ometric pH data. Since the proposed reaction[5] CaL$^-$ + L^{3-} = CaL$_2^{4-}$ corresponds to no change in the proton stoichiometry, there is little to distinguish it from the simple deprotonation reaction of glyphosate. In contrast, direct measurement of [Ca^{2+}] allows an evaluation of complex formation that is independent of the protonation reactions.

Similarly, measurement of total calcium by atomic absorption allows a direct evaluation of CaHL equilibria. The value of log β_{MLH} determined by Martell and Motekaitis[5] is 11.48, compared to the value of 12.18 (9) determined in this study. On the basis of the equilibrium constants determined here and the conditions used by Martell and Motekaitis,[5] K_{sp} may have been exceeded in the earlier potentiometric titration experiments; this would account for their lower value for this formation constant.

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Registry No. Ca(O$_3$PCH$_2$NH$_2$CH$_2$CO$_2$)(H$_2$O)$_2$, 112740-48-4; K$_2$C$_3$H$_6$NO$_5$P, 69200-57-3.

Supplementary Material Available: Listings of general temperature factor expressions (B's) and root-mean-square amplitudes of vibration (Tables S2 and S3) (1 page); a listing of observed and calculated structure factors (Table S1) (6 pages). Ordering information is given on any current masthead page.

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Isolation and Characterization of the Principal Kinetic Products in the Rothemund Synthesis of Sterically Hindered Tetraarylporphyrins. Crystal and Molecular Structures of [Tetrakis(2,6-dichlorophenyl)porphinato]zinc(II) and Bis[(*meso*-2,6-dichlorophenyl)-5-(*o*,*o*′-dichlorobenzyl)dipyrromethene]zinc(II) Complexes

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The Rothemund condensation reaction, the most useful route to hindered 5,10,15,20-tetraarylporphyrins, has been examined in detail in context with the production of tetrakis(2,6-dichlorophenyl)porphyrin, TDCPP, a porphyrin used extensively at present in homogeneous oxygenation and biomimetic heme studies. The principal products from the reaction of pyrrole, 2,6-dichlorobenzaldehyde, and zinc acetate in refluxing 2,4,6-collidine are the bis(dipyrromethene) complex bis[(*meso*-2,6-dichlorophenyl)-5-(*o*,*o*′-dichlorobenzyl)dipyrromethene]zinc(II) (**2**), produced in ca. 40% yield, and the Zn porphyrin [tetrakis(2,6-dichlorophenyl)porphinato]zinc(II), Zn^{II}TDCPP (**1**), produced in ca. 10% yield. In contrast to a previous report, there is no evidence that *meso*,5,5′-trisubstituted dipyrromethenes are formed. Furthermore, no zinc complexes of pyrromethenes nor dipyrromethanes build up to observable levels under the conditions of this aerobic high-temperature condensation reaction. The X-ray crystal structure of **2** coupled with ^{1}H NMR, ^{13}C NMR, infrared, UV-visible, and mass spectral data confirms the formulation of the compound as a Zn^{2+} ion coordinated by two planar bidentate disubstituted dipyrromethene ligands. Although the data indicate that carbon-carbon bond formation and cyclization in **2** to form the metalloporphyrin, **1**, should not be a difficult process, **2** does not produce **1** in appreciable yield under the Rothemund conditions examined in this work. The metalloporphyrin, **1**, isolated from the reaction, crystallizes as its five-coordinate *N*-methylpyrrolidinone (NMP) complex in triclinic space group $P\bar{1}$: $a = 11.470$ (9) Å, $b = 13.155$ (7) Å, $c = 19.894$ (10) Å, $\alpha = 84.25$ (4)°, $\beta = 79.00$ (5)°, $\gamma = 75.59$ (6)°; $V = 2849.3$ (3.3) Å^3, $Z = 2$. The zwitterionic canonical form of the O-bound axial NMP is considerably enhanced upon ligation to the zinc, and the pocket depth defined by the eight phenyl *o*-chloro substituents in **1** is ca. 2.6 Å. Although the spectroscopic data indicate that free-radical bromination of **2** followed by treatment of the product under Rothemund condensation conditions yields some porphyrin, the principal products are brominated derivatives of **1** and **2**.

Introduction

Few areas in chemical research has been as active since 1980 as the use of synthetic transition-metal porphyrins to model the electronic and reactivity features of cytochrome P-450 and to catalyze the oxidation of hydrocarbons and other organic substrates.[1-15] The most recent work has largely focused on the use of 5,10,15,20-tetraarylmetalloporphyrins with bulky substituents on the ortho positions of the aryl rings. These sterically hindered

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(2) References 3-15 involve the use of metallotetraarylporphyrin complexes with bulky ortho substituents on the aryl rings. Many of the studies involve modeling the electronic and reactivity features of cytochrome P-450 by synthetic metalloporphyrins. Papers are listed alphabetically by the principal investigator's last name.

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porphyrin rings obviate μ-oxo dimer formation, offer enhanced stability with respect to oxidative degradation, and generally render highly reactive metalloporphyrin species more stable and tractable than their sterically unencumbered counterparts, such as the corresponding 5,10,15,20-tetraphenylporphyrin (TPP) species.[2–15] The two sterically hindered porphyrin ligands most frequently used in biomimetic high-valent metalloporphyrin studies and homogeneous oxo transfer and related investigations are the tetrakis(2,6-dichlorophenyl)porphyrin ($TDCPP^{2-}$) and the tetramesitylporphyrin (TMP^{2-}) dianions. Despite the importance of these ligands and their complexes, there remain no good preparative routes to these materials. The most successful and extensively practiced synthetic routes to these compounds remain the one-pot condensation reactions starting with the benzaldehyde and the pyrrole.[16–18] The most satisfactory of these one-pot syntheses remains the hot propionic acid aerobic cyclization procedure of Adler and co-workers[16,17] and the Rothemund condensation usually carried out with a heterocyclic base as a solvent in the presence of a metal ion as a template.[17,18] While the propionic acid procedure is generally superior for preparing the unhindered 5,10,15,20-tetraarylporphyrins, the Rothemund condensation is generally superior for preparing the highly hindered 5,10,15,20-tetraarylporphyrins. No synthetic procedure for the most useful 5,10,15,20-tetraarylporphyrins, those with bulky substituents on all ortho positions of the *meso*-aryl rings, affords the porphyrin derivative in greater than 5% yield with the exception of the recent procedure for tetramesitylporphyrin (29%) of Lindsey and co-workers.[17b] Often the yields of TDCPP are closer to 2% in practice. In this paper we examine the Rothemund template synthesis of TDCPP in the presence of zinc(II). We report the structural and spectroscopic properties of the two principal kinetic products from this reaction, the zinc porphyrin [tetrakis(2,6-dichlorophenyl)porphinato]zinc(II), Zn^{II}TDCPP (**1**), as its *N*-methylpyrrolidinone complex, and the zinc bis(dipyrromethene) complex bis[(*meso*-2,6-dichlorophenyl)-5-(*o,o′*-dichlorobenzyl)dipyrromethene]zinc(II) (**2**). The isolation and partial characterization of **2** were described in a preliminary communication.[19] The relationships between these two principal kinetic products are discussed, and the optimization of such Rothemund condensation reactions is addressed within the context of the characteristics and limitations posed by this general type of metalloporphyrin synthesis.

Experimental Section

Materials and Methods. Water used in the preparations was deionized and then fractionally distilled from $KMnO_4$. All other solvents were either reagent grade or glass-distilled grade from Burdick and Jackson and were used as received. Pyrrole and 2,6-dichlorobenzaldehyde were purchased from Lancaster Synthesis. In all reactions the pyrrole was freshly distilled immediately before use. Electronic absorption spectra were recorded on a Hewlett-Packard 8451A spectrometer. The infrared spectra were obtained by using a Perkin-Elmer Model 1430 spectrometer, and the ^1H NMR spectra were recorded on a Nicolet Model 360-B spectrometer operating at 361.0 MHz with a probe temperature of 25 °C or a General Electric Model QE-300 spectrometer operating at 300.0 MHz with a probe temperature of 25 °C. The mass spectra were obtained by using a VG-70S spectrometer. Elemental analyses were performed by Atlantic Microlabs.

Synthesis of [Tetrakis(2,6-dichlorophenyl)porphinato]zinc(II), Zn^{II}TDCPP (1). The same Rothemund condensation produces both **1** and **2**. The following procedure affords an unusually high yield of **1**. To a 500-mL round-bottomed flask containing a magnetic stirring bar and 187 mL of 2,4,6-collidine was added 30 g (0.1714 mol) of 2,6-dichlorobenzaldehyde. The mixture was stirred until all the 2,6-dichlorobenzaldehyde had dissolved, producing a yellow solution. To this was added 31.8 g (0.173 mol) of anhydrous zinc acetate. The resulting yellow slurry was heated to 50 °C, and then 13.05 mL (12.62 g, 0.188 mol) of freshly distilled pyrrole was added dropwise over a period of 8 min. At the end of the addition, the temperature of the solution was 80 °C. If the pyrrole was added at a higher temperature (e.g. reflux), lower yields of Zn^{II}TDCPP (**1**) were observed. The resulting dark solution was refluxed for 26 h while the progress of the reaction was monitored by UV–visible spectroscopy. The well-defined chromophores of **1** (λ_{max} in acetone = 424 nm) and the bis(dipyrromethene) complex (**2**) (λ_{max} in acetone = 500 nm) began to form in ca. 50 and 10 min, respectively.

