

of the amine solutions was corrected for the conductivity of dissolved carbon dioxide by the usual method.<sup>2</sup>

### Results

The limiting equivalent conductances ( $\Lambda_0$ ) of the amines were calculated from their measured conductances by means of Ostwald's dilution law, which has been applied satisfactorily to other weak organic bases.<sup>1</sup> The ionization constants were calculated by the usual equation. The values obtained are shown in Table I.

The limiting equivalent conductances are probably accurate to  $\pm 2$  mhos, and the ionization constants are probably accurate within  $\pm 0.2 \times 10^{-4}$  over the concentration ranges tabulated.

Nonyl- and decylamines were each studied in both pure water and in various dilutions of ethanol. Extrapolation of the equivalent conductances in the ethanol solutions yielded values which agreed with those measured in pure water. Figure 1 shows the curves for three decylamine solutions in various dilutions of ethanol. Ionization constants were obtained in this manner for the homologs above decylamine and for the secondary amines.

Bredig<sup>1</sup> and Hall<sup>4</sup> have reported a difference of about 0.39  $pK$  unit between the lower amines and their corresponding secondary homologs. The values in Table I show an average difference of  $0.37 \pm 0.03$   $pK$  unit.

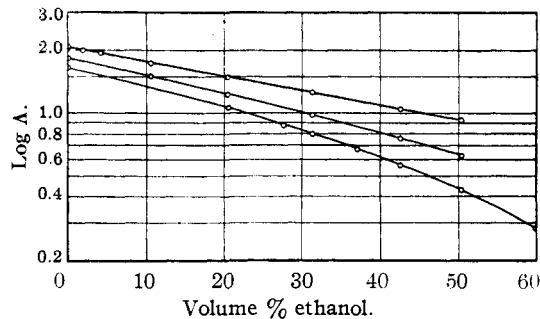


Fig. 1.—Equivalent conductance of decylamine in ethanol: from top to bottom, 0.00080, 0.00322 and 0.00800  $M$ , respectively.

Halford<sup>8</sup> states that lengthening of the hydrocarbon chain of aliphatic acids produces a definite weakening effect in the relative strength of the acids. This effect has not been noted in the amines which we have investigated.

### Summary

Ionization constants have been calculated from conductivity measurements for the normal primary aliphatic amines containing 4 to 18 carbon atoms, inclusive, isobutyl- and isoamylamines, docosylamine, and the symmetrical normal secondary aliphatic amines containing 6, 8, 12, 13, 15 and 18 carbon atoms in each hydrocarbon chain.

CHICAGO, ILLINOIS

RECEIVED NOVEMBER 7, 1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

## The Stereochemistry of Coördination Number Eight<sup>1</sup>

BY LOUIS E. MARCHI,<sup>2</sup> W. CONARD FERNELIUS<sup>3</sup> AND JAMES P. McREYNOLDS

The stereochemistry of compounds of elements exhibiting coördination numbers four and six has been definitely established. However, very little is known concerning the stereochemistry of compounds of elements exhibiting coördination number eight even though many such compounds are known (Table I) and the possibilities for the preparation of many more are great. J. D. Main

Smith<sup>4</sup> presents tables showing (for both mono- and bidentate groups) the types, classes, and isomeric forms theoretically expected for compounds exhibiting coördination numbers four (planar and tetrahedral) and six (octahedral). He intimates that the same has been done for compounds showing coördination number eight, assuming a cubic arrangement. The consideration of possible configurations and the numbers and types of isomers arising from these configurations is a necessary preliminary to any chemical approach to the

(1) This article is abstracted from dissertations presented by Louis E. Marchi to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degrees of Master of Science (March, 1940) and of Doctor of Philosophy (August, 1942).

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(4) J. D. Main Smith, "Chemistry and Atomic Structure," Ernest Benn, Ltd., London, 1924, p. 97.

