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IS

5th Workshop of the Italian Astrobiology Society

Life in a Cosmic Context

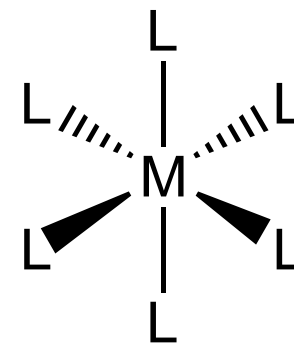
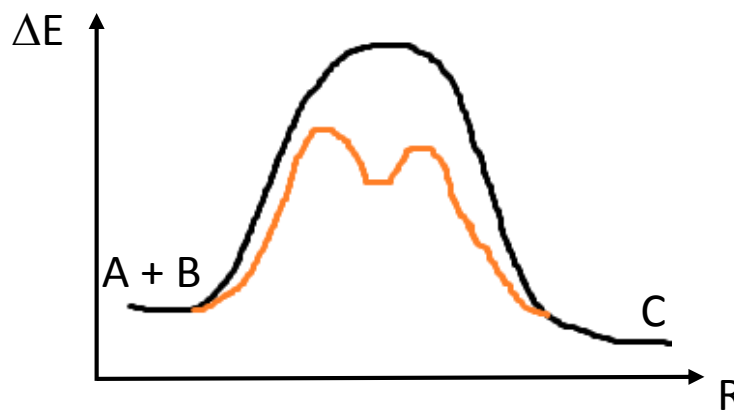
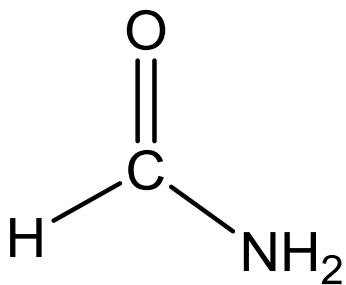
15-17 September 2015, Trieste, Italy



Metal-Formamide Complexes and their Role in Prebiotic Chemical Catalysis

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Tohoku University

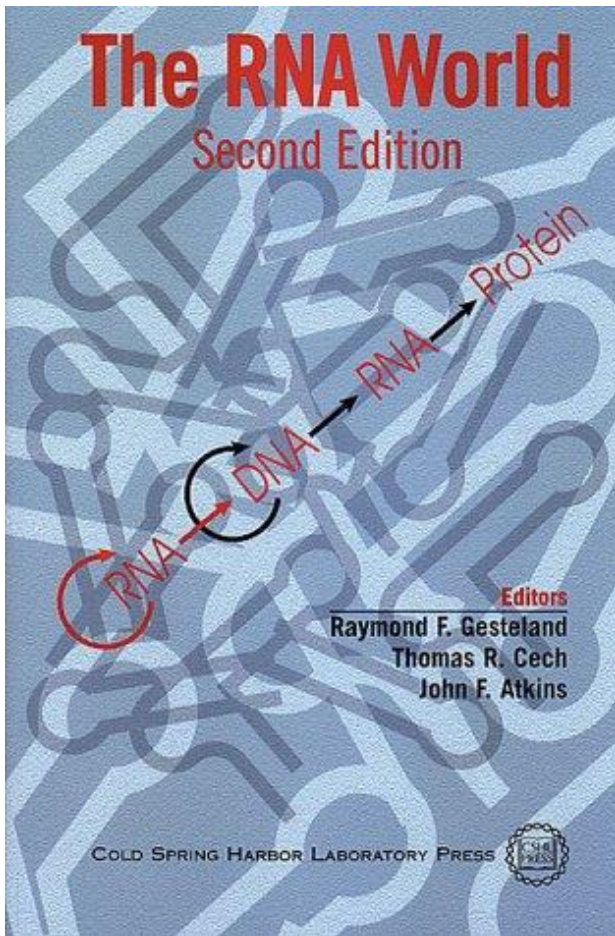


Outline

- RNA \leftarrow nucleobases \leftarrow formamide
- Formamide coordination to metals
- Structure of metal-formamide complexes (Experimental studies)
- **Iron-formamide** complexes (computational studies)
- Homogeneous prebiotic catalysis

The RNA World Hypothesis

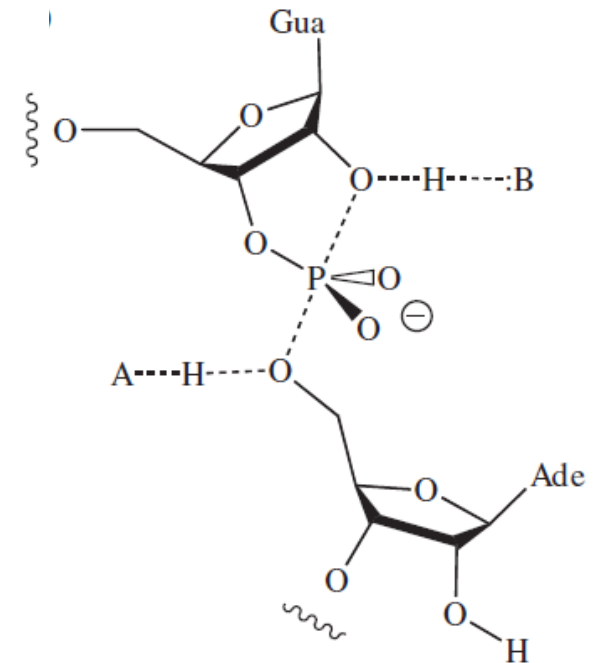
Carl Woese (1967), Leslie Orgel (1968), Francis Crick (1968)



RNA: informational molecule & catalyst (Ribozymes)

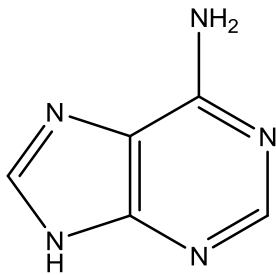


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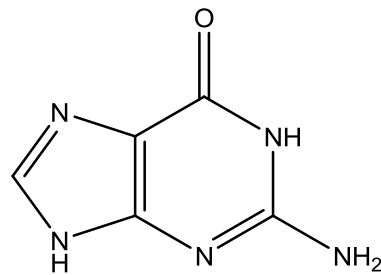


