Possible Isomers for Coördination Compounds with Terdentate Ligands and Ligands of Higher Function

By W. Conard Fernelius and Burl E. Bryant

In the consideration of any particular coördination compound, it is important to know what isomers are theoretically capable of existence. Main Smith[1] has presented tables showing (for both uni- and bidentate groups) the types, classes and isomeric forms theoretically expected for entities (compounds or ions) exhibiting coördination numbers four (square and tetrahedral) and six (octahedral). Marchi, Fernelius and McReynolds[2] similarly have worked out the possible isomeric forms for several classes of various likely configurations for entities exhibiting coördination number eight with uni- and bidentate groups. Recently we have had occasion to work out by means of models the isomeric forms for six-coördinate entities with terdentate groups

TABLE I

ISOMERIC CLASSES AND FORMS FOR THE OCTAHEDRAL CONFIGURATION CONTAINING TERDENTATE GROUPS

| Class symbol | Number of isomeric forms | | | | |
| | Optically active | | Optically inactive | | |
	cis	trans	cis	trans	Total
Type 5					
A_3 3b	..	..	1	1	2
A_3 2b c	..	..	1	2	3
A_3 b c d	2	..	..	3	5
A_2B 3c	..	..	1	1	2
A_2B 2c d	2	..	1	2	5
A_2B c d e	6	6	..	3	15
ABC 3d	2	..	..	1	3
ABC 2d e	6	2	..	1	9
ABC d e f	12	6	..	..	18
Total	30	14	4	14	62
Type 6					
A_3 B_2 c	..	..	1	1	2
A_3 BC d	2	..	..	2	4
A_2B C_2 d	2	..	1	1	4
A_2B CD e	6	..	..	2	8
ABC D_2 e	6	2	..	..	8
ABC DE f	12	4	..	..	16
Total	28	6	2	6	42
Type 7					
$2A_3$	..	..	1	1	2
$2A_2B$	2	..	1	1	4
2ABC[a]	10	2	..	..	12
A_3 B_3	..	..	1	1	2
A_3 B_2C	..	..	1	1	2
A_3 BCD	2	..	..	1	3
A_2B C_2D	4	..	..	1	5
A_2B CDE	6	..	..	1	7
ABC DEF	12	2	..	..	14
Total	36	4	4	7	51

[a] P. Pfeiffer and S. Saure [Ber., **74B**, 935 (1941)] have studied this class to some extent.

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

(2) L. E. Marchi, W. C. Fernelius and J. P. McReynolds, THIS JOURNAL, **65**, 329 (1943); L. E. Marchi, ibid., **65**, 2257 (1943); **66**, 1984 (1944).

and groups of higher function. These are given in Tables I–IV. Optical activity originating within the coördinating groups has been disregarded. Also the customary assumption has been made that adjoining points of attachment on the coördinating groups will always be in the closest adjacent positions (*cis*) in the coördination sphere of the metal.

Symbolism.—It is customary to use lower case letters to represent unidentate groups and pairs of capital letters, bidentate groups: *i.e.*, AA = a symmetrical group like ethylenediamine, the acetylacetonate ion, or $C_2O_4^-$ and AB = an unsymmetrical group like propylenediamine or glycine. In this paper the symbolism A_2 will be used instead of AA. For terdentate groups, A_3 = three equivalent points of attachment such as $HC(CH_2NH_2)_3$, A_2B = two equivalent positions and one different such as $HN(CH_2CH_2NH_2)_2$, and ABC = three non-equivalent positions (possible example is $HSCH_2CH(NH_2)COOH$). For quadridentate groups A_2B_2 would represent such groups as $(H_2NCH_2)_2CHCH(CH_2SH)_2$; ABBA, $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$; and A(B)CD, $H_2NCH_2(HSCH)_2$-

TABLE II

ISOMERIC CLASSES AND FORMS FOR AN OCTAHEDRAL CONFIGURATION CONTAINING QUADRIDENTATE GROUPS

| Class symbol | Number of isomeric forms | | | | |
| | Optically active | | Optically inactive | | |
	cis	trans	cis	trans	Total
Type 8					
A_2B_2 2c	2	..	..	..	2
A_2B_2 c d	4	..	..	..	4
ABBA 2c[a]	4	..	..	1	5
ABBA c d	6	..	..	1	7
$A_2B(C)$ 2d	4	..	..	..	4
$A_2B(C)$ d e	8	..	..	..	8
A_2BC 2d	2	..	1	..	3
A_2BC d e	8	..	..	..	8
A(B)C(D) 2e	8	..	..	..	8
A(B)C(D) e f	16	..	..	..	16
A(B)CD 2e	6	..	..	..	6
A(B)CD e f	12	..	..	..	12
ABCD 2e	6	..	..	1	7
ABCD e f	12	2	..	..	14
Total	98	2	1	3	104
Type 9					
A_2B_2 C_2	2	..	..	..	2
A_2B_2 CD	4	..	..	..	4
ABBA C_2	4	..	..	..	4
ABBA CD	6	..	..	..	6
$A_2B(C)$ D_2	4	..	..	..	4
$A_2B(C)$ DE	8	..	..	..	8
A_2BC D_2	2	..	1	..	3
A_2BC DE	4	..	2	..	6
A(B)C(D) E_2	8	..	..	..	8
A(B)C(D) EF	16	..	..	..	16
A(B)CD E_2	6	..	..	..	6
A(B)CD EF	12	..	..	..	12
ABCD E_2	6	..	..	..	6
ABCD EF	12	..	..	..	12
Total	94	..	3	..	97

[a] The five isomers of this class have been isolated for diammine{α,α'-(o-phenylenediimino)-di-o-cresolato}cobalt-(III) ion by G. T. Morgan and J. D. Main Smith [*J. Chem. Soc.*, **127**, 913, 2030 (1925)].

