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A Novel Optical Complex between an Organic Substrate and a Polyoxometalate. Crystal and Molecular Structure of α-$H_4SiW_{12}O_{40}\cdot 4HMPA\cdot 2H_2O$ (HMPA = Hexamethylphosphoramide)

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A solvated complex of α-$H_4SiW_{12}O_{40}\cdot 4HMPA\cdot 2H_2O$ composed the heteropolytungstate α-$H_4SiW_{12}O_{40}$ and the organic substrate hexamethylphosphoramide (HMPA) has been synthesised, purified, and characterized. The electronic spectra ($\lambda = 220-500$ nm) as well as the ^1H NMR spectra for the title compound dissolved in CD_3CN establish that this complex dissociates into free $SiW_{12}O_{40}{}^{4-}$ and HMPA moieties in solution unless the organic substrate HMPA is present in very high concentrations. The solid reflectance electronic spectra and IR spectra indicate that there is interaction between the α-$H_4SiW_{12}O_{40}$ and the organic substrate. The complex has no photosensitivity under irradiation of sunlight, but under the near-UV light result in a charge transfer by oxidation of the HMPA and the reduction of the polyoxometalate. Light yellow polyhedrons of the title compound crystallize from the aqueous solvent of acetonitrile and aqueous solution as the formula of α-$H_4SiW_{12}O_{40}\cdot 4HMPA\cdot 2H_2O$ in the monoclinic, space group $P2_1$. The unit cell has $a = 12.791(3)$ Å, $b = 22.103(6)$ Å, $c = 15.532(4)$ Å, $\beta = 102.860(10)°$, and $Z = 2$. From the bond-valence parameters, it was found that the four hydrogen atoms of the polyoxometalate were combined with the N atoms of the four HMPA respectively. The title compound shows a certain second-order and third-order nonlinear optical response of $I^{2\omega} = 0.7I^{2\omega}{}_{\mathrm{KDP}}$ and $\chi^{(3)} = 2.63 \times 10^{-11}$ esu, respectively.

Introduction

In the last few years there have been a rapidly growing number of reports in the literature addressing the use of polyoxometalate as both homogeneous and heterogeneous catalysts.[1,2,3] A substantial portion of the reported homogeneous catalystic process are photochemical in nature.[4] There are a lot of papers which disscused the photochemical and the photochromism process of the polyoxometalates.[5] But to our knowledge there are no papers about the nonlinear optical properties of this kind of compound. As we know, the study of nonlinear optical materials is very interesting and vigorous because of the wide usage of this property.[6] During the study of organic nonlinear optical materials, the concepts of "charge-transfer theory",[7] "molecule engineering", and "crystal engineering" were proposed based on a lot of experiments and theories.[8] From theory, we know that if there is a donor and a acceptor in a conjugated molecule, it is easy for charge-transfer to happen in the molecule, and the molecule probably has a second-order coefficent (β). Crystals composed of these kinds of molecules must belong to a noncentrosymmetric space group in order to avoid counteraction of the dipolar nature of the molecules.

It has been reported that the electron donor-acceptor complex may serve as a potential high-efficiency second-order nonlinear optical material.[9] In the title compound the polyoxometalate can be considered to act as an electron acceptor and the organic substrate as a donor. The polyoxometalate has the capacity to reduce and can form crystals, and HMPA has a large dipole moment, has unusually high basicity,[10] and can form a insoluble

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Table 1. Crystallographic Data for α-Dodecatungstatosilic Acid−Tetrakis(hexamethylphosphoramide)−Bis(water)

$C_{24}H_80N_{12}O_{46}P_4SiW_{12}$	fw 3631.2
$a = 12.781(3)$ Å	space group $P2_1$
$b = 22.103(6)$ Å	$T = 20$ °C
$c = 15.532(4)$ Å	$\lambda = 0.710\,73$ Å
$\beta = 102.860(10)$ deg	$\rho_{calc} = 2.822$ g cm^{-1}
$V = 4278$ (2) Å	$\mu = 162.33$ cm^{-1}
$Z = 2$	$R^a = 0.0637$
$R_w = 0.1500$	

[a] $R = \Sigma||F_o| - |F_c||/\Sigma F_o$.

complex with a polyoxometalate acid in aqueous solution. We report here the synthesis, purification, crystal structure, and nonlinear optical properties of the discrete intermolecular complex composed of an organic substrate and a polyoxotungstate.

Experimental Section

Materials. All organic solvents used for the synthesis and physical measurement were of reagent grade and were used without further purification. $H_4SiW_{12}O_{40}\cdot nH_2O$ was prepared by a literature method.[11]

Physical Measurement. C, H, and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer; other elemental analyses were performed on a Jarrell-Ash 1100+2000 ICP quantometer. ^{1}H NMR spectra were obtained with a Bruker Am-500 spectrometer operating at 500 MHz. IR spectra of samples were obtained as KBr pellets on a Nicolet 170SX FT-IR spectrometer. Electronic spectra ($\lambda = 220-500$ nm) were recorded on a Shimazu UV-3100 spectrometer in solution. Solid state diffuse reflectance spectra were recorded on a Shimazu UV-240 spectrometer. An ESR spectrum was recorded on a Bruker ER200-D-SRC spectrometer at X-band. Nonlinear optical properties and crystallography will be described below.

Preparation of the Title Compound. To 20 mL aliquot of a 50 mM aqueous solution of α-$H_4SiW_{12}O_{40}$ was added 1 mL of HMPA with stirring, and a yellow precipitate resulted immediately. The resulting precipitate was collected and then sucked as dry as possible on a fritted-glass funnel. The precipitate was recrystalized from a solvent mixture of acetonitrile and water to yield 0.75 g of yellow crystals. Anal. Calcd for $H_4SiW_{12}O_{40}\cdot 4HMPA\cdot 2H_2O$, C, 7.93; H, 2.20; N, 4.62; P, 3.41; Si, 0.80; W, 61.76. Found: C, 7.80; H, 2.02; N, 4.41; P, 3.37; W, 61.60.

X-ray Crystallography. Collection and Reduction of Intensity Data. A light yellow polyhedron crystal of the title compound was coated with epoxy cement immediately after removal from the mother liquor to avoid crystal destruction by efflorescent desolvation. The crystal was then affixed to the end of a glass capillary and then mounted on the goniometer head of a Siemens P4 four-circle diffractometer. Accurate cell dimensions were obtained by least-squares refinement of 15 centered reflections (λ(Mo Kα) = 0.710 73 Å). The $2\theta/\theta$ scan method was used with a variable scan rate of 3.00−25°min^{-1}. Intensity measurements of three check reflections measured every 97 reflections showed no evidence of significant crystal deterioration. Intensities ($2\theta = 3-55°$) were measured for 9018 reflections of which 7719 independent reflections and the 5052 observed reflections ($I > 2.0\sigma(I)$) were used for further computation. Crystal and data collection parameters along with the values for the residuals after final refinement are summarized in Table 1.

