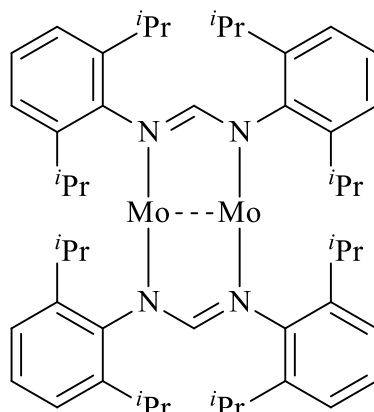


- In 2009, great excitement was generated amongst chemists worldwide with the report of a neutral Mo complex containing two bridging, anionic *N*-donor ligands. The structure of the complex is shown below. ^{*i*}Pr = isopropyl = $-\text{CH}(\text{CH}_3)_2$

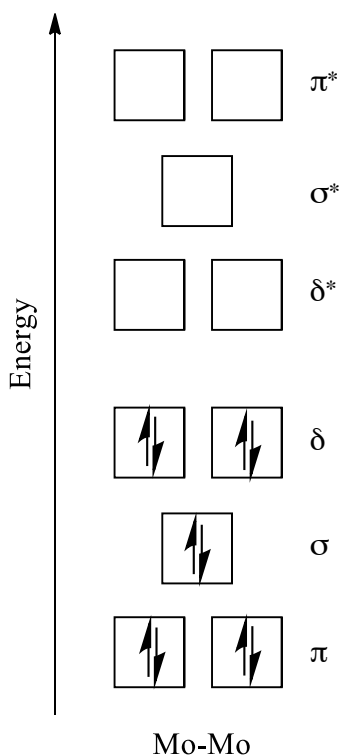


Name the complex by using standard IUPAC nomenclature. For simplicity, the name of the *N*-donor ligand (in its neutral form) can be shortened to “aminidate”.

bis(aminidato)dimolybdenum(I)

The Mo complex above possesses an extremely short Mo–Mo bond (202 pm), much shorter than the bonding distance between Mo atoms in Mo metal (273 pm)!

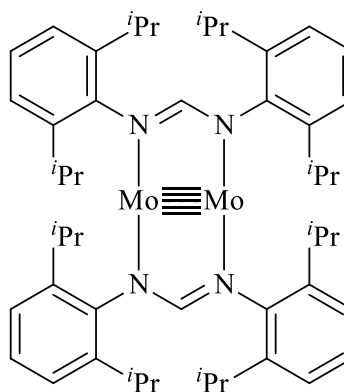
- Propose a reasonable explanation for the very short Mo–Mo bond length in the complex by adding *d*-electrons into the (*partial*) MO scheme shown below.
- Determine the bond order for the metal-metal bond and re-draw the structure of the complex shown above indicating the actual bonding between the two Mo atoms.



(b) Molybdenum is present as Mo(I): $4d^5$. The 2 Mo(I) contribute 10 electrons to the Mo-Mo bonding orbitals. This fills the bonding levels shown opposite:

$$\begin{aligned} \text{bond order} &= \frac{1}{2} (\text{number of bonding electrons} - \\ &\quad \text{number of antibonding electrons}) \\ &= \frac{1}{2} (10 - 0) = 5 \end{aligned}$$

There is a quintuple bond between the metal ions:



Oxidation of the Mo complex by **two** electrons gives rise to a paramagnetic species in which the Mo–Mo distance increases significantly. Give a reasonable hypothesis for the bond-lengthening phenomenon.

Marks
2

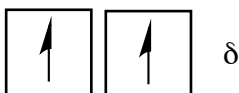
If two electrons are removed, they will come from the bonding orbitals in 2014-N-4 and probably from the δ orbitals. As bonding electrons are removed, the Mo-Mo bond will be weakened. There will 8 bonding electrons remaining:

$$\begin{aligned}\text{bond order} &= \frac{1}{2} (\text{number of bonding electrons} - \\ &\quad \text{number of antibonding electrons}) \\ &= \frac{1}{2} (8 - 0) = 4\end{aligned}$$

As the bond is weaker, it is longer.

Determine the number of unpaired electrons in the oxidised Mo complex.

