Notes

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Isomer Counts for Polynuclear Coordination Compounds

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The number of isomers to be expected for a given type of coordination compound can be determined by means of quite powerful analytical expressions.[1-6] The use of these expressions, however, becomes somewhat complicated for polynuclear coordination compounds when chemistry restricts the distribution of their ligands. For example, Kennedy, *et al.*, found it necessary to use five "restricted forms" in order to apply their technique to the dimer $Nb_2Cl_2(OC_2H_5)_6(C_5H_5N)_2$ while keeping one pyridine bonded to each niobium atom.[6] The technique of systematically eliminating duplicates from an enumeration of all possible permutations has proved more rapid in some cases than the evaluation of cycle indexes for a number of restricted forms. Furthermore, a procedure of this kind has the advantage that it yields not only the total number of isomers but also their individual configurations.

We desired to calculate the number of isomers expected for the dimer depicted in Figure 1a. Since the stepwise application of Polya's theorem[6] appeared to involve the individual evaluation of 12 "restricted forms," we decided to determine the number of isomers by eliminating all duplications from an enumeration of all possible permutations, using the skeleton shown in Figure 1b. The locants a, b, c, . . . follow the system outlined in the "Tentative Rules for Nomenclature of Inorganic Chemistry" recently prepared by a subcommittee of the IUPAC.[7] The eight nonbridging substituents occur as two similar sets of four, *i.e.*, one hydroxyl group, one nonbridging phosphinate group, and two water groups, bonded to the two chromium atoms. There are 12 ways to arrange the four groups in one set about its chromium. When each of these arrangements is combined with the 12 arrangements for the second chromium atom, a total of 144 possible configurations for the dimer results.

The skeleton (Figure 1b) has three mutually perpendicular C_2 axes and belongs to point group D_{2h}. Proper rotation of a configuration about any one of the C_2 axes yields an equivalent configuration. The 144 configurations were sorted out systematically by considering the effect of rotation about each axis on the individual configurations, one by one, and eliminating duplicates. If the ligands are designated H for hydroxyl, P for nonbridging phosphinate, and W for water, the isomer pictured in Figure 1 can be represented by the composite WPWH HWWP in which the ligand symbols are written in the locant order. Proper rotation of WPWH HWWP about C_2 yields PWHW WHPW, about C_2' yields PWWH HWPW, and about C_2'' WPHW WHWP. These four composites then represent the same isomer. Analogous treatment of the remaining composites yields 42 nonequivalent configurations.

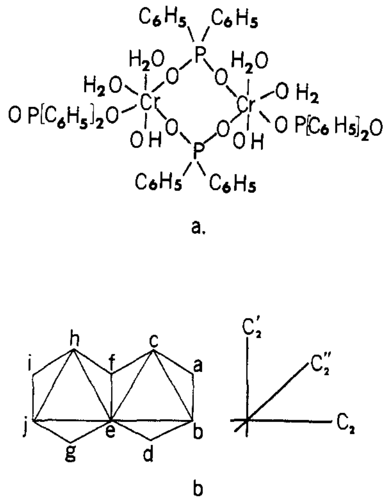

Figure 1.—(a) Probable structure of the chromium(III) dimer and (b) the skeleton of the structure with locants designated.

It is now possible to classify these 42 composites as optically active (mirror plane) or inactive (center of symmetry or plane of symmetry). Those that contain a mirror in the *yz* plane are classed as *meso* in analogy to *meso* organic compounds, *i.e.*, the halves of the dimer compensate each other. There are four such *meso* configurations, four inactive forms with a center of symmetry, and 17 enantiomorphic pairs to make up the 42 nonequivalent forms.