Lilley, *Phil. Trans. R. Soc.* (2011)

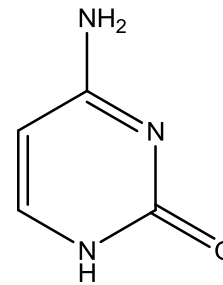
RNA Nucleobases



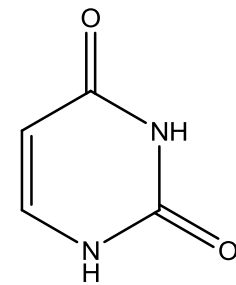
Adenine



Guanine



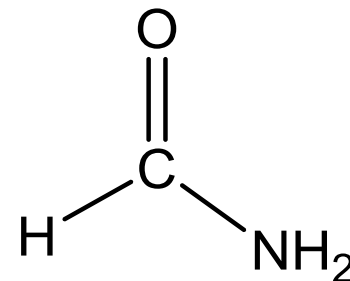
Cytosine



Uracil

Q: What are the possible chemical precursors?

The Formamide Clue:



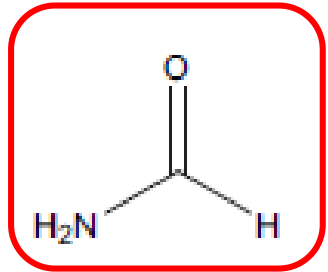
Raffaele Saladino, Ernesto Di Mauro and coworkers:

“...we suggest the possibility that formamide could have jointly provided the main components for the onset of both (pre)genetic and (pre)metabolic processes [concerned with the origins of Life]”

[Saladino et al., *Chem. Soc. Rev.* 41 (2012) 5526]

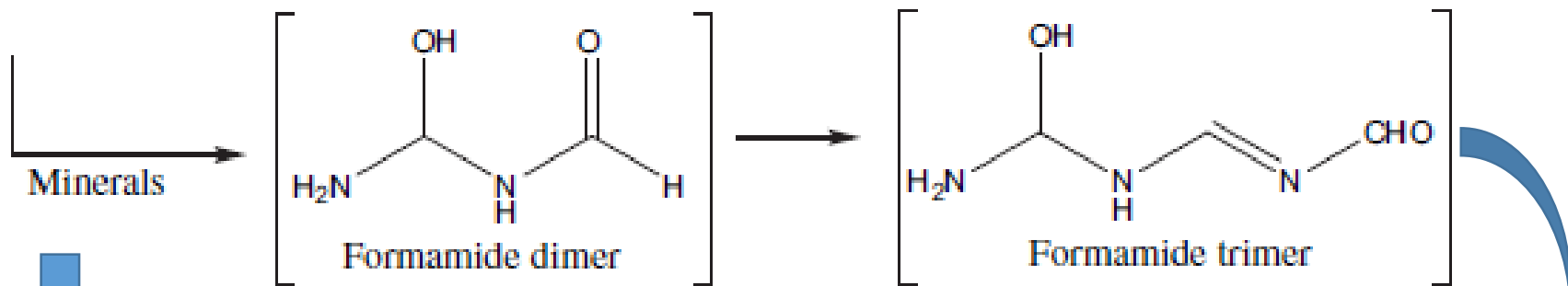
⇒ Wednesday morning session ⇐

Mineral catalysts in prebiotic chemistry



Formamide

Saladino et al., *Res. Microbiol.* (2009)



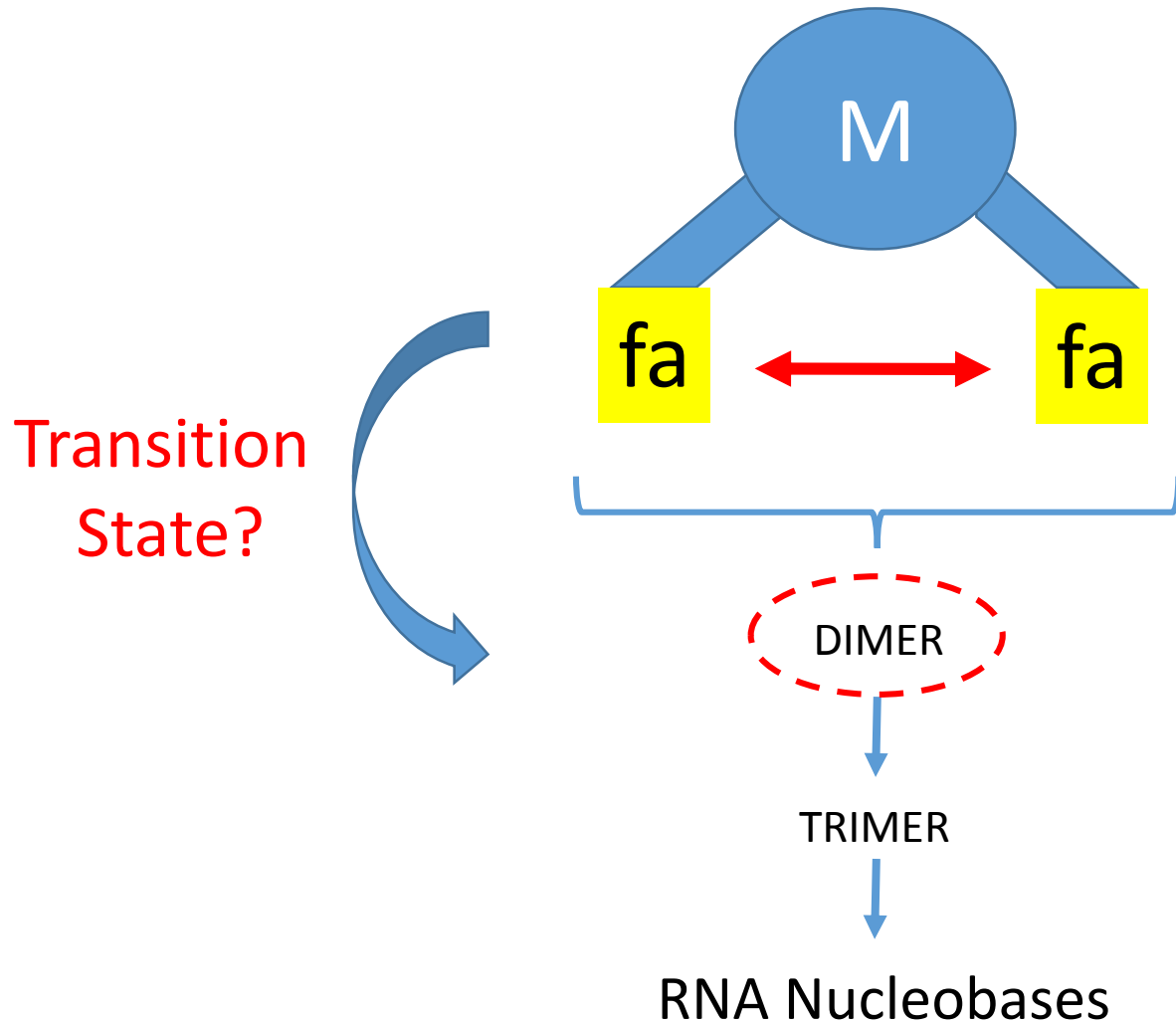
Mineral dissolution
(in formamide or fa/water media)

