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Valence Balance of Magnesium in Mixed (Cl, O) Environments

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Empirical parameters (d_1 and N) are given for the equation $s = (d/d_1)^{-N}$ relating Mg–Cl and Mg–O bond lengths (d, Å) and bond strengths (s, valence units), using structural data from 73 compounds with about 100 different all (Cl), all (O) and mixed (O, Cl) ligand sets. Parameter values are (2.010, 5.10) and (1.62, 4.40) for Mg–Cl and Mg–O, respectively, and deviations from ideal valence sums are discussed.

Introduction

Application of the valence sum rule has led to an extensive set of empirical parameters which can profitably be used in the determination and interpretation of crystal structures [1]. In particular, bond strength–bond length relationships are well established for cation bonding to oxygen, but are scarcely known for other anions. This is partly due to the more restricted structural data which are available for such compounds. Further extension of the parameter set is then of considerable general interest. In an attempt to describe the Mg–Cl bond, using the available all (Cl) and mixed (Cl, O) ligand sets, we have come across fairly high mean deviations from ideal valence values. In view of previous criticism [2] with regard to the validity of the proposed relationship in the case of very short bond distances, we have also independently attempted to derive a parameter set for the Mg–O bond, taking into account that one important function of bond strength – bond length calculations is the establishment of general conceptual schemes by pointing out where disagreements occur.

Results and Discussion

Magnesium–Chlorine Bonding

On the basis of the crystal data for regular chlorine coordinations in the solid state, as in the tetrahedrally coordinated Cs_2MgCl_4 (*d*, 2.303 Å; *s*, 0.50 v.u.) and octahedrally coordinated α-$MgCl_2$, $KMgCl_3$, K_2MgCl_4, $CsMgCl_3$ and $RbMgCl_3$ (*d*, 2.494 Å; *s*, 0.33 v.u.), the parameters (d_1, N) of the equation $s = (d/d_1)^{-N}$ relating bond strengths or bond valences (*s*, valence units) and bond lengths (*d*, Å) are readily derived as (2.010, 5.10). For the gas phase species $(MgCl2)_n$, where the role of π-bonding is claimed to be very minor [3], structural data are only available for the terms with $n = 1, 2$ [3, 4]. As may be seen from Table I, gas phase data for $MgCl_2$ (*d*, 2.18 Å; *s*, 1.0 v.u.) [5] do not comply with the relation described above, or with similar expressions such as $R - R_o = -2k\log s$, as opposed to other analogous cases of gaseous species (*e.g.* $AlCl_3$ and $TiCl_4$). On the other hand, such a fit is not to be expected, according to Brown [6]. Yet, if we consider that $rMg^{2+} - rAl^{3+} = 0.15$ Å, reported experimental data for $MgCl_2(g)$ with Mg–Cl = 2.18 Å stand in good relation to the bond distance of 2.06 Å in $AlCl_3(g)$. The Mg–Cl distance of 2.18 Å has recently also been confirmed theoretically by energy minimization procedures [4]. It should be mentioned, however, that various inconsistencies exist in bond distances of group 2A and 2B dimethyls and chlorides [3]. As to sources of error in the reported bond data used for deriving the parameter set, it is noticed that the experimental values of 2.272–2.303 Å for Mg–Cl bonds in tetrahedrally coordinated Cs_2MgCl_4 and Cs_3MgCl_5 are very reasonable if compared to the average tetrahedral Al–Cl bond length (2.125 Å) and therefore do not appear to be in doubt.

In magnesium compounds there is a trend towards a maximum coordination number compatible with the steric requirements of the ligands. Tetrahedral $MgCl_4^{2-}$ species are rare and occur in Cs_2MgCl_4 (*s*, *l*) [7] and K_2MgCl_4 (*l*) [8]. Mixed salt systems of the type $MgCl_2\cdot nMCl$, such as Cs_2MgCl_4–K_2MgCl_4, also contain the tetrahedral $MgCl_4^{2-}$ ion as the dominant species in the melt [8]. Whereas the coordination number of magnesium changes from six in solid K_2MgCl_4 to four in the melt, Cs_2MgCl_4 melts with retention of the $MgCl_4^{2-}$ tetrahedral

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TABLE I. Bond Strengths and Bond Lengths in Magnesium Chlorine and –Oxygen Coordination Spheres.

