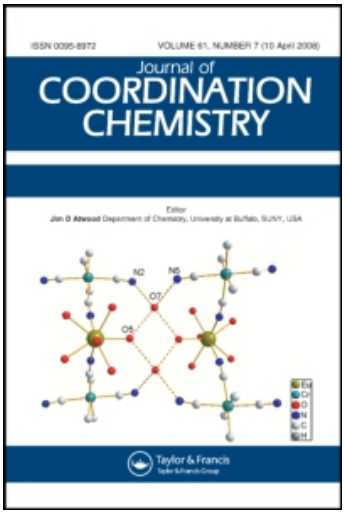


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

STRUCTURAL STUDIES ON PYRAZOLYLPYRIDINE LIGANDS AND COMPLEXES. 2. COMPARISONS BETWEEN BISPYRAZOLYLPYRIDINE LINKAGE ISOMERS AND WITH 2,2',6',2''-TERPYRIDINE JERZY ZADYKOWICZ

Pierre G. Potvin[a]
[a] Department of Chemistry, York University, Toronto, Ontario, Canada

To cite this Article Potvin, Pierre G.(1999) 'STRUCTURAL STUDIES ON PYRAZOLYLPYRIDINE LIGANDS AND COMPLEXES. 2. COMPARISONS BETWEEN BISPYRAZOLYLPYRIDINE LINKAGE ISOMERS AND WITH 2,2',6',2''-TERPYRIDINE JERZY ZADYKOWICZ', Journal of Coordination Chemistry, 47: 3, 395 — 407
To link to this Article: DOI: 10.1080/00958979908022224
URL: http://dx.doi.org/10.1080/00958979908022224

J. Coord. Chem., 1999, Vol. 47, pp. 395–407
Reprints available directly from the publisher
Photocopying permitted by license only

STRUCTURAL STUDIES ON PYRAZOLYLPYRIDINE LIGANDS AND COMPLEXES. 2. COMPARISONS BETWEEN BISPYRAZOLYLPYRIDINE LINKAGE ISOMERS AND WITH 2,2′;6′,2″-TERPYRIDINE

JERZY ZADYKOWICZ and PIERRE G. POTVIN*

Department of Chemistry, York University, 4700 Keele Street, Toronto, Ontario, Canada M3J 1P3

(Received 25 February 1998; Revised 27 May 1998; In final form 18 August 1998)

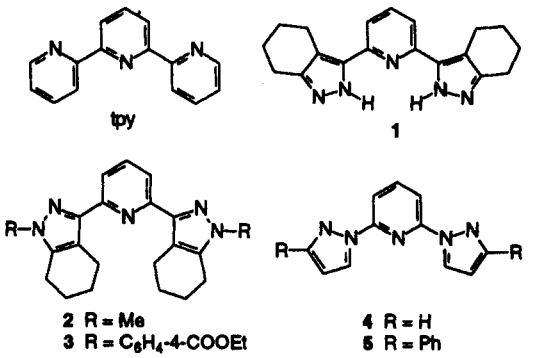
Crystal structures were obtained for the 3(*C*),2′;6′,3″(*C*)-linked bispyrazolylpyridines 2,6-di(2*H*-4,5,6,7-tetrahydroindazol-3-yl)pyridine (**1**), 2,6-di(1-methyl-4,5,6,7-tetrahydroindazol-3-yl)pyridine (**2**), 2,6-di(1-(4-ethoxycarbonylphenyl)-4,5,6,7-tetrahydroindazol-3-yl)pyridine (**3**) and for the homoleptic Ru^{II} complex of **2**, $[Ru(\mathbf{2})_2]Cl_2$, which crystallized with 7 molecules of $CHCl_3$. Ligand **1** adopts the inter- and intramolecularly hydrogen-bonded *syn,syn* rotameric conformation, while **2** and **3** were in the *anti,anti* forms. Relative to the latter, ligand distortions were assessed in **1** (considered as a H^+ complex) and $[Ru(\mathbf{2})_2]Cl_2$. Comparisons were drawn with other tridentate ligands containing a pyridine nucleus, specifically the 1(*N*),2′;6′,1″(*N*″) linkage isomers and 2,2′;6′,2″-terpyridine, in both free and Ru^{II} complexed forms, as well as with their bidentate analogues. Unlike with bidentate ligands, the bonds to the pyridine moiety are shortest, the outer heterocyclic rings are drawn inward and, overall, the ligands remain fairly planar. Flanking substituents remain well splayed out in the 1,2′;6′,1″-linked bispyrazolylpyridines, are more parallel in the 3,2′;6′,3″ linkage isomers and are unfavorably compressed in terpyridines.

Keywords: Bispyrazolylpyridine complexes; linkage isomers; terpyridine complexes; crystal structures; ligand distortions; transition metal binding; intramolecular hydrogen bonding; intermolecular hydrogen bonding

* Corresponding author. Tel.: (416) 736-2100. Ext.: 66140. Fax: (416) 736-5936.
E-mail: pgpotvin@yorku.ca.

