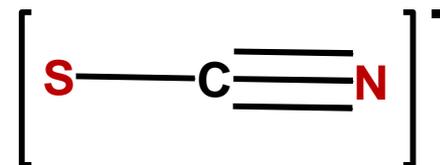
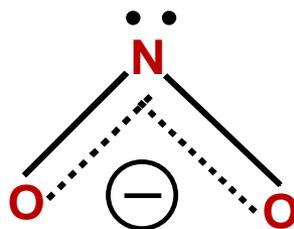
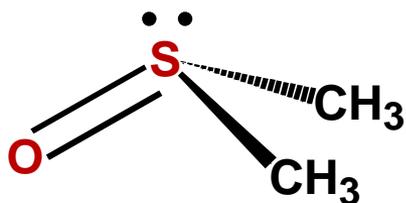


ESPERIENZA 2

Sintesi di complessi di metalli di transizione con dimetil solfossido e con lo ione nitrito: esempi di **leganti ambidentati**

Def.: si definiscono **ambidentati** quei leganti che presentano **due atomi potenzialmente donatori**.



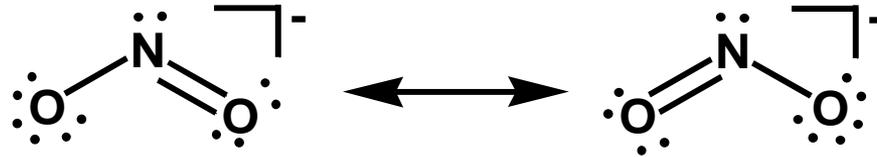
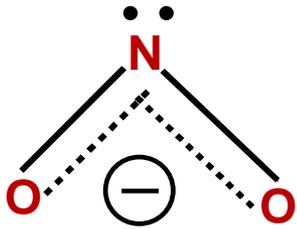
Fattori **elettronici** o **sterici** o **entrambi** indirizzano la coordinazione attraverso uno dei due atomi donatori.

Si possono fare delle previsioni sull'atomo donatore utilizzando la teoria **HARD and SOFT, ACIDS and BASES**.

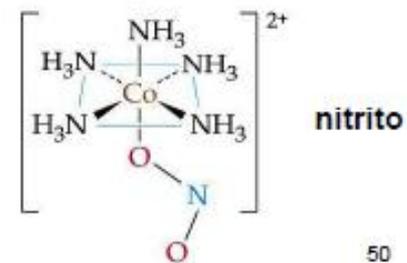
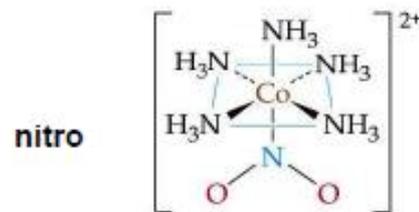
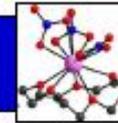
Spettroscopia **IR** allo stato **solido**, **UV-Vis.** ed **¹H NMR** in **soluzione** sono diagnostiche per riconoscere il modo di legame dei leganti ambidentati.

ESPERIENZA 2

Lo ione nitrito

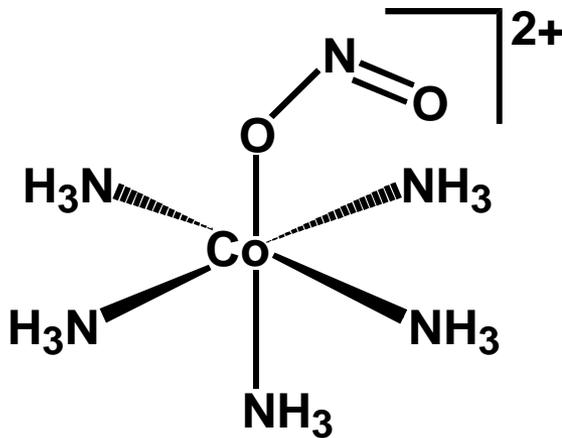
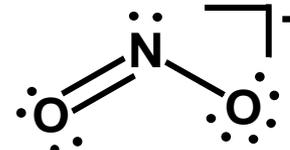
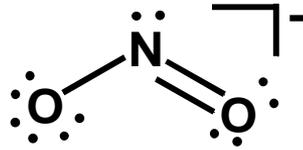
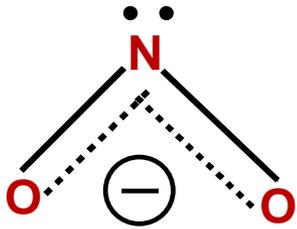