Structure Solution and Refinement. The computer hardware and software for data refinement, structure solution, and structure refinement were a 486 PC, Siemens SHELXTL-PC package, and SHELXL93. The monoclinic space group was uniquely determined to be $P2_1$. The structure was solved by direct methods and completed by a series Fourier synthesis and least-squares refinement. Hydrogen positions were not readily discernible from electron density difference maps. All non-hydrogen atoms were refined anisotropically. The extremes in the final difference map are +1.958 to −2.882 e/Å^3. Least-squares refinement of 456 parameters gave final reliability factors R = 0.0637, R_w = 0.1500, and GOF = 0.972. The data were corrected for absorption by a semiempirical (ψ scan) method.[12] A weighting scheme utilizing weights of the form $w = [\sigma^2(F_o) + (0.0904P)^2]^{-1}$ (where $P = (F_o^2 + 2F_c^2)/3$) was implemented. Scattering factors were those used for neutral atoms.[13] The final positional and thermal parameters are given in Table 2.

Result and Discussion

Synthesis, IR Spectra, Electronic Spectra, and ESR Spectra. Polyoxometalate acid dissolved in an organic donor solvent induces a sizable red-shift in the charge-transfer absorption spectrum of the polyanion, indicating that the electronic interaction between the organic substrate and the inorganic anion has occured which results in a color change of the solution.[14] However, in the case of alkyl aromatics, which were inverstigated as organic substrates for catalytic oxidation, the interaction between organic substrate and inorganic anion is not enough to allow the isolation of stable solid products from the solution.[14a,15] However by the introduction of a basic function, such as an amino group in the organic moiety, it is easy to separate the powder salt of the polyoxometalate.[5c,16] Among several organic substrates, HMPA was chosen due to its strong polarity. When the heteropolytungstate, α- $H_4SiW_{12}O_{40}\cdot nH_2O$, solution was mixed with HMPA, a new material far less soluble in water than either of the components was precipitated from the solution. This complex can be recrystalized from a solvent mixture of acetonitrile and water to yield yellow hydrated polyhedron crystals.

Comparing the IR spectrum of the title compound with the IR spectrum of α-$H_4SiW_{12}O_{40}$, the vibrational band of the $W{=}O_d$ bond of the title compound is split from 981 cm^{-1} into 991 and 971 cm^{-1}, due to the difference in the 12 $W-O_d$ bonds in the complex (see the crystal structure data). The vibrational band of the $Si-O_a$ bond has a red-shift from 928 to 920 cm^{-1}, and the vibrational bands of the $W-O_b$ bond have a blue shift from 880 to 885 cm^{-1}. The $W-O_c$ bond has a splitting of 785 cm^{-1} to 799 and 755 cm^{-1}, due to the contact between the O_c oxygen and the carbon atom of the methyl. The results indicate that the $W-O_b$ bond was strengthened and the Si−O bond was weakened in the title compound, and the anion has a large distorting effect due to the interaction between the carbon atom of the organic substrate and the oxygen atom of the polyoxometalate anion.

Comparison of the UV spectrum of the title compound with that of α-$H_4SiW_{12}O_{40}$ dissolved in a weakly coordinating solvent such as acetonitrile or an aqueous solution indicates that the interactions between HMPA and polyoxometalate are rather weak and the complexes are almost entirely disrupted in solution (Figure 1), but if the solution is concentrated (Figure 2), we find there is a interaction between the organic molecules and the polyanions. The electronic spectra of $PW_{12}O_{40}{}^{3-}$ dissolved in HMPA has been reported,[2d] and the results indicated that the charge-transfer of polyoxometalate anion is obviously influenced by the presence of HMPA. Figure 3 compares the reflectance electronic spectrum of the title compound with that of α-$H_4SiW_{12}O_{40}$. It is interesting to note that the low-energy

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Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å × 10^3)

