CPMAS ^{13}C NMR Spectra of Quinones, Hydroquinones, and Their Complexes. Use of CMR To Follow a Reaction in the Solid State

J. R. Scheffer,*† Y.-F. Wong,† A. O. Patil,‡ D. Y. Curtin,*‡ and I. C. Paul*‡

Contribution from the Department of Chemistry, University of British Columbia, Vancouver, Canada V6T 1Y6, and Department of Chemistry, University of Illinois, Urbana, Illinois 61801.
Received June 29, 1984

Abstract: CPMAS ^{13}C NMR spectroscopy has been employed to follow the reaction at temperatures above 70 °C of the crystalline 1/1 complex of 1,4-benzoquinone with 2,5-dimethyl-1,4-hydroquinone to give the 1/2 complex of 2,5-dimethyl-1,4-benzoquinone–hydroquinone and an equimolar amount of 2,5-dimethyl-1,4-benzoquinone. The redox reaction of a solid mixture of quinhydrone (1,4-benzoquinone–1,4-hydroquinone) with an equimolar amount of 2,5-dimethyl-1,4-hydroquinone gives the 1/2 complex of 2,5-dimethyl-1,4-benzoquinone with 1,4-hydroquinone with no evidence of formation of side products or accumulation of reaction intermediates. During preparation of a mixture of the 1/1 complex of 1,4-benzoquinone–2,5-dimethylhydroquinone with an equimolar amount of 1,4-hydroquinone the partial exchange of one hydroquinone for another in the complex occurs even during mixing of the components at room temperature. An equimolar mixture of 1,4-benzoquinone, 1,4-hydroquinone, and 2,5-dimethyl-1,4-hydroquinone underwent partial complexation at room temperature. These latter two mixtures when heated in the solid state each gave the 1/2 complex 2,5-dimethyl-1,4-benzoquinone–1,4-hydroquinone. As background for this work, CMR spectra of some crystalline quinones, hydroquinones, and their complexes (quinhydrones) have been obtained. The differences between the solid-state and corresponding solution spectra have been shown to be primarily in the multiplicities of some resonances but not others. It is suggested that a primary source of multiplicities in the quinones is CH- - -O interactions of the sort discussed by others in the analysis of the crystal packing patterns of such compounds.

Although CPMAS (cross polarized magic angle spinning) techniques have made high-resolution NMR spectra of solids available to the organic chemist for some time,[1] this methodology has excited relatively little interest as a *general* technique for structure determination of organic molecules or for following the progress of chemical reactions. Although the requisite instrumentation is commercially available, it is expensive and has been employed more often in structural studies involving insoluble solids such as polymers[2] and for special organic molecules whose solid-state structures had some feature which was not readily studied by other techniques.[3] It has been pointed out[4] that interpretation of such spectra may involve complications not found in solution due to the special features of the structure of the crystal such as conformational effects and/or intermolecular interactions not found in solution.

In the course of an investigation[5] of the synthesis and redox rearrangement of complexes of quinones with hydroquinones in the solid state, it became of interest to follow these reactions with high-resolution (CPMAS) ^{13}C NMR. This required an examination of the solid-state NMR spectra of such compounds. Although there have been certain isolated reports, there seems to have been no study of the spectra of members of this family correlating them with their crystal structures. It is apparent that these compounds form a particularly interesting group because of their relatively high degree of molecular symmetry, their typically simple layered structures, the absence of conformational complications, and the well-defined intermolecular hydrogen bonding and C—H- -O interactions which have previously been analyzed in some detail by Bernstein, Cohen, and Leiserowitz.[6]

In this paper we report the high-resolution ^{13}C solid-state spectra of certain quinones and hydroquinones and their crystalline complexes, the quinhydrones. ^{13}C NMR spectroscopy is then employed to follow a solid-state redox reaction of such a complex.

Experimental Section

Sources and purification of the compounds employed here have been described in ref 5a-c. Doping of the quinones **1** and **4** with cupric or manganous chloride was carried out by the method of ref 10, except that the crystallization solvent was methanol rather than water.

Determination of CPMAS ^{13}C NMR Spectra. Spectra were obtained with a Bruker CXP-200 FT NMR spectrometer, operating at an applied field strength of 4.7 T or a ^{13}C resonance frequency of 50.3 MHz. Single-contact spin-locked cross polarization was established under the Hartmann–Hahn[7] matching condition with applied ^{1}H and ^{13}C radio frequency fields of 15 and 60 G, respectively. Samples (200–300 mg) were packed into Delrin spinners and spun at approximately 4.5 kHz estimated from the location of spinning sidebands. A typical cross-polarization time was 5 ms with a recycle time of 10 to 15 s. Each spectrum was obtained with 4K data points, zero filled to 16K prior to Fourier transformation with 2–5 Hz digital filtering. Accumulation of a few hundred to a few thousand transients normally provided spectra with a reasonable signal-to-noise ratio. The ^{13}C NMR signal of liquid benzene was used as an external reference to determine chemical shift values. (The benzene signal was taken as 128.5-ppm downfield from tetramethylsilane.) Estimated error limits of the solid-state spectra are ±0.5

† University of British Columbia.
‡ University of Illinois.

(1) See: (a) Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 201–208. (b) Wasylishen, R. E.; Fyfe, C. A. "Annual Reports on NMR Spectroscopy"; G. A. Webb, Ed.; Academic Press: New York, 1982; Vol. 12, pp 1–80.

(2) Schaefer, J.; Stejskal, E. O. "High Resolution ^{13}C NMR of Solid Polymers" in "Topics in C^{13}-NMR Spectroscopy"; Levy, G. C., Ed.; John Wiley and Sons: New York, 1979; Vol. 3, pp 283–324.

(3) (a) Lyerla, J. R.; Yannoni, C. S.; Fyfe, C. A. *Acc. Chem. Res.* **1982**, *15*, 208–216. (b) Miller, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 7396–7397. (c) Strub, H.; Beeler, A. J.; Grant, D. M.; Michl, J.; Cutts, P. W.; Zilm, K. W. *J. Am. Chem. Soc.* **1983**, *105*, 3333–3334. (d) Schroeter, B.; Rosenberger, H.; Hadzi, D. *J. Mol. Struct.* **1983**, *96*, 301–314. (e) Wasylishen, R. E.; Graham, M. R. *Mol. Cryst. Liq. Cryst.* **1979**, *49*, 225–230. (f) Dalling, D. K.; Zilm, K. W.; Grant, D. M.; Heeschen, W. A.; Horton, W. J.; Pugmire, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 4817–4827.

