

9. BASIC STRUCTURAL FEATURES

the sample standard deviation, as shown in Fig. 9.6.2.1(b) in which four (out of 366) observations are deleted.

The statistics chosen for tabulation effectively describe the distribution of bond lengths in each case. For a symmetrical, normal distribution, the mean (d) will be approximately equal to the median (m), the lower and upper quartiles (q_l , q_u) will be approximately symmetric about the median $m - q_l \approx q_u - m$, and 95% of the observations may be expected to lie within $\pm 2\sigma$ of the mean value. For a skewed distribution, d and m may differ appreciably and q_l and q_u will be asymmetric with respect to m . When a bond-length distribution is negatively skewed, *i.e.* very short values are more common than very long values, then it may be due to thermal-motion effects; the distances used to prepare the table were not corrected for thermal libration.

In a number of cases, the initial bond-length distribution was clearly not unimodal as in Fig. 9.6.2.1(a). Where possible, such distributions were resolved into their unimodal components (as in Fig. 9.6.2.1c) on chemical or structural criteria. The case illustrated in Fig. 9.6.2.1, for Cu—Cl bonds, is one of the most spectacular examples, owing to the dramatic consequences of oxidation state and coordination number (and Jahn–Teller effects) on the structures of copper complexes.

9.6.3. Content and arrangement of table of interatomic distances

Table 9.6.3.1 indicates how the interatomic distances covered in Table 9.6.3.3 are subdivided. Metal–ligand distances are grouped according to the ligand contact atom, which leads to ordering by atomic number of that contact atom. For a given contact atom (H, B, C, *etc.*), the ligands are grouped by type as listed in Table 9.6.3.1. The class of ligand is identified numerically (*e.g.* alkoxides are class 5.3, alcohols class 5.23, ethers 5.24, *etc.*). Particular ligands are identified by a third number (*e.g.* methoxide is ligand 5.3.1). Finally, alternative bonding modes for a particular ligand are denoted by a fourth number [*e.g.* terminal alkoxides 5.3.1.1, bridging (μ_2) alkoxides 5.3.1.2]. In general, the bonding modes are arranged in the sequence $\eta^1, \eta^2, \dots, \eta^n, \mu_2, \mu_3, \dots$, where η^n implies n atoms of the ligand are bonded to metal atoms, and μ_m that m metal atoms are bonded to the ligand. Thus, acetates are represented by entries headed 5.5.2.1 (η^1), 5.5.2.2 (chelating, η^2) and 5.5.2.3 (bridging, μ_2). For each ligand, the metal–ligand bonds then follow a sequence of ascending atomic

Table 9.6.3.1. *Ligand index*

Contact atom	Ligand class	Ligand class identifier
Hydrogen	hydride	1.1
	tetrahydroborate (BH ₄)	1.2
Boron	borohydrides	2.1
	boranes/carboranes	2.2
	boroles, borylenes, other heteroboracycles	2.3
Carbon	carbide (C)	3.1
	carbyne/alkylidyne (CR)	3.2
	vinylidene/alkenylidene (CCR ₂)	3.3
	acetylide/alkynyl (CCR)	3.4
	cyano (CN)	3.5
	isocyanides (CNR)	3.6
	carbon monoxide (CO)	3.7
	thiocarbonyl (CS)	3.8
	carbene/alkylidene (CR ₂)	3.9
	vinyl/alkenyl (CRCR ₂)	3.10
	aryl (C ₆ R ₅)	3.11
	acyl [C(O)R]	3.12
	alkyl (CR ₃)	3.13
	η -alkenes (C ₂ R ₄ , allenes, <i>etc.</i>)	3.14
	alkynes (RCCR)	3.15
	η^3 ligands (allyls, <i>etc.</i>)	3.16
	η^4 ligands (conjugated dienes, <i>etc.</i>)	3.17
	η^5 ligands (dienyls, <i>etc.</i>)	3.18
	η^6 ligands (arenes, <i>etc.</i>)	3.19
	η^7, η^8 ligands	3.20
carboranes, boroles	3.21	
miscellaneous (CO ₂ , CS ₂ , <i>etc.</i>)	3.22	
Nitrogen	nitride (N)	4.1
	nitrene/imide (NR)	4.2
	methyleneamido (N=CR ₂)	4.3
	nitriles (NCR)	4.4
	isocyanate, isothiocyanate (NCO, NCS)	4.5
	dinitrogen (N ₂)	4.6
	diazonium (N ₂ R), diazoalkanes (N ₂ CR ₂)	4.7
	azide (N ₃)	4.8
	nitrosyl, thionitrosyl (NO, NS)	4.9
	amide (NR ₂)	4.10