3. Structure et isomérisation des complexes



ESPERIENZA 2

Lo ione nitrito



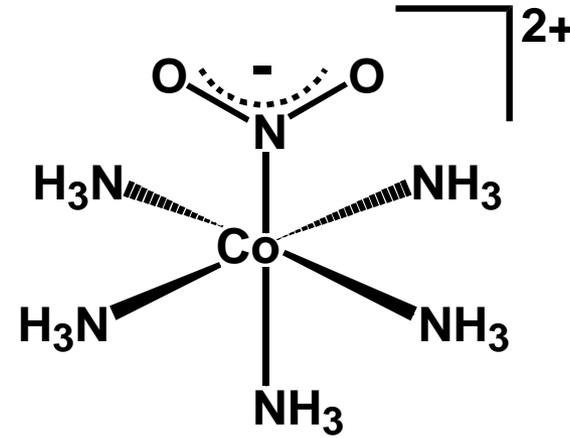
nitrito

Coordinazione via **O**

IR

$$\nu_{\text{N-O}} = 1065 \text{ cm}^{-1}$$
$$1460 \text{ cm}^{-1}$$

UV-Vis. $\lambda_{\text{max}} = 485 \text{ nm}$



nitro

Coordinazione via **N**

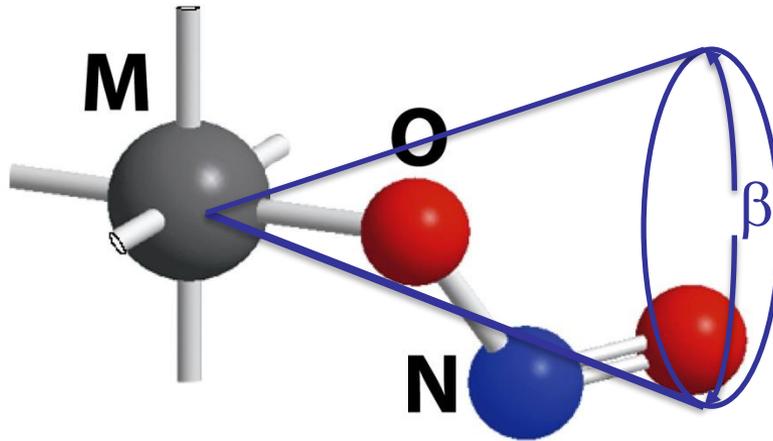
$$\nu_{\text{N-O}} = 1420 \text{ cm}^{-1}$$

$\lambda_{\text{max}} = 455 \text{ nm}$

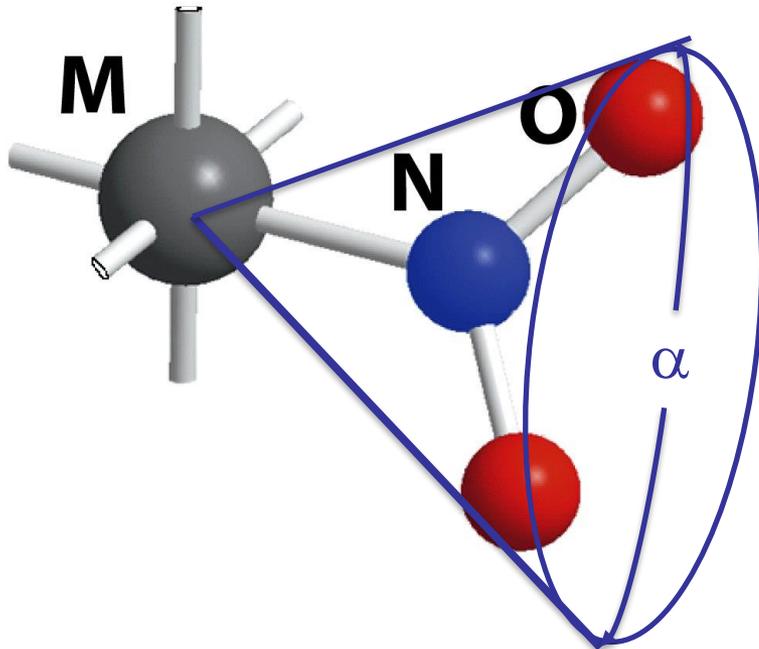
Serie spettrochimica: $\underline{\text{NO}}_2^- < \underline{\text{NO}}_2^+$

