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Metal−Ligand Bond Distances in First-Row Transition Metal Coordination Compounds: Coordination Number, Oxidation State, and Specific Ligand Effects

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Mean metal−ligand bond distances for the coordination ligands isothiocyanate, pyridine, imidazole, water, and chloride, bound to the transition metals Mn, Fe, Co, Ni, Cu, and Zn in their 2+ oxidation states, were collected from searches the Cambridge Structure Database. The metal−ligand bond distances were converted to bond orders through the bond distance-bond order technique, as suggested by Pauling. The mean bond order sums at the 2+ metal centers were found to be independent of coordination number or geometry and to be strongly ligand-dependent; the values (by ligand) are as follows: isothiocyanate = 2.56 ± 0.13; imidazole = 2.13 ± 0.04; chloride = 2.12 ± 0.07; pyridine 1.95 ± 0.10; water = 1.88 ± 0.10. The bond order sum for Fe(III) bound to chloride was found to be 3.09, approximately one bond order unit larger than for the 2+ metal centers bound to chloride. Division of the ligand-specific bond order sums by coordination number allows prediction of the M−L bond distance to within 0.017 Å, regardless of the specific coordination geometry. The physical basis for the ligand-specific variation in bond order sum is also discussed.

Introduction

The variation of metal−ligand (M−L) bond distance with the coordination number of the metal atom in coordination compounds is a well-known but poorly understood phenomenon. Several researchers[1,2] have noticed an increase of M−L distance in discrete molecular compounds as coordination number increases, but little analysis of this trend has been attempted. Some theoretical studies of transition metal coordination compounds have been done,[3,4] but these were limited both in scope and variety of coordination geometries. Bridging this theoretical gap are the well-compiled Shannon−Prewitt tables,[5,6] which give ionic radii of transition metals (and nonmetals) as a function of charge and coordination number. Though these values were collected from essentially ionic materials, the Shannon−Prewitt tables have nonetheless proved useful in analysis of discrete molecular compounds.[7,8] Inspection of the these tables reveals trends which are consistent for a variety of metals, as shown in Table 1.

Table 1. Values from Shannon−Prewitt Tables for Several Transition Metals[a]

coord. no. (geometry)	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
6 (octahedral)	0.97	0.92	0.885	0.83	0.87	0.88
5	0.89	−	0.81	0.77	0.79	0.82
4 (tetrahedral)	0.80	0.77	0.72	0.69	0.71	0.74
4 (square planar)	−	0.78	−	0.63	0.71	−

[a] Octahedral Mn, Fe, and Co are high-spin only, all distances in Å.

As can be seen in Table 1, the difference in ionic radii between octahedral and tetrahedral coordination is consistent (0.15 ± 0.01 Å) for all five 2+ metal ions. Additionally, the difference in radii between tetrahedral and square planar coordination is insignificant for the Fe(II) and Cu(II) ions. Ni(II) has a *smaller* radii in square planar geometry than in tetrahedral, but this is probably due to the non-Aufbau electron filling in d^8 square planar species. These trends suggest that there may be a straightforward relationship between coordination number and metal ionic radii. However, it is unclear to what degree the M−L bonds in coordination compounds, which have aspects of both covalent and ionic bonding,[3,4,9] are accurately modeled by the Shannon−Prewitt values.

As useful as the Shannon−Prewitt tables are, it would be much more convenient to be able to compare bonds between a variety of transition metals and ligand binding atoms on the same scale. The bond distance−bond order (BDBO) technique, as suggested by Pauling,[10] allows us to do just this. In the BDBO technique, bond order is a function of the observed bond distance and the single bond expectation distance between any pair of atoms, which can be calculated from literature sources.[11] The BDBO technique is related to the bond valence model (BVM), which has been extensively developed in geology and material science.[11−14] In the BVM, the total bond order (valence) is equal to the oxidation state of any atom. If this conception is applicable to discrete molecular coordination compounds, then shorter M−L bonds would be expected for

