Contents

CHAPTER 1

Introduction

It is convenient to define organic reagents used in chemical analysis as those carbon-containing substances which, by some form of interaction, enable other ions or molecules to be detected or determined. Such organic reagents find many important applications in the analytical chemistry of inorganic species.[1] Procedures such as complexometric titrations using ethylenediaminetetraacetic acid (EDTA) and selective determinations of metals spectrophotometrically with dithizone, or gravimetrically with 8-hydroxyquinoline, come readily to mind. Recent developments in theoretical chemistry, particularly those arising from the ligand-field theory of transition metal ions and their complexes, have led to a greatly increased understanding of factors in reactions that govern the stability of metal complexes, the nature of their absorption spectra, and other properties of interest to the analyst. This book attempts to present a picture of current chemical theory, more particularly as it relates to reaction between inorganic species and organic reagents. Applications to familiar analytical procedures will be discussed. To keep the account within reasonable limits, however, no attempt will be made to encompass practical details of the processes involved.

Unlike reactions in organic chemistry, most of those in inorganic chemistry involve dynamic equilibria, so that the positions of equilibria and the nature of the products are determined rapidly and directly by free-energy considerations. This is especially true of ionic reactions, and knowledge of the energies involved in such reactions is important in deciding whether, or how far, they can proceed. In some cases, however, including substitution reactions of complexes containing certain metal ions, rates are very slow although the processes involved are thermodynamically favorable. Reasons for this are given in Chapter 5.

Much of the most important group of reactions to be considered are those in which complexes are formed between hydrated metal ions and organic molecules or ions, usually by coordination through one or more atoms of oxygen, nitrogen, or sulfur. Such complex formation is important in analytical chemistry in two ways. It may produce a species that has more useful characteristics for identification or estimation; and alternatively, the concentrations of particular cations can be reduced to levels below those at which they interfere in reactions designed to separate, or otherwise characterize, other molecules or ions.

Metal ions in aqueous solution are themselves complexes because they orient the water molecules immediately surrounding them, leading, especially in the transition and higher-valent metal ions, to definite complexes such as $Al(H_2O)_6^{3+}$ and $Cr(H_2O)_6^{3+}$. This is a consequence of the dipole moments of the water molecules, leading to their spatial orientation by the ionic charge on the metal ion.

For this reason, complex formation in solution is really a replacement process in which one or more of the solvent molecules surrounding an ion is replaced by other ions or molecules, to give species which usually have very different chemical and physical properties. Rates of exchange of water bound to metal ions show wide variation, ranging (for most ions) from exchange times of very much less than a millisecond to a half time ($t_{1/2}$) measured in days (for $Cr(H_2O)_6^{3+}$). The species with which a metal ion reacts to form a complex is known as a *ligand.* In most cases, the formation and dissociation of complexes proceeds rapidly by a succession of equilibrium reactions which, if M signifies a metal ion and L is a ligand, can be written

$$\begin{gathered} M + L \rightleftharpoons ML \\ ML + L \rightleftharpoons ML_2 \\ ML_{n-1} + L \rightleftharpoons ML_n \end{gathered}$$

so that, because of these stepwise equilibria, a series of complexes may coexist in the solution. Ligands may be anions (such as Cl^- or $NH_2CH_2COO^-$) or neutral molecules (such as NH_3 or 1,10-phenanthroline), so that complexes may be cations, neutral molecules, or anions.

For a substance to function as a ligand it must have at least one pair of electrons it can "donate" towards a metal ion. The maximum number of such ligands that are bound by a metal ion is equal to its *coordination number*.

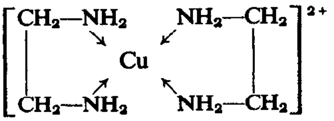
Where, as in this series, each complex contains only one metal ion, the quantity $\bar{n}$, Bjerrum's *formation function*, is independent of metal ion concentration and provides a quantitative measure of the extent of formation of the complexes. This is because $\bar{n}$, which is defined as the average number of ligand molecules bound per metal ion, depends on the ligand concentration.

