UNIT 4: ORD and CD

Part IV: Application of ORD & CD in determining absolute configuration of metal complexes

M.Sc. Semester II

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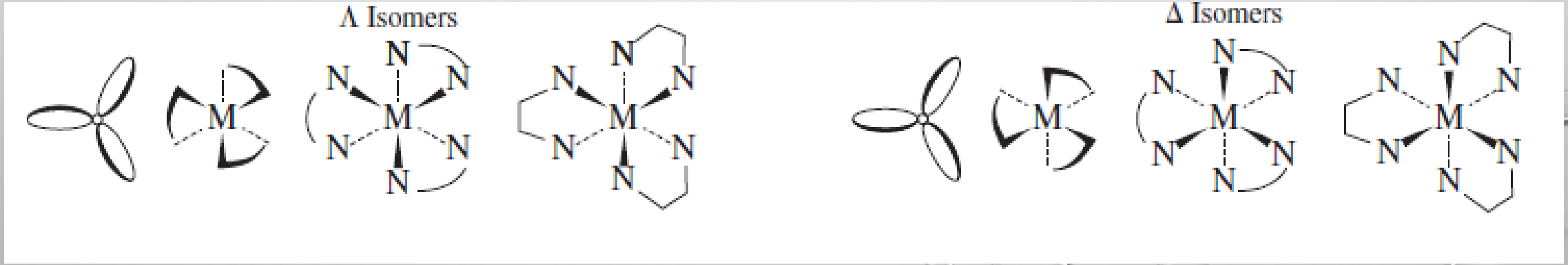
Absolute configuration of Complexes

- It is not possible to assign the absolute configuration simply on the basis of the direction of rotation of the plane of polarized light.

Assignment of configuration

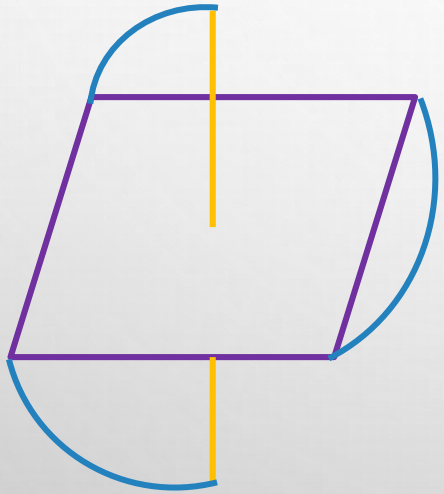
- Complexes with three rings formed via chelating ligands, such as $[Co(en)_3]^{3+}$, can be treated like three-bladed propellers by looking at the molecule down a threefold axis.



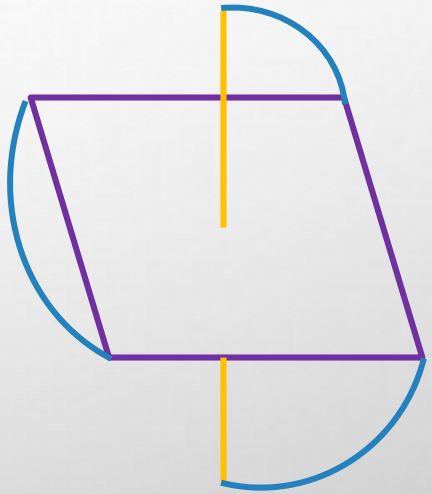
Picture Credit: Inorganic Chemistry, 5th Edition, Miessler & Tarr, Chapter 9.

Absolute configuration of Complexes

To decide the handedness one should view, for example, tris(chelate) down the three fold rotational axis. If the helix thus viewed is right-handed, the isomer is the Δ-isomer, and its mirror image is the Λ-isomer.