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Table 2. 2^+ Metal Radii

	Mn	Fe	Co	Ni	Cu	Zn
radius, from ref 11	1.17	1.16	1.09	1.04	0.87	1.07
S−P radius of octahedral, high-spin, 2+ metals[5,6]	0.97	0.92	0.885	0.83	0.87	0.88
radius, as used	1.17	**1.12**	1.09	1.04	**1.06**	1.07

lower coordination numbers. For example, at a 2+ metal center, the M−L bond orders for a four-coordinate compound would be expected to be ∼0.5 ($0.5 \times 4 = 2.0$), where the M−L bond orders for a six-coordinate compound should be ∼0.33 ($0.33 \times 6 = 2.0$). Thus, knowledge of the metal oxidation state and coordination number allows a prediction of the metal−ligand bond order. Several researchers[15−18] have used this model, referred to as the bond valence sum (BVS) method, in conjunction with X-ray absorption techniques to provide metal−ligand bond distances in metalloprotiens. Some validation of this technique was attempted,[15] but the variety of metal−ligand combinations was quite limited. The Cambridge Structure Database[19] (CSD) provides a ready source of M−L bond distances. Imidazole, isothiocyanate, pyridine, water, and chloride ion were chosen as the ligands in this study, as these ligands are commonly used in coordination compounds and data are available for most of the first-row transition metals. Mean M−N bond distances can be converted to bond orders, and the sums of these bond orders can be assessed as a function of oxidation state and coordination sphere. Not only will this study assess the validity of the BVS approach, but it will also provide data on three important questions in metal−ligand bonding of coordination compounds: (a) do the trends in the Shannon−Prewitt tables accurately reflect the variation in the M−L bond distance as a function of coordination number in discrete molecular coordination compounds; (b) do the M−L bond orders sum to a consistent value, and can this be used to accurately predict M−L bond distances; (c) if the bond order sums vary significantly from 2.0 at 2+ metal centers, is this a function of ligand binding properties?

Experimental Section

BDBO Technique. Conversion from the observed bond distances to bond orders was done through the following equation:[11]

$$bo = \exp[(R_{ij} - d_{ij})/0.37] \qquad (1)$$

where bo is the bond order between atoms i and j, d_{ij} is the observed bond distance and R_{ij} is the single bond expectation distance. The value 0.37 (sometimes called the universal constant) is taken from a number of recent publications,[11−14] and although it differs from Pauling's original value of 0.31,[10] may provide a better fit for a variety of atom pairs. R_{ij} was calculated from literature sources,[11] with two significant changes. It was noticed that the radius values for iron and copper did not closely match the trend seen in the Shannon−Prewitt radii,[5,6] as shown in Table 2. Since a goal of this study was to determine if the Shannon−Prewitt radii values were reproduced in discrete molecular compounds, the radius parameters for iron and copper were adjusted to better fit the trend found in the Shannon−Prewitt tables (see Table 2).

Database Search. Crystallographic data were retrieved for the CSD[19] on the basis of a search for structures containing a first-row transition metals Mn, Fe, Co, Ni, Cu and Zn, with coordination numbers 4, 5, or 6 and at least one example of the ligand of interest. The protocol employed for data selection is summarized in Table 3. No structure containing more than one metal atom in the molecule of interest was retained. Hits were retained for isothiocyanate, water, and chloride only with exact matches of the terminal ligand; for imidazole and pyridine, only nonsubstituted or singly methyl-substituted examples were allowed. No macrocyclic or bridging ligands were retained. Mean M−L bond distances, and their standard deviations, are collected in Table 4 for the nitrogen-binding ligands isothiocyanate, pyridine, and imidazole and in Table 5 for water and terminal chloride. Entries are made in Tables 4 and 5 only for those metal−ligand pairs with data from at least two distinct structure determinations. R_{ij} values for all metal−ligand pairs are also collected in Tables 4 and 5.

Table 3. Database Search Acceptance Parameters

coordinating atoms	nitrogen only for NCS^-, pyridine, and imidazole oxygen only for H_2O nitrogen or chlorine for Cl^- nitrogen, chlorine or bromine for Br^-
ligand types	mono-, bi- or terdentate for 6- and 5-coordinate mono- or bidetate for 4-coordinate
temperature	room temperature (∼295 K) only
R factor	<0.100 for 0 or 1 σ data <0.085 for 2 or 3 σ data <0.070 for 4 (or greater) σ data
geometry	angles from recorded ligand to all other ligands within ±10° of ideal values
spin-state	high-spin only

