CHEMISTRY
A European Journal

A Journal of
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Accepted Article

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To be cited as: *Chem. Eur. J.* 10.1002/chem.201703394

Link to VoR: http://dx.doi.org/10.1002/chem.201703394

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Aza vs. Oxophilicity of SmI_2: A Break of a Paradigm

Sandeepan Maity,[a,b] Robert A. Flowers II*[a] and Shmaryahu Hoz*[b]

Abstract: Ligands that coordinate to SmI_2 through oxygen are prevalent in the literature and make up a significant portion of additives employed with the reagent to perform reactions of great synthetic importance. In the present work a series of spectroscopic, calorimetric and kinetic studies demonstrate that nitrogen-based analogs of many common additives have a significantly higher affinity for Sm than the oxygen-based counterparts. In addition, electrochemical experiments show that nitrogen-based ligands significantly enhance the reducing power of SmI_2. Overall, this work demonstrates that the use of nitrogen-based ligands provides a useful alternative approach to enhance the reactivity of reductants based on Sm(II).

Introduction

The most important advantage of samarium diiodide (SmI_2) as a reducing agent is its versatility in a wide range of reductions and bond-forming reactions that proceed through electron transfer.[1] One of the unique features of the reagent is that its reactivity is controlled by additives that act as ligands.[2] In nearly every instance, ligands accelerate or alter the reactivity of SmI_2 through the interaction of an oxygen atom on the additive (ligand).[2, 3] Although nearly forty years have elapsed since SmI_2 was introduced into organic chemistry, three recent reviews concerning additives used in its reactions, describe only oxygen, but not nitrogen based ligands as additives in reactions.[2, 1k] A great deal of the success in using additives that coordinate to Sm through interaction with oxygen has been proposed to be a consequence of the oxophilicity of Sm(II).[4, 3h, 3i, 3j, 3k] As a consequence, nitrogen based ligands are only sporadically described in the literature.[5] One of the classical example of nitrogen based ligand is sodium or potassium salt of bis (trimethylsilyl) amide which forms strong complex with Sm(II) resulting in thermodynamically stronger reductant.[5b]

In the present paper, we show that in contrast to the aforementioned literature precedent, SmI_2 is significantly more azaphilic than oxophilic and consequently aza ligands are much more effective than the oxygen ligands in enhancing the reducing power of the reagent. The work described herein presents studies on mono as well as bidentate ligands having the general structure of glycols (henceforth referred to as G-ligands). Several diagnostic tools including: a) spectral analyses, b) ligand competition experiments, c) isothermal titration calorimetry and d) cyclic voltammetry are used to demonstrate the high affinity of nitrogen-based ligands for Sm(II).

Results and Discussion

The most straightforward approach to examine coordination of ligands to SmI_2 is visible spectroscopy and this technique is also the fastest and most straightforward tool to apply. In general, spectral changes of the two broad absorptions at 600 nm provide a clear indication of ligand complexation to the SmI_2.[2] Previous work on ligands that coordinate through oxygen (HMPA, MeOH, H_2O) display a broadening or merging of the absorptions at 600 nm.[6] Typically, the visible spectrum of higher affinity ligands displays a broadening of the absorptions at a much lower additive: SmI_2 ratio than lower affinity ligands. Recent work in our groups has provided evidence that amines and other nitrogen-based ligands may have higher affinities than originally indicated from previous studies in the literature.[7] To initially examine the affinity of an amine, we chose n-$BuNH_2$ as a test ligand. Figure 1 shows the results of increasing concentrations of n-$BuNH_2$ on the visible spectrum of 2 mM solution of SmI_2.

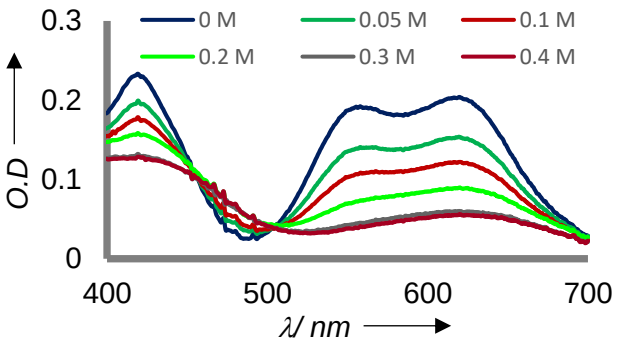

Figure 1. The effect of n-$BuNH_2$ on the spectrum of SmI_2 (2 mM).

Next, the oxygen analog *n*-BuOH was examined at the same concentrations. Surprisingly, the alcohol had no significant impact on the spectrum of SmI_2 (see SI, Figure S1). It should be pointed out that water and MeOH do complex to SmI_2 and significantly affect its spectrum.[6a,c] However higher alcohols, apparently because of steric hindrance, do not. Similarly, while the cyclic diether dioxane has no effect on the spectrum (Figure S2), morpholine and pyrrolidine have significant effect on it (Figures 2). Piperidine also has a significant impact on the spectrum (see SI, Figure S3).

