Transition Metals

Chapter 22

Transition Metals: Occupy the d-block of periodic table
Have d-electrons in valence shell

1A 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8	8B 9	10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113	114	115	116	117	118

Some characteristics of Transition Metals and their compounds:

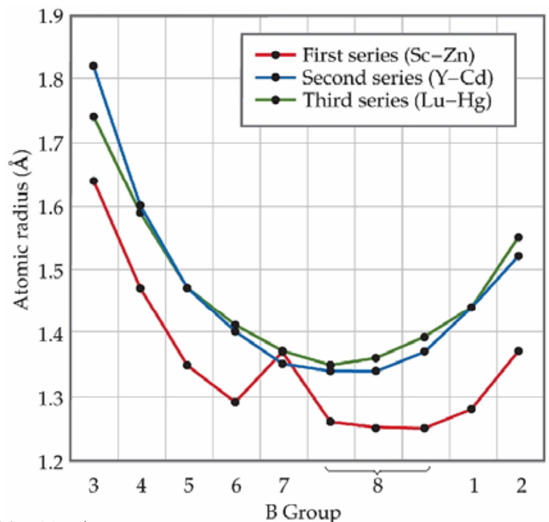
1. Exhibit more than one oxidation state
2. They form an extensive series of compounds known as metal complexes or coordination compounds.
3. Transition metals exhibit interesting magnetic properties.
4. Many of their compounds are colored.
5. Transition metals play important roles in biological systems and modern technology.

There are periodic trends in the transition metals, but they are often complex

(product of several factors, some working in opposite directions – e.g. combining the effects of increasing nuclear charge with the presence of nonbonding d electrons)

Lanthanide contraction – similarity in size, behavior, & properties of 4d and 5d transition elements

We won't worry about details of periodic trends in the transition metals or the exact reasons for them



Recall the Electron Configurations of the transition metals.

Ar $3s^2 3p^6$

K $[Ar]4s^1$

Ca $[Ar]4s^2$

Sc $[Ar]3d^1 4s^2$

Ti $[Ar]3d^2 4s^2$

V

Cr

Mn

Fe

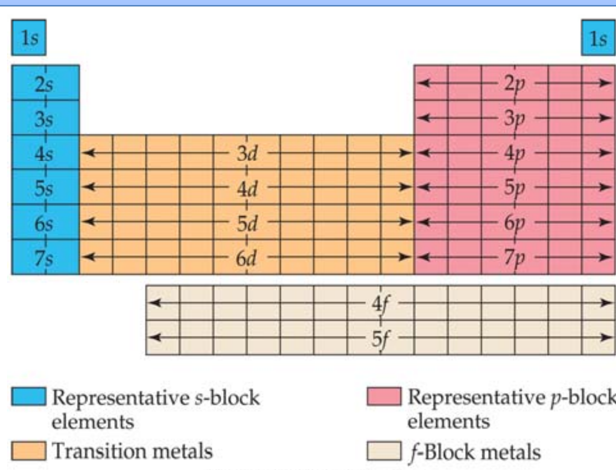
Co

Ni

Cu

Zn $[Ar] 3d^{10} 4s^2$

Use the periodic table to get electron configurations of the First Row Transition metal ATOMS
Sc → Zn



Be able to figure out the electron configuration of transition metal ions.

Transition Metals can have more than one oxidation state.

Ti	$[Ar]3d^2 4s^2$	Ni	$[Ar]3d^8 4s^2$
Ti^{2+}			
Ti^{3+}		Ni^{2+}	
Ti^{4+}			
Ti^{5+}		Ni^{4+}	

Note: 4s is filled before 3d,
but when oxidized,
4s electrons are lost before 3d.

Some trends in Transition Metal Oxidation States can be identified.

Oxidation States:
Highest oxidation states of Sc, Ti, V, Cr, Mn = number of valence (4s + 3d) electrons.

