

***Metalloenzymes as teaching tools for coordination chemistry
From bonding to spectroscopy***

Jordi Cirera

Departament de Química Inorgànica i Orgànica
Insitut de Química Teòrica i Computacional (IQTC-UB)

Bio-Chem-Comp School 2018, Bansko

Outline

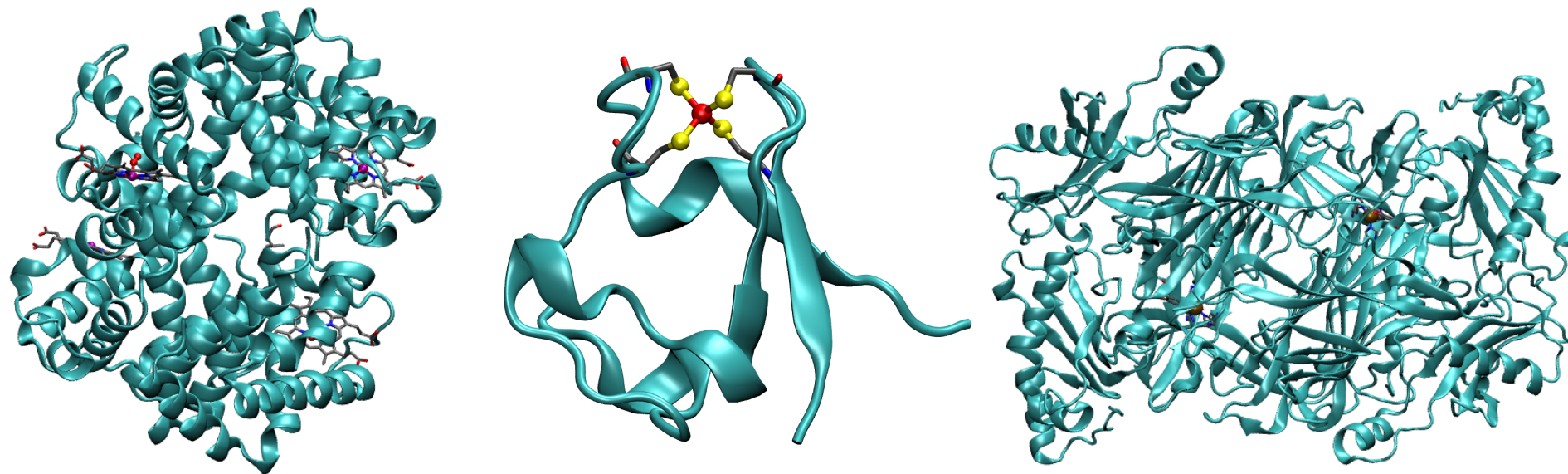
1. *The Protein Data Bank*
 - 1.1 *What is the Protein Data Bank? (RCSD-PDB)*
 - 1.2 *Information contained on the PDB*
 - 1.3 *Working with the PDB*
 - 1.4 *Ligand Explorer*
 - 1.5 *The metal-PDB database*
 - 1.6 *Additional Tools*

2. *Integrating the PDB as a teaching tool for coordination chemistry*
 - 2.1 *Metalloenzymes as illustrative examples*
 - 2.2 *Coordination motifs in active sites*
 - 2.3 *Geometrical data/Coordination modes*
 - 2.4 *Spin-State Information*
 - 2.5 *Absorption Spectroscopy*
 - 2.6 *Electron Paramagnetic Resonance Spectroscopy*
 - 2.7 *Practical Cases*

3. *Summary and Outlook*

Metalloenzymes in coordination chemistry?

Metalloenzymes are usually constrained to bioinorganic courses



They all contain coordination compounds!

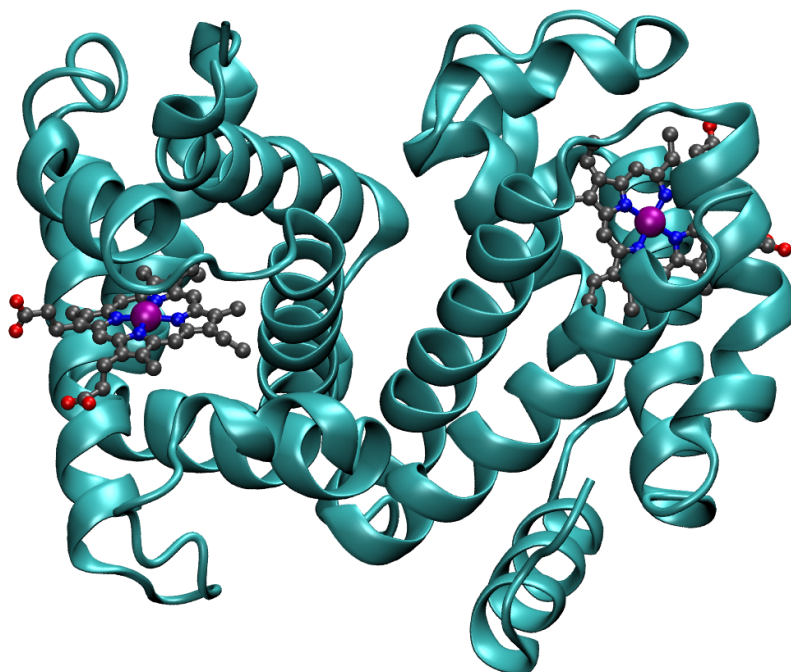
- We can use them to illustrate basic coordination chemistry concepts
- We can use them to illustrate advanced bonding concepts
- We can use them to illustrate spectroscopic techniques
-

The Protein Data Bank

1.1 What is the Protein Data Bank? (RCSB-PDB)

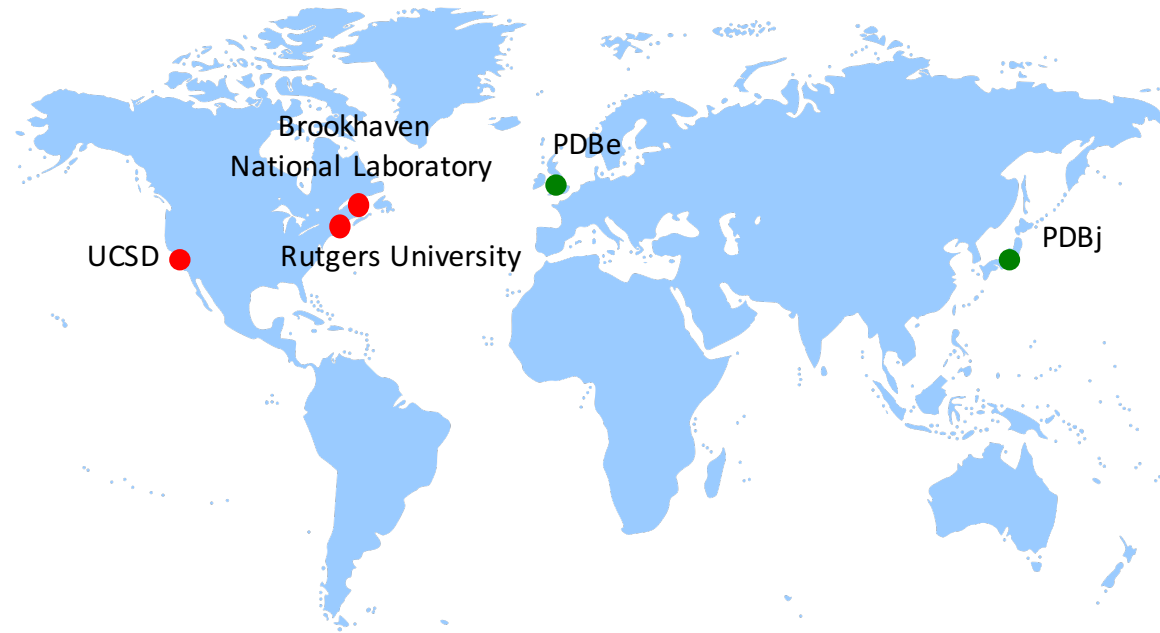


The **PDB** is a database for the three-dimensional structural data of large biological molecules, such as proteins and nucleic acids



- Structural biology
- Genomics
- Bioinorganic Chemistry
- Reactivity of biological systems
- Drug Design
-

1.1 What is the Protein Data Bank? (RCSB-PDB)



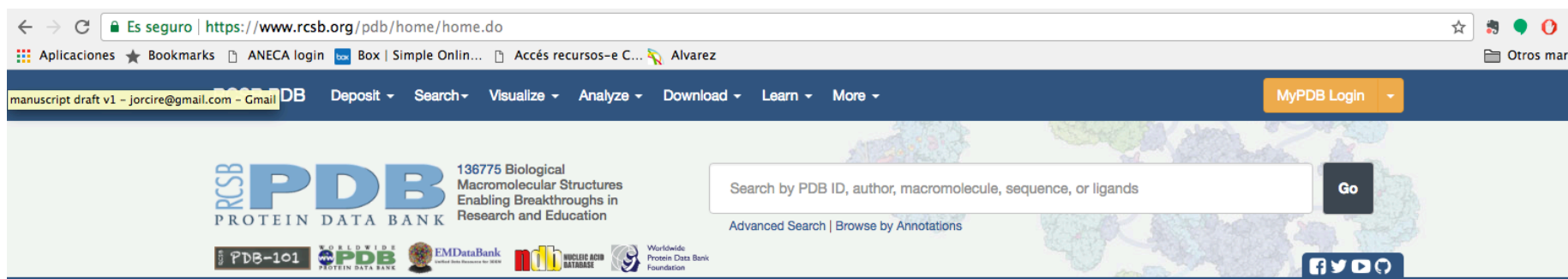
Gordon (SDSC)



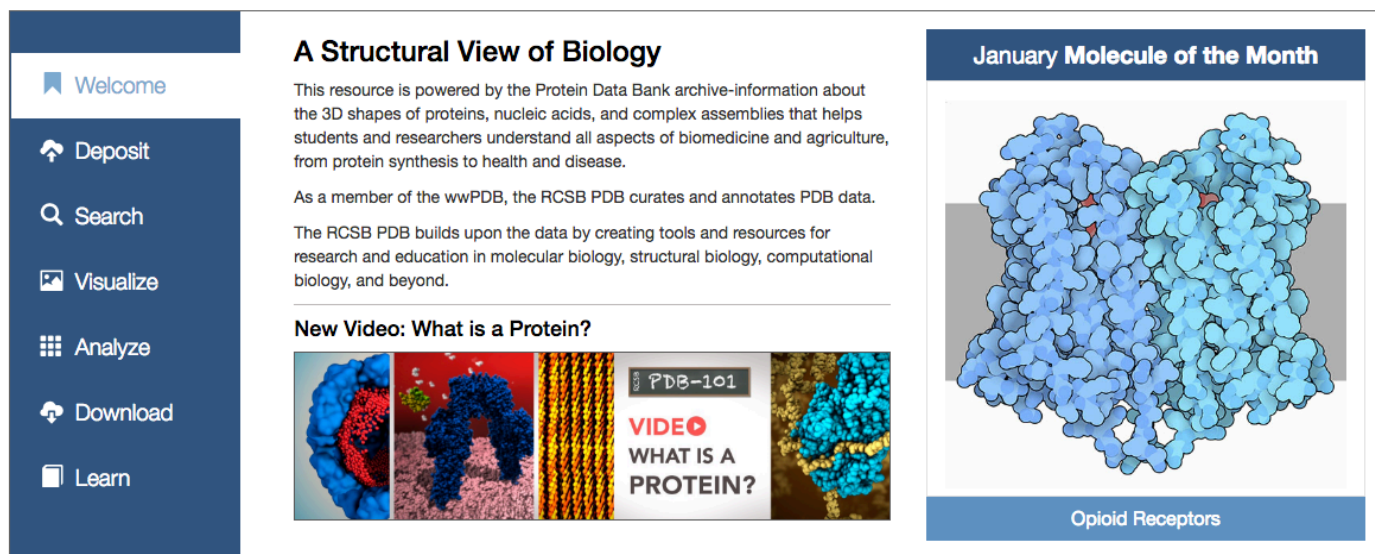
<https://www.rcsb.org/>

1.1 What is the Protein Data Bank? (RCSB-PDB)

- Open access database
- Web based interface (with its pros and cons...)



The screenshot shows the RCSB PDB website homepage. The browser address bar displays "Es seguro | https://www.rcsb.org/pdb/home/home.do". The navigation bar includes links for "Deposit", "Search", "Visualize", "Analyze", "Download", "Learn", and "More", along with a "MyPDB Login" button. The main content area features the RCSB PDB logo, the text "136775 Biological Macromolecular Structures Enabling Breakthroughs in Research and Education", a search bar with the placeholder "Search by PDB ID, author, macromolecule, sequence, or ligands", and a "Go" button. Below the search bar are logos for PDB-101, Worldwide Protein Data Bank, EMDataBank, and the Worldwide Protein Data Bank Foundation. Social media icons for Facebook, Twitter, YouTube, and LinkedIn are also present.

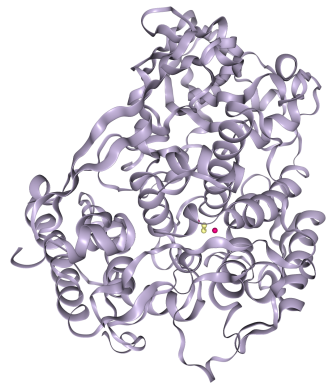


The screenshot shows the content area of the RCSB PDB website. On the left is a dark blue sidebar with navigation links: "Welcome", "Deposit", "Search", "Visualize", "Analyze", "Download", and "Learn". The main content area is divided into three sections:

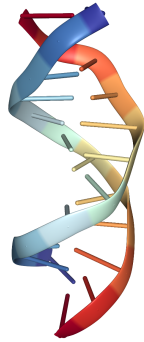
- A Structural View of Biology**: This resource is powered by the Protein Data Bank archive-information about the 3D shapes of proteins, nucleic acids, and complex assemblies that helps students and researchers understand all aspects of biomedicine and agriculture, from protein synthesis to health and disease. As a member of the wwPDB, the RCSB PDB curates and annotates PDB data. The RCSB PDB builds upon the data by creating tools and resources for research and education in molecular biology, structural biology, computational biology, and beyond.
- New Video: What is a Protein?**: A video thumbnail featuring a blue protein structure, a red protein structure, and a yellow protein structure. The text "PDB-101 VIDEO WHAT IS A PROTEIN?" is overlaid on the image.
- January Molecule of the Month**: A large blue protein structure, identified as "Opioid Receptors".