(4) (a) Ariel, S. Scheffer, J. R.; Trotter, J.; Wong, Y.-F. *Tetrahedron Lett.* **1983**, *24*, 4555–4558. (b) McDowell, C. A.; Naito, A.; Scheffer, J. R.; Wong, Y.-F. *Tetrahedron Lett.* **1981**, *22*, 4779–4782. (c) Kessler, H.; Bermel, W.; Foerster, H. *Angew. Chem.* **1982**, 689. (d) Alemany, L. B.; Grant, D. M.; Pugmire, R. J.; Alger, T. D.; Zilm, K. W. *J. Am. Chem. Soc.* **1983**, *105*, 2133–2141. (e) Hexem, J. G.; Frey, M. H.; Opella, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 5717–5719. (f) Hays, G. R. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1049–1052. (g) Chippendale, A. M.; Mathias, A.; Aujla, R. S.; Harris, R. K.; Packer, K. J.; Say, B. J. *Ibid.* **1983**, *1357*–1361. (h) Jeffrey, G. A. "Abstracts" Joint Meeting, 41st Annual Pittsburgh Diffraction Conference and 3rd Canadian Crystallography Conference", Toronto, Oct. 1983, p 16. (i) Taylor, R. H.; Marchessault, R. H.; Stephenson, P. J.; Fyfe, C. A. *Ibid.*, p 21. (j) Henrichs, P. M.; Hewitt, J. M.; Scaringe, R. P.; Linder, M. *Ibid.*, p 15.

(5) Patil, A. O.; Curtin, D. Y.; Paul, I. C. *J. Am. Chem. Soc.* **1984**, *106*, 348–353. (b) Patil, A. O.; Wilson, S. R.; Curtin, D. Y.; Paul, I. C. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1107–1110. (c) Patil, A. O.; Curtin, D. Y.; Paul, I. C. *J. Am. Chem. Soc.* **1984**, *106*, 4010–4015.

(6) (a) Bernstein, J.; Cohen, M. D.; Leiserowitz, L. "The Structural Chemistry of Quinones" in "The Chemistry of the Quinonoid Compounds"; Patai, S., Ed.; John Wiley and Sons: New York, 1974. (b) Berkovitch-Yellin, Z.; Leiserowitz, L. *Acta Crystallogr.* **1984**, *B40*, 159–165.

0002-7863/85/1507-4898$01.50/0

Table I. NMR Spectra of Benzoquinones and Hydroquinones in Solution and the Solid State[a]

	quinones			hydroquinones		
	unsubstd[b] (1)	Me_2[c] (2)	Me_4[d] (3)	unsubstd[e] (5)	Me_2[f] (6)	Me_4[f] (7)
			C=O			
solution	187.6 187.4[g] 187.2[h]	187.9[g]	187.0[g]			
solid	190.0	189.2	184.0			
solution–solid	−2.8 to −2.4	−1.3	+3.0			
			C—OH			
solution				150.5[i] 149.7	147.4	145.5
solid				149.8 148.4 146.9	146.1	145.6
solution–solid				−0.1 to +3.6	+1.3	−0.1
			C—H			
solution	136.6[g] 136.6[h] 136.5	133.6		116.3[i] 115.6	116.8	
solid	137.8	133.8		119.7 118.3 116.9 116.0 115.0	118.3	
solution–solid	−1.3 to −1.2	−0.2		−4.1 to +1.3	−1.5	
			$C—CH_3$			
solution		145.7[g]	140.4[g]		121.1	121.2
solid		147.1	140.9 139.9		123.8	121.5
solution–solid		−1.4	−0.5 to +1.0		−2.7	−0.3
			$C—CH_3$			
solution		15.2[g]	12.2[g]		15.8	12.9
solid		16.3 15.5	12.8 11.5		15.9	12.6 11.9
solution–solid		−1.1 to −0.3	−0.6 to +0.7		−0.1	+0.3 to +1.0

[a] Chemical Shifts (relative to Me_4Si in ppm) are from the present investigation and the solution spectra were measured in Me_2SO-d_6 unless otherwise indicated. [b] Cu^{2+} or Mn^{2+} salts added to improve signal-to-noise ratio.[10] The structure was reported in ref 11. [c] Structure reported in ref 12. [d] Structure reported in ref 13. [e] Structure reported in ref 14. [f] See ref 15. [g] In pyridine-d_5 (ref 16). [h] In $CDCl_3$. [i] In 3:1 (v/v) $CDCl_3$–acetone-d_6.

ppm. Results are presented in Tables I–III. Chemical shift values of the quinhydrone complexes for the carbon atoms not in Table III follow.

Quinhydrone (*monoclinic*) (**1–5**): δ 137.6, 134.1, 118.0.

Quinhydrone (*triclinic*) (**1–5**): δ 136.5, 134.4, 118.5.

2,5-Dimethyl-1,4-benzoquinone–1,4-Hydroquinone (2–5) (1/2): δ 146.7, 132.6, 117.1, 115.5, 16.0.

Tetramethyl-1,4-benzoquinone–Tetramethyl-1,4-hydroquinone (3–7) (1/1): δ 139.5, 119.1, 118.3, 13.7, 12.1.

1,4-Naphthoquinone–1,4-Hydroquinone (4–5) (1/1): δ 134.0, 131.9, 117.8.

1,4-Benzoquinone–2,5-Dimethyl-1,4-hydroquinone (1–6) (1/1): δ 134.4, 134.0, 123.9, 118.2, 15.9.

1,4-Benzoquinone–1,4-Naphthohydroquinone (1–8) (1/1): δ 144.0, 140.4, 136.4, 134.0, 132.3, 128.7, 125.7, 120.6, 117.4, 109.7.

Use of ^{13}C NMR To Follow the Solid-State Conversion of the 1/1 Complex 1–6 to the 1/2 Complex 2–5. In a typical experiment equimolar amounts of the quinhydrone complex **1–5** (4.0 mmol, 872.8 mg) and 2,5-dimethyl-1,4-hydroquinone (**6**) (4.0 mmol, 356.4 mg) weighed to ±0.1 mg were ground with an agate mortar and pestle for approximately 2 min or until no further color change was visible. The mixture had changed from a black and white mixture to a uniform grayish blue powder. The solid-state ^{13}C NMR spectrum was measured before the sample was divided into eight portions and each sealed in a small glass tube. Sample tubes were then heated at about 85 °C in a Kugelrohr oven for various times, cooled with an air gun (blower), and the ^{13}C spectra were taken. After the tubes were heated for about 500 min the redox transformation was completed. The final product showed a characteristic red color of the stable 1/2 complex of **2–5** and its ^{13}C spectrum was identical with that of the stable isomer prepared by other methods.

