

Titanous Ions Destroy Perchlorates

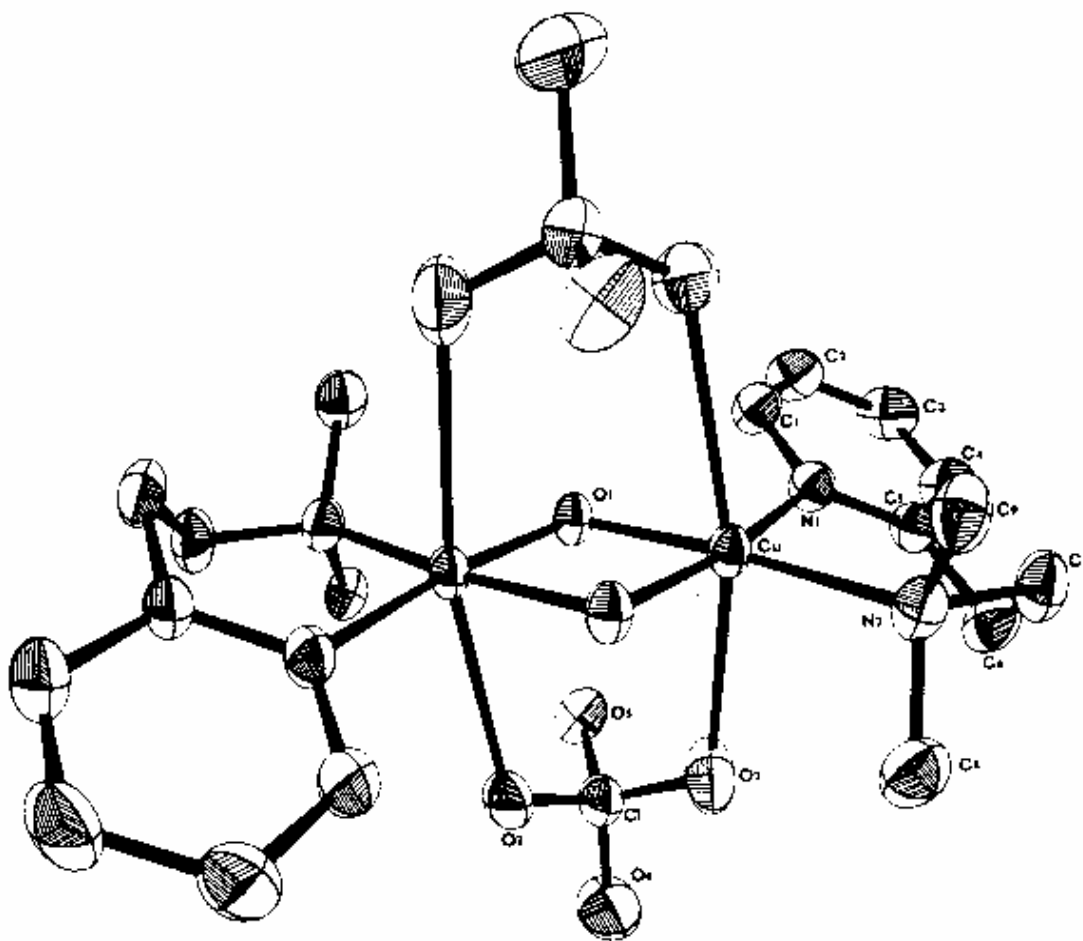
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Summary