In order to use this method it is necessary to know that all possible distributions have been considered and that all rotational permutations have been used. Knowledge of the symmetry elements of the point group for the parent frame suffices for the latter. The number of possibilities to be considered can be readily determined from the number and kinds of groups in question in conjunction with the restrictions on their distribution. For example, the dimer $Nb_2Cl_2(OC_2H_5)_6(C_5H_5N)_2$ examined by Kennedy, *et al.*,[6] has the frame shown in Figure 1b, so the rotational symmetry elements are the three C_2 axes. Since both Cl and OC_2H_5 can serve as bridging groups, there are 10

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(1) A. C. Lunn and J. K. Senior, *J. Phys. Chem.*, **33**, 1027 (1929).
(2) G. Polya, *Z. Krist.*, **93**, 415 (1936).
(3) T. L. Hill, *J. Chem. Phys.*, **11**, 294 (1943).
(4) W. J. Taylor, *ibid.*, **11**, 532 (1943).
(5) I. V. Krivoshei, *Zh. Strukt. Khim.*, **4**, 757 (1963).
(6) B. A. Kennedy, D. A. McQuarrie, and C. H. Brubaker, Jr., *Inorg. Chem.*, **3**, 265 (1964).
(7) We are indebted to Dr. W. C. Fernelius for a draft copy of the tentative rules and helpful comments.

positions among which they can be distributed. The C_5H_5N groups are restricted one to each Nb and not permitted in the bridging positions. This means that one C_5H_5N must be in position a, b, c, or d and the other in g, h, i, or j. There are then only 16 different arrangements possible for the C_5H_5N groups. For each such arrangement there remain eight positions in which the two Cl and six OC_2H_5 groups are to be distributed. They can be placed in these positions in $8!/(6! \times 2!)$ or 28 ways. The total number of possibilities to be considered is then 16×28, or 448. It is possible to eliminate several of these blocks of 28 by considering only the 16 arrangements for the C_5H_5N groups. Only six of the blocks are unique, leaving 6×28, or 168, possibilities for detailed examination. These then reduce to 120 by consideration of rotations that have no net effect on the location of the C_5H_5N groups. These 120 forms include 50 enantiomorphic pairs, six species with centers of symmetry, six *meso* forms, and eight other inactive species, or the total of 70 geometrical isomers calculated by Kennedy, *et al.*[6]

For more symmetrical cases there is a greater number of symmetry elements to consider. An octahedron, point group O_h, for example, has three C_4 axes, four C_3 axes, and six C_2 axes. Therefore, 23 other configurations can be generated from the original octahedral arrangement (nine *via* the C_4 axes, eight *via* the C_3, and six *via* the C_2). It is interesting to note that this relationship leads directly to the calculation of 30 stereoisomers for Mabcdef, *i.e.*, $6!/24$.

Isomer counts for polynuclear species containing chelating ligands are quite rare. (See Table I.) Bailar has devised a scheme for determining the number of isomers for mononuclear octahedral complexes which includes chelated species.[8] However, general analytical methods, even for mononuclear chelated species, have not yet been developed although limited success with mononuclear systems has been claimed by Krivoshei.[9] We have not been able to include chelated species in our procedure, but its mechanics have helped us to examine the rather complicated case of the dimer $(AB)_2M(C)_2M(AB)_2$ in a straightforward manner, with some assurance that all possibilities were considered. There are eight ways the two unsymmetrical chelating groups can be bonded to the four nonbridging positions of the dimer, so that there are 64 possibilities to consider. Again the rotational permutations consist of three C_2 axes. Visual examination leads to the conclusion that there are 24 stereoisomers comprising 10 pairs of enantiomorphs, one *meso* form, one form with a center of symmetry, and two *meso* forms with centers of symmetry.

Table I summarizes the isomer counts we have made along with those already in the literature. More details and tabulations of individual configurations are available.[10]

Acknowledgments.—We are indebted to the Office of Naval Research for partial support of our studies and to Dr. G. H. Dahl for reading Krivoshei's papers to us.