Results and Discussion

Quinones without methyl groups such as 1,4-benzoquinone (**1**) and 1,4-naphthoquinone (**4**) were found to give unsatisfactory solid-state spectra because of their long relaxation times. It has been shown by Ganapathy, Naito, and McDowell[10] that addition of small amounts of paramagnetic dopants such as Cu^{2+} salts improves the signal-to-noise ratio (obtainable in a given period of time) of the solid-state ^{13}C spectra of certain amino acids and heterocyclic compounds. This is brought about by a shortening of the proton relaxation time and occurs without giving rise to an appreciable change in the carbon chemical shifts. The spectra of quinones **1** and **4** in this study were therefore measured with addition of a small amount of a Cu^{2+} or Mn^{2+} salt. The quinones **1–4** show resonances in their solid-state ^{13}C NMR spectra similar to those found in their solution spectra. In general absorption peaks are within 1–2 ppm of the solution values. However, carbon atoms which have equivalent environments when the substance is in solution often are nonequivalent in the crystal—an effect which may or may not show itself as a doubling of certain peaks in the quinone spectra. Examination of the quinone spectral data presented in Tables I and II suggests that in this set of compounds the doubling can often be correlated with the presence of nonequivalence caused by CH···O interactions of a type discussed previously by Bernstein, Cohen, and Leiserowitz[6a] and others.[6b,8,9]

Comparison of the NMR spectra in the solid state with those in Me_2SO solution shows that the solid-state chemical shifts of the carbonyl carbon atoms of 1,4-benzoquinone and 2,5-dimethyl-1,4-benzoquinone which are involved in relatively strong CH···O interactions are shifted downfield 2.6 and 1.3 ppm,

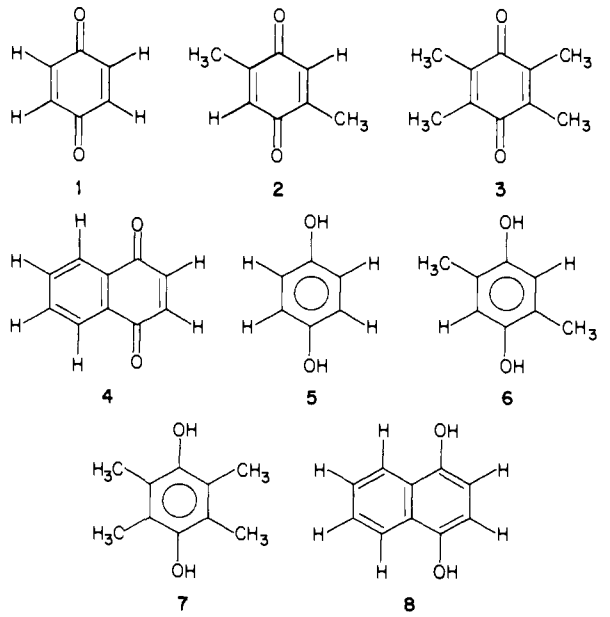
(7) Hartmann, S. R.; Hahn, E. L. *Phys. Rev.* **1962**, *128*, 2042–2053.
(8) Berkovitch-Yellin, Z.; Leiserowitz, L. *J. Am. Chem. Soc.* **1982**, *104*, 4052–4064.
(9) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063–5070.
(10) Ganapathy, S.; Naito, A.; McDowell, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 6011–6015.

Table II. NMR Spectra of Naphthoquinone and Naphthohydroquinone in Solution and the Solid State[a]

carbon positions	frequencies (ppm relative to Me_4Si) naphthoquinone[b] (4)	naphthohydroquinone[c,d] (8)
1,4 (C=O)		
solution	184.9,[e] 184.7	
solid	184.7	
solution–solid	+0.0 to +0.2	
1,4 (C—OH)		
solution		145.3
solid		143.6
solution–solid		+1.7
2,3 (C—H)		
solution	138.6,[e] 138.6	124.5
solid	139.4, 137.8	126.2
solution–solid	−0.8 to +0.8	−1.7
5,8 (C—H)		
solution	126.4,[e] 125.7	121.8[f]
solid	127.7, 127.3	120.1[f]
solution–solid	−2.0 to −0.9	+1.7
6,7 (C—H)		
solution	133.8,[e] 134.1	107.8[f]
solid	137.0, 135.8	109.4[f]
solution–solid	−3.2 to −1.7	−1.6
9,10 (C—CC)		
solution	131.8,[e] 131.4	125.3
solid	131.5	125.1
solution–solid	−0.1 to +0.3	+0.2

[a] Chemical shifts (relative to Me_4Si in ppm) are from the present investigation and the solution spectra were measured in Me_2SO-d_6 unless otherwise indicated. [b] Measured with copper salt added. Crystal structure in ref 17. [c] Crystal structure in ref 18. [d] Solid-state spectrum measured with "flip-back" pulse sequence (ref 19) and assignment helped by the dipolar dephasing method (see ref 20). [e] In $CDCl_3$ (ref 21). [f] Assignment of 5,8 vs. 6,7 not conclusive.

Chart I



respectively, from the positions in solution whereas the carbonyl carbons of tetramethyl-1,4-benzoquinone, having no aromatic CH's with which to interact, show resonances shifted 3 ppm upfield. 1,4-Naphthoquinone, with longer CH---O contacts than those in the first two structures, shows hardly any (0.2 ppm) downfield shift. In this case the CH---O contacts are longer than was the case with the first two quinones above. It may be noted that hydrogen bonding to ketone carbonyl oxygen atoms in solution has been shown[22] to lead to substantial downfield shifts of the C=O resonance by as much as 8 ppm.

1,4-Hydroquinone structures are dominated by OH---O hydrogen bonding. Such hydrogen bonds involve geometrical constraints which prevent formation of layered structures of the type often found with the quinones. A solution study[23] of the effect of dilution of phenol by a series of solvents has shown that H-bond-accepting ability of the solvent leads to shifts to lower field of the phenol ^{13}C–OH resonances. In comparing the spectra of hydroquinones in the solid state with those of solutions in Me_2SO, however, it may be noted that the hydroxyl groups in the crystal are totally involved in hydrogen bonding to adjacent phenolic oxygen atoms. In solution the phenols, being good hydrogen donors, are hydrogen bonded essentially completely to molecules of the solvent, Me_2SO, a good hydrogen bond acceptor. It is not surprising, then, that there is so little difference in chemical shifts of the COH in solution and in the solid state.

