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Supplementary Material Available: Crystal structure tables of experimental parameters, atomic positional parameters, anisotropic thermal parameters, bond lengths, bond angles, torsion angles, and planes for $C_{12}H_{36}Cl_4GaN_2PSSi_4$ (**2b**) and $C_{11}H_{27}AlCl_3N_2PSSi$ (**5**) (17 pages); tables of calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

Quadratic Hyperpolarizabilities of Group 6A Metal Carbonyl Complexes

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Summary: The molecular hyperpolarizabilities of $M(CO)_5$(pyridine), $M(CO)_4$(1,10-phenanthroline), and $M(CO)_5$(styrylpyridine) complexes (M = Cr, Mo, W) have been measured. The relationships between molecular hyperpolarizabilities and molecular modifications on the structures are discussed.

Organometallic molecules should offer the same attributes as organic molecules for nonlinear optics,[1] but interest in organometallic compounds for nonlinear optics (NLO) has been limited to using the second-harmonic generation (SHG) test on powdered materials.[2-7] Results obtained in this way are almost entirely determined by crystallographic and dispersive factors and provide limited information on the inherent molecular hyperpolarizabilities of molecules. Since molecular structure modification is often accompanied by crystallographic changes, powder testing cannot be reliably used to probe structure-property relations. Solution-phase dc electric-field-induced second-harmonic (EFISH) generation is a more appropriate method to extract hyperpolarizability. It allows extraction of a vectorial projection (β) of the quadratic hyperpolarizability tensor along the molecular dipole (μ) direction. When experiments are carried out with radiation of sufficiently long wavelength, EFISH results provide direct information on the intrinsic optical nonlinearity of a molecule.[8] In this paper, we describe EFISH results on group 6A metal carbonyl complexes and draw some conclusions concerning the hyperpolarizabilities of these organometallics.[9]

Table I. EFISH Results for $W(CO)_5$(4-X-pyridine) Complexes

X	solvent^a	$\lambda_{max}{}^b$	μ^c	β^d
H	toluene	332	6.0	-4.4
phenyl	$CHCl_3$	330-340	6.0	-4.5
n-butyl	*p*-dioxane	328	7.3	-3.4
NH_2	DMSO	290	8 (±1)	-2.1 (±0.3)
COMe	$CHCl_3$	420-440	4.5	-9.3
CHO	$CHCl_3$	420-440	4.6	-12

^{a} Solvent in which EFISH experiments were run. ^{b} Absorption maximum (nm) in *p*-dioxane. ^{c} Dipole moment ($\times 10^{-18}$ esu). ^{d} Units are 10^{-30} esu. Error bars represent experimental precision.

Table II. EFISH Results for $W(CO)_5$(4-X-styrylpyridine) Complexes^a

X	λ_{max}	μ	β
H (1)	302, 390	6.4	-5.7
COH (2)	320-420	3.8	-17
NO_2 (3)	322, 425	2.5	-20

^{a} See footnotes for Table I. The solvent is $CHCl_3$.

Metal pyridine complexes are capable of SHG.[2,6] EFISH is ideal for probing the effect of ligand and metal modifications on β in $M(CO)_5$(pyridine) complexes because these complexes are known to have their CT axis along the dipole direction. The low-energy metal to ligand charge-transfer (MLCT) excited states have been extensively studied and involve the low-lying π^*-acceptor orbitals of the pyridine ligands.[10] All measurements reported here have been performed at 1907 nm to minimize dispersive enhancement due to low-energy electronic excitations. EFISH results for a series of simple substituted tungsten pyridines are shown in Table I. The negative sign of β indicates a reduction of the dipole moment upon electronic excitation, which is consistent with the negative solvatochromism observed in this class of compounds.[11] The influence of coordination to the pyridines is clearly significant: pyridine has a β value of only 0.3×10^{-30} esu

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(1) Nicoud, J. F.; Twieg, R. J. In *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987; Vol. 1, p 255.

(2) Tam, W.; Eaton, D. F.; Calabrese, J. C.; Williams, I. D.; Wang, Y.; Anderson, A. G. *Chem. Mater.* **1989**, *1*, 128.

(3) Calabrese, J. C.; Tam, W. *Chem. Phys. Lett.* **1987**, *133*, 244.

(4) Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Bandy, J. A.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. *Nature* **1987**, *330*, 360.

(5) Tam, W.; Calabrese, J. C. *Chem. Phys. Lett.* **1988**, *144*, 79.

(6) Frazier, C. C.; Harvey, M. A.; Cockerham, M. P.; Hand, H. M.; Chauchard, E. A.; Lee, C. H. *J. Phys. Chem.* **1986**, *90*, 5703.

