for the closely related complex molecule $Pd(1,5\text{-}C_8H_{12})(CH_2(SO_2Ph))Cl$.[5] The inner coordination geometry in this case is quite similar to that of $Pd(1,5\text{-}C_8H_{12})(CH(PPhMe_2)(SiMe_3))Cl^+$ with an alkyl Pd–C length of 2.042 (5) Å, a Pd–Cl length of 2.314 (2) Å, lengths of 2.182 (5) and 2.187 (5) Å to olefin carbons trans to the chloro ligand and lengths of 2.311(6) and 2.352 (6) Å to olefin carbons trans to the alkyl carbon atom. This similarity together with other structural features of the complex cation shows that the ylide ligand of $Pd(1,5\text{-}C_8H_{12})(CH(PPhMe_2)(SiMe_3))Cl^+$ bonds in the manner of a simple alkyl zwitterion.

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Registry No. $[Pd(1,5\text{-}C_8H_{12})(CH(PPhMe_2)(SiMe_3))Cl]PF_6$, 71425-94-0.

Supplementary Material Available: A listing of structure factor amplitudes (×10) (11 pages). Ordering information is given on any current masthead page.

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Stereochemistry of Low-Spin Bis(pyridine)(*meso*-tetraphenylporphinato)chromium(II)

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We have been recently interested in the synthesis and definitive characterization of early and middle transition metalloporphyrin complexes both as precursors to dioxygen complexes[2] and also in determining the trends in their spin-state stereochemical relationships.[3] We report herein the structural characterization of the low-spin bis(pyridine)(*meso*-tetraphenylporphinato)chromium(II) complex, abbreviated $Cr(py)_2(TPP)$. This complex is known to react irreversibly with dioxygen.[2] Comparison of the molecular stereochemistry of low-spin $Cr(py)_2(TPP)$ with the high-spin d^4 metalloporphyrin derivatives $Cr(TPP)\cdot 2(toluene)$[4] and several Mn(III) derivatives reveals bond length differences which can be qualitatively rationalized by consideration of the formal d-orbital occupancies.

Experimental Section

The preparation of $Cr(py)_2(TPP)$ has been described.[5] Single crystals were prepared from toluene and obtained as the toluene solvate. Crystals were mounted in thin-walled glass capillaries in a nitrogen-filled drybox to prevent oxidation of the sample. Preliminary examination established a centered monoclinic unit cell whose systematic absences were consistent with the space groups *Ic* or *I*2/*c*, a nonstandard setting of *Cc* or *C*2/*c*. Lattice constants $a = 16.521$ (6) Å, $b = 35.090$ (8) Å, $c = 19.325$ (6) Å, and $\beta = 119.14$ (3)° ($\bar{\lambda}$ 0.71073 Å) came from a least-squares refinement that utilized the setting angles of 60 reflections given the automatic centering routine supplied with the Syntex P$\bar{1}$ diffractometer. These constants led to a calculated density of 1.242 g/cm³ for a cell content of eight molecules. The experimental density was not measured because of the air sensitivity of the sample. All measurements were made at the ambient laboratory temperature of 20 ± 1 °C. The crystal used in all measurements was a needle with approximate dimensions of 0.13 × 0.30 × 0.67 mm.

Diffracted intensities were measured by θ–2θ scanning with graphite-monochromated Mo Kα radiation. The scan range used was 0.7° below Kα_1 to 0.7° above Kα_2. Backgrounds were estimated by profile analysis.[6] All unique data to 2θ of 48.33° were measured. Four standard reflections, measured every 50 reflections, showed a small (~5%) decrease in intensity. Variable 2θ scan rates were used as previously described; the slowest was 1.0°/min and the fastest was 6.0°/min. Net intensities were reduced to relative squared amplitudes, $|F_o|^2$, with correction for absorption of X-radiation ($\mu = 0.27$ mm^{-1}).[7] Reflections having $F_o \geq 3\sigma(F_o)$ were taken to be observed. A total of 3354 unique data were obtained, 43% of the theoretical number possible in the range of $(\sin\theta)/\lambda$ examined.