<https://www.rcsb.org/>

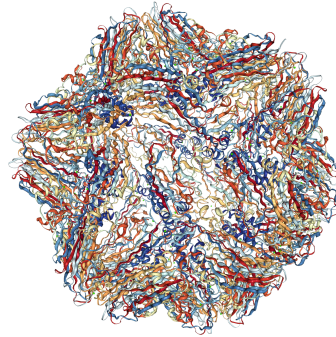
1.2 Information contained on the PDB



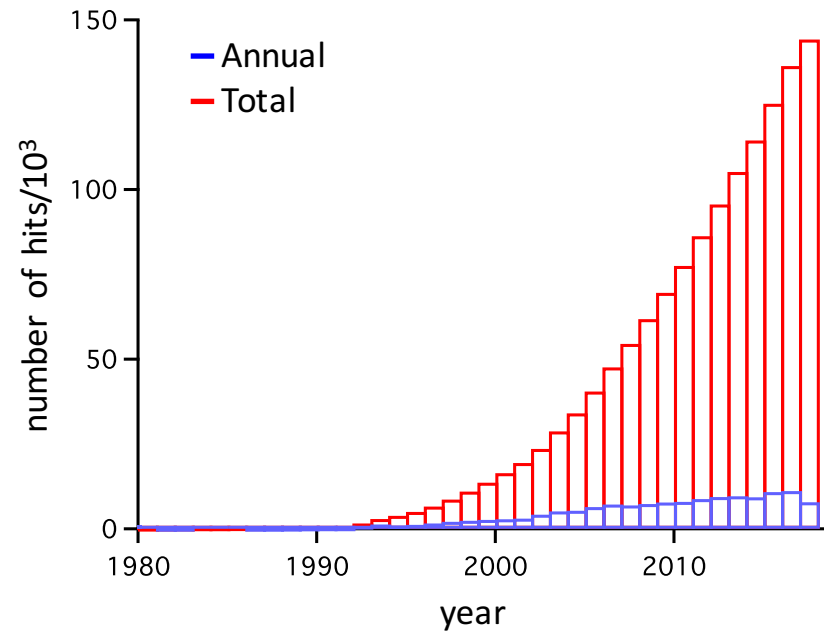
Proteins



DNA/RNA



Virus



<i>Exp. Method</i>	<i>Proteins</i>	<i>Nucleic Acids</i>	<i>Protein/NA Complex</i>	<i>Other</i>	<i>Total</i>
X-Ray	120875	1958	6242	10	129085
NMR	10837	1254	250	8	12349
Electron Microscopy	1735	31	619	0	2385
Other	244	4	6	13	267
Multi Method	117	5	2	1	125
Total	133808	3252	7119	32	144211

1.3 Working with the PDB

- Web based search: we can search by any field!

RCSB PDB Deposit Search Visualize Analyze Download Learn More MyPDB

RCSB PDB 144211 Biological Macromolecular Structures Enabling Breakthroughs in Research and Education

Search by PDB ID, author, macromolecule, sequence, or ligands Go

Advanced Search | Browse by Annotations

PDB-101 Worldwide PDB EMDataBank NUCLEIC ACID DATABASE Worldwide Protein Data Bank Foundation

Welcome

Deposit

Search

Visualize

Analyze

Download

Learn

A Structural View of Biology

This resource is powered by the Protein Data Bank archive-information about the 3D shapes of proteins, nucleic acids, and complex assemblies that helps students and researchers understand all aspects of biomedicine and agriculture, from protein synthesis to health and disease.

As a member of the wwPDB, the RCSB PDB curates and annotates PDB data.

The RCSB PDB builds upon the data by creating tools and resources for research and education in molecular biology, structural biology, computational biology, and beyond.

Award-Winning Videos on Antibiotic Resistance

2018 Video Challenge for High School Students

September Molecule of the Month

Phytase

PDB ID, author, name, DOI, ligands, etc....

Very convenient, but lacks precision

1.3 Working with the PDB

- Web based search: Hemocyanin (the web browser makes a guess....)

The screenshot shows the RCSB PDB website interface. At the top, there is a navigation bar with 'RCSB PDB' and various menu items like 'Deposit', 'Search', 'Visualize', 'Analyze', 'Download', 'Learn', and 'More'. A 'MyPDB Login' button is also present. Below the navigation bar, the PDB logo and tagline '136775 Biological Macromolecular Structures Enabling Breakthroughs in Research and Education' are displayed. A search bar contains the text 'Hemocyanin|' and a 'Go' button. A dropdown menu is open, showing search results categorized into three columns: UniProt Molecule Name, Structural Domains, and Sequence Cluster Name. The UniProt column lists 'Hemocyanin II (4)', 'Hemocyanin 1 (3)', 'Hemocyanin subunit L2 (2)', 'Hemocyanin A chain (2)', 'Hemocyanin AA6 chain (2)', and 'Hemocyanin isoform 1 (1)'. The Structural Domains column lists 'Mollusc hemocyanin... (2)', 'Hemocyanin... (4)', 'C-terminal domain of mollus... [...] (2)', 'Hemocyanin... (4)', 'C-terminal domain of mollus... [...] (2)', and 'C-terminal domain of mollus... [...] (2)'. The Sequence Cluster Name column lists 'Hemocyanin subunit L2'. Below the dropdown, there are sections for 'Help Topics', 'General Help', 'Browsing', 'Search', 'Drug Information', 'Reports', 'Sequence Viewers', and 'Deposition Resources'. A 'Contact Us' button is visible on the right side of the page.

Help Topics | Website FAQ | Glossary | Browser Check | Service Status | Cor

Help Topics

General Help

- File Downloads
- MyPDB
- Large Structures Without PDB Files
- Access to Legacy Theoretical Models
- Obsoleted PDB Entries

Browsing

- Biological Process Browser (GO terms)
- Cell Component Browser (GO terms)
- Molecular Function Browser (GO terms)
- Enzyme Classification Browser
- Transporter Classification
- Transmembrane Proteins
- Source Organism Bowser (NCBI)
- Genome Location Browser
- Medical Subject Headings Browser (MeSH)
- SCOP Classification Browser
- CATH Classification Browser
- Anatomical Therapeutic Chemical Classification Browser
- Protein Symmetry Browser

Search

- Top Ba
- Latest
- Chemi
- Chemi
- Advanc
- Advanc

Drug Information

- Drug and Drug Target Mapping

Reports

- Sequence Details
- Tabular Reports

Sequence Viewers

- Protein Feature View
- Gene View

Deposition Resources

- Prepare Data
- Validate Data
- Deposit Data
- PDBx/mmCIF Dictionary Resources
- wwPDB Resources

UniProt Molecule Name	Structural Domains	Sequence Cluster Name
<ul style="list-style-type: none">• Hemocyanin II (4)• Hemocyanin 1 (3)• Hemocyanin subunit L2 (2)• Hemocyanin A chain (2)• Hemocyanin AA6 chain (2)• Hemocyanin isoform 1 (1)	<ul style="list-style-type: none">• Mollusc hemocyanin... (2)• Hemocyanin... (4)• C-terminal domain of mollus... [...] (2)• Hemocyanin... (4)• C-terminal domain of mollus... [...] (2)• C-terminal domain of mollus... [...] (2)	<ul style="list-style-type: none">• Hemocyanin subunit L2

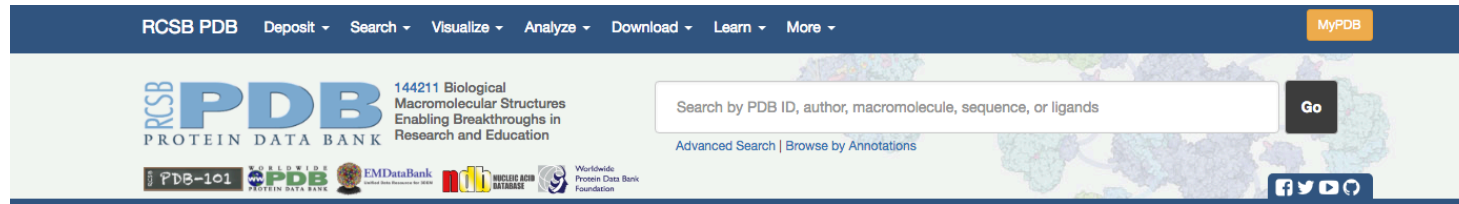
More - Find all

Find all

Close

1.3 Working with the PDB

- Select a particular structure: **1OXY**



← Different tabs



← Download

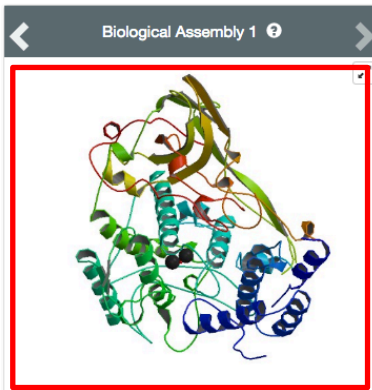
1OXY

← PDB ID

CRYSTALLOGRAPHIC ANALYSIS OF OXYGENATED AND DEOXYGENATED STATES OF ARTHROPOD HEMOCYANIN SHOWS UNUSUAL DIFFERENCES

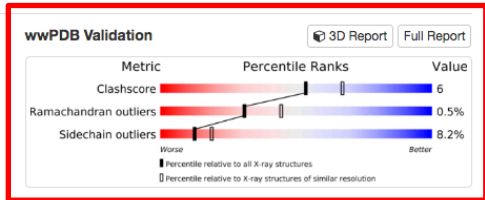
← Title

Display →



DOI: [10.2210/pdb1OXY/pdb](https://doi.org/10.2210/pdb1OXY/pdb)
Classification: [OXYGEN TRANSPORT](#)
Organism(s): [Limulus polyphemus](#)
Deposited: 1995-01-06 Released: 1995-02-27
Deposition Author(s): [Ton-that, H.](#), [Magnus, K.](#)

Experimental Data Snapshot
Method: X-RAY DIFFRACTION
Resolution: 2.4 Å
R-Value Work: 0.171



← Structure validation (blue == better)

This is version 1.2 of the entry. See complete history.

Literature

Download Primary Citation

Crystallographic analysis of oxygenated and deoxygenated states of arthropod hemocyanin shows unusual differences.

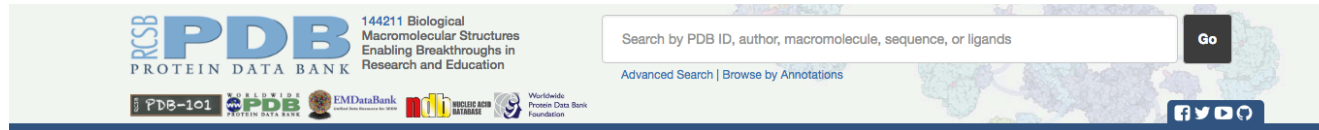
[Magnus, K.A.](#), [Hazes, B.](#), [Ton-That, H.](#), [Bonaventura, C.](#), [Bonaventura, J.](#), [Hoi, W.G.](#)
(1994) Proteins 19: 302-309
PubMed: [7984626](#) Search on PubMed
DOI: [10.1002/prot.340190405](https://doi.org/10.1002/prot.340190405)

← Literature (DOI)

PubMed Abstract:
The X-ray structure of an oxygenated hemocyanin molecule, subunit II of Limulus polyphemus hemocyanin, was determined at 2.4 Å resolution and refined to a crystallographic R-factor of 17.1%. The 73-kDa subunit crystallizes with the symmetry of the sp ...

1.3 Working with the PDB

- Select a particular structure: **1OXY**
Easy to get a very nice picture

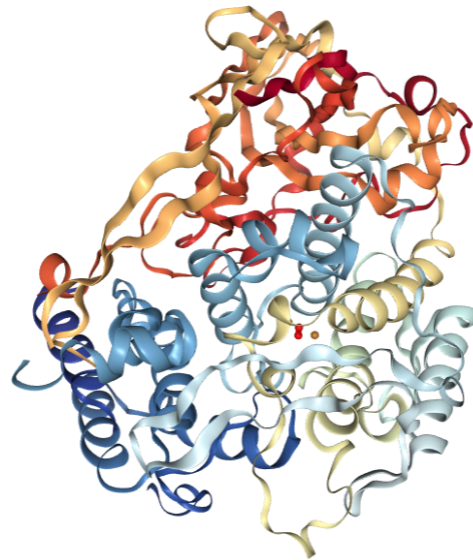


Structure Summary **3D View** Annotations Sequence Sequence Similarity Structure Similarity Experiment

1OXY

CRYSTALLOGRAPHIC ANALYSIS OF OXYGENATED AND DEOXYGENATED STATES OF ARTHROPOD HEMOCYANIN SHOWS UNUSUAL DIFFERENCES

Note: Use your mouse to drag, rotate, and zoom in and out of the structure. Mouse-over to identify atoms and bonds. Mouse controls documentation.



Structure View Electron Density Maps Ligand View

Structure View Documentation

Assembly Bioassembly 1

Model Model 1

Symmetry None

Style Cartoon

Color Rainbow

Ligand Ball & Stick

Quality Automatic

Water Ions

Hydrogens Clashes

Default Structure View

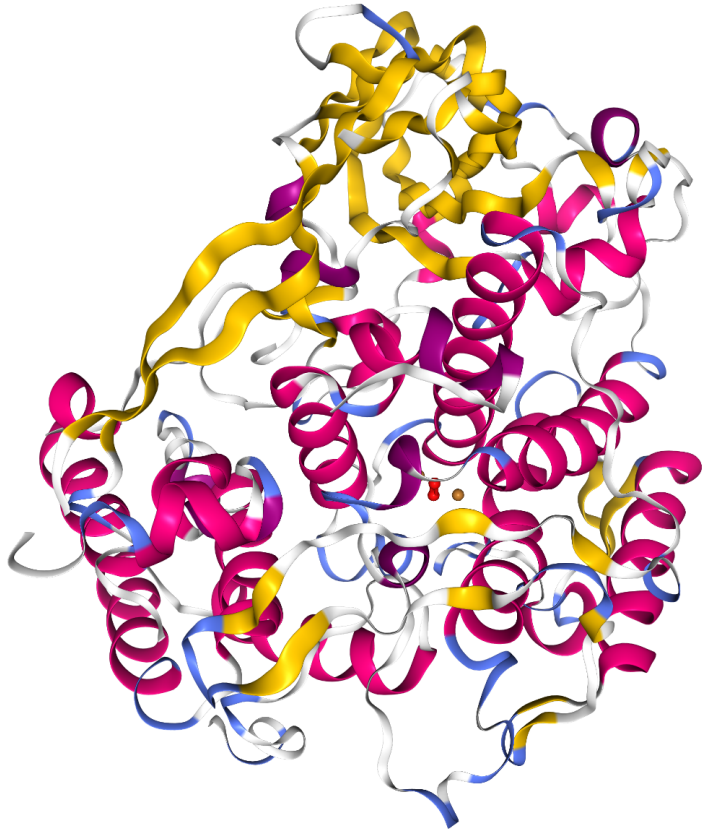
Display Options

Snapshot

Spin Center Fullscreen **Screenshot** Perspective Camera White background Focus

1.3 Working with the PDB

- Select a particular structure: **1OXY**



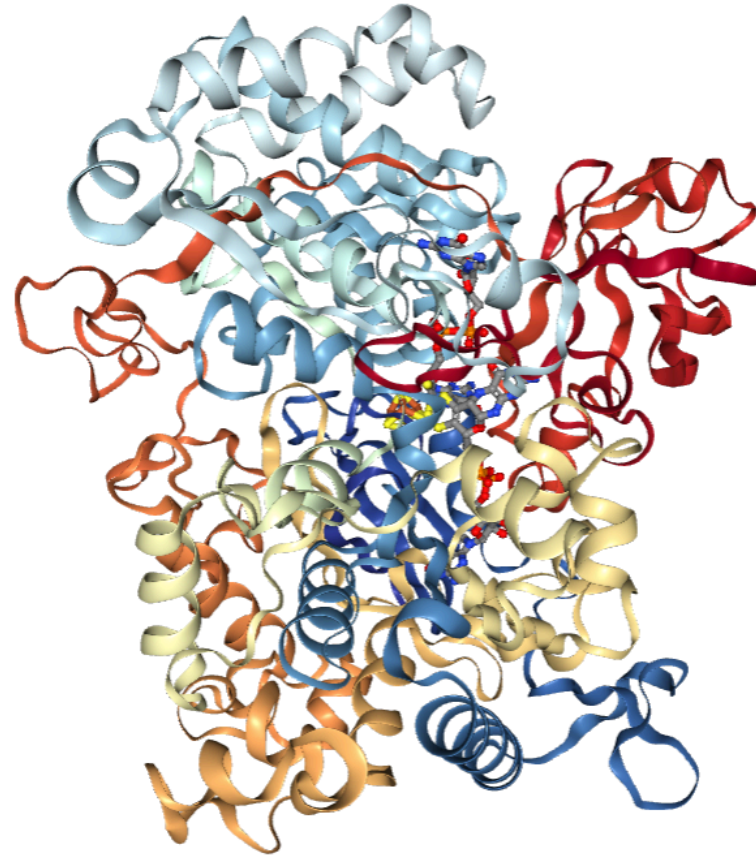
- Title
- Experimental data Snapshot
- Literature (DOI)
- Macromolecules
- Small molecules (Ligand Explorer!!)
- Structure validation (blue == better)
- Display
- Download files (open w/ Mercury)
- Download Citations (Mendeley/EndNote)

PDB Identifier: 4 positions alphanumeric string

1.3 Working with the PDB

- Search for Nitrate Reductase (escherichia coli) (14hits)

Crystal structure of the periplasmic nitrate reductase (NAP) from Escherichia coli (**2NYA**)



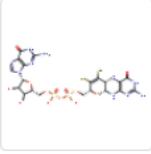


Literature (DOI): [10.1074/jbc.M607353200](https://doi.org/10.1074/jbc.M607353200)

PDB considers everything is not protein is a ligand (ions, metals, drugs, etc...)