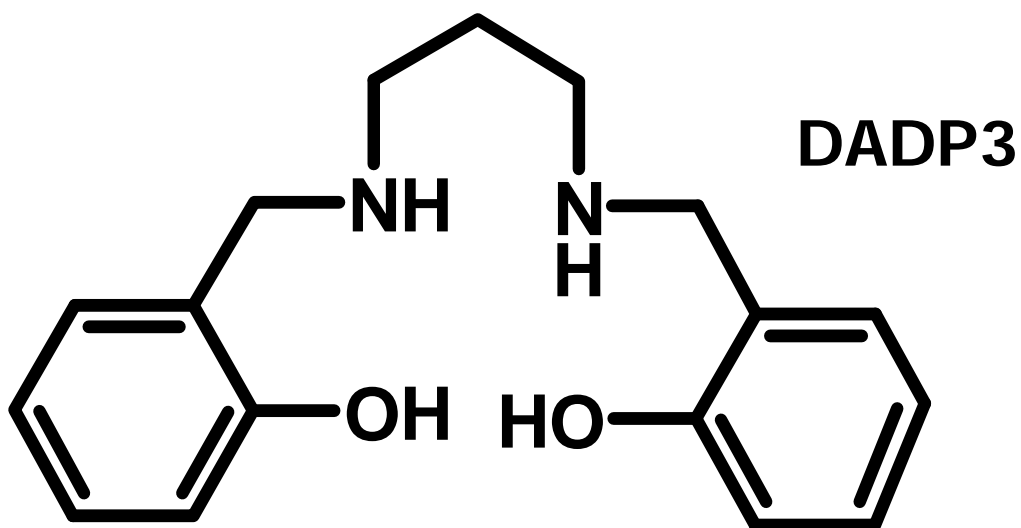
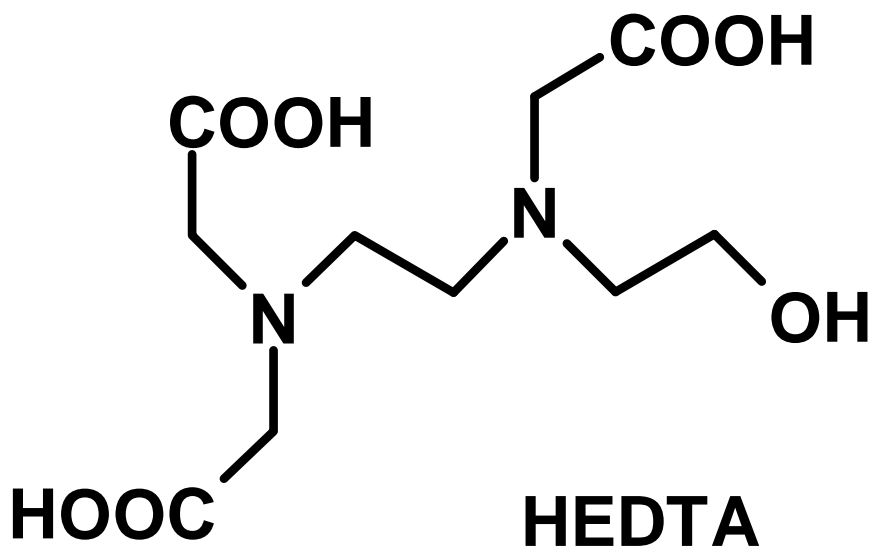
- Last year, in New Orleans, we reported that, in ethanolic media, Ti^{III} reduces perchlorate rather rapidly.
- Evidence indicates an intermediate with *two* Ti^{III} centers.
- We have designed catalysts based on these results. (Patent applied for.)
- Development opportunities exist.

Perchlorato-Cu^{II} complex

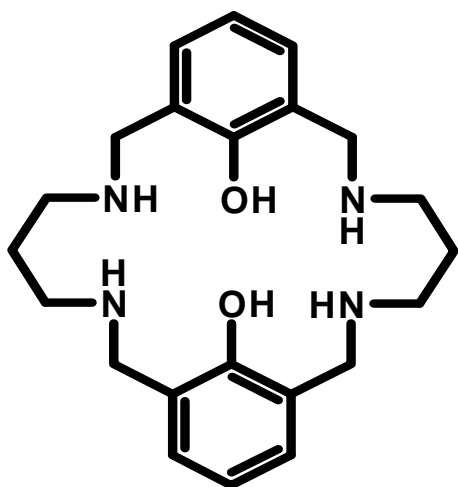
Lewis, Hatfield, Hodgson, *Inorg. Chem.* **13**, 1974, 147.



