

Computation of the Number of Isomers and Their Structures in Coordination Compounds¹

By WILLIAM E. BENNETT

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A method has been developed for the determination of the number of isomers in coordination compounds and has been applied to octahedral, cubic, antiprismatic, and dodecahedral structures and to the binuclear complex with two octahedra bridged on one edge. Examples of each are given.

Introduction

The determination of the number of isomers and their structures in coordination compounds has been approached by using models,² drawings,³ Polyá's theorem,⁴ and the technique devised by Bailar and Mayper.⁵ The first two of these are subject to error and all of them are difficult to apply to complex cases.

The Bailar method has a simplicity which should make it adaptable to computer use. With this adaptation the computation should be fast, error free, and as simple for complex cases as for trivial ones. This paper is a report of our results from the use of this approach.

Method

A structure can be represented in a computer by a set of memory locations which represent positions of ligands in a complex. In each location a number or a character can represent the type of group. As an example the complex ion $\text{Co}(\text{NH}_3)_4\text{Cl}_2^+$ can be represented as in Figure 1.

Similarly chelated structures can be indicated by a second set of memory locations (1' to 6') in which pairs of like digits indicate which locations are bridged by a ligand. For example, the complex ion $\text{Co}(\text{en})_2\text{Cl}_2^+$ could be represented as in Figure 2. The fact that the same number (1) is in location 1' and 3' indicates that those positions are bridged. This is true also for 2' and 4'. In practice we extend this to a second and third set to allow for ligands which are polydentate.

Two identical isomers, when properly oriented, would have the same numbers in memory locations 1 through 6 and matching pairs of numbers in locations 1' through 6'.

The generation of all possible isomers can be accomplished by a permutation together of the numbers in locations 1 through 6 and 1' through 6' to give all possible permutations or, faster, by use of a table of all possible structures. In this work we have used permutations for eight-coordinate structures and an adaptation of the table of Bailar and Mayper⁵ for the octahedral structure.

Orientation of the structures in order to compare them is accomplished by a "rotation" of the symbols. For example, rotation of the complex ion $\text{Co}(\text{en})_2\text{Cl}_2^+$ about the axis through positions 1 and 2 is illustrated in Figure 3. Similarly, rotation about other axes can be simulated by movement of symbols. Conversion from one optical isomer to another can be accomplished in this way also.

The number and kind of rotations needed to compare one isomer to another depends upon the structure. For the octahedral case the maximum number of required rotations of one isomer to compare it to another is 23. This stems from the fact that there are 24 equivalent orientations of the O_h point group. For less symmetrical structures the number is less.

The input of the programs is one structure of the complex in coded form as illustrated above. This structure is then permuted to all possible structures. In the case of chelates a permuted structure is rejected if adjacent functional groups are not in *cis* locations. The structure is then compared to all established isomers. If it does not match or is not an optical isomer of one of them, it is added to the list of established structures. In the matching process the necessary rotations and comparisons are carried out; then the new isomer is converted to its mirror image and the process is repeated.

An advantage of this method is that one can determine the statistical weight of one isomer relative to another. For each established isomer a count is kept of the numbers of times a permutation is identical with it.

The Fortran IV version of the program for the octahedral case is given in Figure 4.

Results and Discussion

Sample results are given for the octahedral case (Table I) and the cubic case (Table II). The numbering system for the cube is as given in Figure 5. In each table the first isomer listed is the one input as data. The interpretation of these coded structures is as given earlier. Since the ligand ABC is tridentate, two sets of *cis* restrictions are needed. Freeman and Liu⁶ have recently isolated all of the isomers, except 3, for the case $\text{M}(\text{ABC})(\text{ABC})$ by using the ligand

(1) Presented in part at the 1966 meeting of the Iowa Academy of Science.

(2) W. C. Fernelius and B. E. Bryant, *J. Am. Chem. Soc.*, **75**, 1735 (1953).

(3) R. F. Trimble, Jr., *J. Chem. Educ.*, **31**, 176 (1954).