Calculation of the Bond Order Sums. The calculated bond order data are also collected in Tables 4 and 5. For the 4-coordinate and most of the octahedral metal−ligand pairs, bond orders were calculated from the compiled mean M−L bond distances using eq 1, and this bond order was multiplied by 4 (for tetrahedral and square planar) or 6 (for octahedral) to arrive at the bond order sum (bo_{sum}). Due to the copious amount of available data, the bo_{sum} of 6-coordinate water and 4-coordinate chloride structures were calculated with the ligand of interest was in all coordination sites. However, octahedral Cu(II) and 5-coordinate complexes required a procedure to correct for geometric inequivalence. Octahedral Cu(II) displays pronounced, *Z*-out, Jahn−Teller distortion. Cu−L bond distances were separated into long and short groups, which were easily discerned as the differences between the means of the two groups were 0.44 Å (for water) and 0.59 Å (for chloride). Bond orders were calculated for each group, and the bo_{sum} for octahedral Cu(II) was found by

$$bo_{sum} = 4(bo_{short}) + 2(bo_{long})$$

Only Cu−ligand pairs with entries from at least two distinct structural determinations in both the long and short groups were recorded.

Five-coordinate compounds were found in both square pyramidal (spm) and trigonal bipyramidal (tbp) geometries; in both cases the coordination sites are geometrically inequivalent. Angles were used to separate M−L distances into basal and apical groups (for spm) or axial and equatorial groups (for tbp). Ligands possessing angles not closely associated with either geometry were discarded. Bond orders were again calculated for each group and the bo_{sum} was found by

$$bo_{sum}(spm) = 4(bo_{basal}) + bo_{apical}$$

$$bo_{sum}(tbp) = 3(bo_{equatorial}) + 2(bo_{axial})$$

Data were recorded only when both groups for a particular geometry (i.e. basal and apical for spm) had entries from at least two distinct structural determinations. Square pyramidal geometry was recorded for the following metal−ligand pairs: Cu−chloride, Cu−imidazole and Cu−water. Trigonal bypyramidal geometry was recorded for Cu−isothiocyanate, Zn−isothiocyanate, and Zn−water.

Handling of Anomalous Data. There are two possible sources of systematic error to bond distances collected in the above manner: non-Aufbau electron filling of the d-orbitals and ligand−ligand interaction. Non-Aufbau d-orbital filling in the form of low-spin, octahedral d^4

