Structural Considerations of Terdentate Ligands: Crystal Structures of 2,2′:6′,2″-Terpyridine and 2,6-Bis(pyrazol-1-yl)pyridine†

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The crystal structures of the terdentate ligands 2,2′:6′,2″-terpyridine (terpy) and 2,6-bis(pyrazol-1-yl)-pyridine (bppy) were determined by single-crystal diffraction studies. The compound terpy crystallizes in the non-centrosymmetric orthorhombic space group $P2_12_12_1$ with a = 3.947(1), b = 16.577(7) and c = 17.840(6) Å; the structure was refined to R = 0.0745 for all 1087 independent data and R = 0.0470 for those 609 data with $F > 6\sigma(F)$. The compound bppy crystallizes in the centrosymmetric orthorhombic space group *Pnma* with a = 11.929(3), b = 21.320(3) and c = 3.889(0) Å; this structure was refined to R = 0.0409 for all 896 independent data and R = 0.0300 for those 723 reflections with $F > 6\sigma(F)$. The structures of the free terpy and bppy ligands were compared directly with the structures of the co-ordinated terpy and bppy ligands in the $[RuL(NO_2)(PMe_3)_2][ClO_4]$ complexes (L = terpy **1** or bppy **2**) in order to determine if any ligand structural changes occur upon co-ordination to ruthenium. To act as terdentate ligands, it was observed that both terpy and bppy must adopt the *cis,cis* ligand configuration as opposed to the *trans,trans* configuration found in the solid state and as the equilibrium configuration in solution. Both terpy and bppy distort upon co-ordination to ruthenium. The greatest distortions for terpy occur primarily at the central pyridine ring. Large distortions were observed for bppy at both in the central pyridine ring and in the terminal pyrazole rings.

The terdentate meridionally co-ordinating ligand 2,2′:6′,2″-terpyridine (terpy) was first isolated by Morgan and Burstall[1] as one of the numerous products from the reaction of pyridine with iron(III) chloride. Since the 1930s, numerous groups have examined terpy, prompted by the use of related ligands, 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen), in photochemical and photophysical processes.[2] Although the crystal structures of some multidentate ligands (for example, bipy and dimethylglyoxime) capable of quantitatively complexing metal ions have appeared in the literature of the 1950s,[3] the crystal structure of terpy has eluded researchers for many years.[4,5] The *trans,trans* configuration of the free ligand, terpy, has been postulated on the basis of ^{1}H NMR studies,[6–9] and ultraviolet spectroscopy[5,10] but until now has not been proven by modern crystallographic techniques. Several derivatized terpy ligands have been found to have the *trans,trans* geometry by X-ray crystal structure analysis.[11]

The crystal structure of 2,6-bis(pyrazol-1-yl)pyridine (bppy), another terdentate, meridionally co-ordinating ligand, has also been solved by X-ray crystallographic methods. This ligand has two pyrazole rings attached to a central pyridine moiety, and was first developed by Jameson and Goldsby[12] as a synthetic analogue of the terpy ligand. The bppy ligand is easily modified synthetically and thus a family of ligands has been developed which allow systematic 'tuning' of the redox and spectroscopic properties of a metal centre (particularly ruthenium) due to convenient variation of the substituents on the pyrazole rings.[13,14] The crystal structure of the bppy ligand is the first for this class of ligands.

With this report, the structures of the free ligands can be compared with the structures of the co-ordinated ligands in the $[RuL(NO_2)(PMe_3)_2][ClO_4]$ complexes (L = terpy **1**[15] or bppy **2**[16]). In this manner, we can compare quantitatively the ligand distortions of terpy or bppy upon co-ordination to an otherwise identical ruthenium centre. In general, we observed that terpy and bppy structurally distort upon ruthenium co-ordination, where the greatest distortional changes occur primarily at the central pyridine ring for terpy, while large distortions at both the central pyridine ring and the terminal pyrazole rings were observed for bppy.

Experimental

The ligands terpy and bppy were synthesised by literature procedures.[12,17] Crystals of terpy were difficult to obtain as crystallization from various solution mixtures resulted in powders or fine needles. Crystals of terpy suitable for X-ray diffraction were obtained after column chromatography using toluene as the eluent. The toluene was removed on a rotary evaporator and, after cooling at atmospheric pressure, crystals formed from the resultant oil. The bppy crystals were isolated from ethanol–water which was heated to boiling and allowed to cool slowly in a Dewar flask.