The structure was solved by the heavy-atom method. Interpretation of the Patterson map in space group *I*2/*c* required positioning of the chromium atoms at 0, *y*, $^1/_4$ and $^1/_2$, 0, $^1/_2$ on a twofold axis and a center of symmetry, respectively. The structure was then essentially solved in the space group *Ic*; when the assumed pseudosymmetry was not broken, it was concluded that the symmetry was real and the true space group is *I*2/*c*. The content of the asymmetric unit of structure is thus two half-molecules of $Cr(py)_2(TPP)$, one having a required twofold axis of symmetry and the other a center of symmetry, and a toluene molecule of solvation. Owing to the large number of parameters, the phenyl groups of the porphinato ligands and the toluene molecule were refined as rigid groups. Individual isotropic temperature factors were assigned to the atoms of the groups and an occupancy factor of 0.8 was assigned to the toluene group. The geometry observed for the phenyl groups in the low-temperature Mn(TPP) structure[8] was employed for the rigid group description. The structure was refined by full-matrix least-squares techniques[9] with standard values for the atomic form factors.[10] A difference Fourier synthesis gave the approximate positions for the hydrogen atoms of the porphinato ligands; these atoms were then assigned to theoretically calculated positions (C–H = 0.95 Å), with isotropic thermal parameters fixed one unit higher than those of the associated carbon atoms, and their contributions to the calculated structure amplitudes were included in subsequent cycles of refinement. The structure was refined to convergence by using anisotropic temperature factors for the chromium atoms, the outer carbon atoms of the porphinato ligands (C_b's and C_m's), and the carbon atoms of the pyridine ligands and isotropic temperature factors for the remaining nongroup atoms.

Final least-squares refinement led to a conventional residual (R_1) of 0.120, a weighted residual (R_2) of 0.109, an error of fit of 2.39, and a final data/parameter ratio of 10.3. A final difference synthesis displayed peak density (~0.5 e/Å³) near each chromium atom and much smaller densities (~0.3 e/Å³) elsewhere in the asymmetric unit. The atomic coordinates and associated thermal parameters of all nongroup atoms are listed in Table I. Rigid-body parameters and the derived atomic coordinates are given in Table II (supplementary material). A listing of observed and calculated structure amplitudes is available (supplementary material).

Discussion of Results

Figure 1 presents a perspective view of the $Cr(py)_2(TPP)$ molecule (**1**) with the required twofold axis of symmetry; Figure 2 presents a view of the $Cr(py)_2(TPP)$ molecule (**2**) with the required center of symmetry. The crystallographic symmetry of both molecules requires the centering of the Cr atoms in the respective porphinato planes. The figures also illustrate the numbering scheme employed for the unique atoms. Individual bond parameters for the two molecules are presented in Tables III and IV.

The bond parameters of the porphinato cores are normal;[11] both cores show only small deviations from planarity. The out-of-plane displacements of individual atoms are shown in Figures 3 and 4 of the supplementary material. The dihedral angles between the five crystallographically independent phenyl

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Table I. Positional and Thermal Parameters in the Unit Cell of $Cr(py)_2(TPP)$[a]