EFFETTI STERICI

NITRITO



NITRO

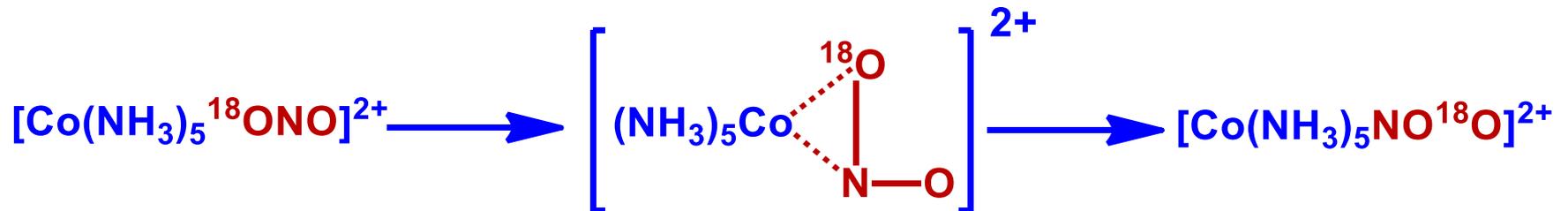


$$\alpha > \beta$$

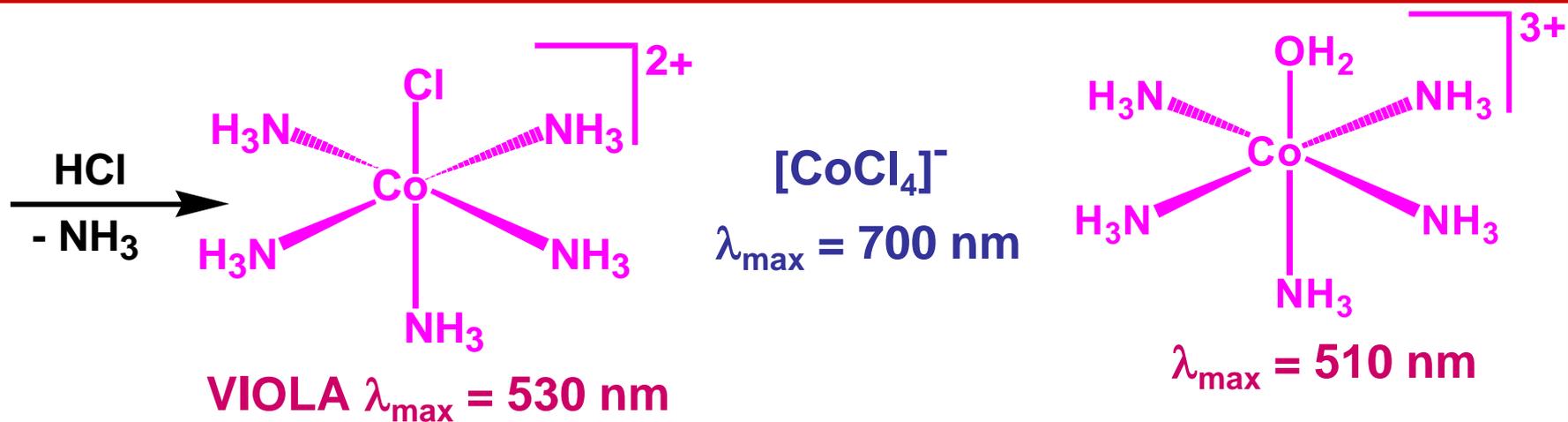
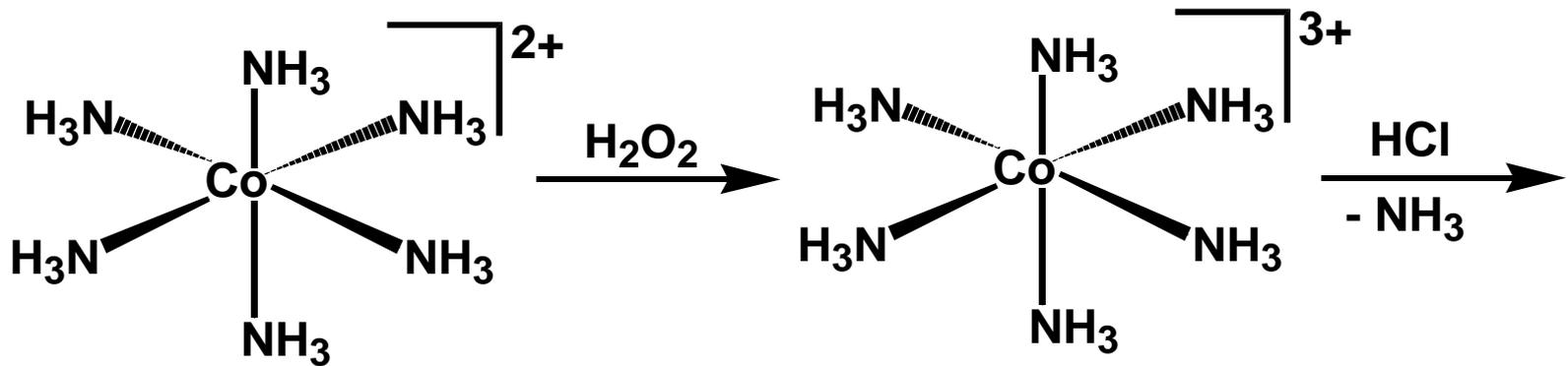
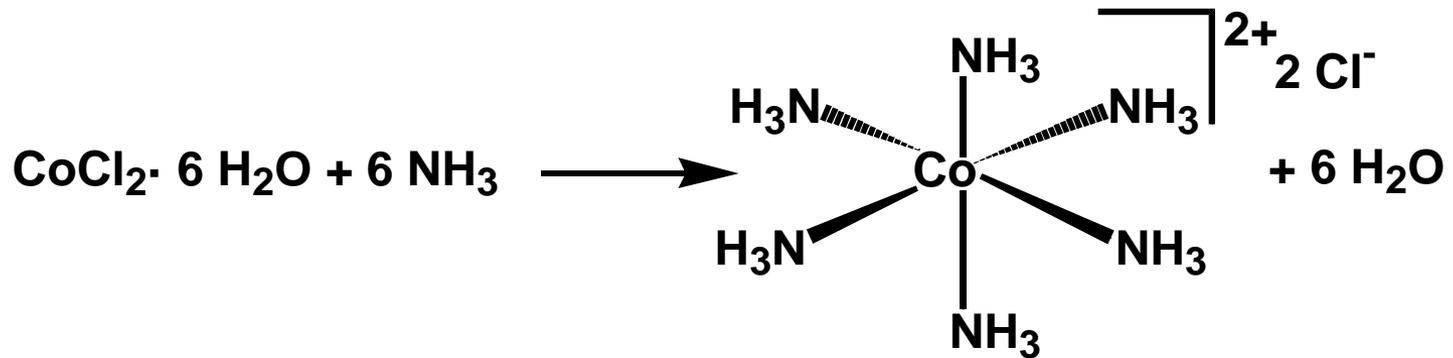
La reazione di **isomerizzazione nitrito/nitro**

Avviene con un **MECCANISMO INTRAMOLECOLARE**.

1. Spettroscopia UV-Visibile: **cinetica del primo ordine**;
2. Sintesi del nitrito derivato con ^{18}O e successiva trasformazione nel nitro derivato: **NON si ha perdita di ^{18}O** .



