J. Braz. Chem. Soc., Vol. 8, No. 1, 83-86, 1997.
Printed in Brazil.

Article

Fine Tuning of the Properties of Organically Modified Heteropolymetalates

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Received: July 5, 1996; September 19, 1996

Oxopolimetalatos organicamente modificados do "tipo Keggin"de formula $[R]_4[SiW_{11}O_{40}(SiR')_2]$, ($R=Bu_4N^+$, R' = $-C_2H_5$, $-C_{10}H_{21}$, $-CH=CH_2$, $-CH_2CH=CH_2$, -OH, $-C_6H_5$, $-C_{10}H_7$, $-C_6H_4NH_2$ (o, p), $-C_6H_4NMe_2$ (p), $-C_6H_4CH=CH_2$, $-C_6H_4CF_3$, $-C_6H_4CH=CHC_6H_5$) foram sintetizados. O núcleo óxido apresentou propriedades redox reversíveis que foram sintonizadas, escolhendo-se o modificador orgânico. As variações nos deslocamentos químicos na RMN de ^{183}W, induzidas pelos modificadores, foram também medidas e ambos os efeitos correlacionados com as propriedades de doação-aceitação eletrônica do radical orgânico. As magnitudes destes efeitos foram comparadas com aqueles causados pelo eletrólito.

"Keggin-type" organically modified oxopolymetalates of formula $[R]_4[SiW_{11}O_{40}(SiR')_2]$, ($R=Bu_4N^+$, R' = $-C_2H_5$, $-C_{10}H_{21}$, $-CH=CH_2$, $-CH_2CH=CH_2$, -OH, $-C_6H_5$, $-C_{10}H_7$, $-C_6H_4NH_2$ (o, p), $-C_6H_4NMe_2$ (p), $-C_6H_4CH=CH_2$, $-C_6H_4CF_3$, $-C_6H_4CH=CHC_6H_5$) were synthesized. The oxide core presented reversible redox properties which were tuned by the choice of the organic modifier. Parallel variations of the ^{183}W NMR chemical shifts were measured and both effects might be related to the electronic donor-acceptor properties of the organic radical. The magnitudes of these effects are compared with those coming from the electrolyte itself.

Keywords: *organically modified oxopolymetalates, redox properties, ^{183}W NMR spectroscopy*

Introduction

Over the last decade, there has been great interest in the study of polyoxometallates (POM) as models for transition metal oxides[1]. These compact oxide clusters of small size (around 10 Å) present unique redox properties and the ability to mimic transition metal oxide features[2]. The redox properties are sensitive to the POM composition and structure. Strong effects are also measured with changes of electrolyte[3]. Recently, the grafting of organic radicals to a Keggin-type oxide core was described[4,5,6]. As a first example of the 'modifier effect', we reported previously the grafting of polymerizable groups to POM structrures as a powerful way to develop mixed organic-inorganic polymers with adjustable properties[7,8].

In this Paper, the interactions between the organic modifier and the oxide core are measured for organically modified POM (OMPOM) with various substituents. Redox potentials (cyclic voltametry) and NMR chemical shifts (^{29}Si and ^{183}W) are used as sensitive probe for such interactions.

Experimental

Synthesis

Pure Keggin OMPOMs of formula $[R]_4[SiW_{11}O_{40}(SiR')_2]$ ($R=Bu_4N^+$, R' = $-C_2H_5$, $-C_{10}H_{21}$, $CH=CH_2$, $-CH_2$

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CH=CH_2, -OH, -C_6H_5, -$C_{10}H_7$, -$C_6H_4NH_2$ (o, p), -C_6H_4N Me_2 (p), C_6H_4CH=CH_2, -$C_6H_4CF_3$, -C_6H_4CH=CHC_6H_5) were synthesized following two procedures previously described[5]. Trichlorosilane (Cl_3SiR') in water or trialkoxysilane ($(OEt)_3SiR'$) in acidified water were added to lacunary Keggin POM $[SiW_{11}O_{39}]^{8-}$ (Table 1). The characterization of a few OMPOMs has already been detailed by elemental analysis, IR, time of flight mass spectrometry, ^{29}Si and ^{183}W NMRs. These analyses assert the grafting of two R' groups, symmetrically anchored to the edges of the hole in the lacunar $[SiW_{11}O_{39}]^{8-}$ cluster, as proposed by Knoth[9] (Fig. 1). All compounds were purified twice by recrystallization in DMF/water or DMF/acetone mixtures and the purity of these compounds was shown to be above 95% (main impurity is $[Bu_4N]_4[SiW_{12}O_{40}]$).