TABLE I  
 COMPOUNDS ILLUSTRATING THE VARIOUS CLASSES FOR COÖRDINATION NUMBER EIGHT

|  | Class   |   | Class |
|--|---------|---|-------|
| OsF <sub>8</sub> <sup>a</sup>  | 8a      | M(C <sub>2</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>4</sub>   | 4AA   |
| [W(CN) <sub>8</sub> ] <sup>-4b</sup>   | 8a      | C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> = acetylacetonate ion  |       |
| [W(OH) <sub>3</sub> (CN) <sub>5</sub> ] <sup>-4b</sup>   | 5a3b    | M = Zr, <sup>e</sup> Ce, <sup>h</sup> Hf, <sup>i</sup> Th, <sup>i</sup> U, <sup>j</sup> Po <sup>k</sup>         |       |
| [W(CN) <sub>8</sub> ] <sup>-3b</sup>   | 8a      | Th(C <sub>2</sub> H <sub>3</sub> NO) <sub>4</sub> <sup>l,i</sup>  | 4AB   |
| [Mo(CN) <sub>7</sub> (H <sub>2</sub> O)] <sup>-4c</sup>  | 7ab     | C <sub>2</sub> H <sub>3</sub> NO = 8-hydroxyquinolate ion   |       |
| [Mo(CN) <sub>8</sub> ] <sup>-4c</sup>  | 8a      | [Cr(C <sub>2</sub> H <sub>3</sub> N <sub>2</sub> ) <sub>4</sub> ]Cl <sub>3</sub> <sup>m</sup>                   | 4AA   |
| [Mo(OH) <sub>4</sub> (CN) <sub>4</sub> ] <sup>-4c</sup>  | 4a4b    | [Cr(C <sub>2</sub> H <sub>3</sub> N <sub>2</sub> ) <sub>4</sub> ]I <sub>3</sub> <sup>n</sup>                    | 4AA   |
| [Mo(OH) <sub>3</sub> (CN) <sub>4</sub> (H <sub>2</sub> O)] <sup>-3c</sup>  | 4a3bc   | C <sub>2</sub> H <sub>6</sub> N <sub>2</sub> = ethylenediamine  |       |
| [Mo(CN) <sub>8</sub> ] <sup>-3c</sup>  | 8a      | [Pb(C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub> <sup>o</sup> | 4AA   |
| SrO·8H <sub>2</sub> O <sup>d</sup>   | 8a      | C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> = orthophenanthroline   |       |
| Sr(OH) <sub>2</sub> ·8H <sub>2</sub> O <sup>d</sup>  | 8a      | [M(C <sub>2</sub> O <sub>4</sub> ) <sub>4</sub> ] <sup>-4</sup>   | 4AA   |
| Ca X <sub>2</sub> ·8NH <sub>3</sub> ; X = Cl, Br, I <sup>e</sup>   |         | M = Zr, <sup>p</sup> Hf, <sup>p</sup> Th <sup>q</sup>   |       |
| Sr X <sub>2</sub> ·8NH <sub>3</sub> ; X = Cl, Br, I  | 8a      | Sn, <sup>r</sup> U <sup>r</sup>   |       |
| Ba X <sub>2</sub> ·8NH <sub>3</sub> ; X = Cl, Br   |         | Sn(C <sub>32</sub> H <sub>18</sub> N <sub>8</sub> ) <sub>2</sub> <sup>t</sup>                                   | 2AAAA |
| Pb X <sub>2</sub> ·8NH <sub>3</sub> ; X = Cl, Br, I  |         |   |       |
| [Ru(H <sub>2</sub> O) <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] <sup>-3f</sup>  | 3AA2b   | C <sub>32</sub> H <sub>18</sub> N <sub>8</sub> = phthalocyanine ion   |       |
| [Ru(H <sub>2</sub> O) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> N) <sub>2</sub> (C <sub>6</sub> O <sub>4</sub> ) <sub>2</sub> ] <sup>-1f</sup> | 2AA2b2c |   |       |