Data Collection and Processing for $C_{15}H_{11}N_3$ (terpy).—A clear crystal with approximate dimensions 0.5 × 0.3 × 0.1 mm was mounted on a Siemens R3m/V four-circle diffractometer; the resulting crystal data and other crystallographic details are reported in Table 1. Items of particular note are as follows. (1) Data were collected for the octants $+h, \pm k, \pm l$. They were averaged with $hkl = h\bar{k}\bar{l}$ and $h\bar{k}l = hk\bar{l}$. Averaging statistics were poor (R_{int} = 0.0709) as might be expected for such a weakly diffracting crystal [only 56% of reflections with 2θ (Mo-Kα) < 40° had $F > 6\sigma(F)$]. (2) Hydrogen atoms were included in the calculated positions based on d(C–H) 0.96 Å[18b] and their isotropic thermal parameters were refined. (3) Refinement led to convergence $[(\Delta/\sigma)_{max} = 0.001]$ with R = 0.0745, R' = 0.1115 and goodness of fit = 0.65 for all 1087 independent

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Experimental data for X-ray diffraction studies on terpy and bppy

	terpy	bppy
Empirical formula	$C_{15}H_{11}N_3$	$C_{11}H_9N_5$
M	233.3	211.2
Crystal size/mm	0.5 × 0.3 × 0.1	0.4 × 0.35 × 0.3
Space group	$P2_12_12_1$	$Pnma$
a/Å	3.9470(10)	11.929(3)
b/Å	16.577(7)	21.320(3)
c/Å	17.840(6)	3.889(0)
U/Å^3	1167.4(7)	989.0(3)
D_c/g cm^{-3}	1.327	1.419
Absorption coefficient/mm^{-1}	0.076	0.087
F(000)	488	440
2θ range/°	5.0–40.0	8.0–50.0
Scan range (ω)/°	0.55 plus Kα separation	0.60 plus Kα separation
Index ranges	$0 \leqslant h \leqslant 3, -15 \leqslant k \leqslant 15, -17 \leqslant l \leqslant 17$	$-14 \leqslant h \leqslant 14, -25 \leqslant k \leqslant 25, -4 \leqslant l \leqslant 0$
Reflections collected	2601	4035
Independent reflections	1087 (R_{int} = 0.0709)	896 (R_{int} = 0.0104)
Reflections [$F > 6.0\sigma(F)$]	609	723
Absorption correction	None	Semi-empirical
Min.,/max. transmission	—	0.9375, 0.9465
Absolute structure	$\eta = 14(9)$	—
Extinction correction/χ	0.006(2) where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-\frac{1}{4}}$	0.013(2)
Hydrogen atoms	Riding model, thermal parameters refined	Positions and thermal parameters refined
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0150F^2$	$w^{-1} = \sigma^2(F) + 0.003F^2$
Number of parameters refined	175	96
Final indices R, R' (all data)	0.0745, 0.1115	0.0409, 0.0398
Indices R, R' (6σ data)	0.0470, 0.0689	0.0300, 0.0366
Goodness-of-fit	0.65	1.64
Data-to-parameter ratio	6.2:1	9.3:1
Largest difference peak/e Å^{-3}	0.35	0.44

Details in common: crystal data colourless, orthorhombic crystal system, Z = 4; data collection Mo-Kα radiation (λ = 0.710 73 Å), highly oriented graphite monochromator, T = 295 K, scan type 2θ–θ, constant scan speed 1.50° min^{-1} in ω, background measurement for stationary crystal and stationary counter at beginning and end of scan each for 25% total scan time, 3 standard reflections every 97; solution and refinement SHELXTL PLUS (VMS)[18a] solution by direct methods, refinement by full-matrix least squares minimizing $\Sigma w(F_o - F_c)^2$, largest and mean Δ/σ 0.001, 0.000.

