Weak Charge-transfer Polyoxoanion Salts: The Reaction of Quinolin-8-ol (Hquin) with Phosphotungstic Acid and the Crystal and Molecular Structure of $[H_2quin]_3[PW_{12}O_{40}]\cdot4EtOH\cdot2H_2O$*

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Different solvated charge-transfer salts between quinolin-8-ol (Hquin) and phosphotungstic acid have been synthesized and characterized. Spectroscopic data support the presence of a sizeable electronic interaction between electron-rich aromatic organics and the inorganic acid, both in the solid state and in solution, provided that a large excess of the organic is present. This interaction is responsible for the formation of photosensitive compounds and provides a rationale for the subsequent facile photo-oxidation of the organic substrate. The crystal and molecular structure of $[H_2quin]_3[PW_{12}O_{40}]\cdot4EtOH\cdot2H_2O$ has been solved by the heavy-atom method and refined to a final $R = 0.083$, for 4 902 reflections with $I \geqslant 3\sigma(I)$: triclinic space group $P\bar{1}$ with $a = 11.721(3)$, $b = 12.818(3)$, $c = 12.878(3)$ Å, $\alpha = 89.20(2)$, $\beta = 104.10(2)$, $\gamma = 117.30(2)$ °, and $Z = 1$. The anion structure consists of an α-Keggin-type molecule in two-fold disorder. The 8-hydroxyquinolinium moieties (three per $[PW_{12}O_{40}]^{3-}$) are stacked approximately along the x direction, with alternative interplanar spacings of 3.25 and 3.57 Å. The crystal structure determination reveals the absence of any substantial, direct interaction between the organic cations and the phosphototungstate anions. Therefore no clear structural basis for the electronic interaction noted above can be given.

Precomplexation between organic substrates and some soluble metal oxides, such as iso- and hetero-polyanions has recently been shown to be a necessary prerequisite for the subsequent photo-oxidation of such organic substrates.[1-3] In the case of some strongly polar, aprotic, organic molecules, such as substituted amides, these donor–acceptor complexes are strong enough to induce large shifts in the electronic spectrum of the polyanion and allow the isolation and structural characterization of stable crystalline compounds.[4-7]

We have observed that other electron-rich molecules, such as alkyl aromatic hydrocarbons, weakly interact with heteropolyanions, which in turn can promote efficient thermal or photochemical catalytic oxidation of alkylbenzenes.[8,9]

In the search for stronger interactions, possibly to be investigated in the solid state, we have examined the reaction between α-$H_3PW_{12}O_{40}$ and several aromatic bases and now report the synthesis and some general properties of different salts of phosphotungstic acid with quinolin-8-ol Hquin, together with the crystal and molecular structure of the weak charge-transfer complex $[H_2quin]_3[PW_{12}O_{40}]\cdot4EtOH\cdot2H_2O$, (1).

In addition to the organic–inorganic interactions, two peculiarities of the chemistry of heteropolyanions are illustrated by the synthetic and structural work presented here. First is the ability of these large, quasi-spherical inorganic anions to promote the stacking and electronic interaction of planar, conjugated organic molecules. Other examples of this property are the mixed-valence tetrathiofulvalene [2-(1′,3′-dithiol-2′-ylidene)-1,3-dithiole] salts.[10,11]

Second is the fact that heteropolyanions can easily and stably bind, through extended hydrogen bonding, a surprisingly large number of organic molecules. In the past the well known use of such ions as precipitants for biomolecules or as non-specific staining agents for electron microscopy has taken advantage precisely of this property.[12-15]

Experimental

Reagents.—All materials and organic solvents were reagent grade (Fluka) and used as supplied. The compounds $[NBu_4]_3[PW_{12}O_{40}]$ and $[Cu(quin)_2]$ were prepared according to literature methods.[8,16] Elemental analyses (C, H, N) were performed either by the Servizio Microanalitico, Area della Ricerca di Roma, CNR, or by H. Malissa Analitische Laboratorien, Elbach, West Germany (other elements).

Preparation of Solvated $[H_2quin]_3[PW_{12}O_{40}]$.—Quinolin-8-ol (290 mg, 2 mmol) was dissolved in hot MeCN (30 cm^3) and added with stirring to a hot solution of $H_3PW_{12}O_{40}\cdot nH_2O$ (1.96 g, 0.68 mmol) in water (50 cm^3). The resulting yellow solution was filtered, stoppered, and set aside to give, after 2 d, 1.55 g (70%) of a yellow crystalline material which approximately analyses as $[H_2quin]_3[PW_{12}O_{40}]\cdot MeCN$ (Found: C, 10.80; H, 0.90; N, 1.54. Calc. C, 10.40; H, 0.80; N, 1.65%). This product (400 mg) was dissolved in boiling, anhydrous ethanol (100 cm^3) to give, in a few days, yellow, *X*-ray-quality crystals which analysed as $[H_2quin]_3[PW_{12}O_{40}]\cdot4EtOH\cdot2H_2O$, (1) (Found: C, 11.75; H, 1.45; N, 1.10; P, 0.95; W, 62.50; EtOH, 5.0; H_2O, 1.0. Calc. C, 11.90; H, 1.50; N, 1.20; P, 0.90; W, 62.40; EtOH, 5.20; H_2O, 1.0%). Thermal gravimetric analysis (t.g.a.) showed that ethanol was lost in two close, but distinct steps of three and one molecule at *ca.* 50 °C, whereas water required a much higher temperature to be eliminated (*ca.* 300 °C). Upon exposure to air (1) slowly lost its ethanol content being converted into $[H_2quin]_3[PW_{12}O_{40}]\cdot2H_2O$ (Found: C, 9.70; H, 0.85; N, 1.25. Calc. C, 9.70; H, 0.85; N, 1.20%). Further confirmation of the stoicheiometry of (1) came from its ^1H n.m.r. spectrum (200 MHz, CD_3CN). Lines due to the ethanol

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

molecules showed the expected intensity ratio with respect to the five multiplets which were assigned as follows to the protons of the H_2quin cations: $\nu_2 = 8.97$, $\nu_3 = 8.09$, $\nu_4 = 9.14$, ν_5, $\nu_6 = 7.85$, and $\nu_7 = 7.58$; $J(H^2H^3) = 5.49$, $J(H^2H^4) = 1.49$, $J(H^3H^4) = 8.48$, $J(H^5H^6) = 8.0$, $J(H^5H^7) = 1.20$, and $J(H^6H^7) = 8.10$ Hz.

Crystallization of the crude salt from other organic solvents was possible and generally gave the corresponding solvates. As an example, from mixtures of dimethylformamide (dmf) and water $[H_2quin]_3[PW_{12}O_{40}]$·3dmf, (**2**) was obtained. (Found: C, 12.40; H, 1.30; N, 2.15. Calc. 12.25; H, 1.30; N, 2.40%).