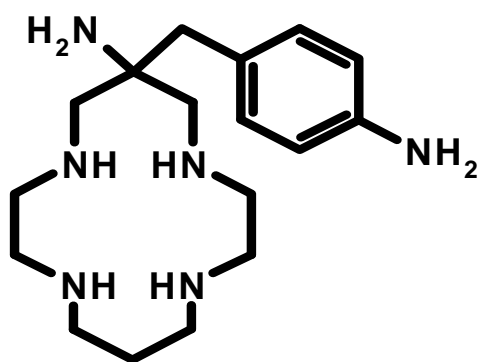
Two Old Ligands



Two New Ligands

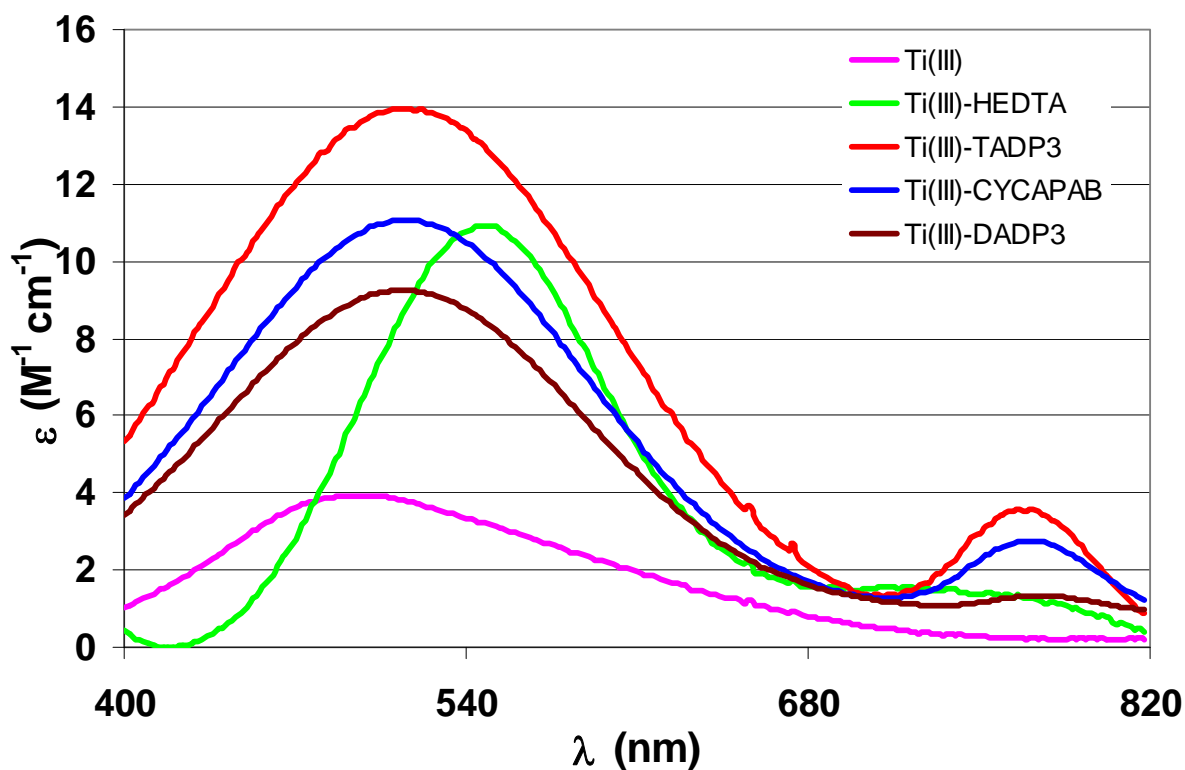


TADP3



CYCAPAB

Ligands Influence Spectra



Suggestions of Dinuclear Ions

- Pecsok & Fletcher (*Inorg. Chem.* 1962, 1, 155) observed that absorption between 730 nm and 800 nm (due to polymers?) slowly developed in Ti(III) solutions of pH 3.9.
- Absorption observed in this spectral region for our systems suggests the presence of dinuclear Ti(III) species.
- Absorption at 778 nm of Ti^{III} complexes followed the trend: **TADP3 > CYCAPAB > DADP3 \cong HEDTA >> Aquoion.**

The $\text{Ti}^{\text{III}}\text{L} - \text{ClO}_4^-$ Reaction

- With reductant in excess, the initial product is chlorate, the final product is chloride.
- With perchlorate in excess, disappearance of Ti^{III} is exponential in time.
- First order rate constant is proportional to perchlorate concentration.

