

probe was measured with a methanol thermometer.<sup>40</sup> Calculations of the self-exchange rate constants were performed as previously described.<sup>15-17</sup> Rate constants are the average of those measured from two different runs, with the values measured on at least two different peaks in each spectrum.

**Sample Preparation and Data Collection.** The Fe(P)Cl complex of interest was dissolved in a mixture of 1.0 mL of acetone-*d*<sub>6</sub> and 0.2 mL of D<sub>2</sub>O. Experiments, particularly on the OEP system, were limited in part by solubility. The acetone/water mixture was used because the compound showed reasonable solubility in this mixture and the reducing agent (aqueous dithionite) could be added without precipitating. Bis-(imidazole) complexes are notably more soluble than the ferric chloride complexes; therefore, it is often helpful to add the 1-MeIm initially to promote dissolution. For Fe(OEC)Cl and Fe(OEiBC)Cl, preparation of solutions was performed in a glovebox, with attempts to minimize light exposure. 1-MeIm (2.0 μL, approximately 50 equiv) was added to each solution. The solution was filtered by using an MSI cameo nylon filter (0.45 μM, Fisher) into a screw-top NMR tube with a septum in the top (Wilmad). The concentrations of the complexes were determined by optical spectroscopy by dilution of an aliquot (5-10 μL of the filtered solution) into 4.0 mL of dichloromethane. Extinction coefficients were as follows:<sup>7</sup> Fe(OEP)Cl, 107 000 at 376.5 nm; [Fe(OEP)(1-MeIm)<sub>2</sub>]Cl, 214 000 at 399.6 nm (this work, based on that for Fe(OEP)Cl); Fe(OEC)Cl, 87 000 at 374.9 nm; Fe(OEiBC)Cl, 51 000 at 377 nm. Solutions for NMR spectroscopy were purged gently with argon for 15 min before the spectra were recorded. At least 15 min was allowed for the sample to reach thermal equilibrium before data were taken. Reduction was achieved by addition of aliquots of degassed aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (saturated Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> in D<sub>2</sub>O diluted 1:5 with D<sub>2</sub>O and degassed with Ar). Samples were reduced a maximum of 10%.

**Error Analysis.** The experimental error in these experiments is larger than usual, due primarily to the fact that individual resonances of the oxidized form could not be matched with the corresponding resonances of the reduced form because neither set of resonances has been assigned. For samples in fast exchange, the resonance frequency of a partially reduced mixture is a linear function of the mole fraction of the reduced component. Therefore, we were able to calculate reasonable resonance frequencies for the reduced species by requiring that all reduced resonances appear within the known total range of resonances in the reduced sample. Under the conditions of these experiments, the procedure gave the resonances of the reduced species within 200 Hz, leading to an uncertainty in the rate constant of 20-40%, depending on the difference in frequencies between the oxidized and reduced resonance for the given proton.

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**Registry No.** [Fe(OEP)(1-MeIm)<sub>2</sub>], 65940-57-0; [Fe(OEC)(1-MeIm)<sub>2</sub>], 78319-98-9; [Fe(OEiBC)(1-MeIm)<sub>2</sub>], 78338-27-9.

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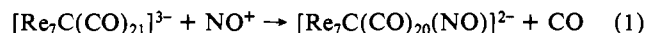
### Electrophilic Substitution of [Re<sub>7</sub>C(CO)<sub>21</sub>]<sup>3-</sup>. Synthesis and Characterization of [N(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[Re<sub>7</sub>C(CO)<sub>20</sub>(NO)]

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Recently, there has been considerable attention focused on reactions of the monocapped octahedral carbide cluster [Re<sub>7</sub>C(CO)<sub>21</sub>]<sup>3-</sup>.<sup>1</sup> This readily available<sup>2</sup> large cluster has been observed

to add both post transition metal<sup>3,4</sup> as well as platinum metal<sup>5,6</sup> electrophiles to the open face opposite the capped face. It is also easily protonated to give [HRe<sub>7</sub>C(CO)<sub>21</sub>]<sup>2-</sup>.<sup>3,4</sup> Beringhelli et al.<sup>7</sup> have recently reported the chemical oxidation of [Re<sub>7</sub>C(CO)<sub>21</sub>]<sup>3-</sup> with C<sub>7</sub>H<sub>7</sub><sup>+</sup>; the radical [Re<sub>7</sub>C(CO)<sub>21</sub>]<sup>2-</sup> is formed first, and then in the presence of carbon monoxide further oxidation to [Re<sub>7</sub>C(CO)<sub>22</sub>]<sup>-</sup> occurs. In this paper we report on the reaction of [Re<sub>7</sub>C(CO)<sub>21</sub>]<sup>3-</sup> with the electrophilic reagent NO<sup>+</sup>, for which we observe net substitution (eq 1).