Primo step di sintesi – $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{Cl})_2$



Photochemical versus Thermal Synthesis of Cobalt Oxyhydroxide Nanocrystals

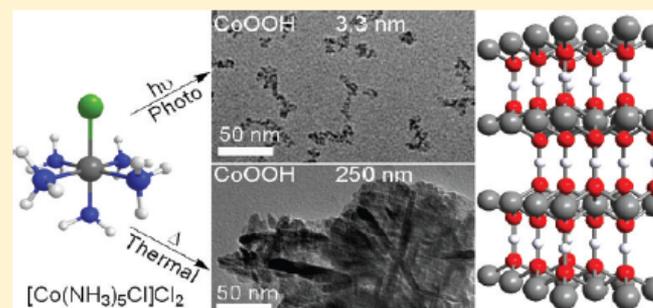
Samuel R. Alvarado,^{†,‡} Yijun Guo,^{†,‡} T. Purnima A. Ruberu,^{†,‡} Andreja Bakac,^{†,‡} and Javier Vela^{*,†,‡}

[†]Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States

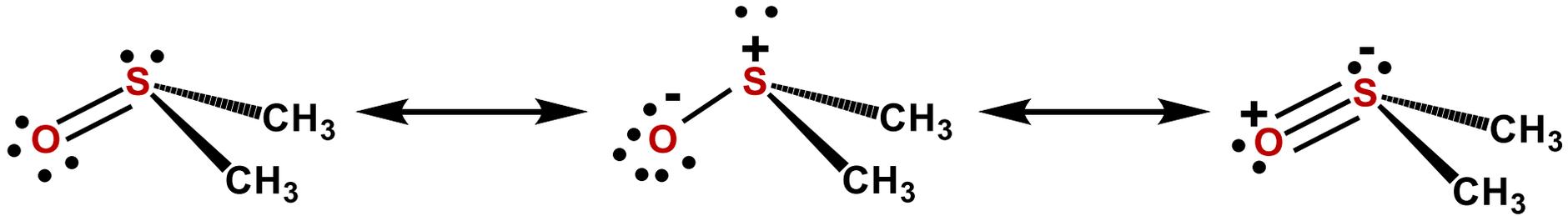
[‡]U.S. DOE Ames Laboratory, Ames, Iowa 50011, United States

Supporting Information

ABSTRACT: Photochemical methods facilitate the generation, isolation, and study of metastable nanomaterials having unusual size, composition, and morphology. These harder-to-isolate and highly reactive phases, inaccessible using conventional high-temperature pyrolysis, are likely to possess enhanced and unprecedented chemical, electromagnetic, and catalytic properties. We report a fast, low-temperature and scalable photochemical route to synthesize very small (~3 nm) monodisperse cobalt oxyhydroxide (Co(O)OH) nanocrystals. This method uses readily and commercially available pentaamminechlorocobalt(III) chloride, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, under acidic or neutral pH and proceeds under either near-UV (350 nm) or Vis (575 nm) illumination. Control experiments showed that the reaction proceeds at competent rates only in the presence of light, does not involve a free radical mechanism, is insensitive to O_2 , and proceeds in two steps: (1) Aquation of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ to yield $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$, followed by (2) slow photoinduced release of NH_3 from the aqua complex. This reaction is slow enough for Co(O)OH to form but fast enough so that nanocrystals are small (ca. 3 nm). The alternative dark thermal reaction proceeds much more slowly and produces much larger (~250 nm) polydisperse Co(O)OH aggregates. UV–Vis absorption measurements and ab initio calculations yield a Co(O)OH band gap of 1.7 eV. Fast thermal annealing of Co(O)OH nanocrystals leads to Co_3O_4 nanocrystals with overall retention of nanoparticle size and morphology. Thermogravimetric analysis shows that oxyhydroxide to mixed-oxide phase transition occurs at significantly lower temperatures (up to $\Delta T = 64^\circ\text{C}$) for small nanocrystals compared with the bulk.



Il dimetilsolfossido

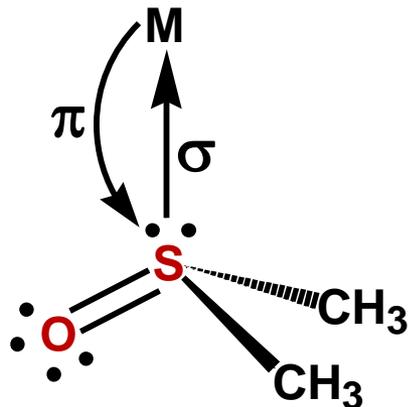


La frequenza IR (cm⁻¹) $\nu = 1/(2\pi c) \sqrt{k/\mu}$

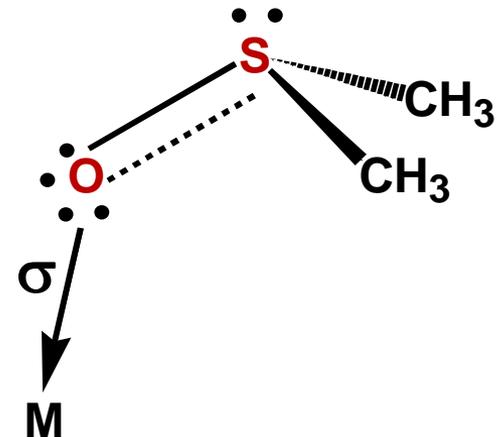
La massa ridotta μ $\mu = m_1 m_2 / (m_1 + m_2)$