Another possible effect of crystal packing on the spectra of 1,4-hydroquinones is the ring-current effect of the aromatic rings. Although the phenols do not crystallize with the nicely layered structures found for several of the quinones, the rings are nevertheless packed in stacks with the carbon atoms of one ring over the aromatic ring of the next molecule in the stack. It can be seen in Table I, however, that the differences in chemical shifts from those in solution are not greater in absolute magnitude than those of the quinones. Levin and Roberts[24] have concluded in a study of [12]paracyclophane that "ring current effects are small and will normally be overshadowed by other kinds of influences on cmr shifts". That generalization seems to apply to the solid-state spectra of the phenols in Tables I and II.

A further difference between phenols in solution and in the solid state is that although the phenol molecule in solution is approximately planar with the hydroxylic proton lying in the plane of the benzene ring and pointed toward one of the two ortho hydrogen atoms as it is in the crystal, the shift of the proton from one side of the oxygen atom to the other is very rapid. The energy barrier in isolated phenol is of the order of 3.5 kcal/mol,[25] and therefore NMR solution spectra show an averaged environment for the two ortho (and the two meta) carbon atoms. The hydroxyl groups of crystalline hydroquinones, on the other hand, are largely ordered and held in place by hydrogen bonding to an adjacent phenolic oxygen. The hydroxyl group can thus provide intramolecular differentiation of the environments of the ortho carbon atoms and lead to a possible difference in chemical shift.

1,4-Hydroquinone (**5**) crystallizes in three modifications,[14] designated as α, β, and γ, whose ^{13}C NMR spectra have been first reported by Ripmeester.[26a] The most readily available form, the α form, crystallizes in space group $R\bar{3}$ with six independent half-molecules in the asymmetric unit.[14a] The spectrum has been

(11) (a) Trotter, J. *Acta Crystallogr.* **1960**, *13*, 86–95. (b) Bolhuis, F.; Kiers, C. Th. *Acta Crystallogr., Sect. B* **1978**, *34*, 1015–1016.
(12) (a) Rabinovich, D.; Schmidt, G. M. J. *J. Chem. Soc. (London)* **1964**, 2030–2040. (b) Hirshfeld, F. L.; Rabinovich, D. *Acta Crystallogr.* **1967**, *23*, 989–1000.
(13) Rabinovich, D.; Schmidt, G. M. J.; Ubell, E. *J. Chem. Soc., Sect. B* **1967**, 131–144.
(14) (a) Wallwork, S. C.; Powell, H. M. *J. Chem. Soc., Perkin Trans. 2* **1980**, 641–646. (b) Lindeman, S. V.; Shklover, V. E.; Struchkov, Yu. T. *Cryst. Struct. Commun.* **1981**, *10*, 1173–1179. (c) Maartmann-Moe, K. *Acta Crystallogr.* **1966**, *21*, 979–982.
(15) Pennington, W. T.; Patil, A. O.; Paul, I. C.; Curtin, D. Y. *J. Chem. Soc., Perkin Trans. 2*, submitted for publication.
(16) Lown, J. W.; Begleiter, A. *Can. J. Chem.* **1974**, *52*, 2331–2336.
(17) Gaultier, J.; Hauw, C. *Acta Crystallogr.* **1965**, *18*, 179–183.
(18) Gaultier, J.; Hauw, C. *Acta Crystallogr.* **1967**, 1016–1024.
(19) Tegunfeldt, J.; Haeberlen, U. *J. Magn. Reson.* **1979**, *36*, 453–457.
(20) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854–5856.
(21) Bowden, B. F.; Cameron, D. W.; Crossley, M. J.; Feutrill, G. I.; Griffiths, P. G.; Kelly, D. P. *Aust. J. Chem.* **1979**, *32*, 769–777.
(22) Maciel, G. E.; Ruben, G. C. *J. Am. Chem. Soc.* **1963**, *85*, 3903–3904.
(23) Maciel, G. E.; James, R. V. *J. Am. Chem. Soc.* **1964**, *86*, 3893–3894.
(24) Levin, R. H.; Roberts, J. D. *Tetrahedron Lett.* **1973**, 135–138.
(25) See, for example: Ginn, S. G. W. *J. Mol. Struct.* **1975**, *28*, 185–191.
(26) (a) Ripmeester, J. A. *Chem. Phys. Lett.* **1980**, *74*, 536–538. (b) Burgar, M. I. *J. Phys. Chem.* **1984**, *88*, 4929–4930.

Table III. Change of C=O and C—OH Resonances on Complex Formation

		C=O			C—OH		
complex	d^a (Å)	soln	solid	complex	soln	solid	complex
1–5							
($P\bar{1}$)	3.2	187.4[b]	190.0	185.8	149.7[c]	149.8	149.4
		187.6[c]			150.5[d]	148.4	
		187.2[d]				146.9	
($P2_1/c$)	3.2			185.7			149.3
2–5 (1/2)	3.2	187.9[b]	189.2	188.1	149.7[c]	149.8	150.5
					150.5[d]	148.4	148.1
						146.9	
3–7	3.5	187.0[b]	184.0	185.0	145.5[c]	145.6	146.1
4–5	3.2	184.7[c]	184.7	185.3	149.7[c]	149.8	150.5
		184.9[e]		184.5	150.5[d]	148.4	148.7
						146.9	
1–6		187.4[b]	190.0	189.5	147.4[c]	146.1	146.4
		187.6[c]					147.3
		187.2[d]					
1–8		187.4[b]	190.0	186.5	145.3[c]	144.1	150.3
		187.6[c]					149.9
		187.2[d]					

[a] Spacing between layers. [b] Pyridine. [c] Me_2SO. [d] 3:1 (v/v) $CDCl_3$–acetone-d_6. [e] In $CDCl_3$ (ref 21).

analyzed and the principal values of the chemical shift tensor for each of the resolved resonances reported.[26b] Although the spectrum is complex, that complexity provides a valuable means of recognizing the presence of α-1,4-hydroquinone. Spectral results for this compound as well as the 2,5-dimethyl derivative **6** and tetramethyl derivative **7** and naphthohydroquinone (**8**) are presented in Tables I and II.