1.3 Working with the PDB

- 2NYA: small molecules menu


Small Molecules				
Ligands 3 Unique				
ID	Chains	Name / Formula / InChI Key	2D Diagram & Interactions	3D Interactions
SF4 Query on SF4 Download SDF File Download CCD File	A, F	IRON/SULFUR CLUSTER Fe ₄ S ₄ LJBDFODJNLIPKO-VKOJMFJBAC		Ligand Interaction
6MO Query on 6MO Download SDF File Download CCD File	A, F	MOLYBDENUM(VI) ION Mo HCNGUXXTNNIKCQ-UHFFFAOYSA-N		Ligand Interaction
MGD Query on MGD Download SDF File Download CCD File	A, F	2-AMINO-5,6-DIMERCAPTO-7-METHYL-3,7,8A,9-TETRAHYDRO-8-OXA-1,3,9,10-TETRAAZA-ANTHRACEN-4-ONE GUANOSINE DINUCLEOTIDE <i>MOLYBDOPTERIN GUANOSINE DINUCLEOTIDE</i> C ₂₀ H ₂₆ N ₁₀ O ₁₃ P ₂ S ₂ VQAGYJCYOLHZDH-ILXWUORBSA-N		Ligand Interaction

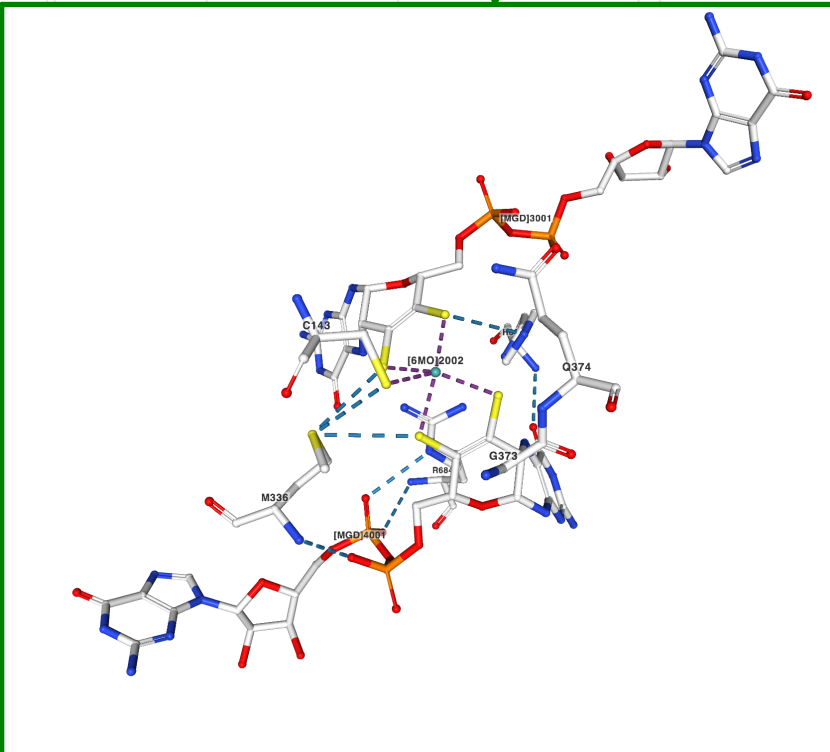
1.3 Working with the PDB

- 2NYA: small molecules menu

Small Molecules

Ligands **3 Unique**

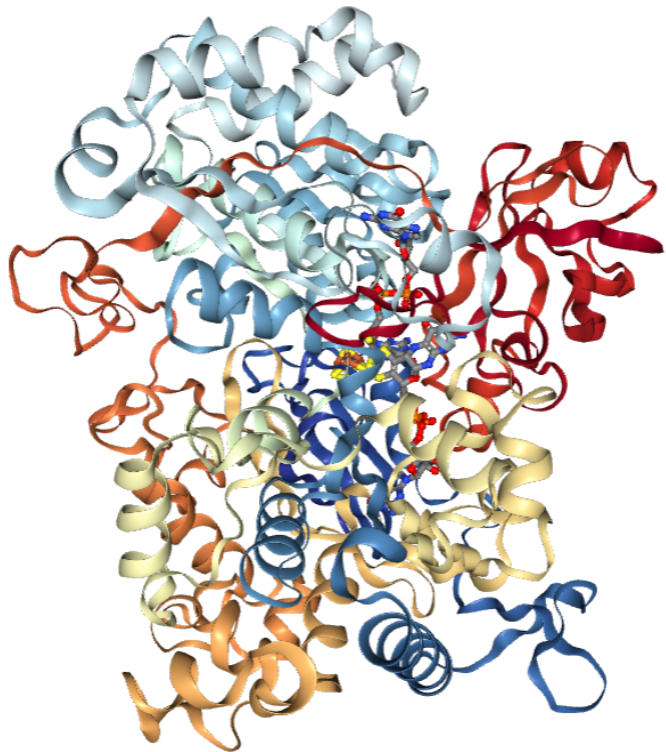
ID	Chains	Name / Formula / InChI Key	2D Diagram & Interactions	3D Interactions
SF4 Query on SF4 Download SDF File Download CCD File	A, F	IRON/SULFUR CLUSTER Fe ₄ S ₄ LJBDFODJNLIPKO-VKOJMFJBAC		Ligand Interaction
6MO Query on 6MO Download SDF File Download CCD File	A, F	MOLYBDENUM(VI) ION Mo HCNGUXXTNNIKCQ-UHFFFAOYSA-N	Mo ⁶⁺	Ligand Interaction
MGD Query on MGD Download SDF File Download CCD File	A, F	2-AMINO-5,6-DIMERCAPTO-7-METHYL-3,7,8A,10-TETRAHYDRO-8-OXA-1,3,9,10-TETRAAZA-ANTHRACEN-4-ONE GUANOSINE DINUCLEOTIDE MOLYBDOPTERIN GUANOSINE DINUCLEOTIDE C ₂₀ H ₂₆ N ₁₀ O ₁₃ P ₂ S ₂ VQAGYJCYOLHZDH-ILXWUORBSA-N		



1.4 Ligand Explorer

- 2NYA: Ligand Explorer: Focuses on small molecules

Small molecules in 2NYA

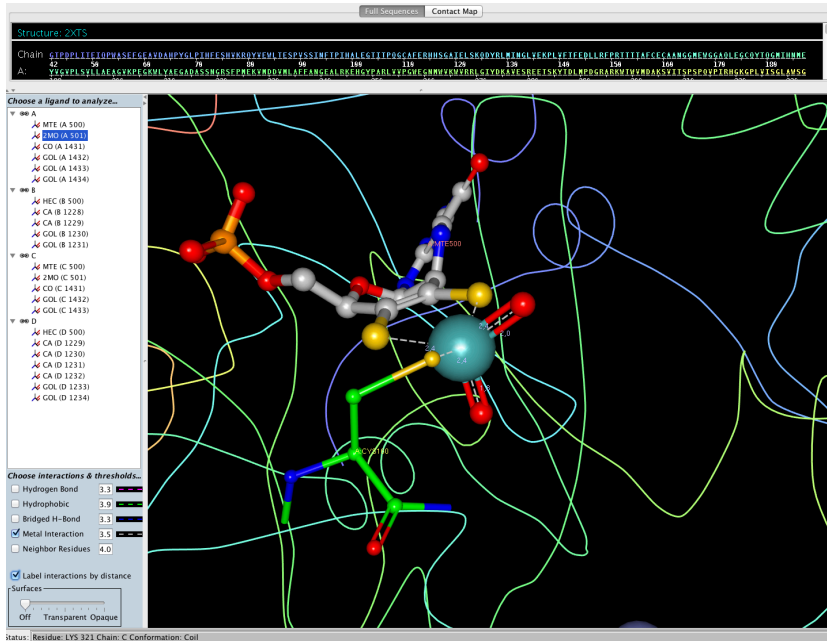


- Visualization options:
- Metal interactions
 - Hydrogen bonds
 - Neighbour residues

1.4 Ligand Explorer

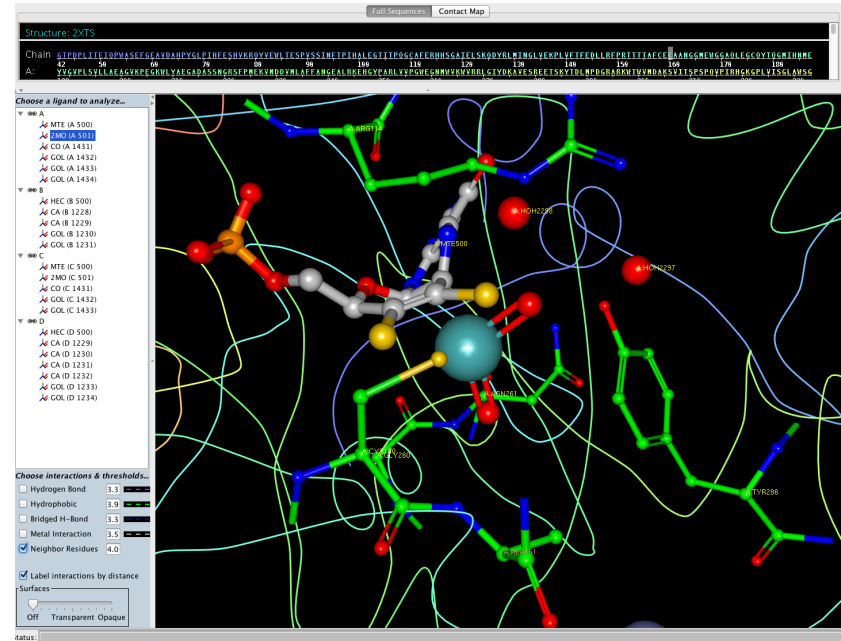
- Visualizing the MoO₂ group (ID: 2MO) on the 2XTS structure

Metal Interactions



3S (2.4 Å)
2O (2.0 and 1.8Å)

Neighbor residues



Backbone: ARG114, MTE500,
ASN261, CYS160, GLY260, ALA161,
TYR282

Two water molecules: HOH2298
HOH2297

1.5 Metal Protein Data Bank (Metal-PDB)

Uses PDB information, but centered in providing with quick access to metal centers in biological systems

The screenshot shows the MetalPDB website interface. At the top, there is a navigation bar with the 'MetalPDB' logo and a search bar. Below the navigation bar, there are three main content areas:

- Left Column:** A news section titled 'We finished to annotate all Molybdenum sites in MetalPDB!!!' with a date of '29/11/2017'. Below this is a small molecular structure diagram. A second news item is dated '25/10/2017' and titled 'MetalPDB Version 2'. It lists seven updates: 1- Information on apo-structures (metal-free), 2- Information on sequences, 3- Information on the secondary structure of the site, 4- Information on the solvent accessibility of the site, 5- Information on the function of the sites (Iron and Copper: completely annotated), 6- New statistics, and 7- Interfaces optimized to improve navigation!. The 'MetalPDB version 2' logo is displayed at the bottom of this section.
- Middle Column:** A search bar labeled 'PDB Id' with a 'Search' button. Below the search bar, a text box states: 'MetalPDB collects and allows easy access to the knowledge on metal sites in biological macromolecules, starting from the structural information contained in the Protein Data Bank (PDB)'. A 'Reference' section follows, citing: 'MetalPDB: a database of metal sites in biological macromolecular structures. Andreini C, Cavallaro G, Lorenzini S, Rosato A. *Nucleic Acids Res.* 2013 Jan;41(Database issue): D312-9. Epub 2012 Nov 15. [PMID: 23155064] Please cite this article to reference MetalPDB in publications.'
- Right Column:** A video player titled 'Basic concepts in MetalPDB'. The video thumbnail shows a 3D protein structure with a play button. The video player interface includes a progress bar showing 0:00 / 0:48.

At the bottom of the page, there is a footer with the text 'Developed at CERM - University of Florence' on the left and the 'West-Life Structures for life' logo on the right.

metalweb.cerm.unifi.it

1.5 Metal Protein Data Bank (Metal-PDB)

Search results for 2nya:

Site Id	Metals	Metals Info	Ligands	Select
2nya_1	Fe, Fe, Fe, Fe	SF4_2001(A)_FE1 SF4_2001(A)_FE2 SF4_2001(A)_FE3 SF4_2001(A)_FE4	SF4_2001(A), CYS_45(A) SF4_2001(A), CYS_17(A) SF4_2001(A), CYS_13(A) SF4_2001(A), CYS_10(A)	<input type="radio"/>
2nya_2	Mo	6MO_5002(F)_MO	CYS_143(F), MGD_6001(F), MGD_7001(F), HOH_7035(F)	<input checked="" type="radio"/>
2nya_3	Fe, Fe, Fe, Fe	SF4_5001(F)_FE2 SF4_5001(F)_FE3 SF4_5001(F)_FE4	SF4_5001(F), CYS_17(F) SF4_5001(F), CYS_13(F) SF4_5001(F), CYS_10(F)	<input type="radio"/>
2nya_4	Mo	6MO_2002(A)_MO	CYS_143(A), MGD_3001(A), MGD_4001(A), HOH_4003(A)	<input type="radio"/>

Showing 1 to 4 of 4 entries

View Previous Next

2NYA(nitrate reductase)

Metal Site

Information on the PDB Chain(s) containing the Site

PDB Chain	Molecule Name	Organism Name	UniProt Id	EC Number
2nya_F	Periplasmic nitrate reductase	Escherichia coli K-12	P33937	1.7.99.4

Information on the Site

Site Name	Nuclearity	Location	Physiological Relevance	Site Image
2nya_2	Mononuclear	Within a Chain	Physiological	

Information on the Function(s) of the Site

Function	Function Details	Metal(s) performing the functions	Reliability
Catalytic	Directly participates to the reaction mechanism of the enzyme	Mo_5002(F)_MO	literature (reference structure = 5hcc)

Information on the Metal(s) in the Site

Metal	Metal Id in PDB	Coordination Number	Coordination Geometry	Endogenous Ligands	Exogenous Ligands
Molybdenum (Mo)	6MO 5002(F) MO	6	trigonal prism (regular)	CYS_143(F)	MGD_6001(F), MGD_7001(F), HOH_7035(F)

Site Classifications

CATH Id	SCOP Id	Pfam Domain
3.40.228.10	-	Molybdopterin

Metal site coordination chemistry

1.5 Metal Protein Data Bank (Metal-PDB)

- How can we search for exogenous groups?

