

9.6. TYPICAL INTERATOMIC DISTANCES: ORGANOMETALLIC COMPOUNDS AND COMPLEXES

Table 9.6.3.2. Numbers of entries in Table 9.6.3.3

Numbers of entries for which < 4 examples are known are given first, followed by numbers of entries for which statistics are quoted (*i.e.* those with > 4 examples).

		Ligand atoms														
		H	B	C	N	O	F	Si	P	S	Cl	As	Se	Br	Te	I
Ligand class	Metal *†	5	4	66	71	79	4	1	32	49	3	2	1	3	1	3
Sc ¹			1, 0	0, 1		0, 4										
Ti ^{2,3}			2, 0	6, 8	14, 5	4, 15	1, 0		1, 2	4, 3	1, 2	1, 0		1, 0		
V ^{4,5,6}			2, 0	8, 8	6, 5	10, 10	0, 1		3, 3	2, 6	0, 2	1, 0				1, 0
Cr ⁷	1, 0	1, 2	9, 15	12, 13	5, 19	0, 1		1, 0	9, 5	1, 7	1, 1	0, 2	1, 0	2, 0	1, 0	1, 0
Mn		0, 3	15, 12	14, 13	14, 10	1, 0		1, 0	5, 6	7, 4	0, 2	0, 2	1, 0	1, 1	0, 1	1, 1
Fe	0, 2	1, 2	10, 33	13, 19	14, 12		0, 1		6, 13	7, 16	0, 2	0, 2	0, 1	2, 0	0, 1	1, 1
Co ⁸	2, 0	0, 4	11, 27	5, 28	18, 22				6, 10	7, 11	1, 2	0, 2		0, 1		0, 1
Ni ^{9,10}	0, 1	2, 1	7, 20	9, 23	9, 18	1, 0			6, 8	12, 13	0, 2	1, 1	0, 1	0, 2		1, 1
Cu ^{11,12}	1, 0	3, 0	1, 11	7, 35	18, 31	3, 0			3, 3	7, 12	0, 3	0, 1	1, 0	0, 3		0, 3
Zn	1, 0	2, 0	3, 2	7, 16	14, 10					7, 3	0, 2			0, 1		0, 1
Y ¹		1, 0	0, 1		2, 6						0, 1					
Zr ¹³		1, 0	6, 8	10, 1	5, 7	0, 1		1, 1	4, 0	0, 2		1, 0				1, 0
Nb ¹⁴			4, 6	3, 5	2, 9	0, 1		2, 0	1, 6	1, 2	0, 1					
Mo ^{15,16}	1, 1	1, 0	11, 25	17, 26	7, 28	1, 1	1, 0	5, 11	3, 20	1, 2	0, 2	1, 0	0, 2	1, 0	0, 2	0, 2
Tc ^{17,18}			0, 1	5, 5	3, 5			1, 2	1, 2	1, 1	0, 1			2, 0		
Ru	0, 1	2, 1	12, 25	19, 9	11, 8		0, 1	2, 13	4, 4	0, 2	0, 2			0, 2		1, 1
Rh	2, 1	0, 2	11, 25	12, 18	11, 14		1, 0	5, 13	6, 7	0, 2	1, 1	0, 1	0, 2	0, 2		0, 2
Pd		0, 1	9, 15	14, 13	6, 6			8, 7	4, 10	1, 2	1, 1		0, 1	0, 1		1, 1
Ag		1, 0	4, 2	8, 6	8, 2	1, 0		2, 3	4, 6	2, 1		1, 0	1, 0	1, 0		1, 2
Cd ¹⁹				3, 14	12, 10			2, 0	6, 4	0, 3				1, 2		0, 1
La§				1, 1	4, 7				1, 0	1, 0						
Ce§			0, 2	0, 1	4, 4				0, 1	1, 0						
Pr§			1, 1	1, 0	2, 5					2, 0						
Nd§				2, 2	7, 5					1, 0						
Sm§			0, 1	2, 1	8, 6											
Eu§			0, 1	0, 1	3, 6											
Gd§			0, 1	1, 0	2, 4											
Tb§					1, 0											
Dy§				2, 1	1, 2					0, 1						
Ho§					0, 1											
Er§			0, 1	1, 1	4, 4					1, 0						
Tm§										0, 1						
Yb§			0, 2	2, 2	3, 2					2, 0						1, 0
Lu§			1, 2	1, 0	0, 1					0, 1						
Hf ¹³			2, 4	1, 0	2, 2			0, 2		1, 0						
Ta ²³	1, 0		5, 7	4, 1	4, 2			2, 2	2, 4	0, 2				1, 0		
W ^{24,159}	0, 2	1, 1	9, 20	10, 7	4, 12	1, 0	1, 0	4, 6	7, 5	1, 2	1, 0	1, 0	0, 1	0, 1		1, 1
Re	0, 2	0, 1	10, 13	9, 9	11, 12	1, 0	0, 1	4, 5	4, 3	0, 2	0, 1	1, 0	0, 2	0, 2		0, 2
Os	0, 2	2, 0	12, 11	9, 7	6, 6		1, 0	4, 6	3, 3	0, 2	1, 0	1, 0	1, 0	0, 1		0, 1
Ir	1, 1	1, 1	11, 12	12, 4	3, 4	1, 0	1, 0	5, 9	5, 5	0, 2		1, 0	0, 2	0, 2		0, 2
Pt	2, 0	0, 1	4, 25	11, 13	8, 10	1, 0	0, 1	6, 13	8, 11	0, 2	0, 1	1, 0	0, 2	1, 0	0, 2	0, 2
Au ²⁵		0, 1	4, 3	6, 0	4, 0			5, 3	7, 3	0, 1				0, 1		1, 0
Hg ²⁶		1, 0	8, 3	10, 5	11, 2		0, 1	3, 2	2, 6	1, 2		1, 0	0, 2	0, 1	0, 1	0, 2
Th§	1, 0		1, 2	0, 3	5, 8			1, 0	0, 1	0, 1						
U§		0, 1	1, 5	7, 5	16, 18	1, 2		1, 0	1, 1	0, 2				0, 1		