Sc $[Ar]3d^1 4s^2$

Mn $[Ar]3d^5 4s^2$

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
				+7				
			+6	+6	+6			
		+5	+5	+5	+5			
	+4	+4	+4	+4	+4	+4		
+3	+3	+3	+3	+3	+3	+3	+3	+3
	+2	+2	+2	+2	+2	+2	+2	+2
								+1

Trend from Sc → Mn:
The maximum oxidation state becomes increasingly unstable.

Sc^{3+}, Ti^{4+}	Are stable. Sc_2O_3 & TiO_4 are stable oxides.
Mn^{7+}	Exists but is easily reduced.
MnO_4^-	Strong oxidizing agent.

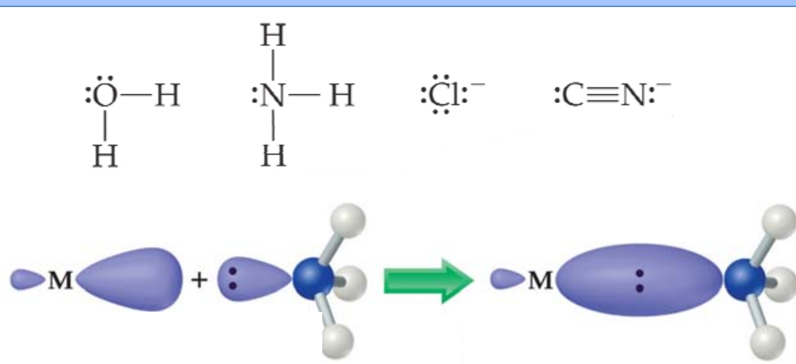
Many transition metals form compounds that have fun colors!

– colors are due to oxidation state and electron configuration...more specifics about that later!

Transition metals form COMPLEXES.

Transition metal ions are Lewis acids →

Ligands are Lewis bases →

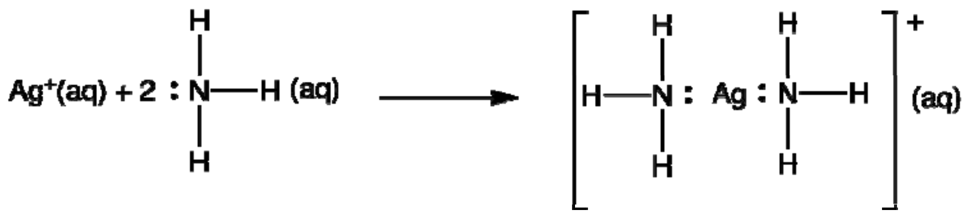


Metal complex is formed when a metal is bonded to molecules or ions.

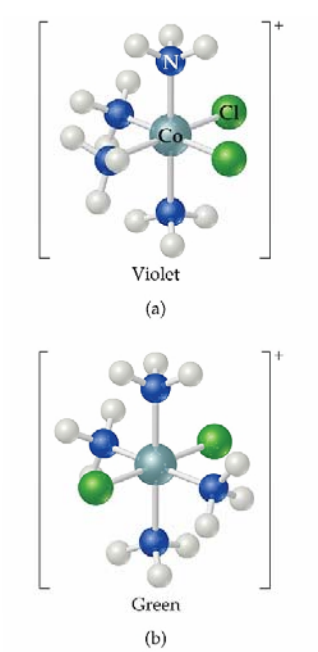
Complex ion: metal complex that is not neutral

Coordination compounds: compounds that contain complexes

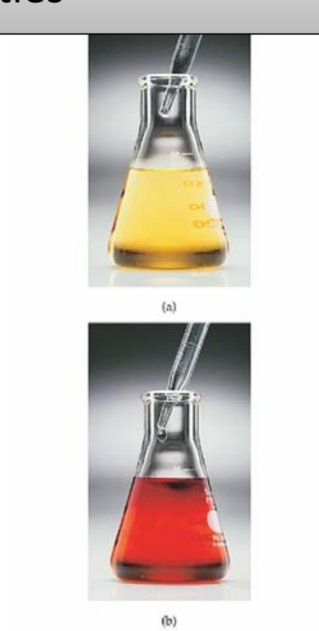
Coordination number: # of atoms directly bonded to a metal



The coordination of the ligand with the metal can greatly alter its physical or chemical properties



EXAMPLE: color



Chemical properties of Metal Complexes differ from the properties of the metal alone.

