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NH-Acid Properties of Porphyrins in Acetonitrile

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Abstract—The thermodynamics of acid dissociation of synthetic porphyrins (H_2P) in alkaline acetonitrile solution is studied. The low stability of the anionic species is attributed to the previously formulated electronic, steric, and solvation factors. The solvent plays an important role in the stabilization of anionic porphyrin species in acetonitrile. The electronic absorption spectra of anionic species of H_2P are analyzed.

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The mechanism and conditions of proton transfer from an acid to a base in the gas and liquid phases differ essentially, mainly owing to the solvation contribution to stabilization of ionic species. These differences are particularly pronounced with complex multicentered macrocyclic molecules (e.g., porphyrins, H_2P) as acids or bases. Factors affecting the stability of ionic (both cationic and anionic) forms of macrocyclic compounds yielded by proton transfer can be subdivided into electronic (polarization), structural (or steric), and solvation factors [1]. These factors are particularly significant for such weak acids and bases with rigidly shielded reaction centers as porphyrins. The contributions of each of these factors to the overall stabilization of the ionic species may differ depending on the structural group to which the given macrocycle H_2P belongs and on the solvent.

In numerous studies concerning the acid–base properties of porphyrins (H_2P) [1–3], most attention was given until recently to the formation and dissociation [equilibria (1), (2)] of protonated species:

$$H_4P^{2+}_{(solv)} \overset{K_3}{\rightleftarrows} H^+_{(solv)} + H_3P^+_{(solv)}\,, \qquad (1)$$

$$H_3P^+_{(solv)} \overset{K_4}{\rightleftarrows} H^+_{(solv)} + H_2P^+_{(solv)}\,. \qquad (2)$$

Mono- and dications of porphyrins were subjected to structural (single-crystal X-ray diffraction, ^{1}H NMR spectroscopy) [4, 5] and thermodynamic [1–3] studies; their excited states were examined [6, 7]. Thus, there are much data on the structure of protonated H_2P species in the solid phase and solution and on the dependence of the base properties of these molecules on the structure of the macrocycle and nature of the solvent. Unfortunately, the anionic species of H_2P [equilibria (3), (4)] were studied insufficiently.

$$H_2P_{(solv)} \overset{K_1}{\rightleftarrows} H^+_{(solv)} + H_3P^-_{(solv)}\,, \qquad (3)$$

$$HP^-_{(solv)} \overset{K_2}{\rightleftarrows} H^+_{(solv)} + P^{2-}_{(solv)}\,. \qquad (4)$$

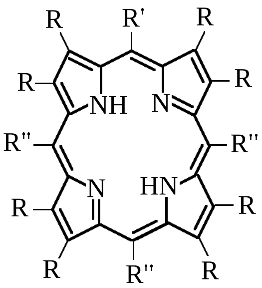
We studied previously [8, 9] the NH-acid properties of compounds H_2P belonging to various structural groups, in DMSO and DMF. As a continuation of these studies, here we report and discuss the thermodynamic parameters of acid dissociation of synthetic porphyrins **I**–**V** in acetonitrile under the action of tetra-*n*-butylammonium hydroxide ($[Bu_4N]OH$).

Porphyrins are usually subdivided into classical (with moderate distortion of macroring planarity and well-known properties [2, 3, 6]) and nonclassical (with nontraditional structure and properties [1, 10]) H_2P. Compounds **I** and **II** examined in this study are typical classical H_2P. There are two types of porphyrins with nontraditional structure: planar highly aromatic H_2P (azaporphyrins, phthalocyanines) and, on the contrary, porphyrins of essentially nonplanar structure [e.g., dodecasubstituted compounds $H_2(\beta\text{-R})_8 \cdot (meso\text{-R})_4P$]. Apparenty, porphyrin **III**, despite its less planar structure compared to **I** [11], can still be considered as classical H_2P. Tetrabenzoporphine **IV**, which is more planar and aromatic compared to compounds **I**–**III**, belongs to the group of rigid nonclassical H_2P, whereas its *meso*-tetraphenyl derivative **V** is a dodecasubstituted H_2P with a nonplanar structure [11].