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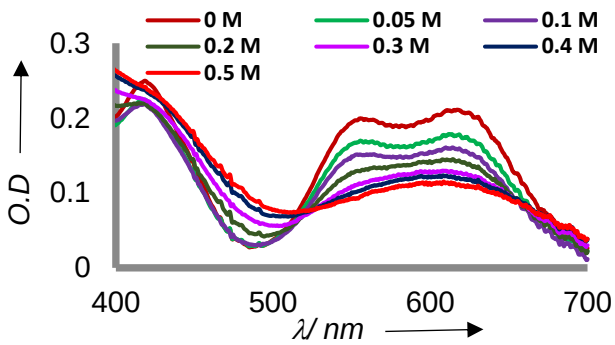

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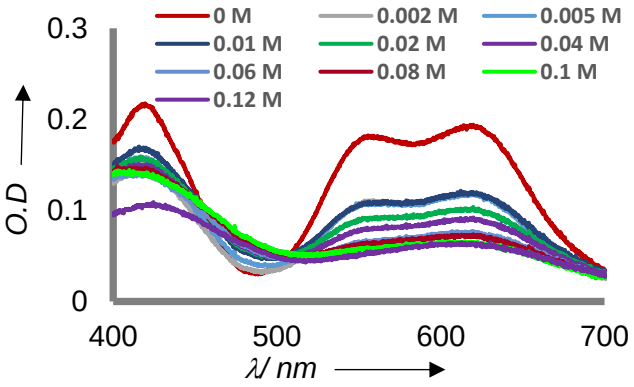

Figure 2. The effect of (a) morpholine and (b) pyrrolidine on the spectrum of SmI_2 (2 mM).

Pyrrolidine is of special importance since it is the aza analog of THF. Its efficiency in coordinating to SmI_2 is apparent from the fact that ca. 0.1M of pyrrolidine is sufficient to displace the THF from its complex with SmI_2 and to reach saturation in the spectrum despite the fact that the concentration of THF as a solvent is two orders of magnitude higher (12.3 M). Overall, these initial experiments demonstrate that a range of amines have an exceptionally high affinity for Sm(II).

Next, we examined G-ligands and there are significant differences with alcohols and amines. In this case, a dioxygen ligand such as ethylene glycol (EG) induces significant change in the spectrum of SmI_2 (Figure 3). This change in behavior is likely due to an entropic effect since the enthalpy gained by the formation of two Sm – O bonds is not over compensated by the high entropic cost of a termolecular reaction required for complexing two mono oxygen ligands.

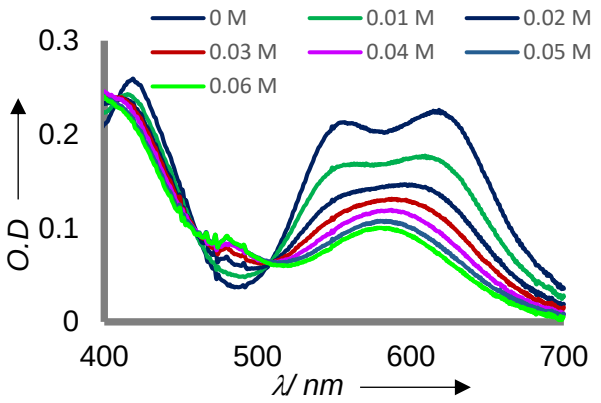

Figure 3. The effect of EG on the spectrum of SmI_2 (2 mM).

Interestingly, when one of the oxygen atoms in EG is replaced by a nitrogen atom, i.e. ethanolamine (EA), the concentration of G-ligand required to achieve spectral saturation are drastically reduced (Figure 4). This effect is even more apparent when ethylenediamine (EDA) is used where the affinity of the ligand for Sm(II) is substantially increased in comparison to EG and EA (Figure 5).

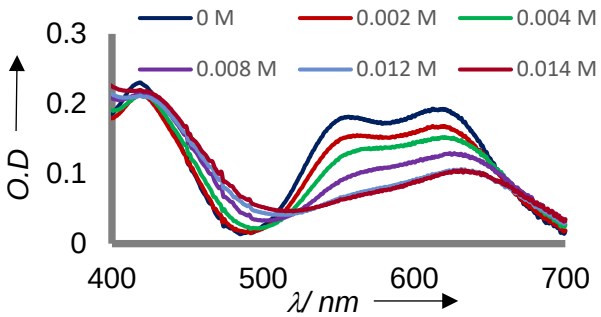

Figure 4. The effect of EA on the spectrum of SmI_2 (2 mM).