atom type	coordinates			anisotropic parameters[b]						
	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B,[c] Å^2
Cr_1	0	1497 (1)	1/4	3.6 (1)	4.0 (1)	4.5 (1)	0	1.4 (1)	0	4.3
Cr_2	1/2	0	1/2	3.1 (1)	4.4 (1)	3.8 (1)	0.0 (1)	1.4 (1)	0.1 (1)	3.9
N_1	158 (5)	1087 (2)	1838 (5)							4.2 (2)
N_2	133 (5)	1901 (2)	1823 (5)							4.2 (2)
N_3	3951 (5)	−276 (2)	5067 (4)							3.5 (2)
N_4	5115 (5)	−439 (2)	4373 (4)							3.5 (2)
N_5	1470 (6)	1483 (2)	3261 (5)							4.5 (2)
N_6	4037 (5)	276 (2)	3938 (5)							3.8 (2)
C_{a1}	149 (7)	689 (3)	1933 (6)							4.0 (2)
C_{a2}	335 (7)	1147 (3)	1212 (6)							4.2 (2)
C_{a3}	260 (7)	1853 (3)	1180 (7)							4.9 (3)
C_{a4}	117 (7)	2290 (3)	1918 (6)							4.7 (2)
C_{a5}	3479 (7)	−144 (3)	5455 (6)							3.8 (2)
C_{a6}	3651 (7)	−644 (3)	4820 (6)							3.8 (2)
C_{a7}	4628 (7)	−777 (3)	4205 (6)							3.8 (2)
C_{a8}	5738 (7)	−475 (3)	4081 (6)							4.0 (2)
C_{b1}	340 (7)	510 (3)	1367 (7)	5.0 (7)	4.0 (6)	5.5 (7)	0.5 (5)	2.2 (6)	0.6 (5)	4.9
C_{b2}	454 (7)	782 (3)	933 (6)	4.5 (6)	4.7 (7)	5.4 (7)	0.8 (5)	2.1 (6)	−0.8 (6)	4.8
C_{b3}	323 (8)	2213 (3)	853 (7)	7.0 (8)	4.5 (7)	6.7 (8)	−0.2 (6)	4.1 (7)	−0.1 (6)	5.6
C_{b4}	242 (9)	2476 (3)	1316 (8)	8.5 (9)	4.2 (7)	7.8 (9)	0.4 (6)	5.0 (8)	0.4 (6)	6.0
C_{b5}	2853 (8)	−434 (3)	5411 (6)	5.0 (7)	5.8 (7)	4.9 (7)	−0.9 (6)	2.7 (6)	−0.8 (6)	5.0
C_{b6}	2972 (7)	−737 (3)	5034 (6)	4.1 (6)	4.9 (7)	5.1 (7)	−1.1 (5)	2.2 (5)	0.1 (5)	4.5
C_{b7}	4942 (7)	−1027 (3)	3792 (6)	4.6 (6)	4.4 (6)	4.6 (6)	0.1 (5)	2.2 (5)	0.1 (5)	4.5
C_{b8}	5599 (8)	−842 (3)	3703 (6)	5.6 (7)	5.3 (7)	4.0 (6)	0.9 (6)	2.3 (6)	−0.1 (5)	4.8
C_{m1}	366 (7)	1502 (3)	898 (6)	4.1 (6)	5.0 (6)	4.2 (6)	0.4 (5)	2.0 (5)	0.1 (5)	4.4
C_{m2}	0	2464 (4)	1/4	6.7 (10)	1.5 (7)	5.2 (9)	0	2.5 (8)	0	3.8
C_{m3}	0	508 (4)	1/4	3.1 (8)	3.7 (8)	5.6 (9)	0	1.5 (7)	0	4.2
C_{m4}	3970 (7)	−873 (3)	4409 (6)	3.5 (5)	3.4 (5)	3.5 (5)	−0.3 (4)	1.4 (5)	0.3 (5)	3.6
C_{m5}	6396 (7)	−200 (3)	4167 (5)	3.4 (5)	4.3 (6)	2.9 (5)	−0.1 (4)	1.2 (4)	−0.4 (5)	3.6
C_{15}	1805 (8)	1341 (3)	3994 (7)	4.4 (7)	7.7 (8)	4.0 (7)	1.3 (6)	0.2 (6)	0.5 (6)	5.5
C_{16}	2758 (10)	1307 (4)	4489 (8)	6.0 (9)	12.7 (12)	7.5 (10)	1.1 (9)	2.3 (8)	−0.3 (9)	8.7
C_{17}	3370 (9)	1428 (5)	4250 (8)	5.7 (9)	12.7 (13)	6.9 (9)	1.9 (8)	1.4 (8)	1.2 (9)	8.4
C_{18}	3032 (9)	1582 (4)	3487 (10)	4.5 (8)	11.3 (12)	11.1 (12)	−0.4 (8)	2.6 (9)	0.8 (10)	8.5
C_{19}	2039 (8)	1612 (4)	2996 (8)	4.5 (7)	8.2 (9)	8.0 (10)	−0.8 (7)	2.5 (7)	0.3 (7)	6.8
C_{32}	4276 (8)	358 (3)	3388 (7)	6.1 (7)	5.1 (7)	4.7 (7)	−0.6 (6)	2.3 (6)	0.2 (6)	5.3
C_{33}	3683 (9)	543 (3)	2660 (8)	5.1 (7)	6.0 (8)	7.3 (9)	0.8 (6)	1.1 (7)	1.7 (7)	6.4
C_{34}	2783 (9)	643 (3)	2540 (7)	7.3 (9)	5.8 (8)	5.3 (8)	−0.1 (7)	1.3 (7)	1.8 (6)	6.3
C_{35}	2534 (8)	548 (4)	3125 (7)	4.5 (7)	7.4 (9)	5.8 (8)	0.7 (6)	0.6 (6)	1.2 (7)	6.2
C_{36}	3185 (8)	363 (3)	3824 (7)	3.7 (6)	6.8 (8)	6.2 (8)	1.9 (6)	1.7 (6)	0.9 (6)	5.4

