Isomerism in coordination compounds pdf

Lecture 6. CHEM1902 Coordinating chemistry Two or more different compounds with the same formula are called isomers. The two main types of isomerism are known among the coordinating compounds. Each of them can be further divided. a) Geometric isomerism b) Optical isomerism a) Coordinating isomerism b) Ionization isomerism c) Hydrate isomerism d) Isomerism interconnection 1. Stereoisomers have the same atoms, the same sets of mates, but differ in the relative orientation of these mates. Ignoring special cases involving esoteric ligands, then: Geometric isomers are possible for both square planar and eight-sided complexes, but not four-walled. Optical isomers are possible for both four-walled and eighth complexes, but not for square planar. The oldest examples of stereoism include Co(III) complexes. In 1889 Jorgensen observed purple and green salts [CoCl2(en)2]+, which Werner later correctly identified as cis- and transgeometric isomers. In 1911, the first resolution of optical isomers was reported by Werner and King for cis-[CoX(NH3)(en)2]2+ complexes, where X=Cl- or Br-. Geometric isomers The number of geometric isomers expected for common stereochemistry are as follows: Square Planar: Composite type no isomers Ma2b2 2 (cis- and trans-) Mabcd 3 (use cis- and trans-relationships) here a, b, c and d refer to monodentate ligands. A number of examples of these types have been isolated and characterized and exhibit very different chemical and biological properties. For example, cis-PtCl2(NH3)2 is an anticancer agent (cisplatin), while the trans-isomer is inactive against cancer (it is toxic) and so is not useful in chemotherapy. cis- and trans-isomers [PtCl2(NH3)2] cis- and trans- refer to the position of 2 groups vis-à-vis each other. In the cis-isomer they are side by side, i.e. at 90 degrees in relation to the central metal ion, while in the trans-isomer they are opposite each other, i.e. at 180 degrees relative to the central metal ion. and | | M ----b a----M----b cis-trans-3 geometric isomers of a square planar complex [PtBrClNH3(pyr)]. The first report on three geometric isomers that were isolated and characterized for [Mabcd] complexes was il'ya Chernyaev in 1928. The above example was reported by Anna Gel'man in 1948. Question. Does cis-amminebromo-cis-chloropyridine platinum(II) uniquely identify isomer (ii) above? Octahedral: Composite type isomers Ma4b2 2 (cis- and trans-) Ma3b3 2 (fac- and mer-) MAA2b2 3 (2 * cis- and 1 trans-) here and b, represent monodentate ligands and AA is bidentate ligand. In the second example, labels are designed to reflect the relative positions of ligands around an eight-sided structure. So; the placement of 3 groups on one side of the octavars leads to the facial isomer, and the placement of 3 groups around the center leads to a meridional isomer. and mer-isomers [RhCl3(pyr)3]. [Mabcdef] is expected to give 15 geometric isomers. In the case of [PtBrClI(NO2)(NH3)(pyr)] several of them were isolated and characterised by Anna Gel'man and reported in 1956. Optical isomers are possible for each of these 15 forms, making a total of 30 isomers. Cis-isomer MAA2b2 may also show optical isomerism, although we will focus mainly on optical isomers of type M (AA)3 (see below). Optical isomers Optical isomers are related as insurmountable mirror images and differ in the direction in which they rotate in flat polarized light. These isomers are referred to as enantiomers or enantiomorphs, and their insurmountable structures are described as asymmetric. Different methods have been used to indicate the absolute configuration of optical isomers such as R or S, Λ or Δ or C and A. IUPAC rules indicate that it is appropriate to use scheme C/A for general eight-sided complexes and that for BIS and tris bidentate complexes the absolute configuration is identified as Lambda Λ (left-handed) and Delta Δ (right-handed). Priorities are intended for mononuclear coordination systems based on standard sequential rules developed for enantiomer carbon compounds cahn, Ingold and Prelog (CIP rules). These rules use the coordinating atom to arrange ligands in the order of priorities so that the highest atomic number gives the highest priority number (the smallest CIP number). For example, a hypothetical complex [Co Cl Br I NH3 NO2 SCN]2- would assign I- as 1, Br as 2, Cl as 3, SCN as 4, NO2 as 5, and NH3 as 6. Here is one isomer where I and Cl, and Br and NO2 were found to trans-k each other. The reference axis of the eight-sided center is the axis containing the strangled CIP priority 1 atom and the transliging atom with the lowest possible priority (the highest numeric value). Atoms in a coordination plane perpendicular to the reference axis are displayed from the ligand with the highest priority (priority CIP 1) and compared by sequences of priority numbers clockwise and counterclockwise. The structure is assigned a C or A symbol depending on whether the sequence is clockwise (C) or counterclockwise (A) lower at the first point of difference. In the example above, this would be C. Two optical