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	z	*U*(eq)[a]
Si(1)	9042(9)	6401(5)	6624(6)	27(2)	O(38)	9472(20)	5831(12)	6226(14)	43(6)
W(1)	8339(2)	7022(1)	4482(1)	45(1)	O(39)	8079(19)	6672(11)	5854(14)	39(6)
W(2)	7038(2)	7509(1)	6021(1)	45(1)	O(40)	9960(17)	6916(9)	6934(12)	25(5)
W(3)	7694(2)	6873(1)	8260(1)	45(1)	P(1)	3198(10)	4926(6)	1529(7)	63(4)
W(4)	9578(2)	5788(1)	8770(1)	45(1)	O(41)	4358(20)	4983(17)	1940(21)	110(14)
W(5)	11003(2)	5260(1)	7113(1)	46(1)	N(1)	2857(30)	4334(15)	1165(23)	117(9)
W(6)	10400(2)	5853(1)	5054(1)	47(1)	N(2)	2989(33)	5349(18)	618(23)	129(10)
W(7)	6574(1)	6111(1)	5156(1)	47(1)	N(3)	2574(29)	5152(21)	2189(26)	148(11)
W(8)	7212(2)	5482(1)	7399(1)	46(1)	C(1)	3194(59)	3689(22)	1680(45)	159(16)
W(9)	8643(2)	4938(1)	5738(1)	44(1)	C(2)	1690(59)	4317(32)	435(49)	199(20)
W(10)	10907(1)	7377(1)	5985(1)	43(1)	C(3)	4063(68)	5499(47)	154(53)	249(26)
W(11)	9607(2)	7865(1)	7512(1)	47(1)	C(4)	2536(73)	5976(36)	596(53)	226(24)
W(12)	11501(1)	6784(1)	8042(1)	45(1)	C(5)	1418(40)	5125(35)	2110(42)	139(13)
O(1)	8263(25)	7322(15)	3491(19)	72(9)	C(6)	3208(67)	5614(53)	3061(55)	254(27)
O(2)	6126(25)	8067(15)	5956(19)	68(9)	P(2)	6913(10)	4722(6)	1429(7)	64(4)
O(3)	7044(24)	7302(14)	8948(18)	64(8)	O(42)	5746(21)	4838(17)	1312(22)	119(14)
O(4)	10123(23)	5467(13)	9794(16)	53(7)	N(4)	7175(30)	4143(15)	1083(25)	117(9)
O(5)	11954(26)	4785(16)	7558(20)	75(9)	N(5)	7291(32)	5195(18)	723(25)	129(10)
O(6)	11107(20)	5761(12)	4290(15)	48(6)	N(6)	7477(29)	4845(20)	2376(24)	148(11)
O(7)	5430(26)	5821(17)	4596(20)	80(10)	C(7)	7973(56)	4037(30)	405(45)	159(16)
O(8)	6324(23)	4993(13)	7543(18)	58(8)	C(8)	6479(69)	3556(28)	1281(57)	199(20)
O(9)	8089(26)	4272(15)	5304(19)	70(9)	C(9)	6291(64)	5534(46)	−56(51)	249(26)
O(10)	11743(25)	7764(14)	5443(19)	66(8)	C(10)	8044(68)	5694(39)	952(53)	226(24)
O(11)	9625(26)	8587(14)	7946(19)	68(9)	C(11)	7154(50)	5305(32)	2945(34)	139(13)
O(12)	12623(20)	6826(12)	8784(15)	43(6)	C(12)	8889(59)	4768(56)	2649(51)	254(27)
O(13)	7477(24)	7613(14)	4941(19)	65(8)	P(3)	1272(9)	7753(5)	1867(6)	46(3)
O(14)	6938(22)	7180(12)	7111(16)	50(7)	O(43)	2355(22)	7484(16)	1878(21)	98(12)
O(15)	8685(22)	6406(13)	9089(16)	56(7)	N(7)	455(27)	7561(17)	1083(21)	117(9)
O(16)	10086(23)	5325(14)	7989(17)	61(8)	N(8)	1365(33)	8474(15)	1658(27)	129(10)
O(17)	11322(21)	5432(12)	5988(15)	47(7)	N(9)	981(33)	7599(20)	2722(24)	148(11)
O(18)	9160(21)	6333(12)	4489(15)	48(7)	C(13)	788(53)	7365(39)	153(33)	159(16)
O(19)	7238(23)	6522(13)	4264(17)	60(8)	C(14)	−496(56)	7132(41)	1344(44)	199(20)
O(20)	6132(20)	6895(11)	5437(15)	42(6)	C(15)	2406(70)	8898(34)	2238(65)	249(26)
O(21)	6810(24)	6163(13)	7996(17)	60(8)	C(16)	496(63)	8923(33)	1496(62)	226(24)
O(22)	8277(19)	5341(11)	8370(14)	38(6)	C(17)	493(56)	7999(32)	3272(35)	139(13)
O(23)	9949(20)	4722(11)	6505(15)	42(6)	C(18)	1448(88)	6934(41)	3285(52)	254(27)
O(24)	9539(22)	5174(13)	4900(16)	52(7)	P(4)	4905(10)	7752(7)	1562(8)	70(4)
O(25)	6518(21)	5859(12)	6320(16)	49(7)	O(44)	3713(20)	7775(16)	1200(21)	100(12)
O(26)	7876(21)	5000(12)	6674(15)	47(7)	N(10)	5345(31)	8332(15)	1878(22)	117(9)
O(27)	7516(25)	5469(14)	5122(19)	68(8)	N(11)	5119(32)	7328(18)	2448(23)	129(10)
O(28)	9536(19)	7405(11)	5142(14)	37(6)	N(12)	5381(30)	7492(20)	824(25)	148(11)
O(29)	8411(20)	7862(11)	6649(14)	40(6)	C(19)	5196(61)	8960(23)	1288(41)	159(16)
O(30)	8776(20)	7425(11)	8197(14)	42(6)	C(20)	6235(66)	8348(32)	2818(45)	199(20)
O(31)	10579(21)	6420(13)	8689(16)	53(7)	C(21)	4249(78)	7322(47)	3139(54)	249(26)
O(32)	11608(20)	6058(11)	7509(15)	43(6)	C(22)	5299(78)	6654(34)	2404(51)	226(24)
O(33)	11063(22)	6594(12)	5583(16)	53(7)	C(23)	4754(50)	7161(33)	66(35)	139(13)
O(34)	10430(22)	7971(13)	6737(16)	53(7)	C(24)	6421(71)	7901(48)	517(55)	254(27)
O(35)	10813(22)	7551(13)	8255(17)	58(8)	O(1W)	3963(58)	6032(40)	6316(46)	249(35)
O(36)	11892(20)	7178(11)	7061(15)	43(6)	O(2W)	6205(76)	3159(54)	5148(62)	314(45)
O(37)	8594(18)	6212(10)	7472(13)	31(5)					

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

tail of the charge-transfer absorption band of the title compound has quite a large red-shift, which is similar to the spectrum of the HMPA solution of $PW_{12}O_{40}{}^{3-}$. This suggests that the interaction between the organic substrate and the polyoxometalate anion must play a role in the observed CT effect if the distance of both is short enough (in concentrated solution or the solid state).[16b] Indeed the purification of the title compound by recrystallization from acetonitrile results in initial breakage followed by complete re-formation of the weak intermolecular HMPA−polyoxometalate interaction in the complex.

That behavior can be also confirmed by compairing the ^1H NMR spectrum of the title compound in CD_3CN with the HMPA standard spectrum (which shows HMPA molecules). The ^1H NMR spectrum of the title compound is similar to those of the other intermolecular molecular complex.[16c] The IR spectra and electronic spectra in the solid indicate that α-$H_4SiW_{12}O_{40}$ and HMPA have interactions in the solid state, and the NMR spectra and electronic spectra in solution indicate that the interaction is very weak in dilute solution.

Although the title compound does not appear to be particularly sensitive to visible light, irradiation in the near-UV region of the pure solid sample immediately induces intense photochromism in solid state. This is assigned to the intervalence charge transfer ($W^{5+} \rightarrow W^{6+}$) IVCT band of $[SiW_{12}O_{40}]^{5-}$,[1d] which indicates that electron transfer occurs between organic substrate and inorganic acid, resulting in the reduction of $[SiW_{12}O_{40}]^{4-}$ to heteropoly blue $[SiW_{12}O_{40}]^{5-}$ with simultaneous oxidation of the organic substrate. This case has been verified by the ESR spectra of the irradiated sample. The low temperature ESR spectra is shown in Figure 4. The appearrance of the Mo^{5+} signal is because small amounts of molybdenum (coming from the raw meterials, about 0.005%) are always contained in the $SiW_{12}O_{40}{}^{4-}$. They behave as selective electron traps under reducing conditions.[17] The signal with $g_{\parallel} = 1.914$, $g_{\perp} = 1.933$, and $A_{\parallel} = 40$ G is ascribed to Mo^{5+}. The second,

