

Answer on Question #76681, Chemistry / Inorganic Chemistry

a) There are three compounds (A, B & C) with the formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. A is violet in colour; when an aqueous solution of A is treated with AgNO_3 , 3 moles of AgCl per mole of A are produced; A doesn't lose any water in a desiccator.

B is grey-green in colour; when an aqueous solution of B is treated with AgNO_3 , it produces 2 moles of AgCl per mole of B; one mole of B loses one mole of water when kept in a desiccator.

C is deep green in colour; when an aqueous solution of C is treated with AgNO_3 , 3 moles of AgCl per mole of C are produced; one mole of C loses two moles of water when kept in a desiccator.

Identify A, B and C and state what type of isomerism these compounds exhibit.

b) Draw the d-orbital splitting diagram for $[\text{Fe}(\text{CN})_6]^{2-}$ and state whether it is

a high-spin or low-spin complex. How would you confirm this experimentally?

) Draw the structure of $[\text{Ni}(\text{CN})_4]^{2-}$, showing the stereochemistry. Use crystal field splitting arguments to explain your answer.

Question 1

a) There are three compounds (A, B & C) with the formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. A is violet in colour; when an aqueous solution of A is treated with AgNO_3 , 3 moles of AgCl per mole of A are produced; A doesn't lose any water in a desiccator.

B is grey-green in colour; when an aqueous solution of B is treated with AgNO_3 , it produces 2 moles of AgCl per mole of B; one mole of B loses one mole of water when kept in a desiccator.

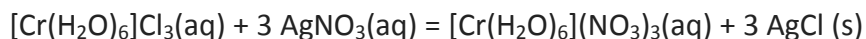
C is deep green in colour; when an aqueous solution of C is treated with AgNO_3 , 3 moles of AgCl per mole of C are produced; one mole of C loses two moles of water when kept in a desiccator.

Identify A, B and C and state what type of isomerism these compounds exhibit.

Solution

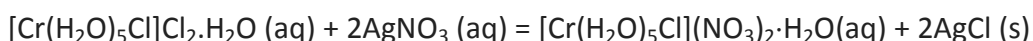
a) Substance A should have three chlorine-ions in the outside coordination sphere and no molecules of water in the outside coordination sphere, as when an aqueous solution of A is treated with AgNO_3 , 3 moles of AgCl per mole of A are produced; A doesn't lose any water in a desiccator.

Therefore A- $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ – Violet, Hexaaquachromium(III) chloride

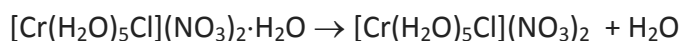


Substance B should have two chlorine-ions in the outside coordination sphere and one molecule of water in the outside coordination sphere, the third chlorine-ion and five molecules of water should be in the inside coordination sphere, as when an aqueous solution of B is treated with AgNO_3 , it produces 2 moles of AgCl per mole of B; one mole of B loses one mole of water when kept in a desiccator.

Therefore B - $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ – grey-green, Pentaquachlorochromium(III) chloride monohydrate

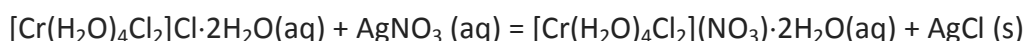


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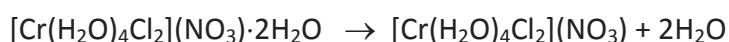


Substance C should have one chlorine-ion in the outside coordination sphere and two molecules of water in the outside coordination sphere, two other chlorine-ions and four molecules of water should be in the inside coordination sphere, as when an aqueous solution of C is treated with AgNO_3 , it produces 1 mole of AgCl per mole of C; one mole of C loses two moles of water when kept in a desiccator.

Therefore C – $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ – deep green, tetraaquadichlorochromium (III) chloride dihydrate.



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Substances A, B and C are hydrate isomers – isomers of crystalline complexes that differ in whether water is present inside or outside the coordination sphere.

The best known examples of hydrate isomerism or Solvate isomerism type of isomerism occurs for chromium chloride $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ which may contain 4, 5, 6 coordinated water molecules.

Note: it seems that there is a mistake in a description of C substance. There should be “one mole of AgCl per mole of C is produced” instead of “3 moles of AgCl per mole of C are produced”, as the described substance would have incorrect chemical formula.

Answer: Hydrate isomerism or Solvate isomerism type of isomerism.

A- $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ – Violet, Hexaaquachromium(III) chloride

B - $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ – grey-green, Pentaquachlorochromium(III) chloride monohydrate

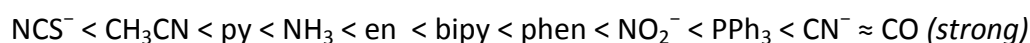
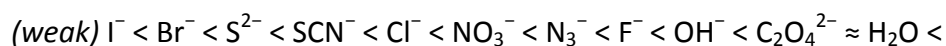
C – $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ – deep green, tetraaquadichlorochromium (III) chloride dihydrate.