### Experimental Section

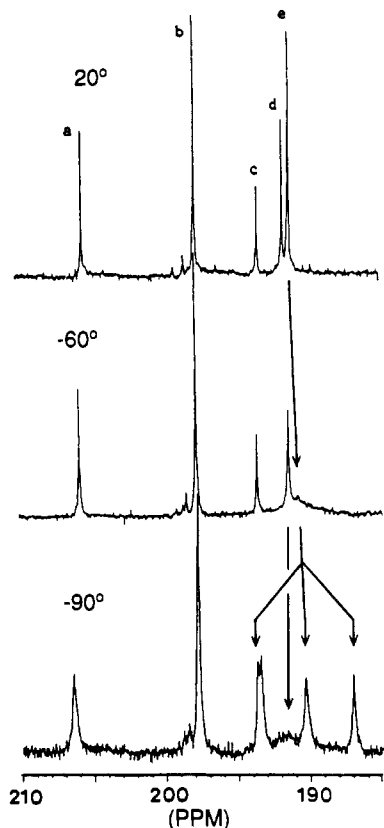
Reactions were conducted under an atmosphere of nitrogen by using standard techniques. Dichloromethane was freshly distilled from calcium hydride. The complex [N(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[Re<sub>7</sub>C(CO)<sub>21</sub>] was prepared as described previously.<sup>2</sup> Infrared spectra were obtained with a Perkin-Elmer 1750 FT-IR spectrometer. <sup>13</sup>C NMR spectra were obtained at 90 MHz with a Nicolet NT-360 NMR spectrometer. Elemental analyses and FAB mass spectra were determined respectively by the Microanalytical Laboratory and the Mass Spectrometry Laboratory of the School of Chemical Sciences. Cyclic voltammetry was performed with a Bioanalytical Systems CV-1B potentiostat and a normal three-electrode cell (Pt working, Ag/AgCl (3 M Cl<sup>-</sup>) reference) at a typical scan rate of 100 mV/s. The dichloromethane solution was 0.1 M in electrolyte ([N(Bu)<sub>4</sub>][PF<sub>6</sub>]) and 0.2 mM in complex. Under our conditions the Cp<sub>2</sub>Fe<sup>0/+</sup> couple (0.2 mM) showed E<sub>1/2</sub> = 0.462 V and ΔE<sub>p</sub> = 74 mV.

**Reaction of [Re<sub>7</sub>C(CO)<sub>21</sub>]<sup>3-</sup> with NOBF<sub>4</sub>.** To a dry 50-mL flask containing [N(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[Re<sub>7</sub>C(CO)<sub>21</sub>] (40 mg, 0.011 mmol) were added dichloromethane (15 mL) and NOBF<sub>4</sub> (2.2 mg, 0.019 mmol). This orange-red mixture turned brownish red after a few minutes of stirring at room temperature. After 2 h the strong IR bands of [Re<sub>7</sub>C(CO)<sub>21</sub>]<sup>3-</sup> at 1978 and 1968 cm<sup>-1</sup> had been replaced by a new, strong band at 1997 cm<sup>-1</sup>, so the reaction mixture was filtered into a second flask. The solution was concentrated to a small volume (ca. 2 mL) by evacuation; then methanol (ca. 10 mL) was carefully layered on top. This mixture was allowed to stand for 2 days at -20 °C. The brown crystals of [N(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[Re<sub>7</sub>C(CO)<sub>20</sub>(NO)] (20 mg, 0.007 mmol, 64%) that formed were separated and dried in vacuo. Anal. Calcd for C<sub>93</sub>H<sub>60</sub>N<sub>3</sub>O<sub>3</sub>P<sub>4</sub>Re<sub>7</sub>: C, 37.45; H, 2.03; N, 1.41; P, 4.15. Found: C, 37.15; H, 2.17; N, 1.31; P, 4.28. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν<sub>CO</sub> 2050 (vw), 1997 (vs), 1988 (s, sh), 1914 (w) cm<sup>-1</sup>; ν<sub>NO</sub> 1693 (w) cm<sup>-1</sup>. IR (KBr): ν<sub>NO</sub> 1697 (w) cm<sup>-1</sup>. Negative-ion FAB mass spectrum (<sup>187</sup>Re): m/z 1911 (Re<sub>7</sub>C(CO)<sub>20</sub>(NO)<sup>-</sup>).