(7) Tam, W.; Wang, Y.; Calabrese, J. C.; Clement, R. A. *Proc. SPIE-Int. Soc. Opt. Eng.* **1988**, *971*, 107.

(8) Interpretation of EFISH results may be hampered if the molecule lacks a clear charge-transfer (CT) axis along the dipole direction; other tensorial components inaccessible by EFISH may contribute to the bulk properties for such compounds. The EFISH response is comprised of a dipolar part derived from the $\mu\beta$ product and an electronic part that originates in the molecular second hyperpolarizability (γ). The electronic component must be determined and substracted from the EFISH response to determine β. The electronic component is determined from third-harmonic generation experiments and can only be obtained on materials that are transparent at the third harmonic (633 nm when a 1.9-μm laser is used).

(9) The details of our EFISH methodology and data analysis are described in: Cheng, L. T.; Tam, W.; Meredith, G. R.; Rikken, G.; Meijer, E. W. *Proc. SPIE-Int. Soc. Opt. Eng.* **1989**, *1147*, 61.

(10) For reviews, see: (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979. (b) Ford, P. C. *Rev. Chem. Intermed.* **1979**, *2*, 267. (c) Adamson, A. W. *Pure Appl. Chem.* **1979**, *51*, 313.

(11) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105.

whereas W(CO)$_5$(pyridine) has a $|\beta|$ value of 4.4×10^{-30} esu.

The dipole moments of W(CO)$_5$(4-X-pyridine) complexes increase with the donating strength of the substituent, X. In the complexes, the pyridine nitrogen lone pair donates into the empty d_{z^2} orbital of tungsten, forming a σ-linkage. Efficient overlap of the pyridine p orbitals with the d_{xz} or d_{yz} orbitals also allows π donation toward the metal center, which acts as a potent ground-state π-acceptor as a result of the carbonyl ligands. It is therefore reasonable to expect that the ground-state dipole moments will be directed along the molecular 2-fold axis with excess charge on the carbonyl oxygen atoms. Due to the low solubility of the complex with X = p-NH$_2$ substituent, this material could not be measured in a low-polarity solvent.

According to the two-state model,[12] a smaller energy gap for the charge-transfer transition should result in a larger β value. We have recently demonstrated the effectiveness of the two-state model in benzene derivatives.[13] Modification of the pyridine ligand is an effective method of lowering the π^*-acceptor orbital and thus reducing the energy gap for the CT transition.[11] The use of 4-substituted pyridines with electron-accepting groups leads to larger β values. This trend can be rationalized, since the use of a strong accepting group should result in more back-transfer of charge upon MLCT excitation. Similarly, the use of pyrazine as a ligand also results in a smaller energy gap for the CT transition[14] and therefore should yield a β value higher than that of the analogous pyridine complex. Indeed, W(CO)$_5$(pyrazine) has a $|\beta|$ value of 6.0×10^{-30} esu (measured in CHCl$_3$, $\mu = 4.0 \times 10^{-18}$ esu), which is larger than the $|\beta|$ value of W(CO)$_5$(pyridine) ($|\beta| = 4.4 \times 10^{-30}$ esu).

Another effective method of increasing the β value is to increase the conjugation length of the molecule. Table II contains results for styrylpyridine derivatives.[15,16] As for the simple pyridine complexes, the increase in β with electron-withdrawing group is consistent with the lowering of the π^*-acceptor orbital and a decrease in the energy gap of the CT transition. The electron-withdrawing substituents once again yield the lowest energy absorption maxima, as expected for the M to L direction of the CT.

To probe the influence of the metal on β, we compare results for the series of complexes M(CO)$_4$(1,10-phenanthroline) (M = Cr, Mo, W). The electronic absorption spectra of a number of M(CO)$_4$L complexes have been determined. For a given L, the variations in band position are not large (<2000 cm^{-1}), and for a given M, the band order is 1,10-phenanthroline > 5-nitro-1,10-phenanthroline.[17,18] The electronic absorption spectra of Cr, Mo, and W complexes all show weak low-energy MLCT bands with λ_{max} = 500, 476, and 492 nm; ϵ_{max} = 5046, 4373, and 7379; and f = 0.13, 0.15, and 0.19, respectively.[19] Consistent with these observations, β values for all three complexes M(CO)$_4$(1,10-phenanthroline) (M = Cr, Mo, W) measured in CH$_2$Cl$_2$ are the same within experimental error in the region -13×10^{-30} esu with dipole moments ranging from 7.5×10^{-18} to 8.4×10^{-18} esu. Once again, the ligand with an electron-withdrawing group yields a higher β value and a lower dipole moment: W(CO)$_4$(5-nitro-1,10-phenanthroline) has a β value of -18×10^{-30} esu and μ value of 4.8×10^{-18} esu. Since the molecular geometries and orbital overlaps are quite different between M(CO)$_4$(1,10-phenanthroline) and W(CO)$_5$(pyridine) derivatives, their β values cannot be directly compared.

