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Organometallic–Polyoxometalate Hybrid Compounds: Metallosalen Compounds Modified by Keggin Type Polyoxometalates

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Hybrid compounds with two functional centers consisting of a metallosalen moiety (M–salen; M = Mn, Co, Ni, and Pd) connected by an alkylene bridging group to a lacunary Keggin type polyoxometalate were synthesized and characterized. In these metallosalen–polyoxometalate compounds (M–salen–POM) it was shown by the use of a combination of UV–vis, ^{1}H NMR, EPR, XPS, and cyclic voltammetry measurements that the polyoxometalate exerts a significant intramolecular electronic effect on the metallosalen moiety leading to formation of an oxidized metallosalen moiety. For the Mn–salen–POM, the metallosalen center is best described as a metal–salen cation radical species; that is, a localized "hole" is formed on the salen ligand. For the other M–salen–POM compounds, the metallosalen moiety can be described as a hybrid of a metal–salen cation radical species and an oxidized metal–salen species, that is, a delocalized "hole" is formed at the metallosalen center. It is proposed that these oxidized metallosalen centers are best characterized as stabilized charge transfer (metallosalen donor–polyoxometalate acceptor) complexes despite the relatively large distance between the two functional centers.

Introduction

The modification of metal centers in organometallic compounds by change of the electronic and steric properties of the coordinating ligand is an ongoing theme important for the control of the reactivity of organometallic complexes. In this context, it is especially intriguing to attain and/or stabilize unusual or rare oxidation states. The possible use of polyoxometalates as modifiers to obtain organometallic compounds of high(er) oxidation states presents an important opportunity because of the strong electron acceptor properties and relatively large bulk of the polyoxometalate (POM) moieties. This approach may in the future be useful in applications such as catalysis by organometallic compounds whereby the presence of a polyoxometalate may lead to the stabilization of high-valent active intermediates. A considerable number of organometallic–(POM) hybrid compounds[1] have already been prepared based on either (a) an electrostatic interaction of organometallic cationic species with polyoxometalate anions,[2] or (b) the attachment of an organic moiety to a metal center incorporated within the polyoxometalate cluster.[3] Here, for the first time, a new and different strategy is presented: the synthesis of an organometallic–POM hybrid compound where the two components are connected by an alkylene group. A series of metallosalen (M–salen, M = Mn, Co, Ni, and Pd) compounds were attached to a Keggin type polyoxometalate through an alkyl bridging spacer, Scheme 1. UV–vis, ^{1}H NMR, EPR, XPS, and cyclic voltammetry measurements clearly showed that indeed there is a significant, most likely through space, electronic effect of the polyoxometalate on the metallosalen leading to stabilization of higher valent oxidation states.

Results and Discussion

Synthesis. The synthetic method, according to Scheme 1, used for the preparation of the M–salen–POM compounds

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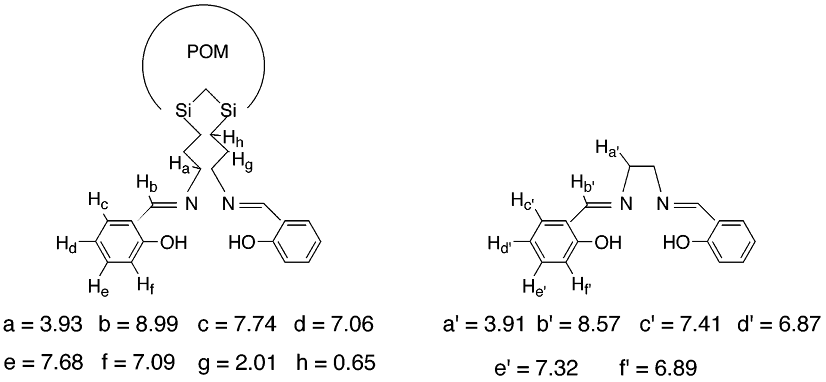
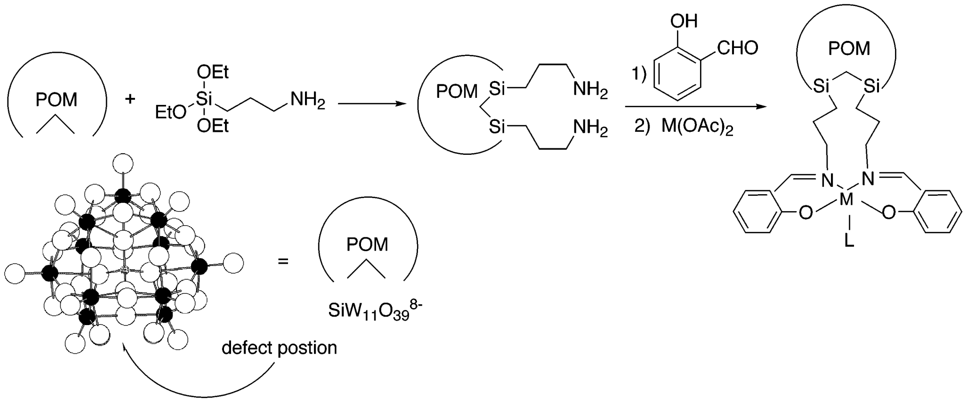


Figure 1. ^{1}H NMR shifts (ppm) for the salen−POM and *N,N′*-ethylenebis(salicylimine) compounds.