Quinhydrones, the crystalline complexes formed by interaction of quinones with hydroquinones, are largely dissociated in solution. However, Griffith, Grant, and Roberts[27] studied the related complexation in solution of trinitrobenzene with benzene, mesitylene, naphthalene, and anthracene. From plots of the donor chemical shifts vs. acceptor concentration, chemical shifts of the pure complexes could be calculated. These extrapolated values indicated that the change in chemical shifts of the hydrocarbons on complexation amounted to −0.8 to +1.3 ppm, depending on the structure of the hydrocarbon and position of the carbon atom. A study by Prins, Verhoeven, and de Boer[28] of changes in the chemical shifts of the chloranil carbon atoms on complexation in solution with several hydrocarbons and with methoxybenzene documented shifts from 0 to −3 ppm whereas the chemical shifts of the hydrocarbon component amounted to −1.9 to +1.2 ppm.

Effects of the charge-transfer interaction associated with quinone/hydroquinone stacking in the crystal made the solid-state spectra of complexes of the above quinones and hydroquinones of interest. The features of the spectra most likely to be of value in the search for such effects of complexing are the resonances due to the carbonyl carbon atoms of the quinone and those due to the hydroxylic carbon atoms of the hydroquinone. These atoms occur in pairs often related by a crystallographic center of symmetry and their resonances are in a region of the spectrum where there is no interference by other absorption. Data for a number of complexes are summarized in Table III.

Both the monoclinic[29] and triclinic[30] polymorphs of quinhydrone have relatively simple spectra (Figure 1). In each case there is only one independent quinone and one hydroquinone molecule in the crystal structure and both lie at crystallographic centers of symmetry so that there is a single resonance for the carbonyl carbon of the quinone and also for the phenolic carbon atom of the hydroquinone component of the complex. These resonances occur at the same chemical shift position in both monoclinic and triclinic complexes. While the hydroquinone phenolic carbon resonance is at the same position as that of one of the three

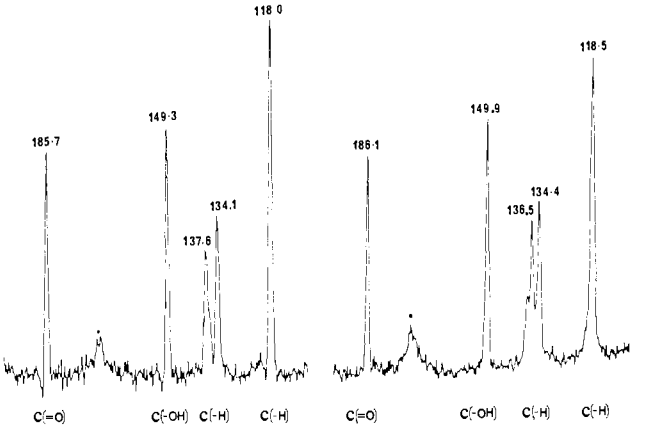


Figure 1. Solid-state CPMAS ^{13}C NMR spectra of (left) monoclinic quinhydrone and (right) triclinic quinhydrone. Spinning sidebands are marked wtih an asterisk.

resonances of the solid α-hydroquinone, the carbonyl carbon resonance in the complex is shifted some 3–4 ppm upfield from the corresponding resonance of solid benzoquinone. Similar upfield shifts on the carbonyl carbon resonance are shown by 1,4-benzoquinone on complexation with 1,4-naphthohydroquinone (**8**) and by 2,5-dimethyl-1,4-benzoquinone (**2**) on formation of the 1/2 complex with 1,4-hydroquinone. Such upfield displacements are consistent both in the direction and order of magnitude with the shifts observed[27] in the solution studies of complexation of chloranil with hydrocarbons. However, the carbonyl carbon resonances of tetramethyl-1,4-benzoquinone (**3**) on complexation with tetramethyl-1,4-hydroquinone (**7**) are shifted downfield. In this case the crystalline quinone has no special CH···O interactions, but in the complex there is hydrogen bonding of the phenolic hydroxyls of the hydroquinone neighbors to the quinone carbonyl oxygen atoms.[31] The carbonyl carbon resonances of 1,4-benzoquinone on complexation with 2,5-dimethyl-1,4-hydroquinone and of 1,4-naphthoquinone (**4**) on complexation with 1,4-hydroquinone (**5**) show a barely observable shift.

The complex of tetramethyl-1,4-quinone with tetramethyl-1,4-hydroquinone (**3**–**7**) has been of particular interest because, although it has the 1/1 composition of a normal quinhydrone, the hydroxyl stretching frequency in the FTIR was found[5b] to occur at 3495 cm^{-1}. The crystal structure,[31] as determined by X-ray diffraction, consists of hydrogen-bonded chains of alternating quinone and hydroquinone molecules but with the hydrogen bonds

(27) Griffith, R. C.; Grant, D. M.; Roberts, J. D. *J. Org. Chem.* **1975**, *40*, 3726–3729.
(28) Prins, I.; Verhoeven, J. W.; de Boer, Th. J. *Org. Magn. Reson.* **1977**, 543–545.
(29) Sakurai, T. *Acta Crystallogr., Sect. B* **1968**, *24*, 403–412.
(30) Sakurai, T. *Acta Crystallogr.* **1965**, *19*, 320–330.
(31) Pennington, W. T.; Patil, A. O.; Paul, I. C.; Curtin, D. Y.. unpublished work.

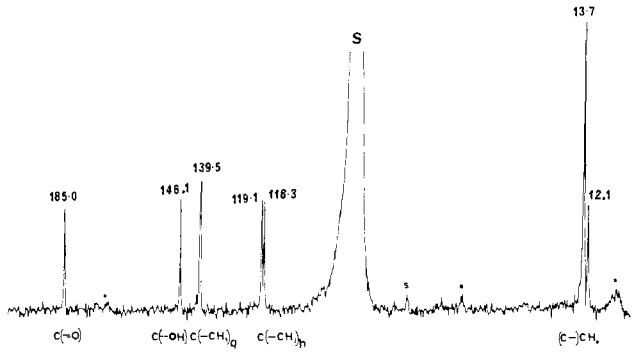


Figure 2. Solid-state CPMAS ^{13}C NMR spectrum of duroquinhydrone. Signals from the Delrin spinner are marked with an S and spinning sidebands with an asterisk.

distorted from the geometry found in less substituted quinhydrones because of the steric effect of the ortho methyl groups. The π overlap between adjacent layers is similar to that of monoclinic quinhydrone but with a somewhat greater separation between layers (Table III). The quinone and hydroquinone molecules each lie at a center of symmetry, and the spectrum (Figure 2) shows the expected single *C*=O and *C*OH resonances. The *C*CH_3 resonance of the quinone is also a single peak, but there are two *C*CH_3 resonances of the hydroquinone molecule (separation of 1 ppm) and two *C*H_3 resonances.

