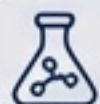


COORDINATION COMPOUNDS · SECTION 5.4.3

Linkage Isomerism

The Macro Impact of Donor-Atom Switching

Exploring ambidentate ligands and the structural pivot points in transition metal complexes that entirely alter their physical properties.



Structural Isomerism

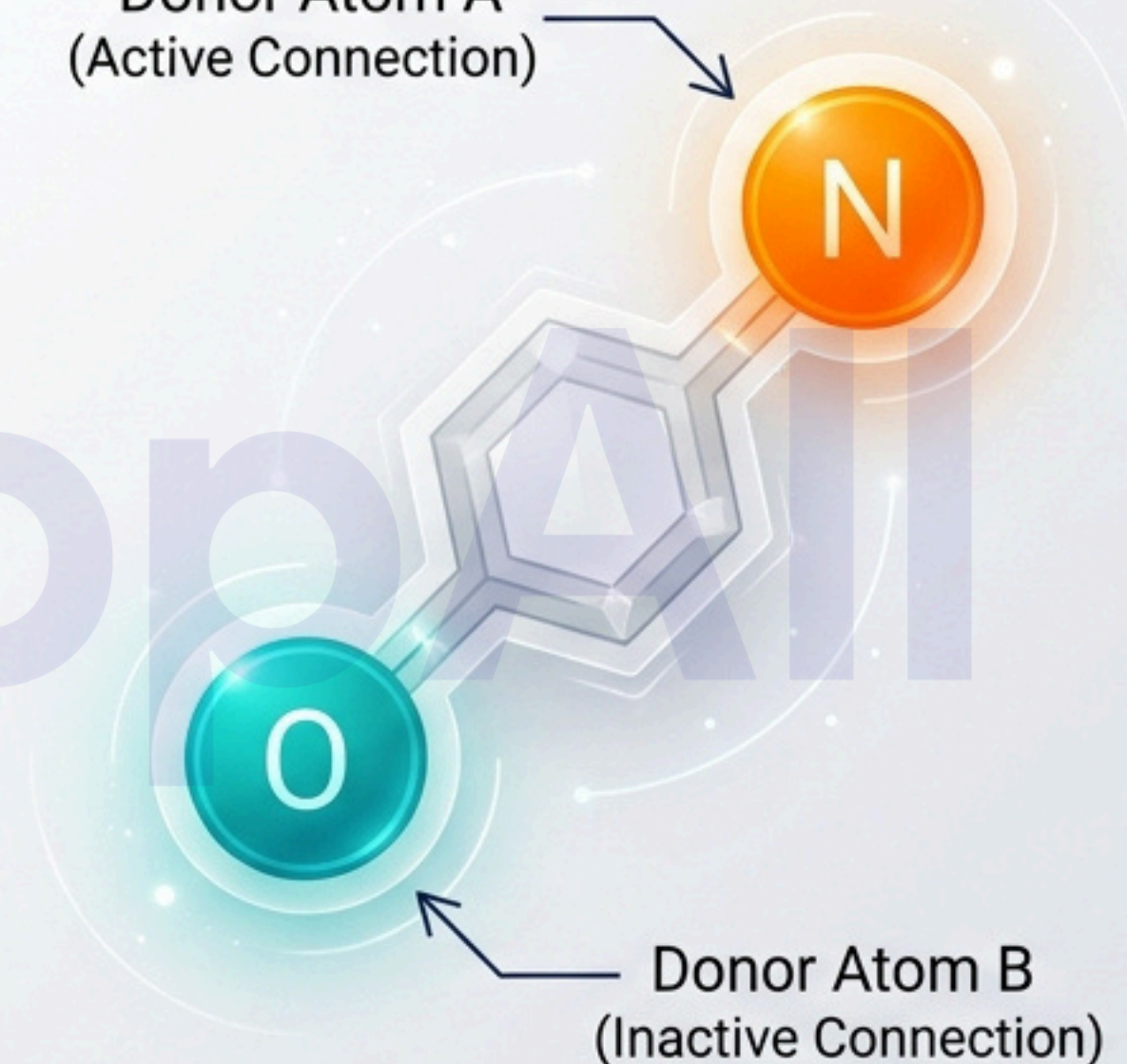
The Ambidentate Ligand

Linkage isomerism is exclusively possible when a coordination compound contains an ambidentate ligand.

What is it?

A ligand possessing two different donor atoms, but which uses only one of them to coordinate with the central metal ion at a given time (e.g., NO_2^- or SCN^-).

Donor Atom A
(Active Connection)



The SCN⁻ / NCS⁻ Pivot

The thiocyanate ion perfectly illustrates linkage isomerism. The overall ligand molecule is identical in both scenarios; only the specific atomic connection point to the central metal switches.

M – SCN



Linked via Sulfur (Thiocyanato)

M – NCS



Linked via Nitrogen (Isothiocyanato)



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The Nitrite Switch: Red vs. Yellow Forms

A single atom's pivot dramatically alters the physical properties of the $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ complex, generating two distinct, visible macroscopic forms.

RED FORM



The nitrite ligand is bound through the Oxygen atom ($-\text{ONO}$).

YELLOW FORM



The nitrite ligand is bound through the Nitrogen atom ($-\text{NO}_2$).

Linkage Isomers at a Glance

A summary matrix of the primary ambidentate ligands and their resulting coordination architectures.

Ligand Ion	Donor Atom	Linkage Formula	Nomenclature
Thiocyanate	Sulfur (S)	M – SCN	thiocyanato-S
Thiocyanate	Nitrogen (N)	M – NCS	isothiocyanato (thiocyanato-N)
Nitrite	Oxygen (O)	M – ONO	nitrito-O
Nitrite	Nitrogen (N)	M – NO ₂	nitrito-N



Note: Both isomers share the exact same chemical formula, differing only in the connectivity of the ambidentate ligand to the central metal.

Key Takeaways



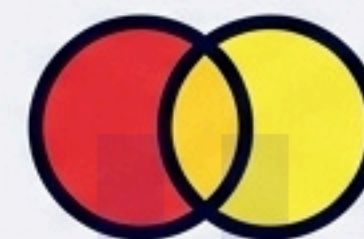
(H3) Ambidentate Requirement

Linkage isomerism exclusively requires ligands that possess multiple, alternative donor atoms (such as NO_2^- or SCN^-).



(H3) The Donor Switch

Isomers are formed when the central metal bonds to a completely different atom situated on the exact same ligand molecule.



(H3) Macroscopic Impact

This microscopic pivot alters electron distributions, causing dramatic macroscopic changes—shifting $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ from red to yellow.



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