Scheme 1. Synthetic Pathway for the Preparation of the M−Salen−POM Compounds



is based on incorporation of a functionalized alkylsilane into the defect position of a lacunary polyoxometalate[4] followed by formation of the salen ligand and metalation. Specifically, first, an organosilane, $RSi(OEt)_3$ (R = $CH_2CH_2CH_2NH_2 \cdot HCl$), was reacted at high dilution[5] with a lacunary polyoxometalate, $[SiW_{11}O_{39}]^{8-}$, leading to incorporation of the organosilane moiety into the defect position of the polyoxometalate and thereby yielding $Q_4[SiW_{11}O_{40}(SiCH_2CH_2CH_2NH_2 \cdot HCl)_2]$ (Q = $(n\text{-hexyl})_4N^+$). The IR spectrum (see Experimental Section) shows peaks of the Keggin structure that was unaffected by the modification by $SiCH_2CH_2CH_2NH_2$ and absorption bands typical of a $SiCH_2CH_2CH_2NH_2$ unit. Likewise the ^{1}H NMR and ^{29}Si NMR spectroscopy (see Experimental Section) showed the expected peaks for both the organic and polyoxometalate moieties. Second, the salen−POM compound was prepared by reaction of $Q_4\{SiW_{11}O_{39}[O(SiR)_2]\}$ with salicylaldehyde to yield $Q_4\{SiW_{11}O_{39}[O(SiR')_2]\}$ (R′ = $CH_2CH_2CH_2N{=}CH(2\text{-}OHPh)$). The molecular structure, as previously discussed,[4b] was confirmed by a combination of IR, ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, and ^{183}W NMR (see Experimental Section). Again, the IR spectrum shows peaks of the Keggin structure that was unaffected by the modification by $SiCH_2CH_2CH_2N{=}CH(2\text{-}OHPh)$ and absorption bands typical of a $SiCH_2CH_2CH_2N{=}CH(2\text{-}OHPh)$ moiety. Also, the ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectroscopy showed the expected peaks and areas for both the organic and polyoxometalate moieties. Importantly, the ^{183}W NMR exhibited six peaks with relative intensities of 2:2:1:2:2:2 characteristic of the C_s symmetry of the polyoxometalate unit. Furthermore, the two ^2J(W−Si) couplings that were observed in the ^{183}W NMR spectrum clearly show the incorporation of the functionalized silane into the lacunary Keggin polyoxometalate. Finally, the salen−POM compounds were metalated by typical metalation procedures to yield the desired metallosalen−POM complexes.

The first indication of the effect of the polyoxometalate as an electron acceptor moiety on the salen group was observed in the measurement of the ^{1}H NMR of the salen−POM compound. Thus, in Figure 1 the ^{1}H chemical shifts of the salen−POM compound are compared with the ^{1}H chemical shifts of the nonmodified salen. Assignment of the chemical shifts was by ^{13}C−^{1}H correlation spectra. Noticeably, there was practically no change in the chemical shift at the alkyl bridging moiety, i.e., the shifts for H_a and $H_{a'}$ were similar. However, there is a consistent downfield shift of between 0.2 and 0.42 ppm in all the aromatic (including conjugated CH=N) hydrogen atoms of the POM modified

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(5) High dilution is necessary to prevent immediate precipitation or salt formation when $K_8SiW_{11}O_{39}$ is contacted with $RSi(OEt)_3$ (R = $CH_2CH_2CH_2NH_2 \cdot HCl$).

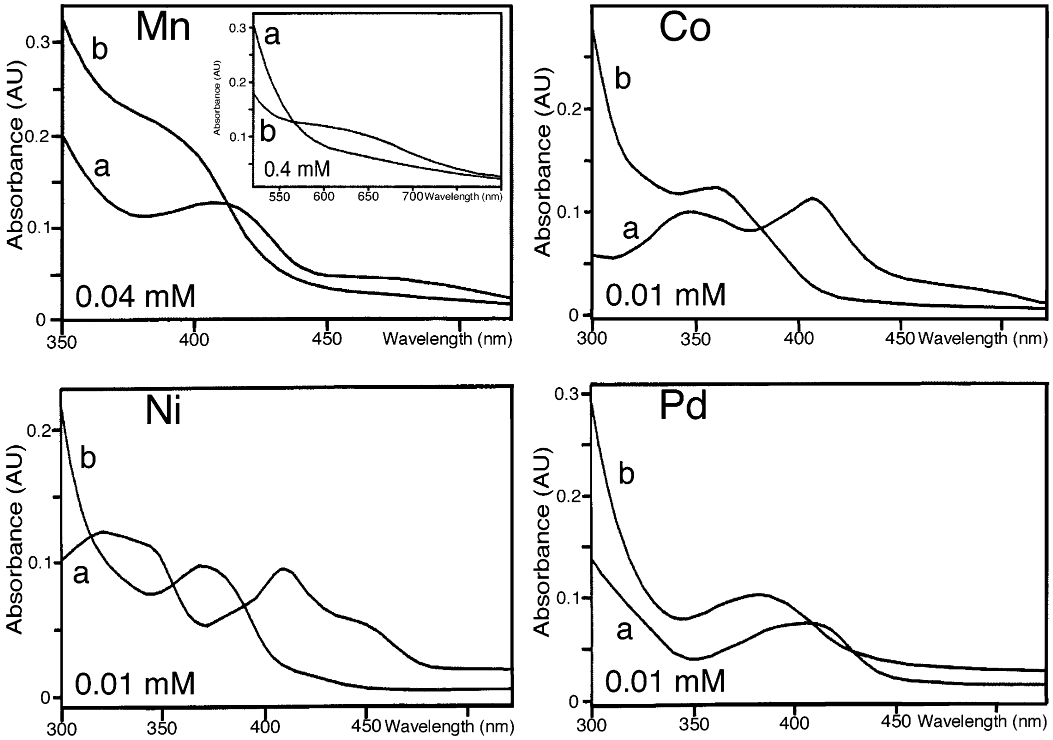

Figure 2. UV−vis spectra of (a) the metallosalen compounds plus $Q_8SiW_{11}O_{39}$ in acetonitrile and (b) the metallosalen−POM hybrid compounds in acetonitrile. (a) Mn: λ_{max} = 410 nm (ϵ = 3750 M^{-1} cm^{-1}). Co: λ_{max} = 348 nm (ϵ = 10000 M^{-1} cm^{-1}), λ_{max} = 408 nm (ϵ =11100 M^{-1} cm^{-1}). Ni: λ_{max} = 322 nm (ϵ = 12300 M^{-1} cm^{-1}), λ_{max} = 410 nm (ϵ = 9400 M^{-1} cm^{-1}). Pd: λ_{max} = 408 nm (ϵ = 7300 M^{-1} cm^{-1}). (b) Mn: λ_{max} (sh) = 390 nm (ϵ = 6250 M^{-1} cm^{-1}), λ_{max} = 600−650 nm (ϵ = 325 M^{-1} cm^{-1}). Co: λ_{max} =358 nm (ϵ = 12200 M^{-1} cm^{-1}). Ni: λ_{max} = 370 nm (ϵ = 9600 M^{-1} cm^{-1}). Pd: λ_{max} = 382 nm (ϵ = 10100 M^{-1} cm^{-1}).

compound versus the nonmodified salen. This indicates a significant electron-withdrawing effect through a relatively large distance between the polyoxometalate and the salen ligand. Importantly, addition of varying amounts of the lacunary polyoxometalate, $[SiW_{11}O_{39}]^{8-}$, had no effect on the NMR spectrum of the salen−POM compound.