The changes in chemical shifts shown by quinone *C*=O atoms on formation of solid quinhydrone complexes seem to be similar in magnitude (but opposite in direction) to the shifts due to the effects of hydrogen bonding and not significantly larger than effects due to other crystallographic interactions. It is thus difficult to distinguish among these various influences. In every case we have studied, however, there are sufficient differences between the uncomplexed solid quinones and hydroquinones on the one hand and their complexes on the other to make the solid-state ^{13}C NMR a valuable method of distinguishing between the complexes and their uncomplexed components.

Two complexes which deserve special mention are those whose interconversion will be described in the following section. The 1/1 complex of 1,4-benzoquinone (**1**) with 2,5-dimethyl-1,4-hydroquinone (**6**) shows carbon resonances which have shifted less than 1 ppm from the corresponding resonances of the crystalline components except for the *C*H atoms of the quinone molecule which shift 3.5 ppm upfield on complex formation. Although the structure of this 1/1 complex has not been determined because single crystals have not been available, this shift suggests that the CH---O interactions found in the quinone may be weaker or absent in the complex. The second complex is the 1/2 complex of 2,5-dimethyl-1,4-benzoquinone (**2**) with 1,4-hydroquinone (**5**).[5c] The quinone *C*=O resonance in this complex is shifted upfield 1.1 ppm, the *C*-CH_3 carbon resonance upfield by 0.4 ppm, and the *C*H carbon 0.8 ppm from their positions in the crystalline quinone. The hydroquinone component shows two *C*OH carbon resonances at 150.9 and 148.4 ppm as might be expected from the different environments of the two hydroquinone molecules in the complex. However, it will be recalled that α-1,4-hydroquinone showed three resonances spread over 2.9 ppm from 149.8 to 146.9 ppm. Although the *C*H carbon atoms could, as seen in the crystal structure,[5c] have produced four resonances, only two resolvable signals were obtained.

A noteworthy difference between monoclinic and triclinic forms of the unsubstituted quinhydrones **1–5** is the difference in the time required to measure their spectra. A satisfactory spectrum of monoclinic quinhydrone required collection of data for 30 h whereas the triclinic polymorph gave a spectrum of comparable signal-to-noise ratio after only 3 h. This difference suggests that a more favorable relaxation mechanism is available for the triclinic form. The reason for the difference is subtle in view of the similarity of the two crystal structures. The volume per molecule of the monoclinic structure is 2.3% greater than that of the triclinic, suggesting that the monoclinic structure should have slightly looser packing with somewhat more molecular motion; the explanation of the implied difference in relaxation times must therefore lie elsewhere. Further studies of the correlation of relaxation time with structure of such polymorphic structures might lead to a better understanding of such effects and provide a valuable method for distinguishing between polymorphic structures. These correlations must be made with caution owing to the fact that proton relaxation in crystals is influenced by the presence of free radical impurities[10] and is likely to be sensitive to the presence of other impurities and crystal defects.

Use of ^{13}C NMR To Follow the Solid-State Redox Rearrangement of the 1/1 Complex of 1,4-Benzoquinone (1) with 2,5-Dimethyl-1,4-hydroquinone (6). In a previous paper[5c] it was shown that Fourier transform infrared spectroscopy (FTIR) could be employed to follow the course of rearrangement of certain quinhydrone complexes to their redox isomers in the solid state. This method had the disadvantage, however, that measurement of the spectra required preparation of mulls in Nujol and therefore introduced the possible complication that preparation of the mull might induce or accelerate reaction. It was in fact noted that reaction was faster when the solid quinhydrone was suspended in Nujol and also that in some cases an appreciable amount of reaction occurred in the cell during the measurement of the FTIR spectrum. The use of ^{13}C NMR as an alternative method of following such reactions therefore appeared attractive.

In the selection of a quinhydrone whose redox reaction was to be studied, it was desirable to choose one which rearranged completely to the redox isomer. This led to the requirement that the hydroquinone component be a substituted one such as 1,4-naphthohydroquinone or 2,5-dimethyl-1,4-hydroquinone and that the quinone molecule be unsubstituted. As a further consideration it was clearly desirable to choose a hydroquinone bearing methyl substituents since methyl groups, by decreasing the relaxation time as a result of their rotation, were found to decrease the time required to obtain spectra of satisfactory quality. The 1/1 complex of 1,4-benzoquinone (**1**) with 2,5-dimethyl-1,4-hydroquinone (**6**) met these conditions. However, it had been shown[5c] to rearrange in the solid state to a complex of 2,5-dimethyl-1,4-benzoquinone (**2**) and 1,4-hydroquinone (**5**) in a ratio not of 1/1 but 1/2, the extra molecule of 2,5-dimethyl-1,4-benzoquinone being eliminated. Stoichiometric considerations thus lead to the following reactions which might be studied.

$$1/1 \text{ complex } \mathbf{1\text{–}6} \rightarrow 1/2 \text{ complex } \mathbf{2\text{–}5} + \mathbf{2} \quad (1)$$

$$1/1 \text{ complex } \mathbf{1\text{–}5} + \mathbf{6} \rightarrow 1/2 \text{ complex } \mathbf{2\text{–}5} \quad (2)$$

$$1/1 \text{ complex } \mathbf{1\text{–}6} + \mathbf{5} \rightarrow 1/2 \text{ complex } \mathbf{2\text{–}5} \quad (3)$$

$$\mathbf{1} + \mathbf{5} + \mathbf{6} \rightarrow 1/2 \text{ complex } \mathbf{2\text{–}5} \quad (4)$$

We have carried out each of these reactions.

When the crystalline 1/1 complex was heated (reaction 1) for 34 h at 67–75 °C, there was obtained a ^{13}C NMR spectrum essentially identical with that of the 1/2 complex **2–5** with additional resonances to be expected from the dimethylquinone **2**. Spectra measured at intermediate time intervals were consistent with the smooth disappearance of the starting complex and formation of a mixture of the 1/2 complex and dimethylquinone.

