J. Am. Chem. Soc. **1993**, *115*, 9997-10003

Star Porphyrazines: Peripheral Chelation of Porphyrazineoctathiolate by Diphosphinonickel Ions

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Received June 7, 1993[•]

Abstract: We have synthesized new pentametallic macrocyclic complexes based on the polynucleating ligand, porphyrazine-2,3,7,8,12,13,17,18-octathiolate, $(\mathrm{pzot})^{8-}$. This ligand can be thought of as a porphyrazine (tetraazaporphyrin) bearing four dithiolene moieties peripherally at the β-pyrrole positions, and we show that a transition-metal ion can be chelated to each of the four peripheral dithiolene moieties. The complexes $[(\mathrm{P{-}P})\mathrm{Ni}]_4[\mathrm{Ni(pzot)}]$ (**2a**, P–P = dppe; **2b**, P–P = dppy; **2c**, P–P = dppb; **2d**, P–P = dcpe) have been synthesized and characterized. Complex **2a** crystallizes in the orthorhombic space group $Cmc2_1$ (No. 36) with 4 macrocycles and 16 solvent molecules (*N,N*-dimethylformamide) in a unit cell of dimensions $a = 24.630(5)$ Å, $b = 20.607(4)$ Å, $c = 30.675(6)$ Å. The $[\mathrm{Ni(pzot)}]^{8-}$ ligand in **2a** coordinates four Ni(P–P) moieties around its periphery with the two thiolate sulfur atoms of each pyrrole binding a nickel ion in a bidentate (S–S) coordination mode. This is in contrast to the reaction of $[\mathrm{Ni(pzot)}]^{8-}$ with $\mathrm{SnR_2X_2}$, which yielded $\mathrm{Ni(pzot)(SnR_2)_4}$ (**1**), where each tin is coordinated in the tridentate (S–N–S) mode, with the thiolate sulfur atoms from two pyrroles and one *m*-nitrogen atom as ligands from the macrocycle (Velázquez, C. S.; Fox, G. A.; Broderick, W. E.; Andersen, K; Anderson, O. P.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 7416–7424). Comparison of the crystal structures of **1**, **2a**, and aquo(octakis(methylthio)porphyrazinato)magnesium(II) (Mg(omtp)), a structurally unconstrained reference compound with eight peripheral methylthio groups, shows that $[\mathrm{Ni(pzot)}]^{8-}$ adjusts to accommodate either the (S–S) or (S–N–S) modes of coordinating the metal ions at the periphery by a swing of the C_β–S bond. ^{1}H and ^{31}P NMR studies have been used to determine the nature of the coordination of the Ni(P–P) units to the $[\mathrm{Ni(pzot)}]^{8-}$ macrocycle in solution. Model compounds were synthesized as structural references to mimic both possible coordination sites of the $[\mathrm{Ni(pzot)}]^{8-}$ ligand. The ^{1}H and ^{31}P NMR chemical shifts of macrocycles **2a–d** and their respective bidentate model complexes clearly indicate that the macrocycle in solution also binds the Ni(P–P) units in a bidentate fashion. The electronic absorption spectra of complexes **2a–d** show a red-shift of the absorbance in the Q-band region due to interaction of the porphyrazine π-system with the four peripheral metal ions.

Introduction

Coordination compounds prepared from ligand systems capable of binding multiple metal ions[1,2] are of importance in studies of electron transfer,[3,4] magnetic interactions,[5-9] optical phenomena,[10,11] excited-state reactivity,[12,13] biomimetic chemistry,[14-16] mixed valency,[17-19] and ionophoric activity.[20] One strategy for the design of multimetallic systems has involved the use of polynucleating macrocyclic ligands,[21,22] and in particular much work has been devoted to the synthesis of porphyrins and phthalocyanines that have been functionalized with appendages that can coordinate metal ions as well.[23-31]

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[•] Abstract published in *Advance ACS Abstracts*, October 1, 1993.

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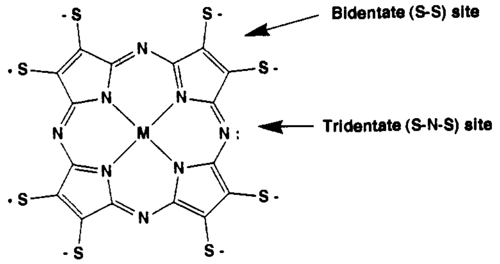
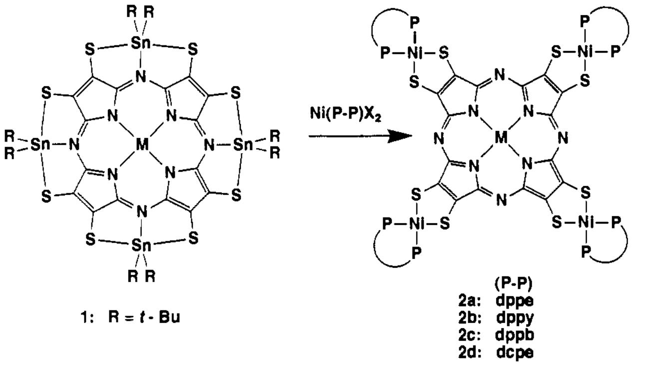
Chart I

