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The first crystallographically established bis-qtpy (qtpy = 2,2′:6′,2″:6″,2‴-quaterpyridine) metal complex

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The first example of a crystallographically established bis-adduct of tridentate 2,2′:6′,2″:6″,2‴-quaterpyridine (qtpy) of formula $[Fe(qtpy)_2][ClO_4]_2$ has been obtained by treating an aqueous solution of iron(II) perchlorate with the ligand in the presence of triethylamine.

Metal complexes of polypyridines[1] have attracted considerable interest for their relevance in supramolecular chemistry. Metal complexes containing two qtpy ligands *per* metal atom are substantially unknown. On the other hand, a spectrophotometric study[2] of the Fe(II)–qtpy system in aqueous solution has suggested that the $[Fe(qtpy)]^{2+}$ and $[Fe(qtpy)_2]^{2+}$ cations have quite remarkable formation constants K_1 and K_2 of 1.5×10^8 and 4.5×10^6, respectively, at 25 °C, with sulfate as counterion at pH 3.0. An earlier report[3] on the reaction between hydrated $Fe(ClO_4)_2$ and qtpy in acetonitrile at 70 °C failed to give the bis-adduct, the product of the reaction being $[Fe(qtpy)(H_2O)_2][ClO_4]_2$ containing the cationic hydrated monoadduct. In view of the conflicting experimental evidence, we decided to reinvestigate the $Fe(ClO_4)_2$–qtpy system.

We have now found that the qtpy bis-adduct $[Fe(qtpy)_2][ClO_4]_2$, **1**, is in fact the only detectable product of the reaction between aqueous $Fe(ClO_4)_2$ and qtpy, provided the pH is maintained at relatively high values by addition of a weakly coordinating tertiary amine and the temperature is raised to 140 °C, see eqn. (1).†

$$Fe(ClO_4)_2{\cdot}6\,H_2O + 2\,qtpy \longrightarrow [Fe(qtpy)_2][ClO_4]_2 + 6\,H_2O \quad (1)$$

A single crystal of **1** was selected for the X-ray diffraction experiment.‡ The molecular structure of the $[Fe(qtpy)_2]^{2+}$ cation is shown in Fig. 1. The iron atom does not achieve regular hexacoordination, and the average Fe–N distance is 2.21 Å, which is longer than the average distance of 1.956 Å observed[7] in the bis(2,2′:6′,2″-terpyridine)iron(II) cation $[Fe(tpy)_2]^{2+}$. In the $[Fe(qtpy)_2]^{2+}$ cation the N···N non-bonding distances between neighbouring rings range between 2.576 and 2.638 Å, whereas for an octahedral coordination geometry a N···N contact of 3.171 Å is expected.[8] As a consequence of this geometrical misfit, each quaterpyridine connects to the metal by three nitrogens only and the resulting small N–Fe–N′ angles between neighbouring nitrogens within the same ligand (mean value 73.4°) produce a heavily distorted octahedron. Contributions to the stabilisation of the system possibly originate from the weak N(8)···Fe interaction at 2.819 Å, which is only 0.6 Å longer than the average Fe–N bond distance, and from the π-stacking between the ring containing N(4) and the coordinated rings containing N(6) and N(7). A similar π-interaction has been suggested for another iron(II) complex with 2,2′:6′,2″-terpyridine.[9]