The effective workup for this reaction took advantage of the greater solubility of **2** and the numerous other dark heterocyclic polycondensation products in toluene relative to the solubility of **1** in this solvent. After the reaction time of 26 h, the 2,4,6-collidine was distilled off in vacuo, leaving a tarry black residue, which was subsequently dried under a full pump vacuum overnight. To the dried residue was added 75 mL of warm (60–70 °C) toluene. The round-bottomed flask with the mixture was then placed in a sonicator for 1 min, and the contents were filtered through a fine-fritted glass funnel. A total of 700 mL of warm toluene (60–70 °C) was needed to dissolve or dislodge the residue in the flask. The dark purple solid on the frit, constituted principally of $Zn(OAc)_2$ and impure **1**, was treated with sufficient warm toluene (60–70 °C, ca. 400 mL) until the supernatant was colorless. Concentration of the supernatant solution on a rotary evaporator produced 0.65 g of **1**. The filtrate contained considerably more than half of the Zn^{II}TDCPP. This metalloporphyrin could be isolated in two ways. The initial method involved concentrating the filtrate to 20% of the original volume followed by adding a minimum amount of toluene at ambient laboratory temperature to the black mixture. The "minimum amount" was defined as that needed to ensure that the mixture could be readily filtered by using a fine-fritted glass funnel. This procedure selectively removed the more soluble dark byproducts. Another crop of **1** (0.188 g) was left on the filter. For the second method of recovering **1** from the supernatant, the filtrate was allowed to stand overnight. A black solid was then separated by using a fine-fritted glass funnel, washed with ca. 75 mL of *n*-heptane, and dried in vacuo overnight. The initial method for recovering the metalloporphyrin from the filtrate usually yields a product of higher purity. The above steps can be repeated up to 10 times and more. The total yield of product for the above preparation after nine such workup cycles was 3.55 g, or a total of 8.7% yield. Combined yields of over 10% are possible with these workup procedures if the investigator has sufficient patience. Impure Zn^{II}TDCPP can be further purified by passage through a column of grade I neutral alumina with toluene as eluant. ^1H NMR (360 MHz, $CDCl_3$): δ 7.67, 7.69, 7.71 (t, 4 H, $J_{m,p\text{-}H}$ = 7.9 Hz, Ph *p*-H), 7.78, 7.80 (d, 8 H, $J_{m,p\text{-}H}$ = 7.9 Hz, Ph *m*-H), 8.75 (s, 8 H, pyr β-H). IR (KBr pellet): 2935 (m), 2865 (w), 1565 (m), 1540 (w), 1435 (s), 1343 (m), 1310 (vw), 1267 (w), 1215 (w), 1200 (m), 1160 (vw), 1075 (m), 1005 (s), 845 (w), 807 (s), 785 (s), 728 (m) cm^{-1}. MS (relative intensity): *m/e* 954 (33), 772 (25), 688 (33), 622 (68), 606 (100).

Anal. Calcd for $C_{58}H_{40}Cl_8N_4O_2Zn = C_{44}H_{20}Cl_8N_4Zn\cdot 2C_7H_8\cdot 2H_2O$: C, 59.34; H, 3.44; Cl, 24.16; N, 4.77. Found: C, 59.24; H, 3.69; Cl, 24.36; N, 4.78. Zn^{II}TDCPP can be recrystallized in high yield from *N*-methylpyrrolidinone (NMP) and water to yield (NMP)-

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Zn^{II}TDCPP·2NMP. ^{1}H NMR (360 MHz, $CDCl_3$; see atom numbering scheme for **1** in Figure 1): δ 1.96–2.04 (quintet, 2 H, $-CH_2CH_2CH_2-$), 2.32–2.36 (t, 2 H, $J_{3,4}$ = 7.9 Hz, $-CH_2CO$), 2.82 (s, 3 H, CH_3), 3.35–3.39 (t, 2 H, $J_{4,5}$ = 7.0 Hz, $-CH_2N$), 7.67–7.71 (t, 4 H, $J_{m,p\text{-}H}$ = 7.9 Hz, Ph *p*-H), 7.78, 7.80 (d, 8 H, $J_{m,p\text{-}H}$ = 7.9 Hz, Ph *m*-H), 8.74 (s, 8 H, pyr β-H). For the quantitative electronic absorption spectra for both (NMP)Zn^{II}TDCPP·2NMP and **2** see Figure 3. The X-ray crystallography is described below.

Synthesis and Isolation of Bis[(*meso*-2,6-dichlorophenyl)-5-(*o*,*o*′-dichlorobenzyl)dipyrromethene]zinc(II) (2). In a typical preparation, described previously, pyrrole (1.68 g, 1.74 mL, 0.025 mol), 2,6-dichlorobenzaldehyde (4.0 g, 0.023 mol), and zinc acetate (4.24 g, 0.023 mol) in 2,4,6-collidine (25 mL) were refluxed for 26 h. After removal of the collidine, the residue was treated, as previously described, to yield Zn^{II}TDCPP (**1**). After four workup cycles, the yield of **1** was 0.38 g, or 7% yield. A 4.5 cm × 60 cm column was wet packed with ca. 450 mL of grade I neutral alumina–toluene slurry. The remaining filtrate was concentrated down to ca. 30 mL, filtered through a fine frit, and applied to the column. At a flow rate of ca. 1 drop/s, ca. 375 mL of toluene eluted from the column before **2** began to elute from the column. At an elution volume of ca. 700 mL, the reaction tar, which still contained a substantial amount of **2**, began to elute from the column. Concentration of the column fractions yielded 0.45 g of pure **2** (8.2% yield). ^{1}H NMR (360 MHz, $CDCl_3$; see atom numbering diagram for **2** in Figure 2): δ 4.11 (s, 4 H, CH_2), 5.81, 5.82 (d, 2 H, $J_{7,8} = J_{17,18}$ = 4.2 Hz, H(8), H(18)), 6.46–6.48 (t with additional splitting, 4 H, $J_{7,8} = J_{17,18}$ = 4.2 Hz, $J_{2,3} = J_{12,13}$ = 4.0 Hz, $J_{1,2} = J_{11,12}$ = 1.3 Hz, H(2), H(7), H(12), H(17)), 6.54–6.55 (dd, 2 H, $J_{2,3} = J_{12,13}$ = 4.0 Hz, $J_{1,3} = J_{11,13}$ = 0.7 Hz, H(3), H(13)), 7.05–7.45 (m, 12 H, Ph *p*-H, Ph *m*-H), 7.75 (s, 2 H, H(1), H(11)). ^{13}C NMR (300 MHz, $CDCl_3$): δ 33.46, 116.84, 117.80, 127.68, 128.05, 128.34, 129.28, 129.70, 132.66, 134.23, 135.69, 135.95, 136.21, 136.68, 138.43, 139.44, 148.49, 163.01. IR (KBr pellet): 3100 (vw), 2935 (vw), 1550 (vs), 1490 (w), 1427 (m), 1398 (s), 1375 (m), 1330 (s), 1250 (s), 1195 (s), 1044 (s), 1005 (s), 918 (m), 886 (w), 850 (m), 795 (m), 780 (m), 765 (w), 715 (s), 700 (w). MS (relative intensity): *m/e* 960 (100), 924 (5), 799 (11). For the quantitative electronic absorption spectra for both (NMP)Zn^{II}TDCPP·2NMP and **2** see Figure 3. The X-ray crystallography is described below.

Anal. Calcd for $C_{50.3}H_{33.2}Cl_8N_4Zn$: C, 57.94; H, 3.21; Cl, 27.20; N, 5.38. Found: C, 57.83; H, 3.21; Cl, 27.35; N, 5.34.

Conversion of 2 into 1. Several oxidants and procedures were used to effect the oxidative cyclization of **2** into **1**. No really satisfactory procedure was found for this transformation. Allylic oxidants such as SeO_2 and MnO_2 do not aid the oxidative cyclization of **2** into **1** under the Rothemund conditions. Several other oxidants produced low yields of Zn porphyrin products, but in all cases, chromatographic and spectroscopic examination of the porphyrin products themselves indicated that additional functionalization of the TDCPP porphyrin ring had occurred. The highest yields of functionalized **1** and **2** products were produced by thermal free-radical bromination of **2** with *N*-bromosuccinimide (NBS) followed by reflux in 2,4,6-collidine. In a typical reaction, 1 g (0.001 mol) of **2**, 0.68 g (0.0038 mol) of NBS, and 472 mL of CCl_4 were mixed and refluxed in a 1-L round-bottom flask for 1 h. The solution was then filtered through a fine frit and the CCl_4 removed by using a rotary evaporator. The bromination product was dissolved in 183 mL of 2,4,6-collidine and refluxed for 6 h. The solution was filtered through a coarse frit, and the collidine was removed by distillation. A UV-vis spectrum of the residue present after distillation showed λ_{max}(acetone) = 426 nm. A 26% yield of **1** was calculated from the UV-visible spectrum of the residue present after distillation. Upon further investigation, the residue was found to contain a complex mixture of **1** and derivatives of **1** and **2**. This residue was dissolved in $CHCl_3$ and applied to a column packed with grade I neutral alumina–$CHCl_3$ slurry. Examination of the column fractions by UV-visible and ^{1}H NMR spectroscopy indicated that a small amount of **1** had been produced and that a mixture of brominated derivatives of **1** and **2** were the main products.