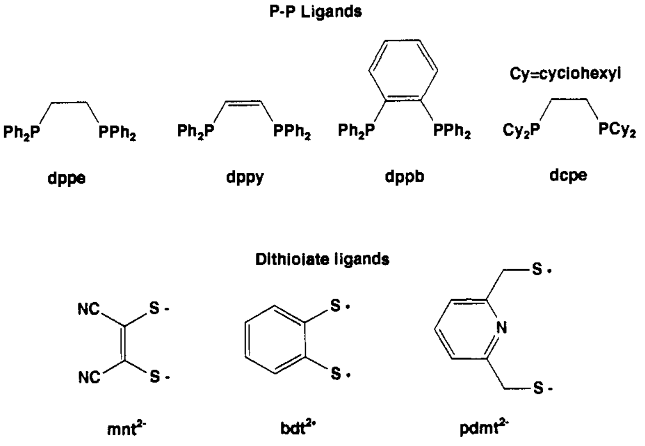


Scheme I



We recently reported the synthesis and structure of a new polynucleating ligand based on the planar porphyrazine (tetraazaporphyrin) ring system.[32,33] Porphyrazineoctathiolate, (pzot^{-8}) (Chart I) consists of a porphyrazine ring substituted with eight thiolate sulfur atoms at the β-pyrrole positions, which permits the coordination of four metal ions at the periphery as well as one at the center. It was originally anticipated that the metal ions would exhibit bidentate (S–S) coordination as in dithiolene complexes,[34,35] leading to metalloporphyrazines peripherally functionalized with four additional transition ions that exhibit a high degree of electronic interaction among themselves and with the central metal ions, through mediation by the conjugated porphyrazine core. However, reaction of $[Ni(pzot)]^{8-}$ with SnR_2X_2 surprisingly yields $Ni(pzot)(SnR_2)_4$, complex **1**, where Sn is coordinated in the tridentate (S–N–S) mode, with two thiolate sulfur atoms and one *m*-nitrogen atom as ligands from the macrocycle (Scheme I). It was inferred, however, that the addition of halide ions induces a novel linkage isomerization whereby the dialkyltin groups bind two halides each and cooperatively migrate to the bidentate chelation site. Consideration of the two modes of binding displayed by $[Ni(pzot)]^{8-}$ led us to reason that the bidentate mode could be enforced through the choice of a peripherally "capping" metal ion complex that provides only two coordination sites in the *cis* configuration. There have been numerous reports that metal ion complexes containing both dithiolene and phosphine ligands are readily synthesized and characterized.[36-62] Therefore, as the first use of this strategy, we have reacted **1**, and also $[Ni(pzot)]^{8-}$, with Ni(P–P)X_2 (Chart II, P–P = a chelating *cis*-diphosphine). The result is a series of multimetallic star porphyrazines, **2a–d** (**Scheme I**), where the peripheral thiolato ligands of $[Ni(pzot)]^{8-}$ are coordinated to the Ni(P–P) moiety in the bidentate mode. The synthesis and spectroscopic properties of this series of novel peripherally chelated pentanickel macrocycles along with the X-ray structure of **2a** are presented in this report. The properties of these complexes are compared to those of related porphyrazines and Ni complexes.

Chart II



Experimental Section

Materials and Methods. Macrocycle **1** was prepared as reported previously.[63] Diphosphines dppe, dppb, dppy, and dcpe[64] (Chart II) were purchased from Strem Chemical and were used as received. Ni(P–P)X_2 complexes (X = Cl, I) were prepared by published procedures[65] and recrystallized from CH_2Cl_2–Et_2O. Disodium 1,2-benzenedithiolate (Na_2-

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(bdt)) was prepared by the reaction of 1,2-benzenedithiol[66] with 2 equiv of NaH in THF under N_2. Disodium maleonitriledithiolate[67] (Na_2(mnt)), and 2,6-pyridinedimethanethiol[68] (H_2(pdmt)), were prepared by the literature methods. THF and CH_2Cl_2 were distilled from sodium/benzophenone ketyl and CaH_2, respectively; DMSO was dried over activated 4-Å molecular sieves.

^1H and ^{31}P NMR spectra were obtained using a Varian XLA-400 spectrometer. The ^{31}P NMR spectra were referenced using the center peak of NBu_4PF_6 as an internal reference and calibrating the field to 5% H_3PO_4–D_2O = 0 ppm. Electronic absorption spectra were recorded using a Hewlett-Packard HP8452A diode-array spectrophotometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY. Fast atom bombardment mass spectra (FAB-MS) were recorded locally by Dr. Doris Hung using a VG-70–250SE instrument. Exact mass measurements were calibrated using KI or CsI standards.

Ni(dppe)(mnt) was prepared by the published procedure[37] as well as a new procedure discussed below. All other Ni(P–P)(dithiolene) complexes were prepared by adding either Na_2(bdt) or Na_2(mnt) in MeOH to a stoichiometric amount of the appropriate Ni(P–P)I_2 in CH_2Cl_2 solution until the color change from purple to orange was complete (<10 min), removing all but ~1 mL of solvent by rotary evaporation, filtering the precipitate, washing with MeOH, and recrystallizing from CH_2Cl_2–Et_2O. Purity was checked by thin-layer chromatography. In each case the Ni(P–P)(dithiolene) complex was more mobile than its corresponding halide and no unreacted halide was observed in the recrystallized products. Yields of 75–95% were obtained.

(Bis(1,2-diphenylphosphino)ethane)(maleonitriledithiolato)nickel(II) (Ni(dppe)(mnt)). Ni(dppe)Cl_2 (144 mg, 0.27 mmol) and Bu_2Sn(mnt)[35] (102 mg, 0.27 mmol) were dissolved in 25 mL of $CHCl_3$ and stirred under N_2 for 3 h. Evaporation of solvent to a minimum volume, filtration of the resulting orange crystals, and copious washing with MeOH gave 109 mg of Ni(dppe)(mnt) in 67% yield. This material was indistinguishable by NMR and TLC (1,2-dichloroethane) from that prepared by the literature method. Repeated attempts at recrystallization yielded tiny and extremely thin square platelike crystals that were unsuitable for single-crystal X-ray structural studies.

[Ni(pdmt)]$_2$(μ-dppe). H_2(pdmt) (800 mg, 4.68 mmol) was dissolved in MeOH (30 mL) under N_2, and NaOMe (600 mg, 11 mmol) was added. To this a solution of Ni(dppe)Cl_2 (2.47 g, 4.68 mmol) in dichlororethane (100 mL) was added dropwise. The resulting orange-red solution was rotary evaporated to a red oil, and the dropwise addition of MeOH caused precipitation of a green solid, which was recrystallized from chloroform–ethanol to give 700 mg of green platelike crystals. (35% yield) mp 173–178 °C, dec. Anal. ($C_{40}H_{38}N_2Ni_2P_2S_4$) Observed (Calc): C, 55.48 (56.23); H, 4.76 (4.48); N, 3.21 (3.28); S, 15.91 (15.01); P, 7.11 (7.25). FAB-MS: 854 (M + H), 715 (M – (pdmt–S)), 683 (M – pdmt), 625 (M – Ni(pdmt)), 456 (Ni(dppe)), 454 ([Ni(pdmt$_2$)]), 399 (dppe). ^1H NMR ($CDCl_3$): δ 7.75 q (dppe, *m*-CH, 8H), 7.4–7.2 m (dppe, *o*-CH, *p*-CH, pdmt, *p*-CH, 14H), 7.08 d (pdmt, *m*-CH, 4H), 4.17 s (pdmt, CH_2, 8H), 2.84 d (dppe, CH_2, 4H). ^{31}P NMR: 27.9 ppm (relative to H_3PO_4).