Λ or D isomer



Δ or L isomer

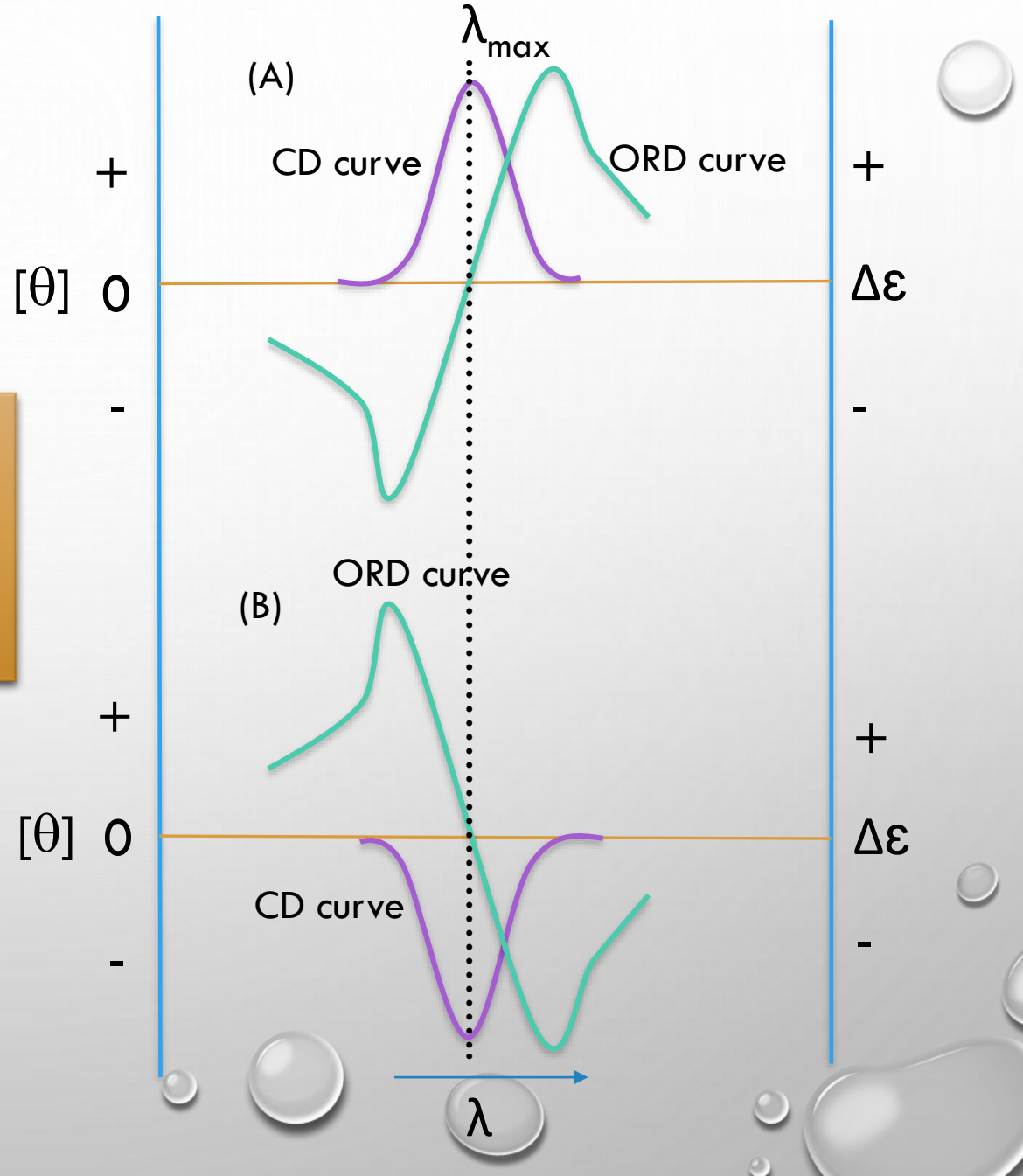
Absolute configuration of Complexes

- ORD and CD are two phenomena associated with d-d transitions that that are useful in assigning absolute configurations.
- A general rule is- ***If, in analogous compounds, corresponding electronic transitions shown Cotton effects of the same sign, the compounds have the same optical configuration.***
- ORD involves measuring the variation of optical rotation with wavelength. There is an abrupt reversal of rotation in the vicinity of absorption band (See Cotton effect, part III).
- If the complex is initially laevorotatory, the ORD curve falls to a minimum, rises rapidly to a maximum, and then slowly falls. If the complex was initially dextrorotatory, the effect is reversed with ORD curve rising first to a maximum, then falling. These represents positive and negative Cotton effects, respectively.

(A) Positive cotton effect

The maximum absorption values
For ORD: 0 (Zero), See green colour curve
For CD : λ_{max} , See violet colour curve
Two graphs represent two enantiomers