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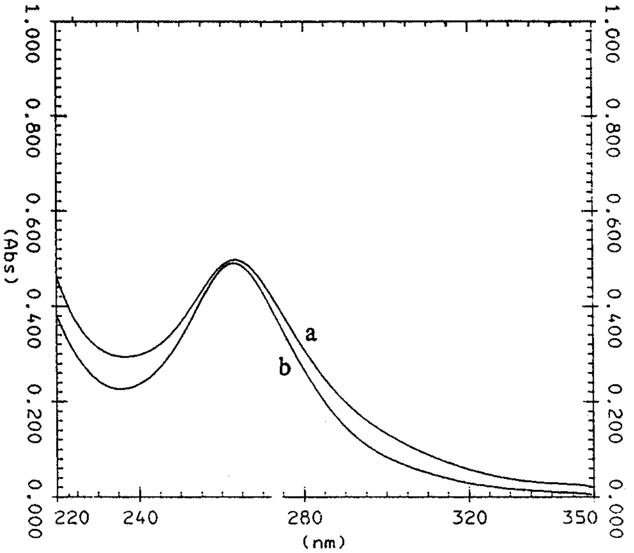

Figure 1. Comparison of the electronic spectra of $H_4SiW_{12}O_{40}$ and the title compound in aqueous solution: (a) $H_4SiW_{12}O_{40}$; (b) the title compound. All spectra were obtained on 5×10^{-5} M solutions in a 1 cm cell at 25 °C.

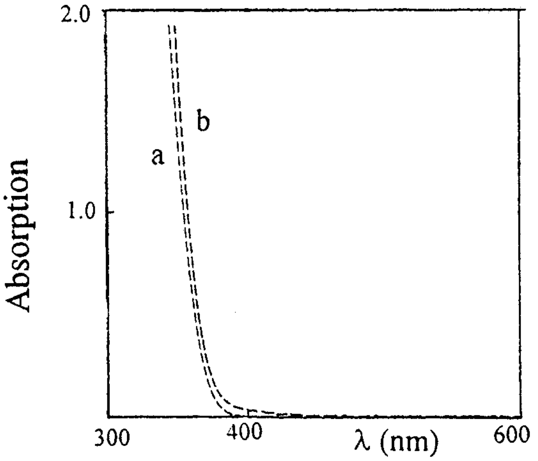

Figure 2. Comparison of the electronic spectra of $H_4SiW_{12}O_{40}$ and the title compound in aqueous solution: (a) $H_4SiW_{12}O_{40}$; (b) the title compound. All spectra were obtained on 5×10^{-3} M solution in a 1 cm cell at 25 °C.

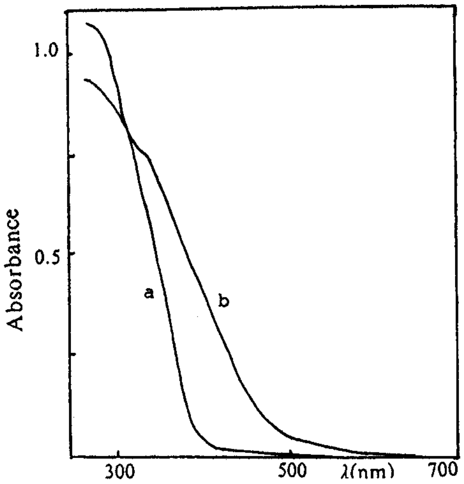

Figure 3. Reflectance electronic spectra: (a) $H_4SiW_{12}O_{40}{\cdot}nH_2O$; (b) the title compound. All spectra were obtained from a pellet which consisted of 40% sample and 60% MgO by weight. The base of the pellet is MgO.

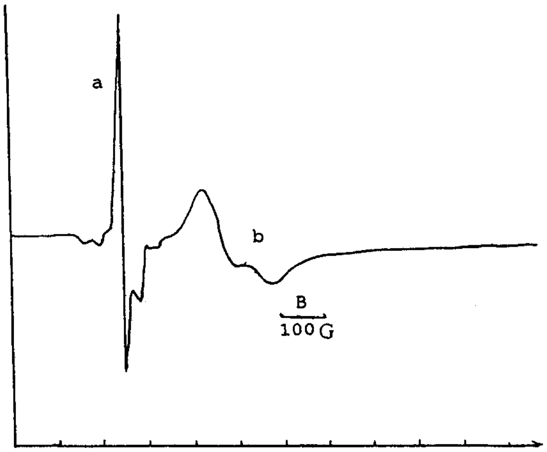

Figure 4. X-Band ESR spectrum of the title compound at low-temperature (110 K). The powder sample was irradiated for 15 min by a 500 W Ac lamp. Signal A is due to molybdenum impurities acting as selective electron traps; signal B is due to the photoreduced silicotungstate anion.

intense and broad signal is assigned to $[SiW_{12}O_{40}]^{5-}$ on the basis of its g value ($g_{\perp} = 1.822$). The fact that these spectra are often isotropic down to quite low temperatures or show small hyperfine values has been ascribed to the rapid intraionic hopping of the unpaired electron, comparable with the ESR time scale.[1d]

From the above result, it turns out that under the specified conditions, charge transfer between the organic substrate and the polyoxometalate anion will take place in the compound.

X-ray Crystal Structure of the Title Compound. Diffraction quality crystals can be grown from a solvent mixture of acetonitrile and water at room temperature.

The intermolecular complex crystallizes as an aquo solvate of formula α-$H_4SiW_{12}O_{40}{\cdot}4HMPA{\cdot}2H_2O$ in a monoclinic crystalline state.

A combined ORTEP plot and numbering diagram of all the non-hydrogen atoms in the asymmetric unit is given in Figure 5. A stereoview of the packing diagram viewed from the *y* axis is given in Figure 6. Selected bond distances and angles are given in Table 3 and Table 4, respectively. Other data and diagrams are included in the supporting informations. All non-hydrogen atoms of the polyoxometalate as well as those of the HMPA and water molecules are shown in Figure 5.

Despite the relatively high quality of the data set, the presence of the numerous heavy atoms in the structure precludes the determination of the hydrogen atom positions. Although we cannot determine the sites of the H^+ of the α-$H_4SiW_{12}O_{40}$ from the X-ray crystal structure, based on the bond-valence parameters,[19] we can obtain the bond orders for the N atoms in the molecule which are 3.13 (N1), 2.43 (N2), 3.01 (N3), 3.11 (N4), 2.55 (N5), 2.84 (N6),2.97 (N7), 2.60 (N8), 3.12 (N9), 3.20 (N10), 2.52 (N11), and 3.01 (N12). This suggests that the every HMPA has combined with a H^+ on N2, N5, N8, and N11, respectively. The W-O bond distance of polyoxometallate are in the range of 1.62−1.77 Å for the terminal oxygen, 1.76−2.00 Å for the bridging oxygens, and 1.91−2.47 for the oxygens of the SiO_4 group. The Si−O bond distances are 1.56, 1.60, 1.63, and 1.63 Å, respectively. The shortest W−O_d distance in the anion, W8−O8, is 1.62 Å, and the longest W−O bond,

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(18) T. Yamase, *J. Chem. Soc., Dalton Trans.* **1991,** 3055.

