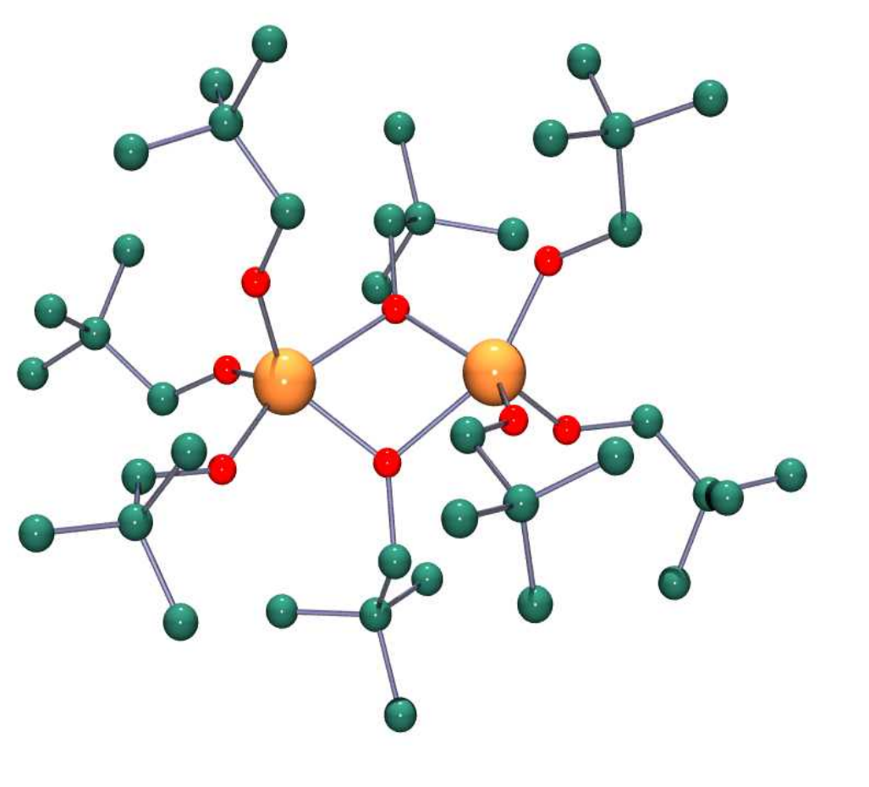
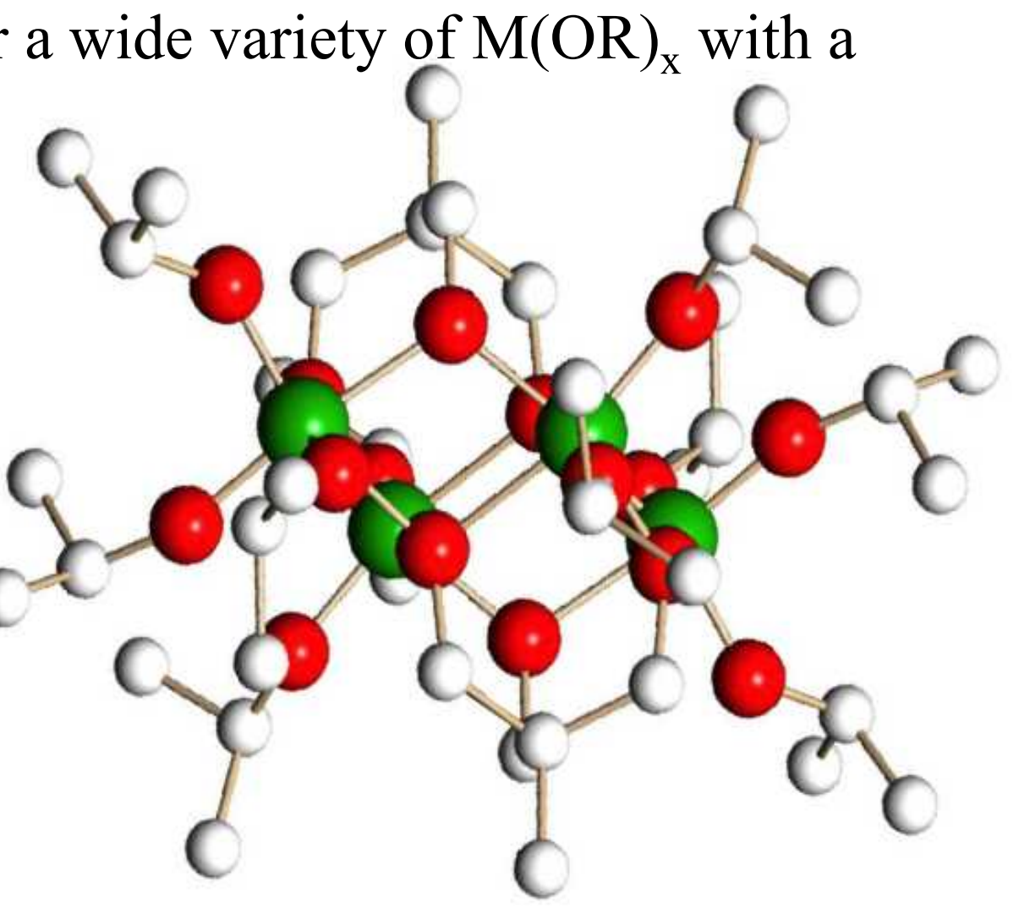
Stable, Water-Soluble Metal Alkoxides

Timothy J. Boyle, Robin M. Sewell, Leigh Anna M. Ottley, Rebecca Raymond, Harry D. Pratt III,
David Ingersoll, Troy D. Russell, Louis J. Tribby (UNM), Timothy N. Lambert, Patrick D. Burton (UNM),
Christopher J. Quintana, Scott D. Bunge, Robert Hromas, M.D. (UNM-SoM)

Introduction

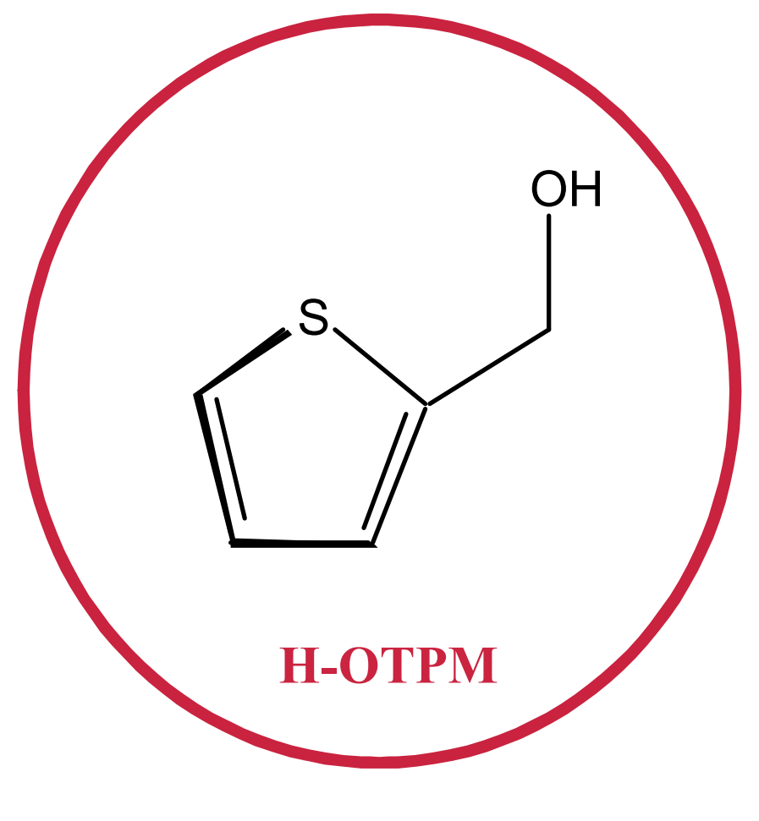
Metal alkoxides ($M(OR)_x$) are of interest for materials production due to their commercial availability, high solubility, high volatility, low decomposition, and many other tunable properties. Often, however, these precursors are air sensitive or more appropriately water sensitive. Therefore, it is necessary to control hydrolysis and condensation rates which is often achieved through ligand modifications. However, due to the rather large radii to charge ratio, hyperoligomerization occurs which leads to uncontrolled structure formation. The use of ligands that occupy more than one coordination sites is often employed in inorganic chemistry as a means to control the undesired oligomerization. For example, the use of cyclopentadienyl ligand which occupies multiple coordination sites on a metal cation led to an entirely new sub-field of study, organometallic chemistry. For metalorganic chemistry and $M(OR)_x$ in particular such a ligand has not been elucidated. We have been exploring the structure types attainable for a wide variety of $M(OR)_x$ with a particular emphasis on the Group 4 cations due to their widespread use in materials production. During these studies we have investigated mono-dentate ligands [i.e., *neo*-pentoxide (ONep)], bidentate [i.e., carboxylate], and tridentate [i.e., *tris*-hydroxymethyl ethane ($THME-H_3$)]. Often polydentate ligands are used with limited success. For early transition metal species, mono-denate ligands do not prevent the oligomerization unless sterically hindering ligands are used (i.e., $OC(CH_3)_3$]. Polydentate ligands, rapidly consume the small charge without necessarily filling the coordination sites or they can lead to oligomerization. To overcome this problem, non-charged atoms present in the ligand but capable of binding are used. In particular, the methoxy ethanol type ligands have been frequently employed but due to their flexible shape, polymers or oligomers are often found to form. Therefore, we have searched for alternative polydentate ligands.