[a] The figure in parentheses following each datum is the estimated standard deviation in the least significant figure. [b] B_{ij} is related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^* a_j^*$. [c] Isotropic thermal parameters as calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

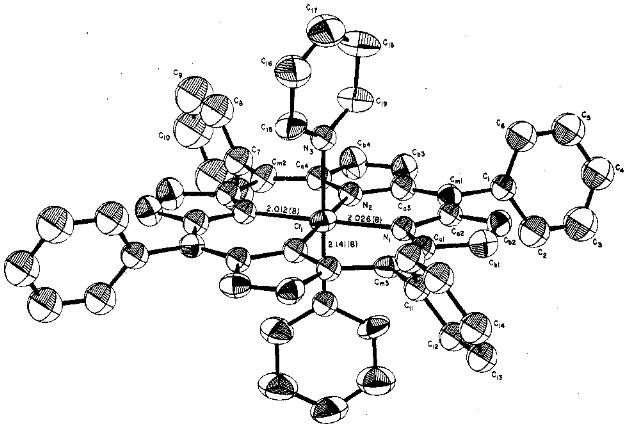

Figure 1. A computer-drawn model in perspective of the $Cr(py)_2(TPP)$ molecule as it exists in the crystal with a required twofold axis. The twofold axis passes through C_{m2}, Cr_1, and C_{m3}. Also included are the special symbols used to identify the atoms and the unique bond lengths of the coordination group.

rings and the mean plane of the cores are in the range 64–83°.

The pyridine ligands are planar to within 0.01 Å. The two pyridine ligands of **1** have dihedral angles of 21° with a NCrN(py) plane, about halfway between the most favorable (45°) and least favorable (0°) orientation for minimizing nonbonded contacts between the axial ligands and the porphinato core. The pyridine ligands of **2** have 32° values for

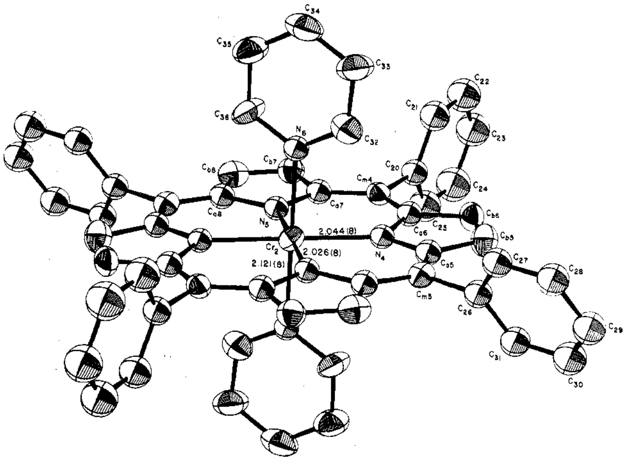

Figure 2. A computer-drawn model in perspective of the second $Cr(py)_2(TPP)$ molecule with a required center of symmetry. The same information as displayed in Figure 1 is also given.

the corresponding dihedral angle. The dihedral angle between the two twofold-related pyridine ligands of **1** are 48°; the two pyridine ligands are required to be coplanar in **2**. The differences in ligand orientations and consequent nonbonded contacts would favor shorter axial bond distances for **2** (2.121 (8) Å) than **1** (2.141 (8) Å) but the differences cannot be regarded as statistically significant. In these circumstances, the average distance of 2.131 Å would appear to be appropriate

Table III. Bond Lengths (Å) in the Coordination Group, Porphinato Skeleton, and Pyridine Ligands of $Cr(py)_2(TPP)$[a]