NMR spectroscopy

^1H, ^{13}C-{^1H} and ^{29}Si-{^1H} NMR spectra were recorded to check the purity of the compounds (Bruker AC250 spectrometer). ^{183}W NMR spectra were recorded on a Bruker AM500 spectrometer following usual procedures[5]. OMPOM salts were dissolved in DMF/DMSO-d_6

Table 1. Properties of $[Bu_4N]_4[SiW_{11}O_{40}(SiR')_2]$ salts. Synthesis procedures for the organo-silicon precursor : (a) $(OEt)_3SiR'$ commercial, (b) Cl_3SiR' commercial, (c) $(OEt)_3SiR'$ from $Si(OEt)_4$; R'Br; Mg/Ether, (d) $(OEt)_3SiH$ commercial; H_2O, (e) $(OEt)_3SiR'$ from $Si(OEt)_4$; R'Br; Mg/THF, (f) $(OEt)_3SiR'$ from $Si(OEt)_4$; R'Br; Li/Ether, (g) $(Cl)_3SiR'$ from $Si(Cl)_4$; R'Br; Mg/Ether. Intermediates $(OEt)_3SiR'$ and $(Cl)_3SiR'$ were purified by vacuum distillation, and characterized by ^1H, ^{13}C and ^{29}Si NMR. $[Bu_4N]_4[SiW_{11}O_{40}(SiR')_2]$ were checked by IR and ^1H NMR spectroscopies.
^{29}Si and ^{183}W NMR chemical shifts in $DMSO_{d6}$-DMF. References; ^{29}Si : $SiMe_4$; ^{183}W : 1.0 M solution of Na_2WO_4 (pH = 10). With respect to the low sensitivities of these techniques, measurements could be only obtained when sufficient quantities of compounds were available.
W1, ... W6 labels are arbitrary assigned in regard to the POM structure.
Electrochemistry: Reduction potentials (*vs.* SCE) for the two first redox stages in Bu_4NBF_4 (0.1M)/DMF electrolytes, scan rate 50 mV/s.

R'	^{29}Si (ppm)		^{183}W chemical shifts (ppm) (relative intensities)						$J_{SiR'-W}$ (Hz)		$E_{reduction}$ Bu_4NBF_4:DMF	
	SiR'	SiO_4	W1(2)	W2(2)	W3(1)	W4(2)	W5(2)	W6(2)				
-CH_2CH_3 (a) (ethyl)	-52.9	-83.9	-106.4	-108.4	-112.6	-128.1	-173.0	-252.4	15.9	5.2	-995	-1560
-$C_{10}H_{21}$(b) (decyl)	-53.0	-84.9	-105.6	-108.4	-112.1	-127.4	-173.4	-253.5	16.0	5.4	-1000	-1570
-CH_2CH=CH_2(a) (allyl)	-57.7	-84.2	-106.2	-107.7	-112.6	-127.3	-171.2	-249.5	16.2	5.5	-965	-1530
-CH=CH_2(a) (vinyl)	-66.6	-84.5	-106.1	-107.1	-112.5	-126.6	-170.8	-247.1	16.6	5.5	-945	-1520
C_6H_5(a) (phenyl)	-66.5	-84.6	-106.1	-106.6	-112.2	-126.3	-169.6	-245.1	16.5	5.5	-930	-1500
-$C_{10}H_7$(c) (naphtyl)	-64.8	-84.5									-960	-1530
-OH (d) (hydroxyl)	-83.1	-84.8							20.2	4.9	-980	-1540
-C_6H_4CH=CH_2(e) (styryl)	-66.4	-84.7									-940	-1500
-$C_6H_4NH_2$, para(f) (p-aminophenyl)	-64.6	-84.3							16.0	5.5	-1000	(x)
-$C_6H_4N(CH_3)_2$, para(f) (diMeaminophenyl)	-66.3	-84.2									-1000	(x)
-$C_6H_5NH_2$, meta(g) (m-aminophenyl)											-890	(x)
-$C_6H_4CF_3$, para (c) trifluoromethylphenyl											-890	(x)
-C_6H_4CH=CHC_6H_5(f) stylbyl											-890	-1250
$SiW_{12}O_{40}$		-85.3					-92.2				-870	-1425