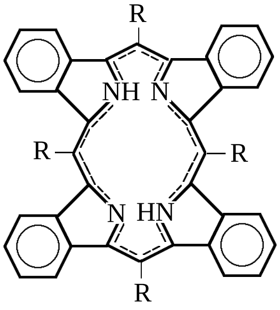
This study is the first successful attempt to exam-

Thermodynamic parameters of acid dissociation [Eqs. (3), (4)] of porphyrins **I**–**V** in $CH_3CN–[Bu_4N]OH$

Comp. no.	pk_i^{298}		ΔG^0, kJ mol^{-1}	ΔH, kJ mol^{-1}	ΔS, J mol^{-1} K^{-1}
I	pK_1	26.58 ± 0.25	152 ± 15	122 ± 12	–101 ± 10
	pK_2	26.54 ± 0.25	151 ± 15	495 ± 50	1154 ± 115
	$pK_{1,2}$	53.15 ± 0.25	303 ± 30	617 ± 62	1053 ± 105
II	pK_1	24.05 ± 0.25	137 ± 10	2 ± 0.2	–453 ± 45
	pK_2	25.00 ± 0.25	143 ± 14	127 ± 13	–54 ± 5
	$pK_{1,2}$	49.05 ± 0.25	280 ± 30	129 ± 13	–507 ± 50
III	pK_1	26.94 ± 0.27	154 ± 15	210 ± 20	188 ± 20
	pK_2	29.52 ± 0.30	168 ± 16	–110 ± 10	–933 ± 90
	$pK_{1,2}$	56.46 ± 0.30	322 ± 31	100 ± 10	–745 ± 70
IV	pK_1	31.00 ± 0.31	177 ± 17	101 ± 11	–255 ± 25
V	pK_1	28.29 ± 0.30	161 ± 16	152 ± 15	–30 ± 3
	pK_2	31.45 ± 0.30	179 ± 18	254 ± 25	252 ± 25
	$pK_{1,2}$	59.74 ± 0.30	340 ± 34	406 ± 40	222 ± 22



I–III



IV, V

R = Et, R' = R'' = H (**I**); R = H, R' = R'' = Ph (**II**); R = R' = Et, R'' = H (**III**); R = H (**IV**), Ph (**V**).

ine the acid properties of porphyrins in acetonitrile (see table). The acid dissociation of H_2P in this solvent is characterized by low dissociation step constants (10^{-24}–10^{-32}), the occurrence of double deprotonation of the porphyrin ligands, and separation of the NH deprotonation steps in the titration curves (Fig. 1a). In DMSO, under similar conditions, only the first step [Eq. (3)] was realized [1, 8]. The deeper dissociation

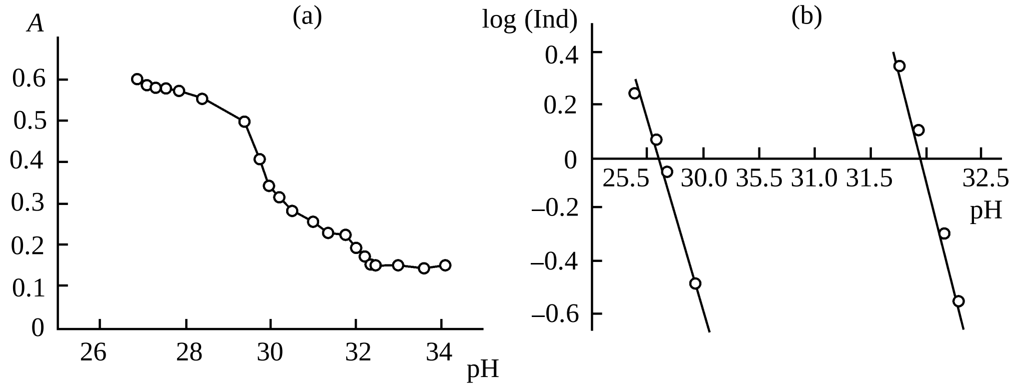


Fig. 1. (a) Titration curve and (b) the corresponding log(Ind) = f(pH) dependences, where Ind is the indicator ratio, Ind = c_{H_2P}/c_{HP^-}, for acid dissociation equilibria (3) and (4) (left and right straight lines, respectively) of *meso*-tetraphenyltetrabenzoporphine **V** in $CH_3CN–[Bu_4N]OH$ at 298 K.