(4) B. A. Kennedy, D. A. McQuarrie, and C. H. Brubaker, Jr., *Inorg. Chem.*, **3**, 265 (1964).

(5) J. C. Bailar, Jr., *J. Chem. Educ.*, **34**, 334, 626 (1957); S. A. Mayper, *ibid.*, **34**, 623 (1957).

(6) W. A. Freeman and C. F. Liu, *Inorg. Chem.*, **7**, 764 (1968).

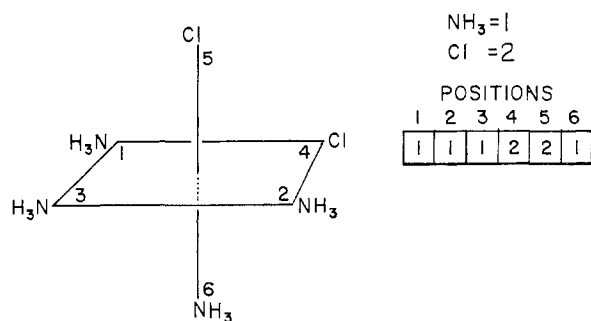


Figure 1.—Representation of the structure of a complex ion.

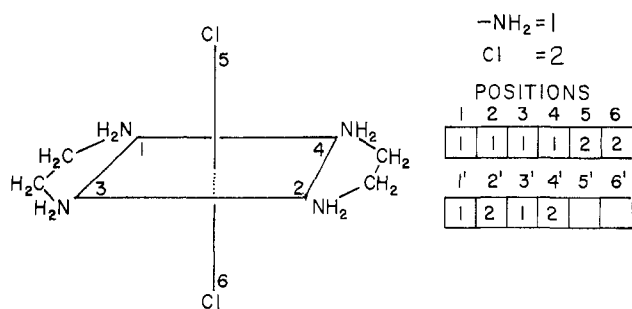


Figure 2.—Representation of a chelated structure.

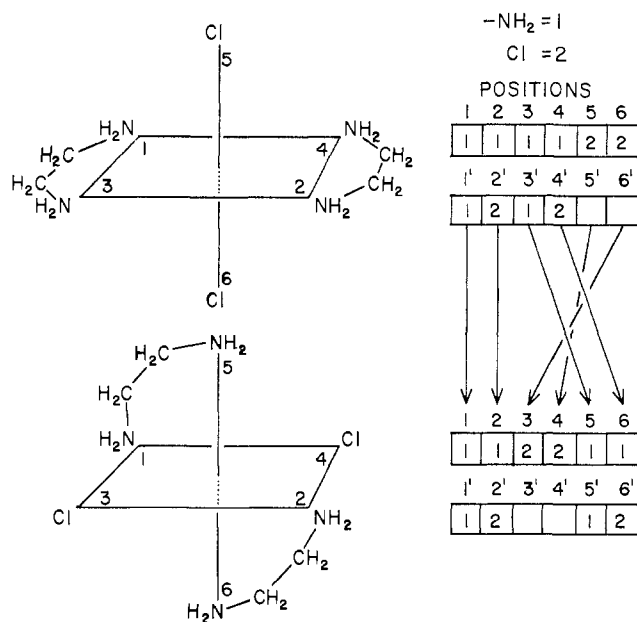


Figure 3.—Representation of the rotation of a complex ion.

TABLE I

STRUCTURES FOR $M(\text{ABC})(\text{ABC})$ ($A = 1, B = 2, C = 3$)

No.	Groups	Chelate 1	Chelate 2	Rel wt
1	113322	123412	000034	1
2 ^a	113232	123241	000403	1
3 ^a	131322	132412	000034	1
4 ^a	131322	142312	000034	1
5 ^a	131232	142132	000304	2
6 ^a	121233	122134	040300	1

^a Has an optical isomer (not shown). Weight includes the optical isomer.

$\text{H}_2\text{NCH}_2\text{CH}(\text{NH}_2)\text{CH}_2\text{COO}^-$. Structure 3 is meridional and cannot accommodate this ligand.