(19) Brown, I. D.; Altermatt, D. *Acta Crystallogr. Sect. B* **1985,** *B41,* 244.

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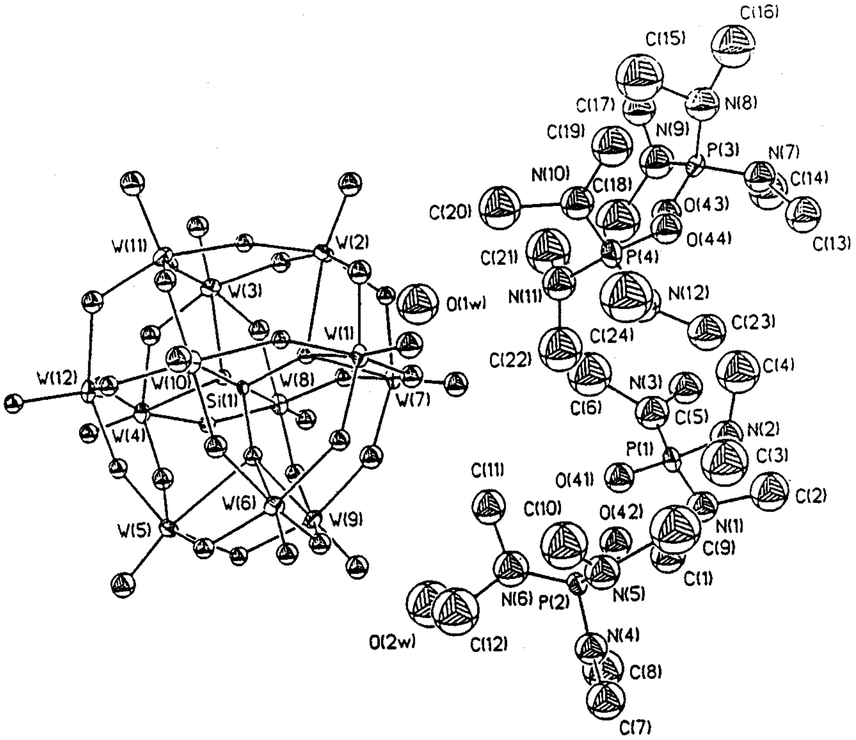

Figure 5. ORTEP of the title compound, showing 50% thermal ellipsoids and atom-numbering diagram of the title compound (recommended atom numbering scheme for Keggin structure as in ref 1a, p 146). The hydrogen atoms of the anion are not indicated for clarity.

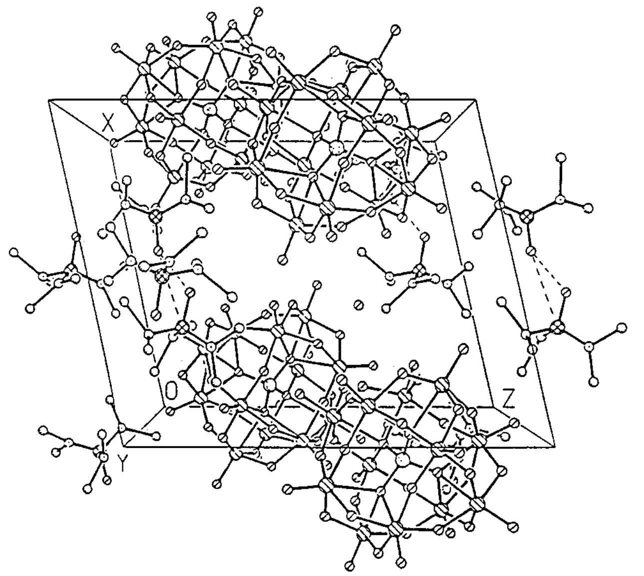

Figure 6. Crystal packing of the title compound viewed down the *y* axis.

W5−O38, is 2.47 Å. This shows that the WO_6 octahedra of the anion is severely distorted.

There is no hydrogen bond in the molecule, but with the solvate−solvate interactions delineated, we can turn to an analysis of the organic solvate−polyoxometalate interactions in the title compound. Such analysis should yield information addressing the effect of the HMPA on the absorption and photochromism of the polyoxometalate. Table 5 summarizes the shortest contact distance between each of the organic molecules and the polyoxometalate oxygens. The other intermolecular contacts less than 4.50 Å are given in the Supporting Information.

There is only one type of shortest contact in the molecules, and it involves the methyl carbon atoms of HMPA. The involved oxygen atoms of the anion are the terminal oxygen atoms and the two types of bridging oxygen atoms. Most of the contacts of solvate−polyoxometalate are quite long, but in some case the contacts are shorter than the sum of the appropriate van der Waals radii.

Table 3. Selected Bond Lengths (Å)

Si(1)−O(38)	1.56(3)	Si(1)−O(37)	1.60(2)
Si(1)−O(39)	1.63(2)	Si(1)−O(40)	1.63(2)
W(1)−O(1)	1.66(3)	W(1)−O(19)	1.76(3)
W(1)−O(28)	1.85(2)	W(1)−O(18)	1.85(3)
W(1)−O(13)	1.94(3)	W(1)−O(39)	2.36(2)
W(2)−O(2)	1.68(3)	W(2)−O(14)	1.87(3)
W(2)−O(20)	1.88(2)	W(2)−O(13)	1.90(3)
W(2)−O(29)	1.97(2)	W(2)−O(39)	2.33(2)
W(3)−O(3)	1.77(3)	W(3)−O(30)	1.86(3)
W(3)−O(15)	1.90(3)	W(3)−O(21)	1.92(3)
W(3)−O(14)	1.95(3)	W(3)−O(37)	2.36(2)
W(4)−O(4)	1.74(3)	W(4)−O(16)	1.81(3)
W(4)−O(15)	1.91(3)	W(4)−O(22)	1.92(2)
W(4)−O(31)	1.92(3)	W(4)−O(37)	2.32(2)
W(5)−O(5)	1.64(3)	W(5)−O(23)	1.89(2)
W(5)−O(17)	1.92(2)	W(5)−O(32)	1.97(2)
W(5)−O(16)	1.99(3)	W(5)−O(38)	2.47(2)
W(6)−O(6)	1.66(2)	W(6)−O(24)	1.85(3)
W(6)−O(17)	1.90(2)	W(6)−O(33)	1.94(3)
W(6)−O(18)	1.95(3)	W(6)−O(38)	2.38(2)
P(1)−N(1)	1.45(3)	P(1)−O(41)	1.48(2)
P(1)−N(3)	1.52(3)	P(1)−N(2)	1.67(3)
N(1)−C(1)	1.64(5)	N(1)−C(2)	1.66(5)
N(2)−C(4)	1.50(6)	N(2)−C(3)	1.72(6)
N(3)−C(5)	1.46(5)	N(3)−C(6)	1.74(7)
P(2)−N(4)	1.46(3)	P(2)−O(42)	1.48(2)
P(2)−N(6)	1.51(3)	P(2)−N(5)	1.66(3)
N(4)−C(7)	1.64(5)	N(4)−C(8)	1.64(5)
N(5)−C(10)	1.46(6)	N(5)−C(9)	1.72(6)
N(6)−C(11)	1.46(5)	N(6)−C(12)	1.77(7)