However, the actual concentrations of the individual complexes are determined by the stepwise equilibrium ratios,

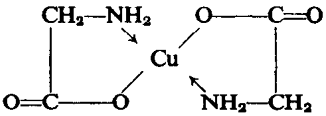
$$K_1 = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]}, \quad K_2 = \frac{[\mathrm{ML}_2]}{[\mathrm{ML}][\mathrm{L}]}, \quad \ldots, \quad K_n = \frac{[\mathrm{ML}_n]}{[\mathrm{ML}_{n-1}][\mathrm{L}]}$$

which are known as *formation constants*, and the overall constant $\beta_n = [\mathrm{ML}_n]/[\mathrm{M}][\mathrm{L}]^n$, which is the *overall stability constant* of the complex ML_n. Methods used in obtaining such constants are described elsewhere,[2] and extensive collections of formation and overall stability constants are available.[3] They show that many factors influence the stability of complexes (in respect of their dissociation into their components), including the nature of the atoms concerned in bond formation, the base strength of the ligand, the stereochemistry of the complexes themselves, and contributions due to resonance. It is the interrelation of these factors that determines the extent to which any reagent shows selectivity towards inorganic species.

One of the greatest effects arises from the formation of complexes in which the ligand is attached to the metal by two or more atoms to form a *chelate compound*. Typical examples include the *bis* complexes of ethylenediamine and of glycine with copper (II) (structures (I) and (II)).

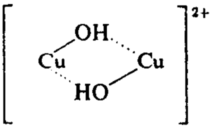


I



II

Whereas (I) is a divalent cation, (II) is a neutral molecule. If five- or six-membered rings are formed in this way, the complex shows a greatly increased stability, an effect further enhanced if the ligand is *multidentate* (so that the complex contains two or more such rings). Ethylenediamine and the dianion of salicylic acid are examples of bidentate ligands. Qualitatively, this *chelate effect* can be explained by saying that, the more points of attachment there are between a ligand and a metal ion, the more difficult it will be for the metal ion to break all the bonds and move away



III

before they can re-form. Polynuclear complex formation can sometimes occur, giving complexes of the type M_mL_n. Examples are fairly common where partial hydrolysis of metal ions is involved, if this leads to *olation* in which metal ions are joined by bridging —OH groups, as in the hydroxo complex ion (III). The mathematical analysis of such systems is complicated because equilibria depend on the metal ion concentration as well as on the ligand concentration.

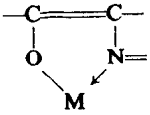
Where concentrations instead of activities are used in their calculation, stability constants vary to some extent with the experimental conditions, reflecting particularly the effects of changes in ionic strength on the activity coefficients of the species concerned. For the present discussion these effects will be ignored.

Some complexes, such as those involving Cr(III) and Co(III), form and dissociate slowly. These "robust" complexes, and the reasons for their existence, are discussed in Chapter 5. Their slowness of reaction prevents their analytical determination by titration procedures.

A ligand is usually an anion or a neutral molecule with basic properties so that, at sufficiently low pH values, it becomes extensively protonated, with consequent reduction in its complex-forming ability. Thus phenols (pK_a 10) are weak acids that form complexes via the phenolate ion. This leads to a progressive decrease in their complexing abilities at pH values less than 10. On the other hand, thiocyanate ion, derived from a strong acid, is almost pH-independent in its complexing ability.

The stability constants of any particular ligand with a series of metal ions fall in a well-defined sequence, depending on the nature of the coordinating groups, so that the analytical ideal of a specific reagent for any individual metal is unlikely to be realized. The number of types of group involved in chelated-ring formation is strictly limited by the requirement that the atoms bonded to the metal in the complex be able to "donate" a pair of electrons to the union. In practice, this almost restricts the choice to N, O, and S. The nitrogen may be present as a primary, secondary, or tertiary amine; a nitro, nitroso, azo, or diazo group; or as a nitrile or an acid amide. Oxygen may coordinate as phenolate or carboxylate ion, (neutral) alcoholic OH, or ether-oxygen, or as —C=O of ketones, aldehydes, and carboxyl groups. Similarly, sulfur bonding may be through ionized thiol and thiocarboxylate anions, through thioethers and thioketones, and through disulfide groups. The main types of reactive group are listed, with the chelating agents in which they occur, in Table 1.1.