(B) Negative cotton effect

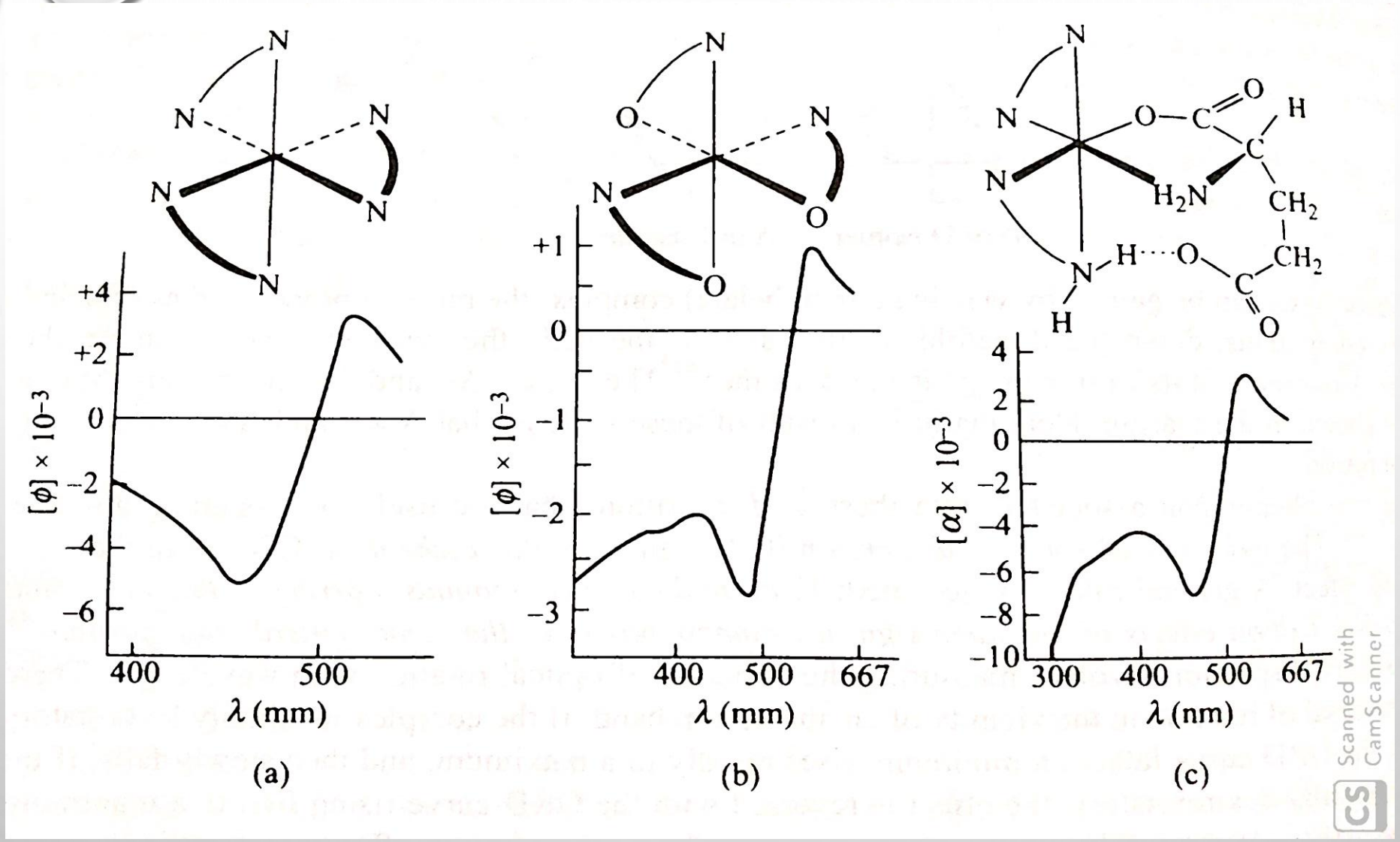


Absolute configuration of Complexes

- ORD curves are useful in the assignment of absolute configurations. For example, the configurations of the enantiomers of
  - tris(ethylenediamine)cobalt(III)
  - Tris(alaninato)cobalt(III), and
  - Bis(ethylenediamine)glutamatocobalt(III)

  are known from X-Ray investigations, and it is found that the three Λ-(D)-configuration could have been assigned to any of these in the absence of x-ray data simply on the basis of the similarity of the ORD spectra to one of the known configuration.

- Complexes having the same sign of CD for a given absorption band will have the same absolute configuration.



Picture Credit: **Inorganic Chemistry: Principles of Structure and Reactivity** James Huheey, Medhi

The absolute configurations and ORD spectra of (a) Λ-$[Co(en)_3]^{3+}$; (b) Λ-$[Co(S\text{-alanine})_3]$; (c) Λ-$[Co(en)_2(S\text{-glu})]^{+}$. All of these complexes have Λ or D configuration

CD data for some Λ-(D)- and Λ-(L)-tris(chelate) complexes of cobalt(III)*

Formula of complex[b]	ν (cm^{-1})	$\varepsilon_l - \varepsilon_r$	Absolute configuration
$(+)_{589}$-$[Co(en)_3]^{3+}$	20,280	+2.18	Λ
	23,310	−0.20	
$(-)_{589}$-$[Co(en)_3]^{3+}$	20,280	−2.18	Δ^c
	23,310	+0.20	
$(+)_{589}$-$[Co(S\text{-pn})_3]^{3+}$	20,280	+1.95	Λ
	22,780	+2.47	
$(+)_{589}$-$[Co(R\text{-pn})_3]^{3+}$	18,500	+1.3	Λ
$(+)_{589}$-$[Co(S\text{-ala})_3]$	18,500	+1.3	Λ
	21,000	−0.2	
$(+)_{495}$-$[Co(S\text{-glu(en)}_2)]^{2+}$	19,600	+2.5	Λ

*Data adopted from **Inorganic Chemistry: Principles of Structure and Reactivity, 4th Ed.** James Huheey, Medhi

End of Chapter 4: ORD & CD

THANK YOU