DALTON COMMUNICATION

Geometrical preferences of complexes of terpyridine *N*-oxide ligands: synthesis and crystal structures of nickel(II) with terpyridine 1,1′,1″-trioxide, terpyridine 1,1″-dioxide and terpyridine 1-oxide

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$[NiL_2][ClO_4]_2$ complexes (L = terpyridine 1,1′,1″-trioxide, terpyridine 1,1″-dioxide and terpyridine 1-oxide) have been prepared and crystallographically characterised; data shows a predictable variation in ligand conformation, such as facial or meridonal binding, which is in agreement with DFT calculations.

The co-ordinating behaviour and subsequent properties of the complexes of pyridine *N*-oxide, 2,2′-bipyridine 1,1′-dioxide, 2,2′:6′,2″-terpyridine 1,1′,1″-trioxide[1] **1** and other aromatic *N*-oxides[2–5] have been the subject of much interest. While earlier work reported the synthesis of the co-ordination complexes of these ligands, subsequent research has centred on the luminescent properties of the lanthanide complexes,[2–4] the catalytic oxidation properties of late transition metal complexes[5] and more recently the synthesis of inorganic polymers.[6]

While studies have been carried out using the terpyridine 1,1′,1″-trioxide,[7] to the best of our knowledge, no crystallographic data of its complexes exist. Thus, we undertook the comparative study of the co-ordination complexes of the series of ligands, terpyridine 1,1′,1″-trioxide, terpyridine 1,1″ dioxide and terpyridine 1-oxide, with a metal centre to determine how the variation in ligand geometry affects the resulting complex and how this may then be used to manipulate known heterocyclic ligands to obtain new variants. The ligands were readily prepared, either by oxidation of 2,2′:6′,2″ terpyridine with H_2O_2/acetic acid to give the trioxide, or by the addition of stoichiometric amounts of mcpba.[8] The nickel(II) complexes of these ligands were then prepared by the addition of $Ni(ClO_4)_2$ to 2 equivalents of ligand resulting in the formation of the product in good yields (60–83%). Microanalytical and spectroscopic data for the complexes are consistent with a 2:1 stoichiometry† and X-ray quality crystals of these products were obtained by the slow diffusion of diethyl ether into an acetonitrile solution. Their structures were determined‡ and are shown in Fig. 1.

The structure of $[Ni(terpyO_3)_2][ClO_4]_2$ **2** [Fig. 1(a)] shows a six-co-ordinate Ni centre in a slightly distorted octahedron and seven water molecules are also included within the lattice. The Ni–O bond lengths are typical of a Ni–O bond for this type of ligand [2.047–2.064(3) Å].[9] The O–Ni–O bond angles are 171.6(1) and 172.5(2)° for the *trans* bond angles and vary from 84.0 to 98.2(1) for the *cis* arrangement of oxygen donors. A point of interest is that the seven-membered chelate rings produce an unstrained structure that contains the ligand in a facial co-ordination mode rather than the meridonal arrangement typical for the parent pyridyl ligand. DFT calculations§ show excellent agreement with the X-ray structure giving Ni–O bond lengths of 2.057–2.170 Å and O–Ni–O angles of 164–171.5° (*trans*) and 83–99° (*cis*). No stable meridonal arrangement could be constructed for this ligand since geometry optimisation led to one of the metal–oxygen bonds being cleaved. Several possible arrangements of these facial ligands exist (Fig. 2) although only one has been observed in the crystal structure. However, the structure is in accord with ^{1}H NMR data for the $[Zn(terpyO_3)_2][ClO_4]_2$ complex[10] which has 11 distinct proton signals as expected from the lower symmetry of the complex in the crystal structure (Fig. 2, isomer **B**).

$[Ni(terpyO_2)_2][ClO_4]_2$ **3** [Fig. 1(b)], also shows the nickel centre in an octahedral geometry with the two terpyridyl units now in a *mer* arrangement. Calculations indicate that significant ligand strain would be introduced by *fac* co-ordination since the calculated total energy of the *fac* complex is some 47 kJ mol^{-1} above that for an energy minimisation based on the observed structure. While the Ni–O bond lengths are not unusual for a pyridine *N*-oxide donor, these distances are significantly shorter than those found in the structures of **2** and $[Ni(terpyO)_2][ClO_4]_2$ **4**, [average Ni–O distances: 2.026(3) *vs.* 2.055(3) and 2.065(5) Å, respectively].