$[Ti(\mu-ONep)(ONep)_3]_2$


$[(\mu-THME)Ti_2(OPr^i)_5]_2$

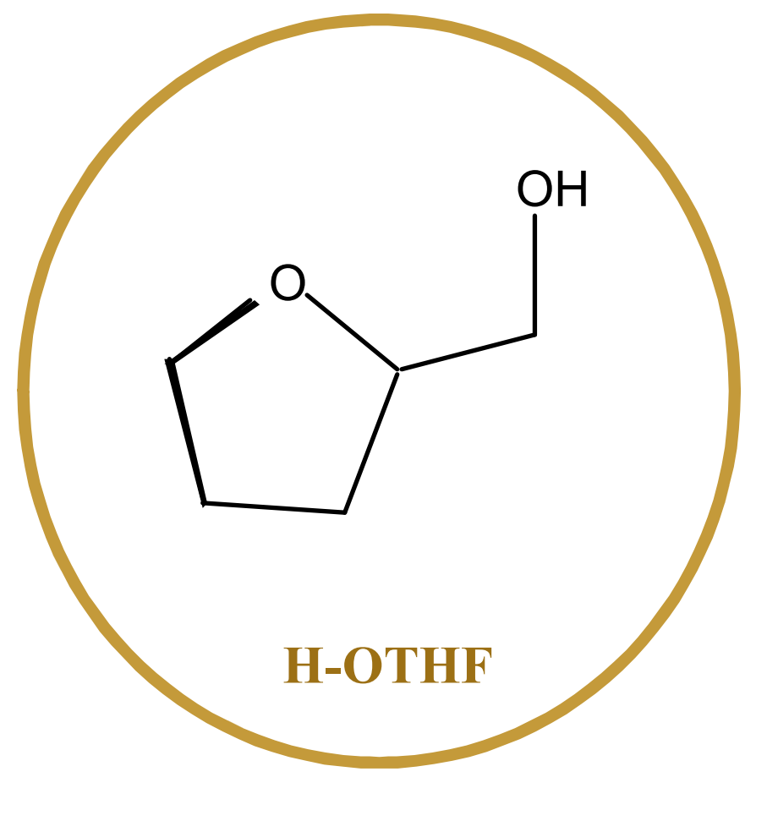
H-OR* Ligands

Of the ligands we have investigated the so-called H-OR* alcohols have become of increased interest. Below are the schematic drawings of the three alcohols we have investigated as a means to control the reactivity of the metal alkoxides. These H-OR* ligands are of interest since they do not significantly deplete the charge but have the potential to fill coordination sites based on the ring heteroatom. Further, the rigidity of the ligand insure site closure of the metal center.



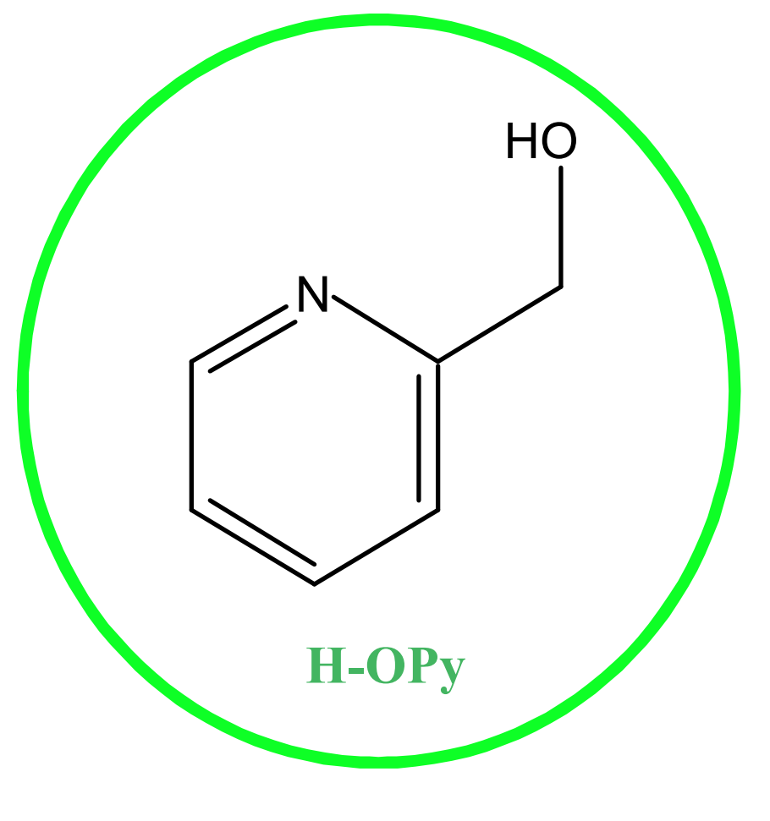
H-OTPM

Thiophene methanol



H-OTHF

Tetrahydrofuran methanol



H-OPy

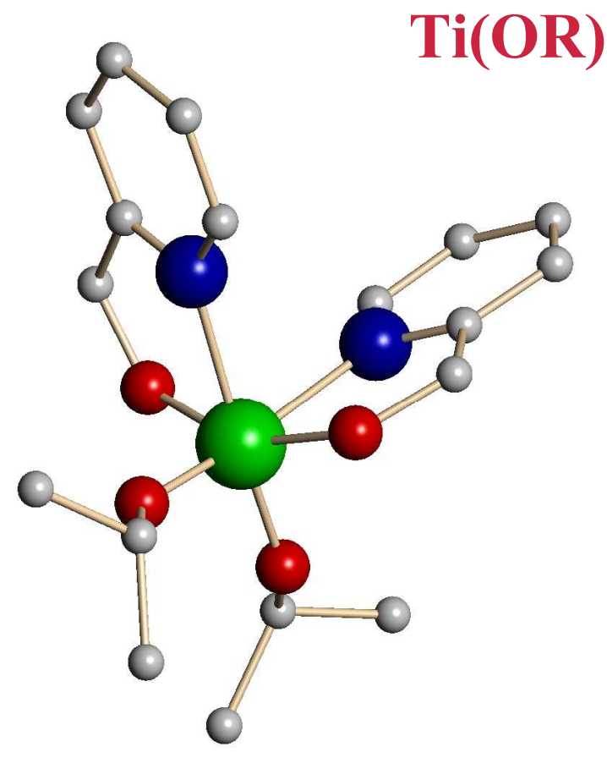
Pyridine methanol

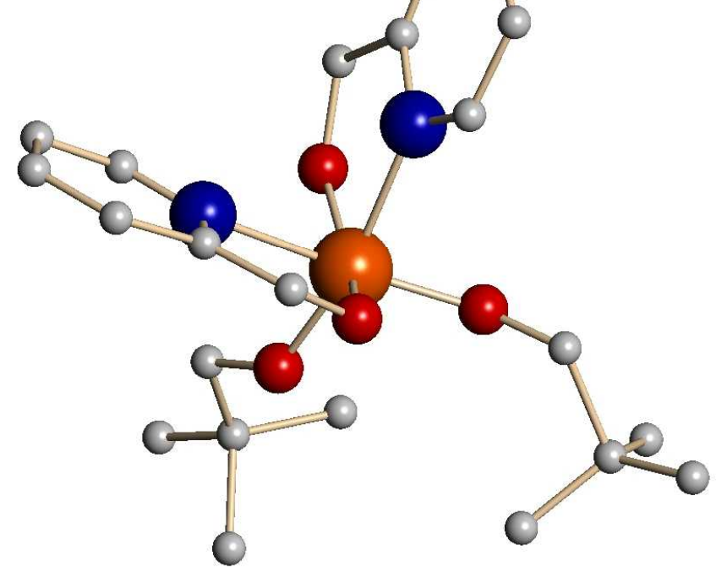
Of these HOR* ligands, the soft S heteroatom does not bind to the hard early transition metals and does not contribute to the controlled construction of $M(OR)_x$. The OTHF ligand was found to bind in a bidentate manner but often only one molecule can be added which limits the utility of this ligand for directed assemblies.

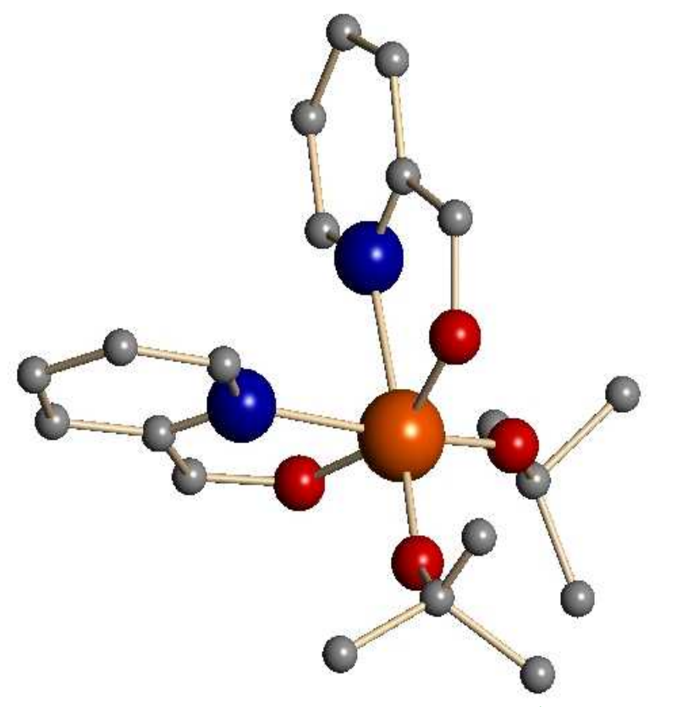
Ti-OPy Derivatives

On the other hand, the OPy ligand has demonstrated some unique properties that make it very useful for planned structure types. Independent of the stoichiometry used, two OPy ligands bind to any Ti alkoxide used as a starting reagent (see eq. 1). The resulting species are octahedrally bound with four sites occupied. The alkoxides are accessible and do not bridge to other metal centers since their coordination sphere is also completely filled.

$$Ti(OR)_4 + 2\ H\text{-}OPy \longrightarrow (OPy)_2Ti(OR)_2$$


$(OPy)_2Ti(OPr^i)_2$


$(OPy)_2Ti(ONep)_2$


$(OPy)_2Ti(OBu^t)_2$

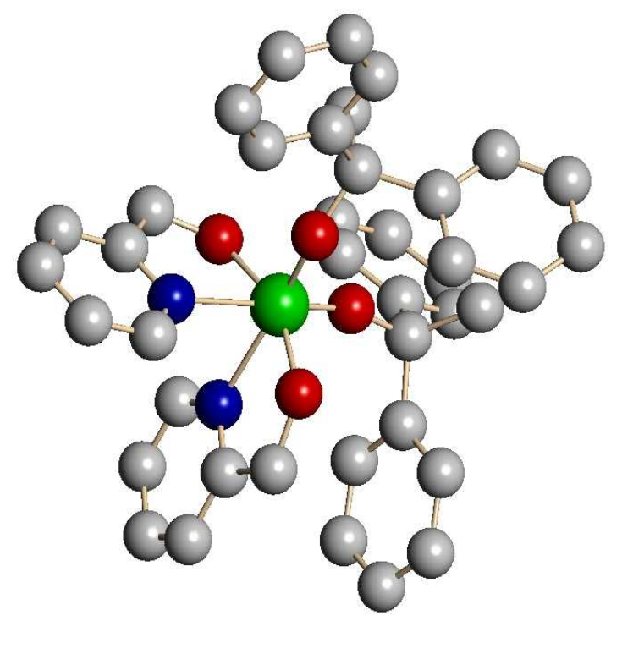
This arrangement appears similar to the bis-cyclopentadienyl derivatives that have become so ubiquitous in the literature. To establish the utility of these precursors, substitution chemistry using the terminal alkoxides is necessary.