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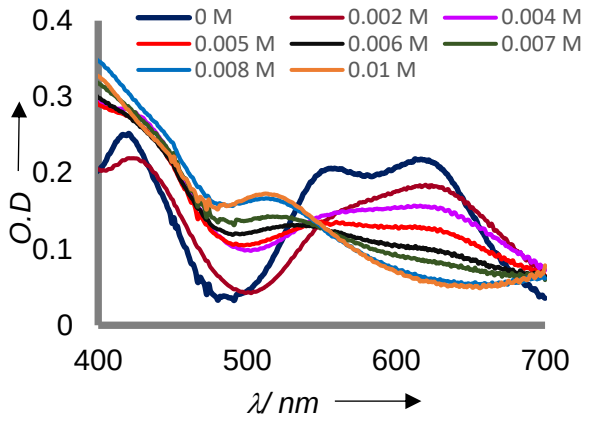

Figure 5. The effect of EDA on the spectrum of SmI_2 (2 mM).

A noticeable feature in the spectrum for the G-ligands is the change in the absorption position of the complexes in the visible spectrum. While the newly formed absorption initiated by the addition of EG is nearly centered between the two original peaks of SmI_2 (similar to MeOH and water), the nitrogen derivatives induce a red shift. In the case of EA, the red shift remains constant with continued addition of the additive. In contrast, EDA induces an initial red shift but further addition induces a blue shift with an absorption centered at approximately 500 nm. This behavior is similar to HMPA which also induces a blue shift in the spectrum of Sm(II).

Figure 6 contains the results described above in a more quantitative manner. In this figure the total OD change to saturation is normalized to 1 and the fraction of the change in the O.D. is plotted as a function of the concentration of the G-ligands. It is clear from this description that the order of reaching complexation saturation is EDA>EA>EG. Another interesting feature of the data is that the addition of a methyl group to EA (*N*-methylethanolamine, NMEA) has a deleterious impact on the affinity of the additive for Sm(II) (Figure S4). This is likely a consequence of steric hindrance.

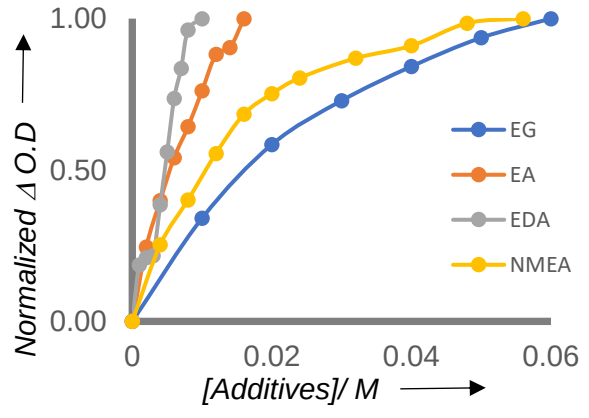

Figure 6. Normalized change in absorbance as a function of G-ligands concentration (SmI_2 2 mM; NMEA = *N*-methylethanolamine).

It is important to note that in the analysis described above, we are making the assumption that the spectral changes can be correlated, at least semi quantitatively, with the degree of complexation of the additives with Sm(II). To further support this supposition, we developed competition experiments between the G-ligands and HMPA, which is known to coordinate strongly to Sm(II).[6b] In the exchange reaction shown in equation 1, the equilibrium will be shifted to the right if the affinity of the G-ligand (G-L) to SmI_2 is higher than that of HMPA.

$$Sm^{+2}(HMPA)_n + mG\text{-}L \rightleftharpoons Sm^{+2}(G\text{-}L)_m + n(HMPA) \quad (1)$$

The characteristic blue shift of the HMPA-Sm(II) complex can be discerned from that of the other ligands and its disappearance can be easily detected. To test this, the addition of EG to a solution of SmI_2 containing HMPA was monitored as shown in Figure 7. The addition of a 10 fold excess of EG (based on [SmI_2]) to the SmI_2-HMPA complex leads to moderate change in the spectrum of SmI_2-HMPA. Nevertheless, the shape of newly generated spectrum resembles SmI_2-HMPA, indicating that HMPA has significantly higher affinity towards SmI_2 over EG under these conditions (Figure 7). At 20 mM of EA the observed spectrum is intermediate between that of the two complexes suggesting that the affinity to SmI_2 of 20 mM of EA is similar to that of 8 mM HMPA to SmI_2 (see SI, Figure S5).

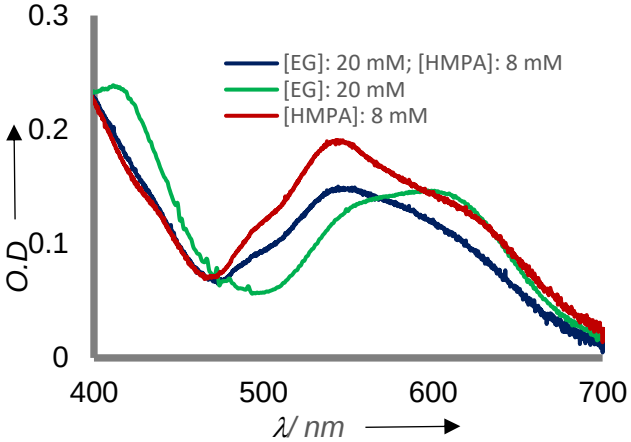

Figure 7. Ligand competition between HMPA and EG (SmI_2 2 mM).