The structure of the mono oxide complex **4** [Fig. 1(c)] was also found to be meridonal, as may be expected when considering that the presence of the 2,2′ bipyridyl fragments requires these two rings to be co-planar meaning that the facial arrangement would be severely strained. Again, the ^{1}H NMR of the analogous zinc complex shows 11 distinct proton signals as expected

From the crystallographic data of this and other studies,[11] it can be shown that the dihedral angle between the aromatic rings is predictable and ranges between 58–60° between two oxide donors, between 29–40° between one oxide and one pyridyl donor and 2–7° between two pyridyl rings. By considering these factors, as well as other steric factors, it is possible to predict the binding modes of the remaining *N*-oxide isomers of terpyridine. Thus, it seems probable that terpyridine 1,1′-dioxide will co-ordinate in a facial manner, while terpyridine 1′-oxide will either co-ordinate in a highly distorted facial manner or bridge between two metal atoms.

Currently we are undertaking both DFT calculations and the synthesis of these other ligand isomers, as well as the higher chain oligiopyridines and aim to determine their co-ordination behaviour.

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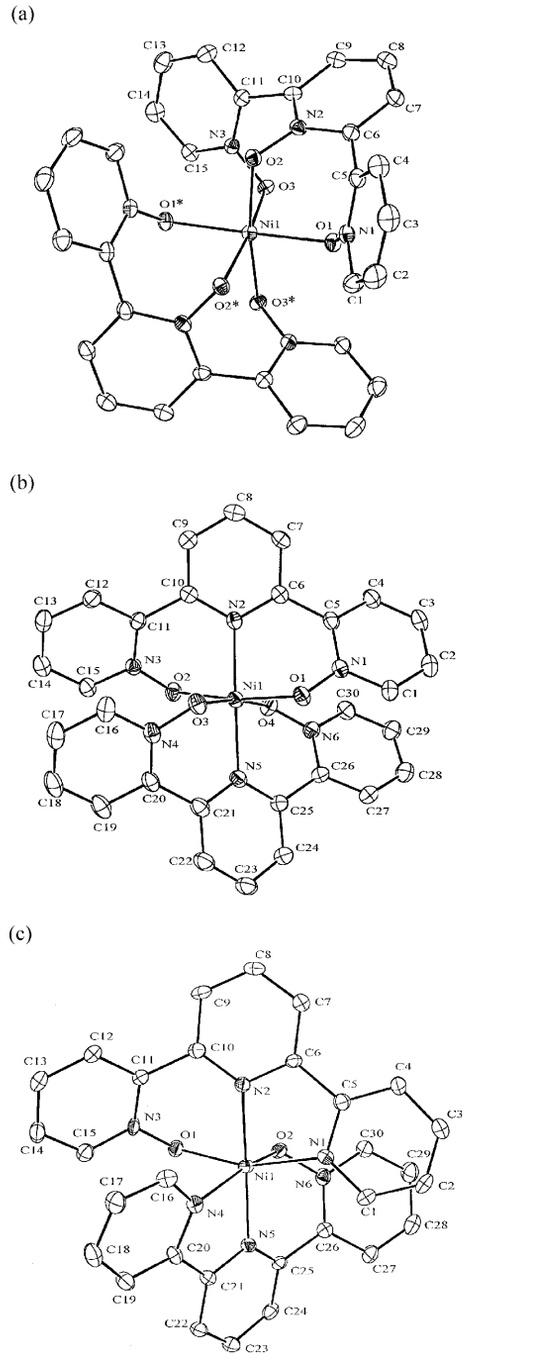