UV−Visible Spectroscopy. Initial evidence of the electronic effect of the polyoxometalate on the metallosalen was observed in the UV−vis spectra, Figure 2. Normally, metalation of salen ligands with $M^{II}(OAc)_2$ yields the corresponding M = Mn(III), Co(II), Ni(II), and Pd(II) salen compounds that can be identified by their distinctive UV−vis spectra (curves a) and colors (brown, dark red, light brown, and yellow, respectively).[6] Addition of the $[SiW_{11}O_{39}]^{8-}$ or $\{SiW_{11}O_{39}[O(SiR)_2]\}^{4-}$ polyoxometalate compounds leaves the metallosalen spectra unchanged with only superposition of the polyoxometalate spectrum (not shown), λ_{max} = 265 nm (ϵ = 62500 M^{-1} cm^{-1}). There is no intermolecular effect of the POM on the metallosalen. Significantly, however, the hybrid metallosalen−POM compounds have different UV−vis spectra (curves b) and colors (green, pale brown, light green, and pale brown, respectively). These spectra all show hypsochromic shifts for the peaks associated with the d−d transitions and are typical for those that have been reported for oxidized metallosalen species, that is, Mn(IV)−salen,[7] Co(III)−salen,[6b] and Ni(II)−salen cation radical compounds.[8] Notably these oxidized species have been previously formed only after application of oxidizing agents or conditions. Oxidized Pd−salen has not yet been reported although other Pd(III) compounds such as Pd(III)-bis(1,4,7-triazacyclononanone) showed a blue-shifted visible spectrum compared to the Pd(II) analogues.[9]

Magnetic Spectroscopy. Additional understanding on the electronic state of the metallosalen moiety in the M−salen−POM hybrid compound was sought, especially in light of the indication from the UV−vis spectra that stable oxidized metallosalen species were obtained when an electron-accepting polyoxometalate was attached to a metallosalen via a three-carbon alkyl spacer. $Mn^{III}Cl$ salen with a high-spin d^4 configuration and Co(II) salen with a d^7 square planar configuration are expected to be paramagnetic species. Indeed, their ^1H NMR spectra showed severely broadened peaks. Similarly the Mn−salen−POM and Co−salen−POM compounds rendered very poorly defined ^1H NMR spectra associated with paramagnetic species. On the other hand Ni(II) and Pd(II)−salen compounds as d^8 species in a square planar configuration are expected to be diamagnetic. Therefore, the nonmodified Ni(II)−salen and Pd(II)−salen compounds have clean, straightforward ^1H NMR spectra shifted

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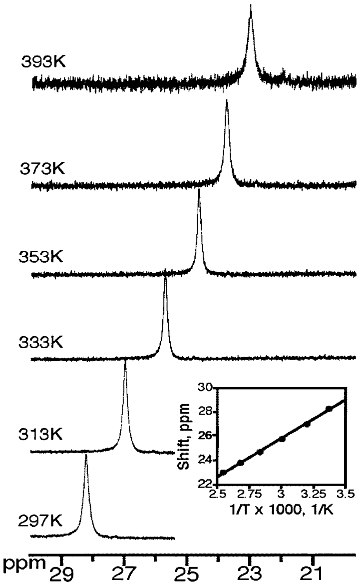

Figure 3. The ^{1}H NMR spectrum of Ni−salen−POM (imine hydrogen) as a function of temperature.

upfield relative to the nonmetalated salen as expected.[10] On the other hand, the ^{1}H NMR spectra of Ni−salen−POM and Pd−salen−POM compounds were both highly broadened and considerably less defined in the aromatic region (6−11 ppm), indicating the existence of a paramagnetic species in both cases. The broadening of the peaks made the assignment of the spectra impossible. Despite this broadening, for Ni−salen−POM a highly downfield shifted peak at 28.3 ppm attributable to the imine hydrogen atom could be observed. This chemical shift was concentration independent. A multitemperature experiment, Figure 3, shows a clean isotropic upfield shift with increasing temperature, correlating well with a Curie type relationship.

For Pd−salen−POM the imine hydrogen was located at 12.1 ppm. In this case, however, the peak broadened with increasing temperature and no isotropic shift was observed. It may be concluded that both the Ni−salen−POM and Pd−salen−POM compounds are paramagnetic compounds with oxidized metallosalen centers; however, for Ni−salen−POM, there is a fast relaxation of the unpaired electron, but for the Pd−salen−POM, there is a slower relaxation. As might have been expected for paramagnetic compounds with fast relaxation, no EPR spectrum was observed for the Ni−salen−POM compound. On the other hand, for the Pd−salen−POM compound as a solid an anisotropic EPR spectrum[9a] was observed with $g_1 = 2.016$, $g_2 = 2.001$, and $g_3 = 1.991$, Figure 4. The slight shoulder at the high-field side is attributable to an impurity from the cavity.

No hyperfine splitting for coupling to ^{105}Pd ($I = {}^5/_2$, 22% abundance) was observed. The position and the anisotropy of the EPR peak indicates that the spectrum cannot be associated with a pure salen ligand cation radical species that would be expected to have an isotropic peak at $g =$ 2.0023. Furthermore, for a purely Pd(III) d^7 complex in a square planar environment, the expected electron configuration is low spin with the single electron occupying the $d_{x^2-y^2}$ orbital. Again, an isotropic EPR spectrum would have been expected.[9a,b] Thus, the anisotropic spectrum for Pd−salen−POM can be explained either by significant departure from a square planar environment for the Pd−salen−POM compound defined as Pd(III)−salen−POM or by electron delocalization within Pd−salen−POM with contributions from both "Pd(III)" and "salen cation radical" species. The concentration of the EPR generating species was not estimated from the spectrum, but the UV−vis spectra would indicate a rather pure compound distinct from the usual Pd(II)−salen.