X-ray Crystallography

Crystallographic Data and Structure Solution for (NMP)-Zn^{II}TDCPP·2NMP. Single crystals of (NMP)Zn^{II}TDCPP·2NMP suitable for X-ray diffraction were grown by adding water dropwise over a period of 3 days to a solution of 40 mg of **1** in 5 mL of NMP. One bright purple crystal (0.2 × 0.42 × 0.38 mm) with well-formed faces was removed from the meniscus of the aqueous NMP solution and attached to the end of a glass fiber with epoxy cement. The fiber was then affixed to a goniometer head and the goniometer mounted on the Syntex (Nicolet) $P2_1$ diffractometer. Cell parameters were determined from least-squares fit of 23 centered reflections (2θ = 3.92–19.55°). The monitoring of two strong reflections over the data collection time indicated that there was no appreciable decomposition of the crystal. The intensity data for (NMP)Zn^{II}TDCPP·2NMP were collected in the triclinic space group $P\bar{1}$ (No. 2) with the cell parameters given in Table I. The data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by conventional heavy-atom/Patterson methods, and all non-hydrogen atoms were refined anisotropically. Blocked-cascade least-squares refinement of 4532 unique reflections ($F_o > 2.5\sigma(F_o)$), 3 < 2θ < 40°, resulted in final residuals R and R_w given in Table I. Other crystal, data collection, and refinement parameters are summarized in Table I. Scattering factors used for both structural determinations were those for neutral atoms.[20] Final positional and thermal parameters for (NMP)Zn^{II}TDCPP·2NMP are given in Table II.

Table I. Crystal, Data Collection, and Refinement Parameters for (*N*-Methylpyrrolidinone)[tetrakis(2,6-dichlorophenyl)porphinato]-zinc(II)–Bis(*N*-methylpyrrolidinone) (**1**·3NMP) and Bis[(*meso*-2,6-dichlorophenyl)-5-(*o*,*o*′-dichlorobenzyl)dipyrromethene]zinc(II) (**2**)

	1·3NMP	**2**
	A. Crystal Data	
formula	$C_{59}H_{47}Cl_8N_7O_3Zn$	$C_{51}H_{34}Cl_8N_4Zn$
fw	1243.00	1051.84
space group	$\bar{P}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	11.470 (9)	10.532 (5)
b, Å	13.155 (7)	15.394 (6)
c, Å	19.894 (10)	16.224 (4)
α, deg	84.25 (4)	70.01 (3)
β, deg	79.00 (5)	76.47 (3)
γ, deg	75.59 (6)	84.28 (3)
V, Å^3	2849.3 (3.3)	2402.8 (1.6)
Z	2	2
D_{calcd}, g cm^{-3}	1.45	1.45
D_{exptl}, g cm^{-3}	...	1.42 (2)
crystal dimens, mm	0.20 × 0.42 × 0.38	0.46 × 0.4 × 0.2
cryst color	bright purple	orange
μ_{calcd}, cm^{-1}	8.68	10.1
	B. Data Collection	
diffractometer	Syntex (Nicolet) $P2_1$	
radiation (monochromatic) (λ, Å)	Mo Kα (0.71069)	
R(merge), R(sigma)	0.0053, 0.0338	0.0067, 0.0403
tot. no. of reflcns	5734	6817
no. of unique reflcns ($F_o > 2.5\sigma(F_o)$)	4532	5124
scan method	ω (Wyckoff)	
2θ range, deg	3–40	3–45
scan speed, deg min^{-1}	3.91–14.65	5.86–14.65
bkgd/scan time	1	1
reflcns measd	$+h,\pm k,\pm l$	$+h,\pm k,\pm l$
temp, °C	20	20
	C. Refinement	
abs cor	none	semiempirical (ψ scan)
max, min transmission		0.901, 0.748
max resid electron density, e Å^{-3}	0.59	0.75 (1.34 Å from C(5A))
R^a	0.0467	0.0683
$R_w{}^b$	0.0428	0.0713
GOF^c	1.723	1.622

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] GOF (goodness of fit) = $[\sum w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$ where n_o is the number of observations, n_v is the number of parameters, and $w^{-1} = (\sigma^2(F) + 0.0002F^2)$ and $w^{-1} = (\sigma^2(F) + 0.0012F^2)$ for **1**·3NMP and **2**, respectively.

Crystallographic Data Structure Solution for 2. Diffraction-quality crystals of **2** were grown by allowing a toluene solution saturated in analytically pure **2** to concentrate by slow evaporation at 25 °C. A representative crystal of the orange-yellow modification with dimensions 0.46 × 0.4 × 0.2 mm was attached to a glass fiber with epoxy cement. The fiber was then placed on the goniometer. The cell parameters given

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(20) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, **1974**; Vol. IV, Table 2.2B.

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å × 10^3) for **1·3NMP**

atom	*x*	*y*	*z*	U_{eq}[a]	atom	*x*	*y*	*z*	U_{eq}[a]
Zn	6803 (1)	7457 (1)	2511 (1)	34 (1)	C(28)	9702 (4)	6809 (4)	−163 (2)	41 (2)
N(1)	6887 (3)	8465 (3)	1643 (2)	35 (1)	C(29)	10483 (4)	6757 (4)	−785 (2)	51 (2)
N(2)	8549 (3)	6655 (3)	2149 (2)	32 (1)	C(30)	11233 (5)	7438 (4)	−941 (3)	59 (3)
N(3)	6973 (3)	6707 (3)	3468 (2)	34 (1)	C(31)	11230 (4)	8168 (4)	−499 (3)	53 (2)
N(4)	5371 (3)	8575 (3)	2987 (2)	34 (1)	C(32)	10461 (4)	8189 (4)	130 (2)	40 (2)
N(1a)	4108 (7)	5949 (7)	2722 (3)	185 (5)	C(33)	9788 (4)	4487 (3)	3403 (2)	35 (2)
C(2a)	5023 (5)	6077 (5)	2528 (3)	87 (3)	C(34)	9934 (4)	3492 (4)	3176 (2)	44 (2)
C(3a)	5631 (7)	4761 (6)	2860 (4)	127 (4)	C(35)	10750 (5)	2624 (4)	3385 (3)	59 (2)
C(4a)	4656 (11)	4474 (9)	3185 (6)	249 (9)	C(36)	11460 (5)	2738 (4)	3838 (3)	70 (3)
C(5a)	3369 (6)	5336 (6)	2995 (4)	136 (5)	C(37)	11360 (5)	3695 (4)	4085 (3)	60 (2)
C(6a)	3143 (9)	6987 (7)	2523 (4)	223 (6)	C(38)	10541 (4)	4560 (4)	3862 (2)	43 (2)
O(7a)	5765 (4)	6505 (3)	2249 (2)	74 (2)	C(39)	4380 (4)	7846 (3)	4849 (2)	38 (2)
C(1)	6016 (4)	9345 (3)	1509 (2)	37 (2)	C(40)	3283 (5)	7545 (4)	5053 (3)	54 (2)
C(2)	6312 (5)	9731 (4)	814 (2)	48 (2)	C(41)	2606 (5)	7714 (5)	5702 (3)	82 (3)
C(3)	7366 (5)	9093 (4)	535 (3)	47 (2)	C(42)	3039 (7)	8191 (5)	6155 (3)	90 (3)
C(4)	7743 (4)	8313 (4)	1061 (2)	36 (2)	C(43)	4112 (7)	8501 (5)	5977 (3)	80 (3)
C(5)	8822 (4)	7539 (3)	994 (2)	34 (2)	C(44)	4764 (5)	8320 (4)	5327 (2)	53 (2)
C(6)	9215 (4)	6789 (3)	1508 (2)	34 (2)	Cl(1)	2755 (2)	9707 (1)	1446 (1)	98 (1)
C(7)	10372 (4)	6034 (4)	1446 (3)	41 (2)	Cl(2)	5837 (2)	11809 (1)	2080 (1)	88 (1)
C(8)	10394 (4)	5463 (4)	2040 (2)	40 (2)	Cl(3)	8716 (1)	5975 (1)	13 (1)	59 (1)
C(9)	9249 (4)	5845 (3)	2483 (2)	33 (2)	Cl(4)	10502 (1)	9070 (1)	715 (1)	66 (1)
C(10)	8913 (4)	5427 (3)	3150 (2)	34 (2)	Cl(5)	9020 (1)	3316 (1)	2614 (1)	65 (1)
C(11)	7846 (4)	5822 (3)	3603 (2)	33 (2)	Cl(6)	10438 (1)	5767 (1)	4173 (1)	63 (1)
C(12)	7497 (4)	5398 (4)	4288 (2)	44 (2)	Cl(7)	2754 (2)	6939 (1)	4485 (1)	87 (1)
C(13)	6450 (4)	6042 (4)	4563 (2)	44 (2)	Cl(8)	6119 (2)	8723 (1)	5115 (1)	85 (1)
C(14)	6122 (4)	6866 (4)	4052 (2)	38 (2)	N(1b)	5222 (4)	5849 (3)	715 (2)	71 (2)
C(15)	5112 (4)	7719 (3)	4147 (2)	35 (2)	C(2b)	4048 (5)	5821 (4)	863 (3)	75 (3)
C(16)	4765 (4)	8505 (3)	3648 (2)	33 (2)	C(3b)	3357 (6)	6879 (5)	610 (4)	99 (4)
C(17)	3715 (4)	9362 (4)	3751 (3)	45 (2)	C(4b)	4265 (7)	7456 (5)	250 (4)	123 (4)
C(18)	3693 (4)	9947 (4)	3153 (3)	45 (2)	C(5b)	5494 (7)	6809 (5)	394 (4)	101 (4)
C(19)	4728 (4)	9457 (3)	2671 (2)	36 (2)	C(6b)	6181 (6)	4965 (5)	885 (4)	103 (3)
C(20)	5022 (4)	9808 (3)	1989 (2)	37 (2)	O(7b)	3610 (4)	5114 (3)	1144 (3)	119 (3)
C(21)	4222 (4)	10830 (4)	1767 (2)	41 (2)	N(1c)	−631 (7)	9176 (8)	3684 (9)	427 (12)
C(22)	3142 (5)	10864 (4)	1543 (3)	60 (2)	C(2c)	−46 (7)	9757 (6)	339 (6)	152 (6)
C(23)	2368 (6)	11796 (5)	1387 (3)	85 (3)	C(3c)	−326 (18)	9882 (18)	2612 (8)	445 (18)
C(24)	2657 (6)	12713 (5)	1456 (3)	92 (3)	C(4c)	−1119 (14)	9197 (11)	2787 (9)	287 (12)
C(25)	3721 (5)	12736 (4)	1657 (3)	73 (3)	C(5c)	−1309 (9)	8659 (7)	3506 (5)	182 (6)
C(26)	4487 (5)	11791 (4)	1815 (3)	53 (2)	C(6c)	−582 (13)	9021 (11)	4338 (7)	343 (13)
C(27)	9669 (4)	7514 (3)	319 (2)	34 (2)	O(7c)	540 (7)	10243 (6)	3517 (6)	289 (7)