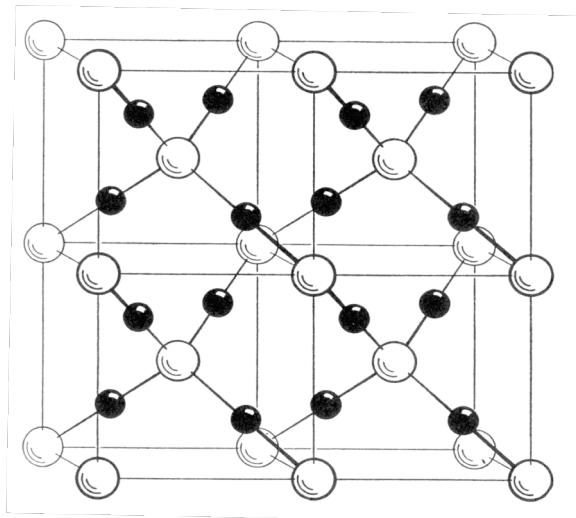
2 electrons remain in the δ orbitals. In accordance to Hund's rule, these occupy separate orbitals with spins parallel to minimise repulsion:



There are 2 unpaired electrons.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Copper oxide is used as a photovoltaic material in solar cells and it crystallizes with the structure shown below. The large white spheres represent the oxygen atoms and the smaller black spheres represent copper atoms.



How many unit cells are represented in the above diagram? Explain your answer.

There are 4 unit cells represented.

A unit cell is the simplest repeating unit of a lattice. Each of the 4 cubes are identical and translation of any one of them will generate the overall structure.

From the solid-state structure shown above, determine the empirical formula for copper oxide.

There are 8 O on the corners plus 1 O in the centre. The O on the corners are shared with 8 other cells so contribute 1/8 to the cell. The O at the centre is unshared so contributes only to this cell. The net contribution is $8 \times 1/8 + 1 = 2$.

The 4 Cu are completely within the cell so only contribute to this cell. The net contribution from Cu is 4.

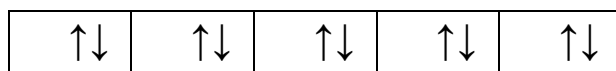
With a Cu : O ratio of 4 : 2, the formula is Cu_2O .

What is the oxidation state of copper in this compound?

With O^{2-} , it must be Cu(I) (i.e +1).

Use the box notation to predict whether the copper ions are paramagnetic.

Cu^+ has 10 electrons in its 3d subshell. They are all paired as shown, so Cu^+ is diamagnetic, not paramagnetic.



ANSWER CONTINUES ON THE NEXT PAGE

Silver oxide is another Group 11 metal oxide and its solid-state structure is identical to that of copper oxide even though the ionic radius for the copper ion (118 pm) is smaller than that of the silver ion (139 pm). Account for this observation.

The anionic radius of O^{2-} is the main factor determining the solid state structure of the oxides. The cations (Ag^+ or Cu^+) fit in the holes within the O^{2-} lattice.

- $K_2[Re_2Cl_8] \cdot 2H_2O$ is an historically important example of a metal-metal bonded complex. Name the complex by using standard IUPAC nomenclature.

