

Large size anion binding with iron(II) complexes of a 5,5'-disubstituted-2,2'-bipyridine ligand†

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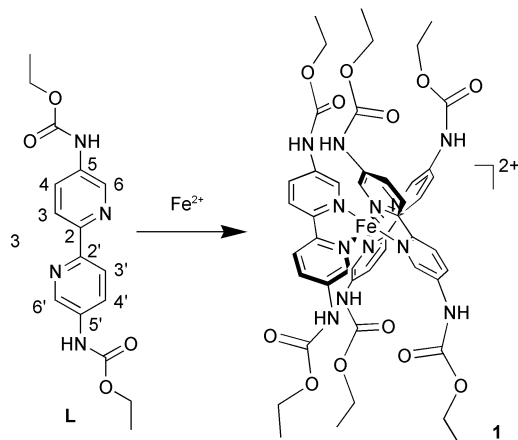
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Three 5,5'-substituted 2,2'-bipyridyl ligands around a metal atom form two clefts which can encapsulate sulfate, perchlorate, or nitrate anions.

Anions play numerous fundamental roles in biochemical systems,¹ for example, the majority of enzymes bind anions as substrates or cofactors, and anions act as nucleophiles, bases, redox agents and phase transfer catalysts in many important processes. In a *Salmonella typhimurium* sulfate transport protein, X-ray crystal studies demonstrated the selective binding of a sulfate anion by H-bond donor/acceptor arrays.² Despite efforts to duplicate such arrays, it remains a challenge for chemists to design and synthesize artificial, abiotic host molecules with the capability of binding anion guests,³ because several factors should be considered, such as anion size and topology, charge density, H-bond donor/acceptor properties and Lewis-base character.

Recently, Ru(II) or Fe(II) complexes of 5,5'-disubstituted-2,2'-bipyridine have been utilized as receptors for chloride ion binding through H bonds.⁴ However, receptors that trap larger ions, such as SO_4^{2-} , ClO_4^- , or NO_3^- are rarely structurally characterized.⁵ We have studied the metal complexes of multi-topic bipyridine-type ligands,⁶ including 5,5'-bis(ethoxycarbonylamino)-2,2'-bipyridine, **L** which possesses both H-bond donors and acceptors. Some interactions were found between the N–H functionalities of the heteroleptic complex $[\text{Ru}(\text{bipy})_2(\text{L})]^{2+}$ and the F atoms of its PF_6^- anions.⁷ Herein, we investigate the homoleptic complex $[\text{Fe}(\text{L})_3]^{2+}$, **1** which forms multi-hydrogen-bond donor/acceptor clefts capable of encapsulating larger anions, such as sulfate, perchlorate, or nitrate.

Mixing a solution of three equivalents of the ligand **L**† in hot ethanol with one equivalent of ferrous sulfate led to a red solution instantaneously, indicating the formation of the Fe(II) bipyridine complex **1** whose composition (m/z 1046/2) was confirmed by electrospray mass spectrometry.† The ¹H NMR spectroscopy in DMSO-*d*₆ solution indicates an equilibrium of



† Electronic supplementary information (ESI) available: synthesis and characterization of **1a–c**. All new compounds were characterised by CHN, ¹H NMR, and ESI-MS. See <http://www.rsc.org/suppdata/cc/b2/b211616b/>