INTRODUCTION

The utility of 2,2′;6′,2″-terpyridine (tpy) in coordination chemistry has spurred the exploration of other tridentate ligands built from combinations of azoles and azines,[1] including the relatively π-rich bispyrazolylpyridines. In previous reports, we presented a series of bidentate,[2] tridentate,[3] pentadentate[4] and macrocyclic[4] ligands based on the novel 3′(*C*′),2-linked 2-(tetrahydroindazol-3-yl)pyridine core, of which **1** is an example. These molecules are prepared by short, high-yielding routes from readily available materials and are amenable to modification at the *N*–H sites to give, for example, **2** and **3**. They constitute linkage isomers of the 1(*N*),2′;6′,1″(*N*″)-linked 2,6-di(pyrazol-1-yl)pyridines **4** and **5**.[5,6]



Despite its long popularity, the crystal structure of free tpy has only recently been obtained by Bessel *et al.*[7] This allowed an analysis of the distortions incurred upon complexation to a Ru^{II} center[8] and a comparison with 2,6-di(pyrazol-1-yl)pyridines in both free and Ru^{II} complexed forms.[7] We have already examined the complexation-induced distortions suffered by the bidentate pyrazolylpyridine linkage isomers and bipyridine (bpy), and pointed out general differences therein between these ligands.[9] We here extend this analysis to include 3,2′;6′,3″-bis(pyrazolyl)pyridines in free and complexed forms, and additionally compare these ligands to other tridentate ligands and to their bidentate analogues.

EXPERIMENTAL

General

The preparations of the free ligands **1**–**3** have been detailed elsewhere.[3,4] Suitable crystals were grown as colorless plates (**1**), colorless prisms (**2** and

TABLE I Crystallographic data

Compound	**1**	**2**	**3**	$[Ru(\mathbf{2})_2]Cl_2 \cdot 7CHCl_3$
Empirical formula	$C_{19}H_{21}N_5$	$C_{21}H_{25}N_5$	$C_{37}H_{37}N_5O_4$	$C_{49}H_{57}Cl_{23}N_{10}Ru$
Formula weight	319.41	347.46	615.72	1702.47
Space group[a]	Cc	$P2_1/m$	$P2_1/n$	$P2_1/c$
Unit cell dimensions	a(Å) 31.536(7)	12.4750(10)	8.4350(10)	20.936(5)
	b(Å) 6.496(2)	10.0560(10)	9.0050(10)	12.550(6)
	c(Å) 17.590(3)	15.402(2)	42.123(5)	30.265(7)
	β(°) 113.92	104.150(10)	95.400(10)	109.940(10)
Volume (Å^3)	3294.0(14)	1873.5(3)	3185.3(6)	7475(4)
Z	8	4	4	4
Density (calcd) (Mg/m^3)	1.288	1.232	1.284	1.513
Absorption coeff. (mm^{-1})	0.080	0.076	0.085	1.072
F(000)	1360	744	1304	3424
Crystal size (mm)	0.8 × 0.2 × 0.1	0.5 × 0.4 × 0.3	0.3 × 0.2 × 0.1	0.9 × 0.4 × 0.05
2θ range for data collection (°)	4.7–44.98	3.78–50.00	3.88–50.02	3.54–45.12
Index ranges	$-1 \le h \le 33$	$-14 \le h \le 14$	$-1 \le h \le 10$	$-1 \le h \le 20$
	$-1 \le k \le 6$	$-1 \le k \le 10$	$-1 \le k \le 10$	$-1 \le k \le 13$
	$-18 \le l \le 17$	$-18 \le l \le 18$	$-50 \le l \le 50$	$-32 \le l \le 31$
Reflections collected	2762	7164	7754	12591
Independent reflections [R(int)]	2276 [0.0446]	3215 [0.1280]	5603 [0.0902]	9561 [0.0905]
Data/restraints/parameters	2276/2/284	3215/0/238	5586/0/417	9538/18/781
Goodness-of-fit on F^2	1.051	1.010	1.016	1.038
R_1/wR_2 indices [$I > 2\sigma(I)$]	0.0852/0.2094	0.0684/0.1528	0.0835/0.1457	0.0819/0.1812
R_1/wR_2 indices [all data]	0.1890/0.2954	0.1504/0.1936	0.2303/0.2262	0.1800/0.2536
Extinction coefficient	0.0006(4)	0.0013(12)	—	—
Largest diff. peak/hole (e Å^{-3})	0.481/−0.339	0.347/−0.284	0.246/−0.246	0.895/−0.503

[a] All crystal systems are monoclinic.