The program for the octahedral case was very fast

TABLE II

STRUCTURES FOR $M(\text{AB})_4$ (Cubic)

No.	Groups	Chelate 1	Rel wt
1	12211221	11223344	1
2	12211212	11223344	4
3 ^a	12211122	11224334	4
4 ^a	12211212	11223443	8
5	12212112	11224433	2
6	12122121	11442233	1
7	12122121	14412233	2
8 ^a	12212112	11342234	2

^a Has an optical isomer (not shown). Weight includes the optical isomer.

and was used to determine the isomers for 88 kinds of complexes. The total computing time was less than 1 min. All of these cases have been investigated by Fernelius and Bryant,² who used models to determine the number of isomers formed by ter-, quinque-, and sexadentate cases, and by Trimble,³ who used drawings to determine the number of isomers formed by mono- to sexadentate cases. Table III

TABLE III

COMPARISON OF THE NUMBER OF ISOMERS AS DETERMINED BY DIFFERENT METHODS

Type	Optical	Inactive	Total	Ref
aaabcd	2	3	5	a, d
AA BC de	0	4	4	b
AB AB cd	10	0	10	a
AB CD ef	8	1	9	b
AB AB AB	10	1	11	a
ABA cde	8	2	10	b
ABA CD e	16	0	16	b
ABC ABC	4	0	4	a
ABA CDC	2	0	2	b
ABA CDE	6	3	9	a, b
ABBA cd	12	3	15	c
ABCD ef	6	2	8	a, c
A ₂ BC de	10	0	10	b
ABCBA d	10	0	10	b
A ₂ BCD e	12	0	12	c
A(B)CDE f	2	2	4	a, b
	4	1	5	c
	6	1	7	a, c
	8	0	8	b
	6	1	7	a, c
	4	1	5	b
	14	0	14	a, c
	10	0	10	b
	4	2	6	a
	8	0	8	c
	6	1	7	a
	8	0	8	b, c
	4	1	5	a
	4	0	4	c
	10	0	10	a
	8	0	8	c

^a This work. ^b Reference 3. ^c Reference 2. ^d Also noted by Kennedy, McQuarrie, and Brubaker.⁴ ^e Also noted by Bailar.⁵

reports these cases in which this computer method differs with the results reported in the above papers.

The eight-coordinate program is much slower⁷ (1 or 2

(7) This could be speeded up by fairly complex modifications.

