A Coordination Geometry Table of the *d*-Block Elements and Their Ions

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Since their discovery by Alfred Werner, coordination complexes have played a very important role in many sub-disciplines of chemistry, including inorganic (*1–3*) and bioinorganic (*4, 5*) chemistry and polymer (*6*) and materials science (*8, 9*). In recent years, the metal–ligand coordination bond has gained importance for the construction of supramolecular complexes and solid-state structures (*7–14*). One of the most basic aspects of coordination chemistry is the geometric preferences for ligand placement about a given metal in a particular oxidation state. Although this type of information is qualitatively summarized in inorganic textbooks (*1–3*), quantitative data on the frequency with which a particular *d*-block element or ion adopts certain coordination geometries is rare (*15*). Such information would be valuable, especially if it were organized within a single table, were compiled by a well-defined set of procedures, were based on reliable data and were analyzed by a standard classification scheme. We present a concise table that quantitatively expresses the frequency of occurrence of the various coordination numbers and geometries for the *d*-block elements and their ions. To our knowledge, a single table presenting this information has never before been compiled.

The Search

Methods for tabulating the coordination geometries will necessarily depend on the source of primary data, the criteria used to select data, and the procedures used to classify the coordination geometries of the selected data. There are two databases from which reliable information such as atomic coordinates can be retrieved. They are the Cambridge Structural Database (CSD) and the Inorganic Crystal Structure Database (ICSD).[1] The table presented here is based on single crystal structures contained within the CSD (Version 5.06) (*16–18*).[2] Consequently, the data represent primarily metal complexes with organic ligands, as opposed to inorganic solids such as minerals.[3]

Using the program QUEST 3D (*17–19*), coordination complexes meeting the "search criteria" outlined below were collected in $E\_z^+\_n$ structure files where E represents the *d*-block element, z^+ is the oxidation state[4] ($z = 0$–VII), and n is the coordination number ($n = 2$–6). Next, the coordination geometry of each structure in these files was classified as one of the standard reference coordination polyhedra (*20*) (Table 1), using an algorithm that searched for the geometry that best fit the observed structure. These data were then tabulated into the coordination geometry table (Tables 2a and 2b).

The criteria used to select structures from the CSD included measures to help insure that entries of high-quality were used in the analysis (i.e., only structures that were

error free and free of disorder and had an *R*-factor (agreement factor) < 12% were included). Measures were also taken to eliminate structure redundancy, including single counting of multiple structure determinations of a particular complex[5] and single counting of coordination

Table 1. Reference Polyhedra[a] (*20*)

Reference Polyhedron	IUPAC Symbol	Ideal ∠L-M-L
linear	L-2	180
bent	A-2	120
trigonal planar	TP-3	120, 120, 120
T-shaped	—	90, 90, 180
pyramidal	TPY-3	109.5, 109.5, 109.5
square planar	SP-4	90, 90, 90, 90, 180, 180
tetrahedral	T-4	109.5, 109.5, 109.5, 109.5, 109.5, 109.5
trigonal pyramidal	—	90, 90, 90, 120, 120, 120
trigonal bipyramidal	TBPY-5	90, 90, 90, 90, 90, 90, 120, 120, 120, 180
square pyramidal	SPY-5	90, 90, 90, 90, 90, 90, 90, 90, 180, 180
octahedral	OC-6	90, 90, 90, 90, 90, 90, 90, 90, 90, 90, 90, 90, 180, 180, 180
trigonal prismatic	TPR-6	70.5, 70.5, 70.5, 90, 90, 90, 90, 90, 90, 131.6, 131.6, 131.6, 131.6, 131.6, 131.6

[a] • = ligand atom; ○ = metal atom.