3) or red plates ($[Ru(\mathbf{2})_2]Cl_2$) by diffusion of ether into $CHCl_3$ solutions. X-ray diffraction data were acquired and the structures were solved as before;[9] significant details and results are presented in Table I. Empirical absorption corrections were applied to the data for **2** (ψ-scans over θ 1.63°–14.93°) and $[Ru(\mathbf{2})_2]Cl_2$ (ψ-scans over θ 0.95°–8.85°). Except for **1**, all non-hydrogen atoms were refined anisotropically. The N–H groups in **1** were located with a difference-Fourier contour map constructed using the Siemens software from a refinement model lacking those hydrogens, and were then fixed at idealized positions with bond lengths of 0.86 Å and refined with a riding model. Anisotropic refinement was applied to the central N–N–C–C–N–C–C–N–N binding fragment of **1** but isotropic refinement was used for all other atoms, in order to maintain a data/parameter ratio of ≥ 8. The absolute structure of **1** could not be determined with certainty (Flack parameter 0 ± 10).

In all cases, the possibility of conformational disorder in the $-(CH_2)_4-$ fragments was explored, as was the utility of refining the positions of the hydrogens attached to nitrogens in **1**. Any particular model was rejected if (i) it failed to provide a statistically significant improvement over a simpler

model according to Hamilton's *R*-ratio test,[10] or (ii) if it led to a chemically unreasonable atomic arrangement or unreasonably long or short bonds, or (iii) if atoms, particularly the nitrogens engaged in H-bonding, became non-positive-definite (negative principal mean square displacements) during anisotropic refinement, or (iv) if the refinement was unstable, or (v) if the occupancy of a given conformer was very small or negative. Also, strong correlations were sometimes observed between parameters in some models. In the end, the inclusion of conformational disorder could not be justified and the positions of the hydrogens attached to nitrogens could not be usefully refined.

By the same criteria, one of the seven $CHCl_3$ molecules (labels ending in A) in the lattice of $[Ru(\mathbf{2})_2]Cl_2$ was found to be disordered. It was modeled with an alternate disposition (39% occupancy) of the Cl atoms about the common C atom (C22A) and the new Cl positions were given labels ending with H. A separate H atom (H22H) was added for the alternate disposition. Because of unusual C–Cl bonds and Cl–C–Cl angles, tetrahedral restraints were also applied to $CHCl_3$ units A, B and H.

Di-(η^3-2,6-di(1-methyl-4,5,6,7-tetrahydro-indazol-3-yl)pyridine)ruthenium(II) Hexafluorophosphate ($[Ru(\mathbf{2})_2](PF_6)_2$)

A mixture of ligand $\mathbf{2}$[3] (0.050 g, 0.144 mmol) and $Ru(DMSO)_4Cl_2$ (0.035 g, 0.072 mmol) was heated to reflux in 10 mL of anhydrous ethylene glycol for 24 h. Subsequently, the mixture was washed with aqueous NaCl and extracted into $CHCl_3$. A red solid was left after the removal of solvent which could be used to grow crystals. For analytic purposes, it was redissolved in MeOH and treated with an excess of NH_4PF_6 in H_2O/MeOH solution to afford $[Ru(\mathbf{2})_2](PF_6)_2$ (0.075 g, 96%) as a red solid; ^{1}H-NMR ($CDCl_3$): δ 1.82 (m, 16H), 2.53 (m, 8H), 2.72 (s, 12H), 2.98 (m, 8H), 7.98 (d, 4H, $J = 7.9$ Hz), 8.09 (t, 2H, $J = 7.3$ Hz) ppm; ^{13}C-NMR: δ 20.86, 21.32, 21.47, 21.73, 34.00, 118.30, 119.00, 136.79, 145.04, 148.19, 154.43 ppm; FAB-MS *m/z* (%) 1087 (10, M + H), 941 (100, M – PF_6), 796 (26, M – 2PF_6). *Anal.* Calcd. for $C_{42}H_{50}N_{10}RuP_2F_{12} \cdot 2H_2O$: C, 44.96; H, 4.85; N, 12.48. Found: C, 44.69; H, 4.51; N, 12.28.

Structural Analysis

The atomic positional parameters from structures cited for comparison with those reported herein were obtained either directly from the literature reports or from databases according to instructions given by the authors.

They were converted to Cartesian coordinates. All calculations ignored the uncertainties in atomic positions. The calculation of the least-squares planes neglected ring substituents, including H. Inter-ring angles in complexes were calculated as the angles between the normals of the least-squares planes of each ring. Interplanar dihedral (twist) angles ψ in complexes were measured while viewing these normals along the centroid-to-centroid axis. Ligand bowing in complexes was measured as the inter-ring angle remaining after correction by rotation about the inter-ring bond of any non-zero ψ to 0°. For the purposes of measuring the "pinch" or "splay" angles of flanking substituents (at 6/6″ in tpy, at pyrazole N^1 in the di(pyrazol-3-yl)pyridines, or at pyrazole C^3 in the di(pyrazol-1-yl)pyridines), hypothetical bond vectors were drawn as the bisectors of the ring angle at the two flanking positions and the angles between these vectors was measured. Free ligands were first converted to their binding conformations (coplanar rings, *syn* binding sites) by rotation of the end rings about the inter-ring bonds.