Fig. 1 Crystal structures of (a) Ni(terpy-1,1′,1″-O_3)$_2$(ClO_4)$_2$ **2**, (b) Ni(terpy-1,1″-O_2)$_2$(ClO_4)$_2$ **3** and (c) Ni(terpy-1-O)$_2$(ClO_4)$_2$ **4** (anions are omitted for clarity). Selected bond lengths (Å) and angles (°) for **2**: Ni(1)–O(1) 2.064(3), Ni(1)–O(2) 2.047(3), Ni(1)–O(3) 2.056(3); O(1)–Ni(1)–O(1*) 172.5(2), O(2)–Ni(1)–O(3*) 171.6(1), O(2)–Ni(1)–O(3) 86.3(1), O(1)–Ni(1)–O(2) 84.0(1), O(1)–Ni(1)–O(2*) 91.1(1), O(1)–Ni(1)–O(3) 96.5(1), O(1)–Ni(1)–O(3*) 88.8(1), O(3)–Ni(1)–O(3*) 90.1(2), O(2)–Ni(1)–O(2*) 98.2(2); for **3**: Ni(1)–O(1) 2.024(4), Ni(1)–O(2) 2.022(4), Ni(1)–O(3) 2.028(4), Ni(1)–O(4) 2.031(4), Ni(1)–N(2) 2.042(5), Ni(1)–N(5) 2.041(5); O(1)–Ni(1)–O(2) 171.9(2), O(3)–Ni(1)–O(4) 171.7(2), N(2)–Ni(1)–N(5) 174.5(2), O(1)–Ni(1)–O(3) 82.8(2), O(1)–Ni(1)–O(4) 98.5(2), O(1)–Ni(1)–N(2) 86.1(2), O(1)–Ni(1)–N(5) 98.3(2), O(2)–Ni(1)–O(4) 81.4(2), O(2)–Ni(1)–N(2) 86.1(2), O(2)–Ni(1)–N(5) 98.3(2), O(3)–Ni(1)–N(2) 90.1(2), O(3)–Ni(1)–N(5) 86.1(2), O(4)–Ni(1)–N(2) 98.2(2), O(4)–Ni(1)–N(5) 85.8(2), O(2)–Ni(1)–O(3) 98.4(2); for **4**: Ni(1)–O(1) 2.067(5), Ni(1)–O(2) 2.062(5), Ni(1)–N(1) 2.059(6), Ni(1)–N(2) 2.025(5), Ni(1)–N(4) 2.055(6), Ni(1)–N(5) 2.044(5), N(2)–Ni(1)–N(5) 178.2(2), N(1)–Ni(1)–O(1) 159.9(2), N(4)–Ni(1)–O(2) 159.4(2), N(2)–Ni(1)–N(1) 79.6(2), N(2)–Ni(1)–N(4) 101.6(2), N(2)–Ni(1)–O(1) 84.6(2), N(2)–Ni(1)–O(2) 94.6(2), N(1)–Ni(1)–O(2) 88.4(2), N(1)–Ni(1)–N(4) 106.8(2), N(1)–Ni(1)–N(5) 101.6(2), O(1)–Ni(1)–O(2) 80.55(19), O(1)–Ni(1)–N(4) 88.4(2), O(1)–Ni(1)–N(5) 93.9(2), N(4)–Ni(1)–N(5) 79.3(2), N(5)–Ni(1)–O(2) 84.2(2).

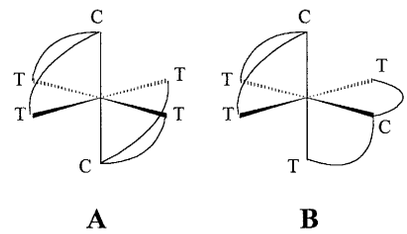

Fig. 2 Possible facial arrangements of terpyridine 1,1′,1″-trioxide about an octahedral centre.