For example: the ease of oxidation of the metal changes when a metal complex forms.

Which is easier to reduce, the metal ion or the complex?

$Ag^+(aq) + e^- \rightarrow Ag(s)$ $E°_{1/2} = +0.80V$

$[Ag(CN)_2]^-(aq) + e^- \rightarrow Ag(s) + 2CN^-(aq)$ $E°_{1/2} = -0.31V$

Complexes are characterized by their Oxidation State and Coordination Number, but the identity of the ligands also matters.

- Oxidation State: "primary valence"
- Coordination Number: "secondary valence"

Early Formula	Color	# of Ions per formula Unit	Free Cl^- Ions in Formula	Complex ion Formula
$CoCl_3 \cdot 6NH_3$	orange	4	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5NH_3$	purple	3	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4NH_3$	green	2	1	trans-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 4NH_3$	violet	2	1	cis-$[Co(NH_3)_4Cl_2]Cl$

The four compounds in the table below have the same oxidation state and coordination number, but clearly they have different properties.

Coordination Sphere is the central atom + ligands bonded to it
Use [ ] to set off components in the coordination sphere

Early Formula	Color	# of Ions per formula Unit	Free Cl^- Ions in Formula	Complex ion Formula
$CoCl_3 \bullet 6NH_3$	orange	4	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \bullet 5NH_3$	purple	3	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \bullet 4NH_3$	green	2	1	trans-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \bullet 4NH_3$	violet	2	1	cis-$[Co(NH_3)_4Cl_2]Cl$

What happens to these complexes when dissolved in water?

Knowing the charge on a complex ion and the charge on each ligand, one can determine the oxidation number for the metal.

$[Cu(NH_3)_4]SO_4$

Charge on the complex:

Coordination #:

Oxidation state of the metal:

$K_2[Ni(CN)_4]$

Charge on the complex:

Coordination #:

Oxidation state of the metal:

Or, knowing the oxidation number on the metal and the charges on the ligands, one can calculate the charge on the complex ion.

Fe^{3+} surrounded by six water molecules

Charge on the complex:

Coordination number:

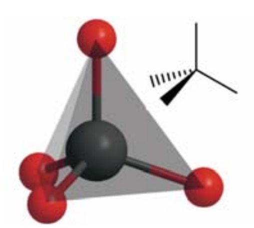
Pt(II) surrounded by two ammonia molecules and two bromide ions

Charge on the complex:

Coordination number:

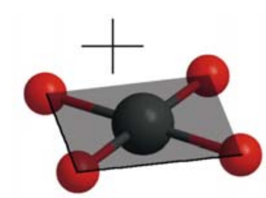
Geometries of Transition Metal Complexes
Geometry for Coordination # = 4