1 with free **L** in the presence of SO_4^{2-} , and **1** shows an increased dissociation with increasing SO_4^{2-} conc. from $(\text{Me}_4\text{N})_2\text{SO}_4$. A 10-fold excess of $(\text{Me}_4\text{N})_2\text{SO}_4$ in a *ca.* 1×10^{-3} M solution of **1** led to complete dissociation evidenced by decolorization and the sole presence of the ligand chemical shifts. In methanol **1** is stable upon addition of SO_4^{2-} . However no significant chemical shift changes are observed for the protons on the carbamate arms in **1a–c** with the increase of SO_4^{2-} , ClO_4^- or NO_3^- concentration, respectively. The X-ray structure of complex $[\text{Fe}(\text{L})_3]\text{SO}_4$, **1a**, is shown in Fig. 1.‡ Three ligands form two clefts through coordination to an iron center. The sulfate anion is encapsulated within one of the clefts through three H bonds between its oxygen atoms and the three NH groups (see caption to Fig. 1). The fourth oxygen atom points outward of the cleft along the quasi C_3 -axis and forms H bonds with CH_3OH and H_2O molecules of crystallization ($\text{O16}\cdots\text{O}(\text{CH}_3\text{OH})$ 2.538 and $\text{O16}\cdots\text{O}(\text{H}_2\text{O})$ 2.857 Å, not shown). The other cleft is empty. The host arms of the filled cleft bend or are pulled inwards for the interaction with the sulfate ion (N \cdots N separations $\text{N4}\cdots\text{N6}$ 5.815, $\text{N6}\cdots\text{N10}$ 5.719, $\text{N10}\cdots\text{N4}$ 5.748 Å), while the arms on the empty side are diverged from each other ($\text{N2}\cdots\text{N8}$ 6.616, $\text{N8}\cdots\text{N12}$ 6.158, $\text{N12}\cdots\text{N2}$ 6.338 Å). Alternatively, the three sides of the H3 triangle around sulfate are $\text{H}(\text{N6})\cdots\text{H}(\text{N4})$ 4.86, $\text{H}(\text{N6})\cdots\text{H}(\text{N10})$ 4.71, $\text{H}(\text{N10})\cdots\text{H}(\text{N4})$ 4.96 Å, while those of the empty side are $\text{H}(\text{N2})\cdots\text{H}(\text{N12})$ 6.08, $\text{H}(\text{N8})\cdots\text{H}(\text{N12})$ 7.10, and $\text{H}(\text{N2})\cdots\text{H}(\text{N8})$ 7.55 Å, respectively. This closing or opening of the cleft is supported by slightly shorter Fe–N bonds towards the filled *versus* the empty cleft in the same ligand. The carbamate with their NH groups in **1a** still lie in the plane of the pyridine rings to bind the large sulfate ion in the cleft. This is different from the $\text{Ru}(5,5'$ -diamide-2,2'-bipy)₃ receptors which trap the smaller chloride anion. There, the H atoms on NH point towards the $\text{Fe}\cdots\text{Cl}$ C_3 -axis.⁴

The perchlorate complex $[\text{Fe}(\text{L})_3](\text{ClO}_4)_2$, **1b** was synthesized by reaction of **L** with $\text{Fe}(\text{ClO}_4)_2$.† Compound **1b** is stable in DMSO-*d*₆ or CD_3OD (by ¹H NMR) and is not sensitive to the addition of ClO_4^- . The structure of **1b** (Fig. 2) is centrosym-

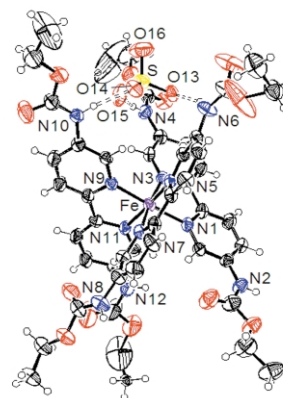


Fig. 1 Structure of **1a**. Fe–N1, 1.997(5); Fe–N3, 1.975(5); Fe–N5, 1.968(5); Fe–N7, 1.973(5); Fe–N9, 1.969(5); Fe–N11, 1.963(5); N6(H) \cdots O13, 2.788(8); N10(H) \cdots O14, 2.812(8); N4(H) \cdots O15, 2.734(8) Å.

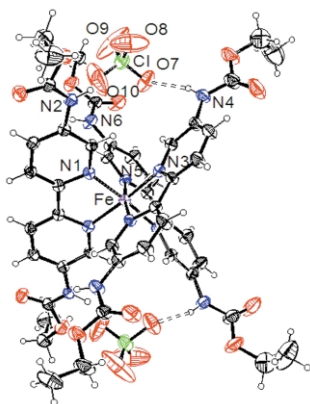


Fig. 2 Structure of **1b**. Fe–N1, 1.960(5); Fe–N3, 1.966(5); Fe–N5, 1.948(5); N4(H)···O7, 2.936(9); N2···O10, 3.924, N6···O10, 3.520 Å.

metric to the Fe atom. § The $[\text{Fe}(\text{L})_3]^{2+}$ host encapsulates two perchlorate anions, each in one cleft, through a H-bond between one oxygen of ClO_4^- and one NH group. Another oxygen atom, O10, is placed between the other two arms with non-H-bonding contacts (see caption to Fig. 2). The remaining two oxygen atoms point outward of the cleft. The other two NH groups are directed away from the perchlorate and form intermolecular hydrogen bonds (not shown). The three sides of the H3 (N3) triangle are H(N4)···H(N6) 5.76 (6.158), H(N4)···H(N2) 5.15 (6.078) and H(N2)···H(N6) 6.28 (6.791) Å, respectively.