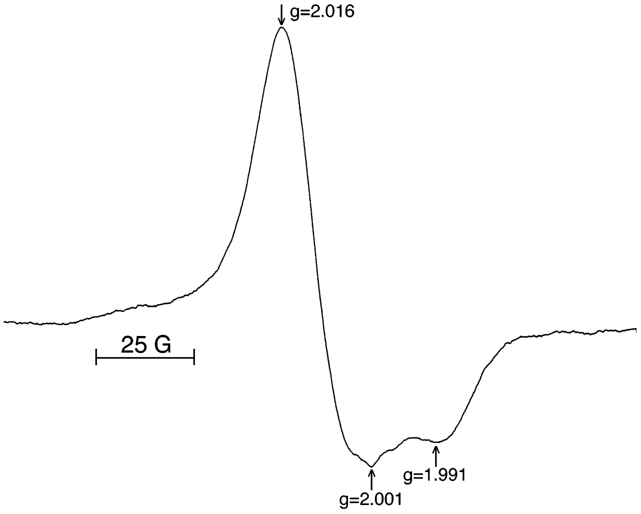

Figure 4. EPR spectrum of solid Pd−salen−POM at 240 K.

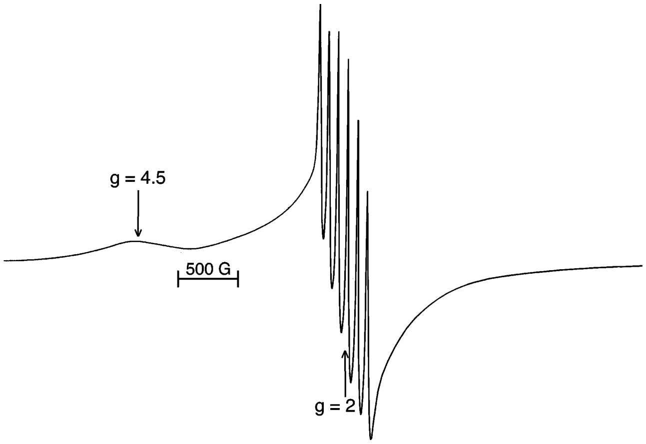

Figure 5. EPR spectrum of solid Mn−salen−POM at 120 K.

Mn(III)−salen compounds are known to be EPR silent in the normal X-band mode but absorb at $g = 8$ in the high-field EPR spectrometers.[7,11] However, the Mn−salen−POM compound is EPR active at the X-band frequency and has a spectrum as presented in Figure 5. The spectrum shown is of a solid compound, but essentially the same spectrum was observed in DMF and DMSO (∼0.1 M). The spectrum shows a major feature (∼95%) at $g = 2$ with a six-line hyperfine

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[10] Ni: δ 7.88 (s, 2H); δ 7.26 (d, 2H); δ 7.15 (t, 2H); δ 6.69 (d, 2H); δ 6.48 (t, 2H); δ 3.41 (s, 4H). Pd: δ 8.19 (s, 2H); δ 7.38 (d, 2H); δ 7.26 (t, 2H); δ 6.83 (d, 2H); δ 6.52 (t, 2H); δ 3.83 (s, 4H).

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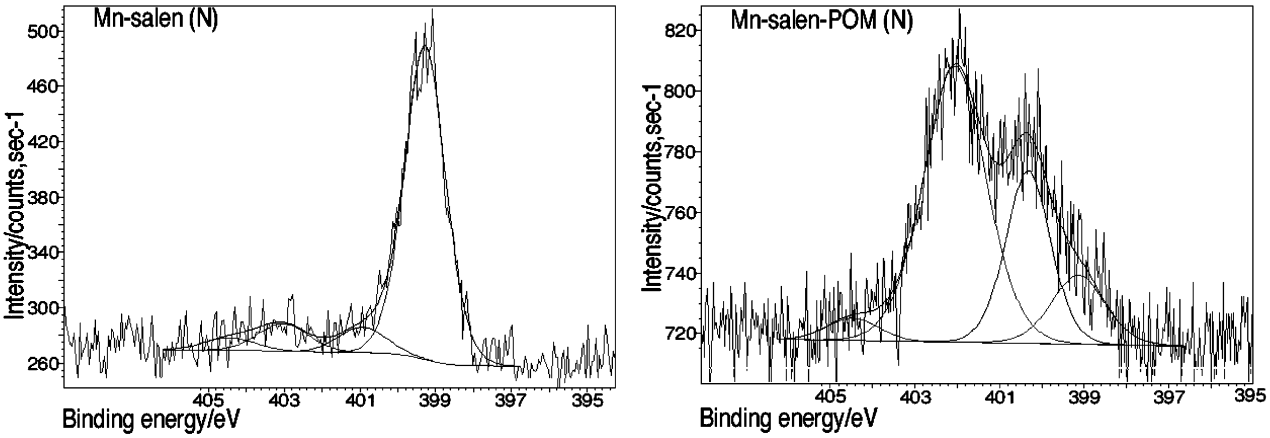

Figure 6. The XPS N (1s) line for Mn–salen and Mn–salen–POM. Solid lines are curve fits of data.

coupling, $A = 81$ G, as may be expected for manganese species ($I = {}^5/_2$) and a minor feature (~5%) at $g = 4.5$. The literature on the EPR spectra of oxidized Mn(IV)salen compounds is inconclusive with both peaks at $g = 2$ and $g = {\sim}4$ of varying relative intensities being reported as associated with Mn(IV) species.[7,12] One practical explanation that has been put forth for the various results is that different *D* (axial) and *E/D* (rhombic) zero-field-splitting parameters, obtained by computer simulation, are possible for different Mn–salen species leading to different EPR spectra.[12b] Room temperature spectra showed the same features albeit at lower intensity.