isomers [Co(en)3]3+ have the same chemical properties and only indicate their absolute configuration do not provide any information about the direction in which the flat polarized light rotates. This can only be determined from measurements and then isomers are further (-) and (+) depending on whether they rotate left or right. left-handed Λ isomer and right-handed Δ isomer To add to the exchange, when measuring on the sodium line D (589nm), tris(1,2-diaminoethane)M(III) complexes (M = Rh (III) and Co (III)) with identical absolute configuration, turn the plane polarized light in opposite directions! Left-handed (Λ)-[Co(en)3]3+ isomer gives rotation to the right and therefore corresponds to (+) isomer. Since the successful resolution of completely inorganic ions (not containing C atoms) (hexol) only a handful of truly inorganic complexes have been isolated as their optical isomers eg. For four-distance complexes, R and S would be used in a similar method to four-walled carbon types, and although it is assumed that four-distance complexes with 4 different ligands should be able to lead to optical isomers, they are generally too unstable and cannot be isolated. 2. Structural isomers There are several types of this isomerism that we often encounter in coordinating chemistry and some of them represent the following. (a) Coordination isomerism: where compounds containing complex anionic and cationic parts can be considered to occur by exchanging certain ligands from the cationic part to the anion part. one isomer [Co(NH3)6] [Cr(C2O4)3] another isomer [Co(C2O4)3] [Cr(NH3)6] b) isomers of ionization: where isomers can be considered to be occurring due to the formation of different ions in the solution. one isomer [PtBr(NH3)3]NO2 -> NO2- anions in a solution another isomer [Pt(NO2)(NH3)3]Br -> Br-anions in solution Note that both anions are necessary to balance the charge of the complex and that they differ in that one ion is directly connected to the medium metal, but the other is not. A very similar type of isomerism results from the replacement of a coordinated group with a solvent molecule (Solvate isomerism). In the case of water, it's called hydrate isomerism. (c) Hydrate isomerism: the best known example occurs with chromium chloride CrCl3.6H2O, which may contain 4, 5 or 6 coordinated water molecules. [CrCl2(H2O)4] Cl.2H2O bright green [CrCl(H2O)5]Cl2.H2O gray-green [Cr(H2O)6]Cl3 purple These isomers have very different chemical properties and react with AgNO3 for cl-ion testing, should find 1, 2, and 3 Cl-ions in the solution, respectively d) Isomerism binding occurs in ambidentate ligands. These ligands are able to coordinate in more than one way. The most famous cases include monodentate ligands SCN- / NCS- and NO2- / ONO-. For example: [Co(ONO)(NH3)5]Cl nitrito isomer -O connected [Co(NO2)(NH3)5]Cl nitro isomer - N connected. Inorganic nomenclature As part of this course, you are required to familiarize yourself with the rules relating to the inorganic nomenclature. Use of coordination compounds A brief overview of some the use of coordination compounds includes: l. Dyes and pigments: Coordinating compounds have been used since the earliest times as dyes and pigments, such as madder dye, which is red, was used by ancient Greeks and others. It is a complex of hydroxyanthraquinone. A more modern example is the pigment of copper fotalokyanin, which is blue. 2. Analytical chemistry: During the laboratory course you have already encountered many such uses. a) Colour tests: Since many complexes are highly coloured, they can be used as colorimetric reagents, e.g. the formation of red 2,2'-bipyridyl and l,l0-phenanthroline complexes as a test for Fe(II) (b) Gravimetric analysis: Here chelation ligands are often used to create insoluble complexes, e.g. complexometric titrations and masking agents: An example is the use of EDTA in the determination of the volume ions of a wide range of metal ions in the solution, e.g. Mixtures of metals, e.g. metal mixtures, can be analysed by carefully adjusting the pH and using appropriate indicators. Alternatively, EDTA can be used as a masking agent to remove a metal ion that would interfere with the analysis of the second metal ion present. 3. Separating agents: Their use as masking agents is related to the use of ligands for separating, i.e. the use of ligands for separating. The addition of EDTA to water is used in boilers, etc., to prevent scaling or accumulation of insoluble calcium salts. 4. Metal extraction: Sometimes some metals may be leached from ores by the formation of stable complexes, e.g. 5. Bio-inorganic chemistry: Naturally occurring complexes include hemoglobin, chlorophyll, vitamin B12, etc. EDTA, and other complexoted substances have been used to accelerate the elimination of harmful radioactive and other toxic elements from the body. (e.g. pb2+). In these cases, soluble metal chelate complexes are formed. 6. Chemotherapy: an example is the use of cis-PtCl2(NH3)2 as an anticancer drug. Return to chemistry coordination curriculum course. 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