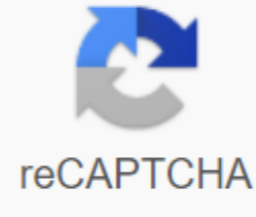




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## Optical isomerism in coordination complexes pdf

Lecture 6. CHEM1902 Coordination Chemistry Two or more different compounds with the same formula are called isomers. Two main types of isomerism are known among the focal compounds. Each of which can be further divided. (a) Geometric Isomerism b) Optical Isomerism (a) Coordination of Isomerism b) Ionization of Isomerism c) Hydrate Isomerism (d) The Link of Isomerism 1. Stereoisomers have the same atoms, the same sets of connections, but differ in the relative orientation of these connections. Ignoring the special cases associated with esoteric ligands, then: Geometric isomers are possible for both square planar and octahedral complexes, but not tetrahedral. Optical isomers are possible for both tetrahedral and octahedral complexes, but not for square planar. The earliest examples of stereoisomerism include Co(III) complexes. In 1889, Jorgensen observed the purple and green salts of  $\text{CoCl}_2(\text{en})_2$ , which Werner later correctly identified as cis and trans-geometric isomers. In 1911, Werner and King reported the first resolution of optical isomers for cis-CoX (NH<sub>3</sub>)<sub>2</sub>, where X'Cl- or Br-. Geometric Isomers Number of geometric isomers expected for common stereo looks, the following: Square Planar: Compound type No. of  $\text{Ma}_2\text{b}_2$  2 (cis- and trans-)  $\text{Mabcd}$  3 (use of 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 they show very different chemical and biological properties. For example, cis-PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> is an anti-cancer agent (cisplatin), while trans isomer is inactive against cancer (it is toxic), and therefore not useful for chemotherapy. cis- and trans-isomers PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> cis- and trans- refer to the position of two groups in relation to each other. In cis-isomer they are next to each other, i.e. at 90 degrees relative to the central metal ion, while in a trans isomer they are opposite to each other, i.e. 180 degrees relative to the central metal ion. a M ----b a----M----b cis-trans- 3 geometric isomers of the square planar complex PtBrClNH<sub>3</sub>(pyr). The first report on three geometric isms, isolated and characterized for  $\text{Mabcd}$ -type complexes, was prepared by Ilya Chernyaev in 1928. The example above was reported by Anna Gelman in 1948. Question. Does cis-aminebromo-cis-chloropiridineline (II) unequivocally identify isomer (ii) above?? Octahedral: Class No. of Isomers  $\text{Ma}_4\text{b}_2$  2 (cis- and trans-)  $\text{Ma}_3\text{b}_3$  2 (fac- and mer-)  $\text{MAA}_2\text{b}_2$  3 (2'cis- and 1 trans) here a, and b, represent the monodentate ligand and AA is a bidentate ligand. In the second example labels are introduced to reflect the relative positions of ligands around the octahedron. So; Placing 3 groups on one person octahedral results in facial isomer and placing 3 groups around the center leads to a meridional isomer. fac- and mer-isomers RhCl<sub>3</sub>(pyr)<sub>3</sub>.  $\text{Mabkdef}$  is expected to produce 15 geometric isomers. In the case of PtBrCl(NH<sub>2</sub>)(NH<sub>3</sub>), some of them were isolated and described by Anna Gelman and registered in 1956. Optical isomers are possible for each of these 15 forms, which is a total of 30 isomers. Cis-isomer  $\text{MAA}_2\text{b}_2$  can also exhibit optical isomerism, although we will focus mainly on optical isomers such as  $\text{M}(\text{AA})_3$  (see below). Optical isomers are associated as non-expensive mirror images and differ in the direction with which they rotate flat-polarized light. These isomers are called enantiomers or enantiomorphs of each other, and their non-layered structures are described as asymmetrical. Various methods are used to indicate the absolute configuration of optical isomers, such as R or S, q or C and A. IUPAC rules state that for common octahedral complexes, the C/A circuit is easy to use and that for bis and tris bidentate complexes, the absolute configuration will be designated Lambda q (left) and Delta q (right). Priorities are assigned to mono-nuclear coordination systems based on standard sequence rules developed for enantiometric carbon compounds cahn, Ingold and Prelog (CIP rules). These rules use a coordinating atom to organize ligands as a priority, so that the highest atomic number gives the highest number of priorities (the smallest number of CIP). For example, the hypothetical complex Co Cl Br I NH<sub>3</sub> NO<sub>2</sub> SCN 2- would appropriate I- as 1, Br as 2, Cl as 3, SCN as 4, NO<sub>2</sub> as 5 and NH<sub>3</sub> as 6. Here's one isomer where I and Cl, and Br and NO<sub>2</sub> were found to be trans-related to each other. The reference axis for the octahedron center is that the axis containing the CIP 1 priority ligating atom and the trans ligating atom is the lowest possible priority (higher numerical value). Atoms in the focal point perpendicular to the reference axis are treated with the ligand having this highest priority (CIP 1 priority), and are compared to the sequences of priorities clockwise and counterclockwise. The structure is assigned to a symbol of C or A, depending on whether the clockwise (C) or anti-clockwise (A) sequence is lower at the first point of difference. In the above example, this will be C. Two optical isomers Co(en)<sub>3</sub> 3 have the same chemical properties and simply denoting their absolute configuration do not give any information about the direction in which they