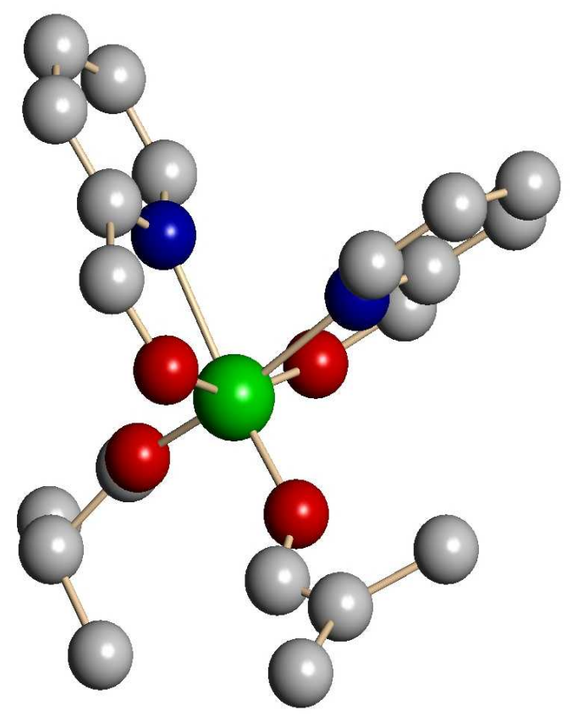
Controlled Derivatization

Using the $(OPy)_2Ti$ moiety as a scaffold, a wide variety of alcohols have been successfully introduced and structurally characterized, ranging from alkyl alkoxides, siloxides, aryloxides, and more complex ligated species. The reaction is fairly simple with high yields that are easily crystallized.

$$(OPy)_2Ti(OR)_2 + 2\ H\text{-}OR \longrightarrow (OPy)_2Ti(OR)_2$$

Alkoxides

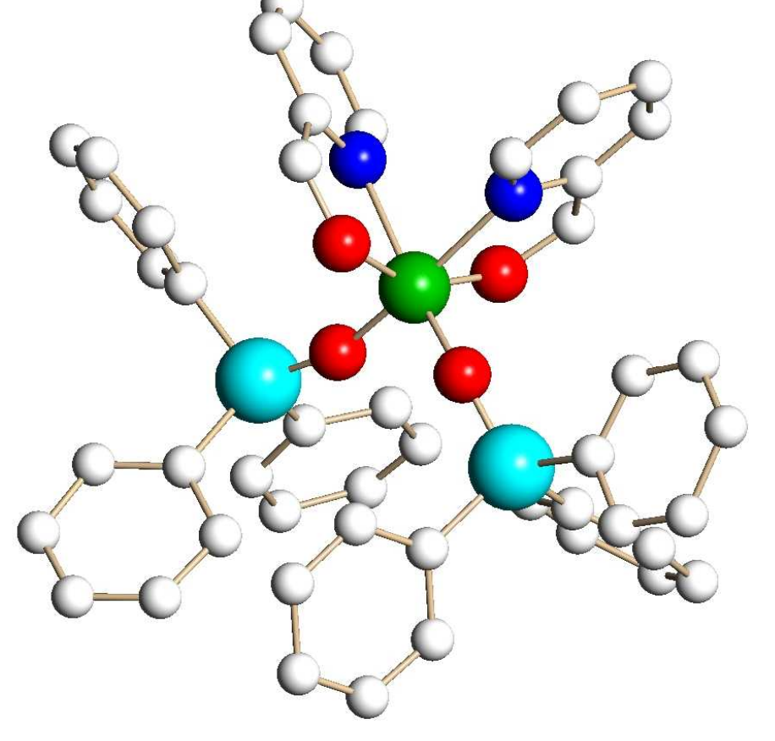

$(OPy)_2Ti(DPE)_2$

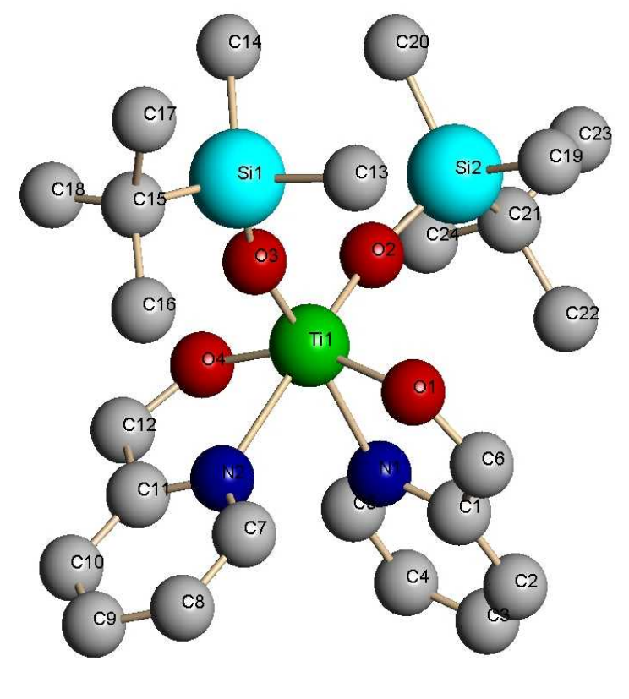

$(OPy)_2Ti(OPr^{Me})_2$

Timothy J. Boyle
Sandia National Laboratories
Advanced Materials Laboratory
1001 University Blvd. SE
Albuquerque, NM 87106
Ph. (505)272-7625
Fx. (505)272-7336
tjboyle@Sandia.gov