<sup>a</sup> Gmelin, "Handbuch der anorganische Chemie," Teil 66, Osmium, 50-51 (1939). <sup>b</sup> *Ibid.*, Teil 54, Wolfram, 258-260 (1933). <sup>c</sup> *Ibid.*, Teil 53, Molybdän, 199-204 (1935). <sup>d</sup> *Ibid.*, Teil 29, Strontium, 71-76, 80-83 (1931). <sup>e</sup> Clark, *Am. J. Sci.*, **207**, 1 (1924). <sup>f</sup> Charonnat, *Ann. chim.*, **16**, 150, 186 (1931). <sup>g</sup> von Hevesy and Lögstrup, *Ber.*, **59B**, 1890 (1926). <sup>h</sup> Scagliarini, *Atti accad. Lincei*, [6] **4**, 204 (1926). <sup>i</sup> Young, Goodman and Kovitz, *THIS JOURNAL*, **61**, 876 (1939). <sup>j</sup> Biltz, *Z. anorg. Chem.*, **40**, 220 (1904). <sup>k</sup> Servigne, *Compt. rend.*, **196**, 264 (1933). <sup>l</sup> Frere, *THIS JOURNAL*, **55**, 4362 (1933). <sup>m</sup> Lang and Carson, *ibid.*, **26**, 759 (1904). <sup>n</sup> Barber, *Compt. rend.*, **136**, 688 (1903). <sup>o</sup> Pfeiffer and Christeleit, *Z. anorg. allgem. Chem.*, **239**, 133 (1938). <sup>p</sup> Tchakirian, *Compt. rend.*, **204**, 356 (1937). <sup>q</sup> Brauner, *J. Chem. Soc.*, **73**, 956 (1898). <sup>r</sup> Rosenheim and Platsch, *Z. anorg. Chem.*, **20**, 309 (1899); Péchard, *Compt. rend.*, **116**, 1513 (1893); *Bull. soc. chim.*, [3] **11**, 30 (1894). Willard and Toribara, *THIS JOURNAL*, **64**, 1759 (1942). <sup>s</sup> Kohlschütter and Rossi, *Ber.*, **34**, 1472 (1901); Kohlschütter, *ibid.*, **34**, 619 (1901). <sup>t</sup> Barrett, Dent and Linstead, *J. Chem. Soc.*, 1733 (1936).

stereochemistry of compounds showing coördination number eight.

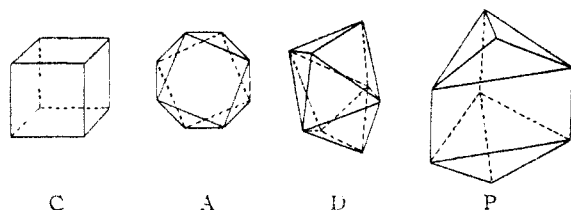


Fig. 1.

The number of possible arrangements of eight groups around a central atom is quite large. The four considered here, Fig. 1, are the cube (C), the square Archimedean antiprism (A), a dodecahedron (D) with triangular faces and with symmetry  $V_d$  and a trigonal prism with two extra bonds along the unique axis (P). In all the configurations, all eight coördinating groups are equidistant from the central atom. Each of these configurations, except the trigonal prism, has been previously suggested<sup>5</sup> and two of these (the

antiprism and the dodecahedron) have been demonstrated experimentally by X-ray methods.<sup>6</sup> The possible combinations and permutations of mono- and bidentate groups are shown in Table II. The classes for which compounds are reported in the literature are marked.

In the preparation of the tables of isomers for the classes and configurations considered, two methods were used. One method was the construction of models and the systematic derivation of the isomers of each class by substitution in the next simpler and the elimination of duplication; the other, the direct calculation by the formula of Lunn and Senior.<sup>7,8</sup> The first method was *allgem. Chem.*, **114**, 25 (1920); 2, Kimball, ref. above in (a); 3, Hoard, paper presented before the Sixth Annual Symposium, Division of Physical and Inorganic Chemistry, Columbus, Ohio, December, 1941. (c) Dodecahedron—1, Hoard and Nordsieck, *THIS JOURNAL*, **61**, 2853 (1939); 2, Kimball, above. (d) Trigonal Prism—Hoard and Nordsieck, and Kimball, considered a trigonal prism having two extra bonds along the normals to two of the rectangular faces. The authors chose a different modification for what at the time seemed good reason but in the light of the referee's comments about the radius ratio the trigonal prism discussed here seems to be a very unlikely configuration for coördination number eight.