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Table 4

Bond Order Sums for 2+ Metal Centers

	Mn	Fe	Co	Ni	Cu	Zn
R_{ij}'s (metal−nitrogen)	1.86	1.82	1.79	1.74	1.76	1.77
(metal−chlorine)	2.12	2.08	2.05	2.01	2.03	2.04
(metal−oxygen)	1.75	1.71	1.68	1.63	1.65	1.66
Isothiocyanate Ion: Mean bo_{sum} = **2.56 ± 0.13**						
octahedral, mean M−L distance (SD)	2.161(25)		2.081(33)	2.070(31)		
mean bo_{sum}/N_{obs}	**2.66**/6		**2.73**/16	**2.46**/101		
M(NCS)$_6$ only			2.119(16)	2.090(10)		
5-coordinate−axial					1.978(35)	2.081(54)
equatorial					1.984(25)	1.983(25)
					2.75/14	**2.55**/4
tetrahedral			1.950(21)	1.919(16)		1.953(24)
			2.60/55	**2.47**/4		**2.44**/18
M(NCS)$_4$ only			1.954(14)	1.918(14)		1.953(12)
square planar				1.859(9)	1.949(19)	
				2.90/3	**2.40**/13	
Pyridine: Mean bo_{sum} = **1.96 ± 0.10**						
octahedral		2.236(21)	2.182(23)	2.139(26)		
		1.95/10	**2.08**/12	**2.04**/109		
tetrahedral						2.064(45)
						1.81/6
square planar				1.907(11)	2.030(26)	
				2.55/5	**1.93**/11	
M(py)$_4$ only				1.919(6)	2.046(−)	
Imidazole: Mean bo_{sum} = **2.13 ± 0.04**						
octahedral		2.204(17)	2.172(23)	2.124(14)		
		2.13/9	**2.14**/6	**2.13**/22		
M(im)$_6$ only			2.168(11)	2.129(4)		
5-coordinate−apical					2.185(62)	
basal					2.041(15)	
				2.19/6		
tetrahedral						2.002(18)
						2.14/13
M(im)$_4$ only						2.000(3)
square planar				1.900(9)	2.004(12)	
				2.60/4	**2.07**/22	
M(im)$_4$ only					2.004(14)	
Terminal Chloride Ion: Mean bo_{sum} = **2.12 ± 0.07** (2.10 ± 0.09 w/Octahedral Ni(II))						
octahedral, mean M−L distance (SD)	2.499(33)		2.436(30)	2.438(38)	2.294(21)/2.886(47)^a	
mean bo_{sum}/N_{obs}	**2.15**/23		**2.11**/13	**1.89**/42	**2.16**/40	
M(Cl)$_6$ only				2.454(62)	2.311(35)/2.99(18)^a	
5-coordinate−apical					2.55(10)	
basal					2.289(51)	
					2.23/23	
M(Cl)$_5$−apical					2.57(−)	
M(Cl)$_5$−basal					2.286(37)	
tetrahedral^b	2.359(25)	2.303(34)	2.259(29)	2.247(28)	2.257(31)	2.255(34)
M(Cl)$_4$ only	2.360(16)	2.318(16)	2.278(16)	2.259(13)	2.256(29)	2.267(20)
	2.09/13	**2.10**/11	**2.16**/51	**2.04**/12	**2.17**/9	**2.17**/100
square planar					2.290(28)	
					1.98/16	
Water: Mean bo_{sum} = **1.88 ± 0.10**						
octahedral	2.181(32)	2.118(35)	2.086(32)	2.059(24)	1.973(27)/2.328(73)^a	2.104(46)
M(H$_2$O)$_6$ only	2.176(27)	2.123(18)	2.088(34)	2.054(17)	1.967(25)/2.41(11)^a	2.088(30)
	1.91/19	**1.97**/11	**1.99**/94	**1.91**/56	**1.91**/48	**1.89**/16
5-coordinate−apical					2.272(35)	
basal					1.968(16)	
axial						2.111(62)
equatorial						1.976(59)
					1.88/7	**1.87**/7
tetrahedral						1.992(10)
						1.63/10
square planar					1.939(17)	
					1.83/15	
M(H$_2$O)$_4$ only					1.944(11)	

Table 4. (Continued)

Bond Order Sums for 2+ Metal Centers: Nitrogen-Binding Ligands

	Mn	Fe	Co	Ni	Cu	Zn
R_{ij}'s (metal−nitrogen)	1.86	1.82	1.79	1.74	1.76	1.77
Isothiocyanate Ion: Mean bo_{sum} = **2.56 ± 0.13**						
octahedral, mean M−L distance (SD)	2.161(25)		2.081(33)	2.070(31)		
mean $\text{bo}_{\text{sum}}/N_{\text{obs}}$	**2.66**/6		**2.73**/16	**2.46**/101		
$M(NCS)_6$ only			2.119(16)	2.090(10)		
5-coordinate−axial					1.978(35)	2.081(54)
equatorial					1.984(25)	1.983(25)
					2.75/14	**2.55**/4
tetrahedral			1.950(21)	1.919(16)		1.953(24)
			2.60/55	**2.47**/4		**2.44**/18
$M(NCS)_4$ only			1.954(14)	1.918(14)		1.953(12)
square planar				1.859(9)	1.949(19)	
				2.90/3	**2.40**/13	
Pyridine: Mean bo_{sum} = **1.96 ± 0.10**						
octahedral		2.236(21)	2.182(23)	2.139(26)		
		1.95/10	**2.08**/12	**2.04**/109		
tetrahedral						2.064(45)
						1.81/6
square planar				1.907(11)	2.030(26)	
				2.55/5	**1.93**/11	
$M(py)_4$ only				1.919(6)	2.046(−)	
Imidazole: Mean bo_{sum} = **2.13 ± 0.04**						
octahedral		2.204(17)	2.172(23)	2.124(14)		
		2.13/9	**2.14**/6	**2.13**/22		
$M(im)_6$ only			2.168(11)	2.129(4)		
5-coordinate−apical					2.185(62)	
basal					2.041(15)	
					2.19/6	
tetrahedral						2.002(18)
						2.14/13
$M(im)_4$ only						2.000(3)
square planar				1.900(9)	2.004(12)	
				2.60/4	**2.07**/22	
$M(im)_4$ only					2.004(14)	