Preparation of $[H_2quin]_3[PW_{12}O_{40}]$·9Hquin.—Mixing hot solutions of quinolin-8-ol (395 mg, 2.7 mmol) in MeCN (15 cm^3) and $H_3PW_{12}O_{40}$·$n$$H_2O$ (980 mg, 0.34 mmol) in water (30 cm^3) gave immediate, quantitative precipitation of an insoluble yellow powder which analysed as $[H_2quin]_3[PW_{12}O_{40}]$·9Hquin, (**3**) (Found: C, 28.65; H, 1.90; N, 3.85; P, 0.80; W, 47.50. Calc. C, 28.05; H, 1.90; N, 3.65; P, 0.65; W, 47.75%). Dissolution of this product was possible only in boiling dmf. However, decomposition occurs and crystals of $[WO_2(quin)_2]$ were obtained.

Preparation of $H_3PW_{12}O_{40}$·$x$$[Cu(quin)_2]$ ($x \approx 30$).—Solid $H_3PW_{12}O_{40}$·$n$$H_2O$ (500 mg, 0.17 mmol) was added to a boiling MeCN suspension of $[Cu(quin)_2]$ (183 mg, 0.52 mmol, 30 cm^3) to give a quasi-clear solution and, immediately after, complete precipitation of an insoluble green-brown powder, which analysed as $H_3PW_{12}O_{40}$·30Cu$(quin)_2$, (**4**) (Found: C, 48.55; H, 2.45; Cu, 14.60; N, 5.65; W, 16.00. Calc. C, 48.35; H, 2.70; Cu, 14.20; N, 6.25; W, 16.40%). Also in this case solubilization was possible in boiling dmf (100 mg, 40 cm^3), but only pure $[Cu(quin)_2]$ could be recovered in this way.

Physical Measurements.—T.g.a. and differential thermal analysis (d.t.a.) were carried out under dry nitrogen on a Stanton-Redcroft STA-781 thermoanalyser. I.r. and optical solution or diffuse-reflectance spectra were recorded, respectively, on a Perkin-Elmer 983-G and 330, or a Beckmann DK2A spectrophotometer. E.p.r. spectra were recorded with a Varian E-9 *X*-band spectrometer equipped with a Bruker BNM-20 gaussmeter and a 6246-A Systron-Donner frequency counter, ^1H n.m.r. spectra by the Servizio NMR, Area della Ricerca di Roma, CNR, using a Bruker WP-200 spectrometer operating at 200 MHz.

Crystal Structure Determination of Complex (**1**).—*Crystal data.* $C_{35}H_{52}N_3O_{49}PW_{12}$, $M = 3\,535.95$, triclinic, space group $P\bar{1}$, $a = 11.721(3)$, $b = 12.818(3)$, $c = 12.878(3)$ Å, $\alpha = 89.20(2)$, $\beta = 104.10(2)$, $\gamma = 117.30(2)°$, $U = 1\,656.7(8)$ Å^3, $Z = 1$, $D_c = 3.545$ g cm^{-3}, $F(000) = 1\,578$, $\lambda(Mo\text{-}K_\alpha) = 0.710\,69$ Å, $\mu(Mo\text{-}K_\alpha) = 220.8$ cm^{-1}.

A yellow prismatic crystal (dimensions 0.5 × 0.3 × 0.2 mm) was affixed inside a Lindmann capillary in which was introduced a small quantity of the mother-liquor in order to avoid desolvation of the crystal. Data were collected on a Nicolet automated four-circle diffractometer at room temperature, by the θ—2θ scan technique with graphite-monochromated Mo-K_α radiation. Intensity measurements of two standards every 50 reflections showed no evidence of significant crystal deterioration. A total of 7 126 independent reflections were collected, 4 902 of which with $I \geqslant 3\sigma(I)$ were used in the refinement. They were corrected for Lorentz-polarization factors; a semiempirical absorption correction, based on a 360° scan around the scattering vector of six selected reflections, was applied.

At the first stage of the analysis we started to solve the structure in the non-centrosymmetric space group $P1$. Patterson and Fourier syntheses provided the locations of W atoms in twelve positions approximately related by a centre of symmetry, and with all equivalent W $\cdots$ W distances of about 3.6 Å. Subsequent Fourier syntheses revealed all the oxygen atoms of the anion. The polyoxoanion shows a structure typical of a disordered 'pseudo-Keggin' molecule, but with site symmetry $m3m$ (O_h), instead of the tetrahedral symmetry of the

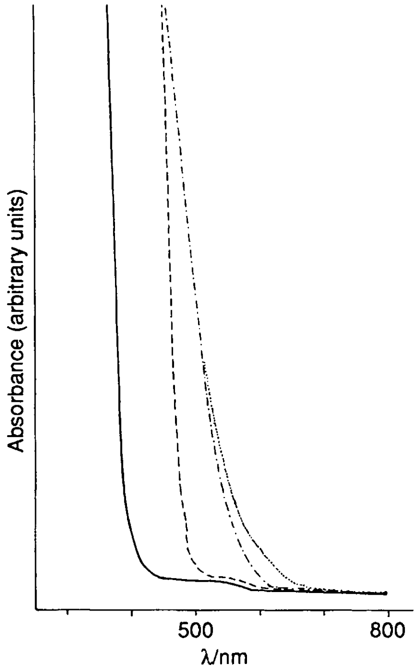

Figure 1. Diffuse reflectance electronic spectra of compounds (**1**) (–•–•–), (**3**) (·····), $[NBu_4]_3[PW_{12}O_{40}]$ (——), and Hquin·HCl (– – – –), in the region 800—300 nm

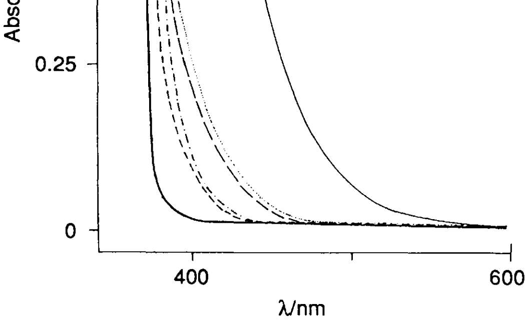

Figure 2. Solution electronic spectra ($c = 1 \times 10^{-2}$ mol dm^{-3}) of $H_3PW_{12}O_{40}$ in MeCN(——), and in 1:1 mixtures of the following substrates in MeCN: ethylbenzene (– – – –), dimethylformamide (–•–•–), mesitylene (— —), *p*-xylene (·····), and 1-chloronaphthalene (——); 5-mm cells

α-Keggin molecule (for this kind of symmetry problem see ref. 17). This fact can be interpreted as an orientational disorder of normal α-Keggin molecules in two positions related by an inversion centre. The central PO_4 group was also disordered with the P atom (at 0,0,0) surrounded by a cube of O atoms at 1.48—1.53 Å with each O site half-occupied.

