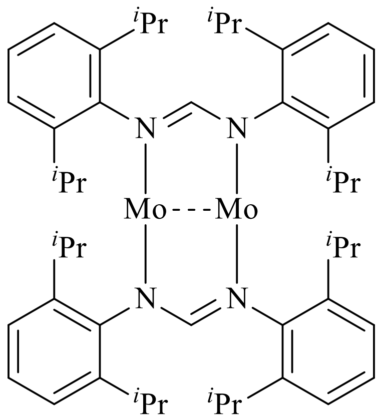
Marks
6

- 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 = $–CH(CH_3)_2$

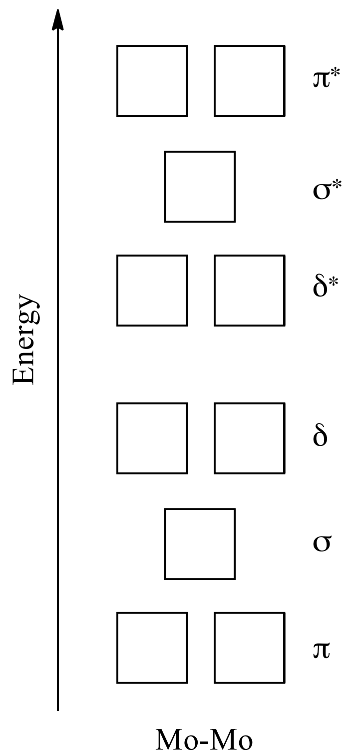


Name the complex by using standard IUPAC nomenclature. For simplicity, the name of the *N*-donor ligand (in its neutral form) can be shortened to "aminidate".

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)!

(a) 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.

(b) 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.



THIS QUESTION CONTINUES ON THE NEXT PAGE.

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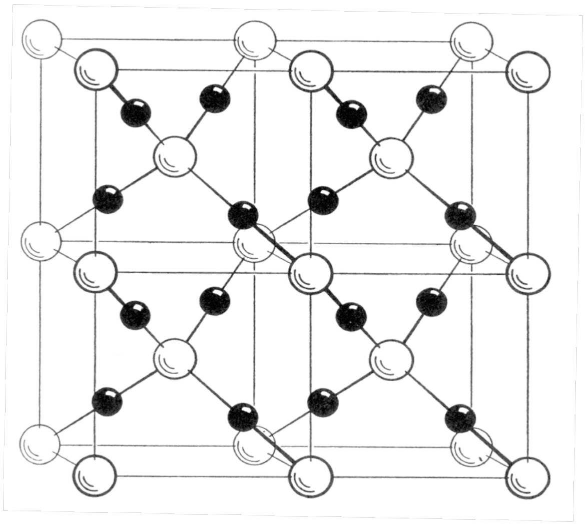
Determine the number of unpaired electrons in the oxidised Mo complex.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 7

- 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.

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

What is the oxidation state of copper in this compound?

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

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.

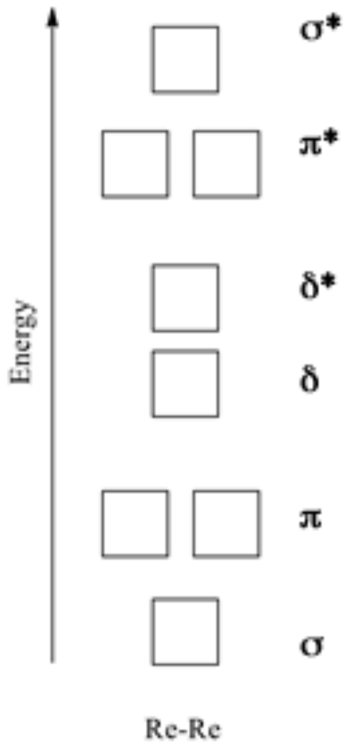
Marks 8

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

What is the oxidation state of Re in this complex?

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

$K_2[Re_2Cl_8]\cdot 2H_2O$ 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.

Marks 6

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

Answer:

The overall formation constant for $[Cu(NH_3)_4]^{2+}$ 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.

$$Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$$

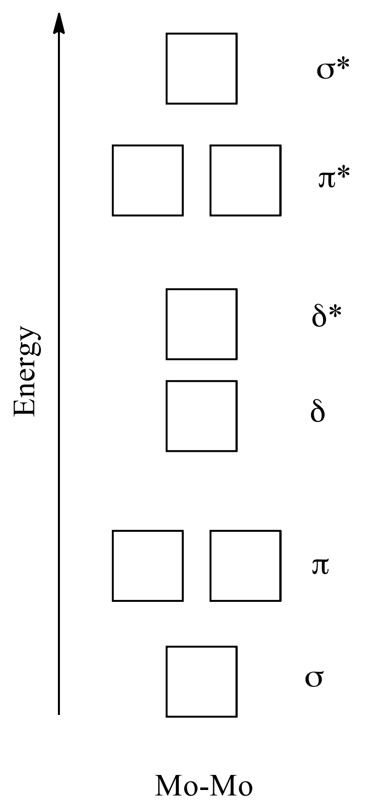
Answer:

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

Marks
6

- The red species $K_4[Mo_2Cl_8]$ is an historically important example of a metal-metal bonded complex. Use standard nomenclature to name the complex salt.

$K_4[Mo_2Cl_8]$ 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.



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.

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 $CoCl_3 \cdot 2en$ 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.

Give the name of the compound.

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

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

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

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

	Marks
• 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 $PtCl_4.4NH_3$ 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.	**5**
Draw the possible structures of the metal complex.	
What types of isomers can be formed by a compound with this empirical formula?	
What is the *d* electron configuration of the Pt in this complex?	

Marks
6

- Alfred Werner, one of the founders of the field of coordination chemistry, made extensive studies of the metal complex $[PtCl_2(NH_3)_2]$. 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?

Draw and name the two isomers.

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

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.