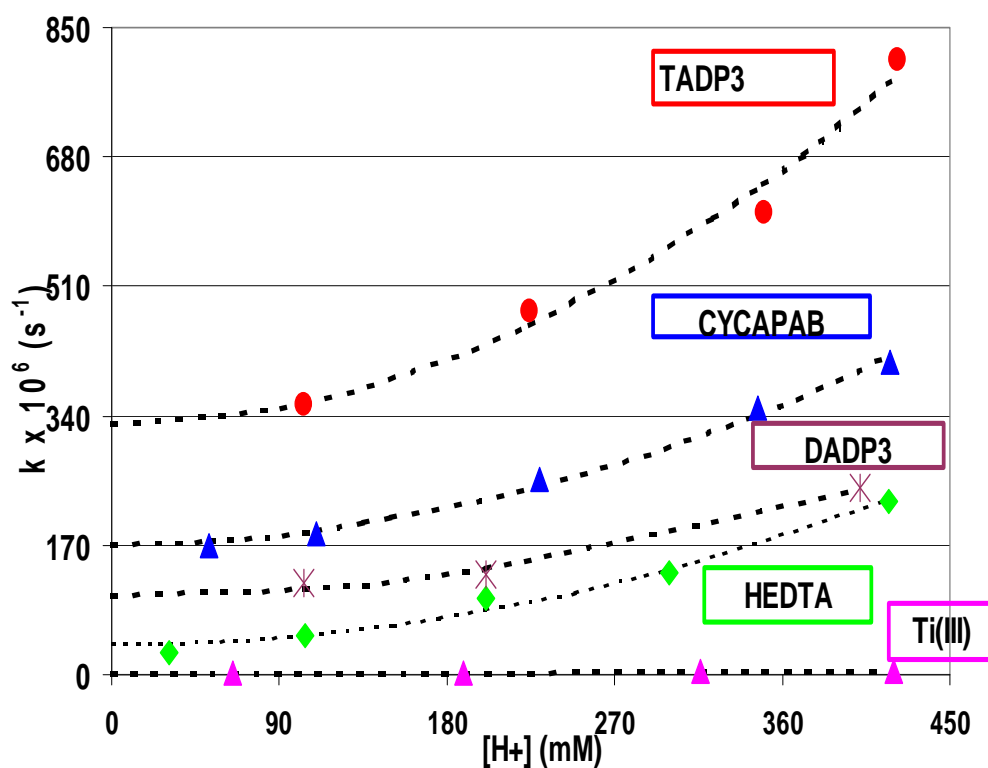
Acid Catalysis

- Pseudo-first order rate constants increase as $[H^+]$ increases.
- Curvature indicates contribution from a rate-law term second order in $[H^+]$.
 $k_{obs} = k_0 + k' [H^+]^2$
- At $[H^+] = 432$ mM, rate constants (k) are:

TADP3 (158) > CYCAPAB (86) > DADP3 (48) ≥ HEDTA (44) > H₂O (1)

- *Species that absorb strongly at 778 nm react rapidly, suggesting a dinuclear complex as intermediate.*

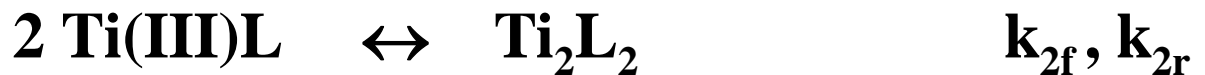
Acid Catalysis Is Nonlinear



An Unusual Kinetic Feature

- Each run yields a first-order rate constant.
- But, strangely enough, the value of that constant *increases* as $[\text{Ti}^{\text{III}}]$ increases.
- A mechanism involving a dinuclear intermediate models this behavior.

