Sample Exercise 24.1 Identifying the Coordination Sphere of a Complex

Palladium(II) tends to form complexes with a coordination number of 4. One such compound was originally formulated as PdCl₂ · 3 NH₃. (a) Suggest the appropriate coordination compound formulation for this compound. (b) Suppose an aqueous solution of the compound is treated with excess AgNO₃(aq). How many moles of AgCl(s) are formed per mole of PdCl₃ · 3 NH₃?

Solution

Analyze: We are given the coordination number of Pd(II) and a chemical formula indicating that NH₃ and Cl⁻ are the potential ligands. We are asked to determine (a) what ligands are attached to Pd(II) in the compound and (b) how the compound behaves toward AgNO₃ in aqueous solution.

Plan: (a) Because of their charge, the Cl⁻ ions can be either in the coordination sphere, where they are bonded directly to the metal, or outside the coordination sphere, where they are bonded ionically to the complex. Because the NH₃ ligands are neutral, they must be in the coordination sphere. (b) The chlorides that are in the coordination sphere will not be precipitated as AgCl.

Solve:

- (a) By analogy to the ammonia complexes of cobalt(III), we predict that the three NH₃ groups of PdCl₂ · 3 NH₃ serve as ligands attached to the Pd(II) ion. The fourth ligand around Pd(II) is one of the chloride ions. The second chloride ion is not a ligand; it serves only as an anion in this ionic compound. We conclude that the correct formulation is [Pd(NH₃)₃CI]CI.
- (b) The chloride ion that serves as a ligand will not be precipitated as AgCl(s) following the reaction with AgNO₃(aq). Thus, only the single "free" Cl⁻ can react. We therefore expect to produce 1 mol of AgCl(s) per mole of complex. The balanced equation is [Pd(NH₃)₃Cl]Cl(aq) + AgNO₃(aq) → [Pd(NH₃)₃Cl]NO₃(aq) + AgCl(s). This is a metathesis reaction (Section 4.2) in which one of the cations is the [Pd(NH₃)₃Cl]⁺ complex ion.



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Table of Contents Ch24 1 Content Mastery Chemistry

- 1. Understanding the eBook Ch24 1 Content Mastery Chemistry
 - The Rise of Digital Reading Ch24 1 Content Mastery Chemistry
 - Advantages of eBooks Over Traditional Books
- 2. Identifying Ch24 1 Content Mastery Chemistry
 - Exploring Different Genres
 - o Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
- 3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Ch24 1 Content Mastery Chemistry
 - User-Friendly Interface
- 4. Exploring eBook Recommendations from Ch24 1 Content Mastery Chemistry
 - Personalized Recommendations

- Ch24 1 Content Mastery Chemistry User Reviews and Ratings
- Ch24 1 Content Mastery Chemistry and Bestseller Lists
- 5. Accessing Ch24 1 Content Mastery Chemistry Free and Paid eBooks
 - Ch24 1 Content Mastery Chemistry Public Domain eBooks
 - Ch24 1 Content Mastery Chemistry eBook Subscription Services
 - Ch24 1 Content Mastery Chemistry Budget-Friendly Options
- 6. Navigating Ch24 1 Content Mastery Chemistry eBook Formats
 - ∘ ePub, PDF, MOBI, and More
 - Ch24 1 Content Mastery Chemistry Compatibility with Devices
 - Ch24 1 Content Mastery Chemistry Enhanced eBook Features
- 7. Enhancing Your Reading Experience
 - o Adjustable Fonts and Text Sizes of Ch24 1 Content Mastery Chemistry
 - Highlighting and Note-Taking Ch24 1 Content Mastery Chemistry
 - Interactive Elements Ch24 1 Content Mastery Chemistry
- 8. Staying Engaged with Ch24 1 Content Mastery Chemistry
 - o Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Ch24 1 Content Mastery Chemistry
- 9. Balancing eBooks and Physical Books Ch24 1 Content Mastery Chemistry
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Ch24 1 Content Mastery Chemistry
- 10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
- 11. Cultivating a Reading Routine Ch24 1 Content Mastery Chemistry
 - Setting Reading Goals Ch24 1 Content Mastery Chemistry
 - Carving Out Dedicated Reading Time
- 12. Sourcing Reliable Information of Ch24 1 Content Mastery Chemistry
 - Fact-Checking eBook Content of Ch24 1 Content Mastery Chemistry

- Distinguishing Credible Sources
- 13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
- 14. Embracing eBook Trends
 - Integration of Multimedia Elements
 - Interactive and Gamified eBooks

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