Next we examined the addition of the higher affinity EDA to the SmI_2-HMPA complex as shown in Figure 8. The presence of as little as 8 mM EDA completely displaces the HMPA from Sm(II) and the resulting spectrum is nearly indistinguishable from the spectrum of SmI_2 containing EDA alone. Thus, the displacement experiment clearly shows that as the number of nitrogen atoms in the G-ligand atoms increases, the complexation ability is enhanced.

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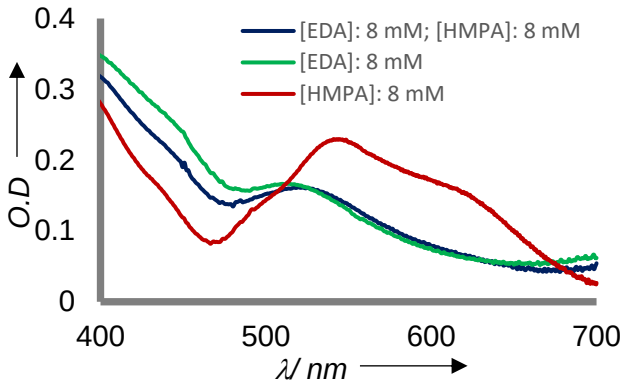

Figure 8. Ligand competition between HMPA and EDA (SmI_2 2 mM).

To this point, we have only considered ligation by sp^3 hybridized atoms. Another question is whether this dominance of nitrogen over oxygen also prevails in sp^2 hybridization. Unfortunately, the high reactivity of imines with SmI_2 prevents an easy spectral measurement. A preliminary competition experiment between THF and p-methoxypyridine (the latter reacts with SmI_2 but at a rate slow enough to enable the recording of its spectrum) showed that it markedly affects the spectrum, however, it takes about 0.4 M in order to reach saturation in the spectrum (Figure S6). A better comparison between the sp^2 ligands should be performed with an sp^2 hybridized oxygen rather than the sp^3 oxygen of THF. Because of the high reactivity of imines, the comparison was achieved through kinetic experiments. In the reaction of SmI_2 (2 mM), with benzophenone imine (10 mM), the SmI_2 vanished in nearly the dead time of the instrument (<3 msec) whereas the reduction of benzophenone (10 mM) was about 30 times slower (Figure 9). Yet the reduction potential of benzophenone imine is much smaller than that of benzophenone itself,[8] suggesting that the enhanced reactivity of SmI_2 with the imine is due to its stronger binding to the sp^2 hybridized nitrogen.

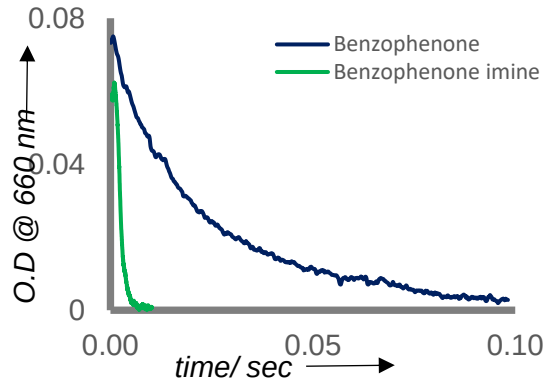

Figure 9. kinetic traces for the reaction of SmI_2 with benzophenone and benzophenone imine.

The equilibria discussed above provide the free energy of the interaction between various amines and Sm(II). While the free energy provides the overall driving force, it includes contributions from enthalpy and entropy. The strength of an interaction is best expressed by the enthalpy and we employed calorimetry experiments to measure the relative affinities between a set of ligands and Sm(II). Simple amines and alcohols have complex stoichiometries, so we examined a crown ether and related aza crowns since these have known, well-defined interactions with metals including Sm(II).[9] The enthalpy of interaction with 15-crown-5, aza-15-crown-5, and 4,10-diaza-15-crown-5 were measured using isothermal titration calorimetry. Figure S7 shows the data for these studies. Both 15-crown-5 and aza 15-crown-5 coordinate in a 2:1 stoichiometry with SmI_2 and the interaction with the aza crown is more exothermic. The 4,10-diaza-15-crown-5 coordinates to Sm(II) in a 1:1 stoichiometry, but the interaction is significantly more exothermic. Since initial part of an isotherm indicates the enthalpy change associated with a complexation process, we have performed ITC titration of 10 mM of SmI_2 with 10 mM of above mentioned three crown ethers by adding 5 μL of aliquot each time (see SI, Figure S8). This experiment allows us to have a more accurate measurement of enthalpy change associated with complexation of SmI_2 and crown ethers (Table 1). As anticipated, complexation phenomenon is more exothermic when more number of nitrogen atom is incorporated in crown ether.

Table 1: ΔH of complexation between SmI_2 and crown ethers

Crown ethers	ΔH (kcal/mol)
15-crown-5	-11.7±0.1
Aza-15-cown-5	-18.4±0.3
4,10-diaza-15-crown-5	-20.0±0.5

Overall, these data demonstrate that the replacement of an oxygen with a nitrogen in the crown ligands leads to a more exothermic interaction with Sm providing further evidence that nitrogen containing ligands have a higher affinity for the metal than oxygen.