Question 2

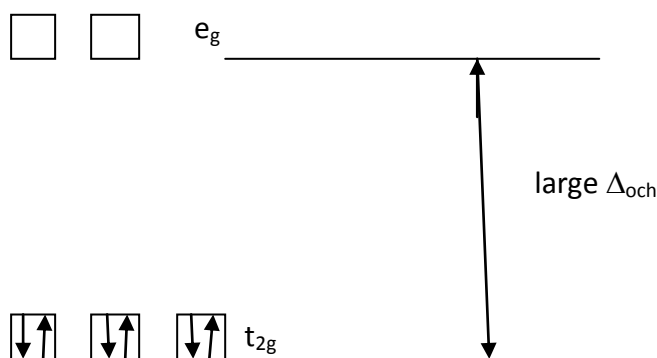
b) Draw the d-orbital splitting diagram for $[\text{Fe}(\text{CN})_6]^{2-}$ and state whether it is a high-spin or low-spin complex. How would you confirm this experimentally?

Solution

- 1) The complex has an octahedral shape (coordination number is 6)
- 2) CN^- is a strong field ligand



- 3) The d-electron configuration for Fe^{2+} is d^6
- 4) The splitting energy is large.



- 5) Has no unpaired electrons, it is diamagnetic.

Conclusion: Low spin

To confirm experimentally that this complex is low spin we should use spectroscopic methods:

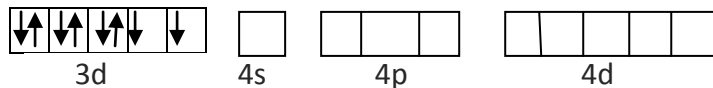
- Optical absorption spectra (low spin complexes with *strong field* ligands absorb light at *shorter wavelengths* (higher energy) in comparison with *high spin* complexes with *weak field* ligands that absorb light at *longer wavelengths* (lower energy))
- electron-spin resonance spectra to determine the magnetism and the filling of the orbitals.

Question 3

) Draw the structure of $[\text{Ni}(\text{CN})_4]^{2-}$, showing the stereochemistry. Use crystal field splitting arguments to explain your answer.

Solution

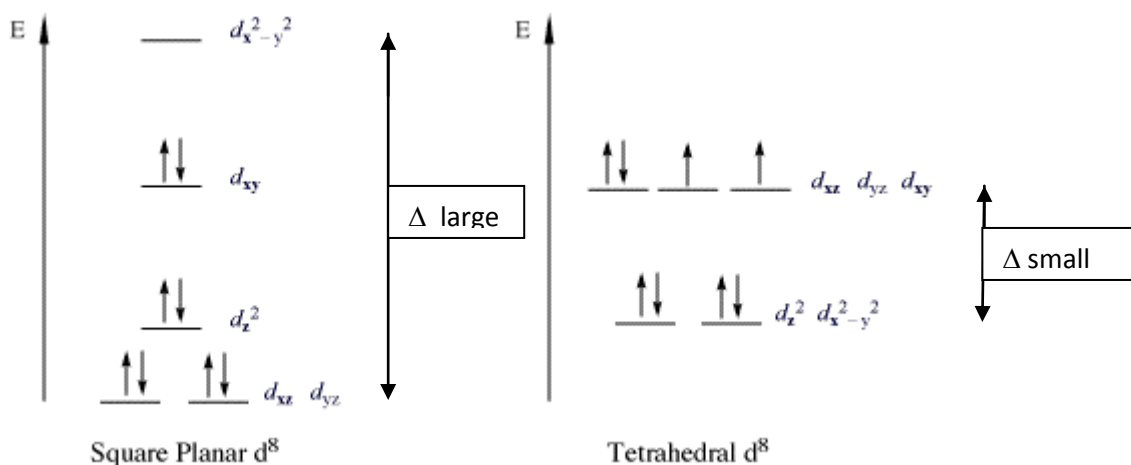
In complex $[\text{Ni}(\text{CN})_4]^{2-}$ oxidation state of nickel is Ni^{2+} . It's d-configuration is d^8 .



There are 4 CN^- ions. Thus, it can either have a tetrahedral geometry or square planar geometry. Since CN^- is a strong field ligand, it causes the pairing of unpaired 3d-electrons, and crystal field splitting energy is large.

In tetrahedral complex Δ_t is relatively small even with strong-field ligands. Δ_t does not exceed pairing energy. Electrons will move to the higher energy orbitals rather than pair. Tetrahedral complexes are high spin.

In square planar complexes Δ is almost always be large even with a weak-field ligands. Electrons tend to be paired rather than unpaired because pairing energy is usually much less than Δ . Square planar complexes are low spin.



Geometry for $[\text{Ni}(\text{CN})_4]^{2-}$ is: square-planar.