Chemical Component Dictionary (<https://www.wwpdb.org/data/ccd>)

- PDB Dictionary: Residues, small molecules,
- Contains accurate chemical descriptors
- Organizes via 3 alphanumeric characters
- Can be accessed via Ligand Explorer


1.5 Metal Protein Data Bank (Metal-PDB)


- How can we search for exogenous groups?

Chemical Component Dictionary (<https://www.wwpdb.org/data/ccd>)

- PDB Dictionary: Residues, small molecules,
- Contains accurate chemical descriptors
- Organizes via 3 alphanumeric characters
- Can be accessed via Ligand Explorer

- PDBeChem (<http://www.ebi.ac.uk/pdbe-srv/pdbechem/>)

EMBL-EBI  Services Research Training About us

 Protein Data Bank in Europe
Bringing Structure to Biology

Chemical Components in the PDB

Share Feedback

▣ [General Information](#)
▣ [How to Use it](#)
▣ [Overview](#)

▣ **Search By**
▣ [Used in PDB Entry](#)

▣ [Useful Links](#)

[Latest Releases](#)

[Modified Ligands](#)

Dictionary of chemical components (ligands, small molecules and monomers) referred to in PDB entries and maintained by wwPDB. It provides comprehensive search facilities for finding a particular component, or determining components in structure entries or vice versa.

To get started, please read the tutorial and help links in the left panel, or use the tool-tips below to quickly proceed with a search.

Currently searching over 25476 ligands.

PDBeChem : Search for a chemical component

Code

Molecule Name

Formula formula range

Non-Stereo SMILES (Has Sub-Structure)

Fragments (Fragment Expression)

Combine Criteria With AND OR

1.5 Metal Protein Data Bank (Metal-PDB)


- **Formula:** Allows us to search for metal/metals and recover the ligands ID


The screenshot displays the PDBeChem search interface. At the top, the EMBL-EBI logo and navigation links (Services, Research, Training, About us) are visible. The main header reads "Protein Data Bank in Europe" and "Chemical Components in the PDB". Below this, a navigation menu includes "General Information", "How to Use it", "Overview", "Search By", "Useful Links", and "Latest Releases". The "Search By" section is expanded to show search criteria: Code, Molecule Name, Formula, Non-Stereo SMILES, and Fragments. The "Formula" field is highlighted with a red box and contains the value "Mo". The "Combine Criteria With" section shows "AND" selected. The "Latest Releases" section lists various release codes (8GA, 8GG, 9J3, 9J6, BWA, BWS, BXG, BXJ, BXM, BZJ) and a "Modified Ligands" section indicating no modified ligands in this release. The footer includes the PDBe logo and logos for PDB and EMDatabank.

PDBeChem (<http://www.ebi.ac.uk/pdbe-srv/pdbechem/>)

1.5 Metal Protein Data Bank (Metal-PDB)

- The ID codes allows to search in the PDB for proteins with a given cofactor

EMBL-EBI  Services Research Training About us

 Protein Data Bank in Europe
Bringing Structure to Biology


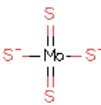
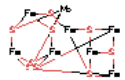
Chemical Components in the PDB

Share Feedback

PDBeChem : Search Results

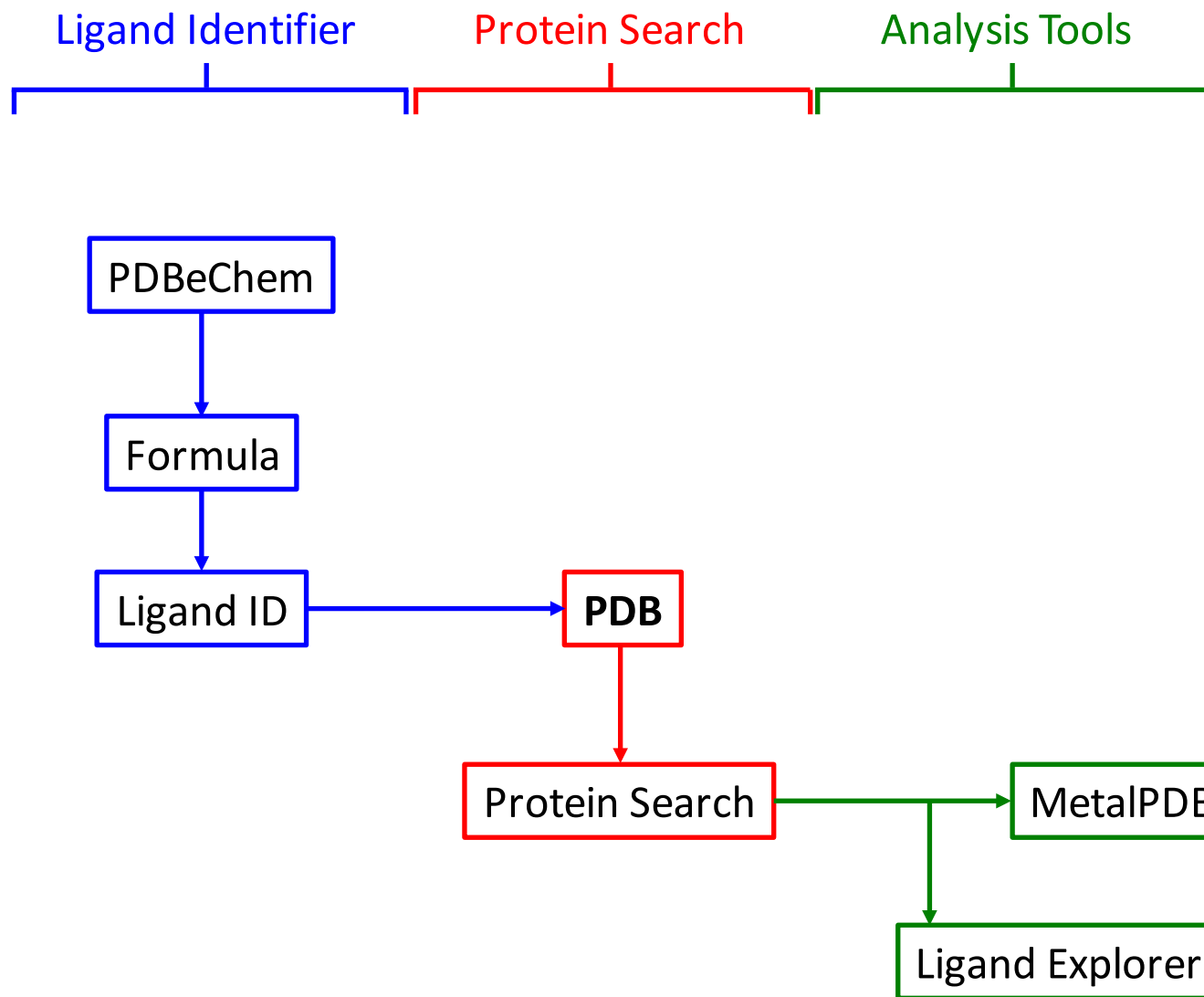
Total number of results: 27

1/1 50 per page

Code	Name	Formula	Structure	Superseded By
2MO	MOLYBDENUM (IV)OXIDE	Mo O2		
4MO	MOLYBDENUM(IV) ION	Mo	Mo ⁺⁴	
4SM	TETRATHIOMOLYBDATE	Mo S4		
6MO	MOLYBDENUM(VI) ION	Mo	Mo ⁺⁶	
CFM	FE-MO-S CLUSTER	Fe7 Mo S9		


PDBeChem (<http://www.ebi.ac.uk/pdbe-srv/pdbechem/>)

1.5 Metal Protein Data Bank (Metal-PDB)



1.5 Metal Protein Data Bank (Metal-PDB)

- **Practical case 1: Search for a structure with chlorophyll**

EMBL-EBI  Services Research Training About us

Protein Data Bank in Europe Chemical Components in the PDB
Bringing Structure to Biology Share Feedback

Dictionary of chemical components (ligands, small molecules and monomers) referred to in PDB entries and maintained by wwPDB. It provides comprehensive search facilities for finding a particular component, or determining components in structure entries or vice versa.

To get started, please read the tutorial and help links in the left panel, or use the tool-tips below to quickly proceed with a search.

Currently searching over 27135 ligands.

Search By

- Used in PDB Entry
- Useful Links
- Download
- Binding Sites
- Chemical search

PDBChem : Search for a chemical component

Code =

Molecule Name =

Formula =


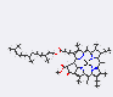
Non-Stereo SMILES (Has Sub-Structure)

Fragments (Fragment Expression)

Combine Criteria With AND OR

Latest Releases

- [8GA](#)
- [8GG](#)

CL2	BETA CHLOROPHYLL A	C55 H72 Mg N4 O5	
CL7	CHLOROPHYLL D	C54 H70 Mg N4 O6	
CLA	CHLOROPHYLL A	C55 H72 Mg N4 O5	
GB0	Bacteriochlorophyll g'	C50 H58 Mg N4 O5	

1.5 Metal Protein Data Bank (Metal-PDB)

- **Practical case 1: Search for a structure with chlorophyll**

The screenshot shows the RCSB PDB website interface. At the top, there is a navigation bar with links for Deposit, Search, Visualize, Analyze, Download, Learn, and More. A search bar contains the text 'CLA' and a 'Go' button. Below the search bar, the results are displayed in a grid format. The 'Ligand ID' column is highlighted with a red box, showing 'CLA'. Other columns include UniProt Molecule Name, Gene View, Protein Feature View, Structural Domains, Membrane Proteins, Author, Organism, and Enzyme Classification. The left sidebar contains navigation options: Welcome, Deposit, Search, Visualize, Analyze, Download, and Learn. The main content area features a section titled 'A Structural View of Bi...' and a promotional banner for the '2018 Video Challenge for High School Students'.

RCSB PDB 144211 Biological Macromolecular Structures Enabling Breakthroughs in Research and Education

WORLDWIDE PDB-101 PDB EMDataBank NUCLEIC ACID DATABASE Worldwide Protein Data Bank Foundation

MyPDB

CLA

Go

close ✕

UniProt Molecule Name	Ligand ID	Gene View	Protein Feature View
<ul style="list-style-type: none">GST class-pi (77)Class... (35)MHC class I molecule (14)Class... (6)Class... (4)GST class-theta (2)	<ul style="list-style-type: none">CLA	<ul style="list-style-type: none">CLASP2... (2)CLASP1... (1)CLASRP...	<ul style="list-style-type: none">cla...cla...

More - Find all

Structural Domains	Membrane Proteins	Author
<ul style="list-style-type: none">Class... (1)DNA polymerase... clamp... (1)Class... (1)Class... (1)Class... (1)Class... (1)class i lysyl... [CATH] (1)	<ul style="list-style-type: none">Class... (1)Class... (1)Claudin... (1)Class... (2)Claudins... (2)CLC-K... class... (2)	<ul style="list-style-type: none">Clancy, S. (236)Clausen, T. (96)Clarke, O.B. (60)Clayton, T. (60)Clark, A.C. (59)Claverie, J.M. (54)

More

Organism	Enzyme Classification
<ul style="list-style-type: none">Cladophorales (1)Platynereis... clam... (1)Mactridae (surf clams) (1)Spisula... clam... (1)Styela clava (1)Cladophora (1)	<ul style="list-style-type: none">1.14.11... Clavaminate... (5)3.4.21... Classical... (6)

More

Welcome

Deposit

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Visualize

Analyze

Download

Learn

A Structural View of Bi

This resource is powered by the Protein Data Bank, which provides the 3D shapes of proteins, nucleic acids, and other macromolecules. This resource helps students and researchers understand all aspects of life, from protein synthesis to health and disease.

As a member of the wwPDB, the RCSB PDB provides research and education in molecular biology, and beyond.

Award-Winning Videos on Ant

2018 Video Challenge for High School Students

BLACTAM ANTIBIOTIC

1.5 Metal Protein Data Bank (Metal-PDB)

- **Practical case 1: Search for a structure with chlorophyll**

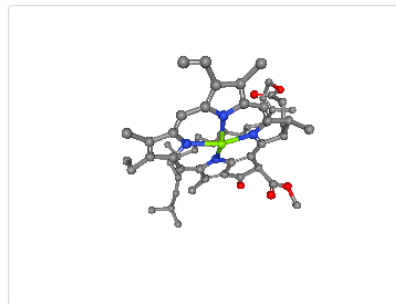
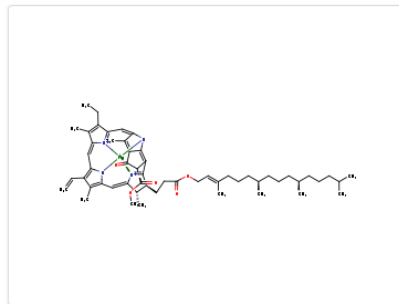
RCSB PDB Deposit Search Visualize Analyze Download Learn More MyPDB

144211 Biological Macromolecular Structures Enabling Breakthroughs in Research and Education

Search by PDB ID, author, macromolecule, sequence, or ligands **Go**

Advanced Search | Browse by Annotations

PDB-101 PDB WORLDWIDE PROTEIN DATA BANK EMDatabank NUCLEIC ACID SOLUTIONS Worldwide Protein Data Bank Foundation



Rotate Hydrogens Labels

CLA
CHLOROPHYLL A

View / Download Files

CLA as a free ligand exists in 94 entries. Examples include: 2E75 2WSE 5XNO

Find related ligands: [Stereoisomers](#) [Similar ligands](#)
[Chemical Structure Search](#)

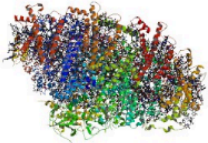
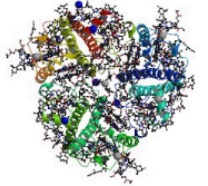
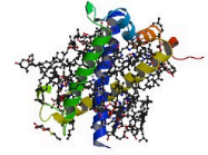
[View summary at Ligand Expo](#)

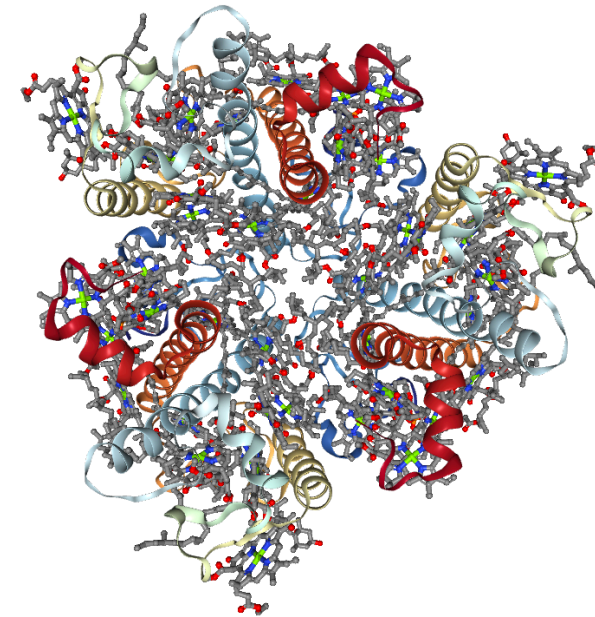
Chemical Component Summary	
Name	CHLOROPHYLL A
Identifiers	n/a
Formula	C ₅₅ H ₇₂ Mg N ₄ O ₅
Molecular Weight	893.49
Type	NON-POLYMER
Isomeric SMILES	<chem>CCC1=C(O)C2=Cc3c(C=C)C(C)c4C=C5[C@@H](C)[C@H](CCC(=O)OC)C=C(C)CCC(C@H)(C)CCC(C@H)(C)CCCC(C)C6=[N+]5[Mg@]5(n34)n3c(=CC1=[N+]25)c(C)c1C(=O)[C@H](C(=O)OC)C6=c31</chem>
InChI	InChI=1S/C55H73N4O5.Mg/c1-13-39-35(8)42-28-44-37(10)41(24-25-48(60)64-27-26-34(7)23-17-22-33(6)21-16-20-32(5)19-15-18-31(3)4)52(58-44)50-51(55(62)63-12)54(61)49-38(11)45(59-53(49)50)30-47-40(14-2)36(9)43(57-47)29-46(39)56-42;/h13,26,28-33,37,41,51H,1,14-25,27H2,2-12H3,(H-,56,57,58,59,61);/q-1;+4/p-1/b34-26+;/t32-,33-,37+,41+,51-;/m1./s1
InChIKey	VIQFHHZSLDFWU-AENIHSZSA-M