At that point we decided to complete the structure analysis in the space group $P\bar{1}$, and to test an eventual ordered structure in the non-centrosymmetric space group $P1$ at the end of the refinement. Subsequent standard and Fourier difference syntheses revealed the remaining non-hydrogen atoms. For one 8-hydroxyquinolinium, H_2quin(a) at $x \approx \frac{1}{3}$, the occupancy factor was 1; a second independent molecule, H_2quin(b), and two water molecules at $x \approx 0$, are near an inversion centre. This results in an overlap with a consequent occupancy factor of 50%. In order to refine the atomic parameters of the disordered

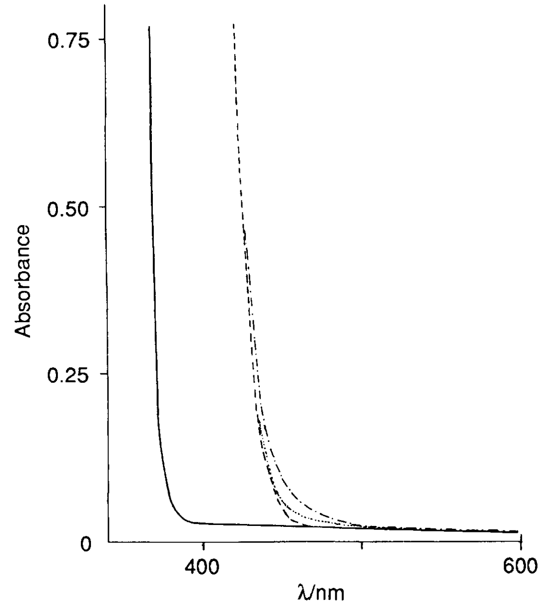

Figure 3. Solution electronic spectra of $H_3PW_{12}O_{40}$ ($c = 1 \times 10^{-2}$ mol dm^{-3}) in pure MeCN (——) or in the presence of 3×10^{-2} (······) or 20×10^{-2} mol dm^{-3} (–·–·–) Hquin; 5-mm cells. The spectrum of Hquin·HCl in MeCN ($c = 1 \times 10^{-2}$ mol dm^{-3}) is also reported (– – – –)

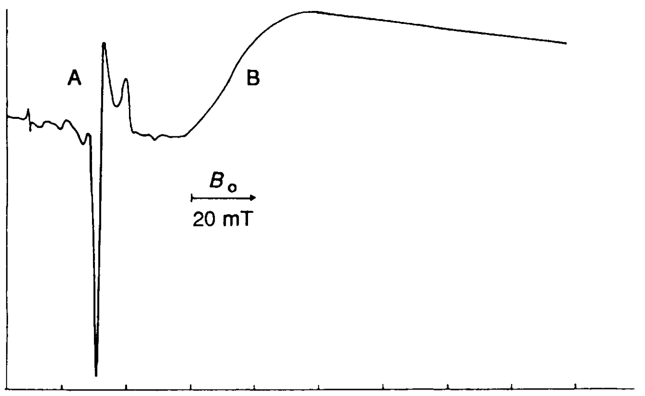

Figure 4. *X*-Band, low-temperature (110 K) e.s.r. spectrum of polycrystalline compound (**1**) after irradiation. Signal A is due to molybdenum impurities acting as selective electron traps, signal B to the photoreduced phosphotungstate anion

Table 1. Atomic co-ordinates of non-hydrogen atoms of complex (**1**), with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
P	0	0	0
W(1)	−0.218 7(1)	−0.281 0(1)	0.038 8(1)
W(2)	−0.245 0(1)	−0.255 7(1)	−0.040 7(1)
W(3)	0.035 1(1)	0.044 3(1)	−0.186 7(1)
W(4)	−0.248 1(1)	−0.026 5(1)	0.074 6(1)
W(5)	−0.284 4(1)	−0.063 8(2)	0.262 4(1)
W(6)	−0.032 4(1)	−0.317(2)	−0.329(2)
O(1a)	−0.317(2)	−0.261(3)	−0.171(2)
O(1b)	−0.083(3)	−0.282(3)	−0.113(2)
O(1c)	−0.291(2)	−0.099(3)	−0.283(2)
O(1d)	−0.087(2)	−0.114(2)	−0.229(2)
O(1e)	−0.297(2)	−0.016(3)	−0.119(2)
O(1f)	−0.076(3)	−0.412(2)	0.059(3)
O(2a)	−0.359(3)	−0.314(3)	0.020(3)
O(2c)	−0.110(3)	−0.183(2)	0.040(2)
O(2d)	−0.327(3)	−0.216(3)	0.180(2)
O(2e)	−0.139(3)	−0.063(2)	0.066(2)
O(2f)	−0.096(3)	−0.388(4)	−0.030(3)
O(3a1)	0.033(4)	−0.360(4)	−0.087(3)
O(3a2)	0.069(4)	−0.189(2)	0.103(2)
O(3d)	0.149(3)	−0.140(3)	−0.096(2)
O(3e)	0.173(3)	−0.049(2)	0.008(2)
O(3f)	0.093(3)	−0.017(2)	−0.074(2)
O(4c)	−0.329(2)	0.093(2)	−0.259(2)
O(4d)	−0.114(3)	0.062(2)	−0.276(2)
O(4e)	−0.364(2)	−0.046(3)	0.111(2)
O(5d)	−0.421(2)	−0.028(3)	0.209(2)
O(5e)	−0.170(3)	−0.058(4)	0.388(3)
O(6e1)	−0.049(4)	−0.128(4)	0.379(3)
O(6e2)	−0.054(4)	0.132(2)	0.034(2)
O(1′a)	0.070(3)		
O(a)	0.320(3)	0.705(3)	0.437(2)
N(a)	0.354(3)	0.775(2)	0.643(2)
C(1a)	0.371(3)	0.816(3)	0.736(2)
C(2a)	0.382(3)	0.751(3)	0.819(3)
C(3a)	0.382(3)	0.642(3)	0.803(3)
C(4a)	0.369(3)	0.599(3)	0.698(3)
C(5a)	0.367(5)	0.495(4)	0.673(4)
C(6a)	0.351(5)	0.467(4)	0.570(5)
C(7a)	0.325(5)	0.524(4)	0.481(4)
C(8a)	0.329(3)	0.630(3)	0.506(3)
C(9a)	0.347(3)	0.665(3)	0.613(3)
O(b)	0.013(5)	0.384(3)	0.559(3)
N(b)	0.018(5)	0.597(3)	0.591(3)
C(1b)	0.021(5)	0.700(3)	0.614(3)
C(2b)	0.011(5)	0.770(3)	0.536(3)
C(3b)	−0.003(5)	0.733(3)	0.432(3)
C(4b)	−0.007(5)	0.628(3)	0.411(3)
C(5b)	−0.020(5)	0.583(3)	0.313(3)
C(6b)	−0.022(5)	0.476(3)	0.297(3)
C(7b)	−0.012(5)	0.406(3)	0.377(3)
C(8b)	−0.003(5)	0.448(3)	0.473(3)
C(9b)	0.005(5)	0.556(3)	0.494(3)
O(c)	0.259(5)	0.634(4)	0.235(3)
C(1c)	0.352(5)	0.621(4)	0.190(3)
C(2c)	0.353(5)	0.672(4)	0.081(3)
O(d)	0.307(5)	−0.067(3)	0.507(4)
C(1d)	0.385(5)	0.057(3)	0.507(4)
C(2d)	0.328(5)	0.123(3)	0.558(4)
O(1w)	0.052(7)	0.448(4)	0.784(4)
O(2w)	−0.053(6)	0.177(5)	0.385(4)