Reaction 2 above proceeds the most cleanly of the four. In Figure 3 is shown a series of spectra measured when the mixture of **6** with the 1/1 complex **1–5**[5c] was heated at approximately 85 °C. The initial spectrum is in good agreement with that to be expected from a summation of the spectra of the complex **1–5** and that of **6**. It is seen that several resonances of the starting material diminish in intensity as reaction proceeds and other resonances grow in. The spectrum at the end of 500 min is essentially identical with that of the expected 1/2 complex of **2–5**. The time required for 50% reaction at 85 °C is approximately 4 h. Particularly significant is the absence of any resonances which appear at an early stage of the reaction and fade away later. This suggests that no appreciable amounts of any reaction intermediates (as, for example, the 1/1 complex of 1,4-benzoquinone with 2,5-dimethyl-1,4-hydroquinone) accumulate during reaction.

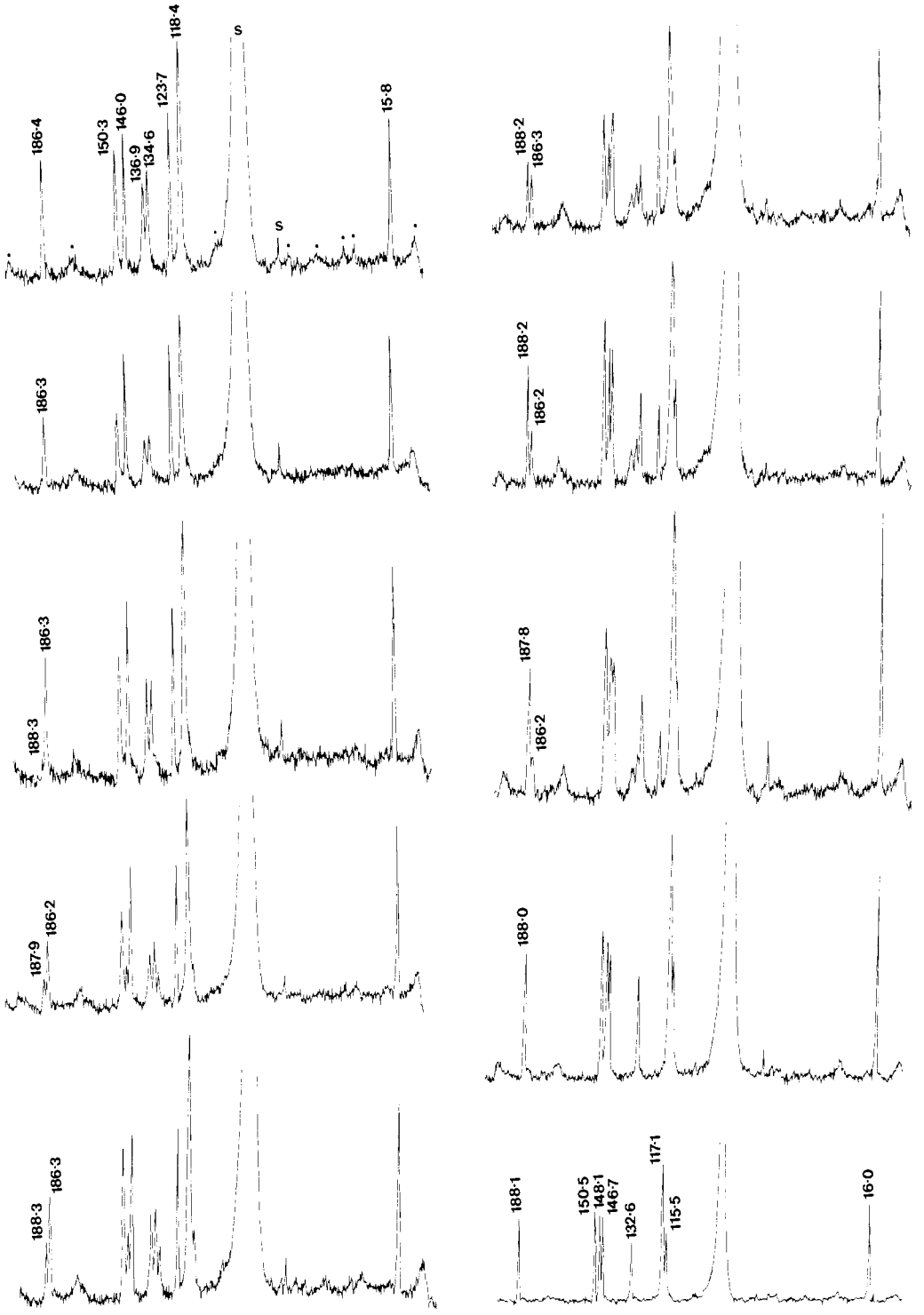


Figure 3. A series of solid-state CPMAS ^{13}C NMR spectra measured when a mixture of 2,5-dimethylhydroquinone (**6**) with the 1/1 complex of benzoquinone–hydroquinone (**1–5**) was heated at approximately 85 °C. Spectra (from top left downward) were measured at 0, 15, 20, 70, 130 min and (from top right downward) 230, 330, 420, and 500 min. At the bottom right is the solid-state spectrum of the 1/2 complex of **2–5** prepared by crystallization.

When the complex of **1** with **6** was mixed with **5** (reaction 3), the spectrum measured before heating indicated that extensive exchange had already occurred. Thus absorption at 188.4 ppm was much less intense than that at 186.3 ppm, characteristic of unsubstituted quinhydrone. The presence of substantial amounts of quinhydrone was also indicated by absorption at 137.3 and 134.8 ppm. There was no absorption characteristic of the redox product, the 1/2 complex of **2** with **5**, however. When this mixture was heated at 115 °C for 10 min, the spectrum obtained was substantially that of the 1/2 complex expected.

When equimolar amounts of **1**, **5**, and **6** were mixed (reaction 4 above), the initial spectrum showed that much of the quinone had disappeared and considerable quinhydrone (**1–5**) had formed although uncomplexed hydroquinone was still present also. After 5 min at 115 °C the mixture showed a spectrum almost identical with that of the 1/2 complex of **2** and **5**.

These results lead to the conclusion that the only mixture which can be counted on not to have undergone exchange of partners during its formation is the mixture of quinhydrone (**1–5**) with dimethylhydroquinone (**6**), presumably the most stable combination. The interchange of one hydroquinone for another in a complex is thus rapid relative to the rate of the redox hydrogen transfer between quinone and hydroquinone molecules. The redox exchange nevertheless occurs rapidly even in the absence of a

medium such as Nujol and is essentially complete after 8 h at 85 °C or 30 min at 115 °C.