Chemical Details	
Formal Charge	2
Atom Count	137
Chiral Atom Count	8
Chiral Atoms	C13, C2A, C3A, C8, CBD, NA, NC, ND
Bond Count	145
Aromatic Bond Count	5
Leaving Atoms	n/a

1.5 Metal Protein Data Bank (Metal-PDB)

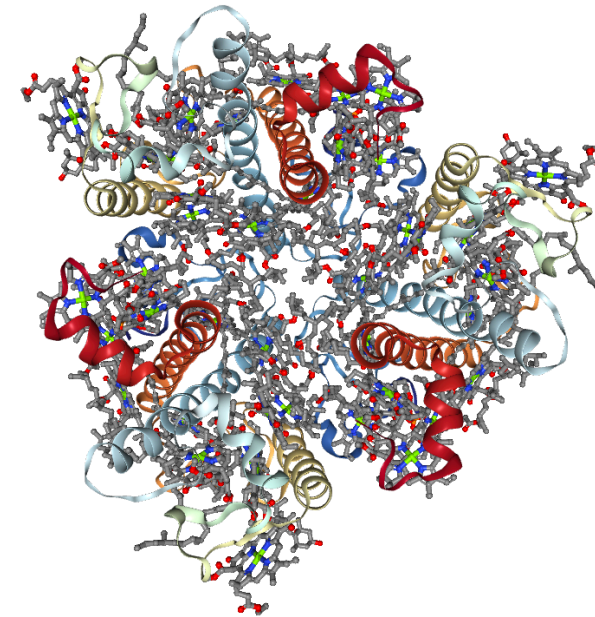
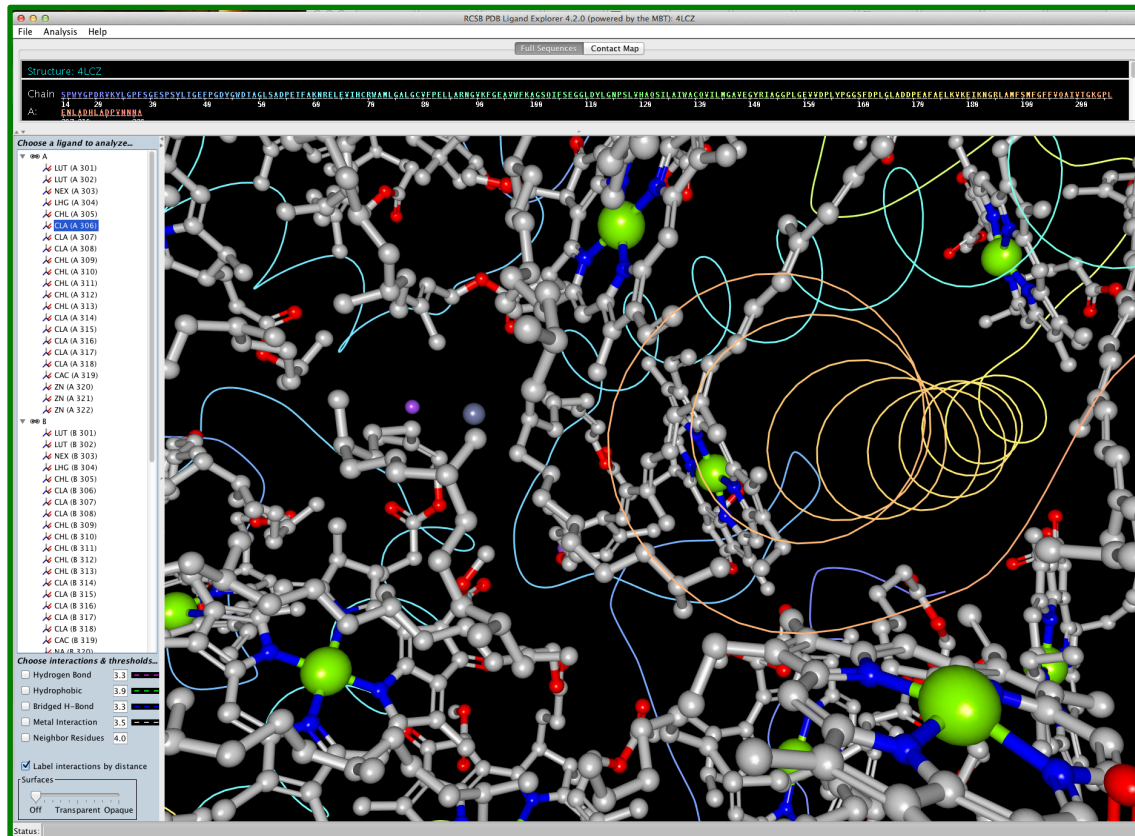
- **Practical case 1: Search for a structure with chlorophyll**

 3D View	4XK8 Crystal structure of plant photosystem I-LHCI super-complex at 2.8 angstrom resolution Qin, X., Suga, M., Kuang, T., Shen, J.R. (2015) Science 348 989-995 Released: 6/10/2015 Method: X-ray Diffraction Resolution: 2.8 Å Residue Count: 6434 Macromolecule: Unique protein chains: 16 Unique Ligands: BCR, CHL, CLA, DGD, HTG, LHG, LMG, LMT, LUT, PQN, SF4, XAT	Download File View File <input checked="" type="checkbox"/>
 3D View	4LCZ Crystal structure of a multilayer-packed major light-harvesting complex Wan, T., Li, M., Zhao, X., Zhang, J., Liu, Z., Chang, W.R. (2014) Mol Plant Released: 5/7/2014 Method: X-ray Diffraction Resolution: 2.6 Å Residue Count: 672 Macromolecule: Major chlorophyll a/b binding prot ... (protein) Unique Ligands: CAC, CHL, CLA, LHG, LUT, NA, NEX, ZN	Download File View File <input checked="" type="checkbox"/>
 3D View	3PL9 Crystal structure of spinach minor light-harvesting complex CP29 at 2.80 angstrom resolution Pan, X.W., Li, M., Wan, T., Wang, L.F., Jia, C.J., Hou, Z.Q., Zhao, X.L., Zhang, J.P., Chang, W.R. PubMed ID is not available. Released: 2/9/2011 Method: X-ray Diffraction Resolution: 2.8 Å Residue Count: 243 Macromolecule: Chlorophyll A-B binding protein (protein) Unique Ligands: CHL, CLA, G3P, HTG, LUT, NEX, XAT	Download File View File <input checked="" type="checkbox"/>



1.5 Metal Protein Data Bank (Metal-PDB)

- **Practical case 1: Search for a structure with chlorophyll**



1.6 Additional Tools



VMD (Visual Molecular Dynamics)
<https://www.ks.uiuc.edu/Research/vmd/>



Mercury
<https://www.ccdc.cam.ac.uk/solutions/csd-system/components/mercury/>



Chimera
<https://www.cgl.ucsf.edu/chimera/>

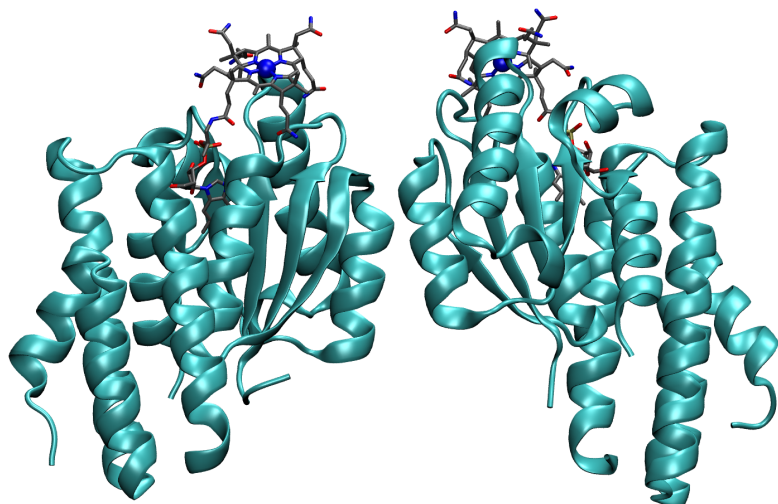
Integrating the PDB as a teaching tool for coordination Chemistry

2.1 Metalloenzymes as illustrative examples

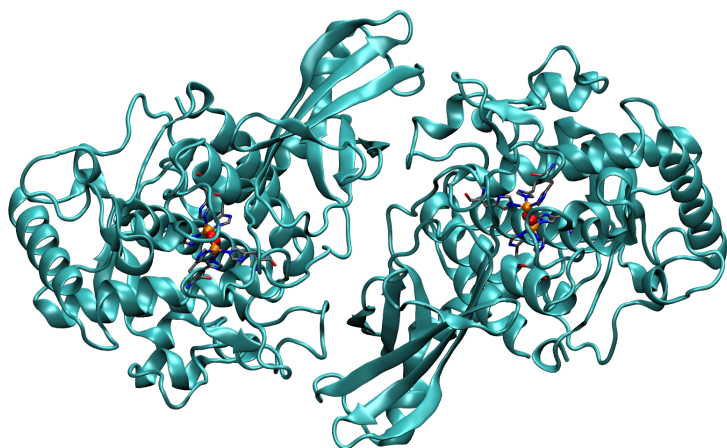
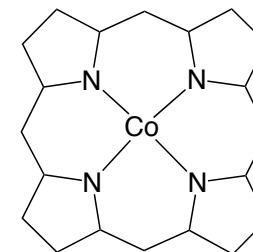
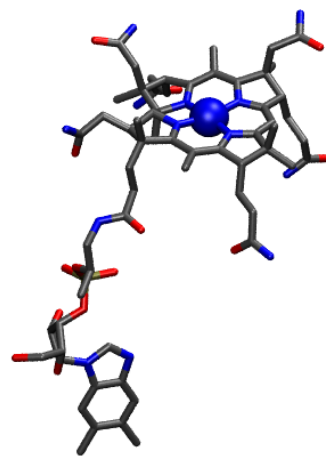
- Metalloenzymes contain metal coordination sites: They can be used as illustrative examples

																		Elements of biological use		Elements in drugs or toxins																			
H																	He																						
Li	Be											B	C	N	O	F	Ne																						
Na	Mg											Al	Si	P	S	Cl	Ar																						
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																						
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																						
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																						
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo																						

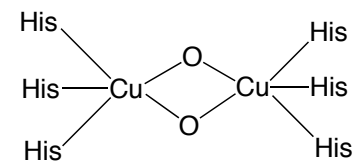
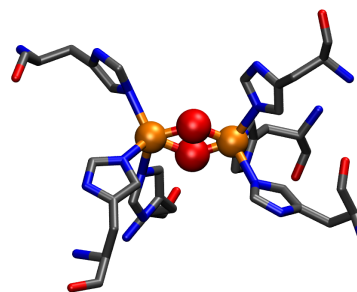
2.1 Metalloenzymes as illustrative examples



cobalamin-binding protein

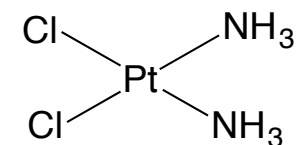
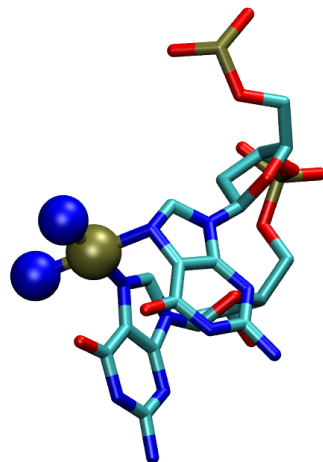
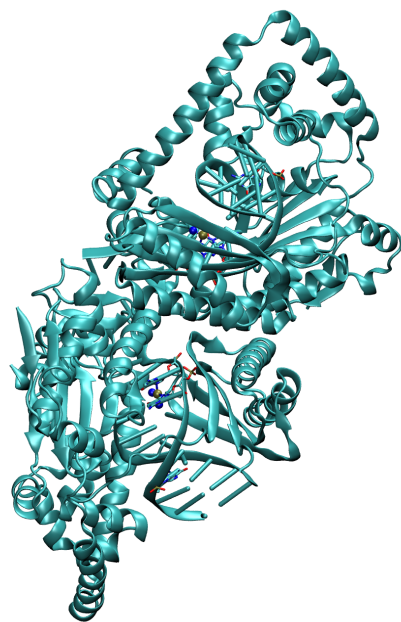


Hemocyanin

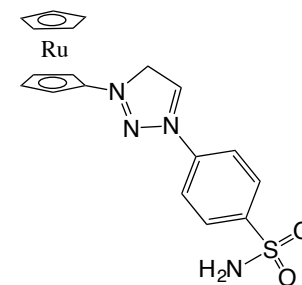
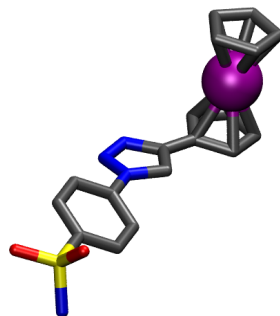


Biological systems allow for a contextualization of coordination chemistry
Visually appealing systems

2.1 Metalloenzymes as illustrative examples

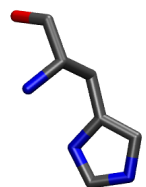


DNA polymerase with DNA containing a major *cis*-platin lesion

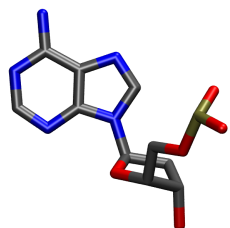


Carbonic anhydrase II in complex with p-(4-ruthenocenyl-1H-1,2,3-triazol-1-yl)benzenesulfonamide