Mechanistic Model

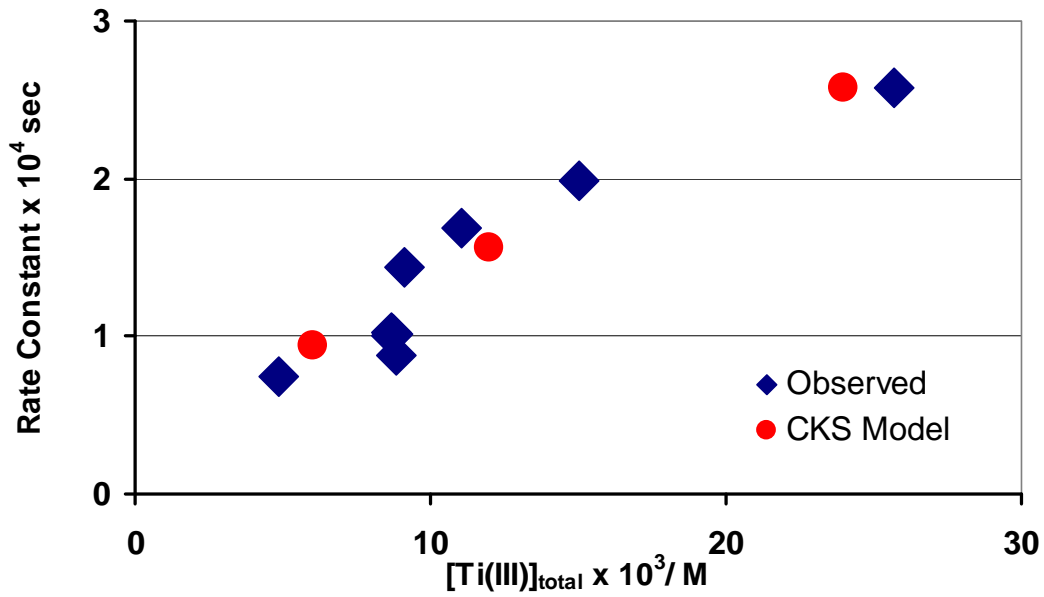


$$k_{1f} = 1000; \quad k_{1r} = 2000;$$

$$k_{2f} = 1000; \quad k_{2r} = 0.1; \quad k_3 = 0.1;$$

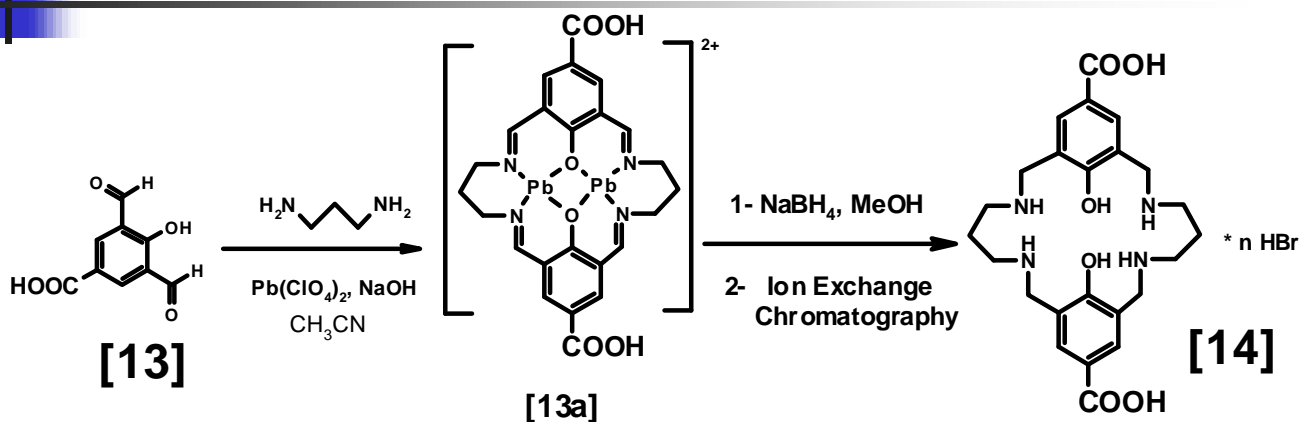
Initial particles = 8000.

The Model Fits



Synthesis of Functionalized TADP3

11,23-Dihydroxycarbonyl-25,26-dihydroxy-3, 7, 15, 19-tetraazatriciclob[19.3.1.19,13]hexacosa-1(25), 9(26), 10, 12, 21, 23-hexaene



■ $^{13}\text{C-NMR}$ ($\text{DMSO } d_6$): 168.1; 154.2; 133.1; 121.3; 120.2; 44.08; 42.00; 23.19.