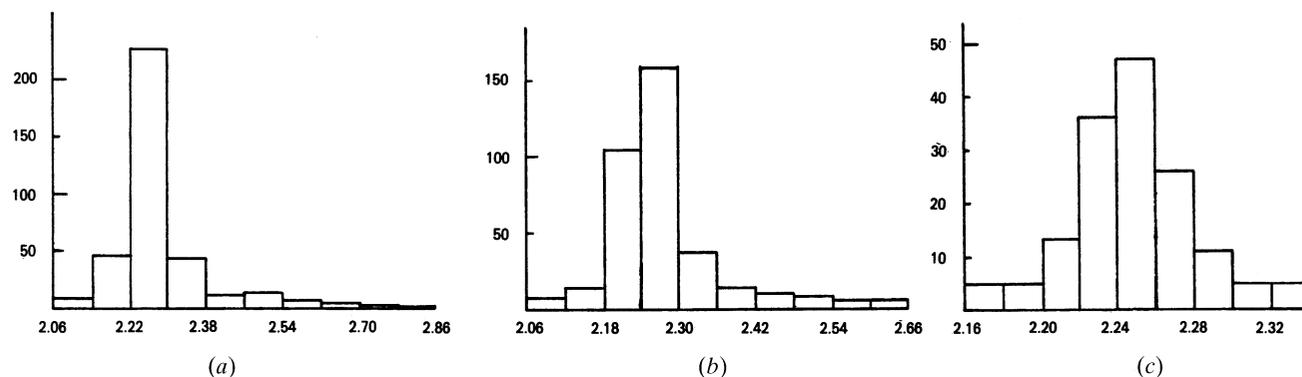


Fig. 9.6.2.1. Effects of outlier removal and subdivision based on coordination number and oxidation state. Cu—Cl: (a) all data; (b) all data without outliers [$> 4\sigma$ (sample) from mean]; (c) all data for which Cu is 4-coordinate, Cu^{II}.

	d	m	σ	q_l	q_u	N
(a)	2.282	2.255	0.105	2.233	2.296	366
(b)	2.276	2.254	0.092	2.232	2.292	362
(c)	2.248	2.246	0.032	2.233	2.263	153

9.6. TYPICAL INTERATOMIC DISTANCES: ORGANOMETALLIC COMPOUNDS AND COMPLEXES

Table 9.6.3.1. *Ligand index (cont.)*

Contact atom	Ligand class	Ligand class identifier
Nitrogen (<i>cont.</i>)	amidinate [RNC(R)NR]	4.11
	Schiff bases	4.12
	phthalocyanines, porphyrins, pyrroles	4.13
	pyrazolate, imidazolate and derivatives	4.14
	pyridine, polypryidyls (bpy, <i>o</i> -phen)	4.15
	pyrazines, pyridazines, pyrimidines	4.16
	other N ₂ ligands (NRNR ₂ , NNR ₂ , NRNR)	4.17
	triazenido (RNNNR)	4.18
	hydrazones and related species (NR ₂ N=CR)	4.19
	oximes	4.20
	<i>N</i> -nitrite (NO ₂)	4.21
	amine (NR ₃)	4.22
	borazines	4.23
	Oxygen	oxo (O)
hydroxy (OH)		5.2
alkoxy, aryloxy, <i>etc.</i> (OR)		5.3
<i>O</i> -ketones (OCR ₂), urea		5.4
carboxylates (O ₂ CR)		5.5
oxalate (O ₂ CCO ₂)		5.6
acetylacetonates [RC(O)CRC(O)CR]		5.7
α , β -diones (<i>e.g.</i> <i>o</i> -quinones)		5.8
carbonate (CO ₃ ²⁻)		5.9
<i>N</i> -oxides (<i>e.g.</i> pyridine <i>N</i> -oxide)		5.10
nitrate (NO ₃ ⁻)		5.11
<i>O</i> -nitrite (NO ₂ ⁻)		5.12
dioxygen, peroxides		5.13
phosphine oxides (OPR ₃)		5.14
phosphate (PO ₄ ³⁻)		5.15
other P—O anions		5.16
<i>O</i> -dialkyl sulfoxides (OSR ₂)		5.17
sulfate (SO ₄ ²⁻)		5.18
other S—O anions (sulfonates, <i>etc.</i>)		5.19
<i>O</i> -SO ₂		5.20
other oxyanions (<i>e.g.</i> ClO ₄ ⁻)		5.21
aqua		5.22
alcohols (ROH)		5.23
ethers (ROR')	5.24	
miscellaneous (η^2 -acyl, η^2 -CO ₂ , μ -NCO)	5.25	
Fluorine	fluoride (F)	6.1
	fluoroanions (BF ₄ ⁻ , PF ₆ ⁻)	6.2
Silicon	miscellaneous	7.1
Phosphorus	phosphorus (P)	8.1
	phosphinidenes (PR)	8.2
	phosphides (PR ₂)	8.3
	oligo-phosphorus ligands (P ₃ , PR ₂ PR ₂ , PRPR, <i>etc.</i>)	8.4
	phosphines (PR ₃)	8.5
	diphosphines (<i>e.g.</i> diphos)	8.6
	phosphites [P(OR) ₃]	8.7
	aminophosphines, cyclotriphosphazanyl, misc. P—N ligands	8.8
Sulfur	sulfides (S)	9.1
	thiolates (SR)	9.2