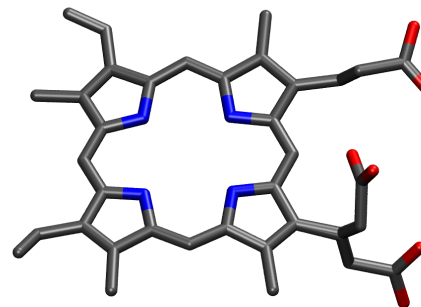
2.2 Coordination motifs in active sites



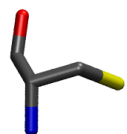
Histidine



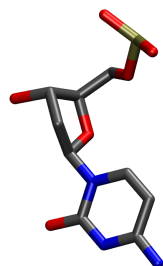
Adenine



chloro/heme group



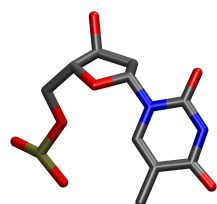
Cysteine



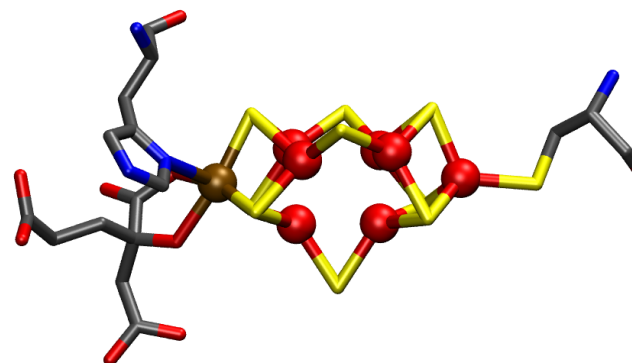
Cytosine



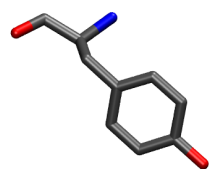
Methionine



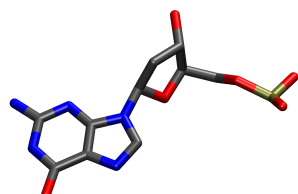
Thymine



Fe-Mo cofactor

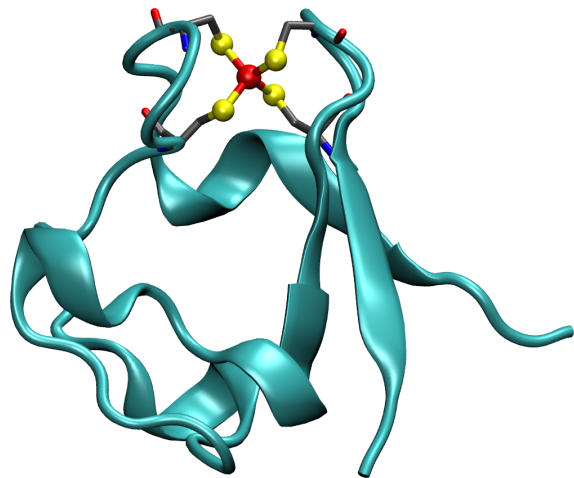


Tyrosine

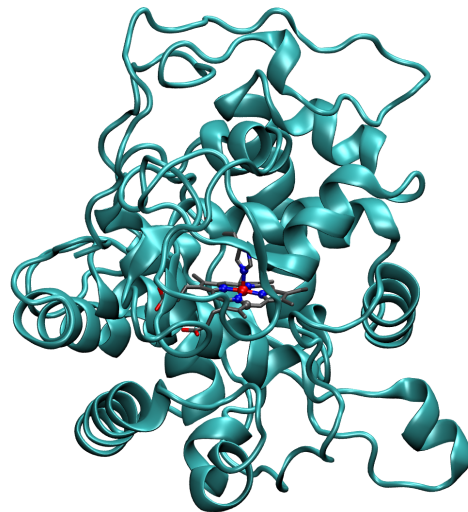


Guanine

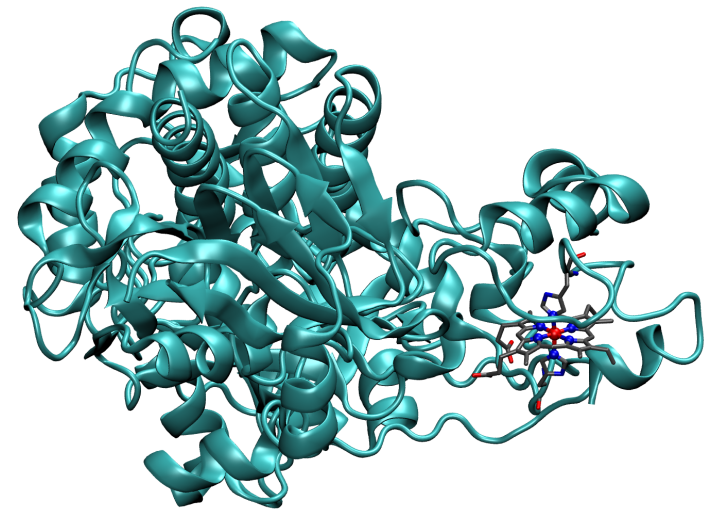
2.3 Geometrical Data/Coordination Modes



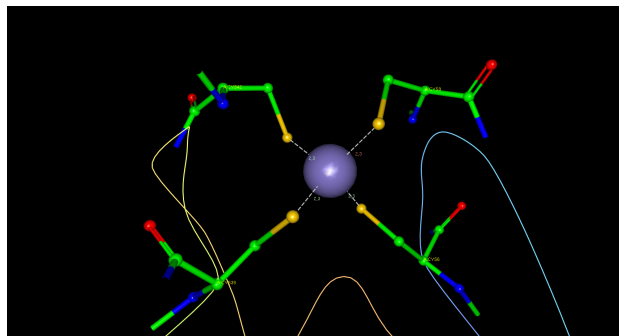
[FeS₄]-Td



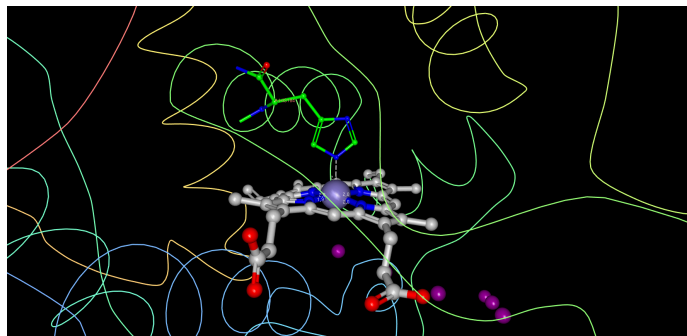
[FeN₅]-SPY



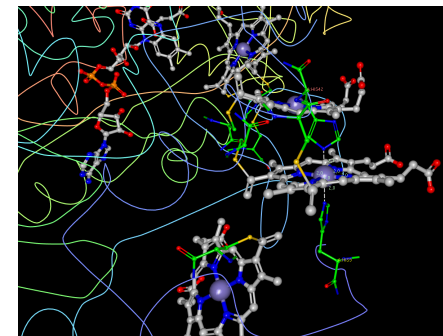
[FeN₆]-Oh



$$r(\text{Fe-S}) = 2.3 \text{ \AA}$$



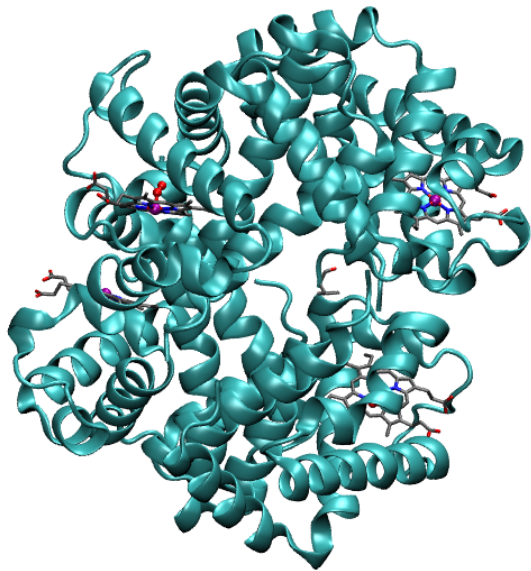
$$r(\text{Fe-N}) = 2.0\text{-}2.1 \text{ \AA}$$



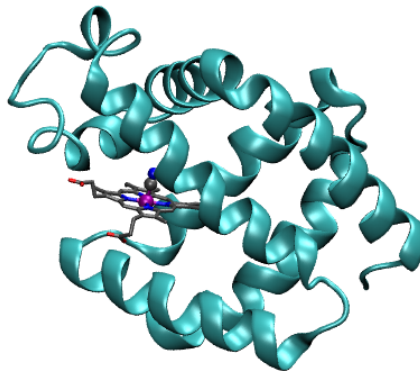
$$r(\text{Fe-N}) = 2.0\text{-}2.1 \text{ \AA}$$

Study of coordination numbers
Donor-acceptor, bonding concepts, metal-ligand bond-length

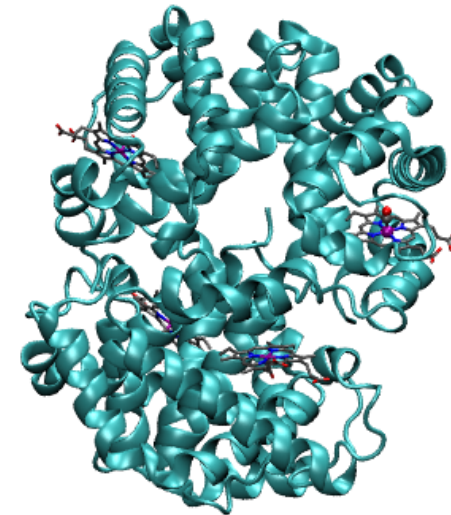
2.3 Geometrical Data/Coordination Modes



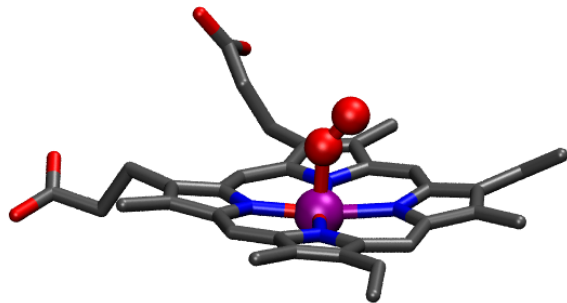
oxy-heme



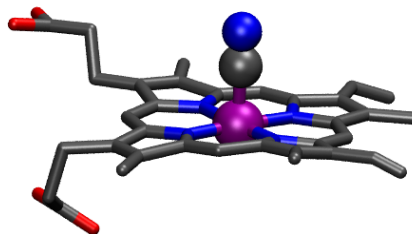
cyano-heme



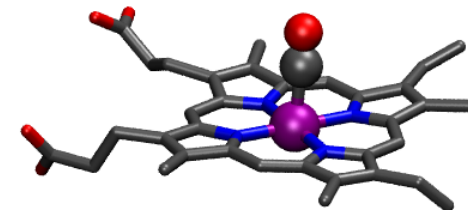
carbonyl-heme



$$r(\text{Fe-CN}) = 1.949 \text{ \AA}$$



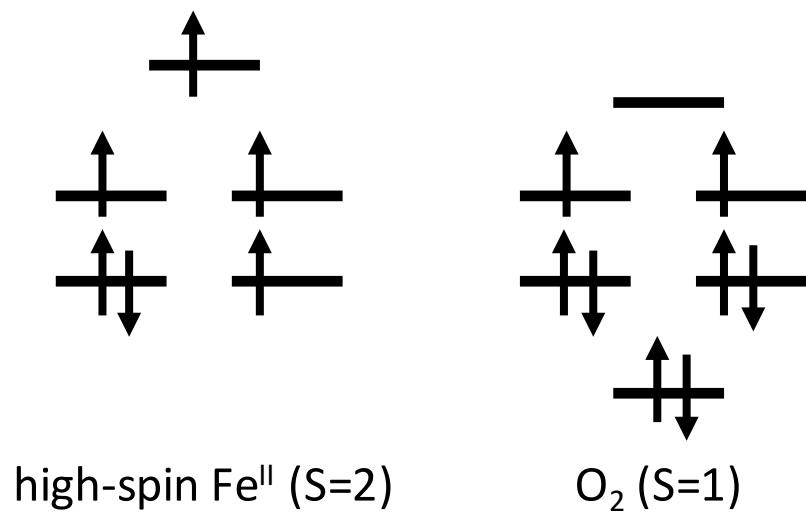
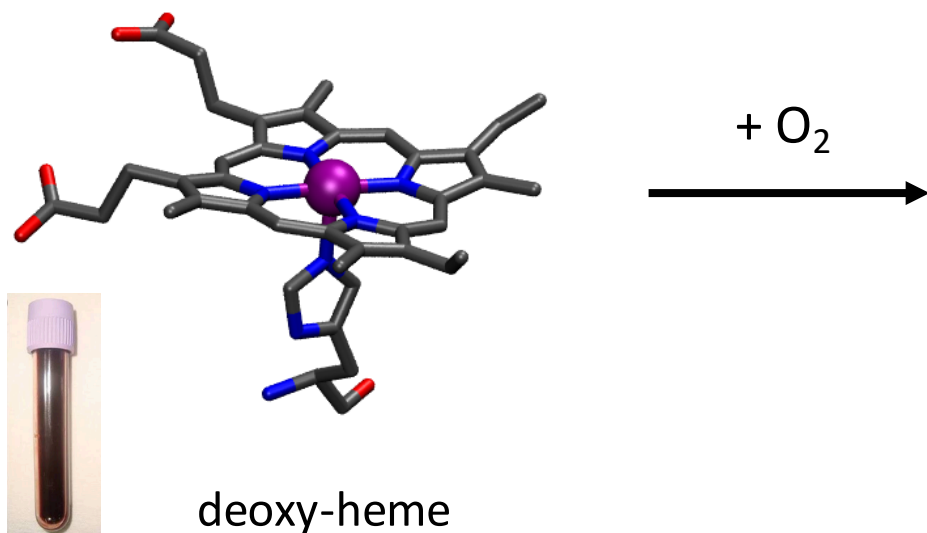
$$r(\text{Fe-CN}) = 1.949 \text{ \AA}$$



$$r(\text{Fe-CO}) = 2.018 \text{ \AA}$$

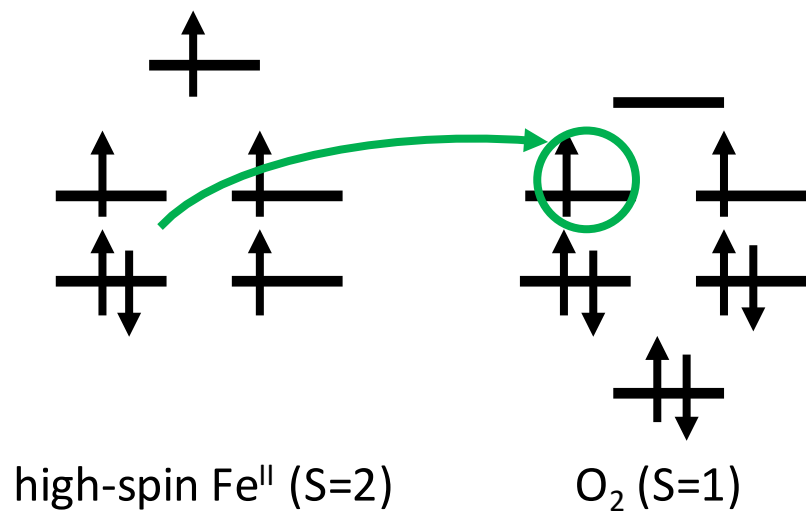
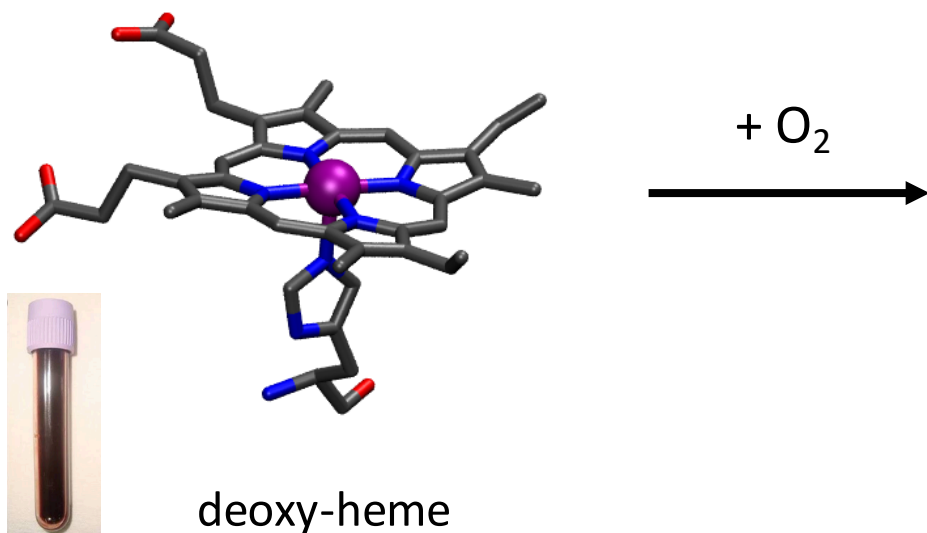
σ -bonding, π -bonding and backbonding