In order to gain more information on the oxidation state of the Mn–salen–POM compound, we carried out room temperature magnetic susceptibility measurements. For Mn–salen–POM we measured an experimental molar susceptibility (χ_m) of 8.514×10^{-3} (cgs units). This value was corrected by measuring the diamagnetic susceptibility (χ_{dia}) of the metal-free salen–POM compound, $\chi_{dia} = -1.023 \times 10^{-3}$. The paramagnetic susceptibility (χ_{para}) was therefore 9.537×10^{-3}. The effective magnetic moment (μ_{eff}) from $\mu_{eff} = 2.828(\chi_{para}T)^{1/2}$ was computed to give a value of 4.8 μ_B. Assuming that only the spin angular momentum contributes to the paramagnetism, the Mn–salen–POM species could be defined as an $S = 2$ (Mn(III), d^3) system. The EPR and magnetic moment measurements are apparently conflicting although the accuracy of the latter is lower both experimentally and due to the "spin-only" assumption.

As will be noted below, vide infra, further X-ray photoelectron spectroscopy measurements strongly argue for the formulation of the Mn–salen–POM compound as mostly a Mn(III)–salen cation radical species rather than Mn(IV)–salen species. Mn(III) cation radical species have not yet been reported for manganese salen compounds; however, several structurally similar Mn(III)–porphyrin cation radical species have been clearly identified.[13] For Mn(III)–porphyrin cation radicals, magnetic moments ranging from 3.9 to 5.7 μ_B and EPR peaks at $g = 2$ and/or 4 (also some species were EPR silent) have been reported depending on the temperature, the identity of the porphyrin macrocycle, and the axial ligands or symmetry at the manganese center. Most notable in his respect is the finding that $(\text{tpp}^{\bullet+})\text{Mn}^{\text{III}}(\text{Cl})(\text{ClO}_4)$ (tpp = tetraphenylporphyrin) also gave a $\mu_{eff} = 4.7$ μ_B and a $g = 2$ EPR signal.[13c] Both the previous $(\text{tpp}^{\bullet+})\text{Mn}^{\text{III}}(\text{Cl})(\text{ClO}_4)$[13c] and the present Mn–salen–POM are structurally similar with a planar macrocyclic ligand and asymmetry in the axial positions. As noted above, the magnitude of the *D* and *E* zero field splitting parameters may be used to explain the EPR spectra. An alternative explanation has also been put forward,[13e] whereby the peak at $g = 2$ reminiscent of a Mn(II) species[14] may be explained by the existence of a Mn(III)–salen cation radical species or the definition of the Mn–salen–POM compound as such wherein the Mn(III) center and the unpaired electron on the salen ligand could be ferromagnetically coupled. In the case of the porphyrin cation radical, the *ungerade* character of the a_{2u} orbital of the macrocycle prevents orbital overlap with the *gerade* d orbitals of the metal.[13e]

X-ray Photoelectron Spectroscopy. XPS was used to directly probe the oxidation states in the solid state of the various elements in the M–salen and M–salen–POM compounds, Figure 6 and Table 1.

Looking first at the metal centers we observed that the binding energies of Mn and Pd were similar for both the M–salen and the M–salen–POM compounds, Table 1 and Figures S1 and S2, although for Mn–salen–POM there was some evidence for the presence of some oxidized manganese centers. On the other hand, for cobalt there was a noticeable increase in the binding energy, 1.3–2.0 eV, in the binding energy of cobalt in Co–salen–POM compared to Co–salen, Table 1 and Figure S3. Apparently, in Co–salen–POM a Co^{3+} moiety can be concluded to partially exist versus a Co^{2+} state in Co–salen. A similar situation was observed for nickel

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Table 1. Corrected Binding Energies (eV) for M$-$Salen and M$-$Salen$-$POM Compounds

	M$-$salen	M$-$salen$-$POM
	Manganese	
Mn 2p	641.7, 643.1	641.5, 643.0
N 1s	399.3	99.3, 400.3, 402.1
3Cl 2p 3/2	197.6	199.0
	Cobalt	
Co 2p 3/2	780.5, 785.9, 795.7	781.8, 787.9, 797.2
N 1s	399.5	399.5, 400.5, 402.3
	Nickel	
Ni 2p 3/2	855.1	856.,0 864.3 (weak)
N 1s	399.5	399.5, 400.5, 402.1
	Palladium	
Pd 3d	338.0, 343.1	337.9, 342.9
N 1s	399.4	399.4, 400.7, 401.9

analogues whereby there was a shift of 0.9 eV and the appearance of a new peak at 864.3 eV indicative of the presence of a Ni^{3+} oxidation state in Ni$-$salen$-$POM.[15] The nitrogen N 1s line, for example Figure 6, shows pronounced changes for all the M$-$salen$-$POM compounds. A new peak at 400.0$-$400.7 eV in the M$-$salen$-$POM compounds supplements the peak at 399.3$-$399.5 eV attributable to the imine nitrogen atom in the M$-$salen compounds. Additional peaks at 401.9$-$402.3 eV are associated with the quaternary ammonium cation;[15] these binding energies are the same as those observed for the tetrahexylammonium salt of $SiW_{11}O_{39}{}^{8-}$ that served as a control. The new peaks at 400.0$-$400.7 eV, shifted significantly by 1.0$-$1.3 eV versus the original imine, 399.3$-$399.5 eV, clearly indicate a more oxidized salen ligand. Note that with all other O and C atoms in the M$-$salen species, the ligand O and C atoms are more difficult to follow due to the O and C atoms in the POM and quaternary ammonium residue. Notably in the Mn$-$salen case there is also a chloride axial ligand, and indeed the Cl 2p 3/2 line shifts by $\sim$1.4 eV from 197.6 eV in Mn$-$salen to 199.0 eV in Mn$-$salen$-$POM. This shift, slightly larger than that of the nitrogen atom, strongly indicates a more positively charged chloride axial ligand in Mn$-$salen$-$POM versus Mn$-$salen. Such changes of the charge on the chloride axial ligand occurring upon oxidation of Mn(III)$-$salen species have been previously noted.[12b]