The tridentate "bite" angles were measured in the same manner as for five-bond C–N–X–C–N–C fragments in bidentate ligands[9] after artificially linking together the terminal rings and ignoring the central ring.

RESULTS

Structure of Unfunctionalized Ligand 1

The *C*-linked tridentate 2,6-di(4,5,6,7-tetrahydroindazol-3-yl)pyridine **1** can exist in three tautomeric forms and in three rotameric conformations involving *syn* or *anti* orientations of the binding sites. Whereas the expected rotamer is *anti,anti*, as occurs with terpyridine itself,[7] the ^{1}H-NMR spectrum of **1** has suggested that the dominant form in solution is the *syn,syn* rotamer of the *in,in* (or 2′,2″-H_2) tautomer,[3] which is presumably stabilized by intramolecular H-bonding. Previous X-ray crystallographic studies of the bidentate analogue has substantiated this explanation, with signs that the ligand backbone became distorted in order to engage in internal H-bonding.[9] This allowed a description of this bidentate analogue as a H^+ complex of the deprotonated form. The bidentate ligand was also engaged in intermolecular H-bonding in the solid phase, though solution studies predicted only the intramolecular variety.[2] As *in,in*-**1** can be regarded as a double H^+ complex and, since it could also engage in both inter- and intramolecular H-bonding, its crystal structure was of interest, particularly to determine the extent of distortion employed to accommodate such binding.

In the crystal structure of **1** (Figure 1), there are two independent but similar molecules in 1:1 ratio (types A and B), neither of which is symmetric. Unfortunately, the low symmetry caused the minimum number of refinement parameters to be high while the number of independent reflections was only modest. An empirical extinction parameter was also required. Nevertheless, the possibility of conformational disorder in the $-(CH_2)_4-$ fragments was explored as was refinement of the $N-H$ positions in view of the H-bonding, especially because of the non-coplanar dispositions of the H-bonding partners. Although there were persistent Fourier peaks in the vicinity of the $-(CH_2)_4-$ chains sometimes coupled with large isotropic temperature factors for the conformationally mobile carbons, the modelling of conformational disorder led to unreasonable structures, as did the refinement of $N-H$ groups.

Sheets of type A molecules alternate with sheets of those of type B and all are stacked along parallel axes, with each molecule lying with the plane of its pyridine ring at about 19.5° from the sheet plane. Any one stack faces an antiparallel but sideways offset stack of molecules of the other type and H-bonds form between nearest neighbors on each. The next pair of H-bonded stacks is a mirror image of the first pair. The two pyridine rings are nearly coplanar (interplanar angle 1.7°) and the two pyridine planes are separated

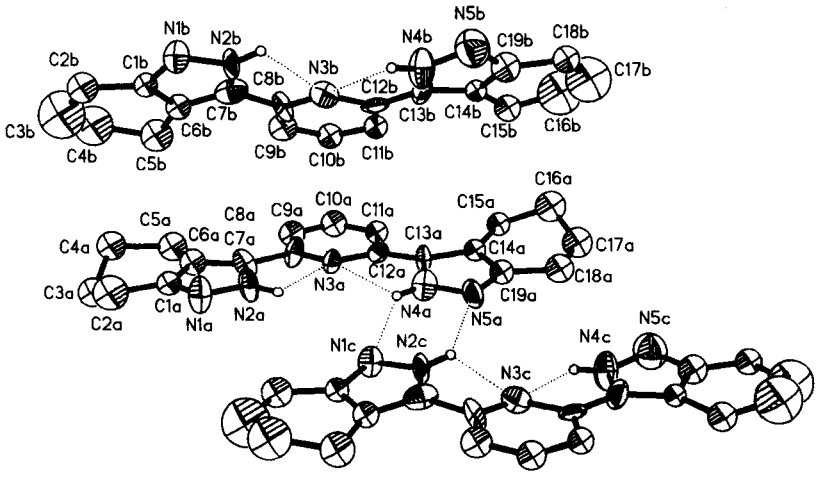


FIGURE 1 ORTEP plot of the crystal structure of compound **1** showing 50% thermal ellipsoids. Units A and B are crystallographically distinct while unit C, with only its nitrogens labelled, is a symmetry equivalent of unit B to show the inter-molecular H-bonding network. All other hydrogens have been omitted for clarity.

by about 1.3 Å. The intermolecular H-bonding involves only one of the two pyrazole nuclei in each molecule and the partner stacks are thereby offset from each other by about half a molecule. The two pyrazoles engaged in intermolecular H-bonding are twisted from their respective pyridine planes (by 11.3° and 7.7°) in order to face each other, while those engaged in only intramolecular H-bonding remained in their respective planes (dihedrals 1.1° and 0.6°). The H-bonding network here differs from that in the bidentate analogue[9] in that the *outer* pyrazole nitrogens (N^1 by the indazole numbering) are the intermolecular H-bond acceptors while each pyridine accepts two internal H-bonds.