Marks
8

potassium octachloridodirhenate(III)-2-water

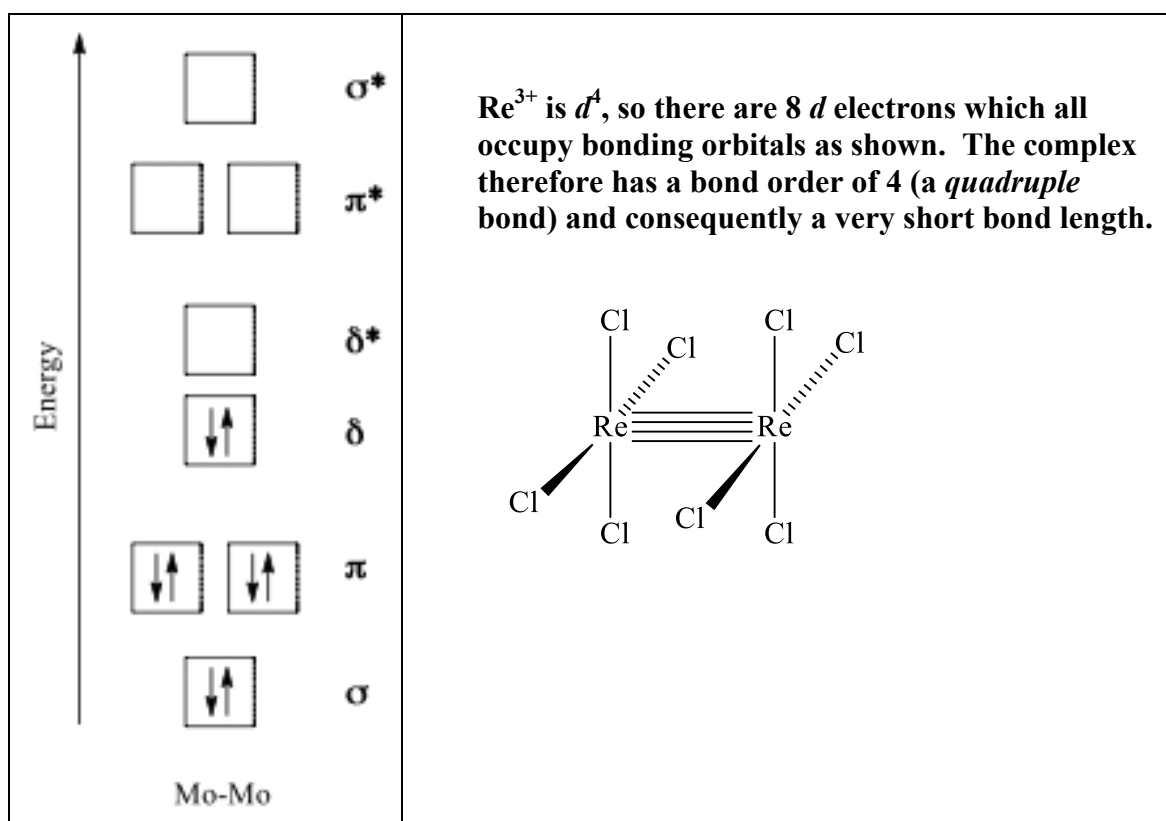
What is the oxidation state of Re in this complex?

III or +3

How many *d*-electrons are on each Re atom in this complex?

4

$K_2[Re_2Cl_8] \cdot 2H_2O$ possesses an extremely short Re–Re bond (224 pm), much shorter than the bonding distance between Re atoms in Re metal (274 pm)! Propose a reasonable explanation for the very short Re–Re bond length in the complex by adding *d*-electrons into the (*partial*) MO scheme shown below. Determine the bond order for the metal-metal bond and draw a structure for the complex.



Reduction of the Re complex by **one** electron gives rise to a paramagnetic species in which the Re–Re distance increases significantly. Propose a reasonable hypothesis for the bond-lengthening phenomenon.

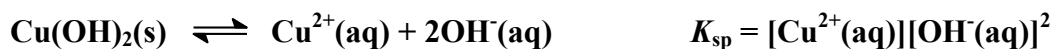
Reduction is the gain of 1 electron. This is added to the lowest available orbitals (the LUMO): the δ^* anti-bonding orbital to give a paramagnetic species.

This reduces the bond order from 4.0 to 3.5, thus weakening and lengthening the Re–Re bond.

- What is the solubility of $\text{Cu}(\text{OH})_2$ in mol L^{-1} ? $K_{\text{sp}}(\text{Cu}(\text{OH})_2)$ is 1.6×10^{-19} at 25°C .

Marks
6

The dissolution reaction and associated solubility product are:



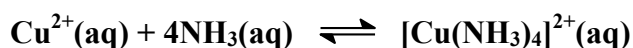
If x mol dissolve in one litre, $[\text{Cu}^{2+}(\text{aq})] = x \text{ M}$ and $[\text{OH}^{-}(\text{aq})] = 2x$. Hence:

$$K_{\text{sp}} = (x)(2x)^2 = 4x^3 = 1.6 \times 10^{-19}$$

$$x = 3.4 \times 10^{-7} \text{ M}$$

Answer: $3.4 \times 10^{-7} \text{ M}$

The overall formation constant for $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is 1.0×10^{13} . Write the equation for the reaction of Cu^{2+} ions with excess ammonia solution.



Calculate the value of the equilibrium constant for the following reaction.



This reaction can be considered to occur via (i) $\text{Cu}(\text{OH})_2$ dissolving followed by (ii) the $\text{Cu}^{2+}(\text{aq})$ ions that form being complexed by ammonia.