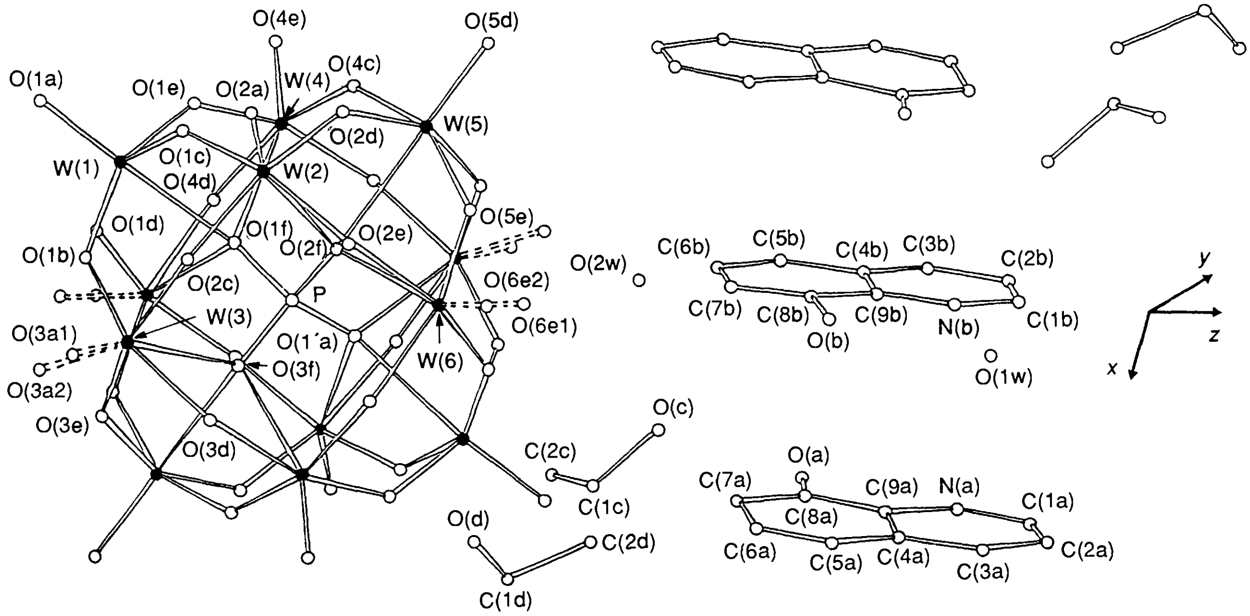

Figure 5. Formula unit and atom-numbering diagram for (recommended atom-numbering scheme for the Keggin structure as in ref. 12, p. 146). The hydrogen atoms are not indicated for clarity

cation, alternate cycles of Fourier difference syntheses and rigid-body least-squares refinements were used. The atomic positions of the two independent ethanol molecules* were not unequivocally determinable by Fourier syntheses owing to a very diffuse electron density. It was therefore necessary to refine them as rigid groups, using the ethanol standard distances and angles.

A further investigation on the oxygens of the anion revealed a displacement of two terminal O atoms [O(3a) and O(6e)] in two disordered positions, split by about 0.9 Å: it was therefore possible to refine separately such half-occupied atomic sites, which are indicated as O(3a1), O(3a2), and O(6e1), O(6e2) (see Figure 5). For the other parts of the anion, the atomic quasi-superposition causes a more or less strong anisotropy of the thermal parameters.

The hydrogens of the H_2quin and of the ethanol molecules were placed in their calculated positions with fixed isotropic thermal parameters equal to the B_{eq} of the carbon atoms to which they are linked. Anisotropic thermal parameters were refined for all non-hydrogen atoms except the disordered ones, for which isotropic refinement was used. Cycles of least squares with the weighting scheme $w^{-1} = \sigma^2(F_o) + 0.000\,652F_o^2$ gave final R and R' values of 0.083 and 0.082 respectively.

Finally we tried to refine the structure in the space group $P1$, by testing the eight models having the following two-fold disordered parts assembled in all possible modes: *i.e.* (1) H_2quin(b) and the related water molecules; (2) the O atoms of the PO_4 group; (3) the terminal O(3a) and O(6e) distributed over the two half-populated sites. Six cycles of full-matrix refinements were performed for each model: all eight converged to essentially equal R of 0.076—0.077. Therefore, the evidence of non-existence of one definitely better non-centrosymmetric solution justifies the choice of the space group $P\bar{1}$.

Neutral scattering factors (f and f' values) were used.[18] Computations were performed on an IBM 4361/4 computer by using the SHELX 76 system of crystallographic programs.[19] Atomic co-ordinates are listed in Table 1.