$M^{n+}(\text{solv})$

RNA
nucleobases

Structure & properties of coordination complexes

Metal-formamide complexes: Role of the Metal Center



Q: How does formamide bind
(coordinate) metal ions?

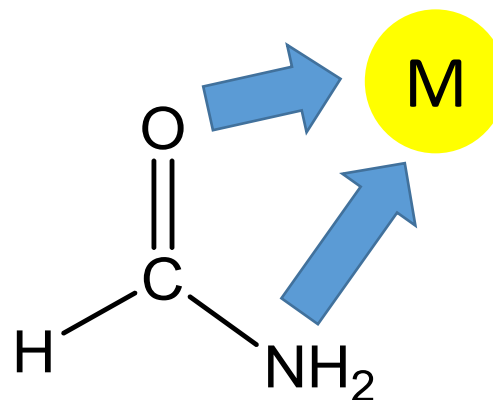
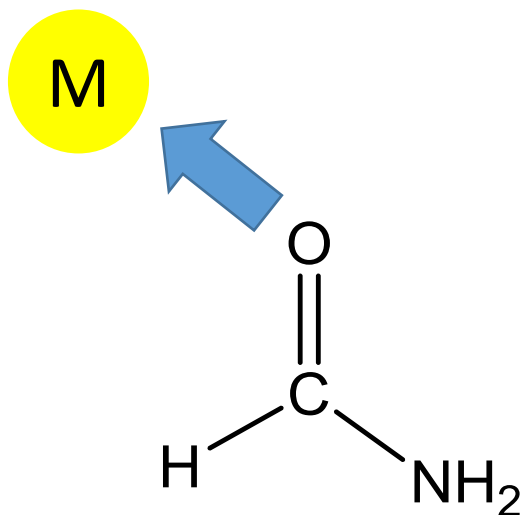
Vibrational spectra of metal formamide complexes

D. B. POWELL and A. WOOLLINS

School of Chemical Sciences, University of East Anglia, Norwich, NR4 7TJ, U.K.

(Received 20 August 1984)

Abstract—Compounds of the form $\text{MX}_2(\text{amide})_n$ have been prepared ($\text{M} = \text{Mn, Fe, Co, Ni, Cu, Cd, Hg, Pd}$ and Pt ; $\text{X} = \text{Cl, Br}$; amide = formamide, *N*-methyl formamide and *N,N*-dimethyl formamide; $n = 1, 2$ and 4) and studied by i.r. and Raman spectroscopy. Complete assignments of the spectra are proposed. The majority of the complexes were found to be oxygen co-ordinated with the exception of $\text{NiCl}_2(\text{nmf})_4$, $\text{NiCl}_2(\text{dmf})_2$ and $\text{CuCl}_2(\text{dmf})_2$ which showed signs of both oxygen and nitrogen co-ordination.



Cambridge Structural Database (CSD)

- Maintained by the **Cambridge Crystallographic Data Centre** (CCDC)
- Home-page: www.ccdc.cam.ac.uk
- ~800,000 crystal structures (X-ray & neutron diffraction analyses)