[Ni(dppe)]$_4$Ni(pzot) (2a).[64] Transmetalation Method. A solution of Ni(dppe)Cl_2 (47 mg, 90 μmol) in DMSO (5 mL) was added to a solution of **1** (31 mg, 20 μmol) in THF (30 mL) and was allowed to stand undisturbed in a closed vessel under ambient conditions for 16 h. The resulting black microcrystalline precipitate was filtered, washed with several portions of THF, and dried in vacuo. Yield, 32 mg (65%). The crystals used for X-ray diffraction were obtained by recrystallization from DMF–Et_2O. Anal. **2a**·4DMSO ($C_{120}H_{96}N_8Ni_5P_8S_8\cdot4(C_2H_6OS)$) Observed (Calc): C, 55.62 (55.69); H, 4.25 (4.38); N, 4.16 (4.06); Ni, 11.24 (10.63); P, 8.69 (8.98); S, 14.52 (13.94). FAB-MS: 2448 (M, **2a**), 2050 (**2a**–dppe), 1652 (**2a** – 2(dppe)). Exact mass: Found (Calc) 2448.0220 (2447.9136).

[Ni(dppe)]$_4$Ni(pzot) (2a).[64] Direct Method. The sodium salt of nickel porphyrazineoctathiolate, [Ni(pzot)]$^{8-}$ was prepared from (octakis(benzylthio)porphyrazinato)nickel(II) (Ni(obtp)), (545 mg, 0.40 mmol) as previously described.[32,33] The Na_8(pzot) was dissolved in degassed water (50 mL) using Schlenk techniques. To this bright-purple solution was added dropwise a solution of excess Ni(dppe)Cl_2 in a degassed *N*-methyl-3-pyrrolidinone (20 mL), resulting in a fine black suspension. Ethanol (50 mL) was added to induce coagulation, and the precipitate was filtered through Celite 545 and washed thoroughly with ethanol. The filter cake was extracted with pyridine (125 mL) and filtered; the filtrate was then dried over $MgSO_4$, filtered again, and taken to dryness on a rotary evaporator. The resulting complex **2a** was dried in vacuo to give 840 mg (85%) of amorphous purple solid. The compound showed the parent ion peak in the mass spectrum (2448) as well as NMR and optical spectra indistinguishable from those of that prepared by the transmetalation procedure.

[Ni(dppb)]$_4$Ni(pzot) (2b).[64] A solution of Ni(dppb)I_2 (76 mg, 90 μmol) in DMSO (5 mL) was added to a solution of **1** (31 mg, 20 μmol) in THF (30 mL) and was allowed to stand undisturbed in a closed vessel under ambient conditions for 36 h. The resulting black microcrystalline precipitate was filtered, washed with several portions of THF, and dried in vacuo. Yield, 32 mg (68%). FAB-MS 2639, 2640 (two predicted highest intensities). Anal. **2b** ($C_{136}H_{96}N_8Ni_5P_8S_8$) Observed (Calc): C, 61.67 (61.87); H, 3.45 (3.67); N, 4.67 (4.27); Ni, 10.82 (11.12); P, 9.18 (9.39); S, 9.79 (9.39).

[Ni(dppy)]$_4$Ni(pzot) (2c).[64] A solution of Ni(dppy)Cl_2 (46 mg, 90 μmol) in DMSO (5 mL) was added to a solution of **1** (31 mg, 20 μmol) in THF (30 mL) and was allowed to stand undisturbed in a closed vessel under ambient conditions for 24 h. The resulting black microcrystalline precipitate was filtered, washed with several portions of THF, and dried in vacuo. Yield, 18 mg (35%). FAB-MS: 2439 (M + H). Anal. **2c** ($C_{120}H_{68}N_8Ni_5P_8S_8$) Observed (Calc): C, 58.08 (59.07); H, 3.39 (3.64); N, 4.96 (4.59); Ni, 11.60 (12.03); P, 10.31 (10.16); S, 10.72 (10.16).

[Ni(dcpe)]$_4$Ni(pzot) (2d).[64] A warmed solution of Ni(dcpe)Cl_2 (47 mg, 90 μmol) in DMSO (5 mL) was added to a nitrogen-purged solution of **1** (31 mg, 20 μmol) in THF (30 mL) and was allowed to stand undisturbed in a closed vessel under ambient conditions for 48 h. The resulting lustrous purple microcrystalline precipitate was filtered, washed with several portions of THF, and dried in vacuo. Yield, 20 mg (65%). FAB-MS: 2549 (M + H). Anal. **2d** ($C_{120}H_{192}N_8Ni_5P_8S_8$) Observed (Calc): C, 57.11 (56.64); H, 7.2 (7.61); N, 4.52 (4.40); Ni, 10.88 (11.53); P, 9.23 (9.74); S, 10.25 (10.08).

X-ray Crystallography of Complex 2a. The crystals were all very thin plates. The largest specimen found was a sheet of dimensions 0.02 × 0.08 × 0.18 mm (3×10^{-4} mm^3); this was used for data collection. It was mounted unprotected in the cold stream on a Siemens P4R diffractometer equipped with a locally modified LT-2 low temperature device keeping the crystal at 120 K. Radiation was Ni-filtered Cu Kα from a Siemens rotating anode source operating at 15 kW. The conditions for reflections present (*hkl*, $h + k = 2n$; *h0l*, $l = 2n$) indicate space group *Cmc*2$_1$ (No. 36) or *Cmcm* (No. 63). Intensity statistics as well as solution and refinement show *Cmc*2$_1$ as the correct choice. The atoms comprising complex **2a** were readily found by direct methods solution. The structure was refined[69] against F^2 using all data with the γ-test version of SHELXL-92.[70] For the main molecule only the space-group required constraints were applied to atoms Ni1, N1, and N5. H atoms were added in calculated positions and included in refinement as riding on their carrying atoms, with isotropic *U* values set to 1.2U_{iso} of these. A number of more or less disordered molecules of dimethylformamide complicated refinement. There are at least seven different, possible sites for dimethylformamide molecules. One of the molecules was well behaved and was used as a model for the others via a SAME restraint.[70] In a difference map two peaks could not be defined as part of anything in particular; they were included as C atoms with 0.5 occupancy. There is also the possibility that disordered diethyl ether is present. The final difference map has two peaks (1.61 and 1.1 e$Å^{-3}$) not associated with the main molecule. The absolute structure of the sample crystal was indicated by the Flack[71] parameter (–0.06(10)). The somewhat high, final *R* value reflects a small, difficult crystal yielding a relatively weak data set, and disordered solvent molecules. The results reported here may not correspond to the ultimate obtainable from the data, but we find no indication that anything of significant chemical value would result from further work. Table I

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[64] Abbreviations: dppe = 1,2-bis(diphenylphosphino)ethane, dppb = 1,2-bis(diphenylphosphino)benzene, dppy = (*Z*)-1,2-bis(diphenylphosphino)ethene, dcpe = 1,2-bis(dicyclohexylphosphino)ethane, mnt = maleonitriledithiolate, bdt = 1,2-benzenedithiolate, pdmt = 2,6-bis(sulfidomethyl)pyridine, pzot = 2,3,7,8,12,13,17,18-porphyrazineoctathiolate. The IUPAC name for **2a** is nickel, tetrakis[(1,2-bis(diphenylphosphino)ethane)nickel(II)]-[μ_5-[21*H*,23*H*-porphyrazine-2,3,7,8,12,13,17,18-octathiolato(10–)-N^{21},N^{22},N^{23},N^{24}:S^2,S^3:S^7,S^8:S^{12},S^{13}:S^{17},S^{18}]].