The discussion up to this point has dealt with the ability of the ligands to coordinate to Sm^{+2}. Yet, the interaction of these ligands with Sm^{+3} is very important because the relative strength of these interactions governs the equilibrium of equation 2 and therefore impact the reduction potential of SmI_2.

$$Sm^{+2} \rightleftharpoons Sm^{+3} + e^- \qquad (2)$$

Since the solubility of Sm^{+3} in THF is low and it does not have a significant absorption in the UV – VIS range, we measured the interactions of the G-ligands with Sm^{+3} indirectly by measuring the ability of Sm^{+3} to pull away G-ligands from their complex with Sm^{+2} (equation 3).

$$Sm^{+2}(G\text{-}L)_n + Sm^{+3} \rightleftharpoons Sm^{+2} + Sm^{+3}(G\text{-}L)_n \qquad (3)$$

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Since SmI_2 has a well-defined visible absorption, the addition of Sm^{+3} to a solution containing a complex of a G-ligand and SmI_2 will strip off the ligand generating free SmI_2. The appearance of the characteristic absorption of SmI_2 will indicate that the G-ligands bind more strongly to Sm^{+3} than to Sm^{+2}.

This strategy is exemplified below for HMPA, an additive that decreases the reduction potential of SmI_2 (making it a more powerful reductant) because it binds more firmly to Sm^{+3} than to Sm^{+2}.[6b, 10] To put it simply, the presence of the strong donor ligand stabilizes the higher oxidation state of Sm. Figure 10 shows the spectrum of SmI_2 (2 mM), after adding 4 mM HMPA. Addition of SmI_3 (2 mM) sequesters HMPA bound to SmI_2 and as a result, the original spectrum of SmI_2 is restored.

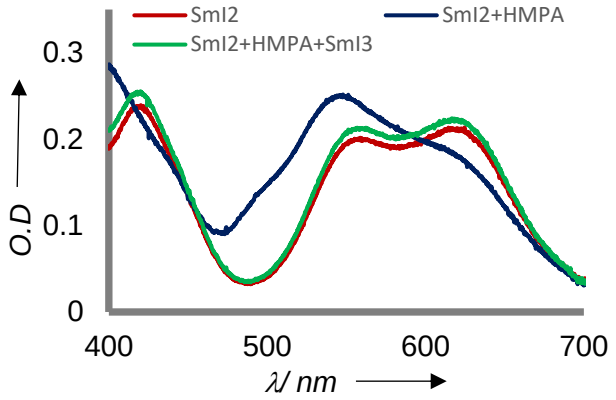

Figure 10. Spectrum regeneration showing the higher affinity of HMPA to Sm^{+3}.

We next carried out the same experiment using EG. Complexation to EG does not affect the spectrum to nearly the same degree as HMPA but nevertheless, some restoration of the could be discerned (Figure S9).

When the nitrogen analog EDA was used, it formed a precipitate with Sm^{+3}, thus masking the results for this G-ligand (Figure S10). However, very good results were obtained with EA and pyrrolidine (Figure 11). These results imply that nitrogen-based ligands have a higher affinity than oxygen containing ligands for Sm^{+3}.

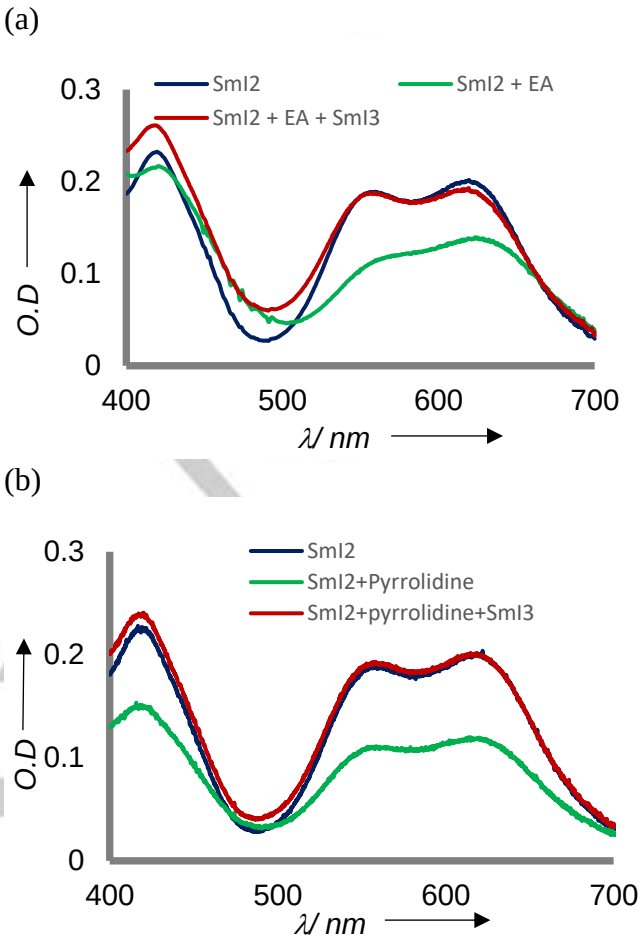

Figure 11. (a) Spectra of, SmI_2 (2 mM); + EA (8 mM); $+Sm^{+3}$ (2 mM). (b) Spectra of, SmI_2 (2 mM); + pyrrolidine (2 mM); $+Sm^{+3}$ (2 mM).