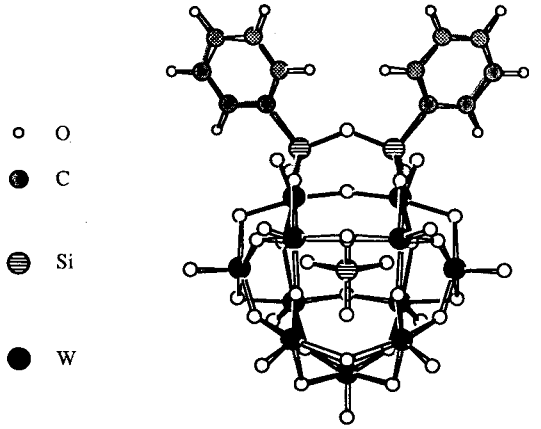

Figure 1. Structure of the phenyl modified Keggin polymetallate $[SiW_{11}O_{40}(SiC_6H_5)_2]^{4-}$.

(80-20) mixtures (0.1 to 0.4 M). Variations of ^{183}W chemical shifts for the different signals were less than ±0.1 ppm with changes of OMPOM concentrations and slight changes of solvent composition. The signal of the silicotungstate salt was used as an internal reference. The spectra of the different compounds exhibited six signals.

Electrochemistry

Electrochemistry measurements were performed in different electrolytes, following usual procedures[10]. In all experiments, the concentration of the electrolyte was 0.1 M in supporting salt, and the concentration of OMPOM was fixed to 10^{-3} M. The working electrode was a 0.07 cm^2 disk of glassy carbon, polished before each measurement (1 μm grain size SiC paste). The reference electrode was a saturated calomel electrode (SCE), except in acetonitrile where an Ag/Ag$^+$ electrode had to be used. Solutions were degazed with dried argon prior to measurements. Cyclic voltammetry experiments were performed with scan rate from 1000 mV s^{-1} down to 1 mV s^{-1} and characteristic potentials were reproducible within 5 mV. Two successive monoelectronic reversible stages proceeded, as shown by the 60 mV measured between reduction and oxidation stages, coulometric measurements and the intensity-scan rate relationship ($I = v^{1/2}$).

Results and Discussion

Table 1 presents the properties of 14 OMPOM as their tetrabutylammonium salts. Variations in the chemical shifts of all nuclei can be seen with the nature of the organic modifier group. ^{29}Si signals are very sharp, and changes in the chemical shifts are noted for both the organic bonded silicon atom and the central oxometallate silicon atom. The first effect is due to σ–π interactions between the organic group and the silicon atoms and parallels those observed for trichloro or trialkoxy silanes[11]. NMR Si-W couplings were observed on this first signal, and their similar values reflect the identical structure of the different OMPOMs. The magnitude of the effect on the second silicon is much lower and one should assume a moderate variation of the silicon partial charge[12]. Changes in chemical shifts are also observed for all W nuclei. The magnitude of this effect varies from 0.8 ppm for W1 to up to 8.4 ppm for W6. Assuming also that this effect arises mainly from changes in the partial charge on the different tungstens, the stonger effect measured on W5 and W6 asserts the proximity of the organic groups to these nuclei[13].

A significant variation in the reduction potentials, measured in DMF/Bu_4NBF_4 was observed for the two first redox steps of the different OMPOMs, ranging from

Table 2. Redox potentials in different supporting electrolytes. All data were normalized with the reference redox couple ferrocene/ferricinium (Fc/Fc$^+$) [0.1M in supporting salt, 0.001 M in polymetalate ; scan rate: 50 mV/s].

R'	Dimethylformamide						Acetonitrile						DMSO	
	Bu_4NBF_4		$NaBPh_4$		$NaBF_4$		Bu_4NBF_4		$NaBPh_4$		$NaBF_4$		$NaBPh_4$	
$-CH_2CH_3$	-1435	-2000	-1370	-1580	-1370	-1590	-1270	-1790	-1040	-1180	-1095	-1260	-1270	-1830
$-C_{10}H_{21}$	-1440	-2010	-1380	-1580	-1380	-1580	-1285	-1790	-1040	Ixx	-1110	xx	-1285	-1830
$-CH_2CH=CH_2$	-1405	-1970	-1340	-1555	-1340	-1560	-1220	-1740	-1025	-1180	-1080	-1255	-1230	-1770
$-CHCH_2$	-1385	-1960	-1335	-1570	-1330	-1570	-1205	-1735	-1020	-1175	-1065	-1250	-1215	-1765
$-C_6H_5$	-1370	-1940	-1315	-1560	-1320	-1560	-1200	-1730	-1025	-1190	-1070	-1260	-1190	-1740
-OH	-1420	-1980	-1320	-1530	-1350	-1560	-1200	-1720	-1150	-1340	-1100	xx	-1250	-1750
$(Bu_4N)_4\,SiW_{12}O_{40}$	-1310	-1865	-1270	-1480	-1280	-1490	-1130	-1650	-970	-1085	-1030	-1145	-1095	-1630
$H_4[SiW_{12}O_{40}]$	-1085	-1240	-1125	-1290	-1090	-1260	-690	-1290	-580	-970	-630	-1010	-1100	-1260
$K_4[SiW_{12}O_{40}]$	-1300	-1690	-1270	-1480	-1280	-1490	-1120	-1540	-1010	-1130	-1035	-1170	-1100	-1640
$K_4[SiW_{11}O_{40}\,(SiPh)_2]$	-1370	-1820	-1320	-1560	-1320	-1560	-1200	xx	-1030	-1190	-1070	-1240	-1200	-1700