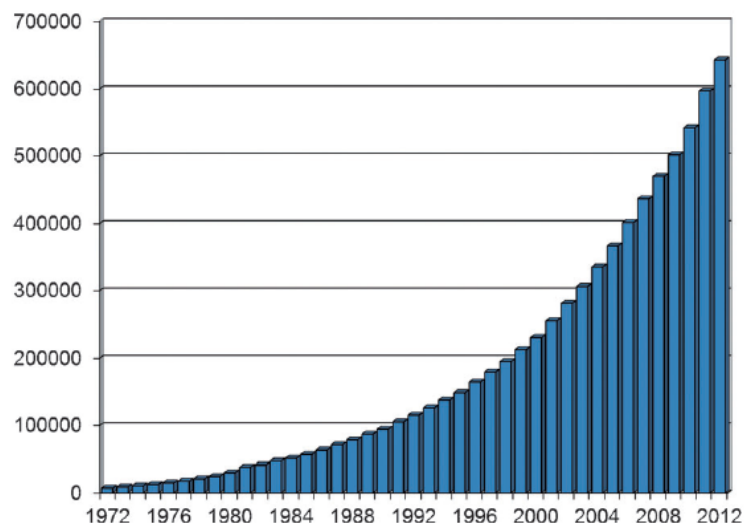
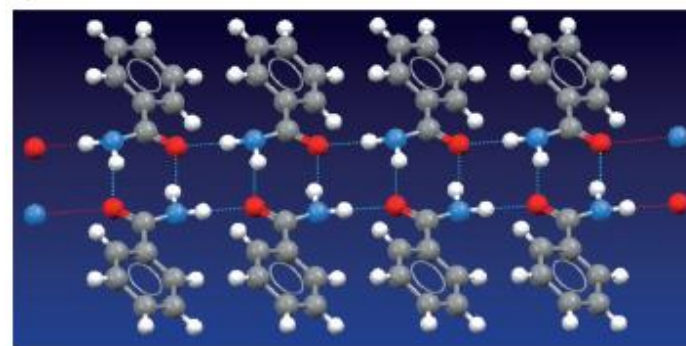
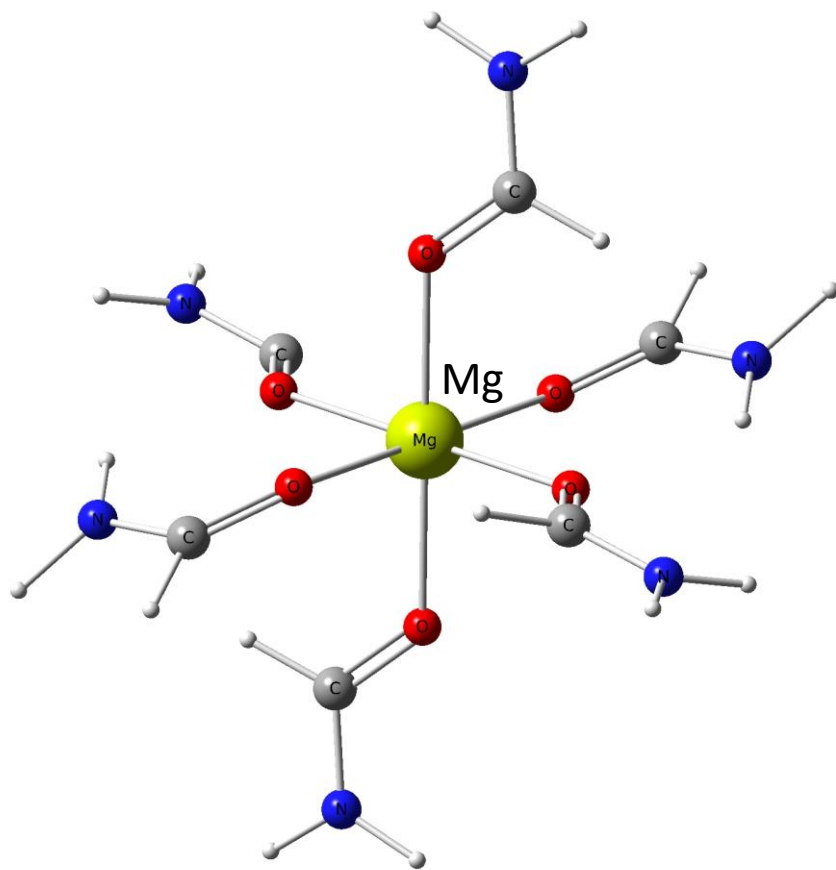


Figure 1. Annual growth of the Cambridge Structural Database from 1970 to 2012.



Packing of benzamide molecular crystal

Crystallographic Data for $[\text{Mg}(\text{fa})_6]^{2+}$ Complex



Oh coordination

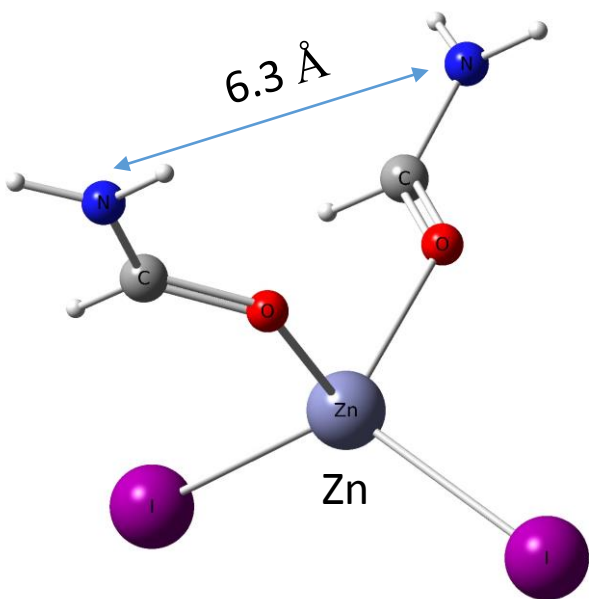
PINFEX

$$d_{\text{NN}} = 4.5\text{-}6.4 \text{ \AA}$$

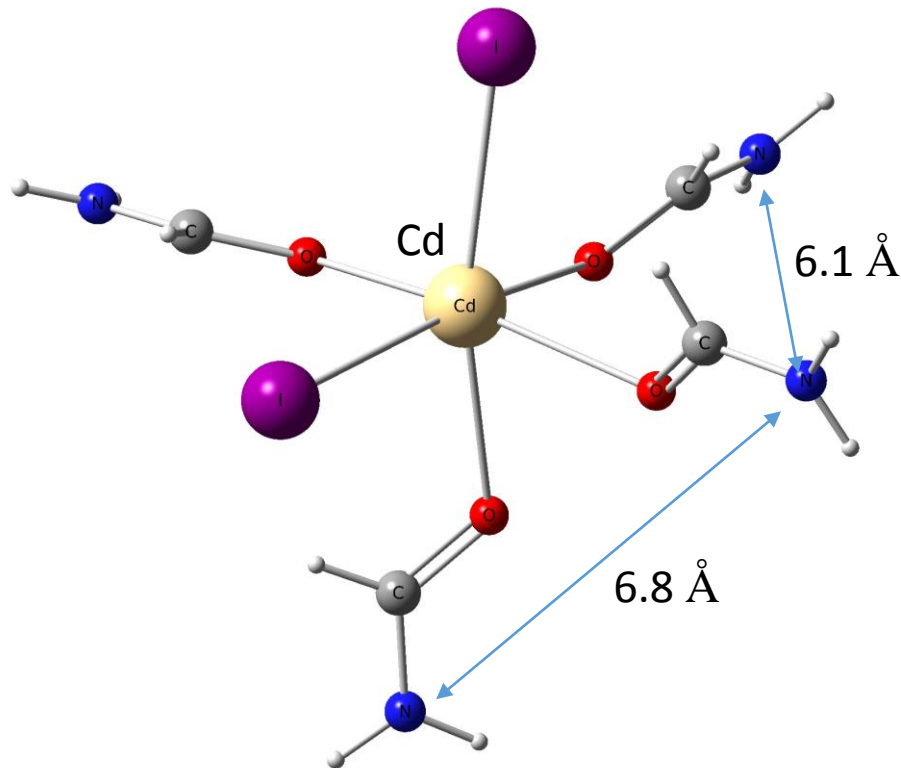
The only known example
of Oh metal complex with
six formamide ligands!!!