Since the relative strength of the interaction of the ligands with Sm^{+3} and Sm^{+2} is known to effect the reduction potential of SmI_2, the impact of NMEA and EG on the reduction potential of SmI_2 was determined using cyclic voltammetry. Depicted in Table 2 are the reduction potentials of SmI_2 as a function of the concentration of, EG, NMEA and *N, N'*-dimethylethylenediamine (NN'DMEDA). The latter two were chosen because at high concentration, EA and EDA precipitates with the generated Sm^{+3} interfering with the measurements. Once again, HMPA data is provided as a benchmark.

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Table 2. Oxidation Peak potential as a function of concentration

Conc. M	HMPA[a]	EG[a]	NMEA[a]	NN'DMEDA[a]
0	-1.13	-1.13	-1.13	-1.13
0.004	-1.59		-1.41	-1.4
0.008	-1.73		-1.6	-1.51
0.01		-1.35		
0.012			-1.69	-1.56
0.016	-1.84		-1.74	-1.57
0.02		-1.43	-1.77	-1.59
0.024			-1.83	-1.6
0.03		-1.5		
0.032			-1.84	
0.04		-1.52	-1.85	
0.05		-1.52		

[a]: [SmI_2]: 2 mM

The data show that HMPA and NMEA reach nearly the same reduction potential although with NMEA, larger concentration of the ligands are necessary, consistent with spectral measurements showing that it has a lower affinity for Sm. EG with its two oxygen atoms has a more modest impact on the redox potential.

Equation 2 is relevant not only to the reduction potential of the complexes, but also to the electronic excitation since in the excited state, where the electron is distanced from the nucleus somewhat resembling Sm^{+3}. Figures 12 (NMEA) and S11 (EG) show that indeed, there is some similarity between the CV data and spectroscopic results. However, bearing in mind that we monitor the change in the OD which is related to the absorption coefficient rather than to the wavelength which corresponds to excitation energy, it is our supposition that the correlation reflects the degree of complexation and indirectly the strength of complexation.

CV data tabulated in Table 2 also suggests that nitrogen containing G-ligands can potentially be employed to carry out reductions of substrates which are recalcitrant towards reduction by SmI_2 when no additives are present. To examine this supposition, the reduction of several substrates shown in Chart 1 were examined. Initial reductions were carried out on cyclohexylmethyl ketone (1), 4-phenyl-2-butanone (2) anthracene (3) and phenanthrene (4) as model substrates in the presence of NMEA and NN'DMEDA. These reactions were also

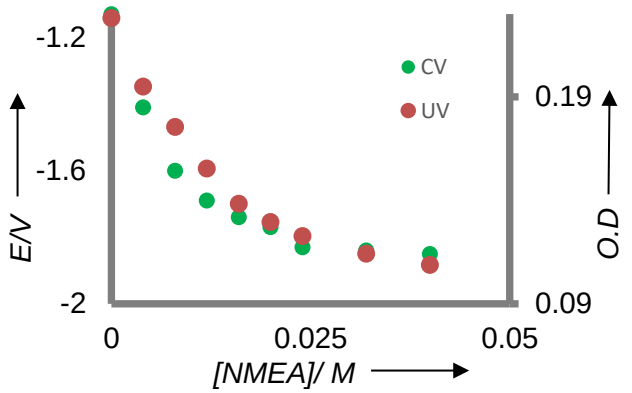

Figure 12. Reduction potential and O.D. of NMEA-SmI_2 complexes as a function of concentration.

performed in the presence of HMPA/TFE for comparison purpose. TFE was used as source of proton in HMPA reaction, since it is known for non-coordinating nature and hence will not disrupt the SmI_2-HMPA complex. Yield of the reactions are tabulated in Table 3. Substrate 1 and 2 were reduced to their corresponding alcohols whereas 3 and 4 were reduced to their dihyro product.

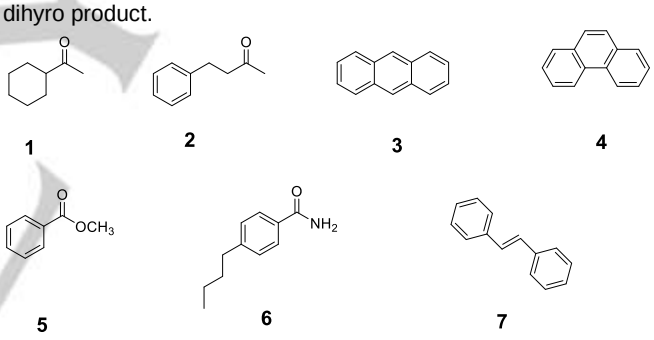

Chart 1. Substrates used for this study

Table 3. Yield of reductions with NMEA[a], NN'DMEDA[a] and HMPA/TFE[a] as additives.