[65] McAuliffe, C. A.; Meek, D. W. *Inorg. Chem.* **1969**, *8*, 904–907.

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[67] Davison, A.; Holm, R. H. *Inorg. Synth.* **1967**, *6*, 8.

[68] Partyka, R. A. U.S. Patent 3,290,316, 1966; *Chem. Abstr.* **1967**, *66*, 115609k.

[69] Neutral atom scattering, *f* and *f'*, and absorption coefficients are from: *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C, Table 6.1.1.3, pp 500–502.

[70] Sheldrick, G. M. *J. Appl. Cryst.* **1993**, in preparation.

[71] Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876–881.

Table I. Crystal Data and Structure Refinement for **2a**

empirical formula	$C_{132}H_{124}N_{12}Ni_5O_4P_4S_4$
formula weight	2488.10
temperature	128(2) K
wavelength	1.541 78 Å
crystal system	orthorhombic
space group	$Cmc2_1$ (No. 36)
unit cell dimensions	a = 24.630(5) Å α = 90°
	b = 20.607(4) Å β = 90°
	c = 30.675(6) Å γ = 90°
volume	15569(5) Å^3
Z	4
density (calc)	1.06 Mg/m^3
absorption coefficient	0.73 mm^{-1}
F(000)	5184
crystal size	0.02 × 0.08 × 0.18 mm
θ range for data collection	2.80–54.04°
index ranges	$0 \leq h \leq 25, 0 \leq k \leq 21, -32 \leq l \leq 0$
reflections collected	4967
independent reflections	4967
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	4952/127/476
goodness-of-fit[a] on F^2	1.025
final R indices[b] [$I > 2\sigma(I)$]	$R1 = 0.1115$, $R_w2 = 0.2777$
R indices (all data)	$R1 = 0.1936$, $R_w2 = 0.3881$
absolute structure parameter	−0.06(10)
largest diff peak and hole	1.618 and −0.671 eÅ^{-3}

[a] Goodness-of-fit = $[\Sigma(w\|F_o| - |F_c\|^2)/(M - N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined. [b] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $R_w2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4]\}^{1/2}$

Table II. Symmetry-Averaged Bond Distances and Angles for Porphyrazine and Phthalocyanine Macrocycles

	1	**2a**	MgOMTP	M(pc)[a]
		Bond Distances (Å)[b]		
Ni–N_p	1.87(3)	1.87(3)		1.88(6)
C_α–N_p	1.366(5)	1.41(1)	1.367(13)	1.376
C_α–C_β	1.449(2)	1.46(3)	1.469(9)	1.453
C_β–C_β	1.373(13)	1.36(1)	1.363(30)	1.395
C_α–N_m	1.321(6)	1.34(3)	1.324(13)	1.328
C_β–S	1.727(6)	1.71(1)	1.739(20)	
S···S	3.74	3.25	3.53	
		Bond Angles (deg)[b]		
C_β–C_β–S	133.4(2)	123.5(5)	128.5(35)	
C_α–C_β–C_β	105.6(5)	107.0(8)	106.8(7)	106.7
C_α–N_p–C_α	104.1(5)	103.5(7)	107.8(6)	108.1
N_m–C_α–N_p	125.9(5)	126.3(12)	127.3(5)	127.7
C_α–N_m–C_α	122.3(1)	120.8(19)	123.9(1)	123.2
N_p–C_α–C_β	112.4(3)	110.0(14)	109.4(7)	109.3
C_α–C_β–S	121.0(5)	129.5(13)	124.7(42)	
N_m–C_α–N_p	121.7(5)	122.8(17)	123.4(6)	123.0
N_p–M–N_p	90.0(2)	90.0(17)	85.8(6)	90
N_p–M–N_p'	180[c]	178.7(1)	148.4(1)	180

[a] Averaged for Mg(pc), Zn(pc), Fe(pc), and Mn(pc) structures, except for Ni–N_p, which is taken from Ni(pc)I. See: Schramm, C. J.; Scaringe, R. P.; Stojakovic, D. R.; Hoffman, B. M.; Ibers, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 6702. [b] Number in parentheses is the standard deviation in the last one or two digits of the values used in the symmetry average. [c] Value is fixed by crystal symmetry.

Table III. Symmetry-Averaged Bond Distances and Angles of Complexes **2a**, Ni(dppe)Cl_2, $[Ni(dppe)_2]^{2+}$, and $[Ni(mnt)_2]^{2-}$

	bond distances (Å)[a]		bond angles (deg)[a]	
compound	Ni–P	Ni–S	P–Ni–P	S–Ni–S
2a	2.158(4)	2.185(4)	86.8(11)	95.4(8)
Ni(dppe)Cl_2[b]	2.195(2)		90.0(5)	
$[Ni(dppe)_2]^{2+}$[c]	2.258(4)		83.3(12)	
$[Ni(mnt)_2]^{2-}$[d]		2.147(2)		92.3(2)

[a] Number in parentheses is the standard deviation in the last digit of the values used in the symmetry average. [b] Reference 73. [c] Reference 74. [d] Reference 75.