Chloride counterions are H-bonded
to the NH_2 groups

Crystallographic Data for M-fa Complexes with Iodide (I⁻)

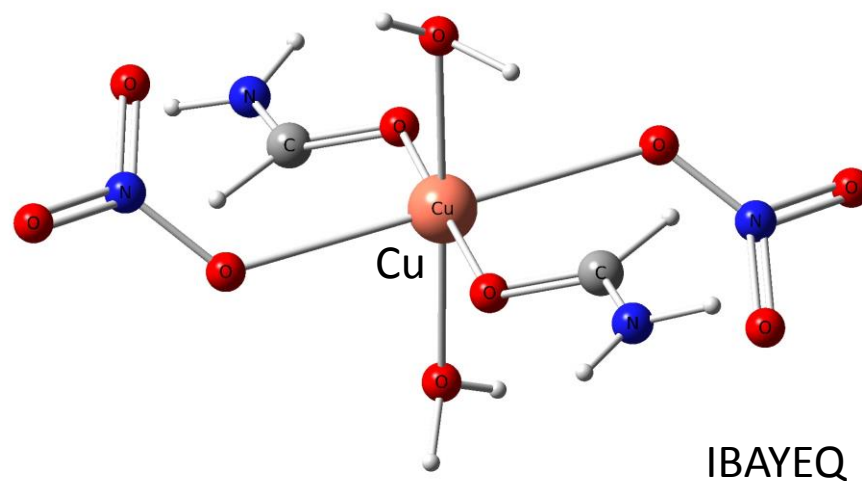
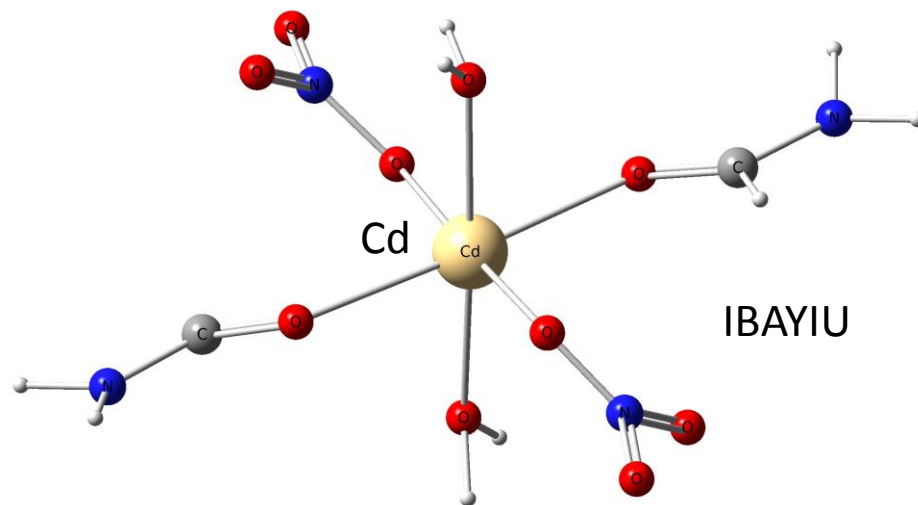
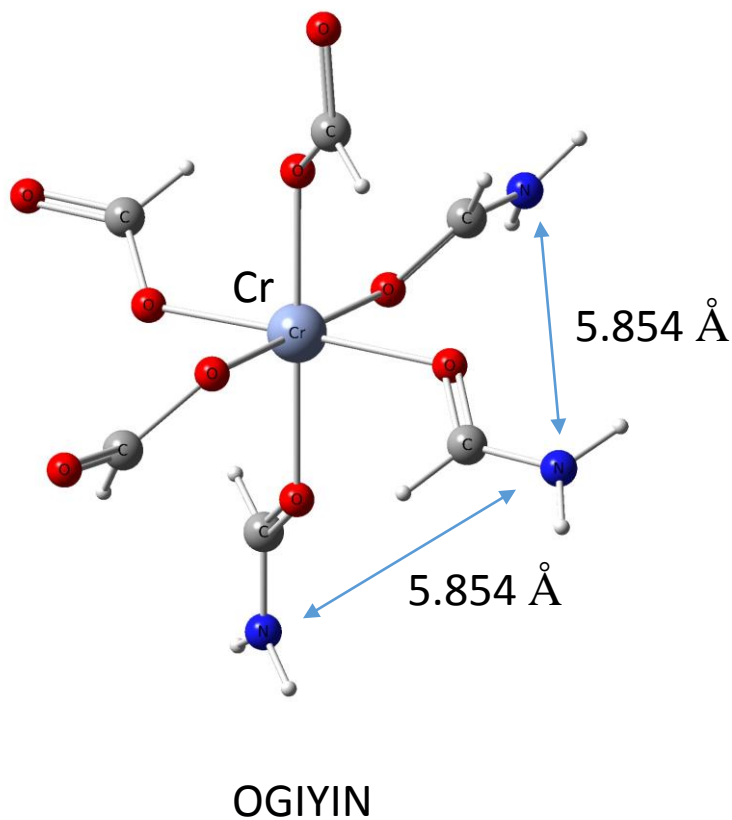