### Results and Discussion

**Synthesis and Characterization of [Re<sub>7</sub>C(CO)<sub>20</sub>(NO)]<sup>2-</sup>.** Treatment of [Re<sub>7</sub>C(CO)<sub>21</sub>]<sup>3-</sup> with ca. 1.5 equiv of NOBF<sub>4</sub> in dichloromethane at room temperature affords [Re<sub>7</sub>C(CO)<sub>20</sub>(NO)]<sup>2-</sup> as the sole product observed by IR spectroscopy. Due to the 1 equiv of [N(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] that is also formed, crystallization by solvent diffusion is necessary to obtain analytically pure product; the isolated yield of [N(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[Re<sub>7</sub>C(CO)<sub>20</sub>(NO)] is then 64%. The formulation follows from elemental analyses and the FAB mass spectrum (M<sup>-</sup>). The presence of a carbide ligand is established by <sup>13</sup>C NMR spectra of [Re<sub>7</sub>\*C(\*CO)<sub>20</sub>(NO)]<sup>2-</sup> (vide infra), which show a resonance at δ 420.9; this position is in good agreement with other Re<sub>n</sub>(μ<sub>6</sub>-C) resonances.<sup>1,2,4,5</sup> The nitrosyl stretching frequency (1697 cm<sup>-1</sup>) is consistent with that expected for a terminal, rather than a bridging, ligand. Analogous electrophilic (oxidative) reactions of NO<sup>+</sup> with anionic carbonyl clusters have been reported;<sup>8</sup> however, neutral clusters are typically substituted by nucleophilic (reductive) reactions with NO<sub>2</sub><sup>-9</sup> or

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**Figure 1.** Carbonyl-region  $^{13}\text{C}$  NMR spectra (90 MHz) for  $[\text{Re}_7\text{C}(\text{CO})_{20}(\text{NO})]^{2-}$ . For assignments see Figure 2.

**Table I.** Carbonyl-Region  $^{13}\text{C}$  NMR Data for Rhenium Carbide Clusters

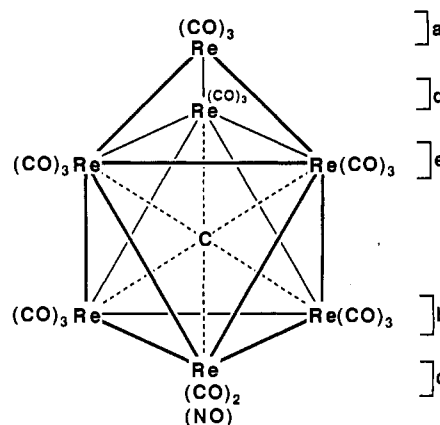
cluster	$\delta(^{13}\text{C})$ (ambient temp)	appearance at low temp	site coord no. <sup>d</sup>	ref
$\text{Re}_7\text{C}(\text{CO})_{20}(\text{NO})^{2-}$	205.6 (3C,a)	one peak	6	this work
	197.8 (6C,b)	one peak	7	
	193.4 (2C,c)	one peak	7	
	191.7 (3C,d)	very broad	8	
	191.2 (6C,e)	three peaks <sup>a</sup>	8	
$\text{Re}_7\text{C}(\text{CO})_{21}^{3-}$	210.2 (3C)	one peak	6	2
	201.1 (9C)	one peak	7	
	195.2 (9C)	broad <sup>b</sup>	8	
$\text{Re}_8\text{C}(\text{CO})_{24}^{2-}$	204.0 (6C)	one peak	6	12
	191.3 (18C)	two peaks <sup>c</sup>	8	

<sup>a</sup> At  $-90^\circ\text{C}$ . <sup>b</sup> At  $-80^\circ\text{C}$ . <sup>c</sup> At  $-100^\circ\text{C}$ . <sup>d</sup> Excluding the  $\mu_6\text{-C}$  ligand.