La costante di forza k è correlata con l'ordine di legame

Coordinazione via **S**



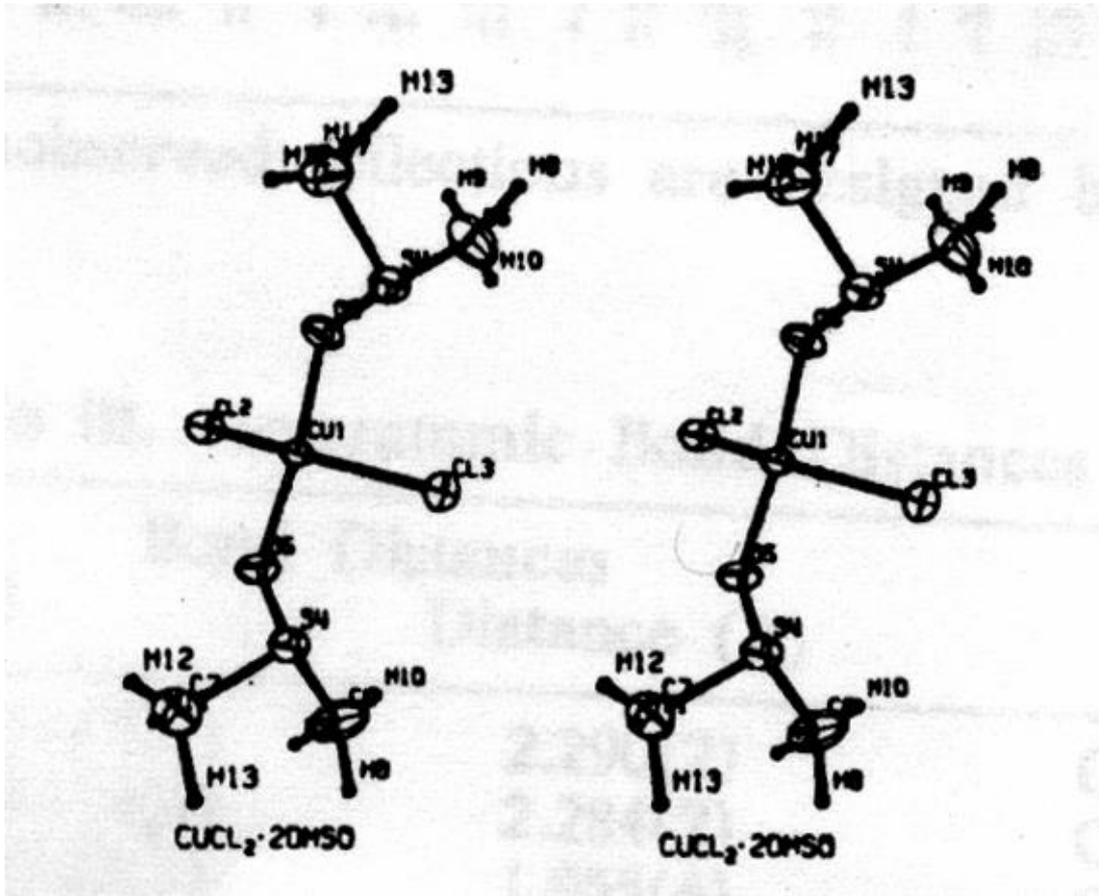
Coordinazione via **O**



Bande IR di stretching del legame S=O

	$\nu_{\text{S=O}}$ (cm ⁻¹)	
DMSO	1020	
[CuCl ₂ (DMSO) ₂]	918	DMSO O-legato
<i>cis</i> -[PdCl ₂ (DMSO) ₂]	1114	DMSO S-legato
<i>cis</i> -[RuCl ₂ (DMSO) ₄]	1122, 1110, 1095 921	DMSO S-legati DMSO O-legato