TABLE I

CLASSIFICATION OF ISOMERS FOR DOUBLE-BRIDGED DIMERS WITH OCTAHEDRAL CENTERS

					Total Isomers	
	Enantio-morphic	Inactive				
Formula[a]	pairs	*Meso*	Center	Other	Geo-metrical	Stereo
$\mathrm{M2Ma_6b_2}$	2	2	2	2	8^{c}	10
$\mathrm{M2Ma_4b_2c_2}$	46	4	4	14	68^{c}	114
$\mathrm{M2M[a_3b]^1[a_3b]^2}$	1^{d}	2^{d}	2^{d}	...	5^{d}	6^{d}
$\mathrm{M2M[a_2bc]^1[a_2bc]^2}$	17	4	4	...	25	42
$\mathrm{M2M(AA)_4}$	1^{e}	1^{e}	...	...	2^{e}	3^{e}
$\mathrm{M2M(AB)_4}$	10	3^{b}	3^{b}	...	14^{b}	24^{b}
$\mathrm{M2^*Ma_5b_2c}$	37	...	...	10	47^{c}	84
$\mathrm{M2^*M(AA)_4}$	1^{e}	1^{e}	...	...	2^{e}	3^{c}
$\mathrm{M2'M(AA)_4}$	2^{f}	...	...	...	2^{f}	4^{f}
$\mathrm{M(2)M[a]^1[a]^2b_6c_2}$	50	6	6	8	70^{c}	120

[a] M2M represents a pair of metal atoms joined by two identical symmetrical bridges. M2*M indicates that there are two different symmetrical bridges, M2′M that one bridge is symmetrical and the other not. M(2)M indicates that the groups being permuted can occupy the bridge as well as nonbridge positions. Symbols enclosed in [ ]^1 are substituents only on the first M, those in [ ]^2 only on the second. [b] Two of the inactive forms possess centers of symmetry and are also *meso* forms. [c] See ref 6. [d] F. Basolo in "Chemistry of the Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, p 290. [e] W. C. Fernelius in "Chemical Architecture," R. E. Burk and O. Grummitt, Ed., Interscience Publishers, Inc., New York, N. Y., 1948, p 93. [f] C. E. Wilkes and R. A. Jacobson, *Inorg. Chem.*, **4**, 99 (1965).

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[8] J. C. Bailar, Jr., *J. Chem. Educ.*, **34**, 334 (1957); S. A. Mayper, *ibid.* **34**, 623 (1957).

[9] I. V. Krivoshei, *Zh. Strukt. Khim.*, **6**, 322 (1965).

[10] A more detailed form of this paper, including tabulations of individual isomers for $\mathrm{M2Ma_6b_2}$, $\mathrm{M2Ma_4b_2c_2}$, $\mathrm{M2M[a_2bc]^1[a_2bc]^2}$, $\mathrm{M2M(AB)_4}$, $\mathrm{M2^*Ma_5b_2c}$, and $\mathrm{M(2)M[a]^1[a]^2b_6c_2}$ has been deposited as Document No. 9535 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting \$3.75 for photoprints, or \$2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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Some Chemistry of Trichlorophosphazosulfuryl Chloride

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Although the chemistry of $PCl_3{=}NSO_2Cl$ has not been extensively investigated, one mode of reaction has been established. Treatment of $PCl_3{=}NSO_2Cl$ with either chlorosulfonic acid[1] or hydrogen fluoride[2] results in protonation of the nitrogen followed by P–N bond cleavage

$$HSO_3Cl + PCl_3{=}NSO_2Cl \longrightarrow HN(SO_2Cl)_2 + POCl_3$$

$$6HF + PCl_3{=}NSO_2Cl \xrightarrow{BF_3} 4HCl + PF_5 + H_2NSO_2F$$

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[1] R. Appel, M. Becke-Goehring, G. Eisenhauer, and J. Hartenstein, *Chem. Ber.*, **95**, 625 (1962).

[2] L. K. Huber and H. C. Mandell, Jr., *Inorg. Chem.*, **4**, 919 (1965).