[a] First values are ligands in *xy* plane, second values are ligands on *z* axis. [b] Values for MCl_4 only or $M(H_2O)_6$ only used to calculate bo_{sum}.

through d^7 metal complexes is a well-known phenomenon. Because electrons are paired in the lower energy level before filling the higher energy (more antibonding) orbitals, the M−L bond distances for low-spin complexes are expected to be shorter than for their high-spin analogues. Therefore, discrimination between low-spin and high-spin complexes can be done on the basis of M−L distances. This was easily accomplished, as the difference in M−L bond distance between low-spin and high-spin complexes was 0.1−0.25 Å in metal−ligand pairs where both occurred. For example, for Fe(II) bound to pyridine, there was a group of 10 Fe−N_{pyridine} distances averaging 2.236 ± 0.021 Å (the high-spin group), a group of 9 Fe−N_{pyridine} distances averaging 2.036 ± 0.017 Å (the low-spin group), and no intermediate Fe−N_{pyridine} distances were observed. In all cases, only distances that were clearly in the high-spin group were included in Tables 4 and 5.

Another well-known form of non-Aufbau electron filling occurs in d^8, square planar complexes such as square planar Ni(II). In this case, the lower four orbitals contain paired electrons and the highest energy (most antibonding) orbital is unfilled. As with the low-spin complexes, this depopulation of the antibonding orbitals results in M−L bond distances shorter than expected. Since there is no alternative to this orbital filling for square planar Ni(II) complexes, the mean M−L bond distances and their associated bo_{sum} have been included in Tables 4 and 5, but these data points do not appear in the figures, nor are they included in the calculation of the mean bo_{sum} for each ligand. As can be seen from Tables 4 and 5, the bo_{sum} for the square planar Ni(II) complexes is always significantly larger than the mean for that ligand, this difference averaging 0.47 bond order units for the three nitrogen-binding ligands.

Finally, one example of (presumably steric) ligand−ligand interaction was observed in the apparently anomalous bo_{sum} for the octahedral nickel−chloride pair. The bo_{sum} of 1.89 is 2.3 σ from the mean of 2.10 be due to steric interaction between the chloride ion and other ligands in the octahedral coordination sphere. There are several factors that support such an interpretation. Nickel is the smallest 2+ metal center, and chloride ion is the largest ligand in Tables 4 and 5, so if steric interaction is ever a problem it should be most apparent in this pair. This steric argument would also explain why, although there are many examples of the less sterically hindered tetrahedral $NiCl_4^{2-}$ complex, there are no square planar structures of $NiCl_4^{2-}$. To investigate this possibility, a bo_{sum} was compiled for octahedral Ni(II) with bromide ion as a ligand. The mean Ni−Br distance was 2.607 Å, giving a bo_{sum} of 1.77, even lower than that of octahedral nickel−chloride complexes and supporting the suggestion that the low value for the octahedral Ni−Cl bond order is caused by steric interactions between the Cl^- and the other ligands in the octahedral coordination sphere.

Discussion

Validity of the Compiled Data. The validity of these data may be judged in a number of ways. Certainly, the standard deviations of the mean bo_{sum} for each ligand is a good measure of the internal validity. The mean bond orders and their standard deviations are visually presented in Figure 1. These values range from ±0.13 bond order units (5.1% of the mean value) for isothiocyanate to ±0.04 (1.9% of the mean value) for