$CHNHCH_2CH_2NH_2$. The meaning of the other symbols follows from these examples.

Use of Terms *cis* **and** *trans.*—For terdentate groups the words *cis* and *trans* are used in the same manner as they are used to designate the isomers of M 3a 3b; *cis* indicates that the three points of attachment of the polyfunctional ligand are on the same face of the octahedron; *trans*, that they are along a plane which passes through the coördination center. For entities with quadridentate groups, *cis* and *trans* refer to the position of the remaining monodentate ligands.

Probability of Realizing Theoretical Possibilities. —Some quadri-, quinque- and sexadentate groups can be postulated (and even prepared) which are not at all likely to coördinate to a common center. Certainly for $\overset{\cdot\cdot}{C}(CH_2NH_2)_4$, only three of the nitrogens can coördinate to a common center; $(H_2-NCH_2)_2CHCH(CH_2NH_2)$ probably will coördinate completely; while *cis*-1,2,3,4-cyclobutanetetramine awaits study to determine whether or not it will coördinate completely. Because of such complications, the classes containing the groups A_4 and A_3B are not considered here. If A_4 were of the type of phthalocyanine, no isomerism is possible for either M A_4 2b or M A_4 b c. Other groups which are difficult of realization or whose coördination to a common center may not be possible are A_5, A_4B, A_3B_2, A_3BC, A_2B_2C, A_6, A_5B, A_4B_2, A_4BC, A_3B_3, A_3B_2C, $A_2B_2C_2$ and A_2B_2CD. These have also been omitted.

TABLE III

ISOMERIC CLASSES AND FORMS FOR AN OCTAHEDRAL CONFIGURATION CONTAINING QUINQUEDENTATE GROUPS

| Type	Class symbol	Optically active	Optically inactive	Total
10	A_2BC_2 d	..	1	1
	ABCBA d	8	..	8
	$A_2BC(D)$ e	2	..	2
	A_2BCD e	4	..	4
	A(B)CD(E) f	4	..	4
	A(B)CDE f	8	..	8
	ABCDE f	12	..	12
	Total	38	1	39

TABLE IV

ISOMERIC CLASSES AND FORMS FOR AN OCTAHEDRAL CONFIGURATION CONTAINING SEXADENTATE GROUPS

Type	Class symbol	Optically active	Optically inactive	Total
11	A_2BBA_2	2	..	2
	ABCCBA[a]	8	..	8
	A(B)CC(B)A	6	..	6
	A_2BCD_2	2	..	2
	$A_2BCD(E)$	4	..	4
	A_2BCDE	4	1	5
	A(B)CDE(F)	8	..	8
	ABCDEF	10	..	10
	Total	44	1	45

[a] An example of this class is being studied by F. P. Dwyer and co-workers, THIS JOURNAL, 69, 2917 (1947); **72**, 1545 (1950); **74**, 4188 (1952).

It seems likely that all groups will not show all the potentialities anticipated for the class to which they belong. Groups may show a preference for certain arrangements because of considerations of steric situations (size, arrangement of atoms, rigid-

idty, etc.). Thus, $H_2NCH_2CH(NH_2)CH_2NH_2$ in contrast to $(H_2NCH_2CH_2)_2NH$ may never be able to coördinate *trans* and
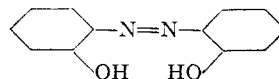
may be sufficiently rigid that it will never coördinate *cis*. The experimental realization of some of the potentialities presented in the tables should not prove too difficult and would contribute greatly to our knowledge of coördination compounds.

A Polarographic Study of the Zinc Thiocyanate Complexes[1]

BY RICHARD E. FRANK[2] AND DAVID N. HUME

Although the thiocyanate complexes of cadmium and mercury are well known and have been extensively studied, very little attention has been paid to complex formation between zinc and thiocyanate ions. The existence of such complex ions is suggested by the fact that solids such as $K_2Zn(SCN)_4 \cdot 2H_2O$ have been isolated by Walden.[3] The only published account of an investigation of the ions in solution is the paper by Ferrell, Ridgion and Riley,[4] who obtained potentiometric data which suggested the existence of a $ZnSCN^+$ ion with a formation constant of the order of 50. Some unpublished polarographic measurements by DeFord[5] pointed to the existence of several complexes in solutions between 0.1 and 2.0 M thiocyanate ion, but the measurements were, unfortunately, not made at constant ionic strength, and since the shifts in half-wave potential observed were of the same order of magnitude as those sometimes observed due to ionic strength effects alone, no quantitative conclusions could be drawn from them. We have, therefore, measured the half-wave potential of zinc ion in potassium nitrate–potassium thiocyanate mixtures with thiocyanate concentrations ranging from 0.2 to 2.0 M at a constant ionic strength of 2.0 M.

Experimental

All measurements were made on a Sargent model XXI recording polarograph at a temperature of 30.0 ± 0.1°. The dropping electrode was made of marine barometer tubing and had a value of $m^{2/3}t^{1/6}$ of 1.355 at zero applied volts vs. the S.C.E. The working anode and reference potential was a saturated calomel electrode which was connected to the polarograph through a large diameter 2 M potassium nitrate agar bridge. All polarograms were started at −0.8 v. and run with a span voltage of 0.4 v. in order to spread out the wave for maximum accuracy of measurement. The initial

(1) This work was supported in part by the Atomic Energy Commission.

(2) On leave from the University of North Dakota, Grand Forks, North Dakota.

(3) P. Walden, Z. anorg. Chem., **23**, 374 (1900).

(4) E. Ferrell, J. M. Ridgion and H. L. Riley, J. Chem. Soc., 1121 (1936).

(5) D. D. DeFord, M.S. Thesis, University of Kansas, 1947.