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DIMENSION ANAME(20)
INTEGER*2 IT(6,4),KF(30,7,4),IR(30,6),IW(6,4)
COMMON IT,KF
C ANAME=TITLE OF PROBLEM
1 READ (5,2) ANAME
2 FORMAT (20A4)
WRITE (6,3) ANAME
3 FORMAT (1H1,20A4)
C DATA=TABLE OF THE 15 D-L PAIRS POSSIBLE
DATA IR(30,1,6,2,6,3,6,4,6,5,6,6,6,3,24,2,4,4,5,5,6,6,4,4,4,5,5,6,6,6,
13,3,5,5,6,6,3,3,4,4,6,6,3,3,4,4,5,5,6,4,6,4,5,5,6,4,6,4,5,5,6,3,
26,3,5,4,6,3,6,3,4,4,5,3,5,3,4,6,5,6,4,5,4,6,5,6,4,5,4,6,5,6,3,5,3,
36,4,6,3,4,3,5,4,5,3,4,3/
READ (5,4) ((IT(N,M),N=1,6),M=1,4)
C READ CODED FORM OF TEST ISOMER IT(N,M) N=1-6 POSITIONS
C M=1 N=1-6 GROUP SYMBOLS M=2-4 N=1-6 CIS CHELATE SYMBOLS
4 FORMAT (4(I12,5I11))
DO 5 N=1,6
DO 5 M=1,4
5 KF(1,N,M)=IT(N,M)
DO 6 N=1,30
6 KF(N,7,1)=1
KF(1,7,2)=1
IC=1
CALL TRANS (ITC)
IF (ITC.EQ.0) GO TO 8
WRITE (6,7)
7 FORMAT (1H1,' TRANS DATA ERROR')
GO TO 1
8 DO 21 NR=2,30
DO 9 NA=1,6
NB=IR(NR,NA)
DO 9 NC=1,4
IW(NA,NC)=KF(1,NB,NC)
9 IT(NA,NC)=IW(NA,NC)
DO 19 ND=1,6
IF (ND.EQ.1) GO TO 16
IF (IW(1,1).NE.IW(ND,1)) GO TO 19
DO 10 NE=1,6
DO 10 NF=1,4
10 IT(NE,NF)=IW(NE,NF)
GO TO (16,11,12,13,14,15),ND
11 CALL ROLL(2,1,4,3,5,6)
GO TO 17
12 CALL ROLL(3,4,2,1,5,6)
GO TO 17
13 CALL ROLL(4,3,1,2,5,6)
GO TO 17
14 CALL ROLL(5,6,3,4,2,1)
GO TO 17
15 CALL ROLL(6,5,3,4,1,2)
GO TO 17
16 CALL TRANS (ITC)
IF (ITC.EQ.1) GO TO 21
DO 18 NE=1,4
CALL MATCH(IC,IM)
IF (IM.EQ.1) GO TO 21
CALL ROLL(1,2,6,5,3,4)
18 CONTINUE
19 CONTINUE
IC=IC+1
KF(IC,7,2)=NR
DO 20 NF=1,6
DO 20 NG=1,4
20 KF(IC,NF,NG)=IW(NF,NG)
21 CONTINUE
WRITE (6,22)
22 FORMAT (1H0,' EVEN NUMBERED STRUCTURES ARE OPTICAL ISOMERS OF PRE
CEEDING STRUCTURES')
WRITE (6,23)
23 FORMAT (1H0,' NO. GROUP CIS. 1 CIS. 2 CIS. 3 STAT. WT')
DO 24 NH=1,IC
24 WRITE (6,25) KF(NH,7,2),((KF(NH,IP,IL),IP=1,6),IL=1,4),KF(NH,7,1)
25 FORMAT (1H ,12,4(3X,6I1),6X,12)
GO TO 1
END
C MATCH THE NEW TEST ISOMER TO ALL ESTABLISHED ONES
SUBROUTINE MATCH (IC,IM)
INTEGER*2 IT(6,4),KF(30,7,4)
COMMON IT,KF
DO 12 NA=1,IC
DO 1 NB=1,6
IF ((IT(NB,1).NE.KF(NA,NB,1)) GO TO 12
1 CONTINUE
DO 8 NC=1,4
GO TO (2,2,3,3),NC
2 NO=3
GO TO 4
3 NO=5
4 DO 7 NE=NO,6
DO 6 NF=2,4
IF (KF(NA,NC,NF).EQ.0) GO TO 6
DO 5 NG=2,4
IF (KF(NA,NC,NF).EQ.KF(NA,NE,NG)) GO TO 9
5 CONTINUE
6 CONTINUE
7 CONTINUE
8 CONTINUE
IM=1
KF(NA,7,1)=KF(NA,7,1)+1
GO TO 13
9 DO 11 NH=2,4
IF ((IT(NC,NH).EQ.0) GO TO 11
DO 10 NI=2,4
IF ((IT(NC,NH).EQ.IT(NE,NI)) GO TO 7
10 CONTINUE
11 CONTINUE
12 CONTINUE
IM=0
13 RETURN
14 CALL EXIT
END
C CHECK FOR VIOLATIONS OF THE REQUIREMENT THAT CHELATING GROUPS BE CI
SUBROUTINE TRANS(ITC)
INTEGER*2 IT(6,4),KF(30,7,4)
COMMON IT,KF
ITC=0
DO 3 NA=1,5,2
NB=NA+1
DO 2 NC=2,4
IF ((IT(NA,NC).EQ.0) GO TO 2
DO 1 ND=2,4
IF ((IT(NA,NC).NE.IT(NB,ND)) GO TO 1
ITC=1
GO TO 4
1 CONTINUE
2 CONTINUE
3 CONTINUE
4 RETURN
5 CALL EXIT
END
C ROTATE THE TEST ISOMER AS INSTRUCTED
SUBROUTINE ROLL(N1,N2,N3,N4,N5,N6)
INTEGER*2 IT(6,4),KF(30,7,4),NT(6)
COMMON IT,KF
DO 2 N=1,4
DO 1 M=1,6
1 NT(M)=IT(N,M)
IT(1,N)=NT(N1)
IT(2,N)=NT(N2)
IT(3,N)=NT(N3)
IT(4,N)=NT(N4)
IT(5,N)=NT(N5)
2 IT(6,N)=NT(N6)
RETURN
END