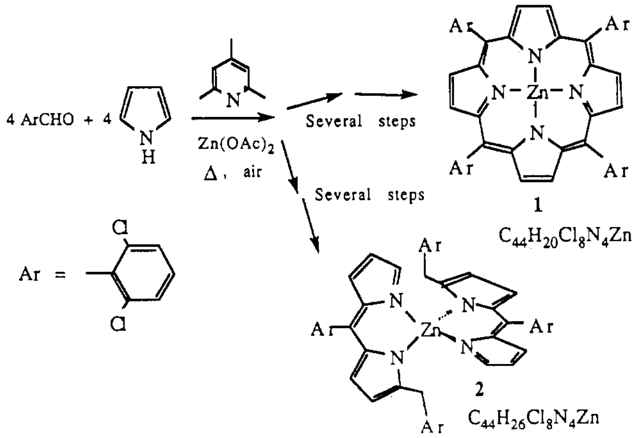
[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

in Table I were determined from 23 standard reflections. The monitoring of several strong reflections indicated that there was no appreciable decomposition of the crystal during data collection. The intensity data for **2**, like those for (NMP)Zn^{II}TDCPP·2NMP, were collected in the triclinic space group $P\bar{1}$ (No. 2). The data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by conventional heavy-atom/Patterson methods. All non-hydrogen atoms were refined anisotropically. Blocked-cascade least-squares refinement of 5124 unique reflections ($F_o > 2.5\sigma(F_o)$), 2θ from 3 to 45°, resulted in final residuals *R* and R_w given in Table I. See Table I for other crystal, data collection, and refinement parameters. Final positional and thermal parameters for **2** are given in Table III.

Results and Discussion

Preparation of the Porphyrin, [Tetrakis(2,6-dichlorophenyl)porphinato]zinc(II). In this work, we specifically examine the Rothemund template condensation of pyrrole and 2,6-dichlorobenzaldehyde in 2,4,6-collidine solvent using Zn^{2+} as a template. These reaction conditions produce as much porphyrin product in our hands as any of a number of other reaction conditions. This reaction is a complex multistep redox condensation process that produces the bis(dipyrromethene) complex bis[(*meso*-2,6-dichlorophenyl)-5-(*o*,*o*′-dichlorobenzyl)dipyrromethene]zinc(II) (**2**) as the principal product and the Zn porphyrin [tetrakis(2,6-dichlorophenyl)porphinato]zinc(II), Zn^{II}TDCPP (**1**) (characterized structurally here as its NMP adduct), as the second most abundant product (Scheme I). The spectrophotometric yields of **1** and **2** in the reaction mixture prior to workup are typically in the ranges of 10% and 40%, respectively. Although some chlorin can be produced in Rothemund condensation reactions exposed to the air, appreciable quantities of this and other possible byproducts, such as the porphomethene and dipyrromethane, do not build up under the conditions in Scheme I (see Experimental Section).

Scheme I



Traylor, Dolphin, and Traylor have already pointed out that the use of higher boiling solvents, such as collidine in place of pyridine, substantially increases the yield of the zinc porphyrin.[6a] Monitoring the course of the reaction by UV–visible spectroscopy and examining the production of **1** from isolated, purified **2** under the reaction conditions (vide infra) indicate that the principal route to **1** does not involve **2**.

It is clear from the present study that the quantities of TDCPP^{2-} available from Rothemund template condensation procedures are limited as much by the lack of good workup procedures as by the inherently low yields of these reactions. Both **1** and **2** can be isolated and purified by taking advantage of the different solubilities of the two complexes and the byproducts in toluene and

Table III. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for **2**

atom	x	y	z	U_{eq}[a]
Zn	1498 (1)	1375 (1)	2851 (1)	47 (1)*
N(1)	141 (4)	2209 (3)	3259 (3)	49 (2)*
N(2)	2964 (4)	1919 (3)	3070 (3)	46 (2)*
N(3)	1437 (4)	24 (3)	3346 (3)	43 (2)*
N(4)	1657 (4)	1422 (3)	1593 (3)	50 (2)*
C(1)	−1139 (5)	2270 (4)	3278 (4)	60 (3)*
C(2)	−1719 (5)	3049 (4)	3464 (4)	60 (3)*
C(3)	−749 (5)	3505 (4)	3557 (4)	54 (2)*
C(4)	431 (5)	2984 (3)	3436 (3)	46 (2)*
C(5)	1662 (5)	3183 (3)	3483 (3)	46 (2)*
C(6)	2830 (5)	2691 (3)	3347 (3)	45 (2)*
C(7)	4074 (5)	2889 (4)	3420 (4)	68 (3)*
C(8)	4933 (6)	2252 (4)	3205 (5)	73 (3)*
C(9)	4224 (5)	1663 (4)	2971 (4)	55 (3)*
C(10)	4735 (6)	891 (4)	2626 (5)	70 (3)*
C(11)	1253 (5)	−536 (4)	4202 (4)	54 (3)*
C(12)	1413 (6)	−1467 (4)	4271 (4)	62 (3)*
C(13)	1729 (6)	−1478 (4)	3414 (4)	59 (3)*
C(14)	1758 (5)	−561 (3)	2831 (3)	46 (2)*
C(15)	2004 (5)	−250 (3)	1896 (3)	48 (2)*
C(16)	1936 (5)	638 (4)	1321 (4)	50 (2)*
C(17)	2091 (7)	938 (5)	373 (4)	79 (3)*
C(18)	1895 (7)	1871 (4)	96 (4)	85 (3)*
C(19)	1634 (6)	2142 (4)	860 (4)	64 (3)*
C(20)	1350 (7)	3098 (4)	904 (5)	84 (3)*
C(21)	2013 (9)	3820 (5)	97 (5)	109 (4)*
C(22)	1398 (17)	4355 (7)	−596 (8)	220 (9)*
C(23)	2034 (25)	5069 (9)	−1282 (10)	360 (16)*
C(24)	3348 (22)	5239 (9)	−1298 (8)	297 (12)*
C(25)	4014 (16)	4698 (9)	−692 (7)	212 (9)*
C(26)	3388 (13)	3991 (6)	22 (5)	150 (6)*
C(27)	2408 (6)	−992 (4)	1463 (4)	61 (3)*
C(28)	1521 (7)	−1485 (5)	1309 (5)	82 (3)*
C(29)	1891 (8)	−2177 (5)	944 (5)	107 (4)*
C(30)	3207 (9)	−2376 (5)	716 (5)	112 (4)*
C(31)	4103 (9)	−1888 (5)	831 (5)	102 (4)*
C(32)	3714 (7)	−1217 (4)	1200 (4)	80 (3)*
C(33)	1747 (5)	4042 (4)	3716 (4)	54 (3)*
C(34)	2021 (6)	4895 (4)	3069 (4)	67 (3)*
C(35)	2090 (7)	5683 (4)	3263 (5)	89 (4)*
C(36)	1915 (7)	5622 (5)	4145 (6)	101 (5)*
C(37)	1669 (7)	4796 (5)	4827 (5)	83 (4)*
C(38)	1570 (6)	4017 (4)	4600 (4)	64 (3)*
C(39)	5940 (5)	409 (4)	2953 (4)	65 (3)*
C(40)	7182 (7)	640 (5)	2474 (5)	81 (4)*
C(41)	8293 (6)	204 (5)	2768 (6)	88 (4)*
C(42)	8130 (7)	−488 (5)	3575 (7)	100 (5)*
C(43)	6929 (7)	−751 (5)	4099 (6)	101 (4)*
C(44)	5840 (6)	−292 (5)	3755 (5)	88 (4)*
Cl(1)	−131 (6)	4128 (3)	−570 (4)	315 (5)*
Cl(2)	4163 (2)	3317 (2)	819 (2)	129 (1)*
Cl(3)	−125 (2)	−1231 (2)	1594 (2)	162 (2)*
Cl(4)	4889 (2)	−608 (2)	1351 (2)	128 (1)*
Cl(5)	2271 (2)	4976 (1)	1943 (1)	103 (1)*
Cl(6)	1215 (2)	2978 (1)	5462 (1)	94 (1)*
Cl(7)	7436 (3)	1516 (2)	1462 (2)	157 (2)*
Cl(8)	4309 (2)	−652 (2)	4427 (2)	137 (1)*
C(1a)	5830 (30)	7552 (14)	3008 (15)	224 (4)
C(2a)	5053 (30)	6904 (14)	2946 (15)	224 (4)
C(3a)	5631 (30)	6142 (14)	2711 (15)	224 (4)
C(4a)	6987 (30)	6028 (14)	2539 (15)	224 (4)
C(5a)	7765 (30)	6676 (14)	2601 (15)	224 (4)
C(6a)	7186 (30)	7438 (14)	2835 (15)	224 (4)
C(1b)	5000	5000	5000	224 (4)
C(2b)	4603 (32)	5829 (26)	5170 (24)	224 (4)
C(3b)	4774 (34)	6528 (27)	4547 (28)	224 (4)
C(4b)	5292 (36)	7072 (26)	3845 (27)	224 (4)
C(5b)	5908 (34)	6216 (27)	3579 (23)	224 (4)
C(6b)	5706 (33)	5320 (27)	3936 (24)	224 (4)