- Tetrahedral



$[Zn(NH_3)_4]^{2+}$

- Square Planar

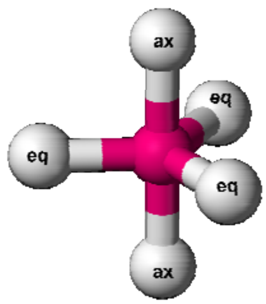


$[Ni(CN)_4]^{2-}$

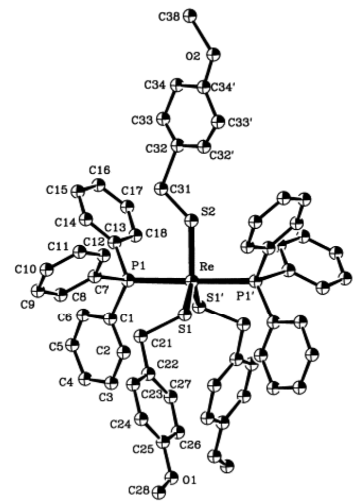
$[PtCl_2(NH_3)_2]$

Geometries of Transition Metal Complexes
Geometry for Coordination # = 5

- Trigonal Bipyramidal



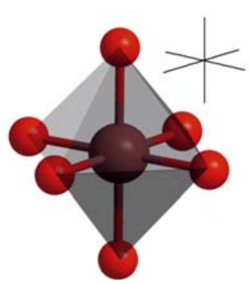
$[Fe(CO)_5]$



$[Re(SCH_2C_6H_4OCH_3\text{-}p)_3(PPh_3)_2]$
$ReL_3(PR_3)_2$

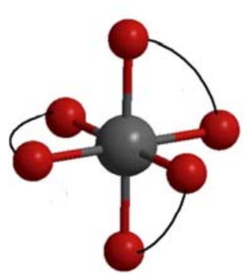
Geometries of Transition Metal Complexes
Geometry for Coordination # = 6

- Octahedral



chromium(III) and cobalt(III) consistently have the same coordination number of 6

$[CoF_6]^{3-}$



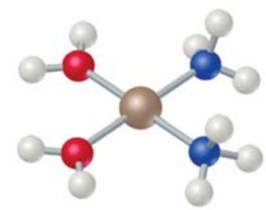
$[Co(\mathit{en})_3]^{3+}$

Special Ligands: Chelating Agents

Chelates are ligands possessing two or more donor atoms.

- Mono-dentate Ligands

  Examples:

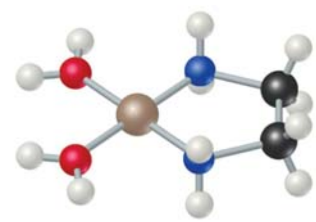


$[Cu(H_2O)_2(NH_3)_2]^{2+}$

- Bi-dentate Ligands

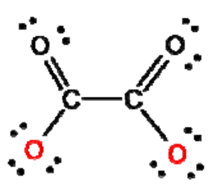
  Example: ethylenediamine = en

  $:NH_2{-}CH_2{-}CH_2{-}\ :NH_2$

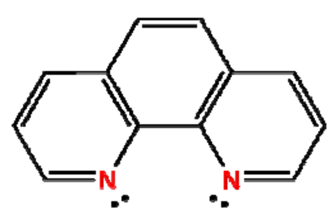


$[Cu(H_2O)_2(en)]^{2+}$

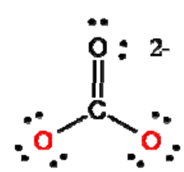
These are examples of Bi-dentate Ligands



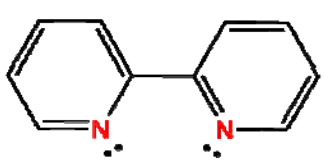
oxalate



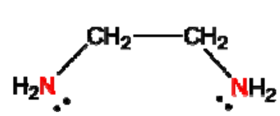
ortho-phenanthroline
(o-phen)



carbonate



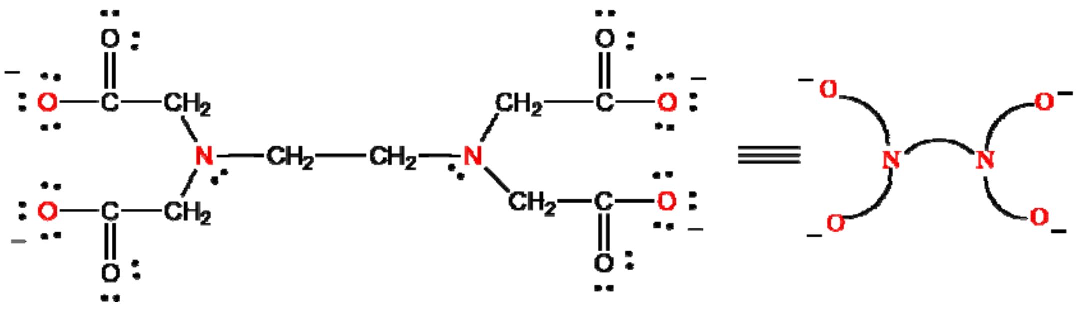
bipyridine
(bipy)