Photochromism studies indicate that the photoexcitation of the ligand to the metal charge-transfer band O→M of MO_6 octahedra in the polyoxometalate lattice lead to the formation of the localized $MO_5(OH)$ center as a result of the transfer of a hydrogen-bonding proton of the cation to the bridging oxygen atom.[18] The lack of hydrogen bond interactions between the

Table 4. Selected Bond Angles (deg)

O(38)−Si(1)−O(37)	109.7(13)	O(38)−Si(1)−O(39)	106.4(13)	O(6)−W(6)−O(33)	98.7(12)	O(24)−W(6)−O(33)	158.9(11)
O(37)−Si(1)−O(39)	110.5(13)	O(38)−Si(1)−O(40)	112.9(14)	O(17)−W(6)−O(33)	87.3(11)	O(6)−W(6)−O(18)	105.3(11)
O(37)−Si(1)−O(40)	107.8(11)	O(39)−Si(1)−O(40)	109.7(13)	O(24)−W(6)−O(18)	89.0(11)	O(17)−W(6)−O(18)	156.5(11)
O(1)−W(1)−O(19)	101.2(14)	O(1)−W(1)−O(28)	101.7(13)	O(33)−W(6)−O(18)	88.0(11)	O(6)−W(6)−O(38)	171.1(11)
O(19)−W(1)−O(28)	157.1(11)	O(1)−W(1)−O(18)	104.5(13)	O(24)−W(6)−O(38)	72.4(10)	O(17)−W(6)−O(38)	74.7(10)
O(19)−W(1)−O(18)	85.0(13)	O(28)−W(1)−O(18)	88.6(11)	O(33)−W(6)−O(38)	86.4(10)	O(18)−W(6)−O(38)	82.0(9)
O(1)−W(1)−O(13)	98.7(14)	O(19)−W(1)−O(13)	89.9(13)	W(2)−O(13)−W(1)	123(2)	W(2)−O(14)−W(3)	147(2)
O(28)−W(1)−O(13)	87.5(12)	O(18)−W(1)−O(13)	156.7(11)	W(3)−O(15)−W(4)	124.0(13)	W(4)−O(16)−W(5)	148(2)
O(1)−W(1)−O(39)	168.1(13)	O(19)−W(1)−O(39)	72.6(10)	W(6)−O(17)−W(5)	124.9(14)	W(1)−O(18)−W(6)	148.9(14)
O(28)−W(1)−O(39)	85.0(9)	O(18)−W(1)−O(39)	85.3(10)	W(1)−O(19)−W(7)	127(2)	W(2)−O(20)−W(7)	125.8(13)
O(13)−W(1)−O(39)	71.5(10)	O(2)−W(2)−O(14)	98.8(13)	W(8)−O(21)−W(3)	123(2)	W(8)−O(22)−W(4)	128.0(13)
O(2)−W(2)−O(20)	98.9(13)	O(14)−W(2)−O(20)	89.8(11)	W(9)−O(23)−W(5)	126.2(13)	W(6)−O(24)−W(9)	122.9(14)
O(2)−W(2)−O(13)	101.3(13)	O(14)−W(2)−O(13)	159.9(12)	W(8)−O(25)−W(7)	149(2)	W(8)−O(26)−W(9)	150(2)
O(20)−W(2)−O(13)	86.1(11)	O(2)−W(2)−O(29)	105.6(13)	W(7)−O(27)−W(9)	149(2)	W(1)−O(28)−W(10)	150.7(14)
O(14)−W(2)−O(29)	86.5(11)	O(20)−W(2)−O(29)	155.5(10)	W(11)−O(29)−W(2)	152.7(14)	W(3)−O(30)−W(11)	150.1(13)
O(13)−W(2)−O(29)	89.1(11)	O(2)−W(2)−O(39)	168.7(11)	W(12)−O(31)−W(4)	148(2)	W(12)−O(32)−W(5)	150(2)
O(14)−W(2)−O(39)	87.0(10)	O(20)−W(2)−O(39)	71.3(10)	W(10)−O(33)−W(6)	149(2)	W(11)−O(34)−W(10)	129(2)
O(13)−W(2)−O(39)	73.0(11)	O(29)−W(2)−O(39)	84.3(9)	W(11)−O(35)−W(12)	124.1(14)	W(10)−O(36)−W(12)	124.3(14)
O(3)−W(3)−O(30)	97.7(13)	O(3)−W(3)−O(15)	102.4(12)	Si(1)−O(37)−W(4)	126.5(13)	Si(1)−O(37)−W(3)	124.6(12)
O(30)−W(3)−O(15)	90.0(11)	O(3)−W(3)−O(21)	103.6(13)	W(4)−O(37)−W(3)	91.8(7)	Si(1)−O(37)−W(8)	122.4(11)
O(30)−W(3)−O(21)	158.5(11)	O(15)−W(3)−O(21)	88.5(12)	W(4)−O(37)−W(8)	91.2(7)	W(3)−O(37)−W(8)	90.1(8)
O(3)−W(3)−O(14)	99.3(12)	O(30)−W(3)−O(14)	86.9(11)	Si(1)−O(38)−W(9)	131(2)	Si(1)−O(38)−W(6)	124.5(14)
O(15)−W(3)−O(14)	158.2(11)	O(21)−W(3)−O(14)	86.6(11)	W(9)−O(38)−W(6)	92.1(8)	Si(1)−O(38)−W(5)	119.8(12)
O(3)−W(3)−O(37)	173.3(11)	O(30)−W(3)−O(37)	85.7(9)	W(9)−O(38)−W(5)	89.7(9)	W(6)−O(38)−W(5)	88.2(8)
O(15)−W(3)−O(37)	71.7(9)	O(21)−W(3)−O(37)	73.5(10)	Si(1)−O(39)−W(2)	124.6(12)	Si(1)−O(39)−W(7)	123.6(13)
O(14)−W(3)−O(37)	86.6(9)	O(4)−W(4)−O(16)	104.5(13)	W(2)−O(39)−W(7)	92.4(8)	Si(1)−O(39)−W(1)	123.3(13)
O(4)−W(4)−O(15)	101.3(12)	O(16)−W(4)−O(15)	154.0(11)	W(2)−O(39)−W(1)	92.2(8)	W(7)−O(39)−W(1)	91.3(8)
O(4)−W(4)−O(22)	103.2(12)	O(16)−W(4)−O(22)	84.6(12)	Si(1)−O(40)−W(12)	124.5(11)	Si(1)−O(40)−W(10)	123.9(10)
O(15)−W(4)−O(22)	85.9(11)	O(4)−W(4)−O(31)	102.7(12)	W(12)−O(40)−W(10)	92.8(8)	Si(1)−O(40)−W(11)	123.1(12)
O(16)−W(4)−O(31)	91.4(12)	O(15)−W(4)−O(31)	86.7(12)	W(12)−O(40)−W(11)	91.8(7)	W(10)−O(40)−W(11)	91.3(7)
O(22)−W(4)−O(31)	154.0(10)	O(4)−W(4)−O(37)	171.0(11)	N(1)−P(1)−O(41)	115(2)	N(1)−P(1)−N(3)	114(2)
O(16)−W(4)−O(37)	81.5(10)	O(15)−W(4)−O(37)	72.4(9)	O(41)−P(1)−N(3)	108(2)	N(1)−P(1)−N(2)	101(2)
O(22)−W(4)−O(37)	70.3(9)	O(31)−W(4)−O(37)	83.7(9)	O(41)−P(1)−N(2)	106(2)	N(3)−P(1)−N(2)	112(2)
O(5)−W(5)−O(23)	100.8(14)	O(5)−W(5)−O(17)	102.9(14)	P(1)−N(1)−C(1)	125(3)	P(1)−N(1)−C(2)	116(3)
O(23)−W(5)−O(17)	86.7(10)	O(5)−W(5)−O(32)	103.8(14)	C(1)−N(1)−C(2)	114(3)	C(4)−N(2)−P(1)	122(3)
O(23)−W(5)−O(32)	155.3(11)	O(17)−W(5)−O(32)	87.7(10)	C(4)−N(2)−C(3)	99(4)	P(1)−N(2)−C(3)	118(3)
O(5)−W(5)−O(16)	104.6(14)	O(23)−W(5)−O(16)	85.6(11)	C(5)−N(3)−P(1)	127(3)	C(5)−N(3)−C(6)	112(3)
O(17)−W(5)−O(16)	152.3(11)	O(32)−W(5)−O(16)	88.3(11)	P(1)−N(3)−C(6)	120(3)	N(4)−P(2)−O(42)	115(2)
O(5)−W(5)−O(38)	169.3(13)	O(23)−W(5)−O(38)	69.8(9)	N(4)−P(2)−N(6)	115(2)	O(42)−P(2)−N(6)	110(2)
O(17)−W(5)−O(38)	72.2(9)	O(32)−W(5)−O(38)	85.6(9)	N(4)−P(2)−N(5)	101(2)	O(42)−P(2)−N(5)	104(2)
O(16)−W(5)−O(38)	80.2(10)	O(6)−W(6)−O(24)	102.3(12)	N(6)−P(2)−N(5)	113(2)	P(2)−N(4)−C(7)	126(3)
O(6)−W(6)−O(17)	98.2(12)	O(24)−W(6)−O(17)	87.2(12)	P(2)−N(4)−C(8)	117(3)	C(7)−N(4)−C(8)	117(3)