[a] Asterisks indicate equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

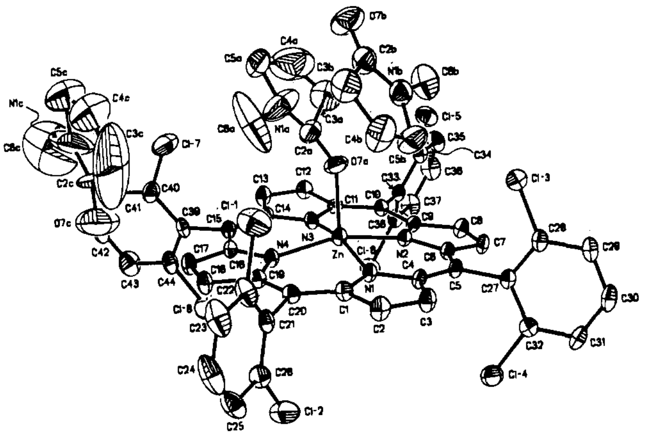


Figure 1. Combined ORTEP and atom-numbering diagram for **1** as its NMP complex, $(NMP)Zn^{II}TDCPP{\cdot}2NMP$. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are at the 30% probability level.

Table IV. Selected Bond Lengths for **1**·3NMP (Å)

Zn–N(1)	2.071 (4)	Zn–N(2)	2.048 (3)
Zn–N(3)	2.075 (4)	Zn–N(4)	2.059 (3)
Zn–O(7a)	2.089 (5)	N(1)–C(1)	1.368 (5)
N(1)–C(4)	1.364 (5)	N(2)–C(6)	1.368 (5)
N(2)–C(9)	1.363 (5)	N(3)–C(11)	1.374 (5)
N(3)–C(14)	1.365 (5)	N(4)–C(16)	1.371 (5)
N(4)–C(19)	1.375 (5)	N(1a)–C(2a)	1.095 (10)
N(1a)–C(5a)	1.320 (12)	N(1a)–C(6a)	1.598 (11)
C(2a)–C(3a)	1.808 (7)	C(2a)–O(7a)	1.161 (8)
C(3a)–C(4a)	1.303 (15)	C(4a)–C(5a)	1.703 (13)
C(1)–C(2)	1.433 (6)	C(1)–C(20)	1.392 (6)
C(2)–C(3)	1.344 (6)	C(3)–C(4)	1.439 (6)
C(4)–C(5)	1.387 (6)	C(5)–C(6)	1.404 (6)
C(5)–C(27)	1.498 (6)	C(6)–C(7)	1.438 (6)
C(7)–C(8)	1.336 (7)	C(8)–C(9)	1.440 (6)
C(9)–C(10)	1.405 (6)	C(10)–C(11)	1.392 (6)
C(10)–C(33)	1.496 (6)	C(11)–C(12)	1.442 (6)
C(12)–C(13)	1.340 (6)	C(13)–C(14)	1.440 (6)
C(14)–C(15)	1.395 (6)	C(15)–C(16)	1.397 (6)
C(15)–C(39)	1.488 (6)	C(16)–C(17)	1.429 (6)
C(17)–C(18)	1.350 (7)	C(18)–C(19)	1.433 (6)
C(19)–C(20)	1.396 (6)	C(20)–C(21)	1.506 (6)
C(22)–Cl(1)	1.725 (7)	C(26)–Cl(2)	1.734 (6)
C(28)–Cl(3)	1.730 (5)	C(32)–Cl(4)	1.738 (5)
C(34)–Cl(5)	1.738 (6)	C(38)–Cl(6)	1.729 (5)
C(40)–Cl(7)	1.721 (6)	C(44)–Cl(8)	1.729 (5)
N(1b)–C(2b)	1.331 (8)	N(1b)–C(5b)	1.434 (8)
N(1b)–C(6b)	1.451 (7)	C(2b)–C(3b)	1.510 (8)
C(2b)–O(7b)	1.205 (8)	C(3b)–C(4b)	1.475 (11)
C(4b)–C(5b)	1.518 (10)	N(1c)–C(2c)	1.175 (14)
N(1c)–C(5c)	1.269 (17)	N(1c)–C(6c)	1.307 (23)
C(2c)–C(3c)	1.638 (21)	C(2c)–O(7c)	1.106 (14)
C(3c)–C(4c)	1.408 (29)	C(4c)–C(5c)	1.534 (19)

the substantially different R_f values for these compounds on regular-phase column chromatography (activated grade I neutral alumina, toluene as the eluant). Reproducible syntheses and workup procedures for **1** and **2** are given in the Experimental Section. The isolated yield of **1** available by these procedures (10% or greater) is substantially higher than the reported yields in the literature for synthesis of the $TDCPP^{2-}$ moiety or other comparably hindered tetraarylporphyrins.

Since only one sterically constrained 5,10,15,20-tetraarylporphyrin or porphyrin complex with substituents larger than hydrogen or fluorine on all the ortho positions of the *meso*-aryl rings had been characterized by crystallography, the tetrakis(2,4,6-trimethoxyphenyl)porphyrin free ligand,[21] we felt that the crystallographic characterization of a metal complex of $TDCPP^{2-}$ was worth some effort. A X-ray crystal structure of such a complex would allow the depth of the pocket defined by the *o*-chlorine atoms and the presence of any unusual structural features associated with this hindered porphyrin ligand to be determined. A derivative of **1** was finally found that produced high-quality single crystals, the five-coordinate NMP derivative

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(21) Gold, K. W.; Hodgson, D. J.; Gold, A.; Savrin, J. E.; Toney, G. E. *J. Chem. Soc., Chem. Commun.* **1985**, 563.