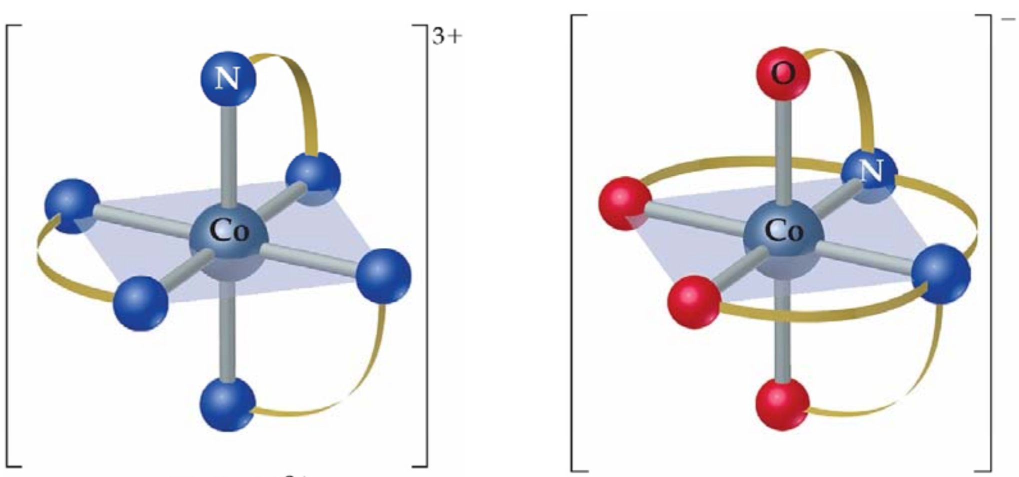
ethylendiamine
(en)

<u>Poly-dentate</u> ligands bind to the metal in more than 2 sites.

Example: ethylenediaminetetraacetic acid (EDTA)



Below are representations of metal complexes with ethylenediamine and EDTA as the ligands.



$[Co(en)_3]^{3+}$

$CoEDTA^-$

EDTA is used to sequester metal ions.

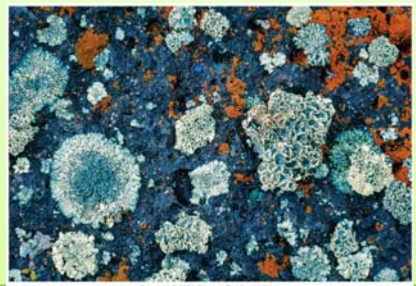
ethylenediaminetetraacetic acid (EDTA)

Applications:

Removes trace metals ions that catalyze food decomposition

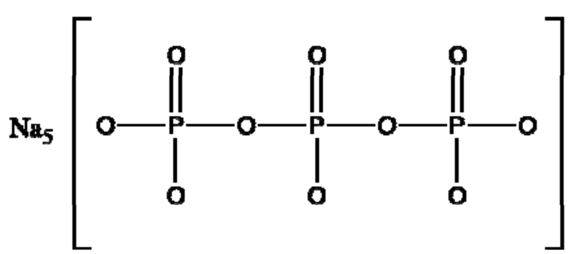
Used in poison control

Used by lichen to obtain minerals from rock.



Chelating Agents can be used to soften water

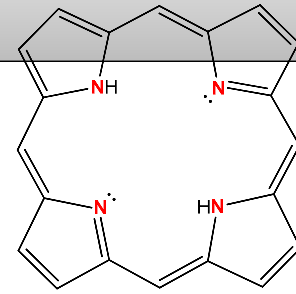
Used in shampoo to remove trace metals from hard water (Ca^{2+} and Mg^{2+}): EDTA