Table 5. Bond Order Sums for 2+ Metal Centers: H_2O and Cl^- Ligands

	Mn	Fe	Co	Ni	Cu	Zn
R_{ij}'s (metal−chlorine)	2.12	2.08	2.05	2.01	2.03	2.04
(metal−oxygen)	1.75	1.71	1.68	1.63	1.65	1.66
Terminal Chloride Ion: Mean bo_{sum} = **2.12 ± 0.07** (2.10 ± 0.09 w/Octahedral Ni(II))						
octahedral, mean M−L dis.(SD)	2.499(33)		2.436(30)	2.438(38)	2.294(21)/2.886(47)[a]	
mean bo_{sum}/N_{obs}	**2.15**/23		**2.11**/13	**1.89**/42	**2.16**/40	
$M(Cl)_6$ only				2.454(62)	2.311(35)/2.99(18)[a]	
5-coordinate—apical					2.55(10)	
basal					2.289(51)	
					2.23/23	
$M(Cl)_5$—apical					2.57(−)	
$M(Cl)_5$—basal					2.286(37)	
tetrahedral[b]	2.359(25)	2.303(34)	2.259(29)	2.247(28)	2.257(31)	2.255(34)
$M(Cl)_4$ only	2.360(16)	2.318(16)	2.278(16)	2.259(13)	2.256(29)	2.267(20)
	2.09/13	**2.10**/11	**2.16**/51	**2.04**/12	**2.17**/9	**2.17**/100
square planar					2.290(28)	
					1.98/16	
Water: Mean bo_{sum} = **1.88 ± 0.10**						
octahedral[b]	2.181(32)	2.118(35)	2.086(32)	2.059(24)	1.973(27)/2.328(73)[a]	2.104(46)
$M(H_2O)_6$ only	2.176(27)	2.123(18)	2.088(34)	2.054(17)	1.967(25)/2.41(11)[a]	2.088(30)
	1.91/19	**1.97**/11	**1.99**/94	**1.91**/56	**1.91**/48	**1.89**/16
5-coordinate—apical					2.272(35)	
basal					1.968(16)	
axial						2.111(62)
equatorial						1.976(59)
					1.88/7	**1.87**/7
tetrahedral						1.992(10)
						1.63/10
square planar					1.939(17)	
					1.83/15	
$M(H_2O)_4$ only						1.944(11)

[a] First values are ligands in *xy* plane, second values are ligands on *z* axis. [b] Values for MCl_4 only or $M(H_2O)_6$ only used to calculate bo_{sum}.

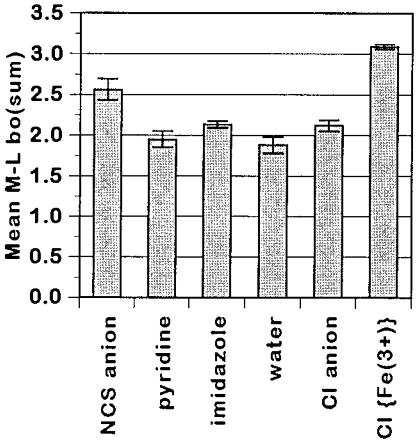

Figure 1. Mean ligand-specific bo_{sum} for 2+ metal centers in 4-, 5-, and 6-coordinate geometries. Error bars denote standard deviations of mean values.

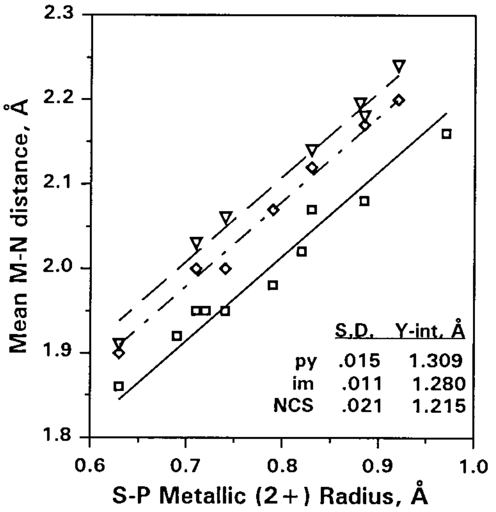

Figure 2. Correlation of metal−ligand distance with Shannon−Prewitt effective ionic radius. Triangles, − − = pyridine; diamonds, − - − = imidazole; squares, — = isothiocyanate. Note that the lines above are not regression lines, but are the slope = 1.00 lines through the mean of the data for each ligand. Standard deviations are calculated using the deviations from this line of ideal agreement.

imidazole. Even for isothiocyanate, the largest value, this standard deviation correlates to an uncertainty of 0.018 Å in the metal−nitrogen bond distance. This is clearly of the same order as the individual standard deviations for each metal, and demonstrates that there is no significant deviation in bo_{sum} between metals bearing the same ligand.