Table V. Selected Bond Angles for **1**·3NMP (deg)

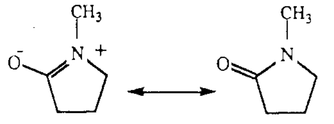
N(1)–Zn–N(2)	88.8 (1)	N(1)–Zn–N(3)	164.5 (2)
N(2)–Zn–N(3)	88.8 (1)	N(1)–Zn–N(4)	88.9 (1)
N(2)–Zn–N(4)	160.6 (2)	N(3)–Zn–N(4)	88.2 (1)
N(1)–Zn–O(7a)	100.2 (2)	N(2)–Zn–O(7a)	102.0 (2)
N(3)–Zn–O(7a)	95.3 (2)	N(4)–Zn–O(7a)	97.4 (2)
Zn–N(1)–C(1)	126.5 (3)	Zn–N(1)–C(4)	126.6 (3)
C(1)–N(1)–C(4)	106.5 (3)	Zn–N(2)–C(6)	126.6 (3)
Zn–N(2)–C(9)	126.6 (3)	C(6)–N(2)–C(9)	106.8 (3)
Zn–N(3)–C(11)	126.1 (3)	Zn–N(3)–C(14)	126.3 (3)
C(11)–N(3)–C(14)	106.5 (3)	Zn–N(4)–C(16)	126.6 (3)
Zn–N(4)–C(19)	125.9 (3)	C(16)–N(4)–C(19)	106.9 (3)
C(2a)–N(1a)–C(5a)	151.5 (9)	C(2a)–N(1a)–C(6a)	107.5 (8)
C(5a)–N(1a)–C(6a)	100.6 (7)	N(1a)–C(2a)–C(3a)	87.8 (7)
N(1a)–C(2a)–O(7a)	158.2 (8)	C(3a)–C(2a)–O(7a)	113.9 (5)
C(2a)–C(3a)–C(4a)	102.9 (7)	C(3a)–C(4a)–C(5a)	110.8 (8)
N(1a)–C(5a)–C(4a)	85.2 (7)	Zn–O(7a)–C(2a)	137.1 (4)
N(1)–C(1)–C(2)	109.7 (4)	N(1)–C(1)–C(20)	124.6 (4)
C(2)–C(1)–C(20)	125.7 (4)	C(1)–C(2)–C(3)	107.1 (4)
C(2)–C(3)–C(4)	107.1 (4)	N(1)–C(4)–C(3)	109.5 (4)
N(1)–C(4)–C(5)	125.0 (4)	C(3)–C(4)–C(5)	125.5 (4)
C(4)–C(5)–C(6)	126.1 (4)	C(4)–C(5)–C(27)	117.3 (4)
C(6)–C(5)–C(27)	116.6 (4)	N(2)–C(6)–C(5)	125.4 (4)
N(2)–C(6)–C(7)	109.1 (4)	C(5)–C(6)–C(7)	125.5 (4)
C(6)–C(7)–C(8)	107.3 (4)	C(7)–C(8)–C(9)	107.6 (4)
N(2)–C(9)–C(8)	109.3 (4)	N(2)–C(9)–C(10)	126.0 (4)
C(8)–C(9)–C(10)	124.7 (4)	C(9)–C(10)–C(11)	125.8 (4)
C(9)–C(10)–C(33)	117.3 (4)	C(11)–C(10)–C(33)	116.9 (4)
N(3)–C(11)–C(10)	124.6 (4)	N(3)–C(11)–C(12)	109.4 (3)
C(10)–C(11)–C(12)	126.0 (4)	C(11)–C(12)–C(13)	107.1 (4)
C(12)–C(13)–C(14)	107.4 (4)	N(3)–C(14)–C(13)	109.6 (3)
N(3)–C(14)–C(15)	125.1 (4)	C(13)–C(14)–C(15)	125.3 (4)
C(14)–C(15)–C(16)	125.7 (4)	C(14)–C(15)–C(39)	117.6 (4)
C(16)–C(15)–C(39)	116.6 (3)	N(4)–C(16)–C(15)	125.6 (3)
N(4)–C(16)–C(17)	109.4 (4)	C(15)–C(16)–C(17)	124.9 (4)
C(16)–C(17)–C(18)	107.2 (4)	C(17)–C(18)–C(19)	107.6 (4)
N(4)–C(19)–C(18)	108.9 (4)	N(4)–C(19)–C(20)	125.6 (4)
C(18)–C(19)–C(20)	125.5 (4)	C(1)–C(20)–C(19)	126.7 (4)
C(1)–C(20)–C(21)	117.1 (4)	C(19)–C(20)–C(21)	116.1 (3)
C(2b)–N(1b)–C(5b)	116.8 (5)	C(2b)–N(1b)–C(6b)	121.9 (5)
C(5b)–N(1b)–C(6b)	121.4 (5)	N(1b)–C(2b)–C(3b)	105.5 (5)
N(1b)–C(2b)–O(7b)	128.2 (5)	C(3b)–C(2b)–O(7b)	126.3 (6)
C(2b)–C(3b)–C(4b)	107.5 (5)	C(3b)–C(4b)–C(5b)	105.8 (6)
N(1b)–C(5b)–C(4b)	103.4 (6)	C(2c)–N(1c)–C(5c)	134.8 (18)
C(2c)–N(1c)–C(6c)	113.5 (15)	C(5c)–N(1c)–C(6c)	111.7 (12)
N(1c)–C(2c)–C(3c)	104.2 (14)	N(1c)–C(2c)–O(7c)	138.7 (16)
C(3c)–C(2c)–O(7c)	116.9 (13)	C(2c)–C(3c)–C(4c)	90.8 (12)
C(3c)–C(4c)–C(5c)	121.5 (15)	N(1c)–C(5c)–C(4c)	88.5 (12)

as its NMP solvate, (NMP)Zn$^{\mathrm{II}}$TDCPP·2NMP. A combined ORTEP and atom-numbering diagram for this complex is shown in Figure 1, and selected bond lengths and angles are summarized in Tables IV and V, respectively. The maximum deviations of various atoms from the mean plane defined by the 24-atom porphyrin core are 0.21 Å (for C(8)), 0.20 Å (for C(7)), 0.16 Å (for C(17) and C(18)), −0.15 Å (for C(12)), −0.12 Å (for C(13)), and −0.11 Å (for C(3)). Negative deviations are toward the side of the porphyrin containing the axial NMP. The metalloporphyrin ring exhibits a modest degree of quasi-S_4 ruffling.

The axial NMP is ligated through the carbonyl oxygen in accordance with the ground-state electronic properties of the ambident amide moiety and with the great majority of amide or peptide complexes in the literature.[22,23] The NMP oxygen–Zn bond length, $d_{\mathrm{Zn-O(ax)}}$ = 2.089 (5) Å (ax = axial). This compares to the $d_{\mathrm{Zn-O(ax)}}$ value of 2.06 Å for the (H$_2$O)ZnTPP structure.[24] The $d_{\mathrm{Zn-O(ax)}}$ value for the five-coordinate perchlorate complex is 2.079 (8) Å. The larger thermal ellipsoids for the axially ligated NMP (NMP$_{\mathrm{a}}$) relative to those of most of the other non-hydrogen atoms indicate a higher degree of thermal motion for this group than for the rest of the metalloporphyrin. The larger thermal parameters for NMP$_{\mathrm{a}}$ notwithstanding, an examination of the $d_{\mathrm{C=O}}/d_{\mathrm{C=N}}$ ratio for this NMP (1.161 (8) Å/1.095 (10) Å = 1.060) relative to those for the unassociated NMP molecules of crystallization, NMP$_{\mathrm{b}}$ (1.205 (8) Å/1.331(8) Å = 0.905) and NMP$_{\mathrm{c}}$ (1.106 (14) Å/1.175 (14) Å = 0.941), indicates that complexation of NMP$_{\mathrm{a}}$ to the Zn ion stabilizes the zwitterionic form of the amide unit (canonical form A) relative to the neutral form (canonical form B). The oxygen atom of NMP$_{\mathrm{a}}$ lies 2.399 and 2.439 Å above the mean N$_4$ and 24-atom planes of the porphyrin, respectively, and the zinc atom is displaced 0.36 Å toward the axial NMP from the mean N$_4$ plane. The latter distance is compared to the analogous displacement from the mean N$_4$ planes in (H$_2$O)Zn$^{\mathrm{II}}$TPP (0.33 Å, estimated)[24-26] and (py)-Zn$^{\mathrm{II}}$TpyP (0.33 Å).[27] The projection of the O(7a)–C(2a) bond of the ligated NMP$_{\mathrm{a}}$ onto the 24-atom plane of the metalloporphyrin nearly bisects the N(3)–Zn–N(4) angle of the porphyrin. Beyond this, there appears to be little structural or electronic rationale for the observed orientation of the atoms in NMP$_{\mathrm{a}}$ relative to that of the porphyrin ring atoms. The Zn–porphyrin nitrogen distances, $d_{\mathrm{Zn-N(por)}}$, average 2.063 Å and are unexceptional for a zinc *meso*-tetraarylporphyrin.