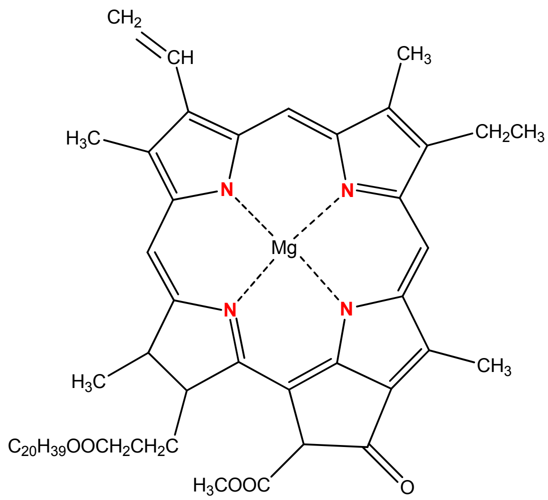


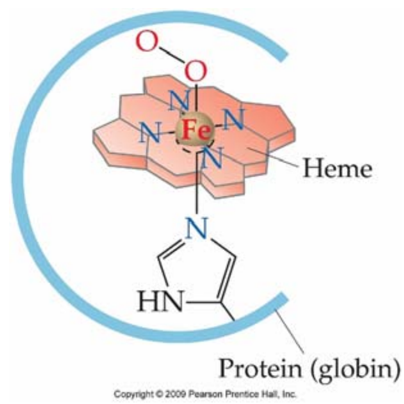
$Na_5P_3O_{10}$ Used in detergents to remove trace amounts of dissolved metals:

Chelating Agents play important roles in biological applications.

Porphine is a flat molecule
Complexes with this molecule are called porphyrins







These are the Important Chelating Agents you need to know.

Chelate	# of Coordination Sites	Charge
Ethylenediamine (en)		
Porphine		
EDTA		
Oxalate ($C_2O_4^{2-}$)		
Carbonate (CO_3^{2-})		

METAL COMPLEXES are very stable.
The formation reactions have large values of K_f.

$$Cu(OH_2)_4^{2+} + 4NH_3 \rightarrow Cu(NH_3)_4^{2+} + 4H_2O$$

$$Cu^{2+}(aq) + 4NH_3 \rightarrow Cu(NH_3)_4^{2+} + 4H_2O$$

K_f VALUES OF SOME COMPLEXES

$[Ag(NH_3)_2]^{+}$	1.7×10^{7}
$[Cu(NH_3)_4]^{2+}$	5×10^{12}
$[Cu(CN)_4]^{2-}$	1×10^{25}
$[Ag(CN)_2]^{-}$	1×10^{21}
$[Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}

THE CHELATE EFFECT: Chelating ligands form *exceptionally stable metal complexes when compared to* related monodentate ligands.

$[Ni(H_2O)_6]^{2+} + 6\ NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6H_2O$ $K_f = 4\times10^{8}$

$[Ni(H_2O)_6]^{2+} + 3\ en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O$ $K_f = 2\times10^{18}$

$[Ni(NH_3)_6]^{2+} + 3\ en \rightleftharpoons [Ni(en)_3]^{2+} + 6\ NH_3$

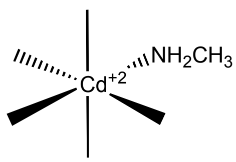
What is the expression for the formation constant for this reaction?

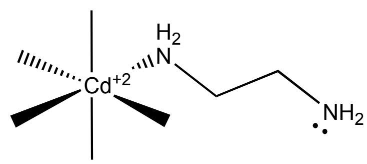
THE CHELATE EFFECT: **Chelating ligands form *exceptionally stable metal complexes when compared to* related monodentate ligands.**

This "chelate effect" is due to :

1) Probability
2) Entropy Effects

Probability Effect:



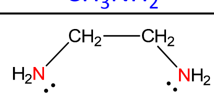


: NH_2CH_3

ΔS for the formation of a chelate is positive.

1) $Cd^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+}$ **ΔH° = −57.3 kJ**

2) $Cd^{2+} + 2en \rightleftharpoons [Cd(en)_2]^{2+} + 4H_2O$ **ΔH° = −56.5 kJ**

	Ligand	ΔH°(kJ)	ΔS°(J/K)	ΔG°
1	**Methyl amine** CH_3NH_2	−57.3		**−37.2kJ**
2		−56.5		**−60.7kJ**

Why is ΔS° so much larger?

$$[Cd(H_2O)_4]^{2+} + 4\ CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+} + 4H_2O$$

$$[Cd(H_2O)_4]^{2+} + 2\ en \rightleftharpoons [Cd(en)_2]^{2+} + 4H_2O$$