Furthermore, the nitrate analogue, $[\text{Fe}(\text{L})_3](\text{NO}_3)_2$, **1c** was synthesized by reaction of ligand **L** with $\text{Fe}(\text{NO}_3)_3$ in the presence of iron powder. † Compound **1c** is stable in DMSO- d_6 or CD_3OD (by ^1H NMR), too. Similar to complex **1b**, the $[\text{Fe}(\text{L})_3]^{2+}$ host encapsulates two nitrate anions in a centrosymmetric fashion (Fig. 3), § each through a hydrogen bonding interaction between one oxygen of the nitrate and one NH group. The two other oxygen atoms of the nitrate ions form only very weak interactions with the adjacent NH groups (see caption to Fig. 3). The three sides of the H3 (N3) triangle are H(N4)···H(N6) 5.02 (5.995), H(N4)···H(N2) 5.70 (6.099), H(N2)···H(N6) 6.29 (6.796) Å, respectively.

In **1a–c** the hydrogen atoms on the NH groups are more or less oriented in the same direction ("homodromic") around the quasi C_3 -axis (passing through Fe and the central atom of the anion). The distance between Fe and Cl in **1b** is 5.907 Å, the distance between Fe and NO_3 in **1c** is 5.576 Å; both are longer than the Fe–S distance of 5.539 Å in **1a**, indicating that the sulfate anion is sited deeper in the receptor cleft than either the perchlorate or the nitrate ions. Except for **1a** there is no distortion of the $\text{Fe}(\text{L})_3$ core. Among the three complexes the sulfate ion shows the strongest interactions with the receptor by

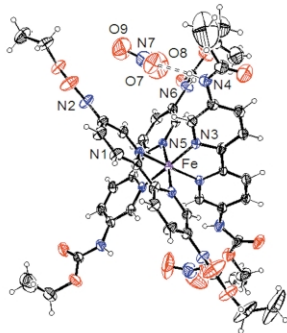


Fig. 3 Structure of **1c**. Fe–N1, 1.970(7); Fe–N3, 1.961(6); Fe–N5, 1.952(6); N4(H)···O7, 2.857(10); N2(H)···O9, 3.215; N6(H)···O8, 3.583 Å.

forming three H bonds and shorter N–H···O bond distances. This may be due to the stronger electrostatic interaction between Fe and the dianionic sulfate compared with the monoanionic perchlorate or nitrate. A correlation with radii of the anions is not clear as different sets of radii are available in the literature with reversed order: SO_4^{2-} 2.18(19)⁸ or 2.58(4),⁹ ClO_4^- 2.25(19)⁸ or 2.40(5), NO_3^- 2.00(19)⁸ or 1.79(6)⁹ Å.

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Notes and references

† The ligand **L** was prepared according to the literature procedures.^{6,10}

§ Crystal data: **1a**·3.2H₂O·0.5CH₃OH, monoclinic, space group $P2_1/c$, $a = 14.0449(10)$, $b = 22.8722(16)$, $c = 18.8110(13)$ Å, $\beta = 100.833(1)^\circ$, $V = 5935.1(7)$ Å³, $Z = 4$, $D_c = 1.356$ g cm⁻³, final R , wR values 0.0825, 0.2158 for 4829 independent reflections with $I > 2\sigma(I)$. **1b**·2H₂O, monoclinic, $C2/c$, $a = 18.459(5)$, $b = 25.212(6)$, $c = 14.755(4)$ Å, $\beta = 117.340(4)^\circ$, $V = 6100(3)$ Å³, $Z = 4$, $D_c = 1.396$ g cm⁻³, final R , wR values 0.0871, 0.2221 for 3116 independent reflections with $I > 2\sigma(I)$. **1c**·2CH₃CH₂OH, monoclinic, $C2/c$, $a = 18.49(6)$, $b = 24.91(8)$, $c = 15.14(5)$ Å, $\beta = 117.69(5)^\circ$, $V = 6178(33)$ Å³, $Z = 4$, $D_c = 1.358$ g cm⁻³, final R , wR values 0.0748, 0.1784 for 2190 independent reflections with $I > 2\sigma(I)$.

Data collection by the ω -scan method, Mo–K α radiation ($\lambda = 0.71073$ Å), graphite monochromator, at 223 K (**1a** and **1b**) or 293 K (**1c**) on a Bruker SMART CCD diffractometer. Structure solution by direction methods (SHELXS-97); and refined by full-matrix least-squares on F^2 (SHELXL-97); all non-hydrogen positions were found and refined with anisotropic temperature factors except for atoms C24' and C48 which are part of a disordered ethyl group in **1a** and were refined isotropically. Graphics were obtained with ORTEP3 for Windows. CCDC reference numbers 198626, 198627 and 198628. See <http://www.rsc.org/suppdata/cc/b2/b211616b/> for crystallographic data in .cif or other electronic format.

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