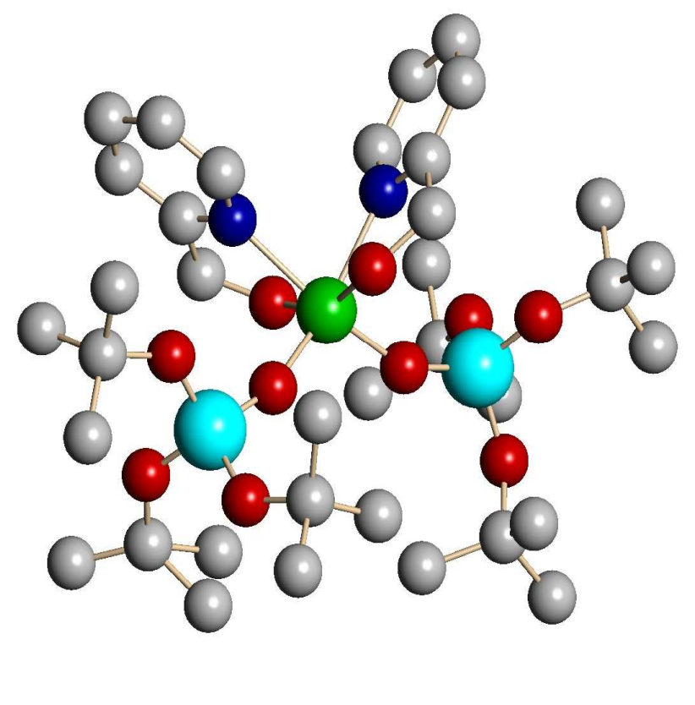
SAND2007-1675P

Siloxides

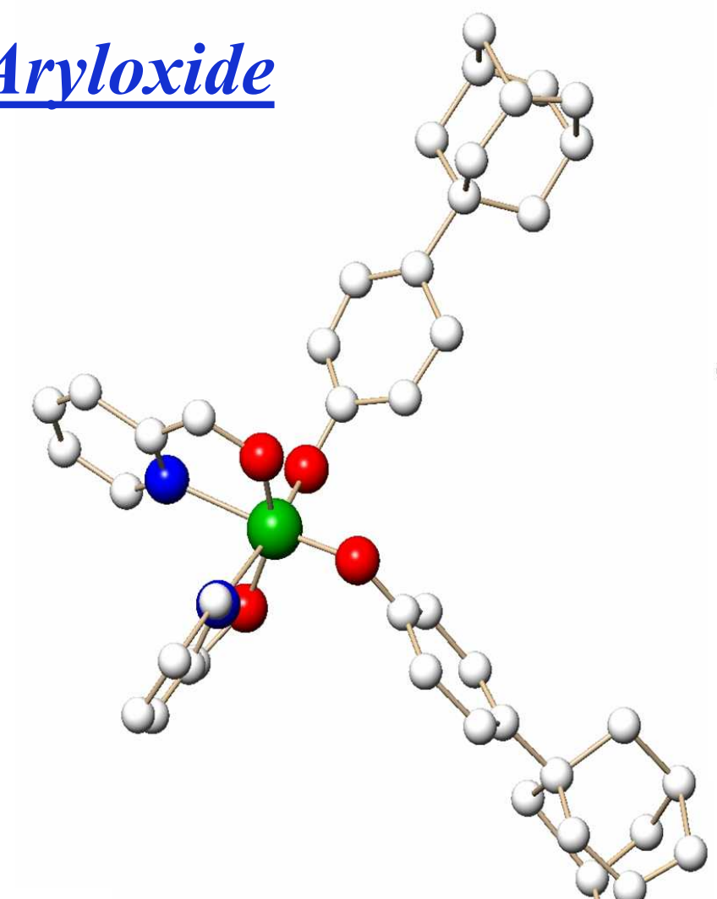

$(OPy)_2Ti(TPS)_2$

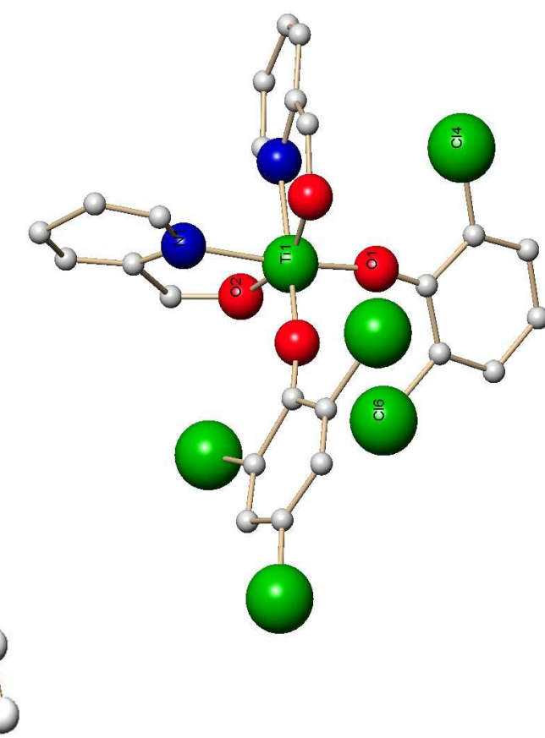


$(OPy)_2Ti(DMBS)_2$

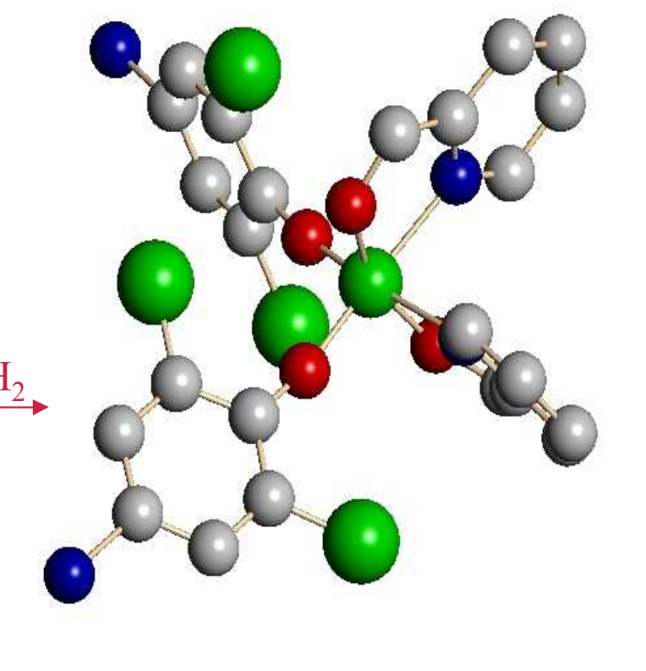

$(OPy)_2Ti(OSiOBu^t)_2$

Aryloxide

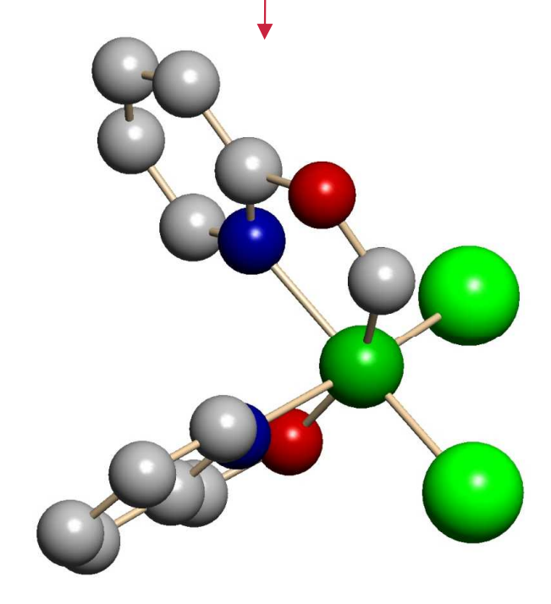

$(OPy)_2Ti(OPh\text{-}Adam)_2$


$(OPy)_2Ti(TCP)_2$

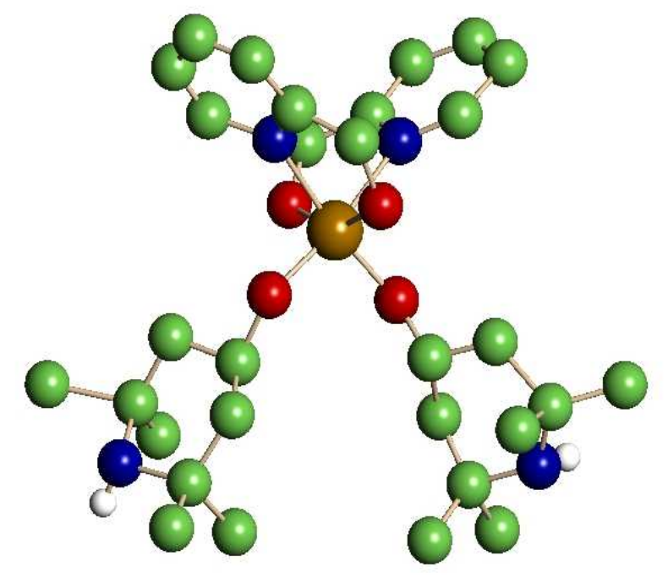
$\xrightarrow{2\ LiNH_2}$

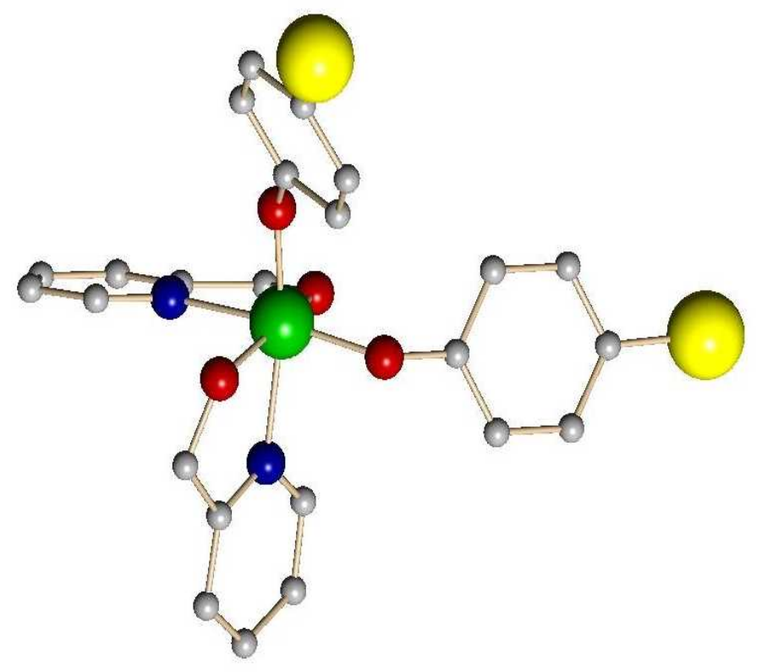

$(OPy)_2Ti(DCN)_2$

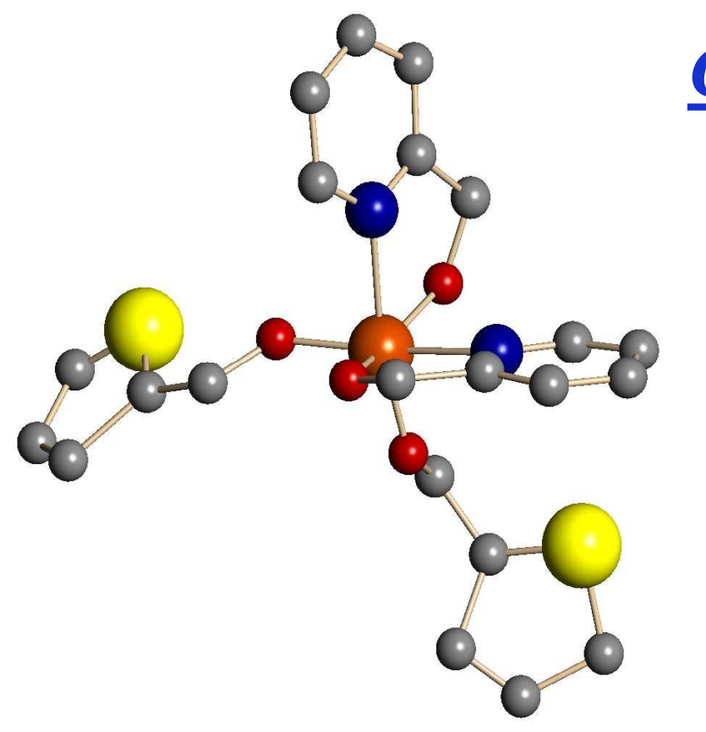
$Ti(ONep)_4 + TiCl_4$
$+ 4\ H\text{-}OPy$