Cyclic Voltammetry. The importance of the intramolecular interaction between the metallosalen and polyoxometalate components in the hybrid compounds can also be gauged by cyclic voltammetry measurements. For example, the simple Mn(III)$-$salen compound has a reduction wave, Mn(III/II), at -0.45 V versus SCE[16] that was unaffected by the addition of the tetrahexylammonium salt of $[SiW_{11}O_{39}]^{8-}$, or $\{SiW_{11}O_{39}[O(SiR)_2]\}^{4-}$, Figure 7 left top (0.5 M Bu_4NBF_4, 0.5 mM Mn$-$Salen, 0.5 mM $Q_5H_3[SiW_{11}O_{39}]$ in DMF). However, for the Mn$-$salen$-$POM compound, Figure 7 left bottom, no reduction wave was observable. A similar situation is easily observed for the nickel-based compounds. For the simple Ni(II)$-$salen compound, a Ni(II/III) oxidation wave at 0.82 V versus SCE[17] was unaffected by the addition of the tetrahexylammonium salt of $[SiW_{11}O_{39}]^{8-}$ or $\{SiW_{11}O_{39}[O(SiR)_2]\}^{4-}$, Figure 7 right top (0.5 M Bu_4NBF_4, 0.5 mM Ni$-$salen, 0.5 mM $Q_5H_3[SiW_{11}O_{39}]$ in DMF). However, for the Ni$-$salen$-$POM compound, Figure 7 right bottom, no oxidation wave was observable.

Essentially identical results were observed (not shown) using a platinum working electrode and for the cobalt and palladium analogues, although in the latter cases there were weak irreversible oxidation waves in the CV measurements for Co(II)$-$salen and Pd(II)$-$salen. From the cyclic voltammetry measurements it would appear as well that there is a change in the oxidation state of the metallosalen moiety upon attachment of the polyoxometalate and not simply a change in the oxidation$-$reduction potential that would have led to the observation of a CV wave at a different potential.

Summary. From the UV$-$vis, ^{1}H NMR, EPR, XPS, and cyclic voltammetry measurements described above it is apparent that the attachment of the $[SiW_{11}O_{39}]^{8-}$ polyoxometalate moiety, via an alkylene ($CH_2CH_2CH_2$) bridge to the metallosalen center, leads to the formation of an oxidized metallosalen unit. This is a purely intramolecular phenomenon since addition of $Q_5H_3[SiW_{11}O_{39}]$ or $Q_4\{SiW_{11}O_{39}[O(SiR)_2]\}$ to metallosalen compounds showed no effect on the spectral or redox properties of the metallosalen compounds. The exact formulation of the oxidized metallosalen group depends very much on the identity of the transition metal. (a) The metallosalen center can be described as a metal$-$salen cation radical species; that is, a localized "hole" is formed on the salen ligand. Especially the EPR and XPS data seem to indicate that this is the best description for the Mn$-$salen$-$POM compound now best formulated as Mn(III)$-$salen$^{+\bullet}$ $-$ POM. (b) The metallosalen center can be described as an oxidized metal$-$salen species, with oxidation localized at the metal center. (c) The metallosalen center can be described as a hybrid of a metal$-$salen cation radical species and an oxidized metal$-$salen species; that is, a delocalized "hole" is formed at the metallosalen center. Especially the XPS and EPR (for Pd) measurements would indicate that this is the case for M$-$salen$-$POM compounds with M = Co, Ni, and Pd as these show properties indicating oxidation of both the salen ligand and the transition metal. It is also interesting discuss the nature of the polyoxometalate$-$metallosalen interaction within the intramolecular complexes. One view would be that the M$-$salen$-$POM compounds exit simply as oxidized metallosalen centers in the presence of the polyoxometalate moiety. However, the observation that addition of the polyoxometalate to a solution of M$-$salen leaves the M$-$salen compounds unchanged, that is, there is no intermolecular stabilization of oxidized M$-$salen species, leads us to suggest that the hybrid M$-$salen$-$POM compounds are best described as charge transfer complexes (metallosalen electron donor$-$polyoxometalate electron acceptor). These proposed charge transfer complexes are formed across the relatively large bond

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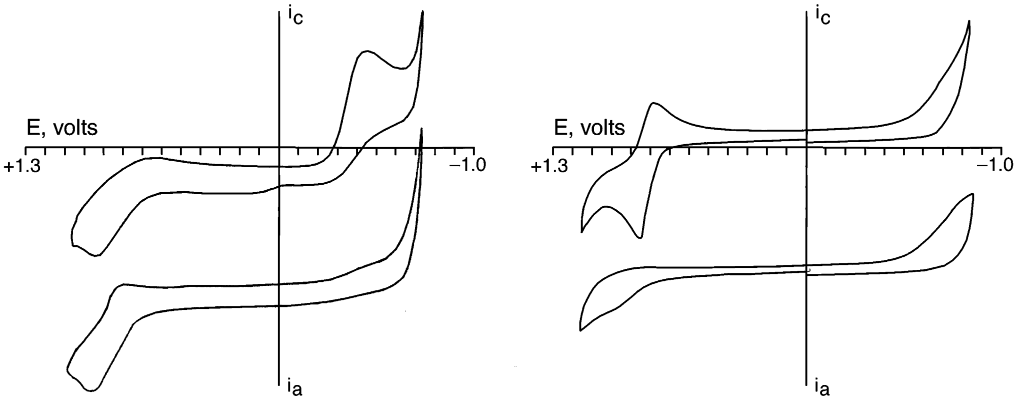

Figure 7. Cyclic voltammograms of M−salen and M−salen−POM compounds. Top left: Mn(III)salen + $Q_5H_3SiW_{11}O_{39}$. Bottom left: Mn−salen−POM. Top right: Ni(II)salen + $Q_5H_3SiW_{11}O_{39}$. Bottom right: Ni−salen−POM.

distance (three-carbon alkyl spacer) separating the metallosalen moiety and the polyoxometalate. Presumably, the interaction between the polyoxometalate and the metallosalen groups is through space. There is no spectroscopic manifestation, notably UV−vis and EPR, of the presence of electron in the polyoxometalate acceptor. Thus, it would appear that the charge transfer is such that the negative charge is delocalized over the complexes, as there is *no* direct evidence of a specific reduced polyoxometalate species. The concept presented in this research will be further developed toward stabilization of high-valent metal−oxo species and toward catalytic applications of M−salen−POM compounds.