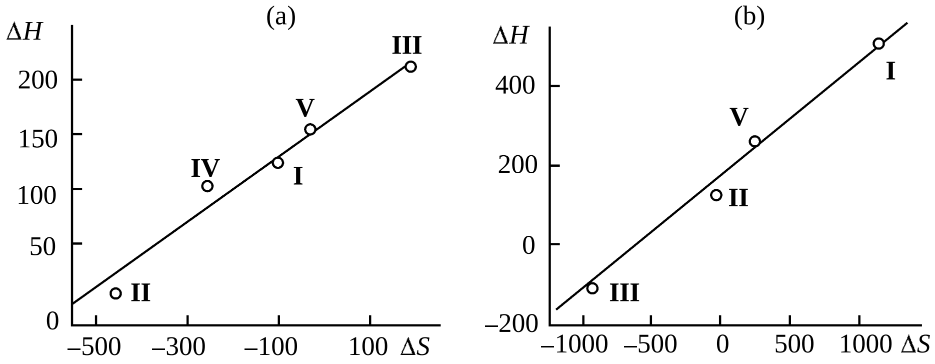


Fig. 2. Solvatothermodynamic compensation effect in acid dissociation equilibria (a) (3) and (b) (4) of compounds **I**–**V** in the acetonitrile–tetra-*n*-butylammonium hydroxide system.

of the porphyrins in acetonitrile is due to the abovementioned factors stabilizing the ionic H_2P species [1], and primarily to the solvation factors.

The NH acidity decreases in the order *meso*-tetraphenylporphine **II** > β-octaethylporphine **I** > *meso*-monoethyl-β-octaethylporphine **III** (see table). *meso*-Tetraphenylporphine **II** is the strongest NH acid owing to the following facts. First, as compared to porphyrin **I**, it is somewhat less planar [11], which makes the NH centers more accessible to an attack of a base. Second, *meso*-phenyl fragments provide efficient delocalization of the excess electron density [6, 12], thus stabilizing the mono- and dianions. β-Octaethylporphine **I** as an acid is weaker than **II** by four orders of magnitude (for both dissociation steps); this is also due to the presence of eight electron-donor ethyl substituents in the β positions, decreasing the polarization of the NH bonds. Introduction of an additional ethyl group into one of the *meso* positions of **I** (i.e., into the main conjugation contour) decreases the acidity of one of the NH bonds in **III** by additional three orders of magnitude (see table), although the pK_1 values for **I** and **III** are close (26.6 and 26.9, respectively). Apparently, the factor of steric distortion, although it is manifested relatively weakly in nonasubstituted H_2P [11], compensates the electron-donor effect of the *meso*-ethyl group in the first dissociation step. At the same time, the pK_2 of **III** is appreciably larger than that of **I**. The nonparallel variation of pK_1 and pK_2 in going from **I** to **III** is caused by the unsymmetrical substitution of **III** and hence by the electronic nonequivalence of the two NH bonds. Similar pattern was observed previously in the acid dissociation of the protonated porphyrin species: The monocation H_3P^+ was detected in the electronic absorption spectra and in the titration curves only when the tertiary N atoms considerably differed in the basicity (e.g., in chlorins, singly N-substituted analogs of H_2P, etc. [1, 6]).

The NH acidity of tetrabenzoporphine **IV**, whose aromaticity is appreciably higher than that of the other H_2P studied, appeared to be unexpectedly low. It is believed that an increase in the aromaticity of porphyrin molecules enhances their acid properties because of activization of the electronic (polarization) component of the macrocyclic effect [13], whereas the structural component, on the contrary, impedes the abstraction of the NH proton with a base. We found that, in contrast to DMF and DMSO (solvents with pronounced electron-donor properties), in CH_3CN the acid properties of **IV** are not enhanced compared to classical H_2P. The strength of rigid nonclassical porphyrins (tetrabenzoporphyrins, porphyrazines) [10] as acids in typical electron-donor solvents such as DMSO is higher than that of classical H_2P because of chemical activation of the NH bonds in electron-donor solvents [14, 15]. Acetonitrile cannot be classed with strong electron donors, because, at a high dielectric constant (ε 36.0), it has relatively low donor number (*DN* 14.1) and high acceptor number (*AN* 18.9) [16]. Apparently, the entropy factor exerts a decisive influence on the thermodynamic stability of anionic H_2P species. Acetonitrile is a dipolar aprotic solvent equally poorly solvating both cations and anions [17, 18]. Probably, solvation of the anionic species is one of the most important factors of their stabilization. Therefore, e.g., tetrabenzoporphine **IV** in acetonitrile is by more than ten orders of magnitude weaker acid (with respect to the first step, pK_1 31.0) than in DMSO (pK_1 18.5 [8]) and especially in DMF (pK_1 12.0 [9]), which better solvate the anions [17]. Under the conditions of our experiment, the anionic H_2P species are strongly unstable, because they are stabilized neither by the solvent nor by the bulky $[Bu_4N]^+$ counterion. Furthermore, as seen from the table, the acid dissociation of H_2P is energy-consuming ($\Delta H > 0$). The linear correlations $\Delta H = f(\Delta S)$ (Fig. 2) show that the energy consumption for the ionization of por-

