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Burmeister J L. Linkage isomerism in metal complexes.
Coord. Chem. Rev. 3:225-45, 1968.
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Linkage isomerism involves the existence of two complexes differing only in the mode of attachment of an ambidentate ligand to the metal atom. This paper describes the synthesis, the physical methods used in structural elucidation, and the factors that determine the formation and stability of 32 linkage isomeric pairs involving seven ambidentate ligands. [The *SCI®* indicates that this paper has been cited in over 270 publications, making it the most-cited paper from this journal.]

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The genesis of this paper may be traced to the moment in 1963 when, hunched over an IR spectrophotometer in a laboratory in Northwestern University's Technological Institute at 1:30 a.m., I watched a pen trace the confirming evidence that I had, indeed, synthesized the first inorganic linkage isomers of the thiocyanate ion.[1] The impacts of this discovery were both immediate and long-range: My doctoral mentor, Fred Basolo, was roused from his slumber by a telephone call to share the joy that always accompanies scientific discovery, light appeared at the end of my PhD tunnel, and, given the green light by Basolo, I initiated a research program that has focused on the coordination chemistry of ambidentate ligands to this very day, some 100 research publications later.

The growth of interest in these "schizophrenic" ligands has paralleled the burgeoning interest in inorganic chemistry. Although the first linkage isomeric pair was isolated 131 years ago, 37 years elapsed before their true nature was predicted,[1] and it was not until the 1960s that this was finally confirmed.[1] In 1962 F.A. Cotton and G. Wilkinson's classic text[2] devoted a grand total of *seven lines* to the subject of linkage isomerism. Sixteen years later, J.E. Huheey[3] allocated *12 pages* to the subject in his widely adopted text. In the same vein, our 1963 thiocyanato/isothiocyanato linkage isomer synthesis represented only the second example of this phenomenon in inorganic chemistry, all previous reports having involved nitrito/nitro linkage isomerism.

The paper that spawned this commentary listed a total of 32 known linkage isomeric pairs in 1968. Eight years later, the number had more than tripled.[4] The most recent comprehensive review,[5] a text that deals solely with the coordination chemistry of the pseudohalide ions, includes a staggering total of 4,217 references, a whopping increase of 56 percent over those cited in the original German version of the text published six years earlier. Growth, indeed!

Historically, the study of the coordination chemistry of ambidentate ligands has proceeded through five relatively distinct phases: (1) the use of ambidentate ligands in basic coordination chemistry studies without regard to their potential ambidentate character, (2) the development of chemical and physical probes for the determination of the bonding modes of ambidentate ligands, (3) the rational synthesis of linkage isomers of ambidentate ligands, (4) the elucidation of the factors that determine the bonding modes adopted by ambidentate ligands, and (5) the extrapolation and application of the understanding achieved in the preceding studies to questions involving bonding in coordination complexes in general.

Relatively recent work in our laboratories emanating from the fifth phase has led to such disparate discoveries as complexes of gold in the highly unusual +2 oxidation state[6] and a study of the *ortho*-metalation reactions of ambidentate phosphonium, arsonium, and sulfonium ylides.[7] Most recently, we have come full circle with our synthesis[8] of structural isomers involving the ambidentate $SeCN^-$ ion.

In retrospect, the significance and utility of my paper may be traced to its timing. Whenever any field of scientific endeavor experiences sudden, rapid growth, a critical review article is needed to organize and codify the seminal studies for the workers in the field, both current and future. I simply struck while the iron was hot.

1. **Basolo F, Burmeister J L & Poë A J.** Linkage isomerism: synthesis of thiocyanato and isothiocyanato isomers of some palladium(II) complexes. *J. Amer. Chem. Soc.* 85:1700-1, 1963. (Cited 45 times.)
2. **Cotton F A & Wilkinson G.** *Advanced inorganic chemistry—a comprehensive text.* New York: Wiley Interscience, 1962. p. 538. (Cited 290 times.)
3. **Huheey J E.** *Inorganic chemistry: principles of structure and reactivity.* New York: Harper & Row, 1978. p. 468-79. (Cited 90 times.)
4. **Balahura R J & Lewis N A.** Linkage isomers: their preparation and reactions. *Coord. Chem. Rev.* 20:109-53, 1976. (Cited 50 times.)
5. **Golub A M, Köhler H & Skopenko V V,** eds. *Chemistry of pseudohalides.* Amsterdam: Elsevier, 1986. 479 p.
6. **Calabro D C, Harrison B A, Palmer G T, Moguel M K, Rebbert R L & Burmeister J L.** Thiocyanation, selenocyanation, and halogenation reactions of dithiocarbamate complexes of gold(I) and silver(I). Generation of gold(II) and silver(II) complexes. *Inorg. Chem.* 20:4311-6, 1981. (Cited 5 times.)
7. **Illingsworth M L, Teagle J A, Burmeister J L, Fultz W C & Rheingold A L.** Crystal and molecular structure of a dinuclear *ortho*-metalated platinum ylide complex. *Organometallics* 2:1364-9, 1983. (Cited 2 times.)
8. **Grygon C A, Fultz W C, Rheingold A L & Burmeister J L.** Structural isomerism involving an ambidentate ligand: the synthesis and characterization of diselenocyanato[bis(diphenylphosphino)methane]palladium(II) and cyano(selenocyanato)[diphenyl(diphenylphosphinomethyl)phosphine selenide]palladium(II). *Inorg. Chim. Acta* 141:205-9, 1988.

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