Possible Isomerism in Octahedral Metal Complexes Containing Three Flexible Bidentate Ligands

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For octahedral complexes containing three flexible bidentate ligands we distinguish five sources of isomerism - metal and ligand asymmetry, conformational, orientation and sequential isomerism. By using the "C_3" projection and simple permutation concepts it is possible to account for, name, total and inter-relate all isomers in this system. The example shows how in a typical system 2244 isomers are distinguished and uniquely named in a simple table. The gaps in the table are also simply explained. Whereas permutation group theory goes straight to totals and "Herumprobieren" counts heads,* this is enlightened Herumprobieren which factorizes, permutes and identifies.

Introduction

There has been considerable recent interest in the conformations assumed by flexible ligands in a variety of metal complexes. Much of this work is concerned with bidentate ligands in octahedral complexes. Studies in these systems are facilitated by the observations of Bailar and Corey[1] that tris(ethylenediamine)cobalt(III) ion can assume only four possible conformational arrangements since there are two possible low-energy conformations for any metal-ethylenediamine ring. By viewing the tris(ethylenediamine)cobalt(III) ion down the C_3 axis (or pseudo C_3 axis) the two ring conformations are distinguised by one having its carbon-carbon bond parallel (lel) to the C_3 axis while the other is oblique (ob) to this direction. Bailar and Corey predicted that the (lel)$_3$ conformer would be the most stable and the (ob)$_3$ the least stable.

This prediction has been justified by subsequent experiment to some extent. For example conformational specificity is displayed by complexes containing optically active[2] or racemic[3] propylenediamine, optically active[4] and racemic[5] *trans*-1,2-cyclohexanediamine, optically active *trans*-1,2-diaminocyclo-

pentane,[6] optically active and racemic 2,3-butanediamine[7] and N-methylethylenediamine.[8]

The observation of various conformational isomers, in some of which different ethylenediamine molecules assume different conformations, has also been described.[9,10]

In complexes of propylenediamine isomerism due to the relative positions of the various methyl groups is sometimes possible and has recently been observed for the ions [CoEDDA(−)pn]$^+$,[11] L[Co(−)pn$_3$]$^{3+}$,[12] [Co en(−)pn$_2$]$^{3+}$,[13] L[Co(+)pn(−)pn$_2$]$^{3+}$,[14] D[Co(−)pn$_3$]$^{3+}$,[14] and *trans*-[Co(NO$_2$)$_2$(−)pn$_2$]$^+$.[14]

With accumulation of all these observations on the one type of system it is now necessary that a suitable nomenclature which distinguishes all possible isomers and also a method for clearly distinguishing and inter-relating these isomers should be proposed. The following is an attempt to do this.

Discussion

We distinguish five possible sources of isomerism in tris(bidentate) metal complexes: (i) Metal Asymmetry; (ii) Ligand Asymmetry; (iii) Conformational Isomerism; (iv) Orientation Isomerism; (v) Sequential Isomerism.

(i) *Metal Asymmetry.* The asymmetry about the metal is referred to as D or L by comparison with D[Co en$_3$]$^{3+}$ ion.[15] Such isomerism will always double

D   L
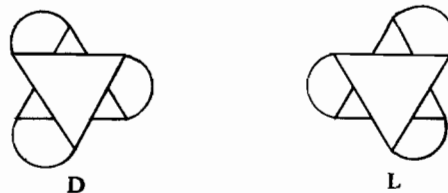
(*) For a discussion of these methods see B. A. Kennedy, D. A. McQuarrie, and C. H. Brubaker, Jr., *Inorg. Chem.*, 3, 265 (1964).
(1) E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, 81 (1959).
(2) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, 81, 290 (1959); F. P. Dwyer, A. M. Sargeson, and T. E. MacDermott, *J. Am. Chem. Soc.*, 85, 2913 (1963).
(3) F. P. Dwyer, A. M. Sargeson, and L. B. James, *J. Am. Chem. Soc.*, 86, 590 (1964).
(4) T. S. Piper and A. J. Karipides, *J. Am. Chem. Soc.*, 86, 5039 (1964).
(5) C. Shäffer, University of Copenhagen, private communication (1967).

(6) D. J. Royer and J. F. Phillips, *Inorg. Chem.*, 4, 616 (1965).
(7) F. Woldbye and G. Borch, Paper presented in Symposium on «Newer Physical Methods in Structural Chemistry», New College, Oxford, July (1966); F. Woldbye in V. Gutmann (Ed.), «Proc. 8.I.C.C.C.», Vienna, p. 103 (1964).
(8) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, 89, 3428 (1967).
(9) J. F. Blount, H. C. Freeman, A. M. Sargeson, and K. R. Turnbull, *Chem. Comm.*, 324 (1967).
(10) P. W. R. Corfield and J. A. Ibers, *Inorg. Chem.*, 7, 842 (1968).
(11) J. I. Legg, *Chem. Comm.*, 675 (1967).
(12) T. E. MacDermott, *Inorg. Chim. Acta*, 2, 81 (1968).
(13) T. E. MacDermott, *Chem. Comm.*, 223 (1968).
(14) T. E. MacDermott, unpublished results (1968).
(15) Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, *Bull. Chem. Soc.*, Japan, 30, 795 (1957).

the number of isomers resulting from other sources.

(ii) *Ligand Asymmetry.* Ligand asymmetry here refers to either an asymmetric centre in the free ligand or to the generation of such an asymmetric centre on complex formation. Such asymmetry is designated R or S according to the definition[16] of Cahn Ingold and Prelog:


where substituent size is $a < b < c < d$.