■ **Elemental Analysis:**

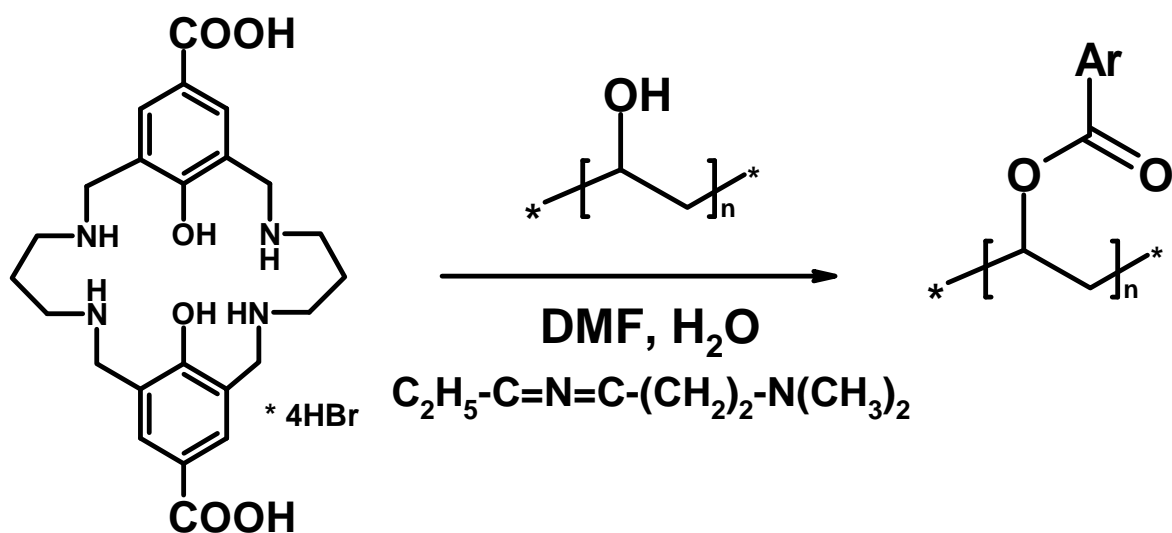
Found: C: 32.98; N: 6.54; Br: 36.71; H: 6.95.

Calculated [$\text{C}_{24}\text{H}_{34}\text{N}_4\text{O}_6 * 4\text{HBr} * 3\text{H}_2\text{O}$] C: 33.17; N: 6.45; Br: 36.78; H: 7.03.

TADP3-PVA ***Semi-Solids*** *

- Polyvinyl alcohol is the solid support of choice ($\langle MW \rangle$ 50-85 Kdal, 97% hydrolyzed)
- Preliminary experiments showed that perchlorate ions are reduced by Ti(III) more rapidly in a PVA environment than in water.
- TADP3-(COOH)₂ is a modified ligand suitable to be covalently bound to the support.

Attachment of TADP3DC to PVA



Assay of Functionalization of PVA

- Spectrophotometric determination of substituted benzene rings ($\lambda_{\text{max}} = 298 \text{ nm}$) is a rapid and reproducible method to assay the degree of PVA functionalization ($\sim 10\%$)
- Cross-linking of PVA chains is likely to occur, due to the presence of two *p*-COOH groups on the ligand.

Results

- Ti^{III} is stable in the presence of PVA (in .2M acid) for more than two weeks.
- Ti^{III} reacts with perchlorate more than two orders of magnitude faster in the presence of PVA than in its absence.
- The PVA surface environment favors reaction.

Heterogeneous Catalysis

- In .2 M acid ,Ti^{III} absorbed on ligand-modified PVA, reacts with perchlorate *more than two orders of magnitude faster* than does Ti^{III} absorbed on PVA.
- Ti^{III} is in excess over ligand.
- The PVA-fixed ligand is an effective catalyst.

A New Chemical Principle

- Ligands that favor dinuclear complex-formation, when attached to a semisolid support with an alcohol-like surface, act as effective catalysts for reduction of perchlorate ions by Ti^{III} .
- The sample system increases rate > 10000 fold.

Prospects

- Ti^{IV} can be reduced to Ti^{III}
 - chemically
 - electro-chemically
 - photo-chemically
- Flow and batch systems can be developed to use this new chemical principle for destruction of perchlorates.

Advantages

- Titania (TiO_2) is cheap, abundant and environmentally benign.
- Optimization of ligand, support-system, and regeneration method can yield rapid, cheap, and safe methods of perchlorate disposal.

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