*No entries for Pm, Pa, and Ac. †Superscripts refer to entries in Appendix 1. §See references 1, 20–23 in Appendix 1.

state is not always well defined, where no assignment was possible then this is indicated by (–) rather than the roman numeral used elsewhere. Finally, cases where the ligand oxidation state is variable are identified (*e.g.* for O₂, *o*-quinones *etc.*) by references to the footnotes at the end of Table 9.6.3.3.

9.6.3.3. Use of the 'Note' column

The 'Note' column refers to the footnotes collected in Appendix 1. These record additional information as follows:

(a) notable features of the distribution of distances, *e.g.* likely bias due to dominance by one structure of substructure, skewness, bimodality (subdivisions of the entry usually follow, which remove these features whenever possible); (b) further details of the chemical substructure, such as the exclusion of structures with particular *trans* ligands; (c) details of exclusion criteria used for a given entry or group of entries, such as the constraint that the two *M*–Cl distances, in bridging (μ_2) chloride complexes, differ by <0.1 Å (section 10.1.1.2); (d)

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references to previously published surveys of crystallographic results relevant to the entry in question. We do not claim that these entries are in any way comprehensive and we would be grateful to authors for notification (to AGO) of any omissions. This will serve to improve the content of any future version of Table 9.6.3.3.

9.6.3.4. Locating an entry in Table 9.6.3.3

Table 9.6.3.2 provides a 'guide' to the contents of Table 9.6.3.3. The number of entries for which individual examples of M -ligand distances are quoted, and the number of entries for which statistics are given in Table 9.6.3.3 are listed for each metal. Inspection of Table 9.6.3.2 shows which element pairs have no bond lengths recorded in Table 9.6.3.3. Thus, while there are no cobalt-fluorine distances in Table 9.6.3.3, there are 6 classes of cobalt-phosphorus distances for which there are examples quoted and 10 for which statistics are given.

Let us say one wished to find typical lengths for cobalt-triethylphosphine ($\text{Co}-\text{PEt}_3$) bonds. Table 9.6.3.1 shows that PEt_3 , a tertiary phosphine, falls under ligand class 8.5. In Table 9.6.3.3, the section dealing with such ligands starts with 8.5.1 (trimethylphosphine) followed by 8.5.2 (triethylphosphine). Under this section, we find that $\text{Co}-\text{PEt}_3$ bonds average 2.208 Å in length (with sample standard deviation $\sigma = 0.039$ Å), and in cobaltacarboranes the average is 2.224 Å, and for ($\eta\text{-C}_5\text{H}_5\text{CoL}_2$) species the average is 2.147 Å.

Polydentate ligands with different elements able to act as contact atoms present particular difficulty. The convention we have adopted is to place the individual $M-L$ interatomic distances under separate entries according to the contact element. Thus, thiocyanate (SCN) appears in ligand class 4.4.5 when N -bonded (*i.e.* isothiocyanate $M-\text{NCS}$) and in ligand class 9.3 when S -bonded ($M-\text{SCN}$). When bridging with both S and N bonded to metals (as in $M-\text{NCS}-M'$), then the $M-N$ distances (as well as *all* intraligand distances) will be under ligand class 4.5 and $M'-S$ distances under ligand class 9.3.