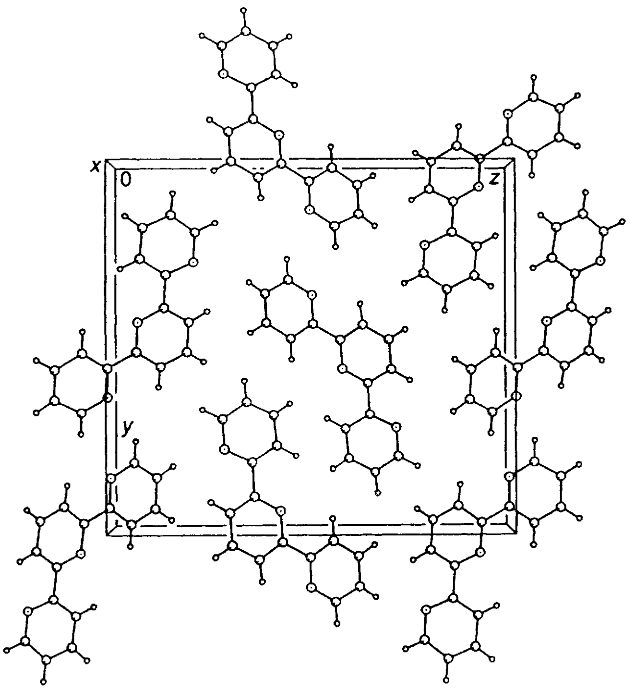

Fig. 1 Packing of molecules in the crystal structure of terpy, viewed down a

reflections and 175 variables [R = 0.0470, R' = 0.0689 for those 609 reflections with $F_o > 6.0\sigma(F_o)$]. (4) Despite the extremely small values for the imaginary components of anomalous dispersion, $\Delta f''(N) = 0.003$ e$^-$ and $\Delta f''(C)$ = 0.002 e$^-$, we tested the chirality of the crystal by 'η-refinement'. The value derived, η = +14(9), suggests that we initially defined the correct chirality.

Data Collection and Processing for $C_{11}H_9N_5$ (bppy).—A clear crystal with approximate dimensions 0.4 × 0.35 × 0.3 mm was mounted on a four-circle diffractometer (Syntex $P2_1$ upgraded to Siemens P3/V); the resulting crystal data and other crystallographic details are reported in Table 1. Items of particular note are as follows. (1) We collected four equivalent forms of data ($hk\bar{l}$, $h\bar{k}\bar{l}$, $\bar{h}k\bar{l}$, $\bar{h}\bar{k}\bar{l}$). The 4035 reflections collected with 2θ (Mo-Kα) < 50° were merged to a set of 896 independent reflections with R_{int} = 0.0104. This data set has 80.7% of its reflections with 2θ (Mo-Kα) < 50° having $F > 6\sigma(F)$. Clearly, this data set for bppy is of superior quality to that for terpy. (2) Hydrogen atoms were located and both their positional and isotropic thermal parameters were refined. (3) The molecule is ordered and lies about a crystallographic mirror plane with atoms N(11), C(14) and H(14) situated precisely at $y = \frac{3}{4}$. (4) Refinement led to convergence [$(\Delta/\sigma)_{max}$ = 0.001] with R = 0.0409, R' = 0.0398 and goodness-of-fit = 1.64 for all 896 independent reflections and 96 variables (R = 0.0300, R' = 0.0366 for those 723 independent reflections with $F_o > 6.0\sigma(F)$].

Additional material available from the Cambridge Crystallographic Data centre comprises H-atom coordinates and thermal parameters for the structures of both terpy and bppy.

Results and Discussion

Structure of $C_{15}H_{11}N_3$ (terpy).—This species crystallizes in space group $P2_12_12_1$ with one very short axis of a = 3.947(1) Å. The crystal packing viewed down this short axis is shown in Fig.

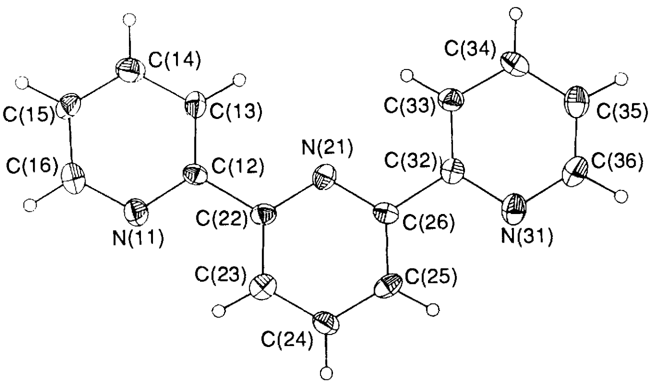

Fig. 2 Labelling of atoms in terpy. (ORTEP II diagram;[19] 30% ellipsoids for non-hydrogen atoms)

Table 2 Atomic coordinates (× 10^4) for terpy with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
N(11)	9 402(15)	6 380(3)	25(3)
C(12)	10 046(16)	5 600(3)	45(3)
C(13)	11 526(18)	5 197(4)	−525(3)
C(14)	12 587(21)	5 634(4)	−1 145(4)
C(15)	12 099(20)	6 440(4)	−1 172(4)
C(16)	10 377(21)	6 799(4)	−579(4)
N(21)	9 596(14)	4 368(3)	773(3)
C(22)	8 808(18)	5 160(3)	718(3)
C(23)	6 976(18)	5 568(4)	1 272(3)
C(24)	6 004(19)	5 164(3)	1 911(3)
C(25)	6 866(18)	4 360(4)	1 977(3)
C(26)	8 637(17)	3 977(3)	1 401(3)
N(31)	8 861(18)	2 758(3)	2 121(3)
C(32)	9 564(16)	3 106(3)	1 455(3)
C(33)	11 007(18)	2 694(4)	855(3)
C(34)	11 736(20)	1 881(4)	938(4)
C(35)	10 905(23)	1 519(4)	1 602(4)
C(36)	9 641(21)	1 970(5)	2 174(4)