Td coordination
DIYGUO

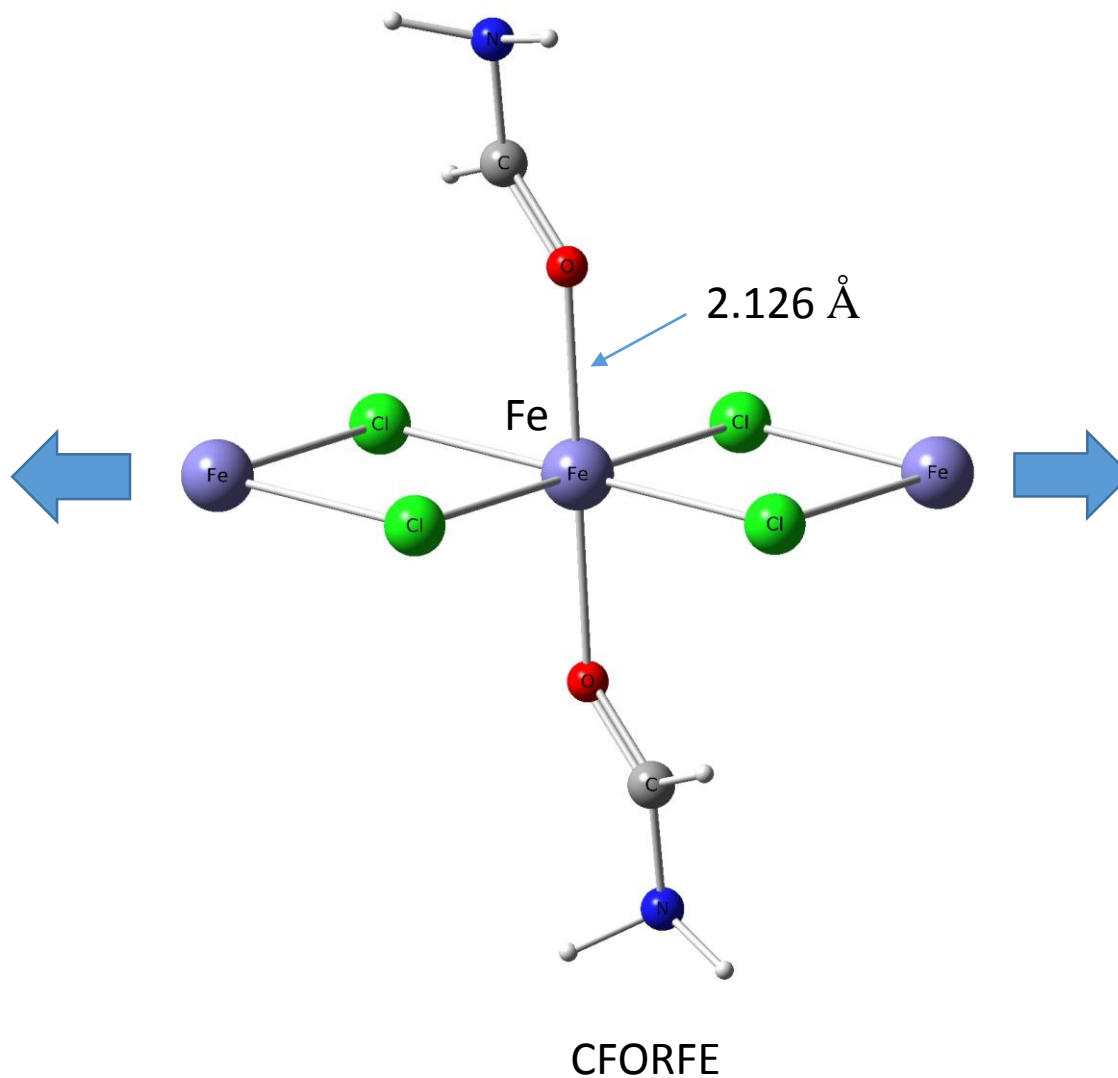


Distorted Oh coordination
XOCKAD

Crystallographic Data for M-fa Complexes with Anions (NO_3^- , HCOO^-) and H_2O



Example of a Polymeric Fe-fa Complex



Summary (crystallographic data)

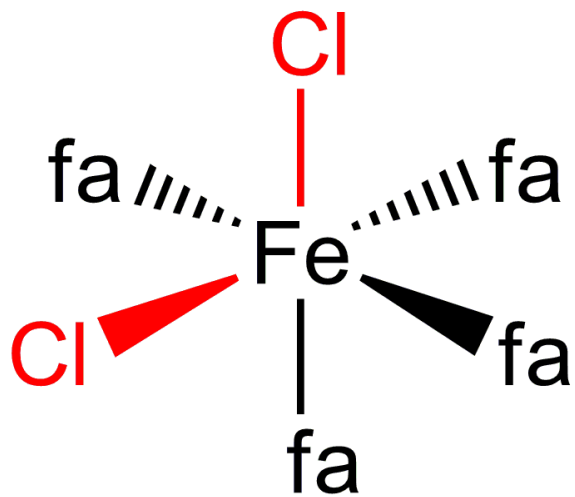
- Formamide (fa) binds the metal ion through its oxygen atom ($\text{O}:\rightarrow\text{M}$)
- No evidence for O and N binding (chelation)
- Other (neutral or charged) ligands can be present on M together with formamide
- Spatial proximity of coordinated fa molecules is achieved in M-fa complexes ($d_{\text{NN}_{\text{min}}} \sim 5.0 \text{ \AA}$)

Table 6. Metal–oxygen and metal–halogen stretching frequencies (cm^{-1}) of the first row transition metal formamide complexes

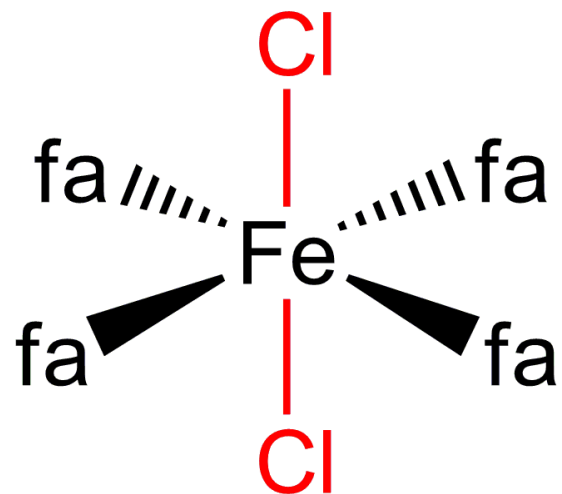
	$\nu\text{M-O}$		$\nu\text{M-X}$	
	i.r.	R	i.r.	R
$\text{MnCl}_2(\text{fa})_4$	234	232	148	136
$\text{FeCl}_2(\text{fa})_4$	250		150	143
$\text{CoCl}_2(\text{fa})_4$	230	224	146	155
$\text{NiCl}_2(\text{fa})_4$	252	237	166	168
$\text{CuCl}_2(\text{fa})_2$	304	298	266	229
$\text{MnBr}_2(\text{fa})_4$		236		114
$\text{CoBr}_2(\text{fa})_4$	235	223	126	116
$\text{NiBr}_2(\text{fa})_4$	287	235	120	128
$\text{CuBr}_2(\text{fa})_2$	290	289	126	130