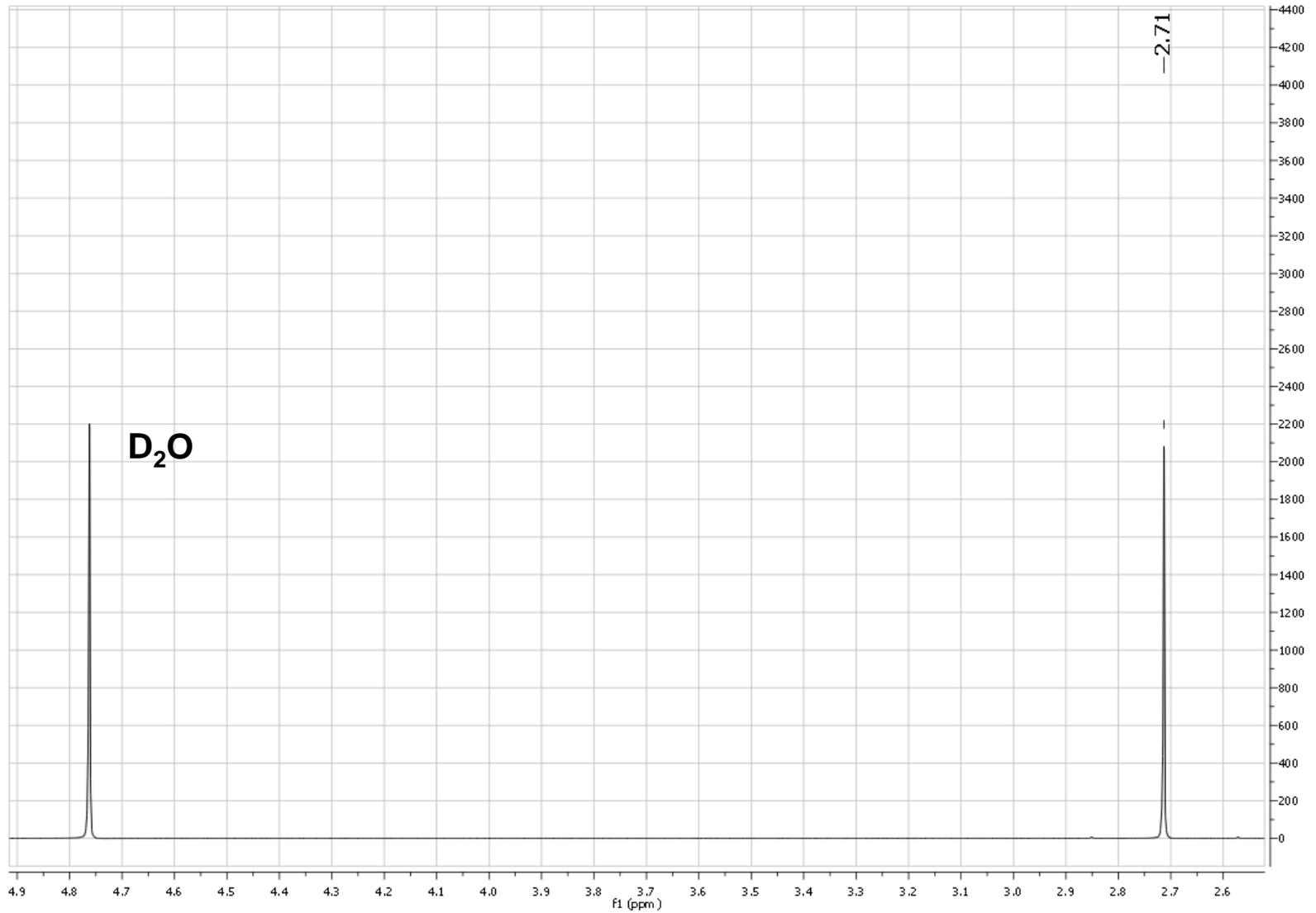
Struttura ai Raggi X di $[\text{CuCl}_2(\text{DMSO})_2]$