Table 2. Bond lengths (Å) with e.s.d.s in parentheses

P–O(1f)	1.53(3)	W(5)–O(5d)	1.68(3)
P–O(2f)	1.50(3)	W(5)–O(5e)	1.92(3)
P–O(3f)	1.48(3)	W(5)–O(3e')	1.90(4)
P–O(1'a)	1.52(4)	W(5')–O(3f)	2.50(3)
W(1)–O(1a)	1.66(4)	W(6)–O(2e)	1.92(4)
W(1)–O(1b)	1.92(3)	W(6)–O(2f)	2.46(3)
W(1)–O(1c)	1.85(3)	W(6)–O(5e)	1.85(3)
W(1)–O(1d)	1.89(4)	W(6)–O(6e1)	1.68(4)
W(1)–O(1e)	1.89(2)	W(6)–O(6e2)	1.72(4)
W(1)–O(1f)	2.50(4)	W(6)–O(1d')	1.88(4)
W(1')–O(1'a)	2.54(4)	W(6)–O(4d')	1.92(3)
W(2)–O(1c)	1.89(2)	W(6')–O(1f)	2.44(3)
W(2)–O(2a)	1.67(4)	O(a)–C(8a)	1.32(5)
W(2)–O(2c)	1.89(3)	N(a)–C(1a)	1.25(4)
W(2)–O(2d)	1.91(3)	N(a)–C(9a)	1.44(5)
W(2)–O(2e)	1.88(4)	C(1a)–C(2a)	1.36(5)
W(2)–O(2f)	2.50(4)	C(2a)–C(3a)	1.41(5)
W(2')–O(1'a)	2.46(4)	C(3a)–C(4a)	1.42(5)
W(3)–O(1b)	1.87(3)	C(4a)–C(5a)	1.36(6)
W(3)–O(2c)	1.88(3)	C(4a)–C(9a)	1.41(5)
W(3)–O(3a1)	1.69(5)	C(5a)–C(6a)	1.33(8)
W(3)–O(3a2)	1.70(4)	C(6a)–C(7a)	1.40(7)
W(3)–O(3d)	1.93(4)	C(7a)–C(8a)	1.38(7)
W(3)–O(3e)	1.91(4)	C(8a)–C(9a)	1.39(6)
W(3)–O(3f)	2.46(4)	O(b)–C(8b)	1.39(5)
W(3')–O(1'a)	2.43(3)	N(b)–C(1b)	1.33(6)
W(4)–O(1e)	1.89(3)	N(b)–C(9b)	1.31(5)
W(4)–O(1f)	2.45(3)	C(1b)–C(2b)	1.36(5)
W(4)–O(4c)	1.89(2)	C(2b)–C(3b)	1.37(5)
W(4)–O(4d)	1.88(3)	C(3b)–C(4b)	1.36(6)
W(4)–O(4e)	1.66(3)	C(4b)–C(5b)	1.34(5)
W(4)–O(3d')	1.85(4)	C(4b)–C(9b)	1.43(5)
W(4')–O(3f)	2.54(3)	C(5b)–C(6b)	1.38(6)
W(5)–O(2d)	1.86(3)	C(6b)–C(7b)	1.37(5)
W(5)–O(2f)	2.49(3)	C(7b)–C(8b)	1.31(5)
W(5)–O(4c)	1.88(2)	C(8b)–C(9b)	1.37(6)

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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* Such solvent molecules have been unequivocally detected and quantitated on the basis of chemical and thermogravimetric analysis, and by means of n.m.r. spectroscopy.

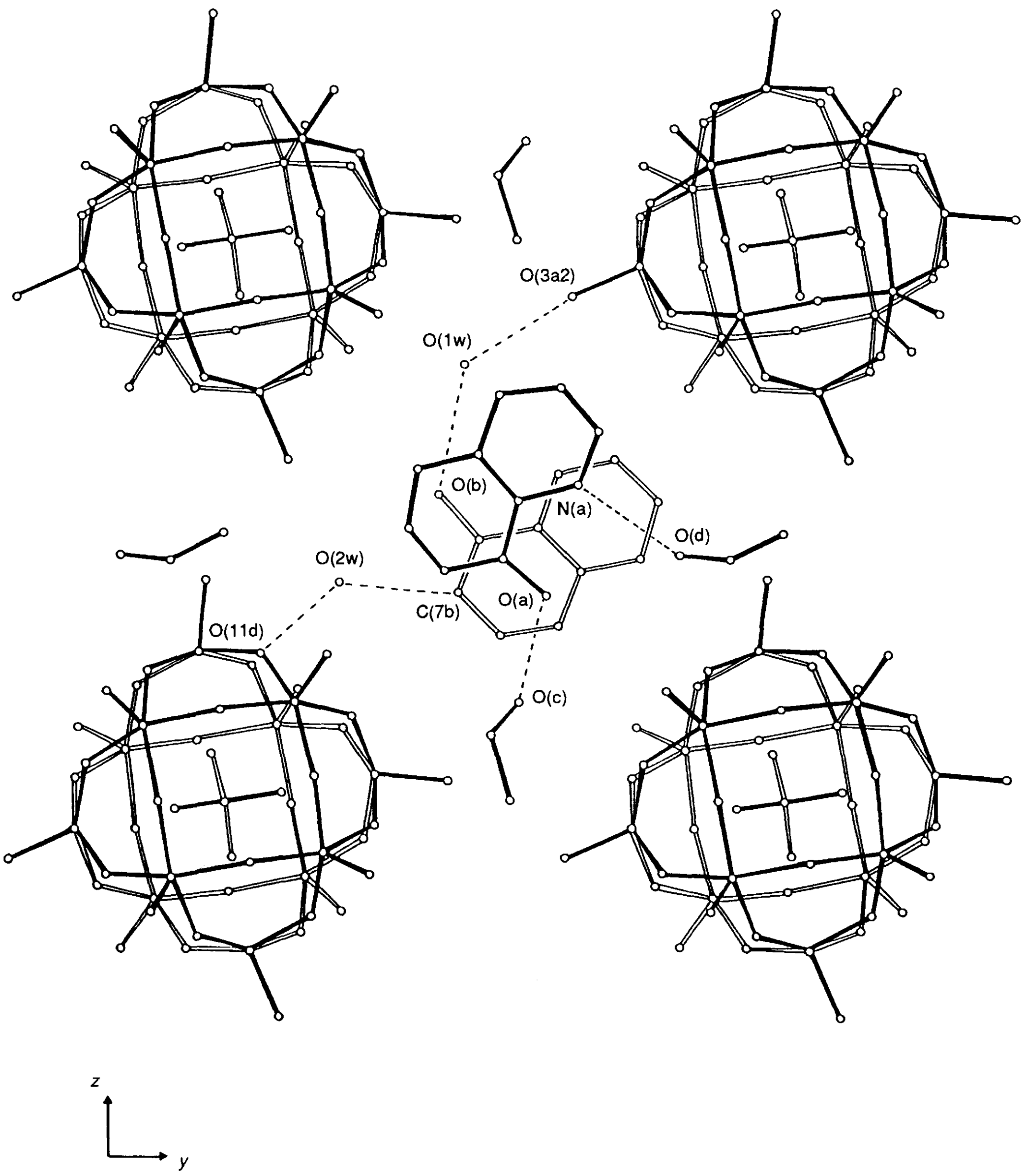

Figure 6. Crystal packing (partial view) projected along the [100] direction with main intermolecular interactions

Results and Discussion

Synthesis and Spectroscopic Properties of Complex (**1**) *and Related Compounds*.—Mixing colourless, concentrated solutions of phosphotungstic acid and various aromatic hydrocarbons, such as xylenes and naphthalenes, gives bright yellow solutions, suggesting that electronic interaction, between the inorganic acid and the organic substrate, occurs, which is able to induce sizeable red shifts in the charge-transfer absorption spectrum of the polyanion.[4,6,8]

However, in the case of the alkyl aromatics which we are also investigating as organic substrates for catalytic oxidation [8,9] the organic–inorganic interaction is not strong enough to allow the isolation of stable, solid products from the solutions. Of course introduction of a basic function, such as an amino group, into the organic moiety allows easy separation of crystalline salts of $H_3PW_{12}O_{40}$. Among several organic bases quinolin-8-ol was chosen because *X*-ray quality crystals of the corresponding salt were easily obtained.

