Correspondence

Designation of Ligand Positions in Coordination Complexes

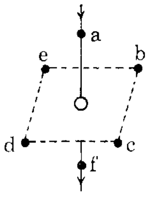
Sir:

The development of methods for uniquely and unambiguously describing ligand positions in coordination compounds has become of considerable importance as a result of recent advances in inorganic and structural chemistry. Enumeration systems have been successfully developed for positions in organic molecules (*e.g.*, IUPAC[1]); but, thus far, a solution of the problem for inorganic structures has not been found.

A table of reference structures for use in unambiguously designating positions in coordination complexes has been prepared in the development of a linear notation system for such compounds.[2] This table contains idealized representations of 22 configurations in which all metal-to-ligand bonds within a coordination sphere are considered to be of equal length. Each structure is assigned what may be called a *class symbol* consisting of two parts: a number, which is in fact the coordination number of the central atom; and an upper-case letter (which is somewhat arbitrarily assigned but reflects frequency of occurrence), to designate a particular geometric arrangement of ligand attachments. This method of describing structures permits simple insertion in proper sequence of any additional structures which may be proposed and also serves as the basis for a simple classification scheme for inorganic complexes.

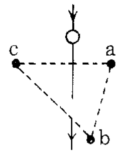
In addition, the positions of ligand attachment in each structure are assigned single lower-case letters, termed *locant designators.* Their assignment is made with reference to the highest-order axis of rotational symmetry of each idealized representation. Conceptually, one travels along the axis until a point is encountered through which a plane passing perpendicular to the axis also passes through one or more positions of ligand attachment. Locant designators are assigned to each ligand position in the plane. The journey down the axis is continued until another such point is encountered and more locant designators are assigned. These steps are repeated until all positions of ligand attachment are assigned locant designators. If several ligand positions occur on one of these planes, designating is done in a clockwise manner with respect to the traversed portion of the axis.

To understand this technique better, consider the octahedral structure (reference structure 6A[2])

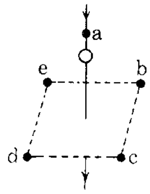


If one starts at either end and travels along the highest-order axis of rotational symmetry, one first encounters a ligand position on the axis, through which a plane could be considered to pass perpendicular to the axis. Locant designator a is assigned to this position. Then one continues until the point is reached at which a plane perpendicular to the axis passes through four ligand positions which are equidistant from position a in the previous "plane." (Coincidence of this point with the coordination center is only accidental.) One of the four positions is arbitrarily chosen to be called position b, and the remaining positions are labeled in the clockwise manner described above. Finally, one proceeds along the axis until the last ligand position is encountered and assigns locant designator f to this position.

In several of the reference structures the two ends of the rotational axis are not equivalent with respect to distribution of the coordination center and ligand positions relative to those ends. For example, consider the trigonal pyramid structure (reference structure 3B[2])



Starting at one end results in encountering the coordination center on the axis before reaching the plane containing the three ligand positions; starting at the other end, one passes through this plane of ligand positions before encountering the coordination center. Consider also the tetragonal pyramidal structure (reference structure 5B[2])



Starting at one end yields an initial contact with a ligand position on the axis, whereas starting at the other end causes one to encounter first a plane containing four ligand positions off the axis. It was arbitrarily decided to start on the end of the axis which would result in the earlier encounter with a ligand position or coordination center on the axis.

In going from one plane containing two or more ligand positions to another plane also containing two or more positions, one proceeds from the last designated position in the first plane to the point in the next plane directly below the position just designated. A clockwise rotation is then begun about the axis, and locant designators are assigned in the usual manner as ligand

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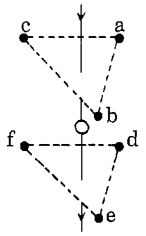
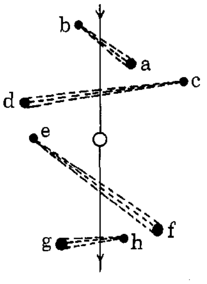
(1) IUPAC, Nomenclature of Organic Chemistry—1957, Butterworths Scientific Publications, London, 1958.