by complex reactions involving neutral  $\text{NO}$ .<sup>10</sup>

Cyclic voltammetry provides a ready distinction between  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$  and  $[\text{Re}_7\text{C}(\text{CO})_{20}(\text{NO})]^{2-}$ . The former shows two chemically reversible oxidations with  $E_{1/2}$  at 0.08 and 0.42 V vs  $\text{Ag}/\text{AgCl}$ ,<sup>2</sup> whereas the latter shows waves with  $E_{1/2} = 0.62$  V ( $\Delta E_p = 160$  mV,  $i_c/i_a = 0.7$ ) and  $E_{1/2} = 0.96$  V ( $\Delta E_p = 210$  mV,  $i_c/i_a = 0.6$ ).<sup>11</sup> Note that  $[\text{Re}_7\text{C}(\text{CO})_{20}(\text{NO})]^{2-}$  is more difficult to oxidize than the analogous dianionic radical  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{2-}$ , consistent with the substitution of a CO ligand by the stronger  $\pi$ -acceptor NO ligand.

**Carbonyl  $^{13}\text{C}$  NMR Spectra.** Representative variable-temperature spectra obtained for  $[\text{Re}_7\text{C}(\text{CO})_{20}(\text{NO})]^{2-}$  (ca. 40%  $^{13}\text{C}$ ) are shown in Figure 1. Five signals are observed at  $20^\circ\text{C}$ ; the positions and intensities are listed in Table I, and the as-



**Figure 2.** Diagram of suggested structure for  $[\text{Re}_7\text{C}(\text{CO})_{20}(\text{NO})]^{2-}$  with assignments of carbonyl  $^{13}\text{C}$  NMR signals.

signments are shown in Figure 2. At  $-60^\circ\text{C}$  resonance e (6 C) is quite broad, but at  $-90^\circ\text{C}$  it appears as three equally intense singlets ( $\delta$  194.0, 190.6, and 187.3, in 1:1  $\text{CD}_2\text{Cl}_2\text{-CF}_3\text{Cl}$ ). At this temperature resonance d (3 C) has nearly disappeared into the base line, but the remaining signals a (3 C), b (6 C), and c (2 C) are largely unaffected. The changes with temperature for resonances d and e are consistent with slowing down localized 3-fold rotation in  $\text{Re}(\text{CO})_3$  units, as has been observed in other instances.<sup>4,5,12</sup> The fact that resonance c represents only two carbonyl ligands at all temperatures measured indicates that it corresponds to a  $\text{Re}(\text{CO})_2(\text{NO})$  unit.

The carbonyl resonances of  $[\text{Re}_7\text{C}(\text{CO})_{20}(\text{NO})]^{2-}$  are assigned by comparison with  $^{13}\text{C}$  NMR data available for two closely related large rhenium clusters, as listed in Table I. The  $\delta$  204.0 singlet of  $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$  corresponds to the carbonyl ligands bonded to the two capping rhenium atoms. For  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ , the farthest downfield resonance at  $\delta$  210.2 also represents the three ligands bonded to the six-coordinate metal cap. Thus, the signal at  $\delta$  205.6 (a) for  $[\text{Re}_7\text{C}(\text{CO})_{20}(\text{NO})]^{2-}$  is assigned to the carbonyls bonded to the rhenium cap. It is important to note that a ca. 5 ppm upfield shift is observed for analogous resonances from trianionic  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$  to the dianionic clusters  $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$  and  $[\text{Re}_7\text{C}(\text{CO})_{20}(\text{NO})]^{2-}$ . This is also seen for other dianionic  $[\text{Re}_7\text{C}(\text{CO})_{21}\text{ML}_n]^{2-}$  derivatives.<sup>4,5</sup> The eight-coordinate metal sites of  $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$  exhibit a carbonyl ligand resonance at  $\delta$  191.3, which is separated into two signals (2:1 ratio) at  $-100^\circ\text{C}$ .<sup>12</sup> Since the upfield signals of  $[\text{Re}_7\text{C}(\text{CO})_{20}(\text{NO})]^{2-}$  at  $\delta$  191.7 (d) and 191.2 (c) show similar dynamic behavior, they are attributed to the carbonyl ligands of the three eight-coordinate rhenium centers. Correspondingly, the  $\delta$  195.2 signal of  $\text{Re}_7\text{C}(\text{CO})_{21}^{3-}$  shows considerable broadening at  $-80^\circ\text{C}$  whereas the  $\delta$  201.1 signal remains sharp, so that these resonances are attributed to the carbonyls bonded to the eight-coordinate and seven-coordinate rhenium sites, respectively. The  $\delta$  197.8 signal (b) of  $\text{Re}_7\text{C}(\text{CO})_{20}(\text{NO})^{2-}$  shows an appropriate upfield shift with respect to that for the corresponding seven-coordinate  $\text{Re}(\text{CO})_3$  site in  $\text{Re}_7\text{C}(\text{CO})_{21}^{3-}$  and likewise remains sharp at low temperatures. The further upfield shift of the 2 C signal (c) at  $\delta$  193.4 compared with the 6 C signal (b) at  $\delta$  197.8 is attributed to the substitution of CO by the stronger  $\pi$ -acid ligand  $\text{NO}^+$ . This is the reverse of the usual downfield shift observed upon substitution of CO by a stronger donor ligand.<sup>13</sup>