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Figure 4.—Fortran program for the octahedral case.

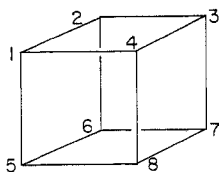


Figure 5.—Numbering system for the cubic structure.

min per structure) and so only a few selected computations were carried out. Some of these were recalculations of binuclear cases in which two octahedra share an edge. These were to repeat those reported by Kennedy⁴ and by Block and Maguire.⁸ Our results agree in all respects with theirs. Sample results for eight-coordinate structures are given in Table IV.

Marchi, Fernelius, and McReynolds⁹ reported the number of isomers for mono- and some bidentate eight-

TABLE IV
ISOMER COUNTS FOR EIGHT-COORDINATE STRUCTURES

Structure	Complex	Optical pairs	Inactive	Total isomers
Binuclear	$M_2a_2b_6$	2 ^f	6 ^f	10 ^f
	$M_2a_2b_2c_4$	46 ^f	22 ^f	114 ^f
	$M_3ab_2c_3$	37 ^{a,f}	10 ^{a,f}	84 ^{a,f}
	$M_2(AA)_4$	1 ^a	1 ^a	3 ^a
	$M_2(AB)(CD)_3$	32	0	64
Cubic	$M_2(AB)_2(CD)_2$	52	8	112
	$M_2(AB)_4$	10 ^a	4 ^a	24 ^a
	$M(AB)_4$	3 ^b	5 ^b	11 ^b
Antiprism	$M(ABCD)CBA$	2 ^b	1 ^b	5 ^b
	$M(AB)_4$	21 ^c	0 ^c	42 ^c
	$M(AB)_4$	7 ^d	0 ^d	14 ^d
Dodecahedron	$M(AB)_4$	4 ^e	0 ^e	8 ^e
	$M(AB)_4$	43 ^c	7 ^c	93 ^c

^a Unsymmetrical bridge. ^b Chelation along an edge only.

^c Chelation along any edge. ^d Chelation only on a square edge.

^e Chelation only on a diagonal edge. ^f See ref 4. ^g See ref 8.

coordinate complexes. We agree with their count for the cubic and antiprismatic $M(AB)_4$ but not with the results for the dodecahedron.

(8) B. P. Block and K. D. Maguire, *Inorg. Chem.*, **6**, 2107 (1967).

(9) L. E. Marchi, W. C. Fernelius, and J. P. McReynolds, *J. Am. Chem. Soc.*, **65**, 329 (1943).

Listings and/or loans of the decks for these programs will be sent on request.

Conclusions

The adaptation of the Bailar method of isomer enumeration to the computer has been shown to be

rapid and reliable. It can be applied to any type of structure.

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JACKSON LABORATORY, ORGANIC CHEMICALS DEPARTMENT,
E. I. DU PONT DE NEMOURS AND COMPANY, INC., WILMINGTON, DELAWARE 19899

Metal Complexes of Azo Dyes. I. Quadridentate Complexes from Bidentate Azo Compounds and Alkanediamines or Ethanolamine^{1b}