(2) P. M. McDonnell and R. F. Pasternack, *J. Chem. Doc.*, **5**, 56 (1965).

sites are encountered. If a ligand position occurs at the point of entry into the new plane, this site is ignored until it is encountered after clockwise rotation is begun. This method of moving between planes is illustrated by the assignment of locant designator d in reference structure 6B[2] and of c, e, and g in 8A[2]



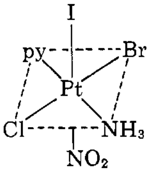
6B trigonal prism



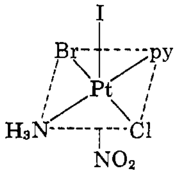
8A dodecahedron with triangular faces

To arrive at an unambiguous designation of positions about a coordination center, one begins by deciding which of the reference structures most closely resembles the coordination complex under consideration. In so choosing, one considers metal-to-metal bonds as equivalent to metal-to-ligand bonds. One next superimposes the coordination sphere onto the appropriate reference structure and assigns the locant designators to the ligand attachments with which they coincide. This designation permits a ready distinction among all isomers having the same empirical formula.

For example, consider some of the possible structures of the compound for which the approved *Chemical Abstracts* name is bromochloroiodonitroammine(pyridine)-platinum. Busch cites two octahedral structures for the complex[3]



I

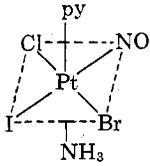


II

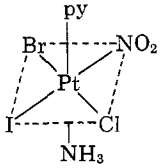
In the name one can differentiate between these isomers by, in turn, superimposing these structures on the reference structure 6A to determine the assignment of locant designators and then inserting the locant designators and class symbol into the name in appropriate positions. One then obtains for these structures such names as the following: for I, *b*-bromo-*d*-chloro-*a*-iodo-*f*-nitro-*c*-ammine-*e*-(pyridine)-*6A*-platinum; and, for II, *e*-bromo-*c*-chloro-*a*-iodo-*f*-nitro-*d*-ammine-*b*-(pyridine)-*6A*-platinum.

To meet the criterion of uniqueness required for most nomenclature and notation systems, one employs an arbitrary set of seniorities in conjunction with the above treatment. With the aid of these rules the relative seniorities of attachments about each coordination center are determined. After choosing the correct reference structure, one permits the coordination sphere to undergo any form of motion permitted to a rigid body until it is aligned with the reference structure so that, insofar as possible, the most senior attachment is made to coincide with locant designator a; the next most senior, locant designator b; etc. In this way two people using the same set of seniority rules will arrive at identical designation patterns.

To illustrate this last point, consider again the names derived above for structures I and II. The assignment of locant designators shown is dependent upon the particular orientation of the structures as they happen to have been drawn. If the representations had been drawn in some other orientation with respect to the plane of the paper, another set of locant designators would have been assigned. Each set would indicate names from which the exact structure could be determined, but more than one complete name would be assigned to each structure because of accidental differences in representations. To prevent this multiplicity of names for individual structures, one can establish an arbitrary set of seniority rules by which representations can be rotated into particular orientations before locant designators are assigned. If one uses the *Chemical Abstracts* modification of the IUPAC rules for ranking ligands in order of increasing seniority (*i.e.*, hydro, oxo, hydroxy, monatomic inorganic anions in alphabetical order, polyatomic inorganic anions in alphabetical order, organic anions in alphabetical order, aquo, ammine, other inorganic neutral and cationic ligands in alphabetical order, neutral and cationic organic ligands in alphabetical order), then in each of the complexes the most senior ligand is the neutral organic pyridine; and, of the four ligands in *cis* positions with respect to the pyridine, the polyatomic nitro group is most senior.[4] One will then rotate any representation of structures I and II into the orientations of structures I′ and II′ respectively. The unique name for structure I (based upon its equivalent representation I′) would be *c*-bromo-*e*-chloro-*d*-iodo-*b*-nitro-*f*-ammine-*a*-(pyridine)-*6A*-platinum; and, for II, *e*-bromo-*c*-chloro-*d*-iodo-*b*-nitro-*f*-ammine-*a*-(pyridine)-*6A*-platinum.

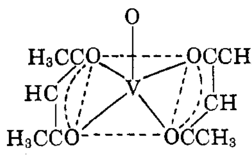


I′



II′

This approach is by no means limited to complexes containing only monodentate ligands. Consider the vanadium(IV) tetragonal pyramidal complex[5]



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[3] D. H. Busch, *J. Chem. Educ.*, **41**, 80 (1964).

[4] "The Naming and Indexing of Chemical Compounds," *Chem. Abstr.*, **56**, 8N (1962).

[5] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry: A Comprehensive Text," Interscience publishers, New York, N. Y., 1962, p. 678.

The complete name would be *a*-oxo-*b*:*c*,*d*:*e*-bis(2,4-pentanedionato)-5*B*-vanadium.