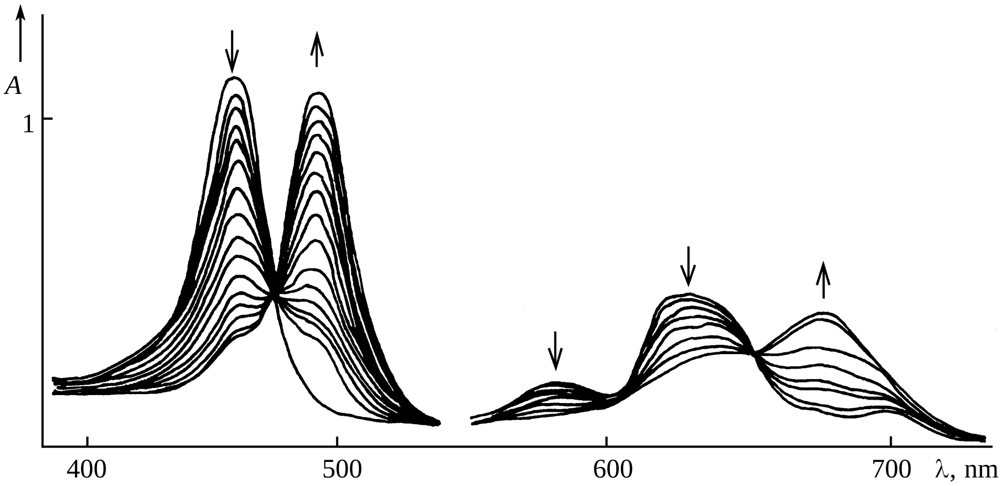


Fig. 3. Evolution of the electronic absorption spectrum in the course of titration of **V** with a solution of tetra-*n*-butylammonium hydroxide in acetonitrile at 288 K. Arrows denote the direction of the spectrum evolution with addition of portions of the base. (*A*) Optical density.

phyrin molecules in processes (3) and (4) is compensated for by the change in entropy due to additional solvation of the ionic species HP^- and P^{2-} in the solution (solvatothermodynamic compensation effect).

Compound **IV** appeared to be a weaker NH acid than its *meso*-tetraphenyl derivative **V** (see table). Hence, as suggested in [19], dodecasubstitution of the porphyrin molecule enhances its acid properties, which is due to two factors: better accessibility of the NH reaction centers in more conformationally labile *meso*-tetraphenyltetrabenzoporphine (**V**) [11] and internal polarization arising from a change in the conformation of the dodecasubstituted ligand [20]. At the same time, it should be noted that the four phenyl groups in **V** are considerably less efficient as “buffers” for delocalization of the excess electron density than those in *meso*-tetraphenylporphine (**II**), because in **V** even partial conjugation of the *meso*-phenyl fragments with the main macroring is sterically impossible [11].