Although in this case the charge-transfer interaction is obviously influenced by the presence of the functional groups, still useful information can be obtained from a careful examination of the crystal and molecular structure.

Figure 1 compares the diffuse-reflectance electronic spectrum of compounds (**1**) and (**3**) with the spectra of the tetrabutylammonium salt of $H_3PW_{12}O_{40}$ and of the organic cation 8-hydroxyquinolinium. Figure 2 reports the solution electronic spectrum of phosphotungstic acid in the presence of large concentrations of different organic substrates. Due to solubility problems, large excesses of Hquin could not be used. However, solution spectra of (**1**) in the presence of Hquin are presented in Figure 3. It is interesting that aromatic hydrocarbons induce quite large shifts of the low-energy tail of the charge-transfer (c.t.) absorption band. In the case of extended aromatic systems, such as α-chloronaphthalene, the effect is much larger than obtained with strongly polar molecules such as dimethylformamide. The essential outcome of these spectra is that the c.t. interaction, responsible for the red shift of the band tail, is essentially a solid-state effect, which survives in solution only if large amounts of the organic are present. Support for this result is given by the ^{1}H n.m.r.

Table 3. Bond angles (°) with e.s.d.s in parentheses

O(1f)–P–O(2f)	110(2)	O(3a2)–W(3)–O(3d)	109(2)	O(2f)–W(6)–O(5e)	64(1)	W(4′)–O(3f)–W(5′)	90(1)
O(1f)–P–O(3f)	108(1)	O(1b)–W(3)–O(3e)	86(1)	O(2e)–W(6)–O(6e1)	115(2)	W(4)–O(4c)–W(5)	141(2)
O(2f)–P–O(3f)	110(1)	O(2c)–W(3)–O(3e)	156(1)	O(2f)–W(6)–O(6e1)	155(1)	W(4)–O(4d)–W(6′)	138(1)
O(1f)–P–O(1′a)	105(1)	O(3a1)–W(3)–O(3e)	116(1)	O(5e)–W(6)–O(6e1)	91(1)	W(5)–O(5e)–W(6)	140(1)
O(2f)–P–O(1′a)	110(1)	O(3a2)–W(3)–O(3e)	88(2)	O(2e)–W(6)–O(6e2)	90(2)	P–O(1′a)–W(1′)	120(1)
O(3f)–P–O(1′a)	113(2)	O(3d)–W(3)–O(3e)	88(1)	O(2f)–W(6)–O(6e2)	153(2)	P–O(1′a)–W(2′)	125(1)
O(1a)–W(1)–O(1b)	102(1)	O(1b)–W(3)–O(3f)	91(1)	O(5e)–W(6)–O(6e2)	108(1)	P–O(1′a)–W(3′)	127(2)
O(1a)–W(1)–O(1c)	103(1)	O(2c)–W(3)–O(3f)	93(1)	O(2e)–W(6)–O(1d′)	154(1)	W(1′)–O(1′a)–W(2′)	90(1)
O(1b)–W(1)–O(1c)	88(1)	O(3a1)–W(3)–O(3f)	159(2)	O(2f)–W(6)–O(1d′)	92(1)	W(3′)–O(1′a)–W(1′)	91(1)
O(1a)–W(1)–O(1d)	103(1)	O(3a2)–W(3)–O(3f)	152(2)	O(6e1)–W(6)–O(1d′)	91(2)	W(3′)–O(1′a)–W(2′)	93(1)
O(1b)–W(1)–O(1d)	83(1)	O(3d)–W(3)–O(3f)	65(1)	O(6e2)–W(6)–O(1d′)	115(2)		
O(1c)–W(1)–O(1d)	154(1)	O(3e)–W(3)–O(3f)	65(1)	O(2e)–W(6)–O(4d′)	84(1)		
O(1a)–W(1)–O(1e)	104(1)	O(1e)–W(4)–O(1f)	65(1)	O(2f)–W(6)–O(4d′)	93(1)	C(1a)–N(a)–C(9a)	126(2)
O(1b)–W(1)–O(1e)	154(1)	O(1e)–W(4)–O(4c)	85(1)	O(5e)–W(6)–O(1d′)	89(1)	N(a)–C(1a)–C(2a)	119(3)
O(1c)–W(1)–O(1e)	89(1)	O(1f)–W(4)–O(4c)	92(1)	O(5e)–W(6)–O(4d′)	157(1)	C(1a)–C(2a)–C(3a)	122(3)
O(1d)–W(1)–O(1e)	88(1)	O(1e)–W(4)–O(4d)	89(1)	O(6e1)–W(6)–O(4d′)	112(2)	C(2a)–C(3a)–C(4a)	119(3)
O(1a)–W(1)–O(1f)	159(1)	O(1f)–W(4)–O(4d)	64(1)	O(6e2)–W(6)–O(4d′)	94(1)	C(3a)–C(4a)–C(5a)	124(3)
O(1b)–W(1)–O(1f)	91(1)	O(4c)–W(4)–O(4d)	156(1)	O(1d′)–W(6)–O(4d′)	88(1)	C(3a)–C(4a)–C(9a)	117(3)
O(1c)–W(1)–O(1f)	93(1)	O(1e)–W(4)–O(4e)	101(1)	W(1)–O(1b)–W(3)	140(1)	C(5a)–C(4a)–C(9a)	119(3)
O(1d)–W(1)–O(1f)	62(1)	O(1f)–W(4)–O(4e)	158(1)	W(1)–O(1c)–W(2)	142(2)	C(4a)–C(5a)–C(6a)	116(4)
O(1e)–W(1)–O(1f)	63(1)	O(4c)–W(4)–O(4e)	103(1)	W(1)–O(1d)–W(6′)	141(1)	C(5a)–C(6a)–C(7a)	129(4)
O(1c)–W(2)–O(2a)	104(1)	O(4d)–W(4)–O(4e)	101(1)	W(1)–O(1e)–W(4)	140(1)	C(6a)–C(7a)–C(8a)	115(4)
O(1c)–W(2)–O(2c)	86(1)	O(1e)–W(4)–O(3d′)	156(1)	P–O(1f)–W(1)	122(1)	O(a)–C(8a)–C(7a)	127(3)
O(2a)–W(2)–O(2c)	102(1)	O(1f)–W(4)–O(3d′)	93(1)	P–O(1f)–W(4)	125(1)	O(a)–C(8a)–C(9a)	116(3)
O(1c)–W(2)–O(2d)	85(1)	O(4c)–W(4)–O(3d′)	88(1)	W(1)–O(1f)–W(4)	92(1)	C(7a)–C(8a)–C(9a)	118(3)