Table 3 Bond lengths (Å) and angles (°) for terpy with e.s.d.s in parentheses

N(11)–C(12)	1.317(7)	N(11)–C(16)	1.339(9)
C(12)–C(13)	1.349(8)	C(12)–C(22)	1.488(8)
C(13)–C(14)	1.388(9)	C(14)–C(15)	1.351(10)
C(15)–C(16)	1.391(10)	N(21)–C(22)	1.353(8)
N(21)–C(26)	1.349(7)	C(22)–C(23)	1.398(9)
C(23)–C(24)	1.376(9)	C(24)–C(25)	1.380(9)
C(25)–C(26)	1.396(8)	C(26)–C(32)	1.493(8)
N(31)–C(32)	1.350(8)	N(31)–C(36)	1.344(9)
C(32)–C(33)	1.391(9)	C(33)–C(34)	1.386(9)
C(34)–C(35)	1.366(10)	C(35)–C(36)	1.360(10)
C(12)–N(11)–C(16)	118.4(5)	N(11)–C(12)–C(13)	123.3(5)
N(11)–C(12)–C(22)	116.1(5)	C(13)–C(12)–C(22)	120.5(5)
C(12)–C(13)–C(14)	118.2(6)	C(13)–C(14)–C(15)	120.1(6)
C(14)–C(15)–C(16)	117.8(6)	N(11)–C(16)–C(15)	122.0(6)
C(22)–N(21)–C(26)	117.5(5)	C(12)–C(22)–N(21)	117.3(5)
C(12)–C(22)–C(23)	120.2(5)	N(21)–C(22)–C(23)	122.5(5)
C(22)–C(23)–C(24)	119.6(6)	C(23)–C(24)–C(25)	118.2(6)
C(24)–C(25)–C(26)	120.0(5)	N(21)–C(26)–C(25)	122.3(5)
N(21)–C(26)–C(32)	116.7(5)	C(25)–C(26)–C(32)	121.1(5)
C(32)–N(31)–C(36)	115.4(5)	C(26)–C(32)–N(31)	114.8(5)
C(26)–C(32)–C(33)	121.7(5)	N(31)–C(32)–C(33)	123.5(5)
C(32)–C(33)–C(34)	118.7(6)	C(33)–C(34)–C(35)	118.0(6)
C(34)–C(35)–C(36)	119.8(6)	N(31)–C(36)–C(35)	124.4(6)

1, the atom labelling in Fig. 2. Atomic coordinates for the non-hydrogen atoms are given in Table 2, interatomic distances and angles in Table 3. The closest intramolecular contacts involve hydrogen atoms 2.93 Å from N(11), 2.91 Å from N(21) and 2.76 Å from N(31). Contacts reported here are for the 'X-ray determined' hydrogen positions. The true internuclear distances [based on *d*(C–H) 1.08 Å][18b] are slightly shorter with values of 2.87, 2.79 and 2.64 Å, respectively.

The bonds linking the rings in the terpy molecule are typical of C–C single bonds between sp^2 hybridized carbon atoms, with C(12)–C(22) 1.488(8) Å and C(26)–C(32) 1.493(8) Å. Inside the ring systems, the C–N distances average 1.342 ± 0.013 Å, ranging from a low value of 1.317(7) Å to a high value of 1.353(8) Å. The C–C bonds inside the rings average 1.378 ± 0.017 Å, ranging from 1.349(8) to 1.398(9) Å. The angles about the C–C bonds linking the rings break down into two significantly different sets. Those angles which involve a nitrogen atom [N(11)–C(12)–C(22) 116.1(5), C(12)–C(22)–N(21) 117.3(5), N(21)–C(26)–C(32) 116.7(5), C(26)–C(32)–N(31) 114.8(5)°] average 116.2 ± 1.1°. Those angles involving only carbon atoms [C(13)–C(12)–C(22) 120.5(5), C(12)–C(22)–C(23) 120.2(5), C(25)–C(26)–C(32) 121.1(5), C(26)–C(32)–C(33) 121.7(5)°] average 120.9 ± 0.7°, 4.7° greater than the average for the angles involving the nitrogen atoms. The three rings are close to coplanar with the torsion angles between the central ring and the rings containing N(11) and N(31) being 5.1 and 7.2°, respectively. The angle between the rings containing N(11) and N(31) (the non-linked rings) is 7.1°.