For the formation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$, the equilibrium constant is:

$$K_{\text{stab}} = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4} = 1.0 \times 10^{13}$$

For the reaction of $\text{Cu}(\text{OH})_2(\text{s})$ with $\text{NH}_3(\text{aq})$, the equilibrium constant is:

$$K = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}[\text{OH}^{-}(\text{aq})]^2}{[\text{NH}_3]^4}$$

To obtain K , K_{sp} is multiplied by K_{stab} :

$$\begin{aligned} K &= K_{\text{sp}} \times K_{\text{stab}} \\ &= [\text{Cu}^{2+}(\text{aq})][\text{OH}^{-}(\text{aq})]^2 \times \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}[\text{OH}^{-}(\text{aq})]^2}{[\text{NH}_3]^4} \\ &= (1.6 \times 10^{-19}) \times (1.0 \times 10^{13}) = 1.6 \times 10^{-6} \end{aligned}$$

Answer: 1.6×10^{-6}

Would you expect $\text{Cu}(\text{OH})_2(\text{s})$ to dissolve in 1 M NH_3 solution? Briefly explain your answer.

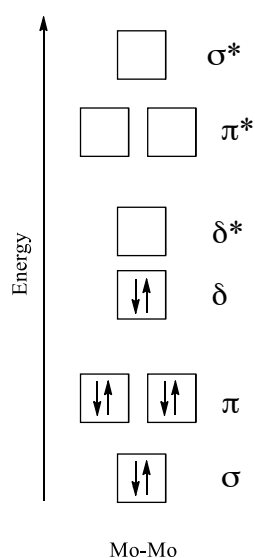
No. Equilibrium constant K is very small so the reaction lies heavily in favour of reactants.

- The red species $\text{K}_4[\text{Mo}_2\text{Cl}_8]$ is an historically important example of a metal-metal bonded complex. Use standard nomenclature to name the complex salt.

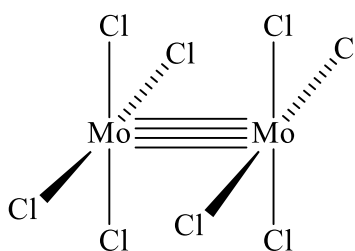
Marks
6

potassium octachloridodimolybdate(II)

$\text{K}_4[\text{Mo}_2\text{Cl}_8]$ possesses an extremely short Mo–Mo bond (214 pm), much shorter than the bonding distance between Mo atoms in Mo metal (273 pm)! Propose a reasonable explanation for the very short Mo–Mo bond length in the complex by adding *d*-electrons into the (partial) MO scheme shown below. Draw a structure for the complex that is consistent with the completed MO scheme and your explanation.



Mo^{2+} is d^4 , so there are 8 *d* electrons which all occupy the σ , π and δ bonding orbitals as shown. With 8 bonding electrons and no anti-bonding electrons, the complex therefore has a bond order of 4 and consequently a very short bond length.



Oxidation of the complex by one electron gives rise to a paramagnetic species in which the Mo–Mo distance increases significantly. Propose a reasonable hypothesis for the bond lengthening phenomenon.

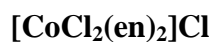
Oxidation is the loss of 1 electron which is removed from the highest occupied molecular orbital: the δ bonding orbital. As this leads to an unpaired electron in this orbital, it is paramagnetic species.

The number of bonding electrons is thus reduced to 7. This reduces the bond order from 4.0 to 3.5, thus weakening and lengthening the Mo–Mo bond.

Marks
6

- When cobalt(II) chloride is reacted with ethane-1,2-diamine (en) and the product is oxidised in the air, a purple compound with the empirical formula $\text{CoCl}_3 \cdot 2\text{en}$ is obtained. When reacted with silver nitrate only one chloride ion is released. The compound can be resolved into its enantiomeric forms.

Give the structural formula of the compound.



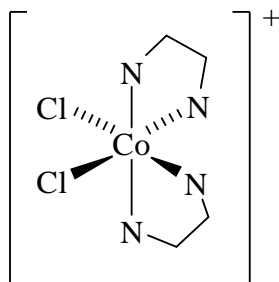
1 chloride ion must be a counter ion as only 1 is released when silver nitrate is added. As en is neutral, it must be coordinate to the metal ion.

Give the name of the compound.

***cis*-dichloridobis(ethane-1,2-diamine)cobalt(III) chloride**

Although the structural formula above gives rise to *cis* and *trans* isomers, only the *cis* form is optically active.

Draw the structure of the metal complex component of the compound.



What is the *d* electron configuration of the Co in this complex?