BY THEODOR A. LISS AND DONALD R. BAER

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o-Halo-*o'*-hydroxydiaryldazo compounds react readily with alkanediamines or ethanolamine in the presence of copper(II) or nickel(II) salts to form in high yield the quadridentate complex of the ligand resulting from nucleophilic displacement of the halogen by the amine. The order of reactivity is I > Br > Cl > F, but even the fluoro compound reacts at room temperature. In polyhaloazo compounds only the *ortho* halogen is reactive under the reaction conditions. 4-(*o*-Bromophenylazo)-3-methyl-1-phenyl-2-pyrazolin-5-one (XI) reacts with ethylenediamine, alone or in the presence of Cu(II), to give the uncomplexed ligand XII, which can be metalized in a separate step with cupric chloride in ethanolamine. The fluoro and bromo compounds Ia and Ic, respectively, also react with ethylenediamine in the absence of metallic salts to form the quadridentate ligand XIV. The *o*-amino-*o'*-halo compounds (XVIIIc and XVIIIId) react with ethylenediamine in a surprising manner to form the reduction product XX. The *o*-bromotriphenylformazan XXI reacts to form a complex of the four-nitrogen ligand XXII in which the copper is five-coordinate. The *o*-(methoxycarbonyl) azo compound XXIII reacts in one step to give the quadridentate complex XXIV.

Metal complexes of azo compounds suitably substituted in the *o, o'* positions constitute an important class of commercial dyes.² Most of these dyes are based on azo compounds which are tridentate and which therefore form bicyclic metal complexes. Quadridentate and quinquidentate azo compounds which form tri- and tetracyclic metal complexes have also been reported.² The requisite multidentate azo compounds were first prepared and were then treated with a metal ion in a subsequent step.

The present work is concerned with the reaction of bidentate azo compounds with alkanediamines or ethanolamine in the presence of copper or nickel salts to form metal complexes of quadridentate azo compounds in one step.

The replacement of the chloro group in *o*-chloro-*o'*-hydroxyazo compounds by hydroxy, alkoxy, alkylamino, and arylamino, as well as other groups, in the presence of cupric salts was first reported by Delfs and coworkers.³ This reaction was subsequently extended and extensively studied by Stepanov and coworkers.^{4,5} Both groups were primarily interested in the new azo

compounds obtained by removing the metal from the first-formed metal complexes, which themselves were not characterized.

Three isolated reports of the use of bifunctional compounds in the metal-catalyzed reaction of *o*-halo-*o'*-hydroxyazo compounds have been located. The patent literature⁶ reports the use of 8-aminoquinoline and formulates the products as quadridentate complexes. Delfs^{3b} mentions the use of ethanolamine in a patent example. Finally, Bamberger and Gross⁷ report the treatment of *o*-chloro-*o'*-hydroxyazo dyes on a fiber with a copper compound and an *ortho*-substituted aromatic amine or a heterocyclic amine. It was suggested that the tricyclic metal complex had formed on the fiber.

The alkanediamines and ethanolamine used in the present work have the advantage of being good solvents for both the azo compounds and the metal salts and simultaneously serve as a base to neutralize the acid generated in the reaction. Much of the earlier work on metal-catalyzed reactions of *o*-halo-*o'*-hydroxyazo compounds was carried out in heterogeneous systems in which two or even three phases were present.

(1) (a) Publication No. 419. (b) The majority of this work was included in a paper presented by D. R. Baer at the Third Internationales Farbensymposium, Interlaken, Switzerland, May 18, 1967.

(2) For a comprehensive review of metal complexes of dyes, see H. Baumann and H. R. Hensel, *Fortschr. Chem. Forsch.*, **7**, 643 (1967).

(3) (a) D. Delfs and R. Knoche, German Patent 571,859 (Sept 29, 1931); (b) D. Delfs, German Patent 658,841 (March 18, 1934); (c) D. Delfs, German Patent 738,900 (Oct 31, 1936).

(4) For paper XXII in the series, see B. I. Stepanov and M. A. Andreeva, *Soviet J. Org. Chem.*, **2**, 2171 (1966).

(5) A review of this work is given by B. I. Stepanov in "Recent Progress in the Chemistry of Natural and Synthetic Colouring Matters," Academic Press, New York, N. Y., 1962, pp 451-471.

(6) German Patent 748,913 (July 25, 1939).

(7) R. Bamberger and R. Gross, *Textil-Praxis*, **16**, 931 (1961); **17**, 485 (1963).