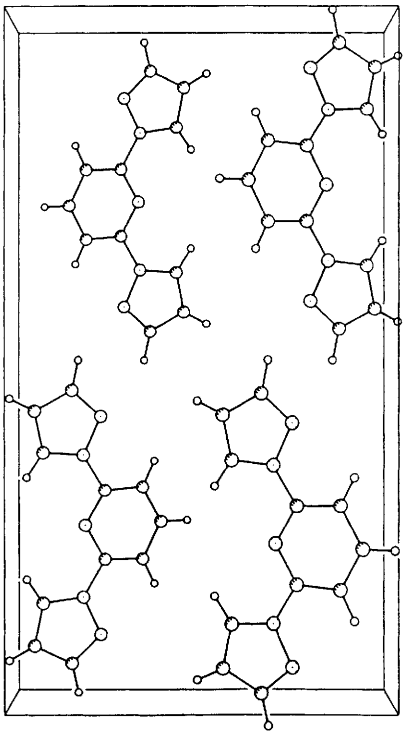

Fig. 3 Packing of molecules in the crystal structure of bppy, viewed down *c*

Structure of $C_{11}H_9N_5$ (bppy).—This species crystallizes in space group *Pnma* with one short axis of *c* = 3.889(0) Å. The crystal packing, viewed down this short axis, is shown in Fig. 3. A general view of the bppy molecule is shown in Fig. 4. Atomic coordinates for the non-hydrogen atoms are given in Table 4, interatomic distances and angles in Table 5. The closest intramolecular contacts involve hydrogen atoms 2.77 Å for N(11) and 2.75 Å from N(21). Contacts reported here are for the 'X-ray determined' hydrogen positions.[18b] [The refined C–H distances range from C(23)–H(23) 0.922(14) to C(22)–H(22) 0.978(13) Å, averaging 0.951 Å.] The true internuclear contacts [based upon *d*(C–H) 1.08 Å] are shorter, with values of 2.64 and 2.68 Å respectively.

The bond linking the rings in bppy is also in the typical single-

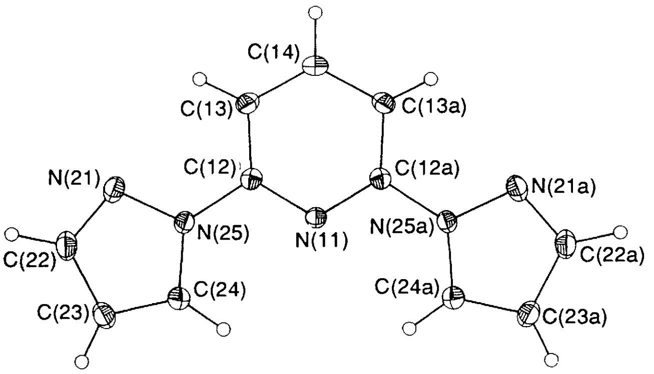

Fig. 4 Labelling of atoms in bppy. There is a crystallographic mirror plane perpendicular to the diagram, passing through atoms H(14), C(14) and N(11) (ORTEP II diagram)

Table 4 Atomic coordinates (× 10^4) for bppy with (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
N(11)	8 196(1)	7 500	646(3)
C(12)	7 679(1)	6 968(1)	−177(3)
C(13)	6 653(1)	6 938(1)	−1 848(3)
C(14)	6 150(1)	7 500	−2 658(5)
N(21)	7 781(1)	5 844(1)	232(3)
C(22)	8 544(1)	5 447(1)	1 368(4)
C(23)	9 490(1)	5 749(1)	2 648(4)
C(24)	9 276(1)	6 366(1)	2 268(3)
N(25)	8 247(1)	6 418(1)	793(3)
H(13)	6 335(10)	6 544(6)	−2 426(31)
H(14)	5 427(14)	7 500	−3 698(44)
H(22)	8 372(10)	4 999(6)	1 224(33)
H(23)	10 121(11)	5 560(6)	3 538(38)
H(24)	9 690(10)	6 732(7)	2 889(32)