(6) Antiprism, [TaF<sub>8</sub>]<sup>-3</sup>, Hoard, ref. 5b; dodecahedron, [Mo(CN)<sub>8</sub>]<sup>-4</sup>, Hoard and Nordsieck, ref. 5c.

(7) Lunn and Senior, *J. Phys. Chem.*, **33**, 1027 (1929).

(5) (a) Cube—1, Morgan and Moss, *J. Chem. Soc.*, **106**, 191 (1914); 2, Pfeiffer, *Z. anorg. allgem. Chem.*, **106**, 26 (1919); 3, Main Smith, ref. 4; 4, Charonnat, *Ann. chim.*, **16**, 150, 186 (1931); 5, Penney and Anderson, *Trans. Faraday Soc.*, **33**, 1363 (1937); 6, Tutida, Kobayashi, and Kuroya, *Rev. Phys. Chem., Japan*, **13**, 151 (1939); 7, Kimball, *J. Chem. Phys.*, **8**, 188 (1940). (b) Antiprism—1, Hüttig, *Z. anorg.*

(8) The details of the operations necessary to take account of the symmetry of the figures considered for the calculation of the numbers of isomers are not included in order to conserve space but may be obtained by writing to Louis E. Marchi.

TABLE II  
CLASSES OF COMPOUNDS THEORETICALLY POSSIBLE FOR COMPOUNDS OF AN ELEMENT EXHIBITING A COÖRDINATION NUMBER OF EIGHT

| Monodentate groups   | Bidentate groups |               |              |  |
|----------------------|------------------|---------------|--------------|--|
|                      | One              | Two           | Three        | Four                                   |
| 8a <sup>+</sup>      |                  |               |              | 4AA <sup>+</sup><br>4AB <sup>+</sup>   |
| 7a b <sup>+</sup>    | AA 6b            | 2AA 4b        | 3AA 2b       | 3AA BB                                 |
| 6a 2b                | AB 6c            | 2AB 4c        | 3AB 2c       | 3AA AB                                 |
| 5a 3b                |                  |               |              | 2AA 2BB                                |
| 4a 4b <sup>+</sup>   |                  |               |              | 2AA 2AB<br>AA 3AB<br>2AB 2CD<br>3AB CD |
| 6a b c               | AA 5b c          | 2AA 3b c      | 3AA b c      | 2AA BB CC                              |
| 5a 2b c              | AA 4b 2c         | 2AA 2b 2c     | 2AA BB 2c    | 2AA BB AB                              |
| 4a 3b c <sup>+</sup> | AA 3b 3c         | AA BB 4c      | 2AA BC 2d    | 2AA AB CD                              |
| 4a 2b 2c             | AB 5c d          | AA BC 4d      | AA 2BC 2d    | AA BB 2AB                              |
| 3a 3b 2c             | AB 4c 2d         | 2AB 3c d      | 2AB c d      | AA 2AB CD                              |
|                      | AB 3c 3d         | 2AB 2c 2d     | 2AB CD 2e    | 3AB CD EF                              |
|                      |                  | AB CD 4e      | 2AB CD 2e    | 3AB CD EF                              |
| 5a b c d             | AA 4b c d        | 2AA 2b c d    | 2AA BB c d   | AA BB CC DD                            |
| 4a 2b c d            | AA 3b 2c d       | AA BB 3c d    | 2AA CD ef    | AA BB CC AB                            |
| 3a 3b c d            | AA 2b 2c 2d      | AA BB 2c 2d   | AA BB CC 2d  | AA BB AB CD                            |
| 3a 2b 2c d           | AB 4c d e        | AA BC 3d e    | AA BB CC d e | AA AB CD EF                            |
| 2a 2b 2c 2d          | AB 3c 2d e       | AA BC 2d 2e   | AA BB CD 2e  | AB CD EF GH                            |
|                      | AB 2c 2d 2e      | AB CD 3e f    | AA 2BC d e   |  |
|                      |                  | AB CD 2e 2f   | AA BC DE 2f  |  |
|                      |                  |               | AB CD EF 2g  |  |
| 4a b c d e           | AA 3b c d e      | 2AA b c d e   | AA BB CD e f |  |
| 3a 2b c d e          | AA 2b 2c d e     | AA BB 2c d e  | AA BC DE f g |  |
| 2a 2b 2c d e         | AB 3c d e f      | AA BC 2d e f  | AB CD EF g h |  |
|                      | AB 2c 2d e f     | AB CD 2e f g  |              |  |
|                      |                  | 2AB c d e g   |              |  |
| 3a b c d e f         | AA 2b c d e f    | AA BB c d e f |              |  |
| 2a 2b c d e f        | AB 2c d e f g    | AA BC d e f g |              |  |
|                      |                  | AB CD e f g h |              |  |
| 2a b c d e f g       | AA b c d e f g   |               |              |  |
|                      | AB c d e f g h   |               |              |  |
| a b c d e f g h      |                  |               |              |  |