Experimental Section

Instrumentation and Techniques of Measurement. The ^1H NMR (400 MHz), ^{13}C NMR (100.613 MHz), ^{29}Si NMR (79.495 MHz), and ^{183}W NMR (16.671 MHz) spectra were measured on a Bruker Avance 400 spectrometer in $CDCl_3$ or DMSO-d_6. The chemical shifts are reported with tetramethylsilane as reference for ^1H NMR, ^{13}C NMR, and ^{29}Si NMR, and 1 M Na_2WO_4 in D_2O as external reference for ^{183}W NMR. The IR spectra were measured on a Nicolet Protegé 460 FTIR; liquid samples were deposited on a KBr disk, and solid samples were prepared ~3−5 wt % as KBr-based pellets. UV−vis spectra were measured in 1 cm quartz cuvettes on a HP8452A diode array spectrometer using spectrophotometric grade acetonitrile as solvent at the conditions given in the caption of Figure 2. The EPR spectra were recorded on a Bruker ER200D-SRC spectrometer (X-band). Samples were placed in a 2 mm quartz tube, and spectra were recorded using microwave frequency 9.52 GHz, microwave power 20 mW, field modulation 3.2 G, receiver gain 5×10^3, time constant 320 ms, and scan time 200 s. The Pd−salen−POM and Mn−salen−POM EPR spectra were measured using solid samples at temperatures varying between 110 and 296 K. The spectra were unchanged in this range, although they were more intense at lower temperatures.

XPS measurements were performed on solid, carefully dried (high vacuum) samples on a Kratos AXIS-HS instrument, using a monochromatized Al Kα source at 75 W (15 kV, 5 mA), and detection pass energies of 20−80 eV. Base pressure at the analysis chamber was $(1-2) \times 10^{-9}$ Torr. An electron flood-gun was used for compensation of extra positive charge. Short and quick scans were always taken first at each fresh spot, followed by repetitive longer scans, in order to account for irreversible beam-induced damage, occurring on a time scale of several hours. These effects, particularly complicating the determination of the metal oxidation state, have limited us in attempting low-noise yet damage-free signals. Yet, the evolution of damage was clear enough to extrapolate our interpretation backward to the damage-free situation. Data processing involved Shirley background subtraction (except for signals superimposed on very sloppy background). Curve fitting was attempted using Gaussian−Lorentzian line shapes, their composition varied according to the detection pass energy (namely, according to the relative contribution of instrumental broadening).

Magnetic susceptibility measurements (Sherwood Scientific MSB-1) using the Evans method were made on solid samples at room temperature. An average from three measurements was taken. The diamagnetic correction was made my measuring the diamagnetic susceptibility (χ_{dia}) of the metal-free salen−POM compound. Cyclic voltammetry measurements were taken from a BAS CV-1B voltammeter using a glassy carbon working electrode, an Ag/AgCl reference electrode, and a Pt auxiliary electrode. Measurements were carried out on 5 mM solutions in DMF with 0.5 M tetrabutylammonium tetrafluoroborate as electrolyte. Scan rates were 100 mV/s at $I/V = 500$ μA/V.

Materials and Synthesis. Commercial reagents (Aldrich, Fluka, Strem) used were of the highest available purity. The known M−salen compounds were prepared according to the known literature procedures.[18] The potassium salt of the lacunary Keggin polyoxometalate, $K_8SiW_{11}O_{39}$, was synthesized by the procedure described by Tézé and Hervé.[19] The tetrahexylammonium ($Q = (n\text{-hexyl})_4N^+$) salt of $\{SiW_{11}O_{39}[O(SiR)_2]\}^{4-}$ where $R = CH_2CH_2CH_2NH_2 \cdot HCl$ was synthesized using a modified procedure previously described as follows:[4b] A diluted and neutralized aqueous solution (pH = 7) of 3 mL of 3-aminopropyltriethoxysilane (13 mmol) was added slowly to a well-stirred solution of 4 g (1.34 mmol) of $K_8SiW_{11}O_{39}$ in 1.2 L of deionized water. When the solution cleared, the pH was adjusted to pH = 1 by addition of a 1 M HCl solution. The solution was vigorously stirred for 24 h. A white sticky precipitate of undesired organosilicate oligomers, $(RSiO_{1.5})_n$, was removed by filtration, and 6 g (14 mmol) of tetrahexylammonium bromide was added to the filtrate. The precipitate was collected and washed with 200 mL of deionized water, 200 mL of 2-propanol, and 200 mL of diethyl ether before drying in a desiccator. The yield was 4.7 g (82% yield). IR (cm^{-1}): 390 (ν_{sym}WOW), 534 (ν_{sym}WOW), 710 (ν_{asym}WOW), 750 (ν_{asym}WOW), 798 (ν_{asym}WOW), 851 (ν_{asym}WOW), 880 (ν_{asym}WOW), 909 (ν_{asym}W=O), 949 (ν_{asym}W=O), 969 (ν_{sym}W=O), 1044 (ν_{asym}Si−O−Si), 1150 (C−N), 1230 (Si−C), 1484 (C−H), 2940 (C−H), 3241 (N−H), 3449 (N−H). ^1H NMR at 400 MHz (DMSO-d_6): δ

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0.62 (t, 4H, $SiCH_2$), δ 0.85 (t, 48H, CH_3), δ 1.26 (m, 96H, $CH_2CH_2CH_2$), δ 1.54 (m, 32H, CH_2), δ 1.74 (m, 4H, $CH_2CH_2NH_2$), δ 2.86 (t, 4H, CH_2NH_2), δ 3.14 (t, 32H, CH_2N^+). ^{29}Si NMR at 79.495 MHz {^{1}H}-decoupled (DMSO-d_6): δ −53.3 (2Si) (for the alkylsilyl groups), δ −85.0 (1Si) (for the polyoxometalate silicon).