Cr_1-N_1	2.026 (8)	$C_{a5}-C_{m5}$	1.372 (12)
Cr_1-N_2	2.012 (8)	$C_{a6}-C_{b6}$	1.410 (12)
Cr_1-N_3	2.141 (8)	$C_{a6}-C_{m4}$	1.401 (12)
Cr_2-N_4	2.044 (8)	$C_{a7}-C_{b7}$	1.441 (13)
Cr_2-N_5	2.026 (8)	$C_{a7}-C_{m4}$	1.368 (12)
Cr_2-N_6	2.121 (8)	$C_{a8}-C_{b8}$	1.441 (13)
N_1-C_{a1}	1.408 (11)	$C_{a8}-C_{m5}$	1.402 (12)
N_1-C_{a2}	1.391 (12)	$C_{b1}-C_{b2}$	1.345 (13)
N_2-C_{a3}	1.367 (12)	$C_{b3}-C_{b4}$	1.336 (14)
N_2-C_{a4}	1.379 (11)	$C_{b5}-C_{b6}$	1.355 (13)
N_4-C_{a5}	1.399 (11)	$C_{b7}-C_{b8}$	1.347 (13)
N_4-C_{a6}	1.380 (11)	N_3-C_{15}	1.341 (12)
N_5-C_{a7}	1.378 (11)	N_3-C_{19}	1.349 (13)
N_5-C_{a8}	1.400 (11)	$C_{15}-C_{16}$	1.394 (15)
$C_{a1}-C_{b1}$	1.424 (13)	$C_{16}-C_{17}$	1.367 (17)
$C_{a1}-C_{m3}$	1.388 (11)	$C_{17}-C_{18}$	1.406 (17)
$C_{a2}-C_{b2}$	1.438 (13)	$C_{18}-C_{19}$	1.443 (15)
$C_{a2}-C_{m1}$	1.398 (13)	N_6-C_{32}	1.334 (12)
$C_{a3}-C_{b3}$	1.439 (14)	N_6-C_{36}	1.349 (11)
$C_{a3}-C_{m1}$	1.394 (13)	$C_{32}-C_{33}$	1.419 (14)
$C_{a4}-C_{b4}$	1.432 (14)	$C_{33}-C_{34}$	1.433 (15)
$C_{a4}-C_{m2}$	1.374 (11)	$C_{34}-C_{35}$	1.419 (15)
$C_{a5}-C_{b5}$	1.425 (12)	$C_{35}-C_{36}$	1.409 (14)

[a] The figures in parentheses are the estimated standard deviations in the least significant figure.

Table IV. Bond Angles (deg) in the Coordination Group and Porphinato Skeleton of $Cr(py)_2(TPP)$[a]