<sup>+</sup> Classes represented in the literature. Capital letters stand for the ligand atoms in bidentate groups; small letters stand for the ligand atom of a monodentate group.

applied only to those classes which were necessary as intermediate steps in deriving one class from another. Because of the mathematical difficulties involved, the second method was applied only to monodentate groups. A number of classes were treated in both ways with perfect agreement.

The possible isomers for all classes containing only monodentate groups are given in Table III.

For the bidentate groups the restriction was imposed that the second position occupied by a bidentate group is the closest adjacent position, thus, for example, no group will fall on the diagonal of a square face.

The isomer numbers for the limited number of

classes containing bidentate groups, which were considered, are given in Table IV.

Inspection of the isomer tables indicates that a complete configurational study of coordination number eight by chemical methods offers insurmountable difficulty. However, due to the large numbers of isomers possible and the probable absence of some of the possible isomers due to their relative instability, it is apparent that the presence of optical activity for certain classes of compounds would exclude one or more of the four proposed configurations; thus, the demonstration of optically active forms for the type 4AA would exclude the cube and the trigonal prism.

TABLE III  
 ISOMERS FOR MONODENTATE GROUPS

| Class      | Con-figuration | Optically active | Optically inactive | Total |
|------------|----------------|------------------|--------------------|-------|
| 8a         | *              | C                | 0                  | 1     |
|            | M              | A                | 0                  | 1     |
|            |                | P                | 0                  | 1     |
|            |                | D                | 0                  | 1     |
| 7a b       | *              | C                | 0                  | 1     |
|            | M              | A                | 0                  | 1     |
|            |                | P                | 0                  | 2     |
|            |                | D                | 0                  | 2     |
| 6a 2b      | M              | C                | 0                  | 3     |
|            |                | A                | 4                  | 2     |
|            |                | P                | 2                  | 5     |
|            |                | D                | 6                  | 4     |
| 6a b c     | M              | C                | 0                  | 3     |
|            |                | A                | 6                  | 1     |
|            |                | P                | 4                  | 6     |
|            |                | D                | 8                  | 6     |
| 5a 3b      | *              | C                | 0                  | 3     |
|            | M              | A                | 4                  | 3     |
|            |                | P                | 4                  | 6     |
|            |                | D                | 8                  | 6     |
| 5a 2b c    | M              | C                | 2                  | 5     |
|            |                | A                | 18                 | 3     |
|            |                | P                | 18                 | 10    |
|            |                | D                | 32                 | 10    |
| 5a b c d   |                | C                | 8                  | 6     |
|            |                | A                | 42                 | 0     |
|            |                | P                | 44                 | 12    |
|            |                | D                | 72                 | 12    |
| 4a 4b      | *              | C                | 2                  | 5     |
|            | M              | A                | 10                 | 3     |
|            |                | P                | 8                  | 8     |
|            |                | D                | 14                 | 8     |
| 4a 3b c    | *              | C                | 6                  | 7     |
|            | M              | A                | 32                 | 3     |
|            |                | P                | 34                 | 14    |
|            |                | D                | 56                 | 14    |
| 4a 2b 2c   |                | C                | 12                 | 10    |
|            |                | A                | 54                 | 6     |
|            |                | P                | 58                 | 18    |
|            |                | D                | 98                 | 16    |
| 4a 2b c d  |                | C                | 26                 | 9     |
|            |                | A                | 102                | 3     |
|            |                | P                | 122                | 18    |
|            |                | D                | 192                | 18    |
| 4a b c d e |                | C                | 64                 | 6     |
|            |                | A                | 210                | 0     |
|            |                | P                | 268                | 12    |
|            |                | D                | 408                | 12    |
| 3a 3b 2c   |                | C                | 14                 | 10    |
|            |                | A                | 64                 | 6     |
|            |                | P                | 74                 | 20    |
|            |                | D                | 120                | 20    |
| 3a 3b c d  |                | C                | 36                 | 12    |
|            |                | A                | 140                | 0     |
|            |                | P                | 164                | 24    |
|            |                | D                | 256                | 24    |