The examined compounds, except the least acidic porphyrin **IV**, in the $CH_3CN–[Bu_4N]OH$ system dissociate in two steps (see table). The monoanionic species HP^- are readily detected in the titration curves (Fig. 1a) but do not give a characteristic electronic absorption spectrum. Figure 3 shows a typical pattern of variation of the spectrum in the course of base titration of H_2P in acetonitrile. Our and published [1, 6] data show that the formation of the porphyrin dianion is accompanied by a bathochromic shift of the strong Soret band and a hypsochromic shift of the long-wave Q_x band (band I) characterizing the strength of the porphyrin chromophore. Apparently, as in the case of formation of acidic dicationic species H_4P^{2+}, the hypsochromic shift is caused by the degeneration of the electronic levels upon formation of the P^{2-} dianion whose symmetry, like that of H_2P^{2+}, is higher (D_{4h}) than that of H_2P (D_{2h}) [6]. This assumption is also confirmed by the fact that the porphyrin dication and diation, having similar symmetry, also have similar absorption spectra (Fig. 3). Also, the formation of the dianion results in filling of the lowest unoccupied molecular orbital of the macroring by a lone electron pair and hence in mutual repulsion of the electron pairs occupying the highest molecular orbials.

Published data on the photophysics of anionic and cationic porphyrin species [1, 6] allow a conclusion that the acid ionization of H_2P, in contrast to its base ionization, is not accompanied by appreciable distortion of the macroring planarity. In particular, the anionic porphyrin species are characterized by small Stokes shifts [$\Delta\nu_1$, Eq. (5)] of bands I in the fluorescence spectra relative to bands I in the absorption spectra. The quantity $\Delta\nu_1$ is one of photophysical characteristics of the nonplanarity of porphyrin macrorings [7, 20]:

$$\Delta\nu_I = \nu_I^{fl} - \nu_I^{abs}. \quad (5)$$

The spectral pattern observed in the formation of cationic species of *meso*-tetraphenylporphine **II** differs from that observed with the other porphyrins, namely, the Q_x band of **II** is shifted bathochromically upon protonation [1, 6, 12]. One of the causes of the bathochromic shift of the Q_x bands in **II** and in other compounds H_2P with *meso* substituents principally capable of conjugation with the main porphyrin macroring (C_6H_5, CH_2=CH, etc.) is the “buffer effect” of the *meso*-phenyl substituent [1, 12]. Namely, partial π conjugation of the *meso* fragment with the macroring arises upon accumulation of excess positive or negative charge in the macroring and leads to the charge delocalization [1, 6]. Apparently, the formation of the anionic forms of **II** favors the conjugation of the phenyl substituents to a considerably lesser extent than in formation of the cationic forms, and the chromophore system is not extended (the Q_x band in the electronic absorption spectrum undergoes no bathochromic shift in the course of deprotonation of *meso*-tetraphenylporphine).

Thus, the study of the acid dissociation of **I**–**V** in the CH_3CN–$[Bu_4N]OH$ system confirms the important role of solvation in the stabilization of extremely unstable anionic species in this solvent, as follows from the values of pK_1 and pK_2. The asymmetric substitution of the molecule exerts a differentiating effect on the dissociation constants of H_2P. Acetonitrile only weakly activates the NH bonds in the molecules of nonclassical H_2P; therefore, the acid properties of such porphyrins in CH_3CN are weaker than in strong electron-donor solvents.

EXPERIMENTAL

Compounds **I**–**V** were prepared, isolated, and identified by published procedures [12, 21]. Acetonitrile was pretreated according to [22]. The water content in the solvent, determined by Fischer titration, did not exceed 0.02%. A solution of tetrabutylammonium hydroxide ($[Bu_4N]OH$) in acetonitrile was prepared from its 1 M solution in methanol (chemically pure grade) after removing the solvent in a vacuum. The acid dissociation constants of **I**–**V** [equilibria (3) and (4)] were determined by spectrophotometric titration (SF-18) with potentiometric monitoring of pH [1, 8, 9] at 288–308 K. The solution emf was measured with an electrode couple consisting of glass (ESL-63-07) and flow-through silver electrodes. The glass electrode was calibrated [emf = f(pH)] with o-cresolphthalein indicator whose acid dissociation constant in acetonitrile is known [18] and the acidity function in the titration range is linear. The character of the acid dissociation of H_2P was judged from the titration curves $A = f(\text{pH})$ (Fig. 1a) and from the slopes of the indicator dependences $\log(\text{Ind}) = f(\text{pH})$ (Fig. 1b). The quantities pK_i and the thermodynamic parameters of processes (3) and (4) were calculated by standard equations.