$(OPy)_2TiCl_2$

Heteroligands

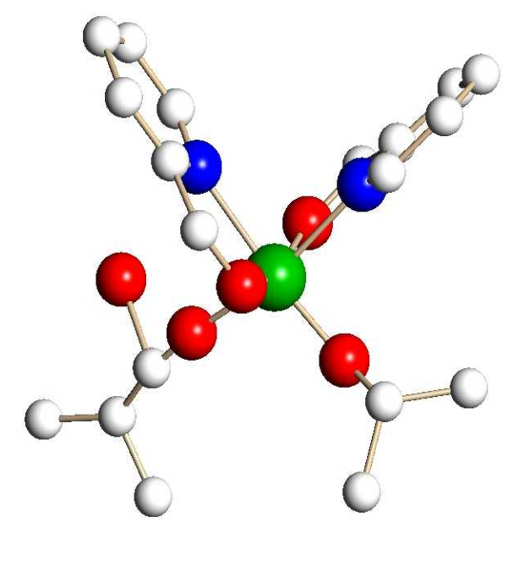

$(OPy)_2Ti(OTMA)_2$

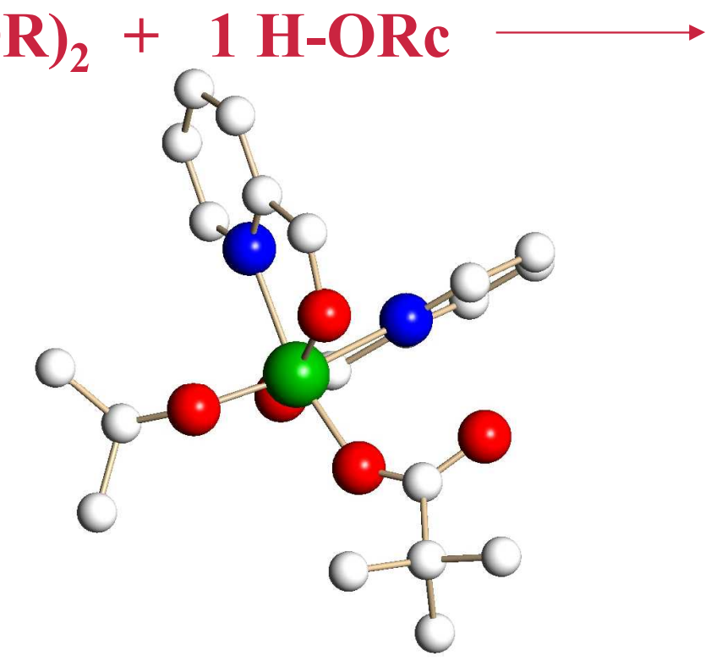

$(OPy)_2Ti(4MP)_2$


$(OPy)_2Ti(OTPM)_2$

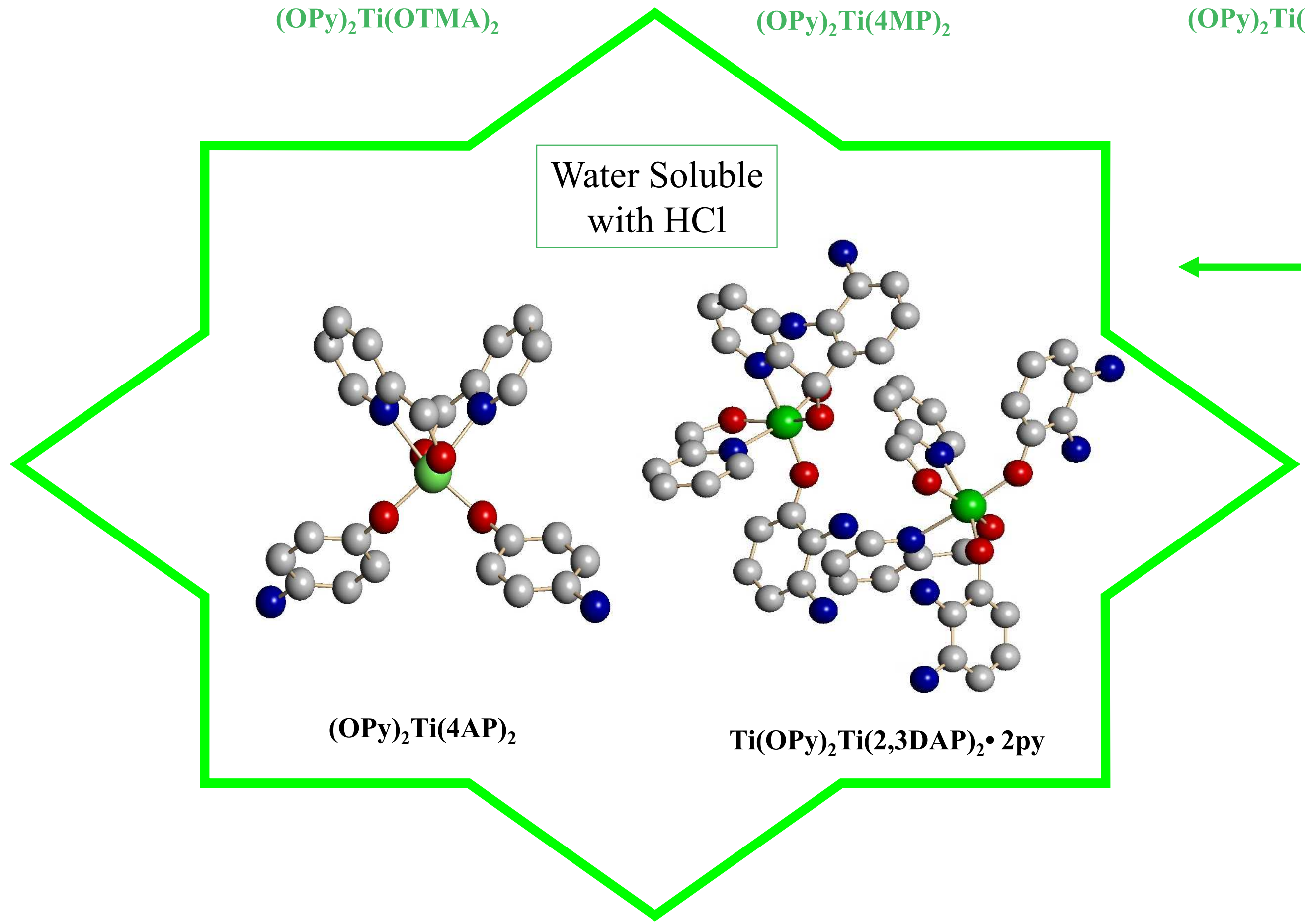
Carboxylates

$$(OPy)_2Ti(OR)_2 + 1\ H\text{-}ORc \longrightarrow (OPy)_2Ti(ORc)(OR)$$


$(OPy)_2Ti(OPc)(OPr^i)$


$(OPy)_2Ti(OBc)(OPr^i)$

Asymmetric substitution is also possible on the $(OPy)_2Ti$ moiety. Using carboxylic acid derivatives (H-ORc), mono-substituted species have been isolated. Furthermore, there was no evidence of esterification occurring!


Water Soluble with HCl

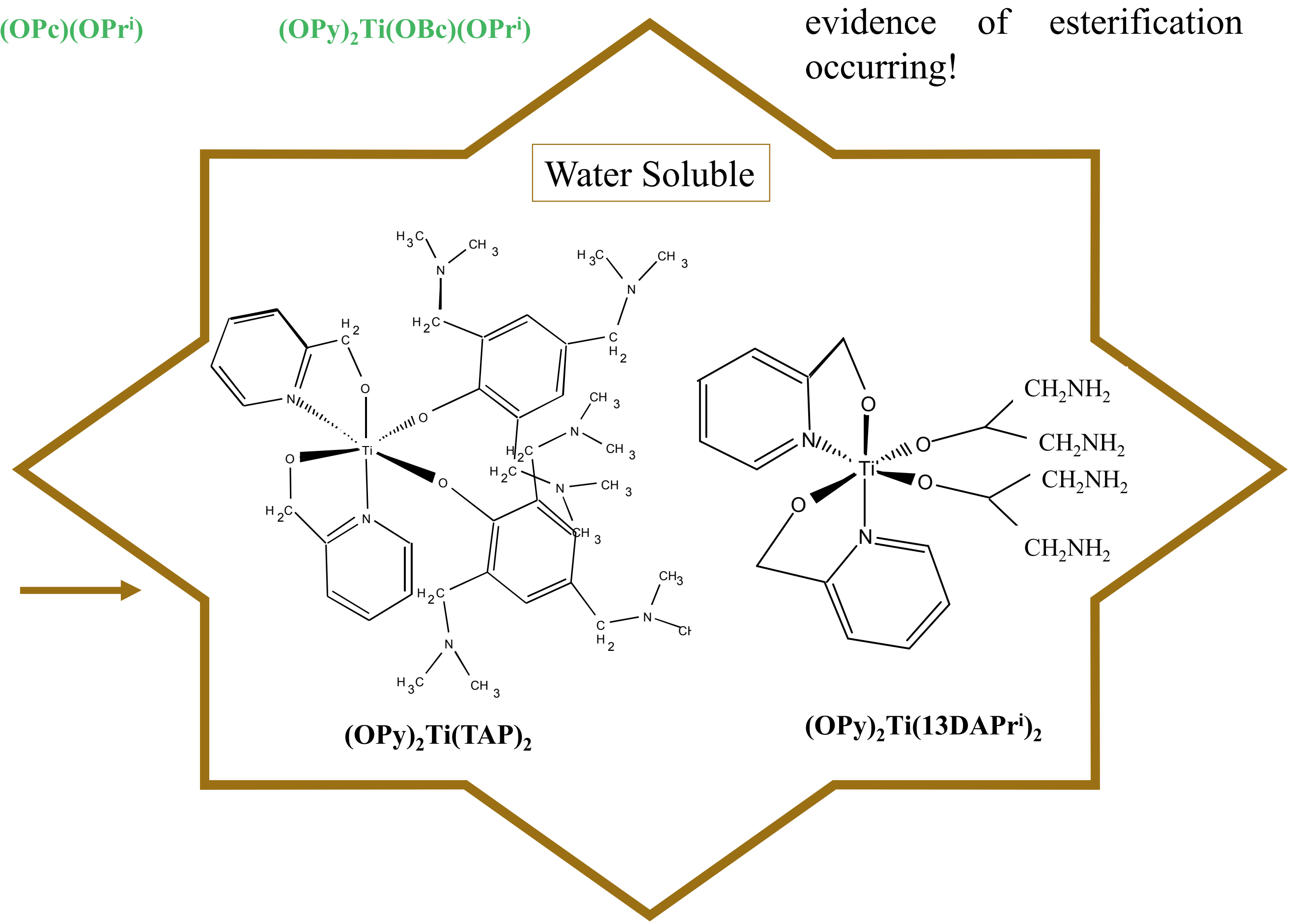
$(OPy)_2Ti(4AP)_2$

$Ti(OPy)_2Ti(2,3DAP)_2\text{•}\ 2py$

Introduction of amine ligands converts the hydrophobic materials to hydrophilic. This water solubilization is assumed to be based on forming *in situ* HCl salts (*vide sinistrorsus*). NMR data confirms structure retention (*vide infra*).

For several of the amide-substituted alkoxides, oils formed (*vide dextrorsus*). NMR data in D_2O confirm the retention of structure in solution (*vide infra*).

