $1^+/1^{2+}$ couple using an optically transparent electrode proceeds isospectrally and results in substantial changes in the UV, vis and NIR regions of the spectrum (Fig. 2). The oxidised solution for 1^{2+} shows $\nu_{\text{max}} = 12.4$ ($\epsilon_{\text{max}} = 1000$), 19 (sh), 22.2 (3 400), 26 (sh) and $32.5 \times 10^3 \text{ cm}^{-1}$ ($15\,500 \text{ M}^{-1} \text{ cm}^{-1}$) at 243 K (Fig. 2). The absorption spectrum of 2^{2+} generated under identical conditions is barely distinguishable from those of 1^{2+} . Re-reduction of both samples at 0 V also proceeds isospectrally and quantitatively regenerates 1^+ or 2^+ , demonstrating the chemical reversibility of this process under these conditions.

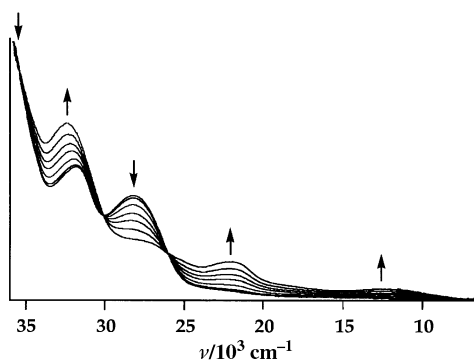


Fig. 2 Oxidation of 1^+ to 1^{2+} by controlled potential electrolysis in $\text{CH}_2\text{Cl}_2/0.5 \text{ M NBU}_4\text{PF}_6$ at 243 K.

The $[\text{C}_6\text{H}_4(\text{OME})_2-1,4]^+$ radical cation exhibits $\nu_{\text{max}} = 21.7$ ($\epsilon_{\text{max}} = 9\,540 \text{ M}^{-1} \text{ cm}^{-1}$), 23.3 (9 040) and $33.3 \times 10^3 \text{ cm}^{-1}$ (13 000) in aqueous solution,¹⁰ but is optically transparent in the range $11\text{--}21 \times 10^3 \text{ cm}^{-1}$.¹¹ The 22.2, 26 and $32.5 \times 10^3 \text{ cm}^{-1}$ bands from 1^{2+} and 2^{2+} quite closely match those shown by $[\text{C}_6\text{H}_4(\text{OME})_2-1,4]^+$; we therefore assign these bands to local excitation transitions within the $[\text{L}^1]^+$ moiety. The $12.4 \times 10^3 \text{ cm}^{-1}$ absorption can be attributed to a $[\text{Tp}^{\text{Ph}}] \rightarrow [\text{L}^1]^+$ LLCT transition. By comparison, the $[(\text{C}_6\text{H}_6)(\text{C}_{10}\text{H}_8)]^+$ complex exhibits a gas-phase intra-dimer CT band at $10.9 \times 10^3 \text{ cm}^{-1}$,¹² while $[(\text{C}_6\text{H}_6)(\text{C}_7\text{H}_8)]^+$ exhibits three such bands, at 8.5, 10.8 and $14.9 \times 10^3 \text{ cm}^{-1}$.¹³ The observation of such a transition for 1^{2+} and 2^{2+} is clear evidence that the intramolecular π - π stacking interaction in these complexes is retained following oxidation. The assignment of the shoulder near $19 \times 10^3 \text{ cm}^{-1}$ is uncertain; we tentatively suggest that this may correspond to a second LLCT transition, or to a $\text{Cu} \rightarrow [\text{L}^1]^+$ MLCT band.

To conclude, we have demonstrated that the intramolecular π - π interaction exhibited by 1^+ and 2^+ is retained following their 1-electron oxidation, but that this interaction has no measurable effect on the kinetic stability of the resultant aryl radical. The unusual longevity of the dimethoxyphenyl radical cation species 1^+ and 2^+ , and those formed from sesterbenzobicyclo[2.2.2]octane² and *ortho*-cyclophane³ derivatives, presumably originates rather in steric protection of the radical

center afforded by the overlying aryl ring. These results demonstrate that the tyrosyl/tryptophan π - π interaction in GOase probably has little or no effect on the chemical reactivity of the tyrosyl radical in this enzyme, except to shield it from external solvent. We are continuing to investigate the effects of π - π stacking on the spectroscopic and luminescent properties of aryl radicals and their complexes, and will report these results in due course.