Substrates	Yield $_{NMEA}$	Yield $_{NN'DMEDA}$	Yield $_{HMPA/TFE}$
1	97[b]	0[c]	99[c]
2	98[b]	17[c]	99[c]
3	95[b]	18[c]	99[c]
4	50[c]	0[c]	0[c]

[a] [SmI_2]: 0.1 M; [Subs]: 0.046 M; [NMEA]: 0.4 M; [NN'DMEDA]: 0.4 M; [HMPA]: 0.4 M and [TFE]: 0.4 M; [b] instantaneous decolorization; [c] reaction time 2 hr.

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Data presented in Table 3 clearly indicates that NMEA is very potent additive to mediated reductions by SmI_2. On the other hand, the reactions with NN'DMEDA were sluggish and resulted poor yields. This could be due to lack of acidic protons which are important for these reductions.[3h-j] It is also important to note that phenanthrene which was not reduced by the HMPA/TFE system, can be reduced up to 50% in the presence of NMEA. Since the additive HMPA is a suspected carcinogen, these initial experiments show that NMEA may be a potential alternative. To determine whether NMEA is indeed potent towards reduction of range of substrates, reduction of methyl benzoate (5), 4-*n*-butylbenzamide (6) and trans-stilbene (7) was carried out. In all cases, good to excellent yields were obtained (Table 4). It is interesting to note that reduction of 4-*n*-butylbenzamide resulted alcohol exclusively. These initial results show that amines are not only good ligands for SmI_2, but they are potential additives for reductions mediated by SmI_2.

Table 4. Yield of SmI_2/NMEA mediated reductions.

Substrate	Product	Yield (%)
5	benzyl alcohol	99[b]
6	4-*n*-butylbenzyl alcohol	99[b]
7	bibenzyl	99[b]

[a] [SmI_2]: 0.1 M; [Subs]: 0.046 M; [NMEA]: 0.4 M [b] instantaneous decolorization

Finally, it is important to consider whether azaphlicity of SmI_2 will have any impact on SmI_2 reductions in the presence of water/amine. Mixtures of water/amine have proven to be one of most efficient and potent additives to carry out reductions of a range of substrates.[11] Hilmersson and others carried out seminal work in this area increasing the substrate scope of this additive.[11b-h] The scope of this additive was further improved by Procter and Szostak who demonstrated that substrates such as carboxylic acid derivatives typically recalcitrant to electron transfer can be reduced by SmI_2/water/amine.[12] Several mechanistic scenarios have been proposed for the reagent combination.[12f, 13] The common theme among the different mechanistic scenarios is the proposal that water coordinates to SmI_2 and amine deprotonates the ligated water. In light of the findings described here, the question is: Can an amine replace water from the coordination shere of SmI_2? Although different amines can be used in the SmI_2/water/amine system, Et_3N is the most commonly used amine, hence we have tried to address whether Et_3N can displace water bound to SmI_2. The ideal experiment in this case would be ligand exchange experiment, similar to HMPA/G-liagnds system. However, instability of SmI_2 in the presence of water and Et_3N prohibits the performance of this measurement. UV-visible spectra study in the presence of Et_3N (0.05 M-0.5 M) shows no change in the shape of SmI_2 spectrum (Figure S12). It known that under similar condition, water significantly changes the shape of SmI_2 spectrum.[13b] The enthalpy of complexation for water and Et_3N measured through ITC experiments was found to be comparable (-2.5 kcal/mole for water and -3.3 kcal/mole for Et_3N). It was shown previously that introduction of alkyl group one oxygen has significant deleterious impact on the coordinating ability.[3j, 4c] We have also seen similar phenomenon when a methyl group was added on the nitrogen of ethanolamine (Figure 6). Based on these findings it is our supposition that water forms much stronger complex than Et_3N and hence despite of azaphilicity of SmI_2, using Et_3N should not have any impact on the key feature of proposed mechanisms where Sm bound water is deprotonated by amine. Nevertheless, amines such as piperidine and pyrrolidine may effectively compete with water coordination and hence choosing right concentration of water and amine may be vital in these cases.

Conclusions

Using several diagnostic tools we have demonstrated that under similar conditions, nitrogen coordinates to SmI_2 stronger than oxygen. This is demonstrated for sp^3 atoms in cyclic and acyclic ligands (n-$BuNH_2$ vs. n-BuOH and THF vs. pyrollidine), bidentate ligands (ethylene glycol vs ethanolamine and ethylenediamine), crown ethers (15-crown-5 vs Aza-15-crown-5 and 4,10-diaza-15-crown-5) as well as for sp^2 hybridized atoms (imine vs. carbonyl). This difference in affinity is even more pronounced for Sm^{+3} resulting in a stronger effect of the aza ligands on the reduction potential of SmI_2. We are currently examining the impact of nitrogen ligand coordination on the reactivity and selectivity of SmI_2-based reductions and the results of this work will be reported in due course.