Compound	Bond Distances (Å)		$\Sigma s^{a,b}$	Structural unit	Reference[c]
	Mg–Cl	Mg–O			
$MgCl_2$(gas)[d]	2.18(2×)	–	1.32(7)	$MgCl_2$[h]	*SPC* 1957, *2*, 472
$MgCl_2$(gas)[e]	2.18(2×)	–	1.32(–)	$MgCl_2$[h]	Ref. 4.
Mg_2Cl_4(gas)[e]	(2.20)[g], 2.30(2×)	–	1.64(–)	$MgCl_3$[i]	Ref. 4
Cs_2MgCl_4	2.296, 2.304(2×), 2.308	–	2.00(1)	$MgCl_4$[j]	*CJC* 1975, *53*, 114 *JCP* 1975, *63*, 3054
Cs_3MgCl_5	2.272(4×)	–	2.14(–)	$MgCl_4$[j]	*AC* 1964, *17*, 506 *JCP* 1970, *53*, 1336
$Mg_3ClB_7O_{13}$(o-rh)	2.614, 3.443	2.023, 2.035, 2.056, 2.064	1.76(1)	$MgClO_4$[k]	*ZK* 1973, *138*, 64
	2.616, 3.447	2.010, 2.050, 2.059, 2.064	1.76(1)		
	2.615, 3.430	2.013, 2.022, 2.038, 2.062	1.80(1)		
$Mg_3ClB_7O_{13}$(o-rh)	2.65, 3.40	2.04(2×), 2.06(2×)	1.75(–)	$MgClO_4$[k]	*AC* 1951, *4*, 310
(cubic)	3.02(2×)	2.04(4×)	1.70(–)	$MgCl_2O_4$[l]	
$Mg_3ClB_7O_{13}$(cubic)[f]	3.025(2×)	2.023(4×)	1.75(1)	$MgCl_2O_4$[l]	*AM* 1973, *58*, 691
β-$Mg_2(OH)_3Cl$	2.587	2.057(2×), 2.086(2×), 2.173	1.91(–)	$MgClO_5$[l]	*ASR* 1953, *B3*, 400
	2.595(2×)	2.081(2×), 2.100(2×)	1.85(–)	$MgCl_2O_4$[l]	
β-$Mg_2(OH)_3Cl$	2.57	2.06(2×), 2.08(2×), 2.14	1.94(–)	$MgClO_5$[l]	*ASR* 1953, *B3*, 400
	2.59(2×)	2.07(2×), 2.10(2×)	1.87(–)	$MgCl_2O_4$[l]	
$Mg_2(PO_4)Cl$	2.623	1.996, 2.055, 2.081, 2.096, 2.422	1.83(1)	$MgClO_5$[l]	*AC* 1972, *B28*, 3461
	2.422, 2.660	1.990, 2.056, 2.086, 2.382	1.89(1)	$MgCl_2O_4$[l]	
$TiMgCl_6(CH_3COOC_2H_5)_4$	2.512, 2.543	2.022, 2.035, 2.042, 2.053	2.08(1)	$MgCl_2O_4$[l]	Ref. 34
$TiMgCl_5(OOCCH_2Cl)\cdot(ClCH_2COOC_2H_5)_3$	2.500, 2.515	2.002, 2.016, 2.021, 2.049	2.16(1)	$MgCl_2O_4$[l]	Ref. 35
$[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$	2.472, 2.495, 2.506, 2.508	2.04, 2.11	2.01(2)	$MgCl_4O_2$[l]	*JOC* 1971, *5*, 28
α-$MgCl_2$	2.517(6×)	–	1.91(3)	$MgCl_6$[l]	*AC* 1963, *16*, 846
$KMgCl_3$	2.496(2×), 2.501(2×), 2.502(2×)	–	1.98(1)	$MgCl_6$[l]	*JCP* 1966, *45*, 4652
K_2MgCl_4	2.470(4×), 2.492(2×)	–	2.07(1)	$MgCl_6$[l]	*CJC* 1975, *53*, 114 *JCP* 1975, *63*, 3054
$RbMgCl_3$	2.48(6×)	–	2.05(–)	$MgCl_6$[l]	*RCM* 1975, *12*, 466
$CsMgCl_3$	2.496(6×)	–	1.99(1)	$MgCl_6$[l]	*JCP* 1970, *52*, 815

[a] Calculated with the following parameter sets (d_1 and N of $s = (d/d_1)^{-N}$): (2.010, 5.10) and (1.62, 4.40) for Mg–Cl and Mg–O, respectively. [b] In valence units. Standard deviations were estimated for the shortest d value of the set. [c] *Cf.* Table II. [d] Electron Diffraction data. [e] *Ab-initio* calculations. [f] Disorder: 400 °C. [g] Estimated value. [h] $D_{\infty h}$ symmetry. [i] Triangular. [j] Tetrahedron. [k] Trigonal to square bipyramid. [l] Octahedron.

complex. Discrete $MgCl_4^{2-}$ tetrahedral species are also present in $(NH_4)_2MgCl_4$ [9] and Cs_3MgCl_5 [10] (isomorphous with Cs_3CoCl_5 [11]) and have also been reported in the gas complex $MgCl_2 \cdot 3AlCl_3$ [12]. Apparently, only the more polarizable ions, such as Cs^+ and $(NEt_4)^+$, are able to stabilize tetrahedral species in the solid phase. No evidence for $MgCl_3^-$ species is available [8, 13], although polynuclear $Mg_2Cl_6^-$ species appear to have been observed [8].