Thus, in such cases the intraligand dimensions will accompany the metal-ligand distances in the first ligand class (*i.e.* the lower-numbered class).

9.6.4. Discussion

Table 9.6.3.3 has been derived from the CSD, and, as a result, does not contain every precisely determined metal-ligand interatomic distance. For example, there are many ammine ($M-\text{NH}_3$), carbonyl ($M-\text{CO}$), halide ($M-\text{Cl}$ *etc.*), and aqua ($M-\text{OH}_2$) complexes that do not fall within the scope of the CSD. For such bond types, and other metal-non-metal bond-length information, the interested reader is referred to the Inorganic Crystal Structure Database (Bergerhoff, Hundt, Sievers & Brown, 1983).

The tabulation given here is a first attempt to obtain average dimensions for (d - and f -block) metal-ligand and intraligand bonds. Inspection of Table 9.6.3.3 shows that, in general, the sample standard deviations of metal-contact-atom interatomic distances are typically larger than those of the intraligand distances [*e.g.* for $\text{Fe}-\text{PPh}_3$ complexes (section 8.5.3), $\text{Fe}-\text{P}$ mean 2.237, σ 0.038 Å, *cf.* $\text{P}-\text{C}$ mean 1.834, σ 0.011 Å]. There are several factors that cause this phenomenon. Firstly, in many (but not all) cases no account has been taken of substituent effects at the metal, such as the *trans* influence of other ligands. In contrast, the substituent pattern at the ligand is usually well defined; therefore, the chemical causes for variation in the metal-ligand and intraligand distances are different. Secondly, it is likely that metal-ligand bonds are softer, *i.e.* have lower force constants, than the intraligand bonds, leading to a broader distribution of distances whatever the *cause* of variation. Finally, it should be noted that a substantial contribution to the standard deviation of both metal-ligand and intraligand distances comes from *random* errors arising most importantly from the rather poor location of light (B, C, N, O, F) atoms in the presence of $5d$, $4f$, and $5f$ metals (La-U). For example, C—O bond lengths

(continued on page 884)

Table 9.6.3.3. Interatomic distances (Å)

Bond	Substructure (coordination number, oxidation state, comment)	d	m	σ	q_l	q_u	n	Note
1.1.1.1 Hydrides (terminal)								27
Fe-H	all BASLIQ10	1.609	1.610	0.004	1.605	1.612	6	
Zn-H	see MAEMAZ11 (1.617)							
Mo-H	see HCYPMO02 (1.684)							
Rh-H	see CONFEO01 (1.578, 1.583)							
Ta-H	see TACPTH (1.769, 1.774, 1.776)							
W-H	all IPPHWH01	1.732	1.734	0.010	1.725	1.740	6	
Re-H	(8), (-)	1.684	1.681	0.015	1.676	1.697	12	
Os-H	all THMPOS01	1.659	1.656	0.017	1.646	1.677	4	
Ir-H	all DETSOK	1.603	1.607	0.021	1.582	1.623	5	
Pt-H	see CAKNEH01 (1.610)							
1.1.1.2 Hydrides (μ_2 -H)								27
Cr-H	see KCPTCR01 (1.725, 1.723)							
Fe-H	all HMYCFE01	1.670	1.670	0.001	1.669	1.672	4	
Mo-H	(6,7), (II,III)	1.842	1.843	0.023	1.819	1.864	4	
Ru-H	(*), (-)	1.782	1.776	0.019	1.773	1.791	22	
Rh-H	(4,*), (I)	1.775	1.768	0.040	1.738	1.811	8	
W-H	(6), (0)	1.900	1.897	0.028	1.876	1.926	5	
Re-H	(8,*), (I,IV)	1.832	1.832	0.039	1.793	1.870	16	
Os-H	(*), (-)	1.817	1.824	0.029	1.798	1.837	34	
Ir-H	see CUSGAY (1.821, 1.847)							
Pt-H	see CAKNEH01 (range 1.656-2.049)							
1.1.1.3 Hydrides (μ_3 -H)								27
Co-H	see HMPCIC01 (1.728, 1.731, 1.742)							
Ni-H	all TCPNIH11	1.691	1.684	0.022	1.673	1.715	9	
Rh-H	see HMPCRH11(1.847, 1.855, 1.873)							