Table 9.6.3.1. *Ligand index (cont.)*

Contact atom	Ligand class	Ligand class identifier
Sulfur (<i>cont.</i>)	<i>S</i> -thiocyanate (SCN)	9.3
	thioketones, thiourea (S=CR ₂)	9.4
	thiocarboxylates (S ₂ CR ⁻)	9.5
	thiocarbamates (S ₂ CNR ₂ ⁻)	9.6
	xanthates (S ₂ COR ⁻), dithio-carbonates	9.7
	trithiocarbonate (CS ₃ ²⁻), thioxanthates	9.8
	α , β -dithiones	9.9
	phosphine sulfides	9.10
	dithiophosphinates (S ₂ PR ₂ ⁻)	9.11
	polysulfur ligands (S ₂ , SSR, <i>etc.</i>)	9.12
	thioethers (SR ₂)	9.13
	<i>S</i> -SO ₂ , <i>S</i> -SO ₃ , <i>etc.</i>	9.14
	disulfides (RSSR)	9.15
<i>S</i> -dialkyl sulfoxides (R ₂ SO)	9.16	
miscellaneous (η^2 -CS ₂)	9.17	
Chlorine	chloride (Cl)	10.1
Arsenic	arsines (AsR ₃)	11.1
	miscellaneous	11.2
Selenium	miscellaneous	12.1
Bromine	bromide (Br)	13.1
Tellurium	miscellaneous	14.1
Iodine	iodide (I)	15.1

number of the metal. For a given metal, the first line of an entry in Table 9.6.3.3 gives statistics covering all appropriate occurrences of metal–ligand distances. Further lines give statistics for metal–ligand distances for subdivision based largely on chemical criteria (*e.g.* metal oxidation state or coordination number). Cases where one atom of a ligand bridges two or more metal atoms were included only when the metal atoms were all of the same type and, unless specified, only when the metal–ligand distances were symmetrical (range for distances ≤ 0.1 Å).

In many instances, the number of structures having interatomic distances involving a given metal for a particular ligand is too small (< 4) for statistics to be quoted. In these cases, individual structures, and the distances in them, are given. These structures are identified by their CSD reference code (*e.g.* BOZMIN); short-form literature references, ordered alphabetically by reference code, are in Appendix 2.

Each line of Table 9.6.3.3 contains nine columns of which six record the statistics of the bond-length distribution described above. The content of the remaining three columns: Bond, Substructure, and Note, are described below.

9.6.3.1. *The 'Bond' column*

This specifies the atom pair to which the line refers. Therefore, in the case of triethylphosphine complexes (section 8.5.2), there are 18 lines, in which the bond column contains P—C, followed by 17 entries for Ti—P through to Au—P, indicating statistics for both intraligand and metal–ligand atom pairs.