Table 5 Bond lengths (Å) and angles (°) for bppy with e.s.d.s in parentheses

N(11)–C(12)	1.331(1)	N(11)–C(12a)	1.331(1)
C(12)–C(13)	1.386(2)	C(12)–N(25)	1.406(1)
C(13)–H(13)	0.950(13)	C(13)–C(14)	1.377(1)
C(14)–H(14)	0.953(17)	C(14)–C(13a)	1.377(1)
N(21)–C(22)	1.318(2)	N(21)–N(25)	1.362(1)
C(22)–H(22)	0.978(13)	C(22)–C(23)	1.391(2)
C(23)–H(23)	0.922(14)	C(23)–C(24)	1.348(2)
C(24)–H(24)	0.954(14)	C(24)–N(25)	1.360(2)
C(12)–N(11)–C(12a)	117.0(1)	N(11)–C(12)–C(13)	124.1(1)
N(11)–C(12)–N(25)	115.1(1)	C(13)–C(12)–N(25)	120.8(1)
C(12)–C(13)–H(13)	120.3(8)	C(12)–C(13)–C(14)	116.9(1)
H(13)–C(13)–C(14)	122.8(8)	C(13)–C(14)–H(14)	119.5(1)
C(13)–C(14)–C(13a)	121.0(2)	H(14)–C(14)–C(13a)	119.5(1)
C(22)–N(21)–N(25)	103.9(1)	N(21)–C(22)–H(22)	117.5(7)
N(21)–C(22)–C(23)	112.6(1)	H(22)–C(22)–C(23)	129.9(7)
C(22)–C(23)–H(23)	126.5(8)	C(22)–C(23)–C(24)	105.0(1)
H(23)–C(23)–C(24)	128.5(8)	C(23)–C(24)–H(24)	132.2(8)
C(23)–C(24)–N(25)	107.2(1)	H(24)–C(24)–N(24)	120.6(8)
C(12)–N(25)–N(21)	120.7(1)	C(12)–N(25)–C(24)	128.0(1)
N(21)–N(25)–C(24)	111.3(1)		

bond range for sp^2 carbon and nitrogen, with C(12)–N(25) 1.406(1) Å. Inside the rings, the C–N bond lengths average 1.335 ± 0.022 Å [1.318(2)–1.360(2) Å] and the C–C bond lengths average 1.376 ± 0.019 Å [1.348(2)–1.391(2) Å]. The N–N bond length is N(21)–N(25) 1.362(1) Å. As in the terpy molecule, the angles about the bond linking the rings are asymmetric, with the angles involving a nitrogen atom being significantly smaller than the angles involving a ring carbon atom about the same central atom. Thus, N(11)–C(12)–N(25) 115.1(1)° as compared to C(13)–C(12)–N(25) 120.8(1)°, a difference of 5.7°; and C(12)–N(25)–N(21) 120.7(1)° as compared to C(12)–N(25)–C(24) 128.0(1)°, a difference of 7.3°. The torsion angle between the central ring and each of the side rings is 3.5°.

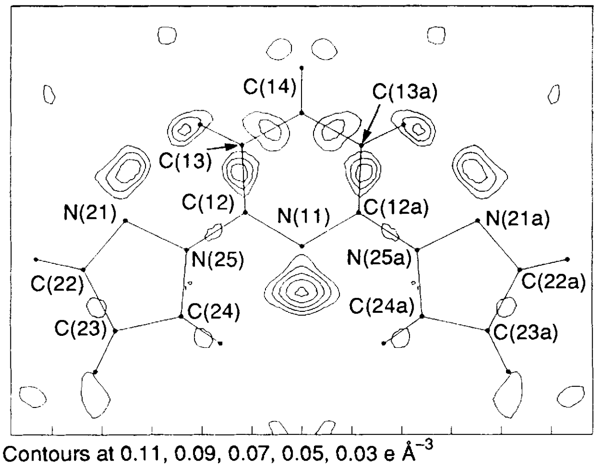

Fig. 5 Residual electron density in final model for bppy. Note features about N(11), N(21) and N(21a), corresponding to lone pairs (This figure is in the same orientation as Fig. 4)

The data set for bppy was far superior to that for terpy. The bppy structure also is in a centrosymmetric space group. We decided, therefore, to investigate the residual electron density for this structural study. A final Fourier difference map for bppy shows significant features corresponding to a lone pair on the nitrogen atom of the central pyridine ring and lone pairs on the symmetry-related free nitrogen atoms of the pyrazole rings (see Fig. 5).

As Constable[4] predicted, the most obvious structural change in terpy and bppy upon co-ordination to a metal centre is the twisting of the terminal pyridine rings (terpy) or terminal pyrazole rings (bppy) from the *trans,trans* configuration to the *cis,cis* geometry. The structure of $[Ru(terpy)(PMe_3)_2(NO_2)][ClO_4]$ **1** provides an example of the structural changes which occur when the terpy ligand is co-ordinated to a ruthenium metal centre.[15] Similarly, the structure of bppy can be compared with the co-ordinated bppy ligand in the $[Ru(bppy)(PMe_3)_2(NO_2)]^+$ **2** complex cation.[16] In general, in order to discuss the changes of bond lengths and angles in terpy and bppy from free compounds to ruthenium co-ordinated ligands, we will use the convention of change of bond length or angle = value from co-ordinated ligand − value from free ligand, where a positive change denotes an increase in bond length or angle upon co-ordination to ruthenium (see Figs. 6 and 7). We assume that a 180° rotation is allowed in the terpy and bppy compounds, thus both the structures of the free compounds and the co-ordinated ligands can be compared in the *cis,cis* geometry.