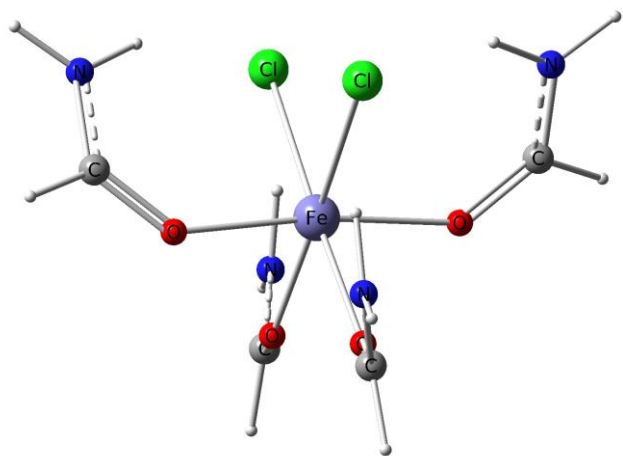
$\text{FeCl}_2(\text{fa})_4$ complex: *cis-trans* isomerism



cis

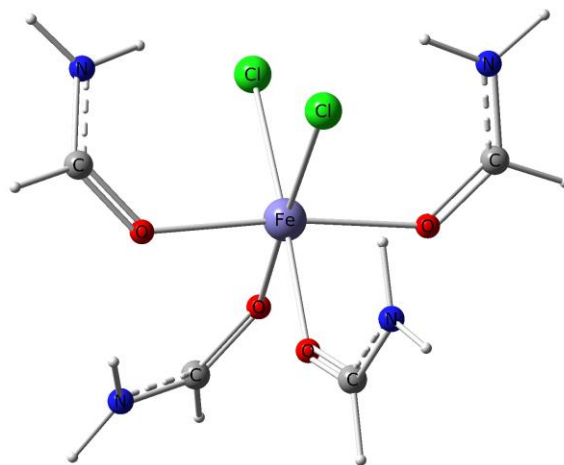
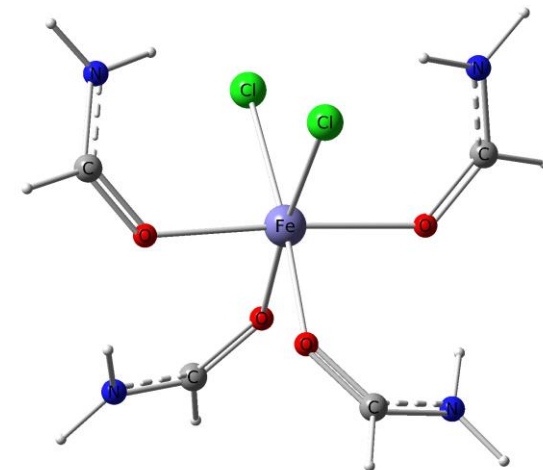


trans

$cis\text{-FeCl}_2(\text{fa})_4$ complexes: rotational isomers

4 x NH...Cl

+stable

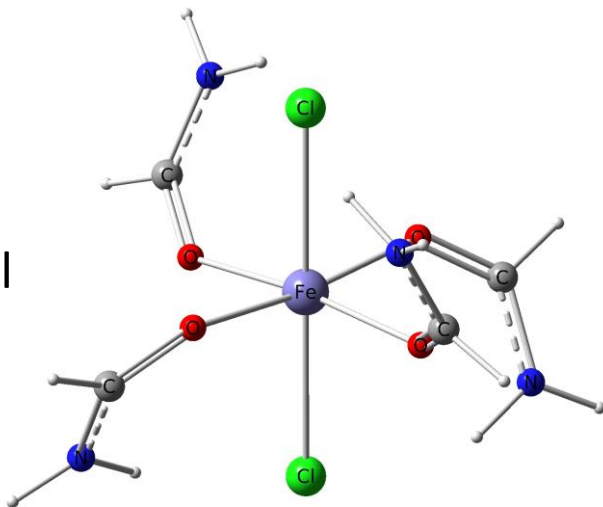
3 x NH...Cl
1 x NH...O2 x NH...Cl
2 x NH...O

-stable

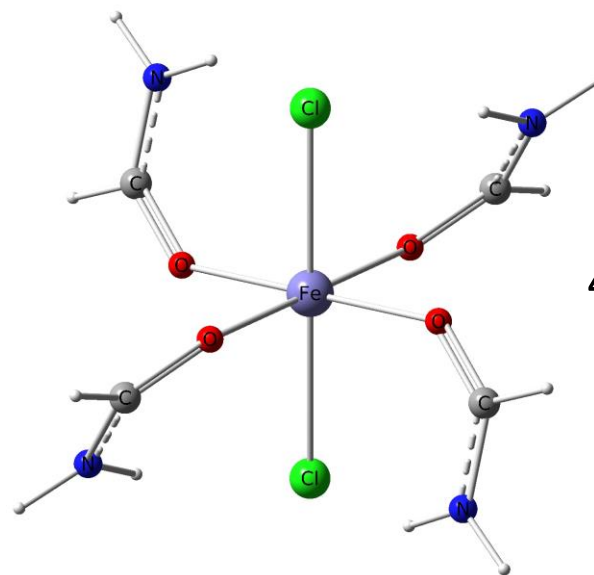
$trans\text{-FeCl}_2(\text{fa})_4$ complexes: rotational isomers