$[\text{CoCl}_2(\text{en})_2]\text{Cl} = \text{Co}^{3+} + 2\text{en} + 3\text{Cl}^-$. As Co is in group 9, it has 9 valence electrons. Co^{3+} has $(9 - 3) = 6$ electrons: $3d^6$

What types of isomers can be formed by a compound with this empirical formula?

Geometrical (*cis* and *trans*) isomers are possible.

The *cis* isomer can form optical isomers.

Which of the possible isomers has formed? Explain the logic you have used in determining this.

As only the *cis* isomer can form enantiomers, it must have been formed.

The *trans* isomer is superimposable (i.e. identical) to its mirror image.

- Alfred Werner, one of the founders of the field of coordination chemistry, prepared a series of platinum complexes that contained ammonia and chloride ions. One of these had the empirical formula $\text{PtCl}_4 \cdot 4\text{NH}_3$ and when reacted with silver nitrate released two chloride ions per formula unit. Write the structural formula of this compound and write the name of this compound.

Marks
5

Ag^+ will react with uncoordinated Cl^- to form AgCl(s) . As it reacts with two Cl^- ions per formula unit, there must be 2Cl^- counter ions.

The remaining 2Cl^- ions and the 4NH_3 molecules are coordinated to the metal.

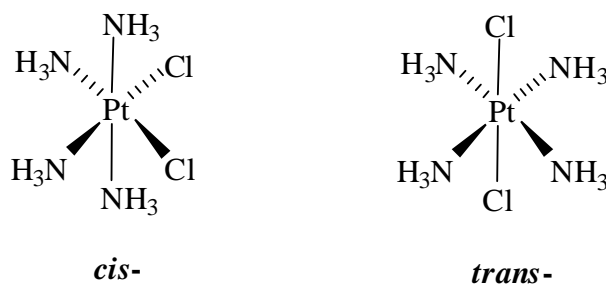
The oxidation number of the metal is +IV. The complex ion is thus $[\text{PtCl}_2(\text{NH}_3)_4]^{2+}$.

The coordination compound is $[\text{PtCl}_2(\text{NH}_3)_4]\text{Cl}_2$.

The name of this compound is tetraamminedichloridoplatinum(IV) chloride

Draw the possible structures of the metal complex.

With 2Cl^- and 4NH_3 ligands, two isomers are possible:



What types of isomers can be formed by a compound with this empirical formula?

Geometric (*cis* and *trans*) isomerism is possible (as above).

What is the d electron configuration of the Pt in this complex?

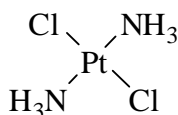
Platinum is in group 10 so Pt(IV) has $(10 - 4) = 6$ d -electrons: $5d^6$.

Marks
6

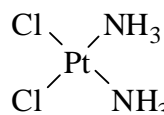
- Alfred Werner, one of the founders of the field of coordination chemistry, made extensive studies of the metal complex $[\text{PtCl}_2(\text{NH}_3)_2]$. He showed that it existed in two isomeric forms and used this information to predict that the compound had a square-planar molecular geometry. What other molecular geometry would need to be considered for such a complex and on what basis did Werner reject this alternative geometry?

As the complex contains 4 ligands bonded to Pt(II) (two Cl⁻ and two NH₃), a tetrahedral geometry also needs to be considered. However, as the angles between all of the bonds in a tetrahedron are the same, tetrahedral $[\text{PtCl}_2(\text{NH}_3)_2]$ would not give rise to two isomers.

Draw and name the two isomers.



trans-diamminedichloridoplatinum(II)



cis-diamminedichloridoplatinum(II)

Why does platinum(II) form square-planar complexes?

There are a number of reasons why platinum(II) forms square-planar rather than tetrahedral complexes. These include:

- Pt(II) is a relatively big cation and so repulsion between the ligands are not too large.
- The Pt-ligands bonds are stronger as, with its $5d^8$ configuration, Pt(II) is able to keep the $d_{x^2-y^2}$ orbital completely empty allowing the ligands to donate into it.

Although the tetrahedral form has less crowding between the ligands, there is no single d -orbital which is directed towards, and can bond with, the ligands.

Which one of the isomers is biologically active? What is its activity? Describe two features of the complex that play important roles in this biological activity.

Only the *cis* isomer is biologically active - it is a potent anti-cancer drug.

The *cis* chloride ligands are easily replaced, allowing Pt(II) to bind to DNA and stop cell replication. It appears that the *cis*-geometry of the Pt-DNA bonds is important in this. The flat nature of the complex means it can approach the DNA closer.