**Pathway of  $\text{NO}^+$  Substitution.** On the basis of the above  $^{13}\text{C}$  NMR analysis, we postulate that the nitrosyl ligand on  $[\text{Re}_7\text{C}(\text{CO})_{21}(\text{NO})]^{2-}$  is substituted on a basal rhenium adjacent to the open face. It is unlikely that X-ray structural analysis could provide a more definitive answer, since resolution of nitrosyl and carbonyl ligands has been difficult in other cases, notably

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$[\text{Os}_{10}\text{C}(\text{CO})_{23}(\text{NO})]^{-8}$ .<sup>8</sup> Given the site of  $\text{NO}^+$  substitution, it is quite possible that  $\text{NO}^+$  initially coordinates at the open face, as in the case of metallic electrophiles, followed by  $\text{CO}$  loss. It is clear that the site of attack is *not* a metal-metal bond involving the capping  $\text{Re}(\text{CO})_3$  moiety, as in the case of  $\text{Os}_{10}\text{C}(\text{CO})_{24}^{2-8}$ . However, we cannot at this stage eliminate the alternative pathway of initial electron transfer followed by coordination of neutral  $\text{NO}$ .

**Acknowledgment.** This work was supported by National Science Foundation Grants CHE 84-07233 to J.R.S. and DMR 86-12860 to the Materials Research Laboratory.

**Note Added in Proof.** Chemical oxidation of  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$  with  $[\text{Cp}_2\text{Fe}]^+$  (1 equiv) followed by  $\text{NO}$  addition also gives  $[\text{Re}_7\text{C}(\text{CO})_{20}(\text{NO})]^{2-}$ .

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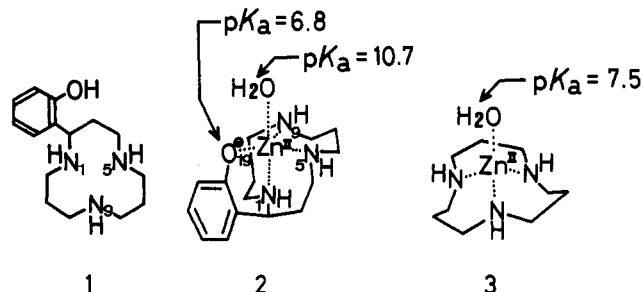
### A Trigonal-Bipyramidal Zinc(II) Complex of a Phenol-Pendant Macrocyclic Triamine

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Received April 27, 1988

Structurally well-defined five-coordinate, trigonal-bipyramidal Zn(II) complexes are scarce,<sup>1</sup> despite the intense synthetic efforts to mimic the active sites in Zn(II)-containing enzymes (e.g. carboxypeptidase A<sup>2,3</sup> or carbonic anhydrase (CA)<sup>2,4</sup>). The Zn(II) in CA is ligated by three imidazoles and a water molecule. This coordination number 4 is considered to expand to 5 in a transient manner or by anion inhibitor binding.<sup>5-7</sup> In a mechanism for CA, the observed  $\text{pK}_a$  value of ca. 7 is assigned to the zinc-bound water, and its conjugate base appears to attack closely positioned carbon dioxide to convert it into bicarbonate ion.<sup>4,8</sup> It was postulated<sup>6,7</sup> that the incoming anions (to five-coordinate) enhance the basicity of  $\text{ZnOH}$  in CA to affect its nucleophilicity.