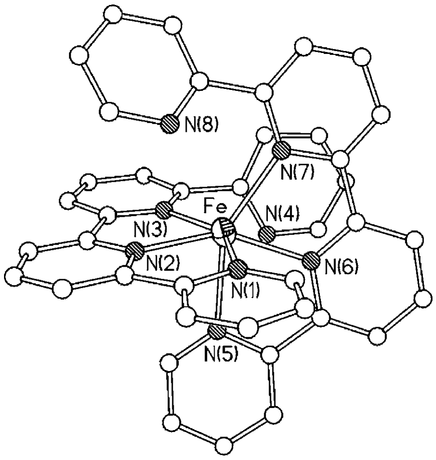

Fig. 1 Structure of the $[Fe(qtpy)_2]^{2+}$ cation. Some relevant bond distances (Å) and angles (°): Fe–N(1), 2.207(8); Fe–N(2), 2.112(7); Fe–N(3), 2.205(7); Fe···N(4), 3.540(8); Fe–N(5), 2.349(9); Fe–N(6), 2.145(7); Fe–N(7), 2.236(8); Fe···N(8), 2.819(9); N(1)–Fe–N(2), 74.7(3); N(1)–Fe–N(3), 148.6(3); N(1)–Fe–N(5), 86.5(3); N(1)–Fe–N(6), 89.5(3); N(1)–Fe–N(7), 102.6(3); N(2)–Fe–N(3), 74.0(3); N(2)–Fe–N(5), 81.4(3); N(2)–Fe–N(6), 150.2(3); N(2)–Fe–N(7), 134.0(3); N(3)–Fe–N(5), 88.0(3); N(3)–Fe–N(6), 118.0(3); N(3)–Fe–N(7), 99.7(3); N(5)–Fe–N(6), 72.4(3); N(5)–Fe–N(7), 144.5(3); N(6)–Fe–N(7), 73.5(3).

It is to be noted that the qtpy bis-adduct of iron(II) was obtained by using an Fe:qtpy molar ratio of 1; while this is in agreement with the high stability of the bis-adduct,[2] the question remains as to why only the mono-adduct of iron(II) was isolated earlier in acetonitrile.[3] We have verified that the mono-adduct $[Fe(qtpy)(H_2O)_2][ClO_4]_2$, crystallographically identical to the product isolated earlier,[3] is formed in an aqueous medium, in the absence of added triethylamine.§

The effect of the weakly coordinating and relatively strong base triethylamine ($pK_a = 10.71$) in our system is therefore quite dramatic (the pH of a 3×10^{-3} M solution of iron(II) perchlorate is 2.4, which increases to 7.5 upon addition of an equimolar amount of Et_3N). The reaction of qtpy (pyridine, $pK_a = 5.17$) with iron(II) was reported to be slow,[2] although no kinetic details were presented. The bis-adduct can be tentatively assumed to be formed under our conditions due to the reduced positive charge on the iron as a consequence of deprotonation of iron(II)-coordinated water by the additional tertiary amine. These studies are being extended to other bivalent transition metal cations.

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Notes and references

† A carefully deaereated aqueous solution (20 ml) of $Fe(ClO_4)_2 \cdot 6\ H_2O$ (0.17 g, 0.47 mmol) was treated under dinitrogen with 2,2′:6′,2″:6″,2‴-quaterpyridine[4] (0.15 g, 0.48 mmol) and NEt_3 (0.07 ml, $d = 0.7275$ g cm^{-3}, 0.50 mmol) in a closed vessel at 140 °C for 5 h. The solution was then cooled over a period of 12 h and red crystals (0.17 g, 80% yield with respect to qtpy) of the air-stable $[Fe(qtpy)_2][ClO_4]_2$ were obtained (Found: C, 53.9; H, 2.8; N, 12.4. $C_{40}H_{28}Cl_2FeN_8O_8$ requires C, 54.9; H, 3.2; N, 12.8%). IR (Nujol, range 1700–400 cm^{-1}): 1601m, 1577m, 1568m, 1397w, 1297w, 1261w, 1243w, 1192w, 1165w, 1099vs, 1085vs, 1019w, 991w, 819w, 797m, 775s, 754w, 669w, 652w, 624s cm^{-1}.

‡ The diffractometric measurements were carried out with an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromated Cu-Kα radiation. A ruby-red prism of dimensions 0.33 × 0.21 × 0.10 mm, glued at the end of a glass fibre, gave the unit cell parameters from the setting angles of 34 strong reflections [$a = 10.392(3)$, $b = 8.867(4)$, $c = 40.177(9)$ Å, $\beta = 91.39(2)°$; monoclinic, $P2_1/n$ (no. 14); $V = 3701(2)$ Å^3; $Z = 4$; $T = 294$ K; $\rho_{calc} = 1.571$ Mg m^{-3}]. The data were collected in the $\omega/2\theta$ scan mode, three standard reflections being monitored every 2 hours for checking crystal decay and equipment stability. Data reduction was by the SDP package.[5] A set of 5730 independent intensity data were collected between $\theta = 4.4$ and 61.9° and corrected for Lorentz and polarisation effects. Only 1859 unique reflections satisfying the condition $I > 2\sigma(I)$ were obtained due to the relatively small dimensions of the crystal and its low diffraction power. A correction for absorption was also applied by using the ψ-scan method. The solution was found by the standard direct methods contained in the SHELX-97 program.[6a] The full matrix least-squares refinement based on F^2 was carried out with the same program by using anisotropic thermal parameters for Fe, Cl and O atoms and placing the hydrogens in calculated positions $\{R(F_o)\ [I > 2\sigma(I)] = 0.0834;\ Rw\ (F_o^2)\ [I > 2\sigma(I)] = 0.1782;\ R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|;\ Rw(F_o^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{\frac{1}{2}};\ w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ]$ where $Q = [MAX(F_o^2,0) + 2F_c^2]\}$. Refined parameters: 292. The PARST program[6b] was also used for geometric calculations. CCDC reference number 156001. See http://www.rsc.org/suppdata/dt/b1/b100360g/ for crystallographic data in CIF or other electronic format.