O(2a)–W(2)–O(2d)	103(1)	O(4d)–W(4)–O(3d′)	88(1)	P–O(1f)–W(6′)	124(2)	N(a)–C(9a)–C(4a)	117(3)
O(2c)–W(2)–O(2d)	154(1)	O(4e)–W(4)–O(3d′)	103(1)	W(1)–O(1f)–W(6′)	92(1)	N(a)–C(9a)–C(8a)	120(3)
O(1c)–W(2)–O(2e)	155(1)	O(2d)–W(5)–O(2f)	64(1)	W(4)–O(1f)–W(6′)	93(1)	C(4a)–C(9a)–C(8a)	123(3)
O(2a)–W(2)–O(2e)	102(1)	O(2d)–W(5)–O(4c)	87(1)	W(2)–O(2c)–W(3)	141(2)	C(1b)–N(b)–C(9b)	124(3)
O(2c)–W(2)–O(2e)	87(1)	O(2f)–W(5)–O(4c)	93(1)	W(2)–O(2d)–W(5)	141(2)	N(b)–C(1b)–C(2b)	121(3)
O(2d)–W(2)–O(2e)	90(1)	O(2d)–W(5)–O(5d)	100(1)	W(2)–O(2e)–W(6)	139(1)	C(1b)–C(2b)–C(3b)	118(3)
O(1c)–W(2)–O(2f)	92(1)	O(2f)–W(5)–O(5d)	157(1)	P–O(2f)–W(2)	124(1)	C(2b)–C(3b)–C(4b)	119(3)
O(2a)–W(2)–O(2f)	159(1)	O(4c)–W(5)–O(5d)	104(1)	P–O(2f)–W(5)	125(1)	C(3b)–C(4b)–C(5b)	125(3)
O(2c)–W(2)–O(2f)	93(1)	O(2d)–W(5)–O(5e)	88(1)	P–O(2f)–W(6)	125(2)	C(3b)–C(4b)–C(9b)	122(3)
O(2d)–W(2)–O(2f)	63(1)	O(2f)–W(5)–O(5e)	63(1)	W(2)–O(2f)–W(5)	91(1)	C(5b)–C(4b)–C(9b)	114(3)
O(2e)–W(2)–O(2f)	64(1)	O(4c)–W(5)–O(5e)	155(1)	W(2)–O(2f)–W(6)	92(1)	C(4b)–C(5b)–C(6b)	122(3)
O(1b)–W(3)–O(2c)	88(1)	O(5d)–W(5)–O(5e)	102(1)	W(5)–O(2f)–W(6)	92(1)	C(5b)–C(6b)–C(7b)	124(3)
O(1b)–W(3)–O(3a1)	110(2)	O(2d)–W(5)–O(3e′)	155(1)	W(3)–O(3d)–W(4′)	140(1)	C(6b)–C(7b)–C(8b)	115(3)
O(2c)–W(3)–O(3a1)	87(2)	O(2f)–W(5)–O(3e′)	92(1)	W(3)–O(3e)–W(5′)	139(1)	O(b)–C(8b)–C(7b)	118(3)
O(1b)–W(3)–O(3a2)	95(2)	O(4c)–W(5)–O(3e′)	88(1)	P–O(3f)–W(3)	127(2)	O(b)–C(8b)–C(9b)	118(3)
O(2c)–W(3)–O(3a2)	115(2)	O(5d)–W(5)–O(3e′)	105(1)	P–O(3f)–W(4′)	122(1)	C(7b)–C(8b)–C(9b)	124(3)
O(1b)–W(3)–O(3d)	155(1)	O(5e)–W(5)–O(3e′)	85(1)	P–O(3f)–W(5′)	125(1)	N(b)–C(9b)–C(4b)	115(3)
O(2c)–W(3)–O(3d)	87(1)	O(2e)–W(6)–O(2f)	64(1)	W(3)–O(3f)–W(4′)	91(1)	N(b)–C(9b)–C(8b)	123(3)
O(3a1)–W(3)–O(3d)	94(2)	O(2e)–W(6)–O(5e)	89(1)	W(3)–O(3f)–W(5′)	92(1)	C(4b)–C(9b)–C(8b)	122(3)

spectrum of complex (**1**), which closely matches the spectrum of the unperturbed 8-hydroxyquinolinium cation (see Experimental section). Secondly we observe that hydrocarbons such as *p*-xylene or Hquin induce similar shifts in the electronic spectrum of $H_3PW_{12}O_{40}$. This suggests that interaction between the electron-rich aromatic backbone and the electron-deficient oxygens of the polyanion must play a role in the observed c.t. effect.

The presence of the interaction discussed above is paralleled by the much higher photosensitivity of complex (**1**) with respect to the free heteropolyacid or its alkylammonium salts. Although (**1**) does not appear to be particularly sensitive to visible light, irradiation in the near-u.v. region of pure solid samples or MeCN solutions of (**1**) immediately induces reduction of $[PW_{12}O_{40}]^{3-}$ with simultaneous oxidation of the organic base. The low-temperature e.s.r. spectrum of polycrystalline, irradiated (**1**) is reported in Figure 4. It is known[20] that small amounts of molybdenum, always contained in $[PW_{12}O_{40}]^{3-}$, behave as a selective electron trap, under reducing conditions. The spectrum of (**1**) shows a signal [$g_{\parallel} = 1.914$, $A_{\parallel}$ not measured, $g_{\perp} = 1.935$, $A_{\perp} = 36.0$ G (3.6×10^{-3} T)] which is ascribed to Mo^{V} and closely corresponds to the spectrum of $[PMoW_{11}O_{40}]^{4-}$.[21] A second, intense and broad, quasi-isotropic signal develops upon further irradiation and is assigned to $[PW_{12}O_{40}]^{4-}$ on the basis of its *g* value ($g_{iso} = 1.828$).[22] The fact that these spectra are often isotropic down to quite low temperatures (14 K for $[PW_{12}O_{40}]^{4-}$) or show small hyperfine values has been ascribed to rapid intraionic hopping of the unpaired electron, comparable with the e.s.r. time-scale.[12] From the above results it turns out that, under the specified conditions, reduction of the polyanion occurs in one-electron steps.