Table 5. Short Nonbonded Distances in the Title Compound

nearest nonbonded C atom	involved atoms of α-$SiW_{12}O_{40}$	dist, Å	sym opern[a]
C2	O4(d)	3.252	2
C4	O16(c)	3.260	2
C4	O12(d)	3.406	2
C13	O31(c)	3.055	2
C13	O35(b)	2.983	2
C17	O1(d)	3.303	3
C17	O10(d)	3.435	3
C18	O6(d)	3.107	3
C23	O12(d)	3.085	2
C24	O14(c)	3.032	1

[a] Key: (1) $+x$, $+y$, $+z - 1$; (2) $+x - 1$, $+y$, $+z - 1$; (3) $+x - 1$, $+y$, $+z$.

HMPA moieties and the polyoxometalate moieties is unexpected. It suggests that the origin of the effect of HMPA molecules on the electronic spectra and photochromism of $SiW_{12}O_{40}^{4-}$ does not have a simple structural basis. The nature of the electronic interactions in the title compound is uncertain, but may resulted from both the van der Waals force and induced-dipole effects. The charge transfer in the complex could involve delocalized excited state or be of a intermolecular donor−acceptor character.

Nonlinear Optical Properties. The title compound crystallized in a nonsymmetric space-group. The second-order nonlinear optical intensities are estimated by measuring powder samples of 76−154 μm in diameter in the form of a pellet. The thickness of a pellet is about 0.8 mm. The pressure in compacting the pellet is 300 MPa. The experimental arrangment for the nonlinear optical properties utilizes a M200 high power Mode-Locked Nd:YAG laser with a 200 ps pulse at a repetition rate of 5 Hz. The selected wave length is 1064 nm. After the selection of the wavelength, the laser beam is split into two parts, one to generate the second harmonic signal in the sample and the other to generate the second harmonic signal in the reference (KDP pellet).

According to the principle proposed by Kurtz and Perry,[21] we estimate the SHG of the title compound. It is $I^{2\omega}{}_{\mathrm{sample}} = 0.7I^{2\omega}{}_{\mathrm{KDP}}$.

The third-order susceptibility, $\chi^{(3)}$, was determined by *Z*-scan techniques.[22] The *Z*-scan experimental apparatus is shown in Figure 7. Using a Gaussian laser beam in a tight-focus limiting geometry, we measure the transmittance of a nonlinear medium through a finite aperture placed in the far field as a function of the sample position (z) measured with respect to focal plane. We placed the sample (1.0×10^{-3} mol/dm^3) having $n_2 > 0$ well in front of the focus (-z in Figure 7). As the sample is moved toward the focus, the increased irradiation leads to a positive lensing effect that tends to collimate the beam, thus decreasing the aperture transmittance. With the sample on the $+z$ side of the focus, the positive lensing effect tends to augment diffraction, and the aperture transmittance is increased. The

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(21) Kurtz, S. K.; Perry, T. T. J. *Appl. Phys.* **1968,** *39*, 3798.
(22) Sheik-bahae, M.; Said, A. A.; Van Stryland, E. W. *Opt. Lett.*. **1989,** *17*, 955.