§ Iron(II) perchlorate (0.25 mmol) and qtpy (0.023 mmol) in 20 ml of water heated at 140 °C for 5 h gave red crystals of $[Fe(qtpy)(H_2O)_2][ClO_4]_2$ exclusively, with the following unit cell parameters (literature data[3] in brackets): $a = 14.613(7)$ [14.633(5)], $b = 11.140(6)$ [11.134(4)], $c = 15.15(2)$ [15.123(6)] Å, $\beta = 98.60(5)$ [98.84(3)]°.

1 (*a*) E. C. Constable, *Adv. Inorg. Chem. Radiochem.*, 1986, **30**, 69; (*b*) E. C. Constable, *Prog. Inorg. Chem.*, 1994, **42**, 67; (*c*) V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni and M. Venturi, *Acc. Chem. Res.*, 1998, **31**, 26; (*d*) E. C. Constable, M. J. Hannon, P. Harverson, M. Neuburger, D. R. Smith, V. F. Wanner, L. A. Whall and M. Zehnder, *Polyhedron*, 2000, **19**, 23 and references therein.

2 A. Bergh, P. O'D. Offenhartz, P. George and G. P. Haight, Jr., *J. Chem. Soc.*, 1964, 1533.

3 C.-M. Che, C.-W. Chan, S.-M. Yang, C.-X. Guo, C.-Y. Lee and S.-M. Peng, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 2961.

4 E. C. Constable, S. M. Elder, J. Healy and D. A. Tocher, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 1669.

5 ENRAF-Nonius SDP V5.0, Delft, The Netherlands, 1989.

6 (*a*) G. M. Sheldrick, SHELX-97, Program for Crystal Structure Analysis (release 97-2), Institüt für Anorganische Chemie der Universität Göttingen, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998; (*b*) M. Nardelli, *J. Appl. Cryst.*, 1995, **28**, 659.

7 A. T. Baker and H. A. Goodwin, *Aust. J. Chem.*, 1985, **38**, 207.

8 (*a*) I. Sotofte and S. E. Rasmussen, *Acta Chem. Scand.*, 1967, **21**, 2028; (*b*) G. J. Long and P. J. Clarke, *Inorg. Chem.*, 1978, **17**, 1394; (*c*) G. J. Long, G. Galeazzi, U. Russo, G. Valle and S. Calogero, *Inorg. Chem.*, 1983, **22**, 507; (*d*) J. S. Haynes, S. J. Rettig, J. R. Sams, R. C. Thompson and J. Trotter, *Can. J. Chem.*, 1986, **64**, 429; (*e*) I. I. Bulgak, V. E. Zubareva, K. I. Turte, Yu. A. Simonov, D. G. Batir, M. D. Mazus and T. I. Malinovskii, *Koord. Khim.*, 1987, **13**, 960; (*f*) J. Lipkowski, *J. Inclusion Phenom. Macrocyclic Chem.*, 1990, **8**, 439; (*g*) C. Roux, J. Zarembowitch, B. Gallois and M. Bolte, *New J. Chem.*, 1992, **16**, 671; (*h*) C. Roux, J. Zarembowitch, B. Gallois, T. Granier and R. Claude, *Inorg. Chem.*, 1994, **33**, 2273; (*i*) B. Singh, J. R. Long, F. F. de Biani, D. Gatteschi and P. Stavropoulos, *J. Am. Chem. Soc.*, 1997, **119**, 7030; (*j*) P. Karsten and J. Strähle, *Acta Crystallogr.*, *Sect. C*, 1998, **54**, 1406; (*k*) Q. Liu, Y. Wei, W. Wang and S. Zhang, *Acta Crystallogr.*, *Sect. C*, 1999, **55**, 127.

9 E. C. Constable, G. Baum, E. Bill, R. Dyson, R. van Eldik, D. Fenske, S. Kaderli, D. Morris, A. Neubrand, M. Neuburger, D. R. Smith, K. Wieghardt, M. Zehnder and A. D. Zuberbühler, *Chem. Eur. J.*, 1999, **5**, 498.