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Table 2a. Distribution of Oxidation States for the *d*-Block Elements
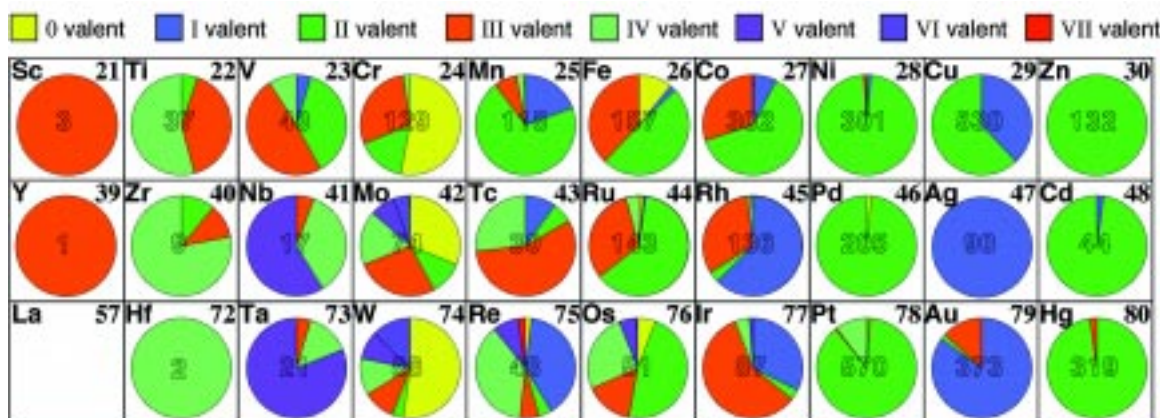
counterions (e.g., [CuCl$_2$]). However, constitutionally identical structural fragments that reside in crystallographically unique sites for a particular complex were analyzed and tabulated individually. Moreover, since ligands that form chelates and π-complexes might have constrained geometries that override or influence the natural coordination preferences of the metal, only complexes whose first coordination sphere consisted exclusively of η^1 (monodentate) ligands were used in the analysis. Ligands were considered to be in the first coordination sphere if they possessed an atom that resided within the distance range $r(M) + r(L) \pm t$ where $r(M)$ and $r(L)$ are the covalent radii of the metal and ligand atom, respectively, and t is a tolerance value set to 0.4 Å (*18*). Coordination complexes with ligands bound to the metal by H, N, C, O, F, Cl, Br, I, Si, S, and P were the only ones used in this analysis.

Classification of coordination geometry was accomplished by a procedure that determined the best fit of the observed structure to one of the ideal coordination polyhedra. The best fit was defined as the minimum deviation in ligand–metal–ligand bond angles (∠L–M–L) between the observed structure and reference polyhedra having the same coordination number. This classification scheme, based entirely on bond angles, has the advantage that it is independent of bond lengths, which will vary as a function of the metal and the ligand atoms bound to it. Since a unique set of angles exists for each of the reference polyhedra, classification is unambiguous. The reference coordination polyhedra considered in this analysis are shown in Table 1 along with the set of ∠L–M–L. The total number of L–M–L valence angles for a polyhedron with coordination number n is $(n/2)(n-1)$.

The minimum deviation in ∠L-M-L was determined by calculating the average angular displacement, Δθ, defined by eq 1, where θ$_i$ represents the ith L–M–L valence angle of the observed structure and θ$_i^\circ$ is the corresponding valence angle of the reference polyhedron under consideration. The average angular displacement is related to the total displacement vector described by Dunitz and Bürgi (*21*), although here we have used the complete set of ∠L–M–L.[6] Next, the geometry of the observed structure was classified as the reference polyhedron that gave the smallest value of Δθ.[7]

$$\Delta\theta = \frac{\sum_{i=1}^{\frac{n}{2}(n-1)} \left| \theta_i - \theta_i^o \right|}{\frac{n}{2}(n-1)} \quad (1)$$

How To Use the Coordination Table

The total number of structures meeting the search criteria for each main transition metal is indicated in the center of the element boxes in Table 2a. This number provides the population that was used to access the distribution of coordination geometries and, therefore, is a means to evaluate the statistical reliability of the data presented in Table 2b. Table 2a also shows pie charts that indicate the distribution of oxidation states observed for each element. For elements having a large enough population, the oxidation state distribution agrees well with the qualitative assessments given in standard inorganic textbooks. Taking copper as an example, it can be seen that a total of 530 coordination complexes were found, of which approximately one-third are copper(I) and two-thirds are copper(II) complexes.