Structure of Functionalized Ligands 2 and 3

Figures 2 and 3 present the structures of the *N,N'*-dimethylated **2** and -diarylated **3**. Here too, the possibility of disorder in the $-(CH_2)_4-$ units arose but, as with **1**, its inclusion could not be justified. The structure of **3**, in the expected *anti,anti* rotameric form,[7] is entirely analogous to that of the bidentate analogue 1-(4-ethoxycarbonylphenyl)-3-(2-pyridyl)-4,5,6,7-tetrahydroindazole[9] but, unexpectedly, that of **2** was not flat, although also *anti,anti*. One pyrazole unit of **2** was nearly coplanar with the pyridine (interplanar angle 6.7°) while the other was strongly twisted out of

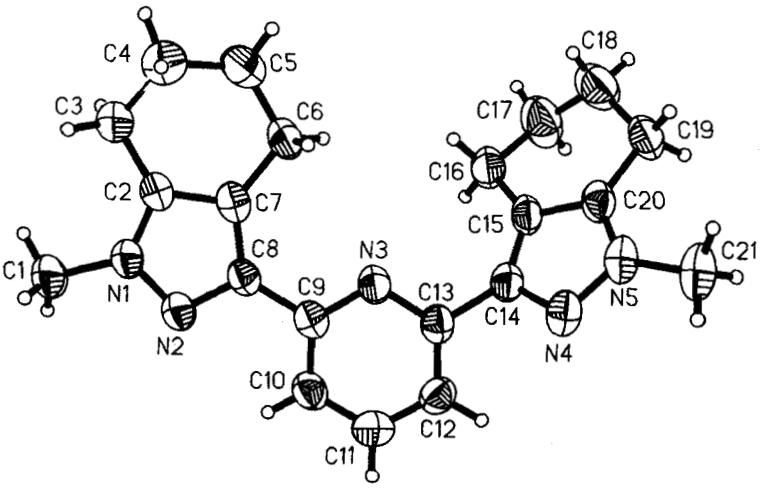


FIGURE 2 ORTEP plot of the crystal structure of compound **2** showing 50% thermal ellipsoids.

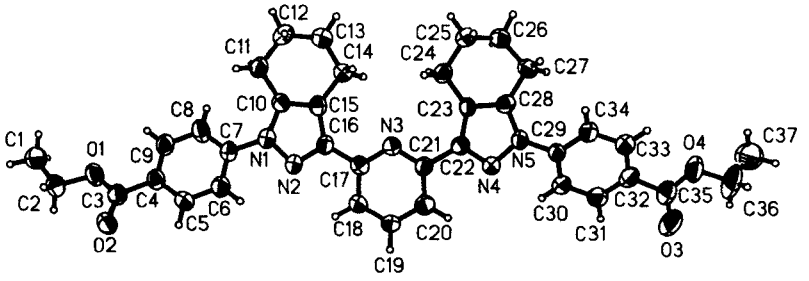


FIGURE 3 ORTEP plot of the crystal structure of compound **3** showing 50% thermal ellipsoids.

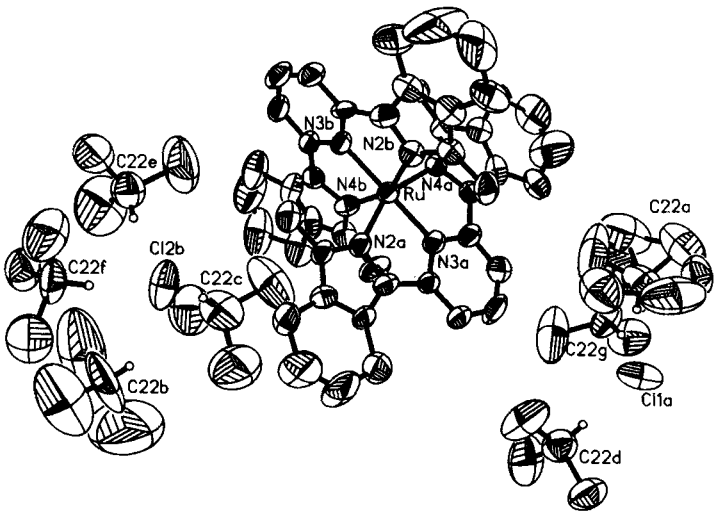


FIGURE 4 ORTEP plot of the crystal structure of $[Ru(\mathbf{2})_2]Cl_2 \cdot 7CHCl_3$ showing 50% thermal ellipsoids. For clarity, H atoms have been omitted from the complex cation, and only the Cl^- ions, the $CHCl_3$ carbons, the metal and the metal-bound nitrogens have been labelled. The ligand numbering is identical to that in Figure 2.

coplanarity (45.8°). In view of the structure of **3**, the lack of coplanarity in solid **2** can be ascribed to intermolecular effects, rather than to intramolecular repulsions.