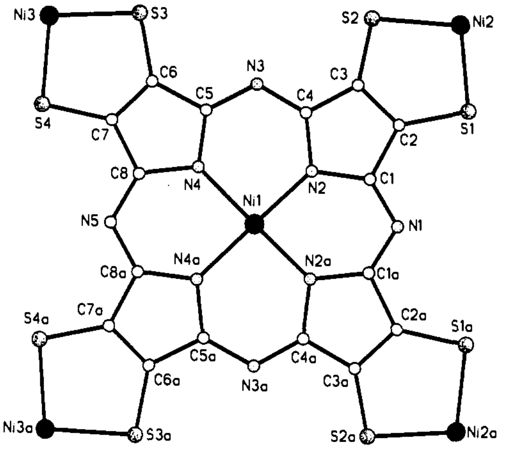


Figure 1. Numbering scheme for the [Ni(pzot)Ni_4] heart of **2a**.

gives the pertinent crystallographic parameters, and Tables II and III give the symmetry-averaged bond lengths and angles. Atomic coordinates, anisotropic displacement parameters, complete listings of bond lengths and angles, hydrogen coordinates, and structure factors appear in the supplementary material. Views of the structure of complex **2a** that include 50% probability thermal ellipsoids are also available in the supplementary material, along with a figure showing displacements of peripheral atoms from the least squares plane of the four pyrrole nitrogens.

Results and Discussion

Synthesis of Pentametallic Macrocycles 2a–d. We chose Ni(P–P)X_2 as a representative capping reagent for preparing pzot complexes containing five transition metal atoms. One route to these complexes involves the transmetalation methodology introduced by Abel[34] and Usón,[35] where solutions of **1** are mixed with the appropriate Ni(P–P)X_2 in slight excess to give macrocycles **2a–d** (Scheme I). Macrocycle **1** is a convenient precursor to the pentanickel complex because it is air-stable and these reactions can be performed under ambient conditions. The transmetalation apparently is facilitated by the presence of a highly polar and/or coordinating cosolvent such as DMSO or *N,N*-dimethylacetamide; in the absence of such a cosolvent there is only partial displacement of the dialkyltin group, as monitored by ^{1}H NMR, when the Ni reagent is in slight excess.

Although $[Ni(pzot)]^{8-}$ is highly air-sensitive, the direct reaction with Ni(P–P)Cl_2 in aqueous *N*-methyl-3-pyrrolidinone under anaerobic conditions also produces the desired product. This route has been used to prepare macrocycle **2a** that is spectroscopically indistinguishable from that formed by transmetalation. The crystallographic and spectroscopic data now presented clearly show that compounds **2a–d** are pentanickel complexes with each Ni(P–P) moiety bound in the bidentate (S–S) mode (Chart I).

Crystal Structure of Macrocycle 2a. The pentanickel complex **2a** crystallizes in the orthorhombic space group $Cmc2_1$ (No. 36) with four macrocycles and several disordered molecules of *N,N*-dimethylformamide per unit cell. The planar macrocycles form linear stacks along the *z*-axis with the central nickel atom, N1, and N5 all residing on the horizontal mirror plane; the molecular numbering scheme is given in Figure 1. The main packing interactions are between the phenyl groups of the phosphine ligands. A common motif in the stacking is a "T" shaped arrangement, where the phenyl rings are oriented perpendicularly to one another. This stacking would leave unfilled space near the porphyrazine moieties; the space is occupied by dimethylformamide molecules, as shown in Figure 2S of the supplementary material.

The molecular structure of **2a**, shown in Figure 2, clearly illustrates the ability of the porphyrazineoctathiolate ligand to adopt the bidentate (S–S) coordination mode as well as the tridentate (S–N–S) mode previously observed in the crystal structure of **1**. The $[Ni(pzot)]^{8-}$ core is essentially coplanar with the least-squares plane of the four pyrrole nitrogens, N2, N4, N2a, and N4a. The maximum displacement of the eight sulfur

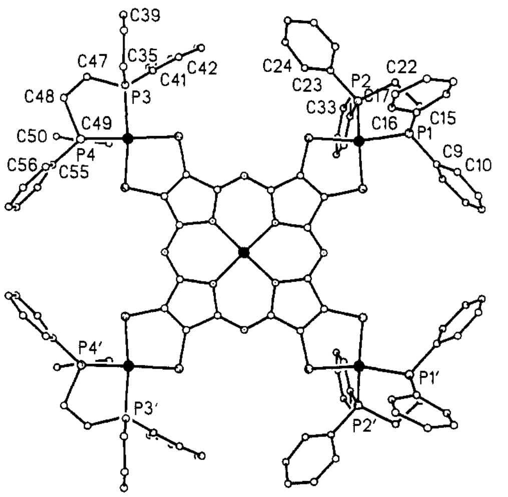


Figure 2. Top view of complex **2a**. For clarity, the hydrogen atoms have been omitted. Numbering scheme for the dppe moieties is included.

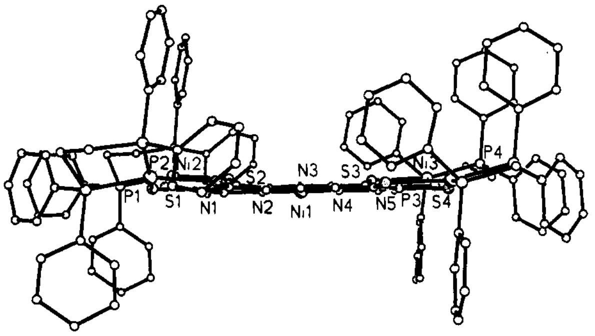


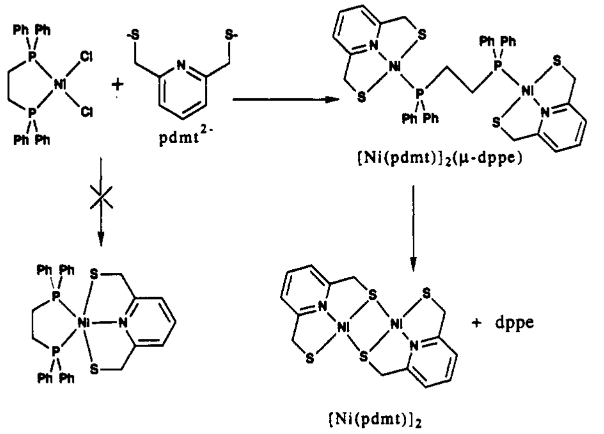
Figure 3. Side view of complex **2a**, with hydrogen atoms omitted.

atoms from this least-squares plane is only 0.045 Å for S2. The Ni ions of the four peripheral Ni(dppe) units are chelated by the pyrroledithiolate moieties with each nickel atom lying slightly (0.061 Å for Ni2) above the least-squares plane. This gives the molecule the contour of a very shallow bowl (Figure 3). The magnitudes of the thermal parameters of the atoms of the polymetallic porphyrazine complex are sufficiently low (supplementary material) to allow definitive analysis of the pzot geometry as a function of the mode of peripheral metal binding.