Changes in the bite angles and in the angles and bond lengths of the ligand-ring systems occur upon co-ordination of terpy and bppy to a ruthenium centre. To approximate the bite angle of the unco-ordinated terpy and bppy compounds, we extended vectors from the lone pairs of the nitrogens of the terminal pyridines (terpy) or pyrazoles (bppy) and the central pyridine to determine the geometric point of intersection. The bite angle for the free terpy and bppy compounds was then defined as the N(terminal ring)–point of vector intersection–N(terminal ring) angle. From our approximations, we estimated the bite angle of terpy, in its unco-ordinated form, to be 128°. The distance of the N(central pyridine) to the point of vector intersection for terpy was approximated at 2.4 Å. For the unco-ordinated bppy compound, the bite angle was approximated to be 116° and the distance of the N(central pyridine) to the point of vector intersection was 3.2 Å.

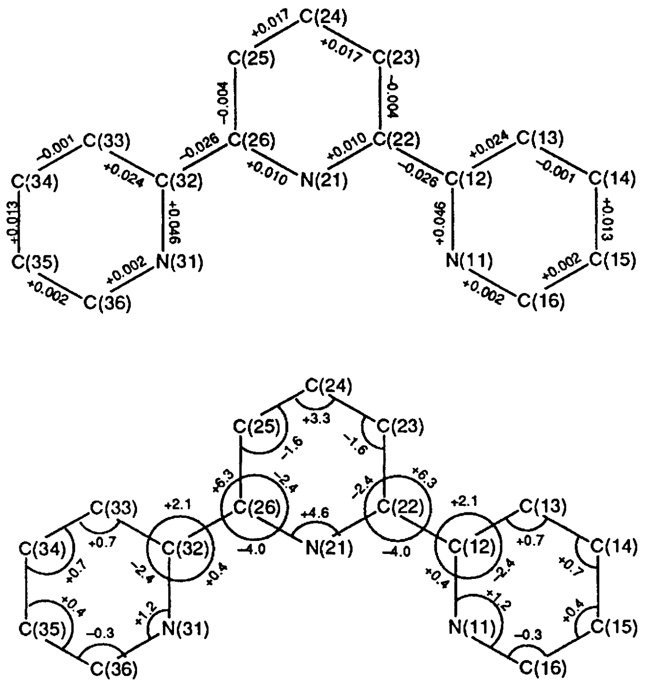

Fig. 6 Average changes in the bond lengths and angles for the terpy ligand due to co-ordination to a ruthenium centre. The average bond length changes are in Å and the average angle changes in °

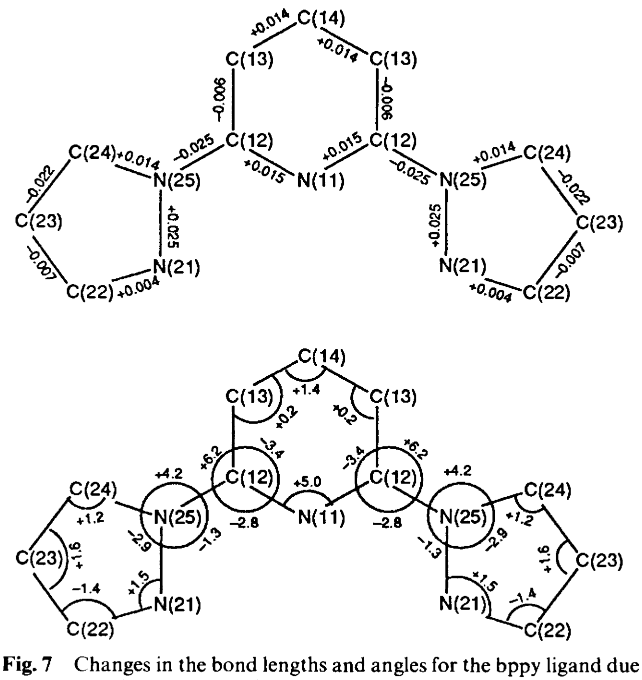

Fig. 7 Changes in the bond lengths and angles for the bppy ligand due to co-ordination to a ruthenium centre. The bond length changes are in Å and the angle changes in °

In the ruthenium complex, **1**, the bite angle of the terpy ligand [where bite angle is defined in the ruthenium complexes as N(terminal ring)–Ru–N(terminal ring)] was determined by crystal-structure analysis to be 158.3(2)°. The N(central pyridine)–Ru bond length of **1** was 1.985(5) Å.[15] In the ruthenium complex **2** the bite angle of the bppy ligand was determined by crystal-structure analysis to be 157.2(2)°, and the N(central pyridine)–Ru bond distance was 1.990(3) Å.[16] Thus, the terpy and bppy ligands have very similar bite angles when co-ordinated to ruthenium. Also, both ligands display very similar N(central pyridine)–Ru bond distances, 1.985(5) Å for terpy and 1.990(3) Å and bppy. In order to co-ordinate to a ruthenium metal centre, terpy and bppy distort from their unco-ordinated structures in different ways. The greatest distortions for terpy occur primarily at the central pyridine ring, while large distortions at both the central pyridine ring and the terminal pyrazole rings were observed for bppy.