Structure of $[Ru(\mathbf{2})_2]Cl_2$

The complex $Ru(\mathbf{2})_2]Cl_2$ was prepared by conventional means from $Ru(DMSO)_4Cl_2$ and **2**, and was characterized as the PF_6^- salt. X-ray diffraction analysis of the chloride salt provided the structure of Figure 4, in which

the complex cation exhibited the expected distorted octahedral coordination of the central metal by two distinct ligand units, and in which both Cl^- counteranions were found to be solvated by a total of seven molecules of $CHCl_3$.

Here too, the possibility of disorder was manifold and was expressed by persistent Fourier peaks near the $-(CH_2)_4-$ units, the Cl^- sites and the $CHCl_3$ molecules, or by large isotropic temperature factors for the affected C and Cl, or by both. As well, three of the four $-(CH_2)_4-$ units showed atypical flatness. The possible inclusion of disorder in each of the $-(CH_2)_4-$ units, at the Cl^- sites and in the $CHCl_3$ molecules was therefore systematically investigated. Only one of the $CHCl_3$ units (unit A) showed disorder that was justifiable on the grounds that it reduced the isotropic temperature factors and the refinement statistics significantly. However, tetrahedral restraints were required for the disordered $CHCl_3$ and for one other unit, owing to short C–Cl bonds and abnormal Cl–C–Cl angles.

DISCUSSION

We measure distortion through several quantities defined graphically in Figure 5 which uses tpy as an example. Free ligands were first computationally converted to their binding conformations (coplanar rings with inter-ring dihedrals $\psi = 0°$ and *syn* binding sites) by inter-ring bond rotations, while complexed ligands were treated as they appear in their complexes. Details of the measurement of the tridentate bite angle θ, the "pinch" or "splay" angle ϕ and the inter-ring dihedral angles ψ (not illustrated) are given in the Experimental Section. Because the angles between flanking substituents (*e.g.* at 6 and 6″ positions in tpy) are affected by intra- and inter-ligand steric congestion, $\pi-\pi$ stacking, as well as any bowing or twisting, we measure the "splay" or "pinch" angles ϕ between hypothetical bond vectors along which would lie an ideal, non-interacting substituent.

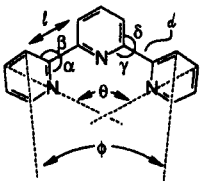


FIGURE 5 Possible distortions of a tridentate ligand.

TABLE II Binding characteristics of free ligands (see Figure 5)[a]

Ligand	$\delta-\gamma$ (°)	$\beta-\alpha$ (°)	d (Å)	l (Å)	ϕ (°)	θ (°)
tpy	3.6	5.7	1.490	2.910	9.8	129.5
bpy	5.3	5.3	1.504	2.972	—	64.4
4	5.7	7.4	1.406	2.957	−33.8	109.6
8	6.8	6.2	1.411	2.944	—	54.6
1	14.4	7.4	1.469	3.198	−20.5	120.7
2	5.2	9.5	1.483	3.092	−33.0	110.5
3	1.0	13.6	1.481	3.145	−32.5	111.0
6	4.3	8.8	1.480	3.070	—	55.1

[a] Averaged values in cases of low symmetry or crystallographically distinct species.

Ligand Readiness for Binding

Despite their different solid-state conformations, the free ligands **2** and **3** display remarkably similar properties (Table II) such as the θ and ϕ values, the pyrazole–pyridine bond lengths d and the closest approach between rings l. Clearly, the nature of the substituent (alkyl *vs.* conjugated aryl) had little effect. Both show negative ϕ, meaning that substituents flanking the outer binding sites would be splayed outward, with bond vectors intersecting behind the central pyridine. Ligand **1**, on the other hand, shows differences that place it intermediate between free **2/3** and complexed **2** (see below), with the terminal rings bent inward (large $\delta-\gamma$), shorter d, larger l, more positive splay angle (ϕ) and larger bite (θ). This supports our description of this unusual occurrence of double intramolecular H-bonding at bent N–H···N angles, which exert the same effects, albeit more weakly, as does metal complexation in causing backbone distortion.

The *N*-linked isomer **4** shows significantly shorter d and l than **2/3** but has similar angles θ and ϕ, which are also negative. In contrast to these bispyrazolylpyridines, tpy shows a shorter d and the closest approach l of all and, thus, the greatest inter-ring (intra-ligand) hindrance. As well, it shows a wider θ and a positive or "pinching" ϕ due to the bond angles within the pyridine rings. Therefore, in complexes, flanking substituents (6 and 6″) would point toward the fourth equatorial site, resulting in strong inter-ligand repulsions. This was indeed observed (see below).