In summary, the M(CO)$_4$L and M(CO)$_5$L complexes show respectable nonlinearities that are comparable to those of p-nitroaniline ($\beta = 9.2 \times 10^{-30}$ esu) and 4-methoxy-4′-nitrostilbene ($\beta = 28 \times 10^{-30}$ esu).[13] The electronic properties of the M(CO)$_5$ and M(CO)$_4$ groups appear to be those of an effective ground-state acceptor and excited-state donor, a characteristic not found in common organic substituents. This characteristic leads to highly nonlinear molecular structures with modest ground-state dipole moments. This is in sharp contrast to conventional donor/acceptor aromatic systems, in which great nonlinearity is accompanied by large dipole moments.

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Registry No. **1**, 41707-83-9; **2**, 129466-97-3; **3**, 129466-98-4; W(CO)$_5$(pyridine), 14586-49-3; W(CO)$_5$(4-phenylpyridine), 129466-95-1; W(CO)$_5$(4-n-butylpyridine), 129466-96-2; W(CO)$_5$(4-NH$_2$-pyridine), 105267-78-5; W(CO)$_5$(4-COMe-pyridine), 60166-30-5; W(CO)$_5$(4-CHO-pyridine), 60166-33-8; Cr(CO)$_4$(1,10-phenanthroline), 14168-63-9; Mo(CO)$_4$(1,10-phenanthroline), 15740-78-0; W(CO)$_4$(1,10-phenanthroline), 14729-20-5; W(CO)$_5$(pyrazine), 65761-19-5; W(CO)$_4$(5-nitro-1,10-phenanthroline), 87655-73-0.

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(12) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.

(13) Cheng, L. T.; Tam, W.; Meredith, G. R.; Rikken, G.; Meijer, E. W. *Proc. SPIE-Int. Soc. Opt. Eng.* **1989**, *1147*, 61.

(14) Pannell, K. H.; Guadalupe de la Paz Saenz Gonzalez; Leano, H.; Iglesias, R. *Inorg. Chem.* **1978**, *17*, 1093.

(15) Complexes **2** and **3** were prepared by the reaction of W(CO)$_5$(THF) with the appropriate styrylpyridine. Data for **2**: 53% yield after chromatography on silica gel with CHCl$_3$ as eluent; ^{1}H NMR (CD$_2$Cl$_2$) δ 10.0 (s, 1 H), 8.8 (m, 2 H), 7.92 (d, J = 8.2 Hz, 2 H), 7.74 (d, J = 8.2 Hz, 2 H), 7.45 (d, J = 16.4 Hz, 1 H), 7.4 (m, 2 H), 7.18 (d, J = 16.4 Hz, 1 H). Anal. Calcd for C$_{19}$H$_{11}$NO$_6$W: C, 42.80; H, 2.08. Found: C, 42.78; H, 2.16. IR (KBr): 2069 w, 1969 w, 1940 m, 1903 s, 1879 m, 1688 m cm^{-1}. Data for **3**: 31% yield after chromatography on silica gel with 25% EtOAc/75% hexane as eluent; ^{1}H NMR (CD$_2$Cl$_2$) 8.8 (m, 2 H), 8.2 (m, 2 H), 7.8 (m, 2 H), 7.44 (d, J = 16.4 Hz, 1 H), 7.4 (m, 2 H), 7.18 (d, J = 16.4 Hz, 1 H); IR (KBr) 2069 w, 1970 w, 1926 m, 1905 s, 1878 m cm^{-1}. Anal. Calcd for C$_{18}$H$_{10}$N$_2$O$_7$W: C, 39.30; H, 1.83. Found: C, 39.25; H, 1.74. Complex **3** has a powder SHG signal 5 times that of urea when irradiated with a 1.06-μm laser. All of the other pyridine complexes in this study were found to be SHG-inactive in the Kurtz powder test.

(16) Wrighton, M. S.; Gray, H. B. *Mol. Photochem.* **1973**, *5*, 179.

(17) Wrighton, M. S.; Morse, D. L. *J. Organomet. Chem.* **1975**, *97*, 405.

(18) Angelici, R. J.; Graham, J. R. *Inorg. Chem.* **1967**, *6*, 988.

(19) Spectroscopic results were obtained in p-dioxane. Spectroscopic results have been reported: Wrighton, M. S.; Morse, D. L. *J. Organomet. Chem.* **1975**, *97*, 405.