Some examples of the types of chelate ring to which these groups give rise are shown in rings (IV) to (IX). Ring (IV) occurs in metal complexes of 8-hydroxyquinoline and its derivatives and in 4-hydroxybenzothiazole. Ring (V) is found in α,α′-bipyridyl, 1,10-phenanthroline, and α,α′,α″-terpyridyl complexes. The ring (VI) is present in metal complexes of dimethylglyoxime and other dioximes, whereas (VII) occurs in complexes of pyrocatechol and its derivatives. Ethylenediamine and glycine give structures (VIII) and (IX), respectively.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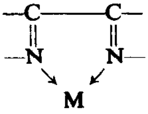
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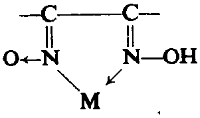
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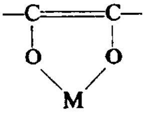
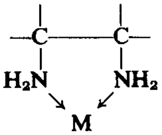

VII


VIII

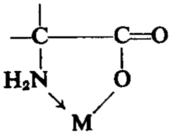
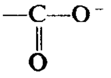
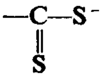

IX

TABLE 1.1

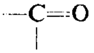
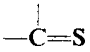
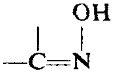
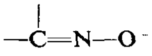
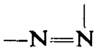
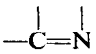
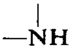
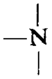
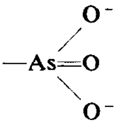
The Main Complex-Forming Groups in Analytical Reagents

Group	Examples
Tertiary N	α,α′-Bipyridine, 4-hydroxybenzothiazole, 8-hydroxyquinaldine, 8-hydroxyquinoline, PAN, 1,10-phenanthroline, picolinic acid, quinaldic acid, α,α′,α″-terpyridyl
(Usually phenolic) —O⁻	Acetylacetone, alizarin, chloranilic acid, cupferron, eriochrome black T, glyoxal-bis(2-hydroxyanil), 4-hydroxybenzothiazole, 8-hydroxyquinaldine, 8-hydroxyquinoline, kojic acid, 9-methyl-2,3,7-trihydroxy-6-fluorone, morin, murexide, α-nitroso-β-naphthol, nitroso-R-salt, PAN, pyrocatechol, rhodizonic acid, salicylaldoxime, salicylic acid, SPADNS, tiron
—S⁻	4-Chloro-1,2-dimercaptobenzene, diphenylthiocarbazone, dithiol, mercaptobenzothiazole, rubeanic acid, thionalide
 $-\underset{\displaystyle \|\atop O}{C}-O^-$	Aluminon, anthranilic acid, EDTA, glycine, mandelic acid, metalphthalein, oxalic acid, picolinic acid, quinaldic acid, salicylic acid
 $-\underset{\displaystyle \|\atop S}{C}-S^-$	Sodium diethyldithiocarbarbamate, zinc dibenzyldithiocarbamate

(*Continued*)

TABLE 1.1 (*Continued*)

The Main Complex-Forming Groups in Analytical Reagents

Group	Examples
 $-\underset{\vert}{C}=O$	Acetylacetone, alizarin, aluminon, chloranilic acid, kojic acid, morin, rhodizonic acid, thionalide
 $-\overset{\vert}{C}=S$	Thiourea
 $-\overset{\vert}{C}=\overset{\overset{OH}{\vert}}{N}$	Dimethylglyoxime, α-furildioxime, nioxime, salicylaldoxime
 $-\overset{\vert}{C}=N-O^-$	α-Benzoinoxime, dimethylglyoxime, α-furildioxime, nioxime
$-N=O$	Cupferron, α-nitroso-β-naphthol, nitroso-R-salt
 $-\overset{\vert}{N}-\overset{\vert}{N}^-$	Diphenylcarbazone, diphenylthiocarbazone
 $-N=\overset{\vert}{N}$	Diphenylcarbazone, diphenylthiocarbazone, eriochrome black T, PAN, SPADNS
 $-\overset{\vert}{C}=\overset{\vert}{N}$	Glyoxal-bis(2-hydroxyanil), murexide.
(Neutral)—OH	α-Benzoinoxime, mandelic acid
$-NH_2$	Anthranilic acid, ethylenediamine, glycine, triaminotriethylamine, triethylenetetramine
 $-\overset{\vert}{N}H$	Thionalide, triethylenetetramine
 $-\underset{\vert}{\overset{\vert}{N}}$	EDTA, metalphthalein, triaminotriethylamine
 $-\overset{O^-}{\underset{O^-}{As}}=O$	Arsonic acids

These groups differ in their relative complexing abilities with different metal ions—for example, the difference between the stability constants of the ethylenediamine complexes of Cu(II) and Zn is much greater than for the corresponding oxalato complexes—but these differences are of degree rather than of kind, so that reagents are rarely specific. Nor, for most analytical purposes, are reagents sufficiently selective to be used directly.