Herein we report the X-ray crystal structure of a Zn(II) complex **2** with a recently developed phenol-pendant macrocyclic triamine [2-(2-hydroxyphenyl)-1,5,9-triazacyclododecane, **1**<sup>9</sup>] that



is distinctly five-coordinate and trigonal bipyramidal with an additional apical  $\text{H}_2\text{O}$  coordination. The ligand was originally designed for an ideal tetrahedral  $\text{N}_3\text{O}^-$  coordinate environment, and its complexations with  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  in aqueous solution were reported.<sup>9</sup>

The corresponding 12-membered macrocyclic triamine (without the phenol pendant) was earlier reported to form a four-coordinate (possibly tetrahedral) Zn(II) complex with an additional aquo ligand **3**, whose ionization (to  $\text{ZnOH}$ ) constant  $\text{pK}_a$  is 7.5.<sup>10</sup> Thus,

**Table I.** Summary of Crystal Data, Intensity Collection, and Refinements

formula	$\text{C}_{15}\text{H}_{24}\text{N}_3\text{OZnClO}_4\cdot\text{H}_2\text{O}$
fw	445.2
cryst system	monoclinic
space group	$P2_1/a$
cell dimens	
$a, b, c, \text{Å}$	16.673 (2), 13.952 (2), 8.286 (1)
$\beta, \text{deg}$	91.73 (1)
$V, \text{Å}^3$	1926.5 (5)
$Z$	4
density calcd, $\text{g cm}^{-3}$	1.536
cryst color	colorless
cryst dimens, $\text{mm}^3$	$0.36 \times 0.11 \times 0.11$
radiation	$\text{Mo K}\alpha$ (graphite monochromated)
$\mu, \text{mm}^{-1}$	1.488
$2\theta$ range, deg	2-55
index range	$+h, +k, \pm l$
scan width, deg	$1.3 + 0.5 \tan \theta$
refinement	block-diagonal least-squares method
no. of measd reflns	4920
no. of indep reflns with $ F_o  \geq 3\sigma(F_o)$	2239
final $R$	0.044
final $R_w$	0.056

**Table II.** Fractional Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Temperature Factors ( $\text{Å}^2$ ) for **2**( $\text{ClO}_4$ )

atom	$x$	$y$	$z$	$B_{\text{eq}}^a$
Zn	1070.9 (4)	1289.2 (4)	5495.9 (7)	3.0
N(1)	1132 (3)	2778 (3)	6106 (6)	3.8
C(2)	1103 (4)	3357 (1)	4641 (7)	4.1
C(3)	1876 (4)	3170 (4)	3724 (7)	4.3
C(4)	2041 (4)	2171 (5)	3088 (7)	4.5
N(5)	2125 (3)	1394 (3)	4345 (6)	4.1
C(6)	2829 (3)	1466 (5)	5465 (8)	4.9
C(7)	2764 (4)	867 (5)	6987 (8)	5.1
C(8)	2187 (4)	1209 (4)	8266 (7)	4.6
N(9)	1321 (3)	1001 (3)	7884 (6)	4.3
C(10)	759 (4)	1460 (5)	8973 (7)	5.0
C(11)	744 (4)	2556 (5)	8899 (8)	5.4
C(12)	499 (4)	2990 (5)	7288 (7)	4.8
C(13)	338 (3)	3212 (4)	3578 (7)	3.9
C(14)	-64 (3)	2321 (4)	3351 (6)	3.2
C(15)	-706 (3)	2308 (4)	2250 (7)	4.3
C(16)	-964 (4)	3107 (5)	1411 (7)	4.9
C(17)	-576 (4)	3961 (5)	1687 (8)	5.8
C(18)	58 (4)	4008 (4)	2761 (8)	4.9
O(19)	146 (2)	1504 (2)	4085 (4)	3.7
O( $\text{H}_2\text{O}$ )	979 (2)	-282 (3)	5112 (5)	4.2
Cl	3004 (1)	4109 (1)	-1436 (2)	5.0
O(1Cl)	2809 (4)	3981 (4)	153 (6)	9.8
O(2Cl)	3600 (4)	4793 (4)	-1562 (7)	10.0
O(3Cl)	3314 (5)	3257 (5)	-2060 (8)	12.8
O(4Cl)	2362 (4)	4412 (7)	-2384 (9)	14.5

$$^a B_{\text{eq}} = \frac{1}{3} \sum_i \beta_i \sum_j a_i a_j$$

the phenolate-pendant coordination in **2** offers the first model for an associative anion interaction.

### Experimental Section

All materials were obtained commercially and were used without further purification. The experimental procedure for the ligand synthesis

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