|            |                 |       |      |       |
|------------|-----------------|-------|------|-------|
| 3a 2b 2c d | C               | 56    | 14   | 70    |
|            | A               | 204   | 6    | 210   |
|            | P               | 252   | 28   | 280   |
|            | D               | 392   | 28   | 420   |
|            | 3a 2b c d e     | C     | 128  | 12    |
|            | A               | 420   | 0    | 420   |
|            | P               | 536   | 24   | 560   |
|            | D               | 816   | 24   | 840   |
|            | 3a b c d e f    | C     | 280  | 0     |
|            | A               | 840   | 0    | 840   |
|            | P               | 1120  | 0    | 1120  |
|            | D               | 1680  | 0    | 1680  |
|            | 2a 2b 2c 2d     | C     | 92   | 22    |
|            | A               | 318   | 12   | 330   |
|            | P               | 392   | 40   | 432   |
|            | D               | 612   | 36   | 648   |
|            | 2a 2b 2c d e    | C     | 192  | 18    |
|            | A               | 624   | 6    | 630   |
|            | P               | 804   | 36   | 840   |
|            | D               | 1224  | 36   | 1260  |
|            | 2a 2b c d e f   | C     | 408  | 12    |
|            | A               | 1260  | 0    | 1260  |
|            | P               | 1656  | 24   | 1680  |
|            | D               | 2496  | 24   | 2520  |
|            | 2a b c d e f g  | C     | 840  | 0     |
|            | A               | 2520  | 0    | 2520  |
|            | P               | 3360  | 0    | 3360  |
|            | D               | 5040  | 0    | 5040  |
|            | a b c d e f g h | C     | 1680 | 0     |
|            | A               | 5040  | 0    | 5040  |
|            | P               | 6720  | 0    | 6720  |
|            | D               | 10080 | 0    | 10080 |

\* indicate that at least one compound is known which belongs to the class. M indicates that the isomer count was also determined by the construction of models and it was found in agreement with the number obtained by the use of Lunn and Senior's method.

 TABLE IV  
 SPECIAL CLASSES OF BIDENTATE GROUPS

| Class  | Con-figuration | Optically active | Optically inactive | Total |
|--------|----------------|------------------|--------------------|-------|
| AA 6b  | C              | 0                | 1                  | 1     |
|        | A              | 2                | 1                  | 3     |
|        | P              | 0                | 2                  | 2     |
|        | D              | 4                | 2                  | 6     |
| AB 6c  | C              | 2                | 0                  | 2     |
|        | A              | 4                | 0                  | 4     |
|        | P              | 0                | 3                  | 3     |
|        | D              | 6                | 3                  | 9     |
| 2AA 4b | C              | 2                | 2                  | 4     |
|        | A              | 12               | 2                  | 14    |
|        | P              | 4                | 2                  | 6     |
|        | D              | 24               | 3                  | 27    |
| 2AB 4c | C              | 8                | 3                  | 11    |
|        | A              | 42               | 3                  | 45    |
|        | P              | 16               | 4                  | 20    |
|        | D              | 100              | 3                  | 103   |