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REFERENCES

1. Andrianov, V.G., Malkova, O.V., and Berezin, D.B., *Uspekhi khimii porfirinov* (Advances in Porphyrin Chemistry), Golubchikov, O.A., Ed., St. Petersburg: Nauchno-Issled. Inst. Khimii S.-Peterb. Gos. Univ., 2001, vol. 3, p. 107.
2. Hambright, P., *Porphyrins and Metalloporphyrins,* Smith, K.M., Ed., Elsevier: Oxford, 1975, p. 233.
3. Berezin, B.D., *Coordination Compounds of Porphyrins and Phtalocyanine,* New York: Wiley, 1981.
4. Senge, M.O., Forsyth, T.P., Nguyen, L.T., and Smith, K.M., *Angew. Chem., Int. Ed. Engl.,* 1994, vol. 33, no. 23/24, p. 2485.
5. Medforth, C.J., *The Porphyrin Handbook,* Kadish, K.M., Smith, K.M., and Guilard, R., Eds., San Diego: Academic, 2000, vol. 5, p. 1.
6. Gurinovich, G.P., Sevchenko, A.N., and Solov’ev, K.N., *Spektroskopiya khlorofilla i rodstvennykh soedinenii* (Spectroscopy of Chlorophyll and Related Compounds), Minsk: Nauka i Tekhnika, 1968.
7. Chirvony, V.S., Hoek, A. van, Galievskii, V.A., Sazanovich, I.V., Schaafsma, T.J., and Holten, D., *J. Phys. Chem. B,* 2000, vol. 104, no. 42, p. 9909.
8. Sheinin, V.B., Andrianov, V.G., Berezin, B.D., and Koroleva, T.A., *Zh. Org. Khim.,* 1985, vol. 21, no. 7, p. 1564.
9. Tsvetkova, I.V., Andrianov, V.G., and Berezin, B.D., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.,* 1994, vol. 37, no. 1, p. 73.
10. Berezin, B.D. and Berezin, D.B., *Uspekhi khimii porfirinov* (Advances in Porphyrin Chemistry), Golubchikov, O.A., Ed., St. Petersburg: Nauchno-Issled. Inst. Khimii S.-Peterb. Gos. Univ., 1999, vol. 2, p. 128.
11. Senge, M.O., *The Porphyrin Handbook*, Kadish, K.M., Smith, K.M., and Guilard, R., Eds., San Diego: Academic, 2000, vol. 1, p. 239.
12. Berezin, D.B., Andrianov, V.G., and Semeikin, A.S., *Opt. Spektrosk.,* 1996, vol. 80, no. 4, p. 618.
13. Lomova, T.N. and Berezin, D.B., *Problemy khimii rastvorov. Biologicheski aktivnye veshchestva v rastvorakh* (Problems of Solution Chemistry. Biologically Active Substances in Solutions), Kutepov, A.M., Ed., Moscow: Nauka, 2001, p. 326.
14. Petrov, O.A., *Koord. Khim.,* 2001, vol. 27, no. 7, p. 483.

15. Berezin, D.B., Toldina, O.V., and Kumeev, R.S., *Zh. Fiz. Khim.*, 2004, vol. 78, no. 8, p. 1427.
16. Fialkov, V.Ya., *Rastvoritel' kak sredstvo upravleniya khimicheskim protsessom* (Solvent as a Means for Controlling a Chemical Process), Leningrad: Khimiya, 1990.
17. Krestov, G.A., Novoselov, N.P., and Perelygin, I.S., *Problemy khimii rastvorov. Ionnaya sol'vatatsiya* (Problems of Solution Chemistry. Ion Solvation), Krestov, G.A., Ed., Moscow: Nauka, 1987.
18. Kolthoff, I.N., Chantooni, M.K., and Bhowmik, S., *Anal. Chem.*, 1967, vol. 39, no. 13, p. 1627.
19. Takeda, J. and Sato, M., *Chem. Lett.*, 1995, no. 11, p. 971.
20. Chirvony, V.S., Sazanovich, I.V., Galievsky, V.A., Hoek, A. van, Schaafsma, T.J., Malinovskii, V.L., and Holten, D., *J. Phys. Chem. B*, 2001, vol. 105, no. 32, p. 7818.
21. Ichimura, K., Sakuragi, M., Morii, H., Yasuike, M., Fukui, M., and Ohno, O., *Inorg. Chim. Acta*, 1991, vol. 182, p. 83.
22. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, New York: Wiley, 1972.