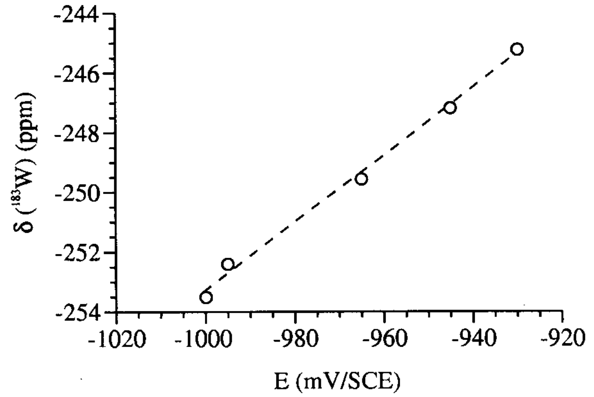

Figure 2. Correlation between electrochemical (reduction potential in Bu_4NBF_4/DMF electrolyte (*vs.* SCE)) and ^{183}W NMR chemical shifts (for W6 atoms) data. The dots represent the decyl, ethyl, allyl, vinyl and phenyl species respectively, from left to right.

1000mV (*vs.* SCE) up to -890 mV. Table 2 reports the data obtained for some of these compounds in different solvents. The ferrocene/ferricinium (Fc/Fc$^+$) couple was used for standardization of all measurements in order to compare the results on a common scale. Severe variation of the redox potentials was observed, depending on both the solvent and supporting salt. Obviously, the solvent strongly affects the redox potentials (it could be parametrized by the acceptor numbers[14]), while the nature of the supporting salt affects mainly the difference between the redox stages. However, the relative redox potentials of the different OMPOMs are not affected by changing the electrolyte. This fundamental observation demonstrates the intrinsic effect of the organic substituent on the redox potential, which appears to be related to the electronic acceptor/donor behavior of the organic substituent. The ability to be reduced is increased when the oxide core is electron depleted, *i.e.*, when the R' organic group is more electronegative[15]. Figure 2 correlates the data obtained from electrochemistry and ^{183}W NMR measurements on some of these compounds. A strong relationship between these two sets of measurements is evidenced by the parallel effects and both should be related to the π-acceptor character of lacunary polyoxometalate[16] and the electronic effect of the organic group. The strong π-conjugation between both organic and inorganic moieties is exalted in comparing the redox potentials of *para* and *ortho* aminophenyl derivatives, respectively -1000 and -890 mV (*vs.* SCE). Only in the first of these compounds, the lone pair may be conjugated with the oxide core, leading to a rather low reduction potential.

This work reports the strong synergy between organic and inorganic components in a series of organically modified heteropolymetalates. Two techniques were used, both measuring the electronic charge on the tungsten core. Electrochemistry averages the charge effect on the whole oxide cluster (EPR of 1e$^-$ reduced species demonstrates the electron delocalization at room temperature), while ^{183}W NMR spectroscopy could provide a selective mapping of the charge on the different tungsten atoms. Moderate conjugation effects were measured and a fine tuning of the redox potential was obtained by the choice of the modifier group. However, for these different compounds, the magnitude of the intramolecular effect is low in comparison with the solvent effect. This could be due to the siloxane bond which is certainly not the best electronic junction. Other modification methods of polyoxometallates have already been described[2,4,16]. They could be a key to obtain functionnalized molecules with unusual behavior for the fields of molecular electronics and non linear optics.

Acknowledment

This work was supported by the CNRS and by the University of Paris XI.

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