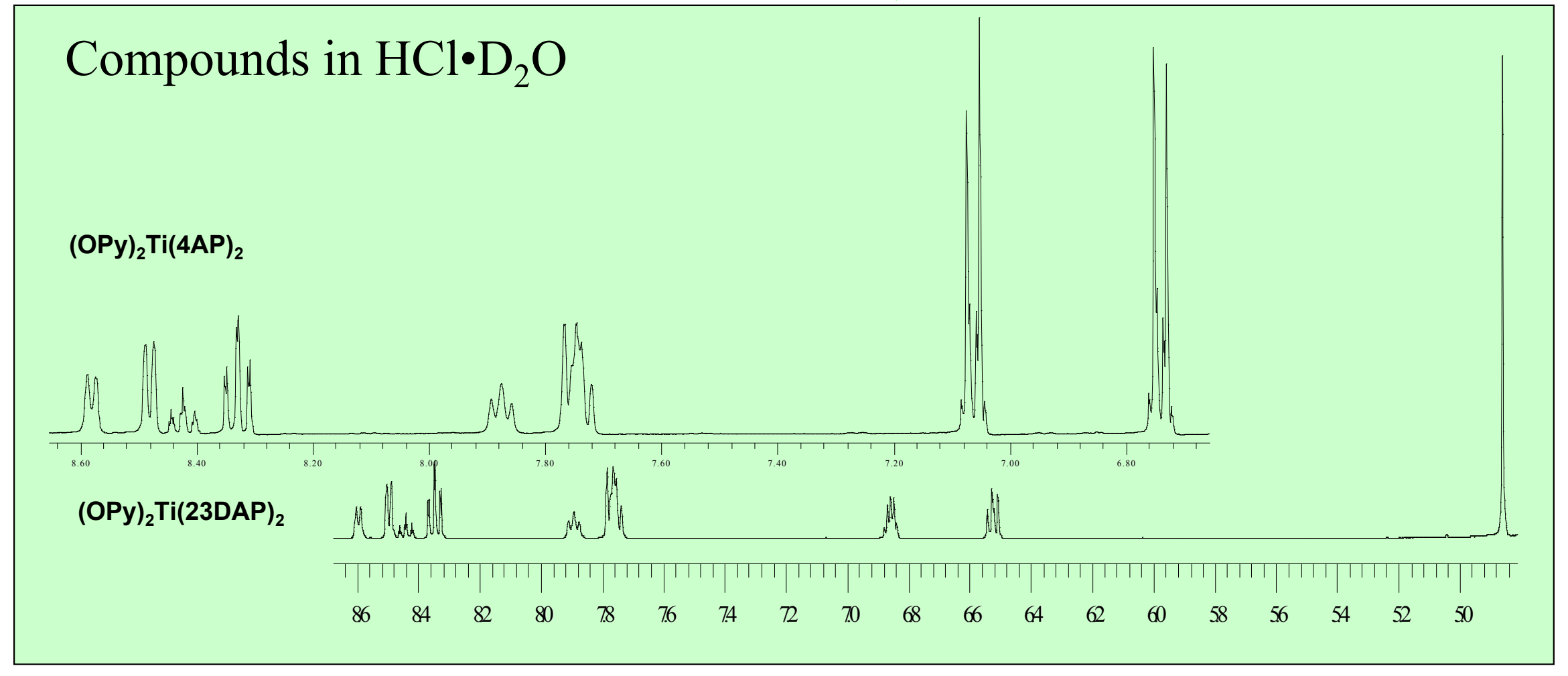
After several months, most samples show no sign of hydrolysis.