To examine how the bond lengths and angles of the [Ni(pzot)]$^{8-}$ core are changed by bidentate (S–S) chelation of the Ni(P–P) units in **2a**, as compared to tridentate (S–N–S) chelation of the *t*-Bu$_2$Sn units in **1**, we use the octakis(methylthio)porphyrazine Mg(omtp) as a structurally unconstrained reference compound. Table II presents selected symmetry-averaged bond distances and bond angles for these three complexes. To our knowledge, there is no reported crystal structure of a Ni(P–P) complex bearing a bidentate dithiolene ligand, even though such complexes have been reported.[37] There are, however, crystal structures of compounds that may serve for comparison: Table III presents a summary of relevant bond distances and bond angles for [Ni(mnt)$_2$]$^{2-}$,[72] [Ni(dppe)$_2$]$^{2+}$,[73] and Ni(dppe)Cl$_2$.[74]

The bond lengths and angles of the [Ni(pzot)]$^{8-}$ core of **2a** are similar to those of Mg(omtp) and complex **1** (Table II), although there appears to be a slight distortion in the geometry of the pyrrole rings of **2a** relative to those of Mg(omtp) and complex **1**. For example, there is an elongation in the bond between the pyrrole nitrogen and its neighboring carbon of $\sim$0.04 Å relative to the case of Mg(omtp). In addition, the bond angle formed by the pyrrole nitrogen and the two neighboring carbon atoms (C$_\alpha$–N$_p$–C$_\alpha$) is decreased by $\sim$4° relative to the case of Mg(omtp). However, the key difference between the structures is seen in the bond angles involving the peripheral sulfur atoms. The data in Table II clearly show that [Ni(pzot)]$^{8-}$ adjusts to accommodate either the (S–S) or (S–N–S) binding modes by a swing of the C$_\beta$–S bond. Thus, the C$_\beta$–C$_\beta$–S bond angle of 128.5(35)° for the unconstrained Mg(omtp) opens up to 133.4(2)° for the tridentate complex **1** and closes to 123.5(5)° for the bidentate complex **2a**. Correspondingly, the interatomic distances between adjacent sulfur atoms decrease from 3.53 Å in Mg(omtp) to 3.25 Å in **2a** and increase to 3.74 Å in **1**. However, the C$_\beta$–C$_\beta$–S bond angle in the [Ni(mnt)$_2$]$^{2-}$ ion is actually smaller by $\sim$3° than the same angle seen in **2a**, suggesting that the geometry of the dithiolate chelation of the nickel atom in **2a** does not merely optimize the binding to the metal ion. Consistent with this, the Ni–S bond in complex **2a** is $\sim$0.04 Å longer than that of the [Ni(mnt)$_2$]$^{2-}$ complex and the S–Ni–S bond angle for **2a** is $\sim$3° larger. This Ni–S bond lengthening in **2a** is accompanied by a shortening of the Ni–P bond of $\sim$0.1 and $\sim$0.05 Å relative to those in the [Ni(dppe)$_2$]$^{2+}$ and Ni(dppe)Cl$_2$ complexes, respectively. The P–Ni–P bond angle for **2a** is correspondingly decreased relative to the case of Ni(dppe)Cl$_2$ to compensate for the increased S–Ni–S bond angle.

Scheme II



Synthesis of Model Compounds. The X-ray structure definitively shows that **2a** *as crystallized* adopts the bidentate coordination geometry. To make definitive structural and spectroscopic assignments of peripherally metallated complexes of [Ni(pzot)]$^{8-}$ in solution, we studied model compounds designed to mimic the structure of the two possible coordination modes of the [Ni(pzot)]$^{8-}$ ligand, namely, tridentate (S–N–S) and bidentate (S–S) (Chart I and Scheme I). The bidentate geometry was simulated using dithiolene ligands (mnt)$^{2-}$ and 1,2-benzenedithiolate ((bdt)$^{2-}$). A series of Ni(P–P)(dithiolene) model complexes was readily prepared by the reaction of the appropriate Ni(P–P)X$_2$ with (mnt)$^{2-}$ or (bdt)$^{2-}$ (Chart II). For example, equimolar amounts of Ni(dppe)Cl$_2$ and Bu$_2$Sn(mnt) react to produce crystalline Ni(dppe)(mnt) (67% yield) identical to that obtained by the method of Bowmaker *et al.*[37,38]. These complexes are orange to pink, air-stable crystalline solids that also are stable to ligand disproportionation in solution for extended periods.

Attempts to model the tridentate (S–N–S) binding mode utilized the chelating ligand 2,6-pyridinedimethanethiolate ((pdmt)$^{2-}$) (Scheme II). Although square-planar and octahedral nickel(II) complexes of this ligand have been reported,[75-77] in our hands the preparation of the five-coördinate Ni(P–P)(pdmt) complexes was unsuccessful, just as other workers were unsuc-

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(72) Eisenberg, R.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 605.

(73) Williams, A. F. *Acta Crystallogr.* **1989**, *C45*, 1002.

(74) Brunner, H.; Vitulli, G.; Porzio, W.; Zocchi, M. *Inorg. Chim. Acta* **1985**, *96*, 67.

(75) Krüger, H.-J.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 1148.

(76) Krüger, H.-J.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 2955.

(77) op den Brouw, P. M.; van der Linden, J. G. M. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 149.

cessful in synthesizing five-coordinate Ni(dppe) complexes.[37,78] The reaction of Ni(dppe)Cl_2 with Na_2(pdmt) results in a green crystalline compound in modest yield. Elemental analysis and ^1H NMR integration results indicated a 2:1 ratio of pdmt to dppe, and the mass spectrum confirms this stoichiometry. The single ^{31}P NMR peak with a chemical shift of 27.9 ppm is characteristic of nonchelated metal diphosphine complexes.[79] This suggests that the structure of **3** consists of two Ni(pdmt) units bridged by a dppe ligand. Upon dissolution, this complex gradually decomposes to give the brown $[Ni(pdmt)]_2$ dimer reported previously[75–77] and free dppe as monitored by NMR. Addition of excess dppe to the solution suppresses the decomposition and allows for satisfactory spectral measurements. Others have previously noted that the $[Ni(pdmt)]_2$ dimer could be dissociated using PPh_3[77] or thiolate ligands.[75] To try to force five-coordination, the reaction was modified by using the rigid diphosphine dppb. However, the reaction of Ni(dppb)I_2 with Na_2(pdmt) gave only $[Ni(pdmt)]_2$ and free dppb as products.