9.6.3.2. *Definition of 'Substructure'*

This column provides details of any subdivision of particular metal–ligand bonds that has been applied. Thus, for terminal

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iron-chlorine bonds (in section 10.1.1.1), the second and third lines of the Fe—Cl entry refer to complexes in which the iron atom is four-coordinate and in oxidation state II and III, respectively. In some cases, subdivision has been carried out

on the basis of ligand substituents in those cases where a well defined subdistribution was observed. For clarity, in a number of cases the ligand structure and numbering scheme are illustrated in Fig. 9.6.3.1. The reader will be aware that formal oxidation

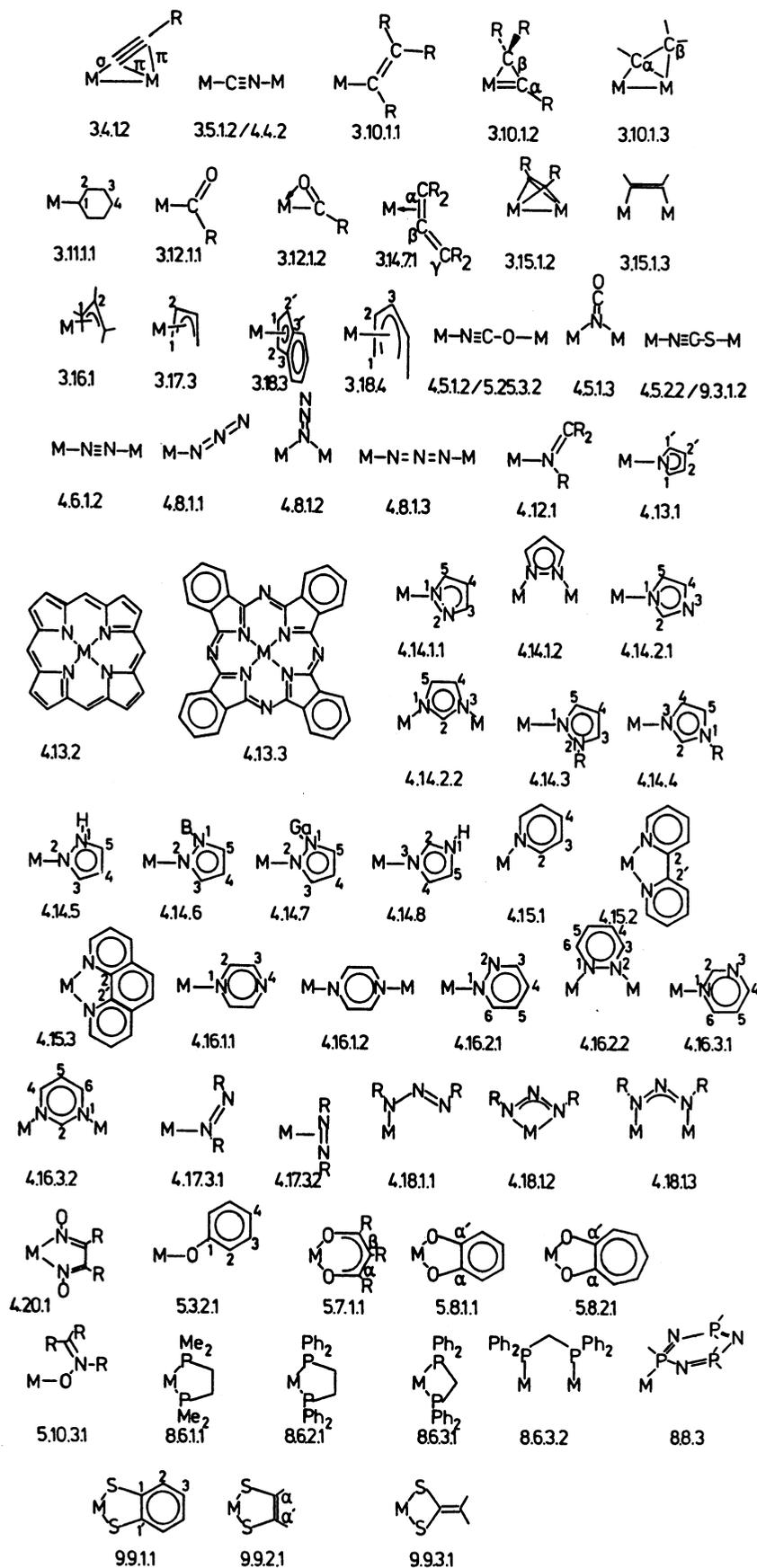


Fig. 9.6.3.1. Diagrams of ligands in Table 9.6.3.3, showing table entry number and ligand atom labelling.

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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
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
Pd		0, 1	9, 15	14, 13	6, 6				8, 7	4, 10	1, 2	1, 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, 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		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
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
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
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
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, 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)							