Notes and references

† Typical experimental procedure: The ligand (0.4 mmol) was dissolved in the minimum amount of hot distilled water. Ni(ClO_4)$_2$·6H_2O (0.073 g, 0.2 mmol) was also dissolved in the minimum amount of distilled water and added to the stirred ligand solution. A precipitate was formed almost immediately which was collected by filtration. Yield 60–83%. Recrystallisation of all complexes was *via* vapour diffusion of diethyl ether into a MeCN solution. For **2**: (Found C, 39.37; H, 3.68; N, 9.07. $C_{30}H_{32}Cl_2N_6NiO_{19}$ requires C, 39.57; H, 3.51; N, 9.23%); IR(KBr)/cm^{-1} 1636s, 1466s, 1435s, 1396s, 1267w, 1222s, 1203s, 1144s, 1119s, 1087vs, 853s, 780s; FAB-MS (NOBA matrix) *m*/*z* 719 (M − ClO_4, 100%). For **3**: (Found C, 45.52; H, 2.79; N, 10.65. $C_{30}H_{22}Cl_2N_6NiO_{12}$ requires C, 45.72; H, 2.81; N, 10.66%); IR(KBr)/cm^{-1} 1588s, 1489w, 1449s, 1426s, 1387w, 1250s, 1214s, 1203s, 1089vs, 852s, 821w, 771s; FAB-MS (NOBA matrix) *m*/*z* 687 (M − ClO_4, 88%). For **4**: (Found C, 47.44; H, 3.11; N, 10.33. $C_{31}H_{26}Cl_2N_6NiO_{11}$ requires C, 47.24; H, 3.32; N, 10.66%); IR(KBr)/cm^{-1} 1599s, 1577w, 1558w, 1480w, 1448vs, 1396w, 1303w, 1262s, 1201s, 1142s, 1117 (sh), 1086vs, 1022s, 844w, 808s, 781s; FAB-MS (NOBA matrix) *m*/*z* 657/655 (M − ClO_4, 36%) 557 (M − 2ClO_4, 9%), 408/406 (NiLClO_4, 100%).

‡ Crystallographic data for **2**: $C_{30}H_{36}Cl_2N_6NiO_{21}$, monoclinic, space group *C*2/*c*, *a* = 22.314(1), *b* = 14.495(1), *c* = 12.678(1) Å, *β* = 107.19(2)°, *U* = 3917.4(6) Å^3, *Z* = 4, *μ*(Mo-K*α*) = 7.23 cm^{-1}, 16433 reflections measured, 3305 unique, 2298 observed reflections [*I* > 3.00*σ*(*I*)]. *R* indices (observed data), *R* = 0.058, *R*′ = 0.062; For **3**: $C_{30}H_{22}Cl_2N_6NiO_{12}$, monoclinic, space group $P2_1/n$, *a* = 15.289(1), *b* = 10.075(2), *c* = 19.771(1) Å, *β* = 97.37(2)°, *U* = 3020.3(5) Å^3, *Z* = 4, *μ*(Mo-K*α*) = 8.99 cm^{-1}, 5359 reflections measured, 3512 observed reflections [*I* > 1.5*σ*(*I*)]. *R* indices (observed data), *R* = 0.063, *R*′ = 0.067; For **4**: $C_{31}H_{26}Cl_2N_6NiO_{11}$, monoclinic, space group $P2_1/n$, *a* = 7.074(2), *b* = 12.042(3), *c* = 38.653(3) Å, *β* = 90.62(2)°, *U* = 3292.2(6) Å^3, *Z* = 4, *μ*(Mo-K*α*) = 0.823 mm^{-1}, 6524 reflections measured, 6005 unique all used [*I* > 3.00*σ*(I)]. *R* indices (observed data), *R* = 0.0698, *R*′ = 0.1548. CCDC reference numbers 152730–152732. See http://www.rsc.org/suppdata/dt/b0/b008993l/ for crystallographic data for 152732 in CIF or other electronic format.

§ For DFT calculations we used the ADF 1999.02[12,13] suite of programs, employing Becke's gradient-corrected exchange functional,[14] and Lee–Yang–Parr's correlation functional (BLYP).[15] Triple-zeta Slater type orbitals were used as basis functions with a polarisation function added for H through Ar and Ga through Kr. The level of frozen core approximation for C, N and O was the 1s orbital and for Ni orbitals up to 2p were fixed. The geometry of each molecule was optimised at the BLYP level of theory with C_2 symmetry assumed for all complexes.

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