2.4 Spin-State Information



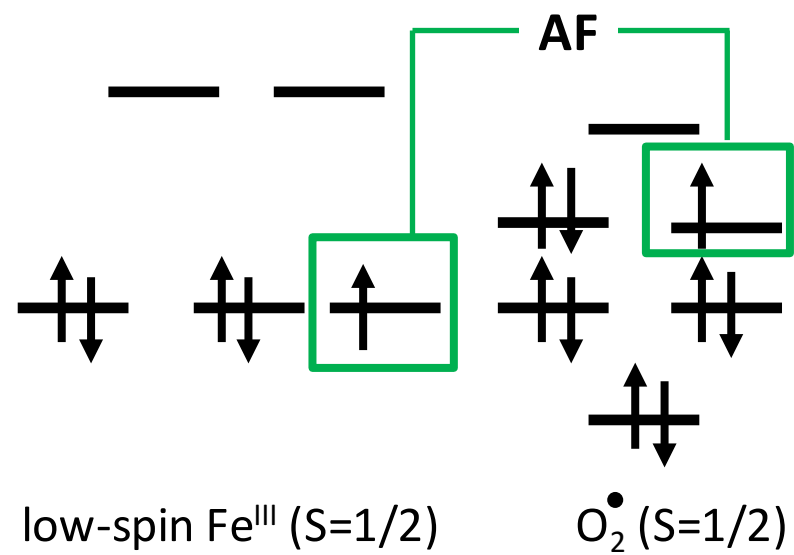
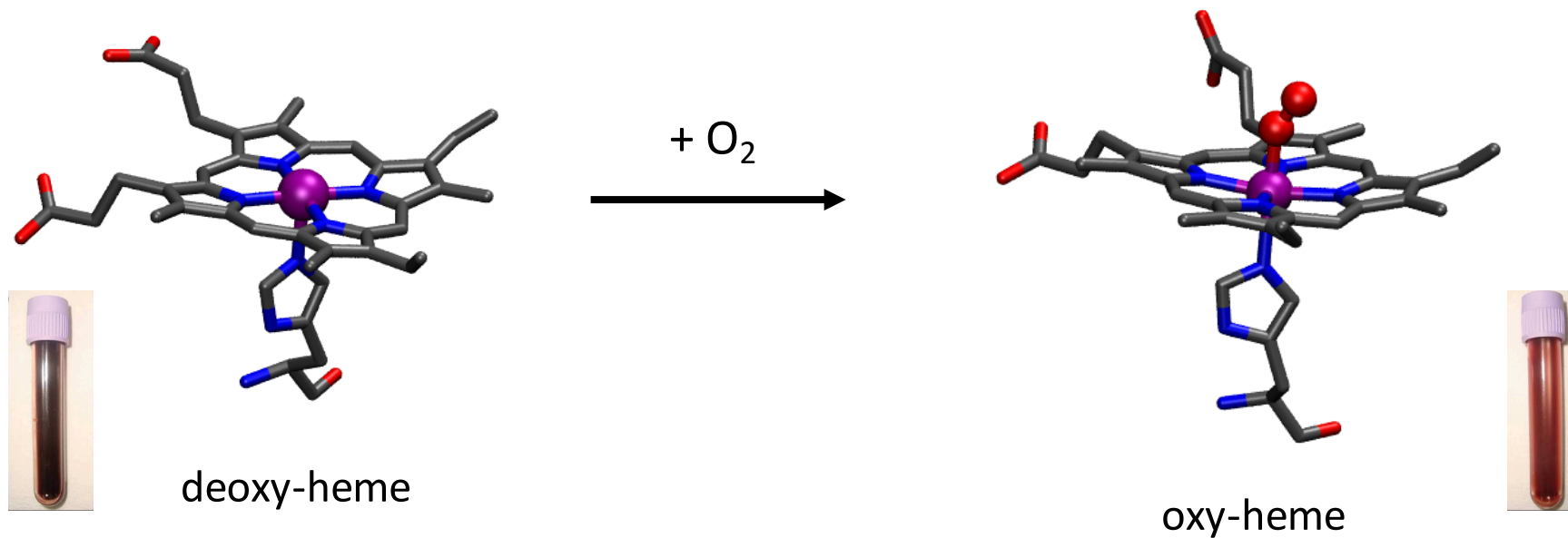
Electronic structure, spin-state, oxidation

2.4 Spin-State Information



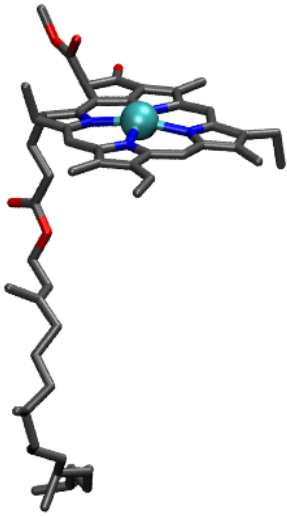
Electronic structure, spin-state, oxidation

2.4 Spin-State Information

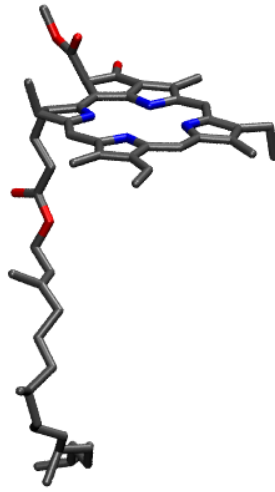


Electronic structure, spin-state, oxidation

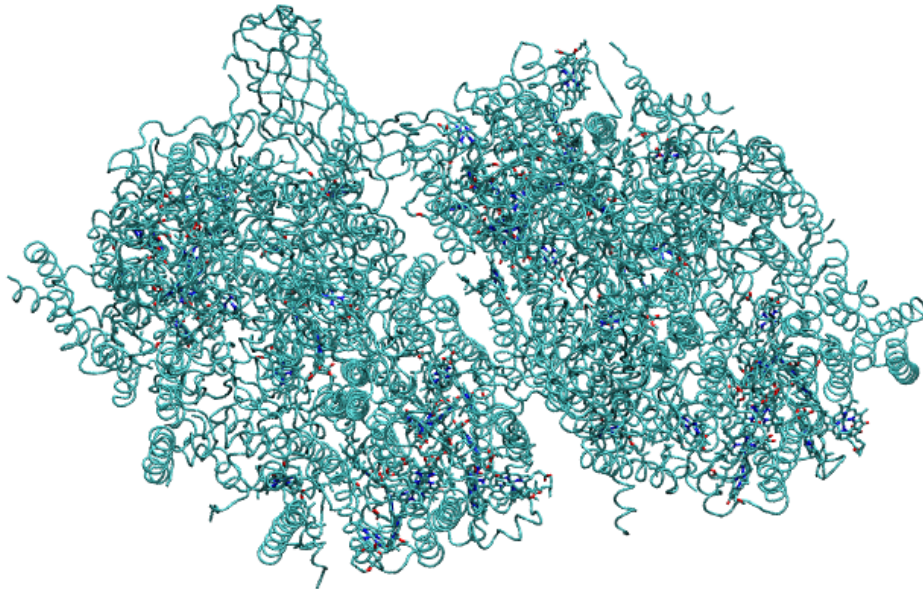
2.5 Absorption Spectroscopy



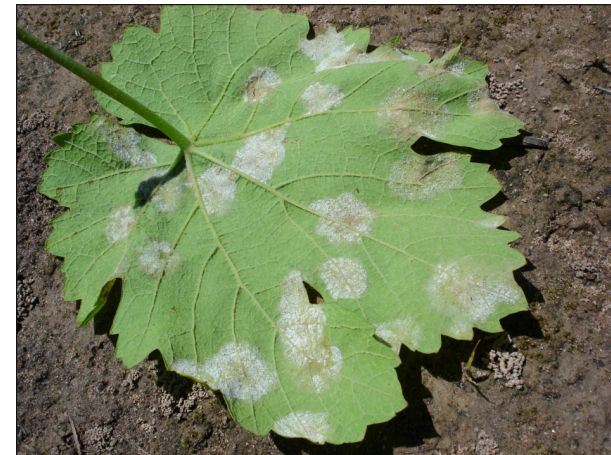
Chlorophyll A



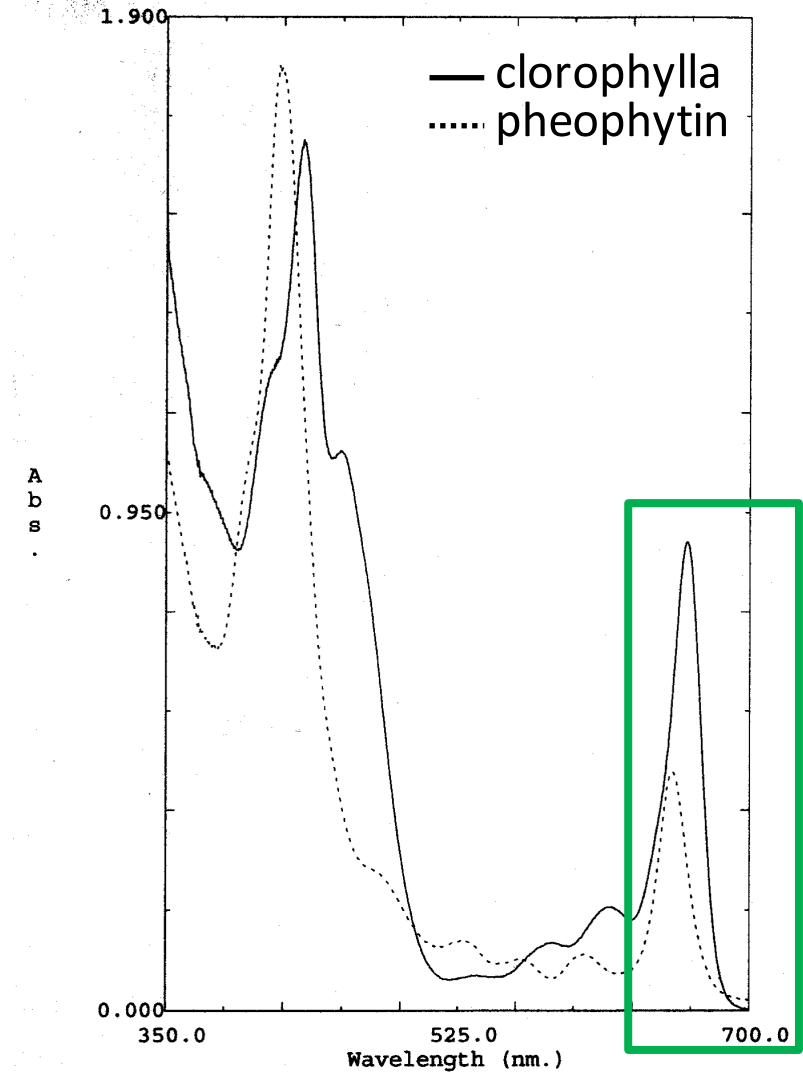
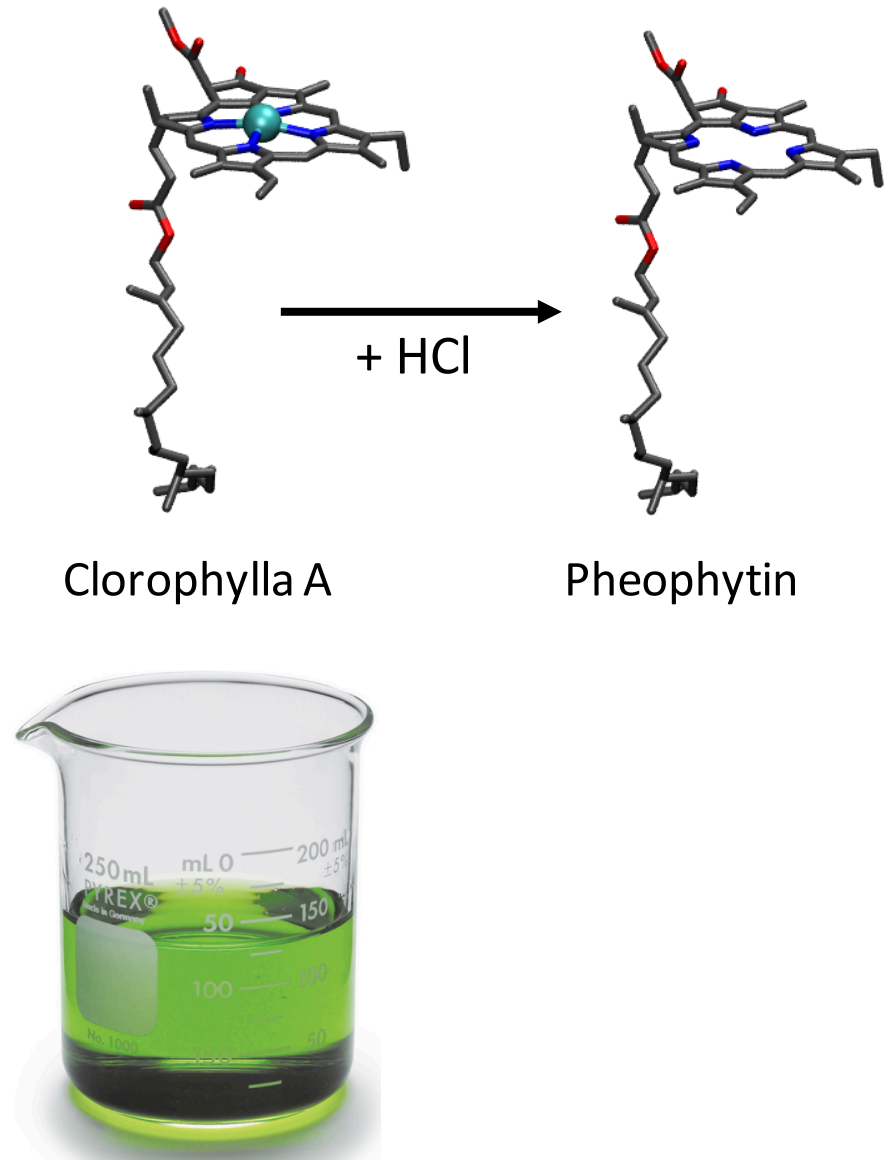
Pheophytin