4 x NH:::Cl

+stable

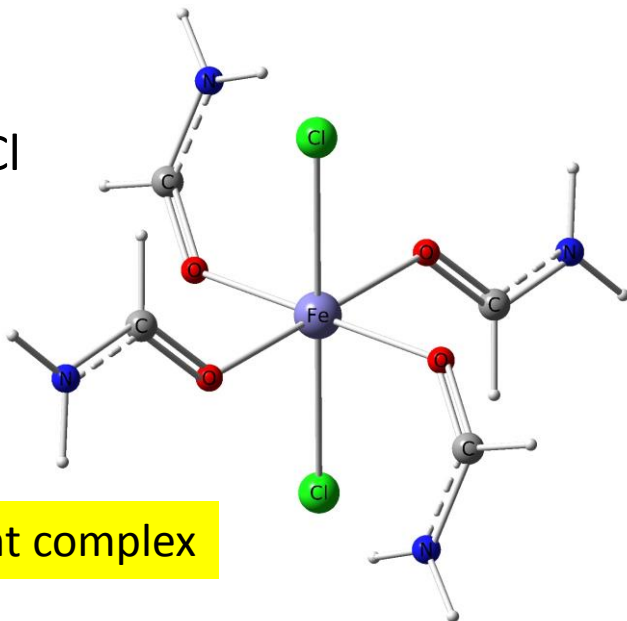


4 x NH:::Cl



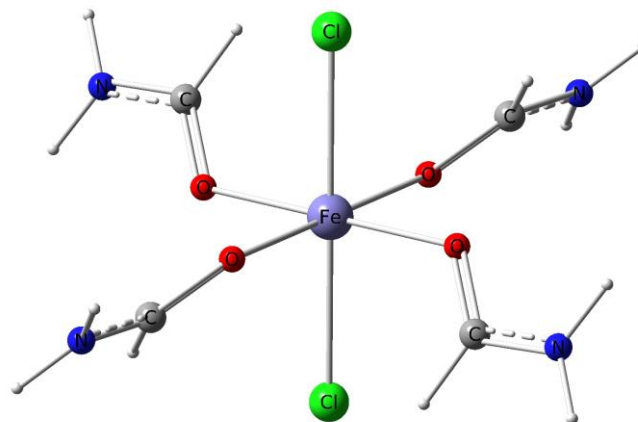
2 x NH:::Cl

Reactant complex

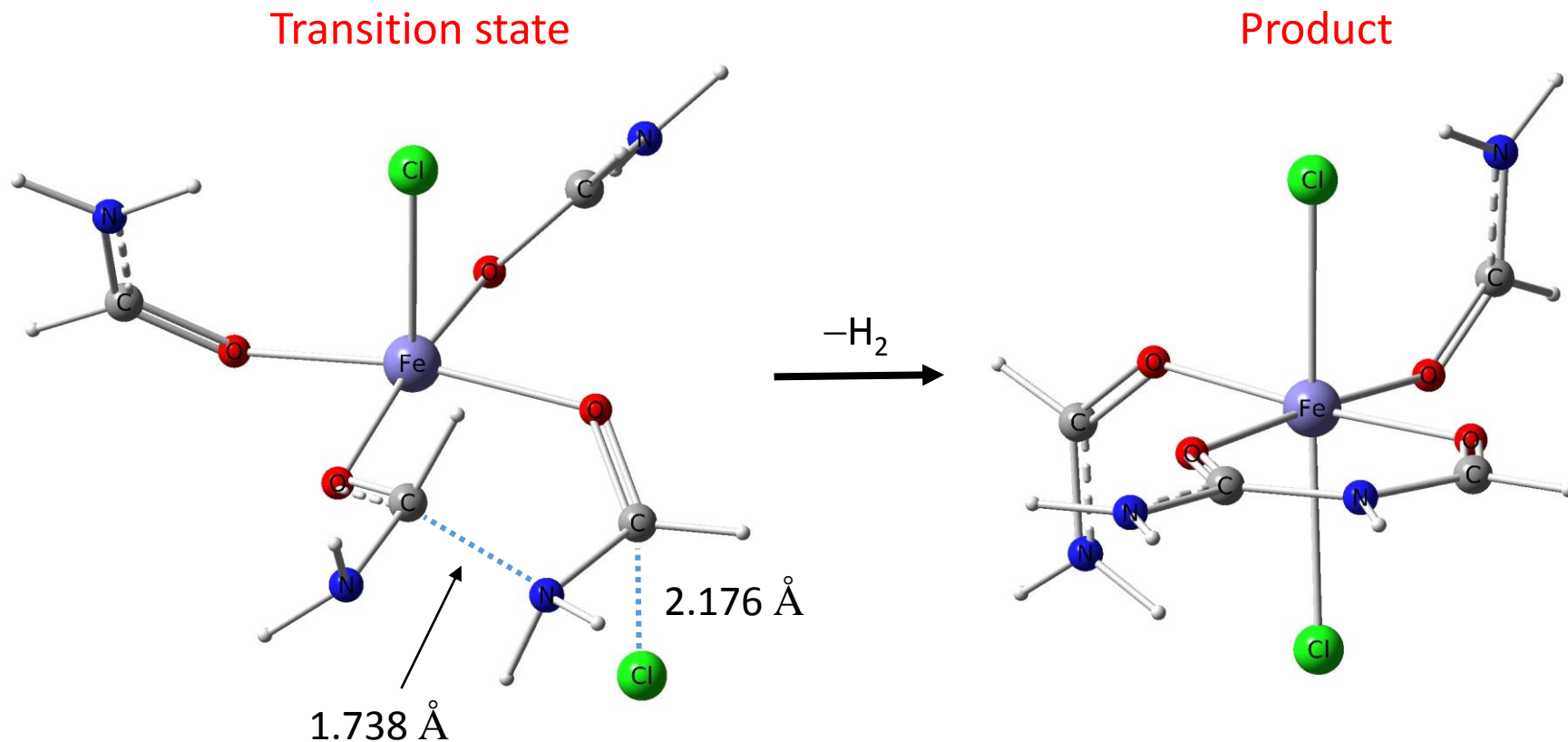


no HBs

-stable



Dimerization Reaction: Transition State Complex & Product



$$\Delta E^\ddagger = 51.0 \text{ kcal/mol}$$

Summary

- Formamide binds metal ions (e.g. Fe^{2+}) derived from the dissolution of minerals
- A pair of formamide molecules can react while bonded to the metal center \Rightarrow Homogeneous prebiotic catalysis may have played a role in the synthesis of RNA nucleobases
- Other synthetic mechanisms are also possible (e.g. high-energy impact)