Table 2b shows the results of the coordination geometry analysis as a set of pie charts subdivided according to metal oxidation state. Each pie chart specifies the frequency distribution of coordination number and geometry for each element or ion. Empty boxes indicate that no structures meeting the above selection criteria were observed for that combination of transition metal and oxidation state. As an example illustrating the use of the table, consider the cobalt(II) ion. Of the 302 cobalt complexes retrieved from the CSD, approximately 60% were found to be in the 2$^+$ oxidation state (see Table 2a). In other words, a reasonably large number of structures (302 × 0.6 ≈ 188) have been used to create the cobalt(II) pie chart in the coordination geometry table. This pie chart can be found in the cobalt element box in the 2$^+$ oxidation state section of Table 2b. From this pie chart, it can be seen that the majority of cobalt(II) structures are classified as either 6-coordinate octahedral (ca. 50%; i.e., 188 × 0.5 ≈ 96 structures) or 4-coordinate tetrahedral complexes (ca. 40%, 71 structures). Complexes of trigonal pyramidal geometry were observed with a frequency of ca. 5% (10 structures), while the remaining cobalt(II) complexes were 2-coordinate linear (ca. 0.5%, 1 structure), 4-coordinate square planar (ca. 1%, 2 structures), 5-coordinate trigonal bipyramidal (ca. 3%, 6 structures), and 5-coordinate square pyramidal (ca. 1%, 2 structures). This agrees well with qualitative comments made in inorganic textbooks about the coordination chemistry of cobalt(II) (*1–3*).

Inspection of the table provides a means to identify those elements and ions with the strongest propensity to adopt particular geometries. For example, the ions most likely to enter into linear coordination are gold(I) and mercury(II). The ion with the greatest propensity to adopt

Table 2b. Coordination Geometries of the *d*-Block Elements Sorted According to Their Oxidation States
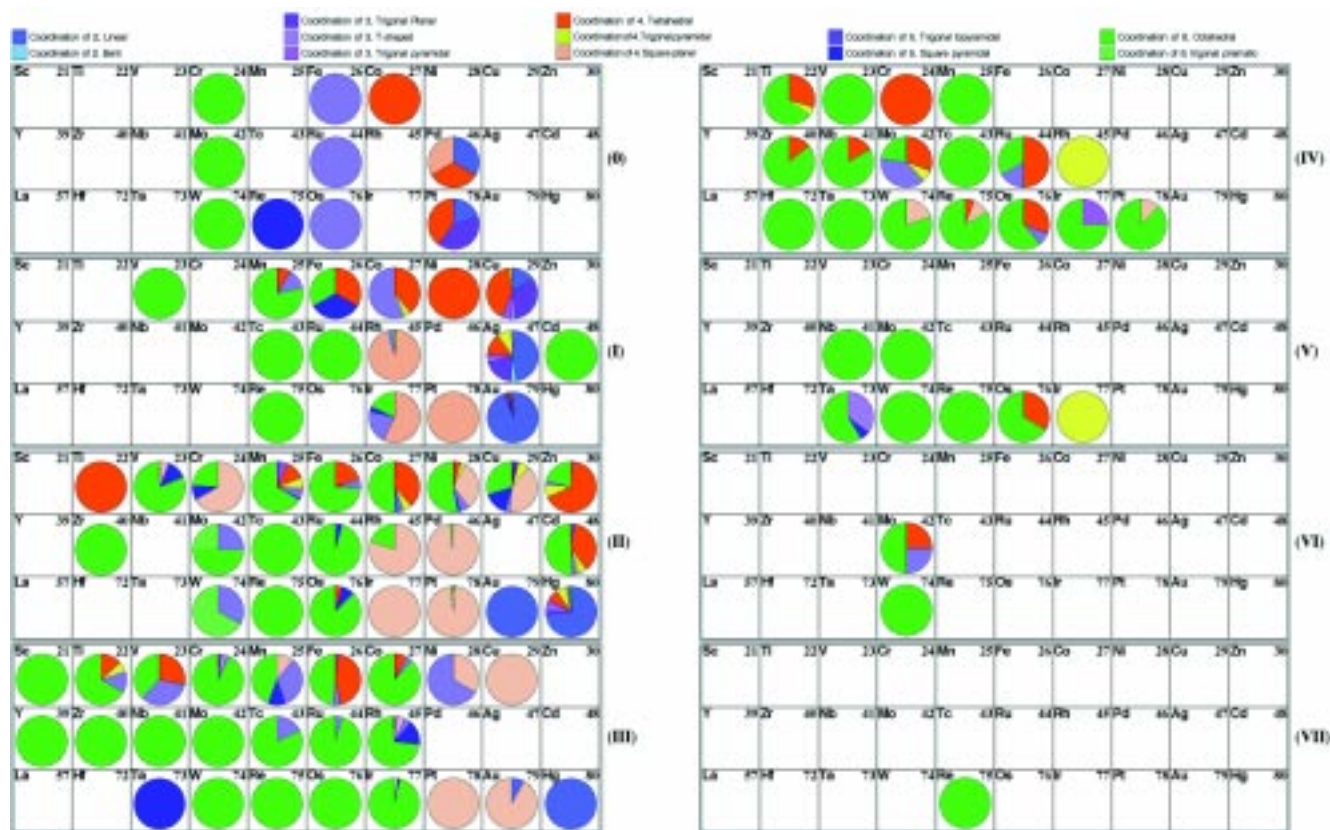
a trigonal planar geometry is copper(I). Tetrahedral coordination is most strongly favored by zinc(II) ions, while platinum(II) and palladium(II) have the strongest bias towards a square planar geometry. The trigonal bipyramidal geometry is adopted sporadically by a number of ions. In contrast, the octahedral geometry is preferred by most of the main transition metals. Of the less commonly encountered geometries, trigonal pyramidal coordination, which is a distorted tetrahedron, is adopted most often by silver(I) (ca. 9%, 8 structures) and zinc(II) (ca. 8%, 11 structures).[8] Also, trigonal prismatic coordination is observed only for tungsten(II) (2 of 3 total structures for this ion) and molybdenum(II) (2 of 8 structures).