Although this designation system has been developed specifically for coordination compounds, it appears to be extensible to other classes of compounds. For example, if the locant designators of some of the reference structures are replaced by corresponding numbers (a by 1, b by 2, etc.), the resulting designation patterns are almost identical with the enumeration system for cage boranes recently suggested by the boron nomenclature subcommittee.[6] In addition, the reference-structure approach may be applicable in the description of the structure of other inorganic compounds such as heteropoly acids. Furthermore, the system is not restricted to application in nomenclature. The table of reference structures has proved to be particularly valuable in the development of a linear notation system for coordination complexes.[2]

[6] R. Adams, *Inorg. Chem.*, **2**, 1087 (1963).
[7] All inquiries should be addressed to this author.

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RECEIVED JULY 20, 1964

The Reactivity of Metal Chelates of 8-Quinolinol-5-sulfonic Acid[1]

Sir:

In a preliminary report on a study of the effect of metal ions on the kinetics of iodination of 8-quinolinol-5-sulfonic acid,[2] the results suggested that the observed decrease in rate might be attributed to the decrease in concentration of the quinolinolate anion (the reactive species). By using lower pH values and higher metal: ligand ratios, we were able to reduce the concentration of ligand anion to sufficiently low values to permit the observation of the iodination of the metal chelates themselves.

Reagents.—Eastman White Label 8-quinolinol-5-sulfonic acid was recrystallized twice from de-ionized water to give long yellow needles and dried at 90° (corrected m.p. 319–321°). Its purity was checked by an iodometric titration: equiv. wt. found, 225.6; calcd., 225.3.

Kinetic Data.—Rate data were obtained by the following titrimetric method. An aqueous solution of iodine was added to the solution and aliquots were withdrawn for titration at appropriate time intervals. The buffer, together with a solution of reagent, and metal ion, if necessary, were diluted to 90 ml. in a 125-ml. glass-stoppered flask immersed in a constant-temperature bath. After the solution had reached the desired temperature, 10 ml. of a solution containing iodine and iodide at the same temperature was added. A timer was started when the iodinating solution had half-emptied into the flask. The stopper was replaced and the contents of the flask mixed. Aliquots (10 ml.) were withdrawn at intervals, quenched in an acidic solution of iodide, and titrated with a 10^{-3} M thiosulfate solution to the starch end point. On the basis of the titer at infinite time it was found that 1 mole of iodine reacted with each mole of ligand in every experiment.

TABLE I

EFFECT OF METAL IONS ON THE RATE OF IODINATION OF 4.54×10^{-4} M 8-QUINOLINOL-5-SULFONIC ACID IN WATER IN 0.1 M ACETATE BUFFER AND 0.02 M KI AT 20° AT pH 5.0

Metal ion	Metal: ligand ratio	k_{obsd}, l. mole^{-1} sec.$^{-1}$ [a]
None	. . .	0.159
Zn(II)	0.50	0.088
	1.00	0.055
	2.00	0.029
	4.00	0.022
	10.0	0.018
	20.0	0.018
	50.0	0.016
	100	0.015
	200	0.011
	500	0.0098
Mn(II)	10.0	0.097
	100	0.049
	500	0.033
Co(II)	10.0	0.014
	100	0.013
Ni(II)	10	0.014
	100	0.012

[a] k_{obsd} calculated from $-d[B^-]/dt = k_{obsd}[B^-][I_2]$.

Results and Discussion.—The rate of iodination of 8-quinolinol-5-sulfonic acid was found to be first order in both 8-quinolinol-5-sulfonic acid and iodine.

Second-order rate constants (k_{obsd}) calculated on this basis were found to fit the experimental data for most of the reaction range (20–80%) to within 3%.[3] Although the precision of these results is not as good as that obtained with the coulometric method,[4] the calculated rate constants are in accord.

In the earlier work describing the effect of metal ions on the reaction kinetics at pH 7.0 and 9.0, only stoichiometric metal: ligand ratios (1:2), were used in order to avoid precipitation due to metal ion hydrolysis. By working at pH 5.0, it was found possible to raise the metal: ligand ratio and thus check on the hypothesis that the reduction in rate observed previously could be attributed solely to the unchelated ligand.

From the data in Table I it may be seen that the rate of iodination does not decrease upon increasing the metal ion concentration in a manner that is consistent with the above hypothesis. The drop in the concentration of free ligand which decreases by several hundredfold in the case of Zn(II), for example, is ac-

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[1] This work was supported by a grant from the National Institutes of Health.
[2] C. Bostic, Q. Fernando, and H. Freiser, *Inorg. Chem.*, **2**, 232 (1963).
[3] C. R. Bostic, Ph.D. Thesis, University of Arizona, 1963.
[4] G. S. Kozak and Q. Fernando, *J. Phys. Chem.*, **67**, 811 (1963).