In addition to compound (**1**), discussed so far, we have briefly examined the possibility that $H_3PW_{12}O_{40}$ might bind additional molecules of Hquin or related compounds owing to its hydrogen-bonding ability. Reaction of phosphotungstic acid with excess of Hquin reproducibly gives a well defined, hardly soluble compound which contains twelve organic molecules per inorganic anion. When a metal complex of Hquin, such as its copper(II) derivative, is used for the same reaction the resulting insoluble powder contains about 30 molecules of the $Cu(quin)_2$ complex per molecule of phosphotungstic acid. I.r. and e.s.r. spectroscopy unequivocally show that the two components are still intact and exhibit spectroscopic features almost identical to those of the free compounds.

Such behaviour is in line with the long known property of

Table 4. Shortest intermolecular distances (Å)

Between anions	
O(3a1) $\cdots$ O(3a2′)	3.37
O(6e1) $\cdots$ O(6e2′)	3.45
Between the anion and the two H_2quin	
O(1a′) $\cdots$ C(7a)	3.27
O(6e1) $\cdots$ C(3b)	2.98
Between the anion and the ethanol molecules	
O(5d′) $\cdots$ C(2c)	3.32
O(4e′) $\cdots$ O(d)	3.20
Between the anion and the water molecules	
O(3a2) $\cdots$ O(1w)	2.90
O(1d′) $\cdots$ O(2w)	2.85
Between the H_2quin and the ethanol molecules	
O(a) $\cdots$ O(c)	2.59
N(a) $\cdots$ O(d)	2.81
Between the H_2quin and the water molecules	
O(b) $\cdots$ O(1w)	2.90
C(7b) $\cdots$ O(2w)	2.75
Between the ethanol and the water molecules	
O(c) $\cdots$ O(1w)	3.24
O(d) $\cdots$ O(2w)	3.29

heteropolyanions to bind and precipitate biomolecules and polar organics and their widespread use as non-specific staining agents for electron microscopy.[12] The interaction has been found to be pH-dependent and has often been qualitatively described as a salt-like electrostatic interaction.[13] However, a detailed description of the arrangement of so many organic molecules around the inorganic ions, based on *X*-ray data, is still lacking. Unfortunately, the growth of compounds (**3**) and (**4**) in single-crystal form appears to be problematic owing to their low solubility or to decomposition when too drastic conditions are used (*e.g.* boiling dmf). At present, attempts employing slow interdiffusion of the two components are underway.

X-Ray Crystal Structure of Complex (**1**).—Figure 5 shows the formula unit $[H_2quin]_3[\alpha\text{-}PW_{12}O_{40}]\cdot 4EtOH\cdot 2H_2O$ together with the numbering for the non-hydrogen atoms: for clarity the PO_4 group and the H_2quin(b) and the water molecules are drawn only in one of the two possible disordered positions related by an inversion centre. Bond distances and angles are given in Tables 2 and 3, respectively. As said before, the polyoxoanion has a two-fold disordered $\alpha[PW_{12}O_{40}]^{3-}$ Keggin-type structure, with W $\cdots$ W distances in the range 3.54—3.56 Å. The W–O distances in the WO_6 octahedra are as in other compounds with the same kind of disorder[23] and similar to those found in normal α-Keggin structures:[24] they are in the range 1.66—1.72 Å for the terminal oxygens, 1.85—1.92 Å for the doubly bridged (2 W) oxygens, and 2.43—2.54 Å for the oxygens of the PO_4 groups. The P–O distances are in the range 1.48—1.53 Å.

The packing arrangement is complicated: the system of polyoxometalate units forms channels, approximately parallel to the *x* direction, into which infinite columns of stacked H_2quin moieties are posed. Within the stack a chain of trimers can be identified, formed by two (non-disordered) H_2quin(a) and one (disordered) H_2quin(b) molecules: the intratrimeric interplanar spacings are 3.25 and 3.57 Å alternately, while the intertrimeric ones are 3.42 Å. The H_2quin molecules interact, *via* hydrogen bonds, with the ethanol or with the two water molecules of crystallization: the water molecules make hydrogen bonds also with two oxygens of polyoxometalates. These main intermolecular interactions are shown in Figure 6, in which an independent molecule of H_2quin(a) and the ethanol molecules at $x \approx \frac{1}{3}$ are drawn with bold lines. The disordered H_2quin(b) and the related hydrogen-bonded water molecules (drawn with less bold lines) are at $x \approx 0$ and are placed in one of the two possible positions around a centre of inversion. Consequently it is the steric hindrance that determines the selection between the two-fold disordered oxygens of the anion: O(3a1) or O(3a2), and O(6a1) or O(6a2), as shown in Figure 6.

In Table 4 are reported the shortest intermolecular distances between the nearest non-bonded non-H-atoms: these distances are quite long, except the H–O $\cdots$ O distances for O(1w) $\cdots$ O(3a2) and O(2w) $\cdots$ O(1d′) between the water molecules and the polyoxometalate, which are compatible with hydrogen bonds. Other hydrogen bonds [O(1w) $\cdots$ O(b), O(a) $\cdots$ O(c), O(d) $\cdots$ N(a), and C(7a) $\cdots$ O(2w)] are present between water or H_2quin and ethanol. In the literature (17 and refs. therein) many structures are described in which polyoxometalates are involved in hydrogen bonds with water molecules.

Conclusion

One interesting outcome of the data presented above is the ability of 'molecular oxides' like $[PW_{12}O_{40}]^{3-}$ to interact with or complex electron-rich aromatic hydrocarbons. In the case of polycyclic molecules, having extended π systems, such complexation is surprisingly strong and definitely larger than observed with other strongly polar organic molecules.

The presence of the above interaction provides an easy path for effective electron exchange between the organic substrate and the photoactivated inorganic anion and rationalizes, on a qualitative basis, the efficient photo-oxidation of aromatic hydrocarbons in the presence of catalytic amounts of different polyanions.

The *X*-ray structure of compound (**1**) has been undertaken with the aim of having a more quantitative description of this organic–inorganic interaction. However, as already found by Williamson *et al.*[6] for related complexes, also in our case one important result is the absence of direct, substantial structural interaction between the organic cations and the polyoxometalate anions. Therefore a clear picture of the spectroscopically observed charge transfer cannot be given on the basis of crystallographic results, in the solid state.

In spite of this it is interesting that these large inorganic, oxide-like anions are capable of forming an extended network of weak hydrogen-bonding interactions, which provide the possibility for binding of large numbers of organic molecules. The facile synthesis of compounds (**3**) and (**4**) experimentally confirms this finding.

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