These synthetic results with model compounds for **2a–d** demonstrate that square-planar Ni(P–P)(dithiolene) complexes are quite stable, whereas five-coordinate Ni(P–P)(S–N–S) complexes are not. They indicate that Ni(P–P) capping groups bound to the tridentate site of the pzot ligand should undergo dissociation and disproportionation reactions similar to those experienced by the Ni(pdmt) complexes, and this would result in intractable oligomeric species because of the multiple S–N–S binding sites on the pzot ligand. In fact, solutions of **2a–d** are stable, which correlates well with the crystallographic data that shows S–S chelation of the Ni(P–P) units.

NMR Spectroscopy of Macrocycles 2a–d and Model Compounds. To study the coordination mode of the Ni(P–P)-capped macrocycles in solution, ^1H and ^{31}P NMR were used to compare **2a–d** with mononuclear Ni(P–P)(dithiolene) complexes that model the bidentate bonding mode. The $(bdt)^{2-}$ ligand is expected to most closely mimic the bidentate binding mode of $[Ni(pzot)]^{8-}$ and the aromatic nature of the porphyrazine; the $(mnt)^{2-}$ ligand should model the binding geometry, but the cyano substituents have an additional electron-withdrawing power, as evidenced by the fact that $(mnt)^{2-}$ complexes show more positive reduction potentials than most dithiolene complexes.[80] The ^1H and ^{31}P chemical shifts for all the compounds studied here are listed in Table IV. These parameters are particularly good markers of structure because of their sensitivity to metal ion coordination and ancillary ligand effects.[79] Specifically, metal ion coordination of diphosphines dppe, dppb, and dppy separates the phenyl proton resonances into meta, para, and ortho peaks in order of decreasing chemical shift.

Inspection of the ^1H NMR chemical shifts for the Ni(P–P) moieties of macrocycles **2a–d** shows an extremely close similarity with those for the models Ni(P–P)(mnt) and Ni(P–P)(bdt) (Table IV). However, small shifts for **2a–d** indicate the presence of ring-current effects exerted by the porphyrazine ring π-system.[81] For example, the phenyl proton chemical shifts for **2a** are slightly higher by 0.06–0.2 ppm relative to the case of the models. Likewise, the ethylene bridge proton resonance of **2a** is shifted downfield by $\gtrsim$0.1–0.2 ppm relative to the case of the model. This contrasts with the ethylene bridge proton resonance of Ni(dppe)Cl_2, whose chemical shift of 2.14 ppm is close the value of 2.10 ppm for free dppe. These same trends can be seen in macrocycles **2b–d**. In the ^1H NMR spectra for the Ni(dppy) macrocycle and the model dithiolenes, the same general features are present with the bridging ethene protons of **2b** shifted downfield, relative to the case of the models, due to the ring current effect of the porphyrazine. The ^1H NMR data for the Ni(dppb) complex **2c** and the two Ni(dppb)(dithiolene) compounds are also similar, with the phenylene protons of the bridge for each complex appearing as poorly resolved shoulders on the more intense phenyl resonances. The (P–P) substituent of **2c** does not show as pronounced a ring current effect for this series, most likely due to the shielding effect of the benzene ring from the dppb ligand. For both the Ni(dcpe) macrocycle **2d** and its dithiolene models, aliphatic cyclohexyl ^1H resonances show a complex pattern occurring from *ca.* 1–2 ppm. In each spectrum, a broad doublet appears above 3 ppm, and this is assigned to the P–H splitting of the ethylene bridge protons. The ^1H NMR spectra for the macrocycle **2d** and its Ni(dcpe)(dithiolene) analogues do not show the same chemical shift trends observed for **2a** and **2b**; the ^1H NMR chemical shifts of **2d** are intermediate between those of the corresponding bdt and mnt analogues. This is undoubtedly due to the absence of phenyl substituents on the phosphine ligand. Within the similarities, interesting subtle differences are observed. The ^1H NMR resonances of macrocycles **2a–d** and the Ni(P–P)(bdt) complexes show the ring current-induced downfield shifts relative to those of the Ni(P–P)(mnt) complexes which lack this aromatic ring current.

Table IV. ^1H and ^{31}P NMR Chemical Shifts for **2a–d** and Ni(P–P)(dithiolene) Complexes[a]

		dithiolene ligand		
(P–P)	assignment	$pzot^{8-}$	mnt^{2-}	bdt^{2-}
2a(dppe)	*m*-CH	7.89 q	7.67 q	7.79 q
	p-CH	7.68 t	7.58 t	7.57 t
	o-CH	7.58 t	7.50 t	7.53 t
	dppe-CH_2	2.68 d	2.44 d	2.57 d
	bdt-CH			7.17, 6.72 dd
	^{31}P	60.7	62.4	59.6
2b(dppy)	dppy-CH	8.10 m	8.01 m	7.93 m
	m-CH	7.89 m	7.66 m	7.77 m
	p-CH	7.66 m	*e*	7.57 m
	o-CH	*e*	7.58 t	*e*
	bdt-CH			7.23, 6.77 dd
	^{31}P	71.2	72.7	70.6
2c(dppb)	dppb-CH	7.82 sh	7.69 sh	7.82 sh
	m-CH	7.77 q	7.65 q	7.73 q
	p-CH	7.67 m	7.57 sh	7.57 m
	o-CH	*e*	*e*	*e*
	bdt-CH			7.19, 6.73 dd
	^{31}P	59.9	61.5	60.6
2d(dcpe)	bridge-CH_2	3.38 m[b]	3.08 m[b]	3.15 m[c]
	1-Cy-CH	2.78 d	1.89 d	1.87 d
	broad d[d]	2.36	2.08	2.30
	broad m[d]	2.00	2.02	2.12
	broad m[d]	1.77	1.78	1.80
	broad d[d]	1.63	1.67	1.69
	sharp s[d]	1.93	1.51	1.58
	complex m[d]	1.47–1.25	1.53–1.26	1.53–1.28
	4-Cy-CH_2	1.15 tt	1.17 tt	1.22 tt
	bdt-CH			7.16, 6.71 dd
	^{31}P	80.7	83.7	80.5

[a] All spectra in DMSO-d_6 unless otherwise specified. Chemical shifts relative to TMS for ^1H and to 5% H_3PO_4–D_2O for ^{31}P. Abbreviations: m = unresolved multiplet, s = singlet, d = doublet, t = triplet, q = quartet, sh = unresolved shoulder peak, dd = doublet of doublets, tt = triplet of triplets. [b] In 2:1 *o*-$C_6D_4Cl_2$–$CDCl_3$. [c] In $CDCl_3$. [d] No definitive assignment for cyclohexyl resonances. [e] Peak is superimposed on previous peak.