rotate the plane of polarized light. This can only be determined by measuring and then isomerizing prefixes (-) and (me) depending on whether they rotate left or right. Left-hander Isomer and right-handed Isomer To add to the confusion, when measured on the Sodium line D (589nm), Tris (1,2-diaminoethane)M(III) complexes (MH Rh(III) and Co(III)) with identical absolute configuration, rotate the plane of polarized light in OPPOSITE directions! Lefty (l)-Ko (en)<sub>3</sub> 3' isomer gives rotation to the right and therefore corresponds to the isomer. After the successful resolution of a completely inorganic ion (non-atom C) (hexol) only a handful of truly inorganic complexes were isolated as optical isomers, such as (NH<sub>4</sub>)<sub>2</sub>Pt(S<sub>5</sub>)<sub>3</sub>.2H<sub>2</sub>O. Tetrahedral complexes R and S will be used similarly to tetrahedral carbon species, and although it is predicted that tetrahedral complexes with 4 different ligands should be able to lead to optical isomers, in general they are too laboratory and cannot be isolated. 2. Structural isomers There are several types of this isomerism often found in the coordination of chemistry and the following represents some of them. (a) Coordination isomerism: where compounds containing complex anion and cation parts can be seen as occurring by exchanging some ligands from the cation to the anion part. one isomer Co(NH<sub>3</sub>)<sub>6</sub> (Cr (C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> another isomer Co(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> (Cr (NH<sub>3</sub>)<sub>6</sub>) Ionization of isomers: where isomers can be considered as occurring due to the formation of different ions in the solution. one isomer (PtBr (NH<sub>3</sub>)<sub>3</sub>NO<sub>2</sub> - NO<sub>2</sub>- anions in the solution of another isomer (Pt (NO<sub>2</sub>) (NH<sub>3</sub>)Br<sup>-</sup> Br-anions in the solution Note that both anion is necessary to balance the charge of the complex, and that they differ in that one ion is directly attached to the central metal. In the case of water, this is called hydrate isomerism. (CrCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>) Cl.2H<sub>2</sub>O Bright Green CrCl(H<sub>2</sub>O)<sub>5</sub>Cl<sub>2</sub>.H<sub>2</sub>O grey-green Cr(H<sub>2</sub>O)<sub>6</sub>Cl<sub>3</sub> Violet These isomers have very different chemical properties and react with AgNO<sub>3</sub> to test for Cl-ions, find 1, 2 and 3 Cl-ions in the solution respectively. d) The link of isomerism occurs with ambidentate ligands. These ligands are able to coordinate in more than one way. The most well-known cases are related to THE mono dentate ligands SCN- / NCS- and NO<sub>2</sub>- / ONO-. For example: Co (ONO) (NH<sub>3</sub>)<sub>5</sub>Cl nitrito isomer-O is attached Co(NO<sub>2</sub>) (NH<sub>3</sub>)<sub>5</sub>Cl Nitro Isomer - N attached. As part of this course, you should familiarize yourself with the rules associated with the inorganic item. Using coordination connections A brief overview of some The use of coordinating compounds includes: 1. Dyes and pigments: Coordination compounds have been used since ancient times as dyes and pigments, for example, a more insane dye, which is red, was used by ancient Greeks and others. This is a hydroxiantrahinone complex. A more modern example is the pigment of the media Phthalo beingan, which is blue. 2. Analytical Chemistry: You have already encountered many such uses during a laboratory course. (a) Color tests: Because many complexes are colored, they can be used as colorful reagents, for example. formation of red 2,2'-bipyridil and 1,10-phenanthroline complexes as a test for Fe (II) (b) Gravimetric analysis: Here chelate ligands are often used to form insoluble complexes such as Ni (DMG)<sub>2</sub> and Al (oxine)<sub>3</sub> (see laboratory guide). (c) Complex imagery and camouflage agents: an example of this is the use of EDTA in the voluminous definition of a wide range of metal ions in a solution, such as n<sub>2</sub>, Pb<sub>2</sub>, Ca<sub>2</sub>,Co<sub>2</sub>, Ni<sub>2</sub>, Cu<sub>2</sub>, etc. In addition, EDTA can be used as a camouflage tool to remove metal ion, which will interfere with the analysis of the second metal ion present. 3. Sequestr agents: Related to their use as camouflage agents is the use of ligands for sequester, i.e. to effectively remove unwanted ions from the solution in industrial processing, for example, EDTA is used to soften water. Adding EDTA to water is used in boilers, etc., to prevent scaling or accumulating insoluble calcium salts. 4. Metal mining: Sometimes some metals can leach out of their des by forming stable complexes such as Ag and Au, like cyanide ion complexes. 5. Bio-inorganic Chemistry: Natural complexes include hemoglobin, chlorophyll, vitamin B12, etc. EDTA and other complex agents have been used to accelerate the elimination of harmful radioactive and other toxic elements from the body. (e.g. Pb<sub>2</sub>). In these cases, soluble metal chelate complexes are formed. 6. Chemotherapy: The example here is the use of cis-PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> as an anti-homulth drug. Return to the chemistry coordination course plan. Image copyright © 1996-2015 by Robert J. Lancashire, all rights are protected. Return to Chemistry, UWI-Mona, Home Page Created and Maintained by Professor Robert J. Lancashire, Department of Chemistry, University of the West Indies, Mona Campus, Kingston 7, Jamaica. Established in March 1996. Links are verified and/or last changed on April 6, 2015. Url

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