In all cases, the tridentate "bite" was about twice the size of the "bite" of the appropriate bidentate analogue bpy,[11] **6**[9] or **8**,[12] but Table II reveals that bidentates and tridentate ligands are otherwise similar.

Ligand Distortion in Complexes

In comparing complexes with free ligands, we can identify five notable effects of complexation on the structures of tridentate ligands and these

TABLE III Measures of ligand distortions in complexes (see Figure 5)[a]

	$\Delta(\delta-\gamma)$ (°)	$\Delta(\beta-\alpha)$ (°)	Δd (Å)	Δl (Å)	ψ (°)	$\Delta\phi$ (°)	$\Delta\theta$ (°)	*Ref.*
Oligopyridines								
$[Ru(tpy)(bpy)(pz)]^{2+}$ [b]	+10.2	+4.4	−0.006	+0.168	0.2	+17.2	+15.9	16
$[Ru(tpy)(PMe_3)_2(NO_2)]^+$	+10.4	+1.6	−0.025	+0.154	1.1	+13.7	+12.9	8
trans-$RuCl_2(tpy)(CO)$	+10.6	+2.2	−0.020	+0.160	3.6	+13.7	+13.9	17
$[Ru(tpy)(bpy)(pz)]^{2+}$ [b]	+5.4	+4.7	−0.056	+0.084	11.4	—	—	16
$[Ru(bpy)_3]^{2+}$	+4.8	+4.8	−0.030	+0.062	7.9	—	—	18
$[Ru(\mathbf{6})_2(bpy)]^{2+}$	+13.2	−1.1	−0.094	+0.086	6.7	—	—	9
$[Ru(\mathbf{7})(bpy)(OH_2)]^{2+}$	+1.8	+8.3	−0.065	+0.049	3.7	—	—	19
Pyrazol-1-ylpyridines								
$[RuCl(\mathbf{5})(PMe_3)_2]^+$	+8.7	+2.6	−0.008	+0.107	1.7	+9.1	+12.1	14
$[Ru(\mathbf{7})(bpy)(OH_2)]^{2+}$	+8.5	+3.0	−0.011	+0.124	4.0	+10.6	+11.4	17
$[Ni(\mathbf{9})_3]^{2+}$	+2.1	+4.3	−0.026	+0.123	10.9	—	—	20
Pyrazol-3-ylpyridines								
$Ru(\mathbf{2})_2^{2+}$	+13.9	+6.2	−0.028	+0.202	1.7	+21.2	+21.2	c
1 (as H^+ complex)	+9.2	−2.1	−0.014	+0.106	5.1	+12.5	+10.2	c
$[Ru(\mathbf{6})_2(bpy)]^{2+}$	+7.2	+11.9	−0.004	+0.201	1.3	—	—	9

[a] Averaged values in cases of low symmetry or crystallographically distinct species.
[b] pz = pyrazine.
[c] This work.

are set against the effects on the analogous bidentate ligands in Table III. The Ru complex of a chiral version of **4** (**7**) is included for additional comparison.

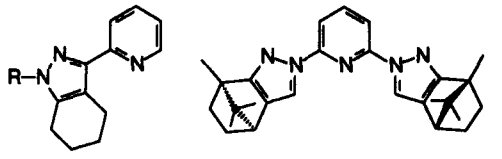
(1) The shortest M–N bonds are those to the central pyridines. In the bidentate ligands, the metal forms shorter bonds to azole nitrogens than to pyridine.[9]

(2) Upon complexation, the inter-ring bonds d tend to become shorter in an attempt to bring the outer rings closer to the metal. This is even more pronounced in the bidentate ligands.[9]

(3) Upon complexation, changes in the angles α to δ reveal that the outer rings are bent inward, toward the metal, as measured by increases in the difference $\beta-\alpha$, with the greatest angular distortions at the central pyridines, as gauged by increases in $\delta-\gamma$. In bidentate ligands, the distribution of these angular distortions is more variable.[9]

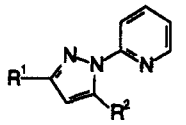
(4) As a result of this inward bending of the outer rings, the bite angle θ increases and the splay angle ϕ becomes more positive, *i.e.* any substituents flanking the outer binding sites are drawn toward each other. In the case of tpy, which is already "pinched", this results in strong inter-ligand repulsions. An example is the Ru^{2+} complex of 6,6″-diphenylterpyridine which is photolabile, presumably owing to this congestion.[13] In contrast, the 3-phenyl groups in **5** are comfortably splayed outward upon complexing to Ru,[14] whereas the 1-CH_3 groups of

complexed **2** are more parallel.