The validity of taking M−L bond distances from compounds with a variety of ligands can be judged by looking at the octahedral complexes containing water ligand and those tetrahedral complexes containing chloride ion. If one looks at all octahedral compounds containing water at one coordination site and any oxygen-binding ligand at the other five sites, the mean M−O bond order for all six metals studied is 0.32 ± 0.02. If one only looks at $M(H_2O)_6^{2+}$ complexes (as in Tables 3 and 4), the mean M−O bond order is still 0.32 ± 0.02. Similarly, the mean M−Cl bond order for tetrahedral metal(II) complexes with chloride in at least one site is 0.55 ± 0.02, insignificantly different from the value of 0.53 ± 0.01 for the M−Cl bond order in tetrahedral MCl^{2-} complexes. This shows that the protocol outlined in Table 3 provides consistent M−L bond distances regardless of the specific composition of the coordination sphere.

Correlation of M−L Distances with Shannon−Prewitt Values. The data clearly show that the trends found in the Shannon−Prewitt tables of effective ionic radii are strongly predictive of the changes in M−L bond distances in coordination compounds. As mentioned above, the mean difference in effective ionic radii between octahedral and tetrahedral geometries is 0.15 ± 0.01 Å for the six 2+ metal centers in this study. For all metal−ligand pairs which displayed both octahedral and tetrahedral geometry in this study, the mean difference in M−L bond distance was 0.14 ± 0.02 Å, an insignificantly different value. A direct comparison of collected M−L bond distances to effective ionic radii is given in Figure 2. (For clarity's sake, only the nitrogen-binding ligands are shown. Results are similar for chloride and water, the values being: for Cl^-, sd = 0.016 Å, *y* intercept = 1.551 Å; for H_2O, sd = 0.017 Å, *y* intercept = 1.212 Å.) The data show a strong correlation, with standard deviations from ideal agreement ranging from 0.011 to 0.021 Å. Given the recent suggestion[20] that there is inherent flexibility of 0.01 to 0.02 Å in the M−L bond distances of coordination compounds, uncertainties of prediction in this range appear particularly satisfactory.

Furthermore, the *y* intercepts plotted in Figure 2 give a relative radius parameter for the ligands. It is clear that isothiocyanate shows significantly shorter binding distances than either pyridine or imidazole, the differences being 0.094 Å (3.6σ) between NCS^- and pyridine and 0.065 Å (2.7σ) between NCS^- and imidazole. In the BVS method as implimented by Thorpe and others,[15−18] it is assumed that all nitrogen-binding ligands would have the same bond distance for any particular metal center and geometry. The above shows that this is not the case, and such an assumption could introduce significant error into BVS modeling. However, ligands similar to pyridine and imidazole could probably be expected to yield reproducible values, since their bo_{sum} is very close to 2.0.

Modeling Metal−Ligand Bond Distances. A further measure of the accuracy of these data is the degree to which the mean bo_{sum} specific to each ligand, in conjunction with the coordination number, are able to reproduce the observed M−L bond distances. We can predict the metal ligand bond distances by essentially reversing eq 1 above, to wit:

$$d_{\text{predicted}} = R_{ij} + [(\ln(\text{mean bo}_{\text{sum}}/\text{coord no}))(-0.37)] \quad (2)$$

The plot of observed versus predicted M−L distance is given in Figure 3, where the line represents ideal agreement with slope = 1.00 and *y* intercept = 0.00. The standard deviation from linearity for this plot is 0.017 Å, again in the range suggested by Orpen.[20] Since the predicted values were generated by division of the ligand-specific mean bo_{sum} by the coordination number, this plot also demonstrates the strong dependence of M−L bond distance on coordination number, regardless of the specific (i.e., tetrahedral vs square planar) coordination geometry. Additionally, because the R_{ij} distances were adjusted to mirror the trends in the effective ionic radii, the strong correlation in Figure 3 reinforces that the observed changes in M−L bond distances in these coordination compounds are well modeled by the Shannon−Prewitt values. Furthermore, these data suggest a basis for both the effective ionic radii and the observed M−L bond distances. The required bo_{sum} at a metal center in a coordination compound appears to be a function of the oxidation state of the metal center and the specific ligands involved in coordination to that center. That sum must be satisfied, whether the coordination number is 4, 5, or 6. The M−L bonds in 4-coordinate compounds are shorter than those in octahedral compounds because the four ligands must provide the same total bond order as six of the same ligands in an octahedral compound. This finding is in basic accord with the BVM, providing that the formal oxidation state of the metal may be altered by the specific ligands present.