Although the structure of the starting complex **1-6** is not known, it is presumed to have the essential features of the other 1/1 quinhydrones and to consist of hydrogen-bonded chains of alternating quinone and hydroquinone molecules stacked to form charge-transfer complexes in a second direction. The structure of the product **2-5** is more complicated.[5c] Clearly, extensive repacking accompanies reaction. The details are not known, but the change is complicated since it involved loss both of an electron pair and of two protons, one from each end of a hydroquinone molecule, presumably to two different quinone neighbors.

Although the potential of ^{13}C NMR as a tool for the study of reactions in the solid state is very great, it is apparent that its application is not nearly as straightforward as might have been anticipated from NMR studies in solution.

Acknowledgment. We are indebted to the National Science Foundation (USA) (Grant CHE 82-09393) for partial support of this work.

Registry No. 1, 106-51-4; **2**, 137-18-8; **3**, 527-17-3; **4**, 130-15-4; **5**, 123-31-9; **6**, 615-90-7; **7**, 527-18-4; **8**, 571-60-8; **1·5** (1:1), 106-34-3; **1·6** (1:1), 87970-32-9; **1·8** (1:1), 87970-33-0; **2·5** (1:2), 87970-37-4; **3·7** (1:1), 96914-21-5; **4·5** (1:1), 60706-28-7.

Spectral, Electrochemical and Base-Binding Studies of Heterodinuclear Ruthenium-Cobalt Complexes of *meso*-α,α,α,α-Tetra(nicotinamidophenyl)porphine

C. Michael Elliott,* J. Kenneth Arnette, and R. R. Krebs

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 85023. *Received December 26, 1984*

Abstract: The spectral, electrochemical, and ligand addition properties of metal complexes of the modified porphyrin $(nic)_4H_2TPP$ have been examined. The porphyrin has the feature that two metal ions may be coordinated and held in close proximity to each other, one ion in the porphyrin ring and the other coordinated to the pyridine-like nitrogens of the nicotinamide pickets. The results for the $RuCl_2(nic)_4CoTPP$ complex studied indicate that the "neutral" fixed axial ligand $Ru^{II}Cl_2$ has very little effect on the electrochemistry and spectroscopy of the cobalt porphyrin when compared with simple CoTPP. However, oxidation of Ru(II) to Ru(III) greatly increases the Lewis acid strength of Co(II) relative to the strength of that center in CoTPP. The binding constant for the Ru(III)-Co(II) species with pyridine is found to be three orders of magnitude larger than that for Ru(II)-Co(II); the binding constant for Ru(III)-Co(III) with pyridine is seven orders of magnitude greater than that for Ru(III)-Co(II). In the presence of high concentrations of *N*-methylimidazole, the Ru(III)-Co(III) appears to form a bis-adduct, presumably by allowing partial entry of a 1-MeIm molecule into the porphyrin pocket.

The preparation and study of metal complexes containing multiple metal centers in well-defined geometric arrangements are of considerable interest. This fact is especially true when the metals are arranged so that they can exert a significant influence on one another with respect to such properties as redox potential, magnetic ground states, and propensity for ligand binding. Aside from the purely fundamental aspects of metal-metal interactions, multiple metal centers are known to be important in many unique catalytic processes carried out by some enzymes.[1] They have been implicated without proof in an even larger number of biological reactions.[1] Synthetic multimetal systems, therefore, are often useful in helping to better understand complex biological systems. Also, they sometimes possess properties of both fundamental and practical interest which are absent in the separate monomeric units.[2-4]

For a number of years we have been interested in heterodinuclear complexes of the ligand *meso*-α,α,α,α-tetra(*o*-nicotinamidophenyl)porphyrin. We have reported, in preliminary form, studies on a variety of complexes of the form $RuCl_2(nic)_4TPPM$ where M is a metal species coordinated in the porphyrin pocket.[5] Herein we report a detailed study of the cobalt complex from this series, primarily from the standpoint of its redox and ligand binding properties. A major factor that makes these complexes unique is the ability to convert the ruthenium center from an overall neutral Ru(II) species (which exerts only a very modest effect on the porphyrin bound cobalt center) into a cationic Ru(III) species. As will be presented subsequently, this simple change in ruthenium oxidation state, and thus charge, induces dramatic but indirect effects in the chemistry of the cobalt, e.g., drastically increasing the binding constant for certain nitrogenous bases at the cobalt(II) center.

Experimental Section

Synthesis. The structure of the ligand α,α,α,α-$(nic)_4H_2TPP$ is given in Figure 1.

α,α,α,α-(nic)$_4$H$_2$TPP (1). *meso*-Tetra(*o*-aminophenyl)porphyrin (H_2TAPP) was prepared by the method of Collman.[6] The α,α,α,α-atropisomer was separated by the methods of Collman,[6] Elliott,[7] or Lindsey.[8] Nicotinoyl chloride hydrochloride ((nic)Cl·HCl) was prepared by dissolving 10 g of nicotinic acid in 100 mL of CH_2Cl_2 containing 15 mL of thionyl chloride ($SOCl_2$, Fisher, reagent) and a few drops of *N*,*N*-dimethylformamide (DMF). The solution was stirred and refluxed for 0.5 h. Upon cooling, fine, slightly yellow crystals formed which were isolated by filtration, washed with $CHCl_3$, and dried, all under an N_2 atmosphere.

The ligand α,α,α,α-$(nic)_4H_2TPP$ was synthesized by dissolving α,α,α,α-H_2TAPP (1.00 g) in 100 mL of dry CH_2Cl_2. To this solution, 6

(1) For example, see: Ibers, J. A.; Holm, R. H. *Science (Washington, D.C)* **1980**, *209*, 223.
(2) Collman, J. P.; Marrocco, M.; Elliott, C. M.; L'Her, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *124*, 113-131.
(3) Collman, J. P.; Marrocco, M.; Denisevich. P.; Koval, C.; Anson, F. C. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *101*, 117.
(4) Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Anson, F. C.; Koval, C. *J. Am Chem. Soc.* **1980**, *102*, 6027.
(5) Elliott, C. M.; and Krebs, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 4301.
(6) Collman, J. P.; Gagnê, C. A.; Reed, C. A.; Halbert, T. R.; Lang, G.; Robinson, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 1427.
(7) Elliott, C. M. *Anal. Chem.* **1980**, *52*, 666.
(8) Lindsay, J. *J. Org. Chem.* **1980**, *45*, 5215.

0002-7863/85/1507-4904$01.50/0