E-1

Type of task: Linking examples to principles

Subject matter: Coordination complexes

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**Notes**

Based on data in Table 31.4 Moeller, *Chemistry with Inorganic Qualitative Analysis*, 3rd Ed, 1989, Harcourt Brace Jovanovich, 812 .

*Linking examples to principles ...*

Instructors regularly use examples to illustrate and clarify general propositions. While the link between the example and the principle may be obvious to the instructors, students do not necessarily understand the connection. Students may understand examples of a principle when the examples have been presented to them but their understanding is challenged more deeply if they are required to identify examples of a principle from a range of possibilities. In such a case, one also needs to be able to identify non-examples and to recognise why they are non-examples.

*This task ...*

This task involves students using a table of dissociation constants of metal ion complexes to select examples that illustrate a number of propositions relating to the chemistry of such complexes. For example, to illustrate the proposition ‘the stability of halide complexes usually decreases in the order I->Br->Cl-’, students might use [CdCl4]2-, [CdBr4]2- and [CdI4]2- which have dissociation constants of 9.3  10-3, 2  10-4 and 8  10-7 respectively.

Linking examples to principles: Coordination complexes

The dissociation constant, Kd, of a complex is a measure of its thermodynamic stability. The smaller the value of Kd, the smaller the tendency for a complex to dissociate and the greater its thermodynamic stability.

**Use the table of overall dissociation constants following to select appropriate examples to illustrate the following propositions:**

(You can refer to complexes by numbers if you want to.)

•  Metal ions differ widely in the stability of the complexes they form, even those with the same ligand and coordination number.

•  The higher the oxidation state of a metal, the more stable the complexes it forms with a given ligand. The ligand-metal bond strength is higher for higher oxidation states of the metal.

•  For a given metal ion, the stability of halide complexes usually decreases in the order I->Br->Cl-.

•  The cyanide ion is like a halide ion in many respects but its complexes with metal ions are far more stable.

•  Chelate ring formation greatly increases the stability of complexes. Mono-amines are rather poor coordinating agents, but diamines, if they can form five membered rings, give extremely stable complexes.

•  The formation of fused chelate rings (rings with one or more bonds in common) gives complexes that are more stable than those containing rings that are not fused.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Complex | Kd |  | Complex | Kd |
| 1 | [Ag(NH3)2]+ | 6.2  10-8 | 18 | [Cu(OH)4]2- | 7.6  10-17 |
| 2 | [Cd(NH3)4]2+ | 1  10-7 | 19 | [Zn(OH)4]2- | 5  10-21 |
| 3 | [Cu(NH3)4]2+ | 1  10-13 | 20 | [CaP2O7]2- | 1  10-5 |
| 4 | [Ni(NH3)6]2+ | 1  10-9 | 21 | [MgP2O7]2- | 2  10-6 |
| 5 | [Zn(NH3)4]2+ | 3.46  10-10 | 22 | [CuP2O7]2- | 2.0  10-7 |
| 6 | [AgCl2]- | 9  10-6 | 23 | [Ag(en)]+ | 1  10-5 |
| 7 | [CdCl4]2- | 9.3  10-3 | 24 | [Cd(en)2]2+ | 2.60  10-11 |
| 8 | [PdCl4]2- | 6  10-14 | 25 | [Co(en)3]2+ | 1.52  10-14 |
| 9 | [AgBr2]2- | 7.8  10-8 | 26 | [Co(en)3]3+ | 2.04  10-49 |
| 10 | [CdBr4]2- | 2  10-4 | 27 | [Fe(ox)3]4- | 6  10-6 |
| 11 | [PdBr4]2- | 8.0  10-14 | 28 | [Fe(ox)3]3- | 3  10-21 |
| 12 | [CdI4]2- | 8  10-7 | 29 | [Cu(gly)2] | 5.6  10-16 |
| 13 | [Ag(CN)2]- | 8  10-22 | 30 | [Zn(gly)2] | 1.1  10-10 |
| 14 | [Cd(CN)4]2- | 8.2  10-18 | 31 | [Cu(edta)]2- | 1.38  10-19 |
| 15 | [Au(CN)2]- | 5  10-39 | 32 | [Zn(edta)]2- | 2.63  10-17 |
| 16 | [Fe(CN)6]4- | 1.3  10-37 | 32 | [Cd(CH3NH2)4]2+ | 2.82  10-7 |
| 17 | [Fe(CN)6]3- | 1.3  10-44 |  |  |  |
|  |  |  |  |  |  |

Overall dissociation constants of some common complexes. The names and structures of en, ox, gly and edta appear below.



Linking examples to principles: Coordination complexes

**SOLUTIONS:**

•  Metal ions differ widely in the stability of the complexes they form, even those with the same ligand and coordination number.

Sets of examples that illustrate the proposition are **2, 3, and 5; 7 and 8; 9, 10 and 11; 13 and 15; 18 and 19; 20, 21 and 22; 29 and 30; 31 and 32.**

•  The higher the oxidation state of a metal, the more stable the complexes it forms with a given ligand. The ligand-metal bond strength is higher for higher oxidation states of the metal.

Sets of examples that illustrate the proposition are **16 and 17; 25 and 26; 27 and 28**.

•  For a given metal ion, the stability of halide complexes usually decreases in the order I->Br->Cl-.

Sets of examples that illustrate the proposition are **7, 10 and 12; 6 and 9**.  **8 and 11** are not consistent with the proposition.

•  The cyanide ion is like a halide ion in many respects but its complexes with metal ions are far more stable.

Sets of examples that illustrate the proposition are **7, 10 or 12 and 14; 6 or 9 and 12**.

•  Chelate ring formation greatly increases the stability of complexes. Mono-amines are rather poor coordinating agents, but diamines, if they can form five membered rings, give extremely stable complexes.

Sets of examples that illustrate the proposition are **33 and 24; 1 and 23; 2 and 24**.

•  The formation of fused chelate rings (rings with one or more bonds in common) gives complexes that are more stable than those containing rings that are not fused.

Sets of examples that illustrate the proposition are **29 and 31; 30 and 32**.