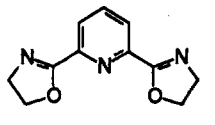


6 R = C_6H_4-4-COOEt

7



8 R^1 = Fc, R^2 = H
9 R^1 = R^2 = CH_3



10

(5) Tridentate ligands generally retain planarity in their complexes, as do the bidentate 3,2-linked pyrazolylpyridines like **6**.[9] In contrast, bipyridine (*e.g.* in $Ru(bpy)_3^{2+}$) and 1,2-linked pyrazolylpyridine complexes (*e.g.* of **9**) lose planarity, with strong twisting about the inter-ring bonds (non-zero dihedral angles ψ between least-squares planes) and/or bowing of the rings (angles between least-squares planes that exceed the dihedral angles ψ).[9] The tridentate complex $[Ru(\mathbf{5})(Me_3P)_2Cl]^+$ also shows very strong bowing and the 3-Ph groups are not orthogonal to the pyrazoles.[12] Since the Ph groups are splayed outward, the bowing cannot be attributed to interference with the Cl ligand at the fourth equatorial site but might be due to repulsions by the axial phosphines.

The complex *trans*-$[RuCl_2(\mathbf{10})(C_2H_4)]$ provides an additional example of a *C*-linked tridentate.[15] Although we have no crystal structure of free **10** with which to compare, we find that complexed **10** resembles none of the other tridentate ligands closely. As expected, it has the same inter-ring bond length (d) as complexed **2** and similar bite (θ), but shows significant inter-ring hindrance (l) like tpy and complexed **5**, and a splay angle (ϕ) intermediate between those of **5** and **2** in their complexes.

References

[1] E.C. Constable, *Adv. Inorg. Chem. Radiochem.* **30**, 69 (1986).
[2] Y. Luo and P.G. Potvin, *J. Org. Chem.* **59**, 1761 (1994).
[3] P. van der Valk and P.G. Potvin, *J. Org. Chem.* **59**, 1766 (1994).
[4] R. Dash and P.G. Potvin, *Can. J. Chem.* **70**, 2249 (1992).
[5] D.L. Jameson and K.A. Goldsby, *J. Org. Chem.* **56**, 4072 (1990).

[6] A.A. Watson, D.A. House and P.J. Steel, *J. Org. Chem.* **56**, 4072 (1991); D.D. Lecloux and W.B. Tolman, *J. Am. Chem. Soc.* **115**, 1153 (1993); A.J. Downard, G.E. Honey and P.J. Steel, *Inorg. Chem.* **30**, 3733 (1991).
[7] C.A. Bessel, R.F. See, D.L. Jameson, M.R. Churchill and K.J. Takeuchi, *J. Chem. Soc., Dalton Trans.* 3223 (1992).
[8] R.F. Leising, S.A. Kubow, M.R. Churchill, L.A. Buttrey, J.W. Ziller and K.J. Takeuchi, *Inorg. Chem.* **29**, 1306 (1990).
[9] Y. Luo and P.G. Potvin, *J. Coord. Chem.* (1998) (in press).
[10] W.C. Hamilton, *Statistics for the Physical Sciences* (Ronald Press, New York, 1964).
[11] L.L. Merritt and E.D. Schroder, *Acta Crystallogr.* **9**, 801 (1956).
[12] R.J. Less, J.L.M. Wicks, N.P. Chatterton, M.J. Dewey, N.L. Cromhout, M.A. Halcrow and J.E. Davies, *J. Chem. Soc., Dalton Trans.* 4055 (1996).
[13] J.R. Kirchoff, D.R. McMillin, P.A. Marnot and J.-P. Sauvage, *J. Am. Chem. Soc.* **107**, 1138 (1985).
[14] C.A. Bessel, R.F. See, D.L. Jameson, M.R. Churchill and K.J. Takeuchi, *J. Chem. Soc., Dalton Trans.* 2801 (1991).
[15] H. Nishiyama, Y. Itoh, Y. Sugawara, H. Matsumoto, K. Aoki and K. Itoh, *Bull. Chem. Soc. Jpn.* **68**, 1247 (1995).
[16] P.T. Gulyas, T.W. Hambley and P.A. Lay, *Aust. J. Chem.* **49**, 527 (1996).
[17] G.B. Deacon, J.M. Patrick, B.W. Skelton, N.C. Thomas and A.H. White, *Aust. J. Chem.* **37**, 929 (1984).
[18] D.P. Rillema, D.S. Jones and H.A. Levy, *J. Chem. Soc. Chem. Commun.* 849 (1979).
[19] W.-H. Fung, W.-C. Cheng, W.-Y. Yu, C.-M. Che and T.C.W. Mak, *J. Chem. Soc. Chem. Commun.* 2007 (1995).
[20] A.T. Baker, N.J. Ferguson, H.A. Goodwin and A.D. Rae, *Aust. J. Chem.* **42**, 623 (1989).