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Notes and references

† Analytical data for $4 \cdot \text{BF}_4$: Found: C 58.1, H 6.2, N 13.8%; calcd. for $\text{C}_{43}\text{H}_{55}\text{B}_2\text{CuF}_4\text{N}_9\text{O}_2$: C 58.0, H 6.2, N 14.1%.

‡ Crystal data for $4 \cdot \text{BF}_4 \cdot 2\text{CHCl}_3$: $\text{C}_{45}\text{H}_{57}\text{B}_2\text{Cl}_6\text{CuF}_4\text{N}_9\text{O}_2$, $M_r = 1129.86$, monoclinic, $P2_1/n$, green prism, $0.56 \times 0.49 \times 0.30 \text{ mm}$, $a = 11.8709(2)$, $b = 20.8196(3)$, $c = 21.6065(4) \text{ \AA}$, $\beta = 98.7150(11)^\circ$, $U = 5278.34(15) \text{ \AA}^3$, $Z = 4$, $T = 150(2) \text{ K}$, $\mu(\text{Mo-K}\alpha) = 0.778 \text{ mm}^{-1}$; Enraf-Nonius KappaCCD diffractometer, 34102 measured reflections, 11965 independent, $R_{\text{int}} = 0.058$; $R(F) = 0.053$, $wR(F^2) = 0.151$, $S = 1.019$. Both solvent molecules were disordered, one over two equally occupied orientations and one over three orientations with occupancies of 0.5, 0.25 and 0.25. All C-Cl bonds were restrained to 1.75(2) \AA , and Cl...Cl distances to 2.86(2) \AA . All non-H atoms with occupancy ≥ 0.5 were refined anisotropically. CCDC 182/1760. See <http://www.rsc.org/suppdata/cc/b0/b006005o/> for crystallographic files in .cif format.

§ In addition to these oxidative voltammetric processes, $4 \cdot \text{BF}_4$ exhibits an irreversible $\text{Cu}(II/I)$ reduction at $E_{\text{pc}} = -0.58 \text{ V}$, with an associated daughter wave at $E_{\text{pa}} = +0.25 \text{ V}$. A weak daughter wave at $E_{\text{pa}} = +0.03 \text{ V}$ becomes apparent following multiple scanning of the $4^+/4^{2+}$ oxidation.

- M. A. Halcrow, E. J. L. McInnes, F. E. Mabbs, I. J. Scowen, M. McPartlin, H. R. Powell and J. E. Davies, *J. Chem. Soc., Dalton Trans.*, 1997, 4025.
- W. Grimme, H. T. Kämmerling, J. Lex, R. Gleiter, J. Heinze and M. Dietrich, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 205.
- S. Mataka, K. Shigaki, T. Sawada, Y. Mitoma, M. Taginuchi, T. Thiemann, K. Ohga and N. Egashira, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 2532.
- D. Werst, *J. Phys. Chem.*, 1992, **96**, 3640.
- J. P. Klinman, *Chem. Rev.*, 1996, **96**, 2541.
- A. J. Baron, C. Stevens, C. Wilmot, K. D. Seneviratne, V. Blakeley, D. M. Dooley, S. E. V. Phillips, P. F. Knowles and M. J. McPherson, *J. Biol. Chem.*, 1994, **269**, 25 095.
- A. L. Rheingold, B. S. Haggerty and S. Trofimenko, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1983.
- M. A. Halcrow, L. M. L. Chia, X. Liu, E. J. L. McInnes, L. J. Yellowlees, F. E. Mabbs, I. J. Scowen, M. McPartlin and J. E. Davies, *J. Chem. Soc., Dalton Trans.*, 1999, 1753; L. M. L. Chia, S. Radojevic, I. J. Scowen, M. McPartlin and M. A. Halcrow, *J. Chem. Soc., Dalton Trans.*, 2000, 133.
- F. E. Woodward, R. D. Goodin and P. J. Kinlen, *Anal. Chem.*, 1984, **56**, 1920.
- P. O'Neill, S. Steenken and D. Schulte-Frohlinde, *J. Phys. Chem.*, 1975, **79**, 2773.
- C. T. Johnston, T. Tipton, D. A. Stone, C. Erickson and S. L. Trabue, *Langmuir*, 1991, **7**, 289.
- M. Matsumoto, Y. Inokuchi, K. Ohashi and N. Nishi, *J. Phys. Chem. A*, 1997, **101**, 4574.
- K. Ohashi, Y. Nakane, Y. Inokuchi, Y. Nakai and N. Nishi, *Chem. Phys.*, 1998, **239**, 429.