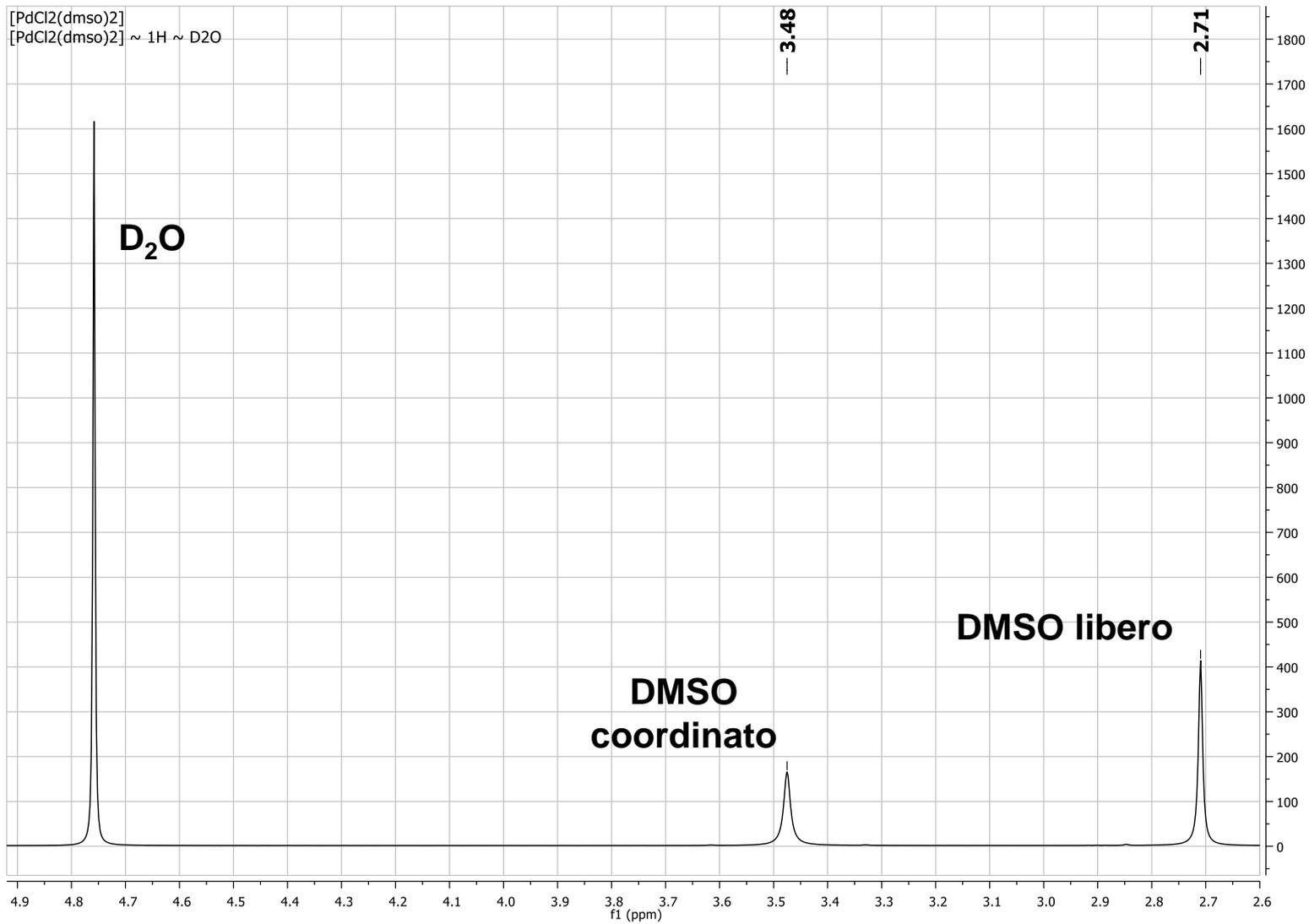
Geometria a sella, d^9

Angolo di legame
Cl-Cu-Cl 146°

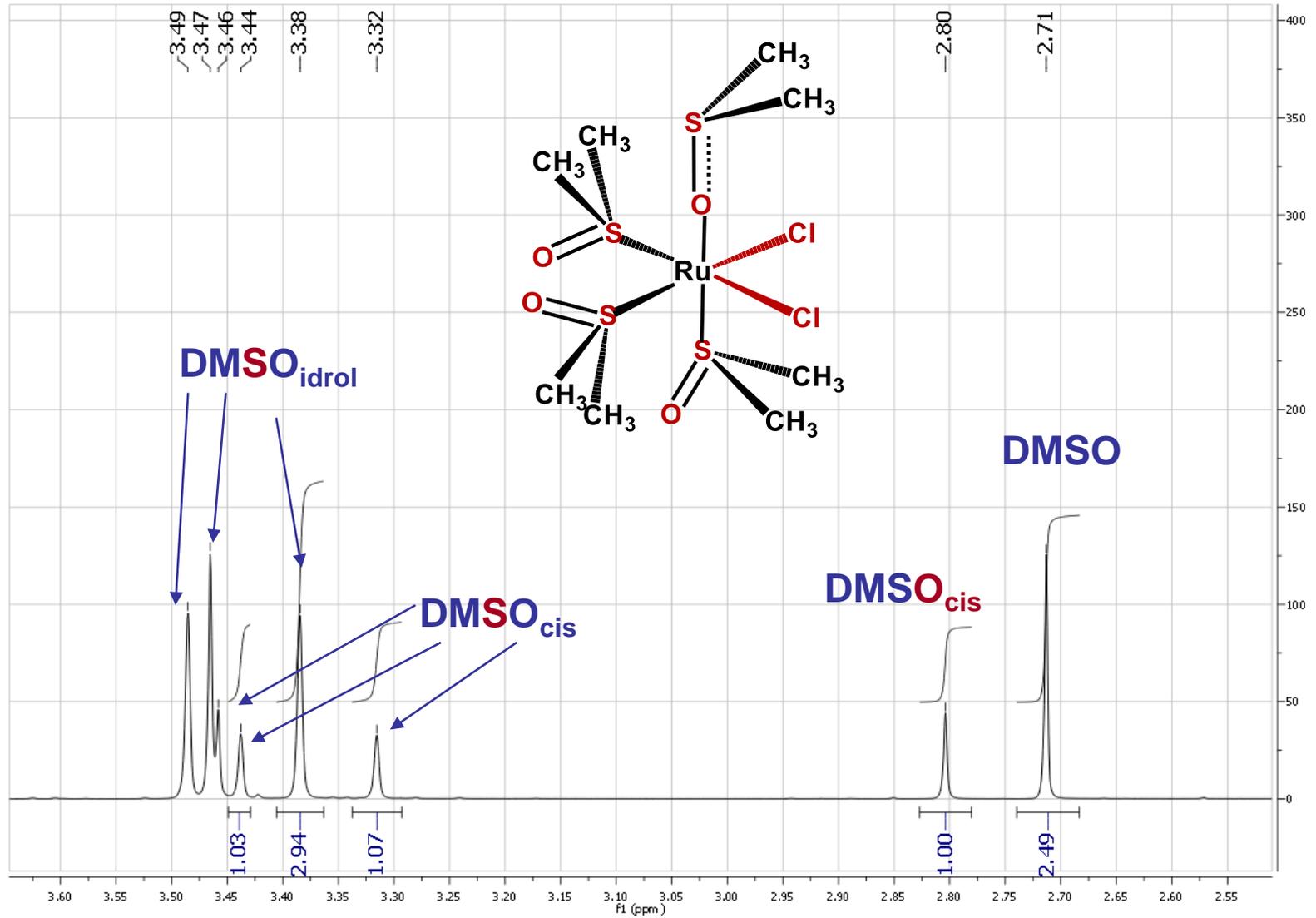
Spettro ^1H NMR in D_2O , a t.a. di DMSO