Metal ions, in turn, fall into three reasonably sharp classifications, as shown by the examples in Table 1.2. These three groups comprise:

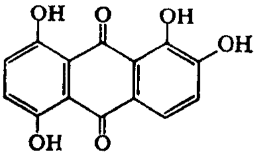
1. Ions in which the electronic distributions approximate to those of the inert-gas atoms, He, Ne, A, Kr, Xe, and Rn. Examples include Na^+, Ca^{2+}, and Al^{3+}.
2. Ions in which the *d* or *f* orbitals are only partially filled. These are the transition metal ions.
3. Ions with filled *d* orbitals, such as Ag^+, Zn^{2+}, and Ga^{3+}.

TABLE 1.2

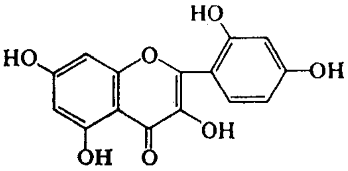
Division of Metals in Terms of Electronic Structure

1. Those metals giving ions resembling the inert gases							
Li	Be	B					
Na	Mg	Al					
K	Ca	Sc	Zr(IV)				
Rb	Sr	Y	Hf(IV)				
Cs	Ba	La, Ce-Lu	Th(IV)				
2. Metals with ions having partly filled *d* or *f* orbitals							
Ti	V	Cr	Mn	Fe	Co	Ni	Cu(II)
Nb	Mo	Tc	Ru	Rh	Pd	Ag(II)	
Ta	W	Re	Os	Ir	Pt	Au(III)	
Rare earths and actinides							
3. Metals whose ions have filled *d* orbitals							
Cu(I)	Zn	Ga	Ge	As			
Ag(I)	Cd	In	Sn	Sb	Te		
Au(I)	Hg	Tl	Pb	Bi	Po		

Some overlapping occurs. For example, in many of their complexes Fe(III) and Mn(II) show properties more closely resembling "inert-gas" ions.

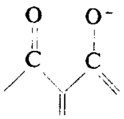


X

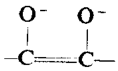


XI

Ions in the first group react preferentially with oxygen-containing anionic ligands such as carboxylate ions and the anions of quinalizarin (X) and morin (XI), in which the important parts of the ligands are the groupings (XII) or (XIII). Thus, quinalizarin is used in alkaline solution for the colorimetric determination of Be, Mg, B, and Al; it also reacts with Sc and the rare earths but, in neutral or weakly acid solutions, many other metal ions, including Zr and Th, also give colors. Similarly, in acid solutions morin is used to estimate Zr, Th, Sc, and Al, whereas in strongly alkaline solutions it is almost specific for Be.



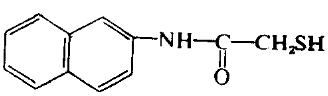
XII



XIII

Transition-metal ions form more stable complexes with ligands containing polarizable portions such as amino groups and heterocyclic nitrogen atoms. There is some overlap in properties between the ions to the right of the transition-metal series and the earliest of those with filled *d* shells, so that ethylenediamine also forms strong complexes with Zn, Cd, and Hg.

The third group in Table 1.2 also prefers highly polarizable ligands, especially if the latter have suitable vacant orbitals into which some of the *d* electrons can be "back-bonded." This condition favors sulfur-containing ligands, so that a reagent such as thionalide (XIV) forms insoluble complexes with Cu, Ag, Au, Cd, Hg(II), Tl, Sn(II), Pb, As, Sb, Bi, Pt, and Pd. Here again, some overlap with the higher members of the transition metals is evident.



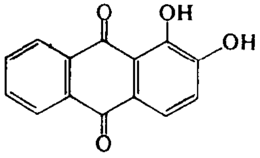
XIV

A reagent such as dithizone, where metal binding takes place through nitrogen and sulfur groups, has an even broader "spectrum" of metal reactivity, which embraces a large part of the transition metal and the "filled *d* orbital" series.