The existence of one such asymmetric centre in each ligand, for example, results in eight possible combinations: RRR, RRS, RSR, SRR, RSS, SRS, SSR, SSS. In some cases (*e.g.,* AB AB AB see Table I) some of these possibilities will be duplicates and care must be taken to omit these.

Ligand asymmetry does not refer to the mirror isomerism of certain metal-chelate rings; this is treated under Conformational Isomerism.

(iii) *Conformational Isomerism.* Conformational isomerism may occur with all flexible bidentate or multidentate ligands although conformational specificity is often encountered. The total number of isomers will be increased by a factor equal to the number of different conformational arrangements the particular compound may assume.

For example, flexible 5-membered metal-ligand rings may assume one of two conformations. These are designated δ or λ according to whether the two lines joining the donor atoms (D) and the bridging atoms (B) define a right or left-handed helix. One line constitutes the axis and the other is a tangent to the helix.
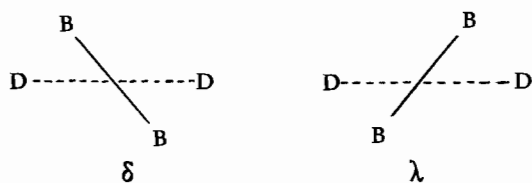
Where a tris(bidentate) complex contains three such five-membered rings there are eight conformational arrangements: δδδ, δδλ, δλδ, λδδ, δλλ, λδλ, λλδ, λλλ. In some cases two or more of these arrangements may be indentical (*e.g.,* see AA AA AA etc., in the Table I).
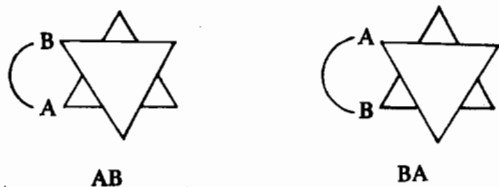
(iv) *Orientation Isomerism.* Orientation isomerism only occurs when the bidentate ligand has distinguishable donor sites (AB) and when, at the same time, the other two ligands are distinguishable. This orientation is indicated by reference to the " C₃ " projection and writing AB when the A donor is presented on the octahedral face closer to the viewer

(16) R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem. Intern. Ed.* (Engl.), *5,* 385 (1966); *Experientia, 12,* 81 (1956).

Table I. Isomers of Octahedral Metal Complexes containing Three Flexible Bidentate Ligands

and BA when this orientation is reversed. We also define


AB   BA

that the normal projection will present the majority of most heavily substituted donor sites on the front octahedral face.

Normally a formula or name does not distinguish the ends of a ligand. As has already been proposed[13] this can be indicated by starring the ligand whose more heavily substituted donor is remote from the viewer, e.g. [Co en(−)pn(−)pn*]$^{3+}$ etc.

In general there are four possible orientation arrangements e.g. AB CD EF, BA CD EF, AB DC EF, and AB CD FE. If we simply number the ligands 1,2,3 then this isomerism is indicated by 1 2 3, 1*2 3, 1 2*3, 1 2 3*.

Orientations such as 1*2*3 need not be considered here since they will be accounted for under sequential isomerism.

(v) *Sequential Isomerism.* In this system the "C₃" projection presents the viewer with the three ligands in a clockwise sequence. Since there are two ways of arranging three different objects about the apices of an equilateral triangle there are also two possible sequential isomers in this system, e.g. AB CD EF and AB EF CD.
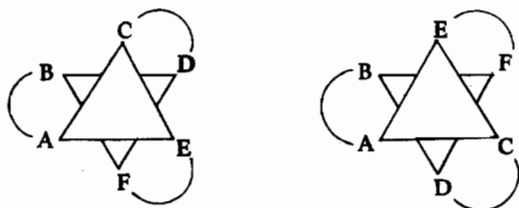
This isomerism is indicated in a formula or name by writing the ligands in their clockwise sequence.

In the table sequences are designated 1 2 3 and 1 3 2 respectively.

Application. By superimposing the isomerism generated by each of the above five sources in a stepwise procedure it is a simple matter to write down or draw in projection any isomer of any tris-(bidentate) octahedral metal complex. Furthermore the total number of isomers for any given system is readily available. Indeed this procedure factorizes this total and the number of isomers for a system where a particular source of isomerism is being ignored is also readily available.

Example. To illustrate the simplicity and usefulness of this system we now tabulate the entire system of tris(bidentate) metal complexes from AA AA AA to AB CD EF. For the purpose of this illustration we assume: (i) all ligands are flexible; (ii) all ligands form 5-membered metal-ligand rings; (iii) all ligands such as AB, CD etc. not only have distinguishable donor sites but also contain one centre of asymmetry. We also require that all symmetrical ligands AA, BB etc. are optically inactive (i).

These assumptions are geared to our own interest in ethylenediamine and propylenediamine complexes. They clearly do not constitute a limitation to the method. They are invoked in this example to obviate pedantry.

The Table I lists the ten tris(bidentate) complexes and the isomerism stemming from each of the five sources listed above. Any given isomer is represented by a set of five symbols which are one in each section and in a horizontal array.

Any set of five symbols represents a unique isomer. Where there is a gap in the table isomers which would have been generated by a symbol in that position are all either identical to, or rotational isomers of, other isomers already represented in the table. The relationships of these «duplicate» isomers to the already catalogued isomers is indicated by a letter which represents one of the following operations: (a) identity; (b) a rotation of 180° about the in-plane bisector of the angle subtended at the metal by one of the ligands; (c) a rotation of 120° positive or negative about the principal screw axis; (d) either (b) or (c) arbitrarily; (e) either (a) or (c) depending on the rest of the system.