Table VI. Selected Bond Lengths for **2** (Å)

Zn–N(1)	1.976 (4)	Zn–N(2)	1.983 (5)
Zn–N(3)	1.958 (4)	Zn–N(4)	1.984 (5)
N(1)–C(1)	1.336 (7)	N(1)–C(4)	1.395 (8)
N(2)–C(6)	1.391 (8)	N(2)–C(9)	1.334 (6)
N(3)–C(11)	1.341 (6)	N(3)–C(14)	1.395 (8)
N(4)–C(16)	1.404 (8)	N(4)–C(19)	1.323 (6)
C(1)–C(2)	1.386 (9)	C(2)–C(3)	1.358 (9)
C(3)–C(4)	1.422 (7)	C(4)–C(5)	1.387 (8)
C(5)–C(6)	1.391 (7)	C(5)–C(33)	1.510 (9)
C(6)–C(7)	1.415 (9)	C(7)–C(8)	1.345 (9)
C(8)–C(9)	1.425 (10)	C(9)–C(10)	1.484 (10)
C(11)–C(12)	1.397 (9)	C(12)–C(13)	1.357 (9)
C(13)–C(14)	1.405 (7)	C(14)–C(15)	1.393 (7)
C(15)–C(16)	1.372 (7)	C(15)–C(27)	1.514 (9)
C(16)–C(17)	1.420 (9)	C(17)–C(18)	1.360 (9)
C(18)–C(19)	1.400 (10)	C(19)–C(20)	1.495 (9)



A B

The size of the pocket constituted by the four chlorines on each side of the porphyrin ring can be defined by examination of a few distances. The minimum distance between chlorines on adjacent phenyl rings and on the same side of the porphyrin ring is $d_{\mathrm{Cl(6)\cdots Cl(8)}}$ = 5.613 Å, while the maximum such distance is $d_{\mathrm{Cl(5)\cdots Cl(7)}}$ = 8.032 Å. The distances to chlorines on opposite phenyl rings but on the same side of the porphyrin ring are $d_{\mathrm{Cl(4)\cdots Cl(8)}}$ = 9.254 Å and $d_{\mathrm{Cl(3)\cdots Cl(7)}}$ = 10.11 Å. The depth of the cavity averages approximately 2.6 Å. The ^{1}H NMR spectrum for (NMP)Zn$^{\mathrm{II}}$TDCPP·2NMP, in CDCl$_3$ (see Experimental Section) is that expected for a diamagnetic metalloporphyrin of the structure illustrated in Figure 1[28] and indicates that the NMP moieties are in rapid exchange on the ^{1}H NMR time scale at 25 °C.

Isolation of the dipyrromethene moieties derived from the starting 2,6-dichlorobenzaldehyde and pyrrole in the form of complex **2** was not expected. Normally, dipyrromethenes, as well as dipyrromethanes, pyrromethenes, and some of the other possible

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[22] (a) Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 385. (b) Rao, Ch. P.; Rao, A. M.; Rao, C. N. R. *Inorg. Chem.* **1984**, *23*, 2080. See also references cited in each.

[23] Hill, C. L.; Williamson, M. M. *Inorg. Chem.* **1985**, *24*, 2836.

[24] The original report of $d_{\mathrm{Zn-O(ax)}}$ = 2.20 (6) Å by Hoard and co-workers was for a disordered (H$_2$O)ZnTPP structure.[25] Subsequently, Scheidt in his definitive review on metalloporphyrin stereochemistry[26] estimated a corrected value of $d_{\mathrm{Zn-O(ax)}}$ = 2.06 Å.

[25] Glick, M. D.; Cohen, G. H.; Hoard, J. L. *J. Am. Chem. Soc.* **1967**, *89*, 1996.

[26] Scheidt, W. R. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, **1978**; Vol. III, Part A, Chapter 10, p 482.

[27] Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 3761.

[28] Janson, T. R.; Katz, J. J. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, **1979**; Vol. IV, Part B, Chapter 1.

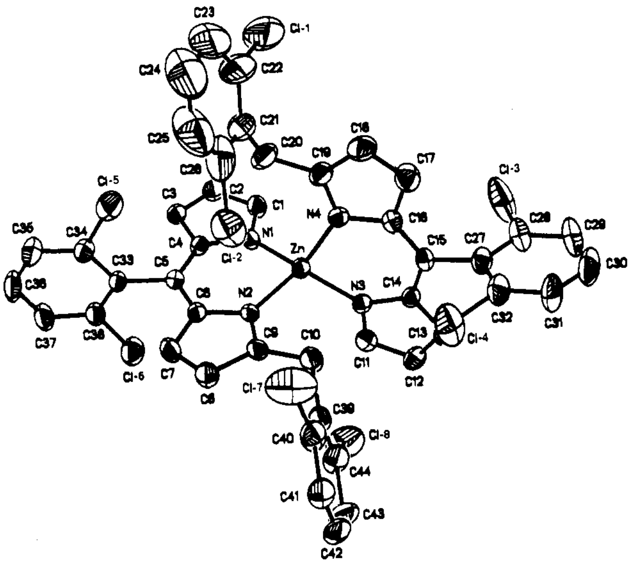


Figure 2. Combined ORTEP and atom-numbering diagram for **2**. Hydrogen atoms and toluene molecules of crystallization are omitted for clarity, and thermal ellipsoids are at the 30% probability level.

Table VII. Selected Bond Angles for **2** (deg)

N(1)–Zn–N(2)	95.1 (2)	N(1)–Zn–N(3)	123.9 (2)
N(2)–Zn–N(3)	114.6 (2)	N(1)–Zn–N(4)	115.0 (2)
N(2)–Zn–N(4)	115.3 (2)	N(3)–Zn–N(4)	94.5 (2)
Zn–N(1)–C(1)	130.0 (5)	Zn–N(1)–C(4)	123.0 (3)
C(1)–N(1)–C(4)	106.1 (5)	Zn–N(2)–C(6)	123.7 (3)
Zn–N(2)–C(9)	129.1 (4)	C(6)–N(2)–C(9)	107.2 (5)
Zn–N(3)–C(11)	129.9 (4)	Zn–N(3)–C(14)	124.3 (3)
C(11)–N(3)–C(14)	105.4 (4)	Zn–N(4)–C(16)	123.0 (3)
Zn–N(4)–C(19)	129.8 (4)	C(16)–N(4)–C(19)	106.9 (5)
N(1)–C(1)–C(2)	112.2 (6)	C(1)–C(2)–C(3)	106.3 (5)
C(2)–C(3)–C(4)	107.8 (5)	N(1)–C(4)–C(3)	107.6 (5)
N(1)–C(4)–C(5)	124.7 (5)	C(3)–C(4)–C(5)	127.7 (6)
C(4)–C(5)–C(6)	128.4 (6)	N(2)–C(6)–C(5)	124.1 (5)
N(2)–C(6)–C(7)	108.0 (5)	C(5)–C(6)–C(7)	127.8 (6)
C(6)–C(7)–C(8)	107.9 (6)	C(7)–C(8)–C(9)	106.8 (6)
N(2)–C(9)–C(8)	110.0 (5)	N(2)–C(9)–C(10)	121.8 (6)
C(8)–C(9)–C(10)	128.2 (5)	N(3)–C(11)–C(12)	112.2 (6)
C(11)–C(12)–C(13)	105.7 (5)	C(12)–C(13)–C(14)	108.3 (5)
N(3)–C(14)–C(13)	108.4 (5)	N(3)–C(14)–C(15)	123.6 (4)
C(13)–C(14)–C(15)	127.9 (6)	C(14)–C(15)–C(16)	128.5 (6)
N(4)–C(16)–C(15)	124.3 (5)	N(4)–C(16)–C(17)	107.7 (5)
C(15)–C(16)–C(17)	127.9 (6)	C(16)–C(17)–C(18)	107.1 (7)
C(17)–C(18)–C(19)	107.3 (6)	N(4)–C(19)–C(18)	111.1 (5)
N(4)–C(19)–C(20)	121.4 (6)	C(18)–C(19)–C(20)	127.5 (5)

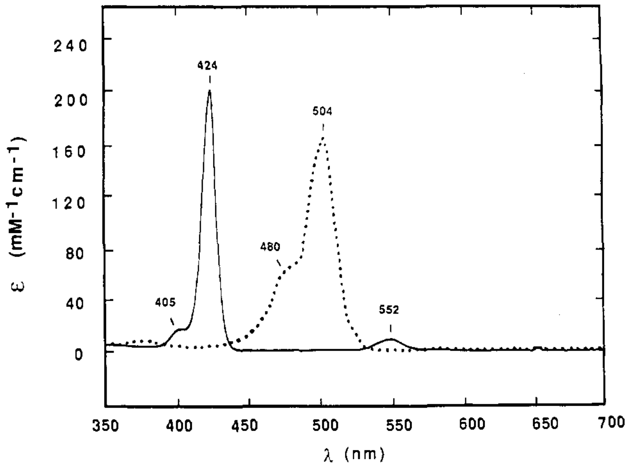
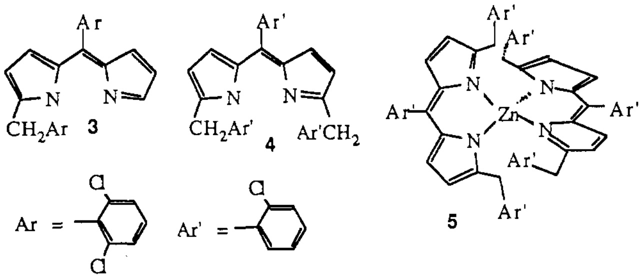


Figure 3. Electronic absorption spectra (λ = 350–700 nm) of **1** and **2**. Both solutions were recorded as 0.1 mM solutions in toluene at 25 °C.