Spettro ^1H NMR in D_2O , a t.a. di $\text{cis-}[\text{PdCl}_2(\text{DMSO})_2]$

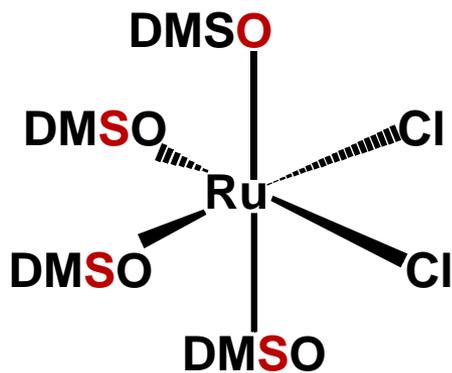


Spettro ^1H NMR in D_2O , a t.a. di $[\text{Ru}(\text{Cl})_2(\text{DMSO})_4]$



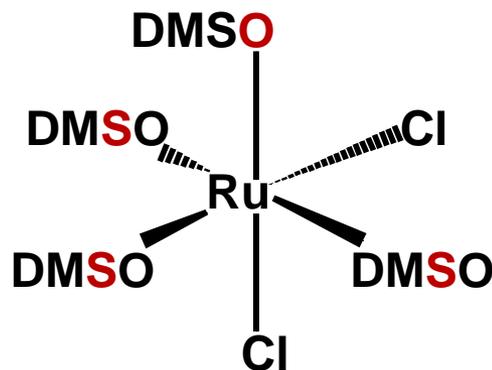
Considerazioni sullo spettro ^1H NMR in D_2O , a t.a. di $[\text{Ru}(\text{Cl})_2(\text{DMSO})_4]$

1. tutti i singoletti cadono a frequenze più alte, cioè a campi più bassi del singoletto del DMSO libero, per cui sono dovuti a DMSO legato;
2. 3 molecole di DMSO S-legate e 1 molecola di DMSO O-legata



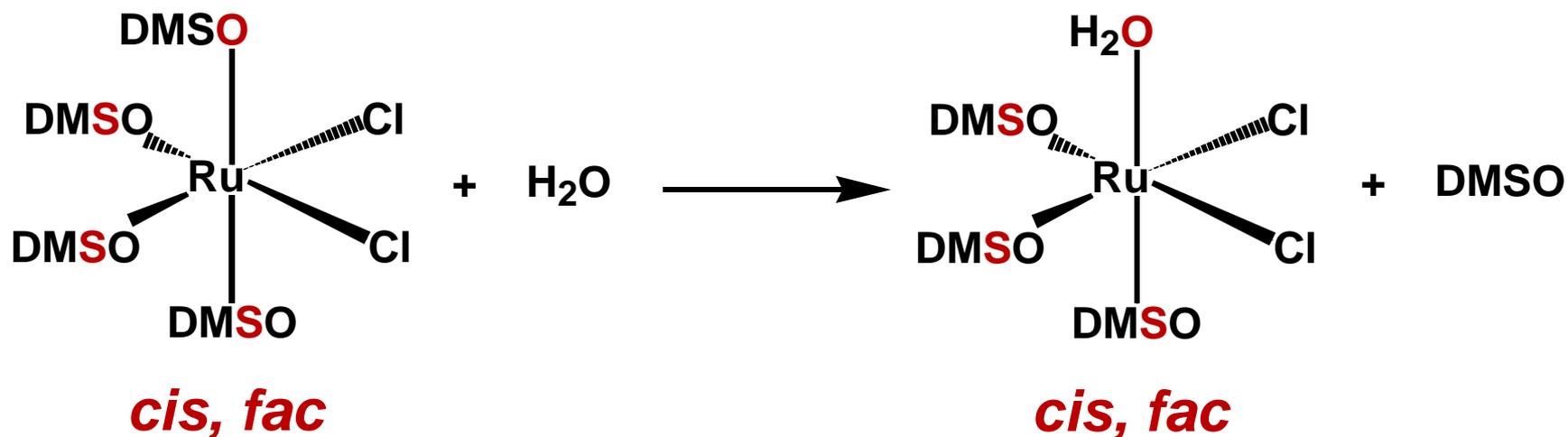
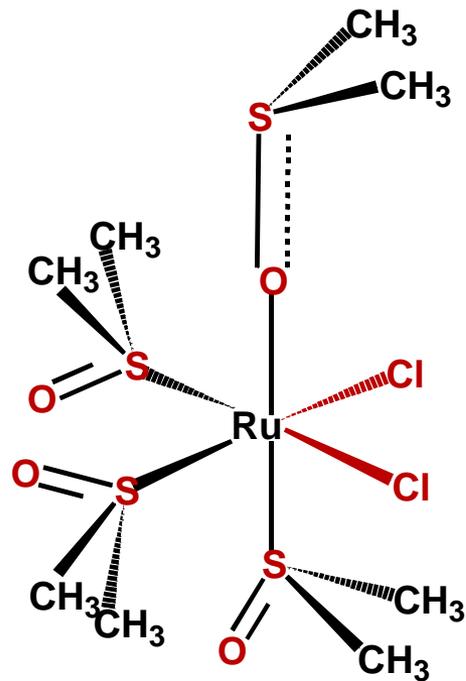
cis, fac

1:1:1:1



cis, mer

Conclusioni su
 $[\text{Ru}(\text{Cl})_2(\text{DMSO})_4]$



Conclusioni

Correlazioni dei risultati sperimentali con la teoria HARD and SOFT, ACIDS and BASES:

[CuCl₂(DMSO)₂]: il Cu²⁺ è uno ione **HARD**;
il **DMSO** si coordina attraverso l'atomo di **ossigeno** che è una base **HARD**;

[PdCl₂(DMSO)₂]: il Pd²⁺ è uno ione **SOFT**;
il **DMSO** si coordina attraverso l'atomo di **zolfo** che è una base **SOFT**;

[RuCl₂(DMSO)₄]: il Ru²⁺ è uno ione **BORDERLINE**;
alcune molecole di **DMSO** si coordinano attraverso l'atomo di **ossigeno** altre attraverso l'atomo di **zolfo**.