The tetrahexylammonium salt of the POM−salen compound $\{SiW_{11}O_{39}[O(SiR'_2)]\}^{4-}$ (R′ = $CH_2CH_2CH_2N{=}CH(2\text{-}OHPh)$ was synthesized by dissolving 0.9 g (0.21 mmol) of $Q_4\{SiW_{11}O_{39}[O(SiR)_2]\}$ in 3 mL of salicylaldehyde. Trimethylorthoformate (8 mL) was added as drying agent, and the mixture was stirred overnight at 25 °C. During the reaction a yellow precipitate (product) was formed, collected by filtration, and washed with dry ether several times. The yield was 0.92 g (90%). IR (cm^{-1}): 390 (ν_{sym}WOW), 533 (ν_{sym}WOW), 710 (ν_{asym}WOW), 750 (ν_{asym}WOW), 802 (ν_{asym}WOW), 855(ν_{asym}WOW), 884 (ν_{asym}WOW), 920 (ν_{asym}W=O), 949 (ν_{asym}W=O), 967 (ν_{asym}W=O), 1045 (ν_{asym}Si−O−Si), 1152 (C−N), 1277 (Si−C), 1384, 1466, 1484 (C−H), 1610, 1630 (C=N), 2873 (C−H), 2934 (C−H), 2961 (C−H). ^{1}H NMR at 400 MHz (DMSO-d_6): δ 0.65 (t, 4H, $SiCH_2$), δ 0.86 (t, 48H, CH_3), δ 1.27 (m, 96H, $CH_2CH_2CH_2$), δ 1.55 (m, 32H, CH_2), δ 2.01 (m, 4H, CH_2CH_2N), δ 3.15 (t, 32H, CH_2N^+) δ 3.93 (t, 4H, $CH_2N{=}$), δ 7.06 (t, 2H, *p*-Ar−OH), δ 7.09 (d, 2H, *o*-Ar−OH), δ 7.68 (t, 2H, *p*-Ar−CN), δ 7.74 (d, 2H, *o*-Ar−CN), δ 8.99 (s, 2H, CHAr), δ 12.10 (s, 2H, OH). ^{29}Si NMR at 79.495 MHz {^{1}H}-decoupled (DMSO-d_6): δ −53.1 (s, 2Si), δ −85.0 (s, 1Si). ^{13}C NMR at 100.613 MHz (DMSO-d_6) (ppm): 9.36, 13.61, 20.96, 21.85, 23.02, 25.39, 30.57, 54.93, 57.62, 114.19, 116.92, 120.11, 134.69, 138.89, 161.30, 167.96. ^{183}W NMR at 16.671 MHz (DMSO-d_6) (ppm): −91.7 [2], −106.7 [2, ^2J(W−Si) = 23.8 Hz], −111.3 [1], −124.8 [2, ^2J(W−Si) = 28.5 Hz], −172.4 [2], −248.1 [2].

The M−salen−POM compounds were prepared by metalation of the salen−POM precursors, $Q_4\{SiW_{11}O_{39}[O(SiR'_2)]\}$, with metal acetate salts, $M(OAc)_2{\cdot}nH_2O$. Mn−salen−POM: 1.5 g (0.32 mmol) of $Q_4\{SiW_{11}O_{39}[O(SiR'_2)]\}$ and 0.15 g (0.64 mmol) of $Mn(OAc)_2{\cdot}4H_2O$ were dissolved in 5 mL of DMF. The solution was heated at 105 °C under Ar for 1 h with vigorous stirring and then stirred under air for another 1.5 h. Saturated aqueous NaCl, 3 mL, was added dropwise, heating and stirring were discontinued, the reaction mixture was cooled to 5−10 °C, and then 10 mL of water was added while the solution was maintained at 5−10 °C. The precipitate that formed was filtered and washed with warm (50 °C) water and then with ether. The crude green product was dissolved in acetonitrile and filtered, and the solvent was evaporated. A green product, 1.46 g (95% yield), was obtained. Note that for Mn−salen compounds metalation of the salen moiety with manganese(II) acetate always leads to a Mn(III) species.[6a] Co−salen−POM: 1.5 g (0.32 mmol) of $Q_4\{SiW_{11}O_{39}[O(SiR'_2)]\}$ was dissolved in degassed DMF (5 mL) and heated to 70 °C under argon with stirring. A solution of 80 mg (0.32 mmol) of cobalt acetate tetrahydrate in DMF was added, and the reactants were maintained at 70 °C for an additional 45 min before being cooled to 25 °C. Methanol (30 mL) was added, and the precipitate was filtered and washed thoroughly with methanol and ether before vacuum drying. A pale brown product, 1.48 g (95%), was obtained. Ni−salen−POM: 1.5 g (0.32 mmol) of $Q_4\{SiW_{11}O_{39}[O(SiR'_2)]\}$ was dissolved in degassed DMF (5 mL) and heated to 70 °C under argon with stirring. A solution of 80 mg (0.32 mmol) of nickel acetate tetrahydrate in DMF was added, and the reactants were maintained at 70 °C for an additional 45 min before being cooled to 25 °C. Methanol (30 mL) was added, and the precipitate was filtered and washed thoroughly with methanol and ether before vacuum drying. A brown product, 1.30 g (94%), was obtained. Pd−salen−POM: 1.5 g (0.32 mmol) of $Q_4\{SiW_{11}O_{39}[O(SiR'_2)]\}$ was dissolved in degassed DMF (5 mL) and heated to 70 °C under argon with stirring. A solution of 72 mg (0.32 mmol) of palladium acetate was added, and the reactants were maintained at 70 °C for an additional 45 min before being cooled to 25 °C. Methanol (30 mL) was added, and the precipitate was filtered and washed thoroughly with methanol and ether before vacuum drying. A pale brown product, 1.52 g (96%), was obtained.

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Supporting Information Available: Figures showing the XPS data for the metal binding energies for Mn−salen−POM, Pd−salen−POM, and Co−salen−POM. This material is available free of charge via the Internet at http://pubs.acs.org.

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