Experimental Section

General: All the reagents were purified prior to their use by following standard procedures. The liquid reagents were distilled under argon and degassed with argon prior to use. The THF was dried and freshly distilled off sodium/benzophenone under an argon atmosphere. The SmI_2 was freshly prepared prior to use by stirring samarium metal and 1,2-diiodoethane at room temperature. The concentration of SmI_2 was determined by UV-visible spectroscopic measurements (λ 619 nm; □ = 635). The spectral, cyclic voltammetric, caloriemetric titration and kinetic experiments were carried out in clean and dry glassware under a nitrogen atmosphere.

Cyclic Voltammetry: Cyclic voltammetry was performed in a single potentiostat from Bio Logic Scientific Instruments. Glassy carbon, $Ag/AgNO_3$ in acetonitrile and Pt wire were used as working, reference and counter electrode, respectively. The glassy carbon electrode was polished with polishing alumina and then washed thoroughly before each sets of measurements. The reference electrode had a potential of 0.542 V with respect to SHE. Tetrabutylammonium hexafluorophosphate (0.1

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M) was used as a supporting electrolyte. The SmI_2 concentration was 2 mM for all set of experiments.

Isothermal Titration Calorimetry: ITC measurements were carried in MicroCal Calorimetry instruments. In a typical experiment, SmI_2 (10 mM) solutions in acetonitrile are taken inside cell of instrument and 200 mM solution of ligands are injected (5 μL/injection) from pipettes. The ligands concentrations for determining ΔH of complexation was 10 mM. Enthalpy change upon addition of ligands to metal ions was plotted against molar ratio.

UV-visible Spectral Measurements: Spectral measurements were performed with a Stopped Flow Spectrometer. To record the spectra of SmI_2 in the presence of different concentrations of additives, SmI_2 and corresponding additive were taken in two different syringes and mixed with stopped flow machine and wavelength was scanned over a range to obtain the spectrum. The concentration of SmI_2 in all the experiments was 2 mM.

Ligand exchange reactions: Two kinds of ligand exchange experiments were performed. In one type of experiment we studied displacement of HMPA, complexed to SmI_2, by other ligands such as ethylene glycol. In these experiment, SmI_2-HMPA complex was taken in one syringe and ligands of interest was added to another syringe and they were mixed with the stopped flow instrument followed by wavelength scan to record the spectrum of system. A series of experiments were conducted with changing the ligand concentration with fixed SmI_2/HMPA concentration to observe the displacement of HMPA with ligand of interest. The concentration of SmI_2 and HMPA for all the experiments were 2 mM and 8 mM respectively.

In another type of experiment, we have determined relative affinity of a ligand towards Sm^{2+} vs Sm^{3+}. In this experiment, SmI_2 and SmI_3 was taken together in one syringe and another syringe was filled with ligand of interest. Two different solutions were mixed through stopped flow instrument followed by scan of wavelength to record the spectrum. The spectrum was compared to the spectrum of SmI_2 and SmI_2 with that ligand. The concentration of SmI_2 as well as SmI_3 for all the experiments was 2 mM.

Kinetics: Stopped flow kinetic measurements were performed with a Stopped Flow Spectrometer. The reactions were performed under pseudo-first-order condition (SmI_2: 2 mM; substrates: 10 mM). The rates of reactions were monitored by following the disappearance of the SmI_2 absorbance at 660 nm.

Preparative reaction: In a typical procedure, to a 5 mL of 0.1 M of SmI_2, 0.23 mmole of substrate [cyclohexylmethyl ketone (0.029 g), 4-phenyl-2-butanone (0.034 g), anthracene (0.041 g), phenanthrene (0.041), methyl benzoate (0.015 g), 4-n-butylbenzamide (0.02 g) and trans-stilbene (0.041 g)] and 2 mmole of N-methylethanolamine (0.15 g) was added. Reaction quenched by passing air through solution. The reaction mixture was diluted with 30 mL of dichloromethane and treated with 20 mL of 0.1 M HCl. The aquous layer was further washed with 2x20 mL of dichloromethane. The organic layer was washed with braine solution, dried over MgSO4 and concentrated under reduced pressure. The crude product was analyzed with NMR to get the yield of reaction. In each case the weight of crude material was measured to make sure 90 % or above organic material was recovered.

Acknowledgements

SH thanks Israel Science Foundation for supporting this work at Bar-Ilan University. RAF is grateful to the National Science Foundation (CHE 1565741) for support of the work at Lehigh University.

Keywords: N ligands • chelates • samarium • amines • affinity

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10.1002/chem.201703394

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In spite of the prevalence ligands that coordinate to SmI_2 through oxygen in synthesis, experimental results demonstrate that nitrogen-based ligands have a significantly higher affinity for the reagent and provide a powerful reducing system.

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