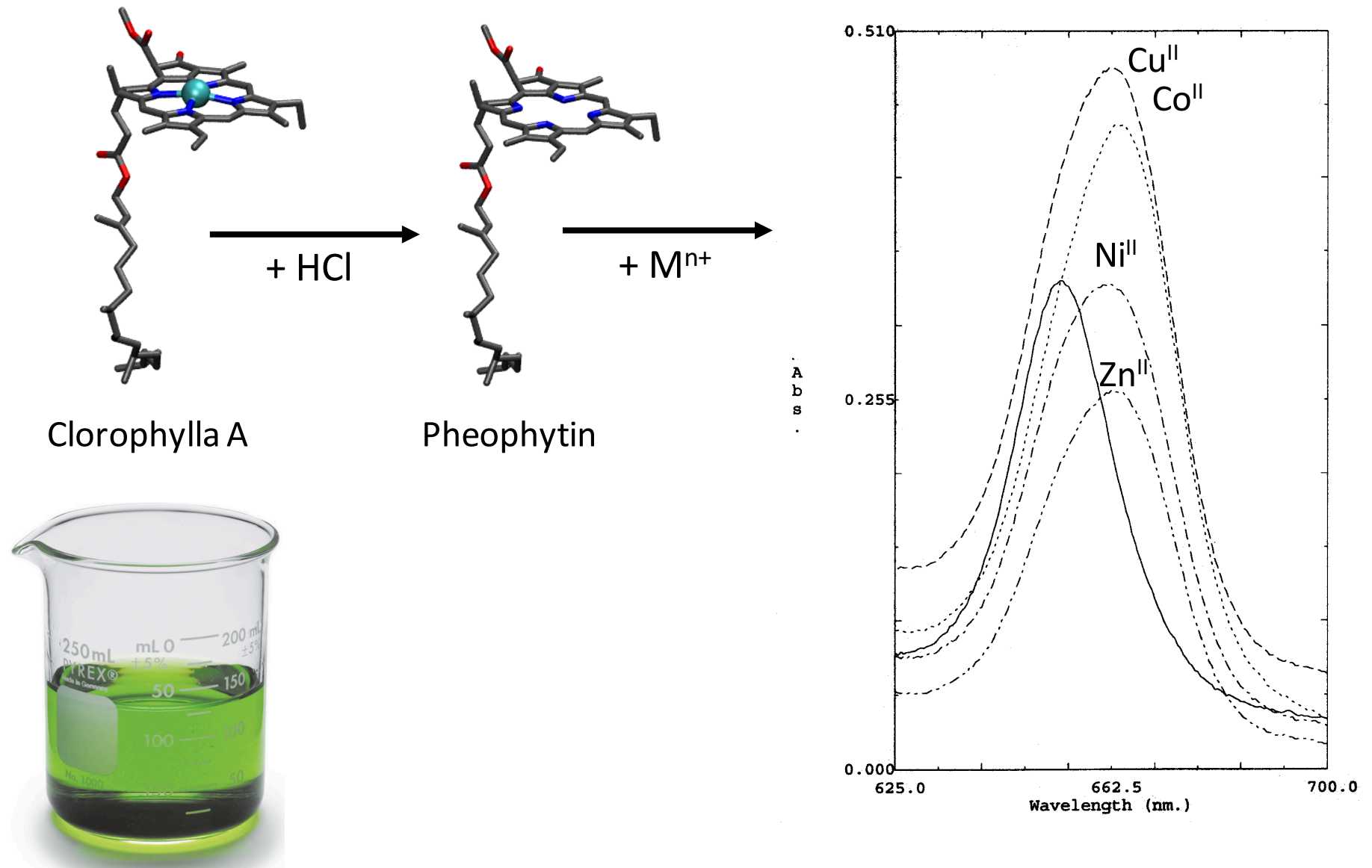
Photosystem II



2.5 Absorption Spectroscopy



2.5 Absorption Spectroscopy



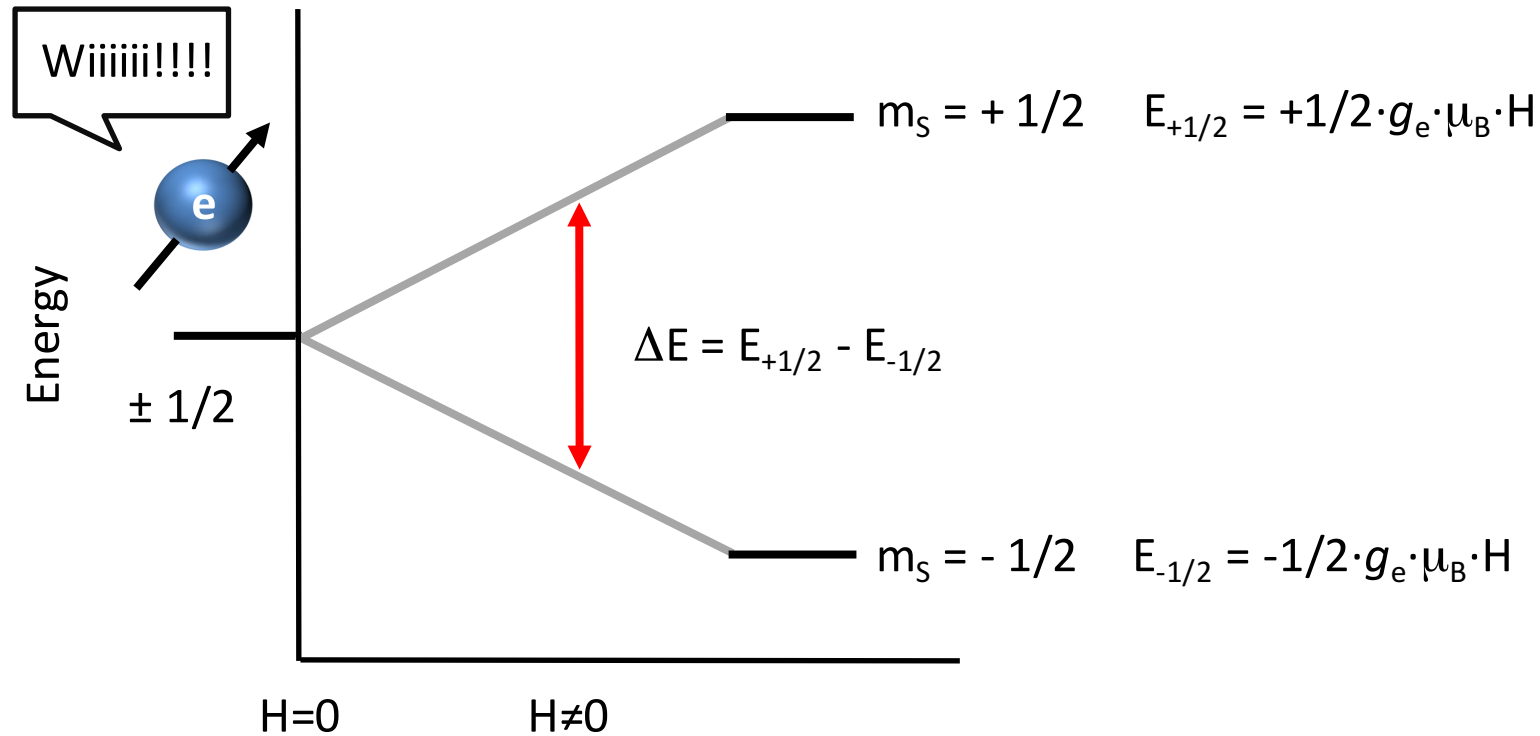
Color can be tuned via metal exchange
Changes in electronic spectra: Spectrochemical series of metals

2.6 Electron Paramagnetic Resonance

Physical origin of the EPR signal

Zeeman effect: $\rightarrow \mathbf{H} = g_e \cdot \mu_B \cdot \mathbf{H} \cdot \mathbf{S} \rightarrow E = m_S \cdot g_e \cdot \mu_B \cdot H$

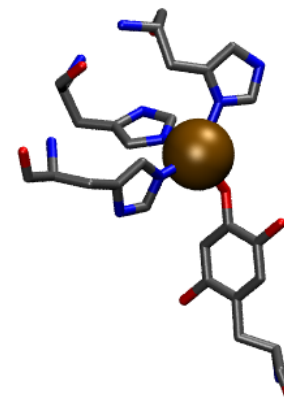
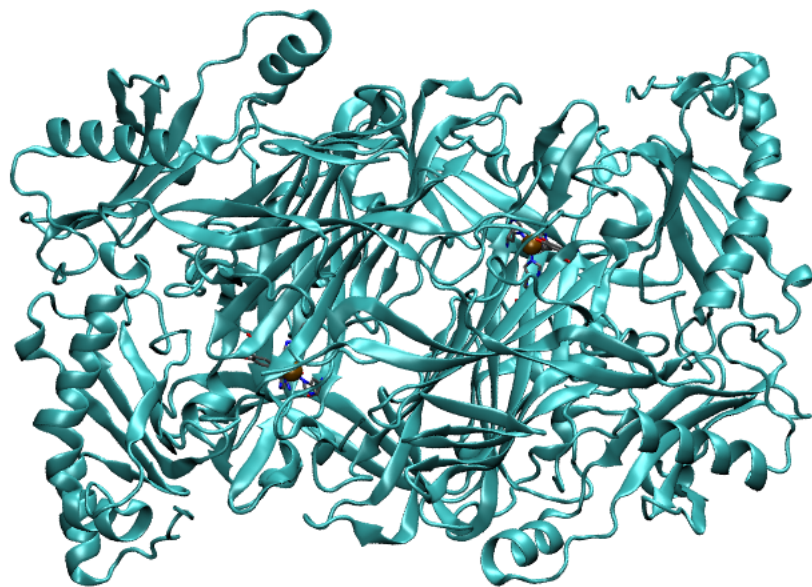
Selection Rule
 $\Delta M_S = \pm 1$



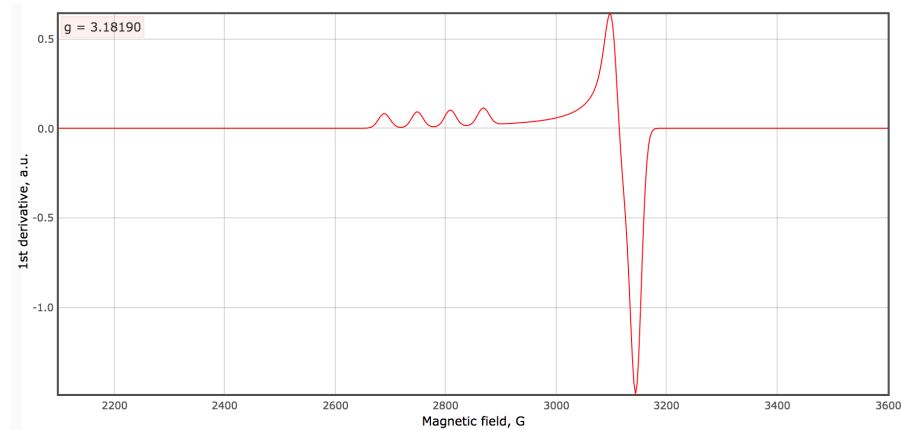
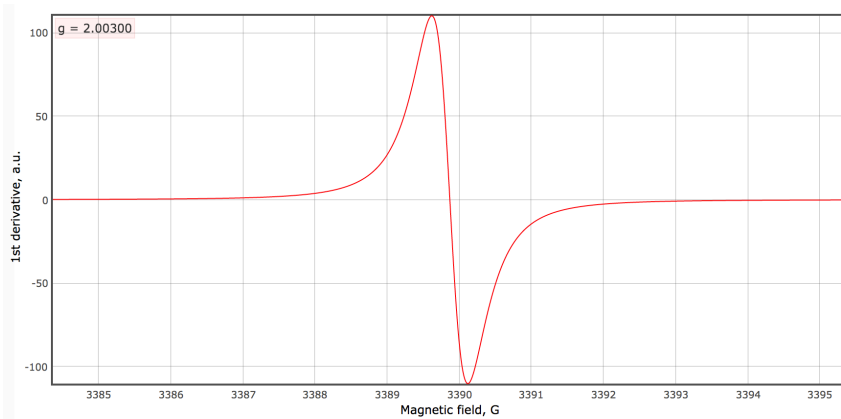
Fundamental equation of EPR spectroscopy

$$\left. \begin{array}{l} \Delta E = g_e \cdot \mu_B \cdot H \\ \Delta E = h\nu \end{array} \right\} \boxed{h\nu = g_e \cdot \mu_B \cdot H}$$

2.6 Electron Paramagnetic Resonance



Single Cu^{II} d⁹ ion



Free electro EPR spectra
Cu^{II}spectra (g_x , g_y and g_z)

2.7 Practical Cases

- How many *homo sapiens* structures contain the $[\text{WO}_4]^{2-}$ motif?
- “Zinc fingers” are proteins involved in repairing and replication processes of DNA
 - Search for the 2EPC structure
 - Visualize the Zn^{2+} cation using Ligand Explorer software
 - Write down the name of the Zn coordinating amino-acids
 - Write down the four Zn-L metal-ligand bond lengths
- Search for the *cis*-platin $[\text{PtCl}_2(\text{NH}_3)_2]$ identifier
 - Recover one structure in which *cis*-platin is interacting with the DNA (5N26)
 - Visualize the structure in Mercury
 - Visualize the structure using the Ligand Explorer software
 - Search for neighbour residues
 - Write down all Pt-L metal-ligand bond lengths

2.7 Practical Cases

- How many *homo sapiens* structures contain the $[\text{WO}_4]^{2-}$ motif?

ID: WO4; homo sapiens 6

- “Zinc fingers” are proteins involved in repairing and replication processes of DNA
 - Search for the 2EPC structure
 - Visualize the Zn^{2+} cation using Ligand Explorer software
 - Write down the name of the Zn coordinating amino-acids
 - Write down the four Zn-L metal-ligand bond lengths

ID: Zn; CYS247, CYS250, CYS267 and HIS263: 2.3, 2.2, 2.3 y 2.1 Å

- Search for the *cis*-platin $[\text{PtCl}_2(\text{NH}_3)_2]$ identifier
 - Recover one structure in which *cis*-platin is interacting with the DNA (5N26)
 - Visualize the structure in Mercury
 - Visualize the structure using the Ligand Explorer software
 - Search for neighbour residues
 - Write down all Pt-L metal-ligand bond lengths

ID: CPT; LYS68 and HIS136; 2.1, 2.1 Å (Pt-NH₃ 2.1 and 2.0 Å)

2.7 Practical Cases

Written report 1:

1. The protein's name, PDB code, and its function
2. A picture of the binding site from the X-ray
3. ChemDraw representations of a number of inorganic complexes that display similar coordination chemistry and activity, giving Conquest refcode and IUPAC names
4. A brief account of the synthesis of the chosen analogue
5. Key literature references

Written report model 2:

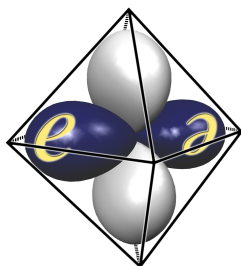
1. Protein function (e.g., electron transfer–ligand exchange, ligand modification) and its relation to the nature of the binding site: the coordination number and geometry, whether it is hard or soft, or has a vacant coordination site
2. The oxidation state of the metal
3. The suitability of the metal for the purpose for which it is used. Can other metals provide a similar function?
4. A critical evaluation of the model complexes available
5. A brief explanation of what can be added to our knowledge from wet chemistry, analysis, and spectroscopy

3. Summary and Outlook

- The **PDB** is an open access structural database with tons of information (allows the student work on his own!!)
- In combination with **Metal-PDB** and **PDBeChem** can be used to scan for metalloenzymes
- Metalloenzymes can be used to illustrate coordination chemistry basic ideas
- Metalloenzymes can be used to illustrate spectroscopic techniques
- Possibility of designing specific curricular problems for both coordination chemistry and bioinorganic courses

Acknowledgments

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