It must be emphasized, however, that although these considerations indicate in broad outline the preferred types of ligand for particular classes of metal ions they are by no means exclusive. Instead, all ligands might be expected to interact with all metal ions, to an extent that depends largely on the nature of the donor groups on the ligand. To achieve the degree of selectivity desired in analytical work it is usually necessary to exploit differences in two or more physical or chemical properties. Some of the more common properties that are used in this way include:

1. The production of a characteristic color. This may be:
   - (i) for the direct spectrophotometric estimation of the species giving rise to the color.
   - (ii) for detecting an endpoint, e.g. by means of an indicator in acid-base or oxidation-reduction titrations, or by adsorption of an indicator onto a precipitate.
2. Differences in solubility. This may be made the basis of a gravimetric method or used volumetrically, or trace constituents may be separated by coprecipitation.
3. The use of "masking" reagents to prevent a species other than the one being studied from participating in a reaction.
4. Differences in distribution between solvents at controlled pH values.
5. Differences in ion-exchange and chromatographic behavior.
6. Differences in volatility.
7. Oxidation or reduction to other valence states.

All these properties of inorganic species can be profoundly modified by the use of suitable organic reagents. Sometimes, too, modification of a reagent improves its analytical usefulness. For example, in dilute mineral acid solutions, zirconium and hafnium (also Ti, Th, Sn, and Al) form intensely colored but sparingly soluble "lakes" with alizarin (XV) and other hydroxyanthraquinones such as purpurin (1,2,4-trihydroxyanthraquinone) and quinalizarin (X) as well as morin (XI) and quercetin (which differs from morin only in the position of one of the hydroxyl groups on the phenyl side chain). Insertion of a sulfonic acid group into alizarin confers water solubility without otherwise affecting the reaction, which is the basis of colorimetric methods for estimating these metals. This book attempts to elucidate the factors that give rise to these effects.



XV

Our understanding of the factors governing such properties has, in recent years, been materially assisted by developments in theories of chemical bonding. In particular, we have been assisted by the union of two treatments which superficially are quite different. On the one hand, the sizes, shapes, and directions of orbitals were held to be very important in determining whether or not chemical combination could occur. Apparently opposed to this was the suggestion that molecules were held together by nondirected, nonspecific electrostatic forces. The combination of these two approaches, to give the ligand-field theory, is described in Chapter 2.

It is hoped that this theoretical background will, in turn, increase the possibilities of predicting with some confidence the kinds of substances most suitable for particular determinations, the experimental conditions that should be used, and the nature and magnitude of the effects of modifying the structures of the reagents.

References

1. See, for example, Sandell, E. B., *Colorimetric Determination of Traces of Metals*, Interscience, New York, 3rd ed., 1959; Feigl, F., *Spot Tests in Inorganic Analysis*, Elsevier Publishing Co., Amsterdam, 5th ed., 1958; Feigl, F., *Chemistry of Specific, Selective and Sensitive Reactions*, Academic Press, New York, 1949; and Welcher, F. J., *Organic Analytical Reagents*, Van Nostrand, New York, 4 vols., 1947–1948.
2. Rossotti, F. J. C., and H. Rossotti, *The Determination of Stability Constants*, McGraw-Hill Book Co., New York, 1961.
3. Bjerrum, J., G. Schwarzenbach, and L. G. Sillén, eds., *Stability Constants of Metal-Ion Complexes; Part I: Organic Ligands; Part II: Inorganic Ligands*, Chemical Society, London, 1957–1958.

CHAPTER 2

Chemical Bonds

The complete mathematical solution of the Schrödinger wave equation for the hydrogen atom, permitting as it does the accurate prediction of the spectrum and other physical properties of this species, represents one of the greatest achievements in physical chemistry.[1] It also provides the foundation for much of our present understanding of chemical bonding, stereochemistry, and spectra. A grasp of some of the fundamental properties and consequences of this wave equation is essential to much that is discussed elsewhere in this book.