TABLE IV (Concluded)

| Class  | Con-figuration | Optically active | Optically inactive | Total |
|--------|----------------|------------------|--------------------|-------|
| 3AA 2b | C              | 2                | 2                  | 4     |
|        | A              | 16               | 1                  | 17    |
|        | P              | 2                | 3                  | 5     |
|        | D              | 34               | 2                  | 36    |
| 3AB 2c | C              | 20               | 0                  | 20    |
|        | A              | 94               | 0                  | 94    |
|        | P              | 20               | 6                  | 26    |
|        | D              | 242              | 6                  | 248   |
| 4AA    | C              | 0                | 2                  | 2     |
|        | A              | 6                | 0                  | 6     |
|        | P              | 0                | 1                  | 1     |
|        | D              | 10               | 1                  | 11    |
| 4AB    | C              | 6                | 5                  | 11    |
|        | A              | 42               | 0                  | 42    |
|        | P              | 6                | 4                  | 10    |
|        | D              | 110              | 5                  | 115   |

The authors are indebted to Mrs. Barbara J. Miller, nee Everhart, for assistance in the construction of models and to Professors E. N. Lassette and J. K. Senior for their interest and assistance in the mathematical portion of the work.

### Summary

Complete isomer tables for monodentate and partial isomer tables for bidentate groups for four likely configurations for compounds of elements exhibiting coordination number eight—the cube, the square Archimedean antiprism, a dodecahedron with triangular faces and symmetry  $V_d$  and a trigonal prism with two extra bonds along the unique axis—have been developed.

COLUMBUS, OHIO

RECEIVED OCTOBER 21, 1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

## The Stereochemistry of Coordination Number Eight. Optical Activity of Potassium Tetra-oxalato-uranium-IV<sup>1</sup>

BY LOUIS E. MARCHI<sup>2</sup> AND JAMES P. McREYNOLDS

The study of the structural configuration of compounds of elements exhibiting coordination number eight has been carried out chiefly by the use of X-ray crystal analysis.<sup>3,4,5</sup>

The authors<sup>6</sup> have carried out a study of the isomer requirements of four types of configuration which are possible for coordination number eight. The configurations considered are the cube (C), the square Archimedean antiprism (A), a trigonal prism (P) with two extra bonds along the unique axis, and a dodecahedron (D) with triangular faces and symmetry  $V_d$ . The isomer count for compounds containing four symmetrical bidentate groups 4AA, such as the oxalate group, is given for each of the four structures in Table I.<sup>6</sup> The number of isomers for this type of compound is so large that a complete proof of structure by isomer isolation does not seem possible. However, the proof of the presence of optical isomers will

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(3) Natta, *Gazz. chim. ital.*, **58**, 870 (1928).

(4) Hoard and Nordsieck, *THIS JOURNAL*, **61**, 2853 (1939).

(5) Hoard, paper presented before the Sixth Annual Symposium, Division of Physical and Inorganic Chemistry, American Chemical Society, Columbus, Ohio, Dec. 29–31, 1941.

(6) Marchi, Fernelius and McReynolds, *THIS JOURNAL*, **65**, 329 (1943).

TABLE I  
ISOMERS FOR COMPOUNDS HAVING FOUR SYMMETRICAL BIDENTATE GROUPS

| Class symbol | Con-figuration | Optically <sup>a</sup> active | Optically inactive | Total |
|--------------|----------------|-------------------------------|--------------------|-------|
| 4AA          | C              | 0                             | 2                  | 2     |
|              | P              | 0                             | 1                  | 1     |
|              | A              | 6                             | 0                  | 6     |
|              | D              | 10                            | 1                  | 11    |

<sup>a</sup> Optically active isomers are listed as individuals, the number of racemic pairs represented is one-half the number listed.

rule out two structures, the cube and the trigonal prism. This study was carried out to determine if such an elimination could be made by chemical methods and shows that the elimination can be made.

### Experimental

#### Resolution of Potassium Tetra-oxalato-uranium-IV

1. Potassium tetra-oxalato-uranium-IV was prepared by the method of Kohlschütter.<sup>7</sup> However, the starting material was  $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$  instead of uranyl ammonium carbonate. The product was purified by repeating the precipitation from water solution by alcohol.

2. Resolution was attempted with brucine, cinchonine and strychnine. The brucine salt was too insoluble and the cinchonine salt was too soluble to give good fractionation. The strychnine salt was not sufficiently soluble to carry out satisfactory fractional crystallization but its

(7) Kohlschütter and Rossi, *Ber.*, **34**, 1472 (1901); Kohlschütter, *ibid.*, 3619.