The chemical shifts in the ^{31}P NMR spectra of the square-planar Ni(P–P)(dithiolene) complexes depend strongly upon the substituents on the diphosphine ligand as witnessed by the fact that Ni(dppe) and Ni(dppb) complexes have chemical shifts of ~60 ppm but those with Ni(dppy) and Ni(dcpe) have chemical shifts of ~70 and ~80 ppm, respectively. Nevertheless, the ^{31}P NMR data for macrocycles **2a–d** are very similar to those for their respective dithiolene models (Table IV). Each pzot complex exhibits one ^{31}P chemical shift that is within a few ppm of the ^{31}P resonances for the respective model compound. For example,

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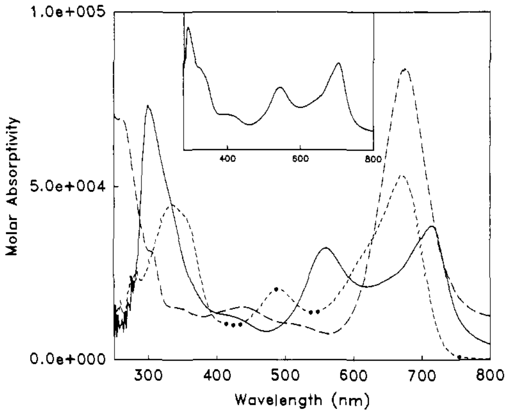

Figure 4. Optical absorption spectra of complex **2a** (20 μM in DMSO) (solid line), Ni(obtp) (20 μM in C_6H_5Cl) (short-dashed line), and complex **1** (20 μM in CH_2Cl_2) (long-dashed line). Inset: complex **2d** (20 μM in DMSO).

the ^{31}P NMR spectrum of macrocycle **2a** shows one phosphorus resonance with a chemical shift intermediate between those of mononuclear complexes Ni(dppe)(mnt) and Ni(dppe)(bdt). This same pattern is seen for both the Ni(dppy)-capped macrocycle **2b** and the Ni(dcpe)-capped macrocycle **2d**. The ^{31}P NMR chemical shift of the Ni(dppb)-capped macrocycle **2c** is again very close to those of the models but is slightly lower than that of either mononuclear complex. Thus, aromatic ring currents appear to fine-tune chemical shifts of ^{31}P as well as of ^1H NMR spectra.

The extreme similarity between the ^1H and ^{31}P NMR spectra of **2a–d** and analogous Ni(P–P)(dithiolene) complexes (Table IV) gives definitive evidence that pentametallic complexes **2a–d** coordinate the nickel atoms at the periphery in the bidentate (S–S) mode seen in the crystal, rather than in the tridentate (S–N–S) mode adopted by the tin-capped macrocycle **1**. For example, in all cases, the macrocycles **2a–d** have a ^{31}P chemical shift within 1 ppm of those for their corresponding Ni(P–P)(bdt) complexes and about 2 ppm lower than those for their corresponding Ni(P–P)(mnt) complexes. Indeed, five- and six-coordinate nickel complexes are typically paramagnetic,[37] and thus one would expect the ^1H NMR spectrum of a macrocycle capped by pentacoordinate Ni(II) in the (S–N–S) mode to be vastly different from that of the model compounds with four-coordinate Ni(II), contrary to observation.

Electronic Absorption Spectra. Complexes **2a–d** show a characteristic five-peak absorption spectrum in solution that bears little resemblance to the spectrum of the precursor **1**, where Sn binds in the tridentate mode, and also shows noticeable difference from those of nickel octakis(alkylthio)porphyrazines (Figure 4); the absorption maxima for complexes **2a–d** are given in Table V. Compounds **2a–d** display an intense absorbance at about 300 nm and a shoulder at about 330 nm; this shoulder is a well-resolved peak for **2d** only (Figure 4, inset). The peak at 300 nm corresponds well to the Ni → P charge-transfer band seen in other nickel(II) diphosphine complexes,[37] and its high intensity is due to the presence of four such moieties per macrocycle. The 330-nm feature for **2a–d** is seen as a distinct peak for octakis(alkylthio)porphyrazines (Figure 4) and is the "Soret" $\pi \rightarrow \pi^*$ transition of the porphyrazine ring system. This absorption is suppressed in complexes such as **1**, where the *m*-nitrogen is bound to the metal atoms (Figure 4), but appears in the spectra of **2a–d**, where the nickel ions coordinate in the bidentate, dithiolene mode. There are also two intense bands for **2a–d** at ~555 and ~730 nm which are relatively invariant with respect to the phosphine ligand. It is plausible to assign these as transitions that correlate with the ~490 and ~672-nm bands seen for Ni(obtp), which have been assigned as n–π^*[24,82] and π–π^*,[83] respectively, where the red shift for **2a–d** is due to interactions with the peripheral metal chelates.

Table V. Electronic Absorption Maxima for Star Porphyrazines **2a–d** in DMSO

complex	absorption maxima (nm)
2a	300, 330 sh,[a] 412, 558, 716
2b	309, (~330 sh), 388, 556, 714
2c	302, (~330 sh), 410, 553, 713
2d	291, 326 sh, 394, 544, 706

[a] sh = shoulder on maximum at *ca.* 300 nm. Where wavelength value is given in parentheses, the shoulder is not clearly discernable from the major peak.

Summary

Compounds **2a–d** represent the first set of examples of peripherally chelated *star* porphyrazines where the $[Ni(pzot)]^{8-}$ ligand is encircled by four additional transition-ion units. The structural assignments made from the spectroscopic studies of both **2a–d** and their respective model compounds in solution are in full agreement with the X-ray crystal structure of **2a**, showing unambiguously that **2a–d** adopt the bidentate coordination mode in solution as well as in the solid state. These results confirm our previous observation that the porphyrazineoctathiolate ligand can act as an ambidentate polynucleating ligand bearing both bidentate and tridentate chelation sites at the periphery. The optical spectra of **2a–d** suggest that the peripheral metal chelates and the porphyrazine ring can have significant electronic interaction.

Acknowledgment. This work was supported by the National Science Foundation (Grants CHE-9107589 and DMR-9119832).

Supplementary Material Available: Table 1, additional crystallographic details; Table 2, atomic coordinates and equivalent isotropic displacement parameters; Table 3, bond lengths and angles for **2a**; Table 4, anisotropic displacement parameters; Table 5, hydrogen coordinates and isotropic displacement parameters; Figures 1S and 2S, views of the structure containing 50% thermal ellipsoids; and Figure 3S, displacements of atoms from the porphyrazine plane (15 pages); listing of structure factors (13 pages). Ordering information is given on any current masthead page.

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