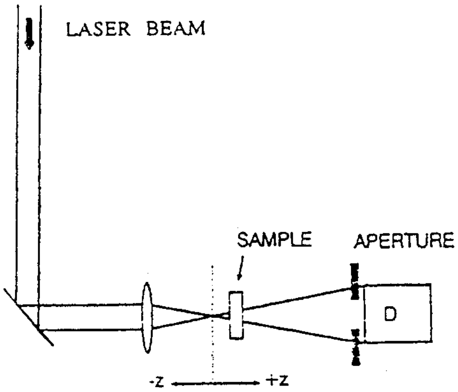

Figure 7. *Z*-Scan (aperture) experimental apparatus.

approximate null at $z = 0$ is analogous to placing a thin lens at the focus that results in a minimal far-field pattern change. For still large $+z$ the irradiation is reduced and the transmittance returns to the original linear value. We normalized this value to unity.

Third-order nonlinear optical properties of the title compound were investigated with a 200 ps pulse of 532 nm radiation at a frequency of 5 Hz using the same laser as the second-order nonlinear experiment. A CH_3CN solution of the compound was placed in a 1 mm quartz cell and used for all the optical mearsurements. The sample is very stable toward air and laser irradiation.

The NLO properties of the title compound are relatively simple. It is dominated by nonlinear refraction, as illustrated in Figure 8b. The nonlinear absorption of the title compound is negligible (Figure 8a). The valley−peak pattern of the normalized transmittance curve obtained under closed aperture configuation shows characteristic self-focusing behavior of the propagating light in the sample.

The valley and peak occur at equal distances from the focus with the valley-peak separation $\Delta Z_{V-P} = 8.1$ mm(see Figure 8b), fitting eq 1, where ω_0 is the laser beam waist radius (33 ± 5 μm) and λ is the laser wavelength (532 nm). This result suggests that observed optical nonlinearity has a third-order dependence on the incident field.

$$\Delta Z_{V-P} = 1.72\pi\omega_0/\lambda \qquad (1)$$

The difference between normalized transmittance values at valley and peak portions, ΔT_{V-P} is related to nonlinear refractive index n_2 ($m^2\ W^{-1}$) by eq 2 and eq 3, where $\Delta\Phi_0$ and I_0 are the on-axis phase shift and on-axis irradiance, both at focus, respectively, and α_0 and L are the linear absorption coefficient and optical path of the sample.[23] In our experiment, $S = 0.3$.

$$\Delta T_{V-P} = 0.406(1 - S)^{0.25}|\Delta\Phi_0| \qquad (2)$$

$$\Delta T_{V-P} = 0.371|\Delta\Phi_0|$$

$$\Delta\Phi_0 = \frac{2\pi}{\lambda} I_0 \frac{1 - e^{-\alpha_0 L}}{\alpha_0} n_2 \qquad (3)$$

The parameters ΔT_{V-P}, I_0, α_0, and L were measured to be 1.74, 3.26 GW cm^{-2}, 0.8 m^{-1}, and 1.0×10^{-3} m respectively (see Figure 8). Accordingly, the n_2 value of interest was calculated to be $1.22 \times 10^{-17}\ m^2\ W^{-1}$. Experiments with varied I_0 show that n_2 so measured is indeed independent of I_0, consistent with the notion that $n = n_0 + n_2 I$ and the observed NLO phenomenon is third-order in nature.

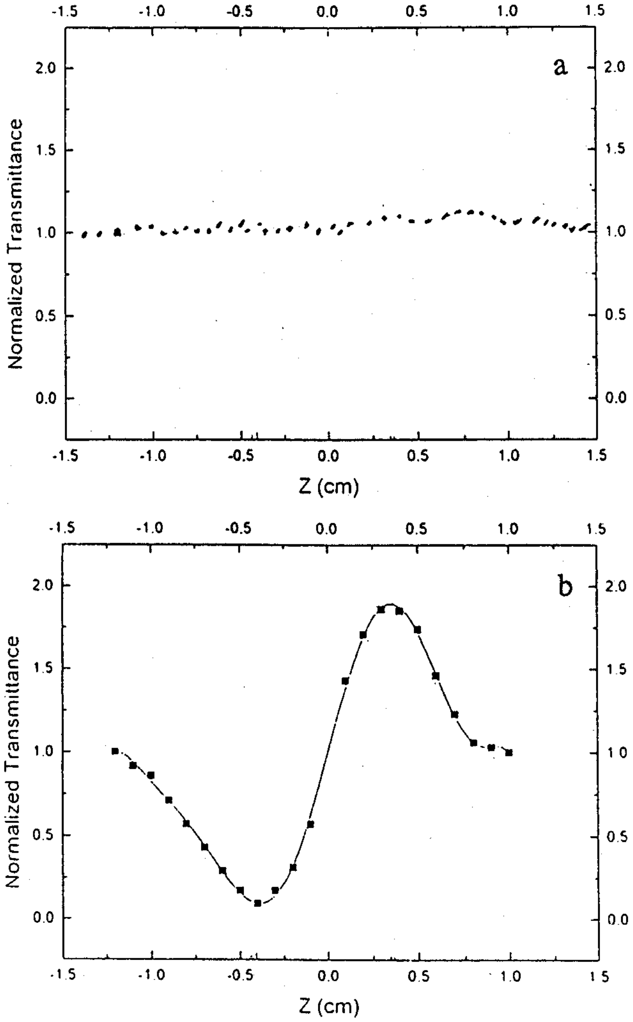

Figure 8. *Z*-Scan data of 1.1×10^{-3} M of the title compound at 532 nm with I^0 being 3.26 GW m^{-2}: (a) collected under the open aperture configuration showing very small NLO absorption; (b) collected under the closed aperture configuration showing the self-focusing effect.

Since the transparency region of the title compound extends from visible to near-IR, dispersion of n_2 in the wavelegth range 0.5−1 μm is expected to be negligible. If we ignore the contribution of NLO absorption, the third-order NLO susceptibility $\chi^{(3)}$ of the title compound can be calculated from the n_2 value by using the following equation.

$$\chi^{(3)} = \chi^{(3)}_{Re} = cn^2_0 n_2/80\pi = 2.63 \times 10^{-11}\text{esu}$$

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Supporting Information Available: Tables giving details of the X-ray structural data collection, bond lengths and angles, intermolecular contacts, and anisotropic displacement parameters (9 pages). Ordering information is given on any current masthead page.

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