$N_1Cr_1N_2$	90.1 (3)	$N_4C_{a6}C_{m4}$	124.2 (10)
$N_1Cr_1N_1''$	89.4 (5)	$C_{m4}C_{a6}C_{b6}$	127.2 (10)
$N_2Cr_1N_2''$	90.5 (5)	$N_5C_{a7}C_{b7}$	109.2 (9)
$N_1Cr_1N_3$	88.0 (3)	$N_5C_{a7}C_{m4}$	126.7 (10)
$N_2Cr_1N_3$	91.0 (3)	$C_{m4}C_{a7}C_{b7}$	124.1 (10)
$N_4Cr_2N_5'$	90.4 (3)	$N_5C_{a8}C_{b8}$	108.6 (9)
$N_4Cr_2N_5$	89.6 (3)	$N_5C_{a8}C_{m5}$	124.7 (10)
$N_4Cr_2N_6$	91.0 (3)	$C_{m5}C_{a8}C_{b8}$	126.7 (10)
$N_5Cr_2N_6$	90.8 (3)	$C_{a1}C_{b1}C_{b2}$	108.4 (10)
$C_{a1}N_1C_{a2}$	106.5 (9)	$C_{a2}C_{b2}C_{b1}$	108.2 (10)
$C_{a3}N_2C_{a4}$	105.2 (9)	$C_{a3}C_{b3}C_{b4}$	105.0 (11)
$C_{a5}N_4C_{a6}$	107.2 (8)	$C_{a4}C_{b4}C_{b3}$	109.3 (10)
$C_{a7}N_5C_{a8}$	106.6 (8)	$C_{a5}C_{b5}C_{b6}$	107.6 (10)
$N_1C_{a1}C_{b1}$	108.5 (9)	$C_{a6}C_{b6}C_{b5}$	108.7 (10)
$N_1C_{a1}C_{m3}$	125.0 (1)	$C_{a7}C_{b7}C_{b8}$	107.8 (10)
$C_{m3}C_{a1}C_{b1}$	126.5 (10)	$C_{a8}C_{b8}C_{b7}$	107.7 (10)
$N_1C_{a2}C_{b2}$	108.5 (10)	$C_{a2}C_{m1}C_{a3}$	125.4 (10)
$N_1C_{a2}C_{m1}$	125.5 (10)	$C_{a4}C_{m2}C_{a4}''$	127.3 (14)
$C_{m1}C_{a2}C_{b2}$	125.0 (10)	$C_{a1}C_{m3}C_{a1}''$	125.5 (14)
$N_2C_{a3}C_{b3}$	111.6 (10)	$C_{a6}C_{m4}C_{a7}$	126.4 (10)
$N_2C_{a3}C_{m1}$	124.6 (11)	$C_{a5}'C_{m5}C_{a8}$	125.2 (10)
$C_{m1}C_{a3}C_{b3}$	123.7 (11)	$Cr_1N_1C_{a1}$	127.5 (7)
$N_2C_{a4}C_{b4}$	108.9 (10)	$Cr_1N_1C_{a2}$	126.0 (7)
$N_2C_{a4}C_{m2}$	124.5 (11)	$Cr_1N_2C_{a3}$	128.2 (8)
$C_{m2}C_{a4}C_{b4}$	125.6 (11)	$Cr_1N_2C_{a4}$	126.6 (8)
$N_4C_{a5}C_{b5}$	107.9 (9)	$Cr_2N_4C_{a5}$	126.0 (7)
$N_4C_{a5}C_{m5}'$	126.8 (10)	$Cr_2N_4C_{a6}$	126.4 (7)
$C_{m5}'C_{a5}C_{b5}$	125.3 (10)	$Cr_2N_5C_{a7}$	125.6 (7)
$N_4C_{a6}C_{b6}$	108.5 (9)	$Cr_2N_5C_{a8}$	127.7 (7)

[a] The numbers in parentheses are the estimated standard deviations in the least significant figure.

for further consideration. This axial distance is considerably shorter than that observed in the isoelectronic manganese(III) porphyrins. In Mn(Cl)(py)(TPP),[12] the Mn–N(py) bond distance is 2.444 (4) Å, and in $[Mn(1\text{-}MeIm)_2(TPP)]^+$,[13] the Mn–N(Im) bond distance is 2.308 (3) Å. This difference in the axial bond lengths is attributable[3] to the population of the $3d_{z^2}$ orbital in the high-spin Mn(III) derivatives and its depopulation in the low-spin Cr(II) complex.

The average chromium–porphinato nitrogen bond distance is 2.027 (13) Å, comparable to the 2.033 (1) Å Cr–N bond distance observed in four-coordinate Cr(TPP)·2(toluene).[4] Thus although the addition of two axial pyridine ligands to Cr(TPP) leads to a high-spin to low-spin conversion, there is little change in the equatorial coordination parameters, since both complexes contain an unoccupied $d_{x^2-y^2}$ orbital. A similar high to low spin conversion was observed by Tsutsui et al.,[14] who noted that chromium(II) mesoporphyrin IX dimethyl ester was high spin in solution and low spin in the solid state. Presumably, in the solid state intermolecular interactions lead to six-coordinate species. As noted previously,[4] the chromium–porphinato nitrogen bond distances in the chromium(II) porphyrins appear short compared to the one other known Cr(II) structure[15] and also to known Cr(III)–N bond distances.[16] This emphasizes, as in other porphinato derivatives, the strong complexing nature of the porphinato ligand.

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Registry No. $Cr(py)_2(TPP)$, 67113-84-2.

Supplementary Material Available: Table II, rigid-body parameter listings, Figures 3 and 4, formal diagrams of the porphyrin cores showing the displacement of each atom from the mean plane of the core, and listings of the observed and calculated structure factor amplitudes (×10) (21 pages). Ordering information is given on any current masthead page.

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Kinetics of the Reaction between Bis(O-substituted xanthato)nickel(II) and 2,2′-Bipyridine in Benzene

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Grant and co-workers, in a series of related papers,[1] have studied the kinetics and the mechanism of the addition of bidentate bases to several nickel(II) complexes; in particular these authors have examined the effect of substituents at the

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