2,2′:6′,2″-Terpyridine must distort at the 2,6 positions of the central pyridine ring to provide effective terdentate co-ordination to the ruthenium metal centre.[4] The magnitudes of the changes in bond lengths and bond angles are not symmetric, due to the lack of symmetry of the terpy ligand in the crystal structures. Thus, we will discuss the average structural changes for the terpy ligand. The 2,6 positions of the central pyridine are described as C(22) and C(26) (Fig. 6), and an average decrease of 4.0° was observed at the C(32)–C(26)–N(21) [C(12)–C(22)–N(21)] angle upon co-ordination of the terpy to the ruthenium centre. We propose that the 4° pivoting by the terminal pyridines about the 2,6 positions of the central pyridine in concert with the 4.6° increase about N(21) of the central pyridine are the primary angular distortions needed to allow terpy to function as a terdentate ligand.

There are several notable changes in bond length in terpy upon co-ordination to ruthenium. The C(12)–C(13) [C(32)–C(33)] bond increases by an average of 0.024 Å, the C(12)–C(22) [C(26)–C(32)] bond decreases by an average of 0.026 Å, and the C(12)–N(11) [C(32)–N(31)] bond increases by an average of 0.046 Å. While these bond length changes are significant, they do not contribute significantly towards the positioning of the terminal pyridines closer to the ruthenium centre.

In addition to our structural analysis of terpy, we can analyse the structural changes that a second terdentate ligand, bppy, undergoes upon co-ordination to ruthenium. The structural changes of the bppy ligand upon co-ordination to ruthenium can be envisioned in terms of maximizing the co-ordination of all three nitrogen donor atoms. The central pyridine structurally distorts by an increase of 5.0° at the N(11) position, an increase of 1.4° at the C(14) position, and a decrease of 3.4° at the C(12) position, while most of the bond lengths remain essentially unchanged. This distortion of the central pyridine results in a pivoting of the terminal pyrazole groups by 2.8° about the C(12) positions, which brings the terminal pyrazole groups closer to the ruthenium centre.

Other notable changes in the bppy ligand upon co-ordination to ruthenium involve the C(12)–N(25) bond, which contracts by 0.025 Å, the C(23)–C(24) bond, which contracts by 0.022 Å, and a lengthening of the N(21)–N(25) bond in the terminal pyrazole ligands. The shortening of the C(23)–C(24) bond results in a distortion about N(25), where the C(12)–N(25)–C(24) angle increases by 4.2°, the N(21)–N(25)–C(24) angle decreases by 2.9°, and the C(12)–N(25)–N(21) angle decreases by a relatively small 1.3°. While these ligand changes are significant, they do not contribute significantly towards the positioning of the terminal pyrazole groups closer to the ruthenium centre.

Our crystal-structure data of unco-ordinated terpy may have relevance to the structure of terpy in solution. The dihedral angle of terpy in solution has been estimated by several research groups. Fielding and Le Fevre[9] proposed a dihedral angle for terpy in solution of up to 28°, based on the observed dipole moment of 0.9 D (D ≈ 3.35 × 10^{-30} C m). Thummel and Jahng[5] suggested a dihedral angle for terpy in solution of 20–50° based on ultraviolet spectroscopy. In contrast to these studies, Nakamoto asserted,[10] based on ultraviolet spectroscopic measurements, that only small twists of the terminal pyridine rings from the plane of the central pyridine occur in solution. In his report, Nakamoto compared the crystal structure of bipy with the electronic spectroscopy of bipy and then extended his argument on bipy to include terpy, and contended that terpy would have small twists due to the *trans,trans* geometry of terpy in the solution state. No crystal structure data regarding unco-ordinated terpy were available at the time; our crystal-structure results now support Nakamoto's argument. In the crystal structure of terpy the three pyridine rings of the terpy ligand are close to coplanar with dihedral angles of 5.1 and 7.2°. (The angle between the two terminal pyridine rings of terpy is 7.1°.) This is possible because the closest intramolecular contacts involve hydrogen atoms 2.87 Å from N(11), 2.79 Å from N(21) and 2.64 Å from N(31).

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