Conclusions

We have presented one rendition of a coordination geometry table of the *d*-block elements and their ions. The table provides quantitative data on the frequency with which a particular element or ion adopts various oxidation states, coordination numbers, and coordination geometries. The information is based on reliable data, and the sample size for many of the ions is large enough to provide meaningful statistics. However, it should be stressed that many other procedures could have been used to construct such a table, especially with regards to how the structural data are selected. One of the shortcomings of the table is that the influence of ligand type (e.g., soft vs. hard; Lewis-base strength) on promoting particular coordination modes (*15*) is lost. Nonetheless, we believe the table presented here is an accurate indicator of the occurrence of coordination number and geometry as a function of element and oxidation state. The concise format of this table makes it a valuable reference, which we would now like to make widely available. This information can also be downloaded from the Internet as individual GIF files from URL *http://www.sulfur.scs.uiuc.edu/*.

Notes

1. These databases are updated regularly and can be accessed through suitable programs. A third database, the Protein Data Bank (PDB), contains the structures of proteins that have been reported in the literature.

2. The CSD can be used as a powerful teaching tool for illustrating important concepts in organic and organometallic chemistry, such as the Bürgi–Dunitz angle in addition reactions in sp^2 systems, the "umbrella" inversion in ammonia, and the directional propensities of hydrogen-bonded systems.

3. Structures with at least one organic moiety are included in the CSD; the ICSD contains inorganic structures such as minerals. For example, while the structure of potassium carbonate will not be found, the structure of $[Cu(CH_3CN)_4]PF_6$ can be retrieved from the CSD.

4. We found that the most reliable way to search oxidation state in the CSD is by compound name.

5. For entries with multiple structure determinations, the entry with the lowest R-value was chosen.

6. The complete set of angles is overdetermined for reference polyhedra with $n \geq 2$.

7. All of the analyses, such as choosing the structure with the lowest R-value for multiple structure determinations and the classification of the coordination geometry, were done by a FORTRAN program.

8. Trigonal pyramidal coordination is the only mode observed for rhodium(IV) and iridium(V). However, the number of structures observed for these ions is too small [2 for rhodium(IV) and 1 for iridium(V)] to allow for a statistically meaningful analysis.

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