heterocyclic intermediates produced under conditions of the Rothemund condensation, would not be expected to be particularly stable with respect to either further condensation or redox processes followed by further condensation, certainly not under the conditions of the principal reaction examined here (see Scheme I and Experimental Section).[18,29] Clearly the bidentate coordination of the dipyrromethene units to the Zn^{2+} ion in **2** stabilizes these units with respect to subsequent oxidation and/or condensation processes. Several structural features of **2** are apparent from the combined ORTEP and atom-numbering diagram for the complex given in Figure 2 and from the selected bond lengths and angles given in Tables VI and VII, respectively. The bidentate ligands are quite planar. The maximum deviation from the mean plane defined by the atoms Zn^{2+}, N(1), C(1)–C(9), and N(2) in the case of one ligand is 0.08 Å (for Zn^{2+}), while the maximum deviation from the mean plane defined by the atoms Zn^{2+}, N(3), C(11)–C(19), and N(4) in the case of the other ligand is 0.11 Å (for C(15)) and 0.16 Å (for Zn^{2+}). The planarity of these groups and the C(4)–C(5), C(5)–C(6), C(14)–C(15), and C(15)–C(16) distances (Table VI) confirm that they are indeed the conjugated dipyrromethene groups, and not the saturated dipyrromethane groups. The ^1H NMR, ^{13}C NMR, infrared, UV–visible, and mass spectral data all support the structure for **2** shown in Figure 2, and the NMR data suggest strongly that this structure persists in solution (see Experimental Section). The quantitative electronic absorption spectra of **1** and **2** are shown in Figure 3. The more extensively conjugated chromophore of the porphyrin ligand **1** relative to the dipyrromethene ligands in **2** is directly reflected in the relative molar extinction coefficients for the two compounds at λ_{max} (205 000 M^{-1} cm^{-1} for **1** versus 164 000 M^{-1} cm^{-1} for **2**). Interestingly, the molar extinction coefficient of the Soret band of the metalloporphyrin increases dramatically upon axial ligation by NMP.

Initially, it was surprising that the isolable dipyrromethene produced in these Rothemund condensation reactions was the *meso-* and 5-disubstituted derivative **3** in context with the existing pertinent literature. The most thoroughly investigated Rothemund condensation related to the one addressed in this paper was that in the study of Badger et al. examining the preparation of [*meso*-tetrakis(*o*-chlorophenyl)porphinato]zinc(II) from *o*-chlorobenzaldehyde and pyrrole.[18d] These authors reported that *meso*,5,5′-trisubstituted dipyrromethenes **4** were formed in this reaction and that the related zinc bis(dipyrromethene) complex **5** was a prominent product. The ^1H NMR spectral data (incomplete) and the infrared data given by these authors are compatible with either ligated disubstituted dipyrromethenes such as **3** or trisubstituted dipyrromethenes such as **4**. Although the analytical data reported by these authors for **5** (chlorine to nitrogen ratio of 3 to 2) implicate the presence of **4**, not the di-*o*-chloro analogue of **3**, it is curious that in the reaction we have examined here, the hexachloro analogue of **4** does not accumulate in appreciable yield, while **3** is produced in at least 40% yield based on the reactant 2,6-dichlorobenzaldehyde!



3

4

5

The fact that **2** is the major product of the reaction, and not the dodecachloro analogue of **5**, brings us to the final point to be addressed: specifically, that **2**, *unlike the latter complex*, is relatively well set up to facilitate the final redox cyclization to the metalloporphyrin, **1**. As is readily seen in Scheme I, **2** could, in principle, be converted into **1** by effective removal of six hydrogen atoms ($6H^+ + 6e^-$) coupled with the formation of two

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[29] Paine, J. B., III. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, **1978**; Vol. I.; Part A, Chapter 4.

carbon–carbon bonds. The fact that the positions to be oxidized and activated in **2** with respect to cyclization to **1** are the benzylic carbons of the (2,6-dichlorophenyl)methyl substituents at the 5-position of the dipyrromethene groups suggests that synthetic strategies for converting **2** into **1** would logically be based in large part on the use of selective allylic oxidants. Unfortunately, not only did **2** fail to convert to **1** in reasonable yield under the Rothemund conditions (refluxing freshly distilled 2,4,6-collidine solution exposed to the air) but the use of several allylic oxidants including selenium dioxide or manganese dioxide failed to improve the quantity of metalloporphyrin produced. Free-radical bromination of **2** followed by refluxing the brominated products in 2,4,6-collidine exposed to the air produced a UV–visible chromophore indicative of the presence of **1**. However, subsequent analysis of the products of this reaction demonstrated that they were primarily a mixture of polybrominated derivatives of **1** and **2**. Independently it was shown that **1** could be brominated by NBS. A note by Traylor and Tsuchiya that has recently appeared reporting the production of a zinc complex of octabrominated TDCPP upon bromination of Zn^{II}TDCPP by NBS establishes the susceptibility of at least the β-pyrrole hydrogens of **1** to bromination by this reagent under typical free-radical conditions.[15] Inasmuch as the Fe complex of the octabrominated TDCPP appears to be the most oxidatively resistant metalloporphyrin yet prepared, the possible conversion of **2** into the brominated TDCPP derivatives by the procedures given here warrants further attention.

Acknowledgment. This research was supported by the National Science Foundation (Grant No. CHE-8715322).

Registry No. **1**, 100506-72-7; **1**·3NMP, 112816-27-0; **2**·C_7H_8, 100655-02-5; NBS, 128-08-5; 2,6-dichlorobenzaldehyde, 83-38-5; pyrrole, 109-97-7; *meso*-(2,6-dichlorophenyl)-5-(*o,o'*-dichlorobenzyl)dipyrromethene, 112839-60-8.

Supplementary Material Available: For the structure determination of **1**·3NMP, complete table of bond lengths (Table SI), complete table of bond angles (Table SII), and tables of anisotropic temperature factors (Table SIII), hydrogen coordinates and temperature factors (Table SIV), nonbonded distances (Table SV), and torsion angles (Table SVI) (12 pages); a table of observed and calculated structure factors (Table SVII) (27 pages). Ordering information is given on any current masthead page. All the supplementary data for the X-ray crystallographic structure determination of the bis(dipyrromethene) complex of zinc, **2**, have already been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

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Chlorination of Bis(ethylenediamine)cobalt(III) Complexes Containing Chelated N,S-Bound (*R*)-Cysteine and Cysteamine: Novel Oxidative Ring Expansion Reactions

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Exhaustive chlorine oxidation of the sulfur center in the N,S-bonded (*R*)-cysteine and cysteamine complexes $[Co(en)_2(NH_2CH(R)CH_2S)]^{2+}$ leads to a remarkable rearrangement involving an increase in the ring size of the original amino thiolate from five-membered to six-membered, concomitantly with the conversion of S-bonded thiolate to (necessarily) O-bonded sulf*o*nate. For the cysteine derivatives, some linkage isomeric product, $[Co(en)_2(NH_2CH(CH_2SO_3)COO)]^+$, accompanies the formation of the chelated amino sulfonate $[Co(en)_2(NH_2CH(CO_2H)CH_2SO_2O)]^{2+}$. Details of the stereochemistry of these rearrangements are reported and mechanisms proposed. Also reported are studies of H exchange and the hydrolysis and interconversions of linkage isomers, which bear on structural assignments and relative isomer stabilities as well as the mechanisms for base hydrolysis of pentaaminecobalt(III) species.

Introduction

Recent interest in the reactions of coordinated thiols has precipitated several reports on a remarkable range of reactions.[1-9] Metal(III) thiolates can be oxidized to coordinated sulf*e*nate, sulf*i*nate, monothiooxalate, sulf*e*namide, and disulfide with reagents such as hydrogen peroxide, hexaquacobalt(III), neptunium(VI), and acetic anhydride/dimethyl sulfoxide. We report here yet another oxidation, and one that took an unexpected course.

It was anticipated that Cl_2 oxidation of Λ-$[Co(en)_2((R)\text{-cys-}N,S)]^{2+}$ (**1**) in water would follow that documented[1] for H_2O_2 (Figure 1), where the sulf*e*nate **3** and ultimately the sulf*i*nate **4** are formed. Similarly, exhaustive oxidation by Cl_2 was expected to give the sulf*i*nate **4**, the sulfur being protected by the cobalt against conversion through to the sulfonate ((*R*)-cysteic acid). Our initial interest was vested in the specificity of the first oxidation step, which was expected to give a mixture of the sulf*e*nate diastereoisomers (**3a**,**b**).[1] These isomers differ only in the chirality of the (optically stable) sulfur center. The problem is discussed in detail elsewhere,[10] and this article will be largely concerned with the second oxidation step with Cl_2.

Results and Discussion

Chlorine Oxidation of $[Co(en)_2((R)\text{-cys-}N,S)]^{2+}$. Controlled oxidation of **1** in H_2O using *N*-chloro- or *N*-bromosuccinimide (1 equiv) as the source of X^+ gave, as anticipated, the stable chiral sulfenate **3** (Figure 1), the isomer ratio being much higher (>20/1) than that found for H_2O_2 (2.3/1).[1] However, excess Cl_2 rapidly (ca. 5 s, 20 °C) gave a pink solution, rather than yellow-brown **4**, from which two products were readily separated by ion-exchange chromatography on Dowex resin using HCl as the eluant. The first band was an orange 1+ ion (**5**, ca. 20%) and the second a pink 2+ ion (**6**, ca. 80%). Each was crystallized readily as a Cl^-, ClO_4^-, $ZnCl_4^{2-}$, or $S_2O_6^{2-}$ salt. Neither product corresponded to the expected sulf*i*nate **4**. The same two products, in the same

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