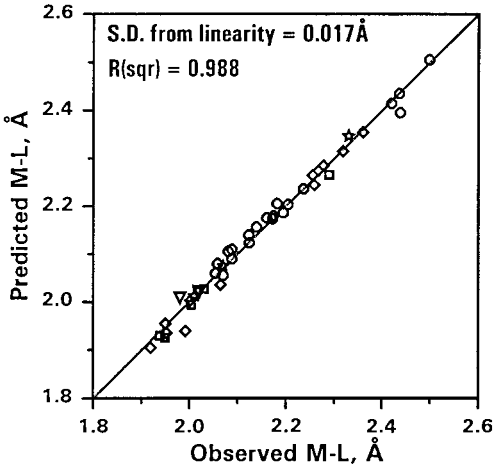

Figure 3. Observed versus predicted metal−ligand bond distance for 2+ metal centers. Solid line indicates ideal correlation ($x = y$). Key to symbols: ○ = octahedral, ▽ = trigonal bipyramid, ☆ = square pyramid, ◇ = tetrahedral, □ = square planar.

To establish the dependence of bo_{sum} on oxidation state for (much less numerous) 3+ metal centers, the bo_{sum} was calculated for octahedral (high-spin only) and tetrahedral Fe(III) bound to chloride ligands. The bo_{sum} is 3.11 for octahedral $Fe^{III}-Cl$ (N_{obs} = 114) and 3.07 for tetrahedral $Fe^{III}-Cl$ (N_{obs} = 283); in both cases very nearly one bond order unit larger than the mean bo_{sum} of 2.12 ± 0.07 found for the 2+ metals bound to chloride. Therefore, the basic premise of the BVM—that the valence sum at any atom will be approximately equal to the oxidation state of the atom—is shown to be an important factor in determining this bo_{sum}. However, it is clear that the specific ligands involved also make a significant contribution to this value. These results may also explain the apparent flexibility of M−L bonds in coordination compounds observed by Orpen and co-workers.[20] Because the bond orders are found in a range from 0.3 to 0.45 for 6-coordinate complexes and 0.40−0.65 for 4-coordinate complexes, the force constants of these bonds are necessarily much less than a formal single bond, and as such these bonds should be more prone to deformation by both intra- and intermolecular steric forces.

The ligand-specific bo_{sum} may be understood in terms of a Lewis acid−base interaction. A strong Lewis base has nonbonding (and perhaps π-bonding) electron density available for a Lewis acid, such as a positively charged metal center. This available electron density strengthens the metal−ligand interaction and results in a shorter M−L bond distance, so that the bo_{sum} at 2+ metal centers increases from the expected value of 2.0. When weak Lewis bases act as ligands, the nonbonding electrons are not readily available and the bo_{sum} decreases. From Figure 1, this qualitative relationship is clearly evident, with water (a poor Lewis base) having the lowest bo_{sum}, isothiocyanate (a good Lewis base and potentially a good π-donating ligand) having the highest bo_{sum} and pyridine and imidazole displaying intermediate values. Unfortunately, the available values that might be used to correlate this effect (gas-phase

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(20) Martin, A.; Orpen, A. G. *J. Am. Chem. Soc.* **1996**, *118*, 1464.

proton affinity, Hammett parameters) are not really appropriate to the realities of ligand−metal interaction, so quantification of this relationship must await further work in this area.

Concluding Remarks

These results show that M−L bond distances are determined by the need of the metal center to obtain a specific bo_{sum}, which is a function of the oxidation state of the metal and the specific ligands involved in coordination. Coordination number does not effect bo_{sum}, but it does effect individual M−L bond orders, in that four ligands in a tetrahedral or square planar compound must supply the same bo_{sum} as six ligands in an octahedral compound. The BDBO relationship supplies a simple and flexible formula to apply the Shannon−Prewitt effective ionic radius values to a variety of metal−ligand pairs, and allows prediction of M−L distances to 0.017 Å, providing that bo_{sum} is known for the specific ligand. In the BVS method, the assumption of equal binding strength for all ligands sharing a common binding atom is somewhat in error, but ligands similar to pyridine and imidazole should provide reproducible values. While the trend is clear that stronger Lewis bases result in larger bo_{sum}, further study is needed to quantify this relationship.

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Supporting Information Available: A complete list of CSD refcodes for the structures used to compile Tables 3 and 4 (7 pages). Ordering information is given on any current masthead page.

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