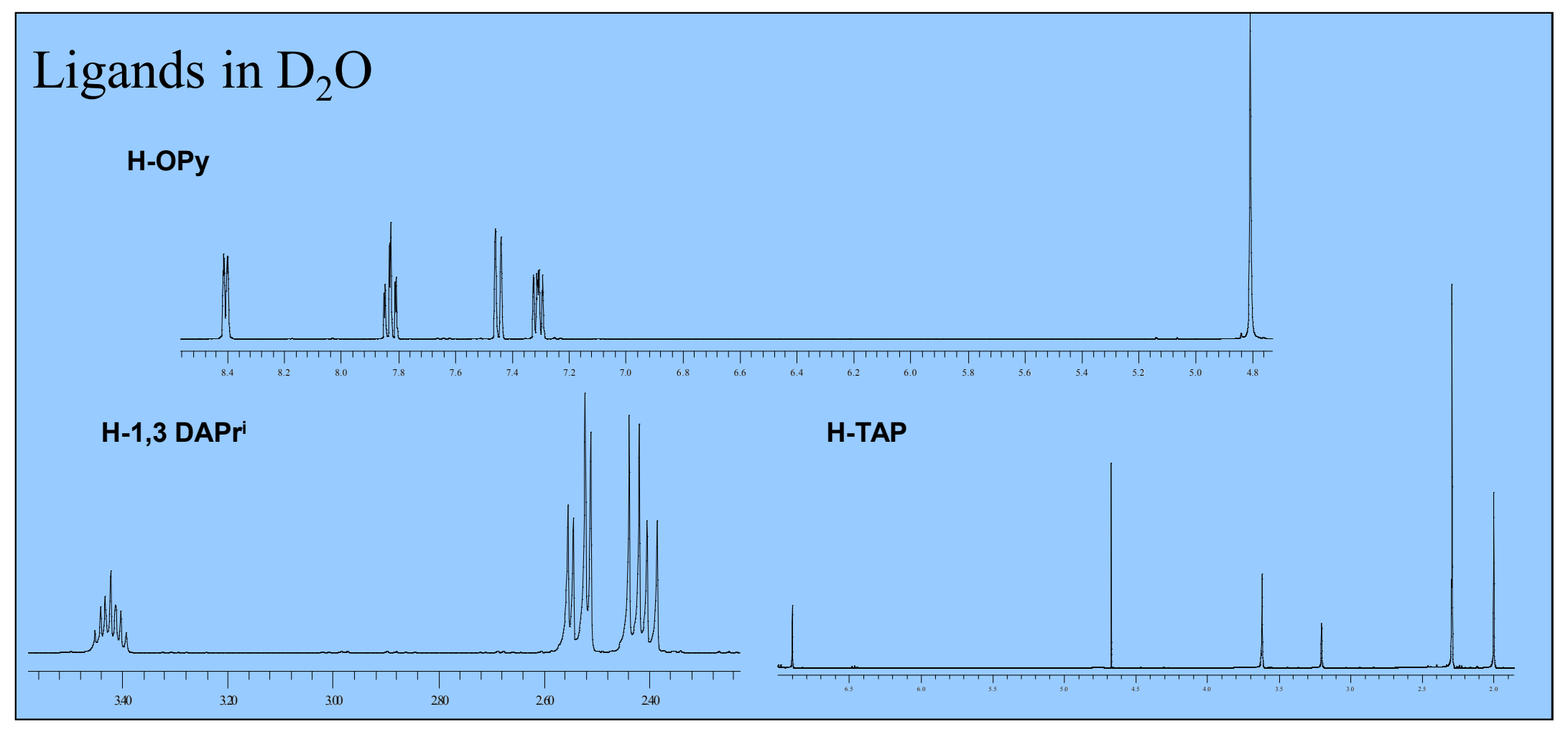


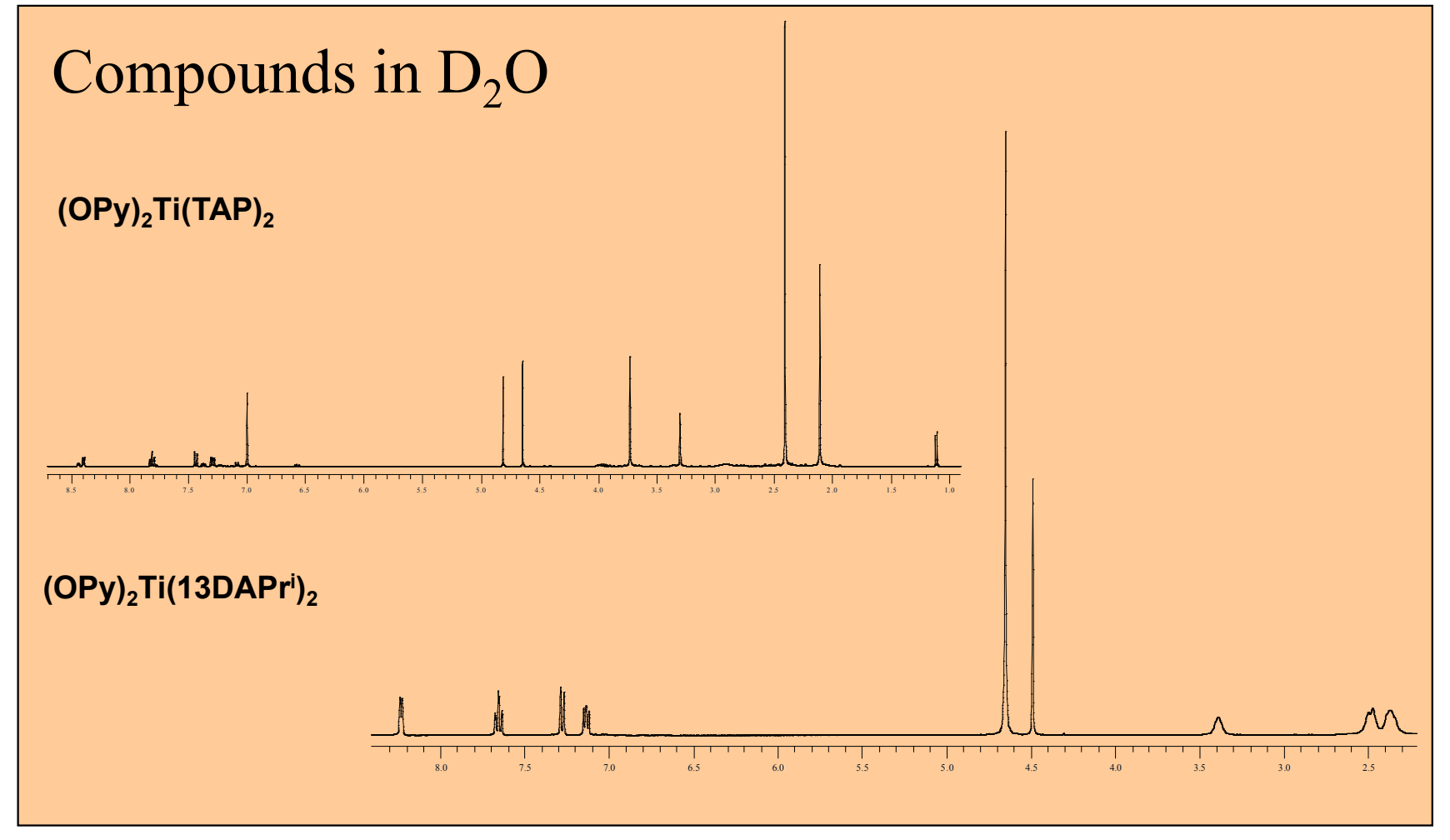
Water Soluble

$(OPy)_2Ti(TAP)_2$

$(OPy)_2Ti(13DAPr^i)_2$

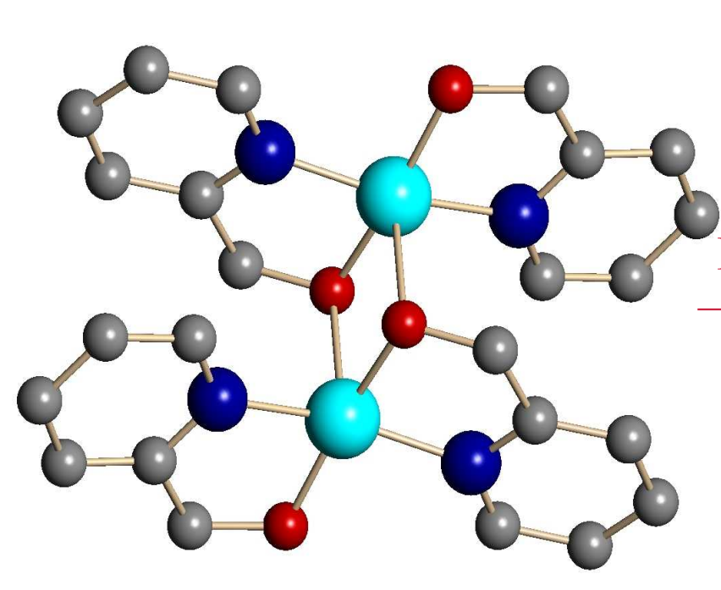

Compounds in HCl•D_2O


Ligands in D_2O

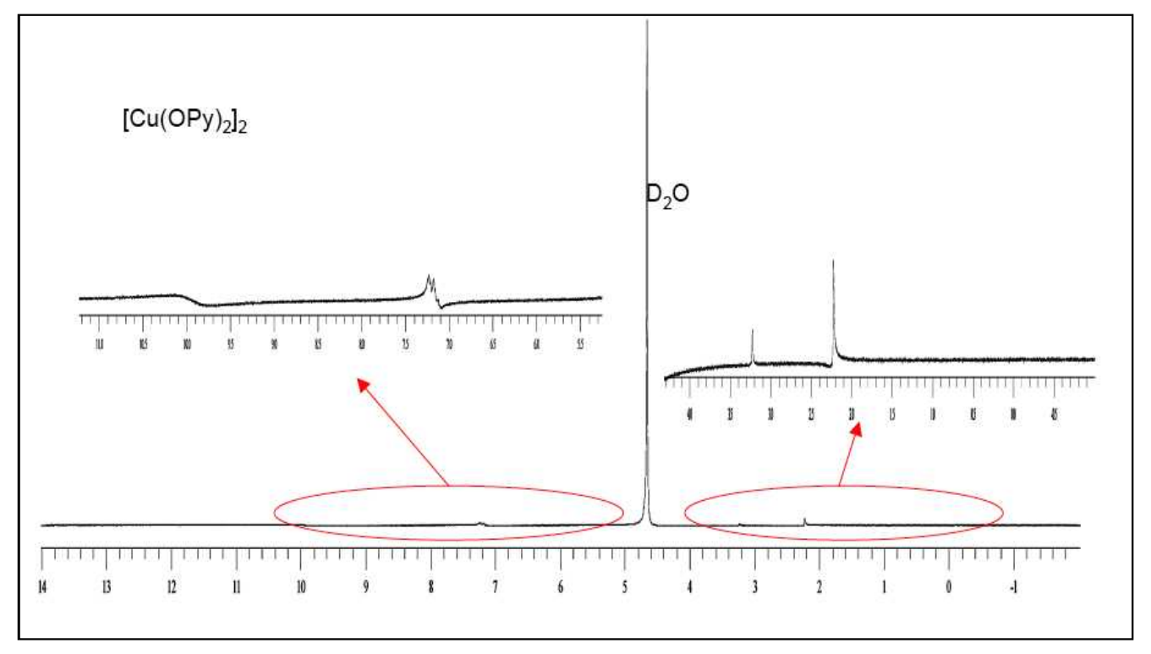

Compounds in D_2O

Copper

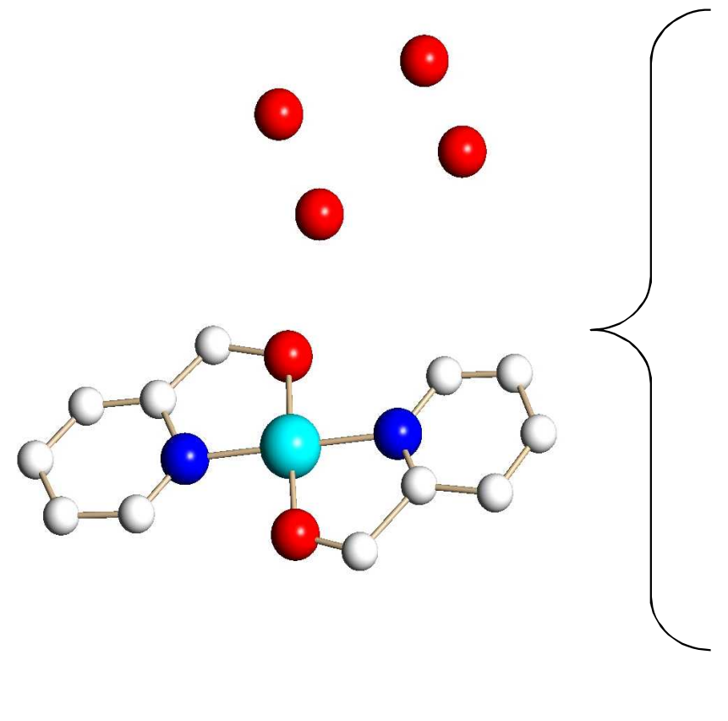
$Cu(OEt)_2 + 2\ H\text{-}OPy \longrightarrow$