2.1 Atomic Orbitals

The Heisenberg uncertainty principle and the wave character of the electron prohibit the exact location, at any instant, of the position of an electron in any atom. All that can be obtained from the wave equation is information about the average time spent by an electron in any small element of space. By constructing contours of the space within which electrons spend, say, 99% of their time, the volumes they occupy can be visualized. These volumes are known as "orbitals," and any orbital can contain a maximum of two electrons. Chemical-bond formation results from the overlap of filled and unfilled orbitals of different atoms, molecules, or ions, resulting in a greater spreading out in space ("delocalization") of the electrons concerned. The electron density in any region of an orbital is proportional to the square of the wave function, ψ.

A further, crucial factor that must be taken into account is the mathematical sign that the wave function takes in any totally enclosed part of an orbital. This sign (*which has nothing to do with electronic charge*) is somewhat analogous to "phase." Where parts of overlapping orbitals have the same sign for ψ, so that the wave functions are "in phase," chemical bonding can occur; if they are of opposite sign, then the orbital resulting

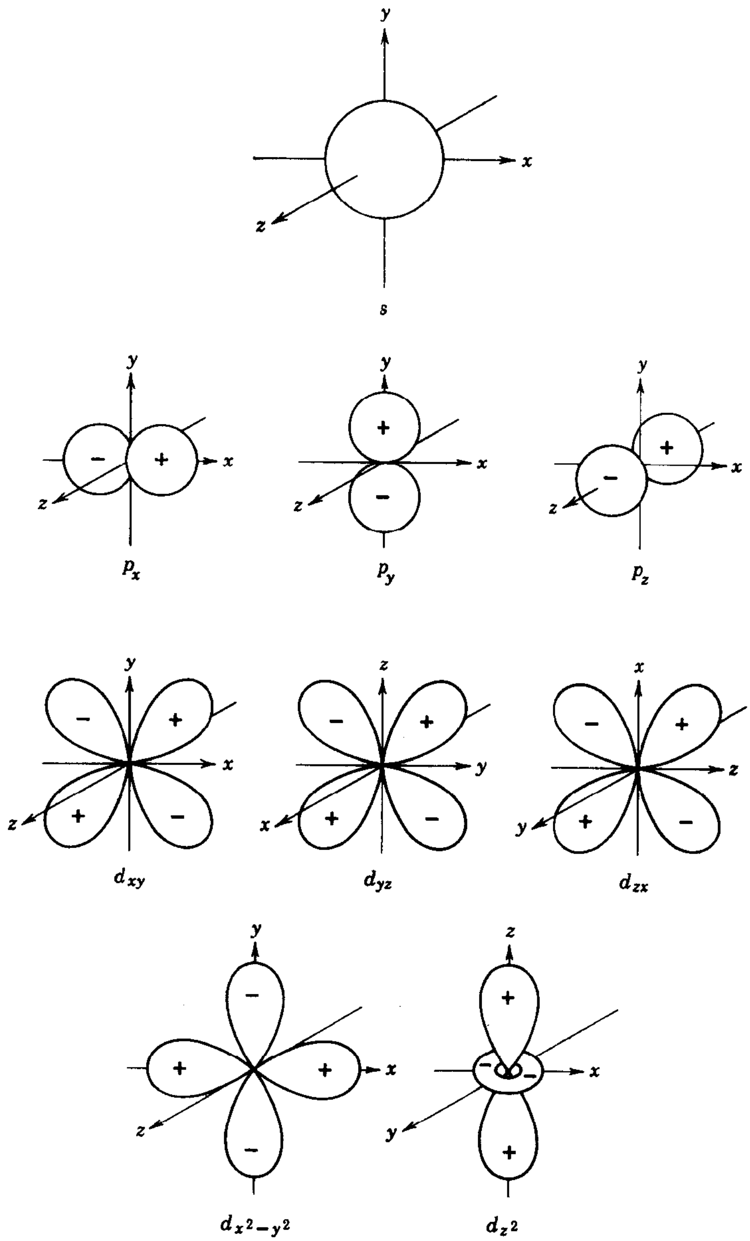


Fig. 2.1. Shapes of atomic orbitals. The *p* orbitals lie along each of the *x*, *y*, and *z* axes. The lobes of the d_{xy}, d_{yz}, and d_{zx} orbitals lie in the corresponding planes, in directions bisecting the axes. The $d_{z^2-y^2}$ and d_{z^2} orbitals lie along the *x* and *y*, and *z* axes, respectively.