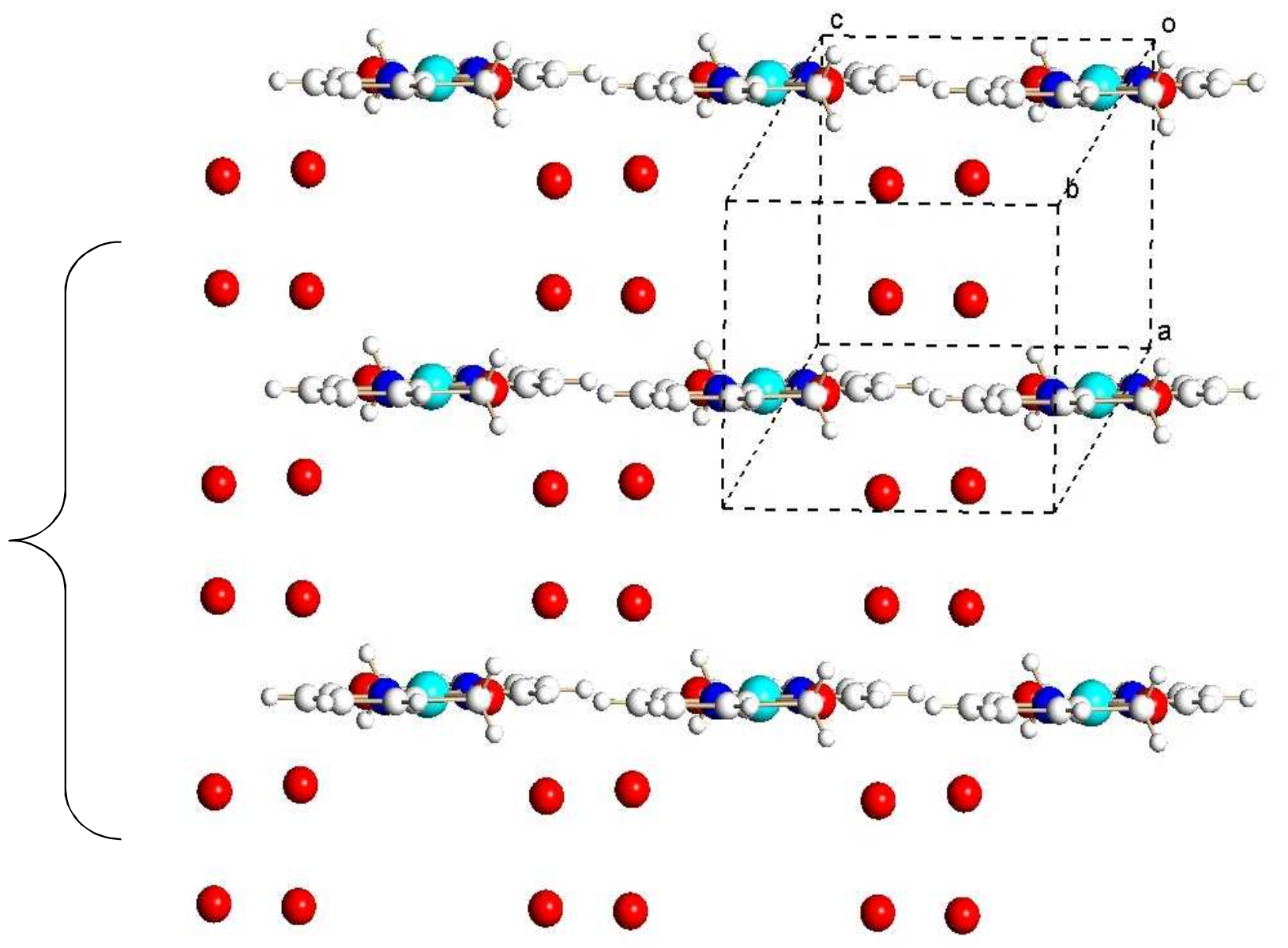

$[Cu(\mu\text{-}OPy)(OPy)]_2$

$\xrightarrow{H_2O}$



$\downarrow H_2O$

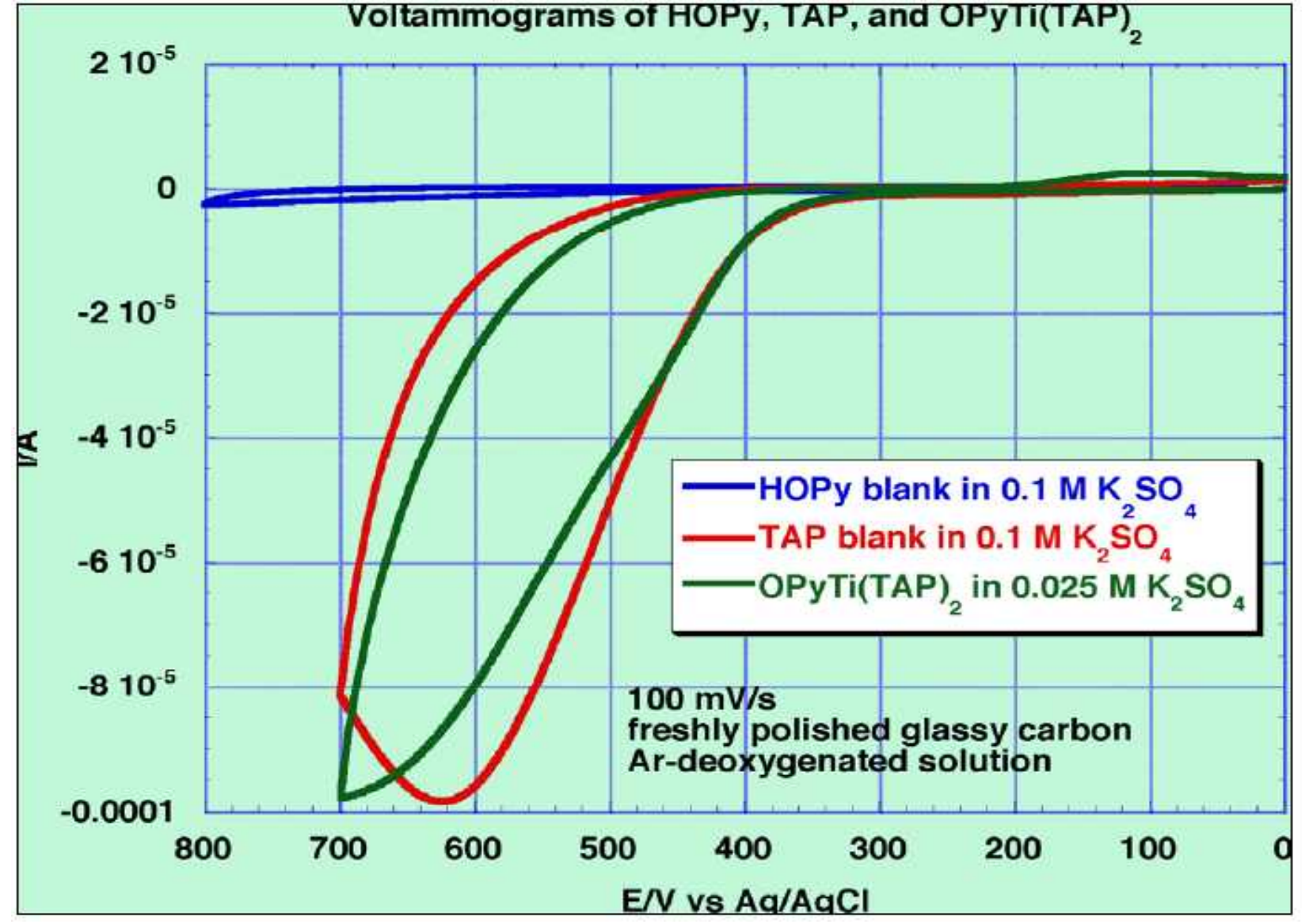

$[Cu(\mu\text{-}OPy)(OPy)\text{•}4\ H_2O$



Expansion of Unit Cell of $[Cu(\mu\text{-}OPy)(OPy)\text{•}4\ H_2O$

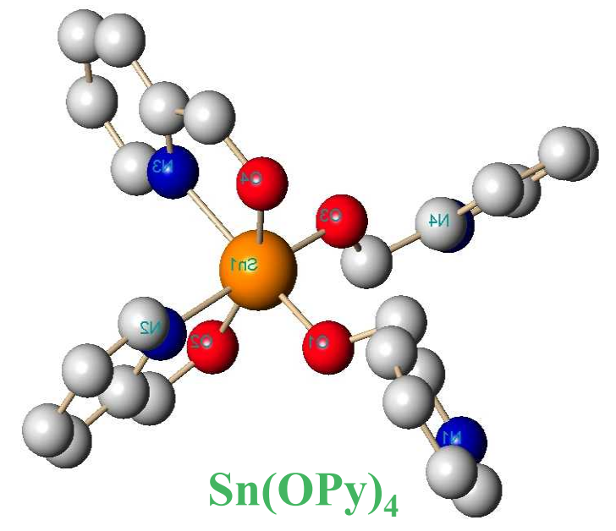
$(OPy)_2Ti(TAP)_2$

Cyclic voltammetry reveals $(OPy)_2Ti(TAP)_2$ acts electrochemically like the TAP ligand.



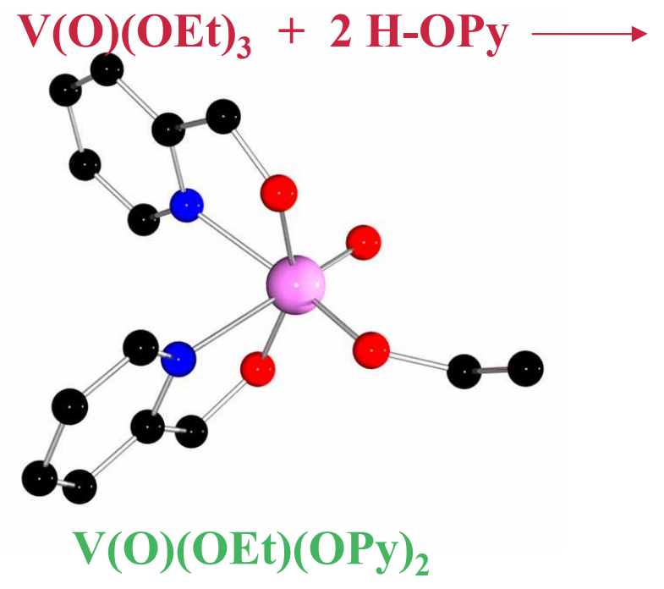
Tin

$Sn(NR_2)_4 + 4\ H\text{-}OPy \longrightarrow$

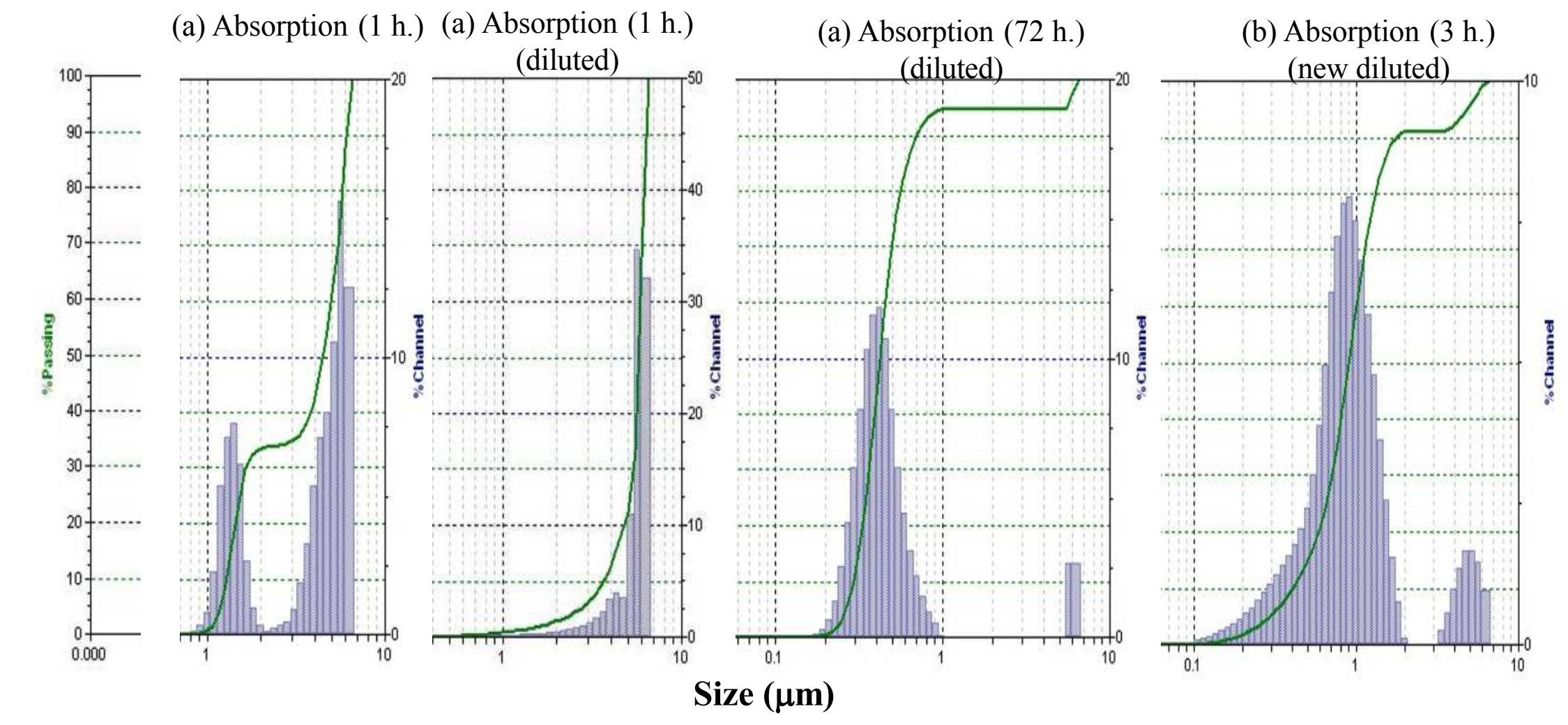

$Sn(OPy)_4$

Vanadium

$V(O)(OEt)_3 + 2\ H\text{-}OPy \longrightarrow$


$V(O)(OEt)(OPy)_2$

Dynamic light scattering was undertaken for $(OPy)_2Ti(TAP)_2$ in water. Two samples: (a) almost dissolved and (b) one fully dissolved.



Summary and Conclusion

We have synthesized and characterized metal alkoxides from across the periodic table derivatized with the bidentate OPy ligand. Investigations reveal the "$(OPy)_2Ti$" moiety is stable to controlled substitution under standard inert atmosphere conditions. If the substituent on this moiety has NR_2 groups, they can be easily solublized in water using HCl to form the *in situ* salt. In addition, the $DAPr^i$ and TAP derivatives have been characterized as water soluble *and* stable oils, possibly forming micelles on the order of 1 μm. A number of the OPy derivatives for other metals were also identified and characterized as water stable as well.

This work supported by the Department of Energy, Office of Basic Energy and Science and the United States Department of Energy under contract number DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the United States Department of Energy.