Among the crystal data for mixed (Cl, O) ligand sets of Table I those referring to boracite are worth considering. Whereas the cubic modification [14] has been described by a point-atom structure for the borate framework with space–time averaging of Mg and Cl within the cavities, in orthorhombic boracite [15] the nature of the cavities in the borate framework is claimed to be responsible for the unusual coordination. We notice that the cation–oxygen distances are quite normal but that the cation–chlorine distances are anomalously long. This is particularly evident if we compare the boracite data with structural results for MgO_4Cl_2 units with similar Mg–O bond lengths, such as $TiMgCl_6(CH_3COOC_2H_5)_4$, $TiMgCl_5(OOCCH_2Cl)$, $(ClCH_2COOC_2H_5)_3$ and β-$Mg_2(OH)_3Cl$. Our considerations indicate the need for a careful re-examination of boracite, with special regard to Mg and Cl positions.

As may be seen from Table I, except from boracite structures, Mg–Cl bonds usually range from about 2.2 to 2.65 Å (0.60 to 0.25 v.u.). Even longer bonds (2.79 Å) are reported for five coordinate Mg to three coordinate Cl in $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$ [16]. The exceptional ability of the chlorine atom to bridge two or more atoms undoubtedly contributes to the wide range in bond distances and greatly expands the structural possibilities for organomagnesium chlorides.

In compounds with mixed (Cl, O) coordination spheres the Mg–O bonds are usually confined to the range of 1.99–2.10 Å (0.40–0.30 v.u.), whereas Mg–Cl distances cover the range of 2.42–2.66 Å (0.40–0.25 v.u.); two-coordinate Cl bridge distances more often correspond to about 2.50 Å (0.33 v.u.). The latter distance is similar to that found in $[MgCl_3]_\infty^{n-}$ chains, as in $CsMgCl_3$ [17]. Apart from the discrepancies discussed above, calculated valence sums for mixed (Cl, O) ligand sets around magnesium conform to the expected value, with a mean deviation of 4.0%.

Magnesium–Oxygen Bonding

As rather few all-(Cl) ligand sets are available (*cf.* Table I), as opposed to mixed (Cl, O) environments, confidence in the (d_1, N) parameter set for Mg–O bonding was found to be highly desirable. Previous parameter values of (1.622, 4.290) have been reported by Brown and Shannon (hereinafter B & S) [18]. Using an extensive subset of the structural data of Table II, it appears that other parameter sets minimize the deviations from ideal values (Fig. 1). As a result, the values indicated by B & S would appear to be quite arbitrary. Closer examination of the problem shows that the presently available data set reflects the very strong tendency to form octahedral bonds and accounts for the findings of Fig. 1.

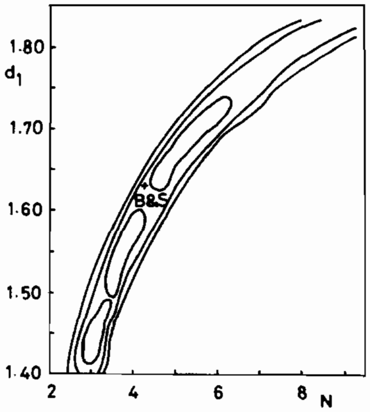

Fig. 1. Parameter values (d_1, N) minimizing discrepancy to ideal valence value of Mg in oxomagnesium environments. B & S refers to findings of ref. 18.

Magnesium shows a range of oxygen coordinations from eight in pyrope garnet to four in melilite. Amongst the reference structures with regular oxygen coordinations, which are primarily to be used to derive the (d_1, N) parameter values, we noticed a considerable spread in bond distances. If we deliberately ignore spinel structures due to the uncertainty in the degree of inversion, and other compounds with cation substitution such as (Ca, Na, K) (Mg, Al)Si_2O_7, the only remaining data referring to tetrahedral structures then relate to $Mg[PO_2(OC_2H_5)_2]_2$ [19], K_6MgO_4 [20] and Na_2MgSiO_4 [21]. Surprisingly, in these compounds the average Mg–O distances differ widely, namely from 1.901(5) to 2.01(2) Å.

As to trigonal bipyramidal and related structures, no regular coordinations are known, as expected. The average bond lengths range from 2.005–2.042 Å for such compounds of Table II.

In almost-regular octahedral coordinations the mean Mg–O distance is usually between 2.057 and 2.076 Å (average 2.065 Å) but with some noticeable exceptions of underbonding, as in MgO, $MgCl_2 \cdot 10H_2O \cdot 2(CH_2)_6N_4$, $Mg(OH)_2$ and Mg_6MnO_8, with bond distances exceeding 2.10 Å. Similarly, in other structures, such as $[Mg(POCl_3)_6][Ti_2Cl_{10}] \cdot 2POCl_3$ and $[Mg(POCl_3)_6][TiCl_6]$, very low mean bond length values have been reported (2.037(9) and 2.019(9) Å, respectively). The overall octahedral Mg–O distance amounts to 2.064 Å, in fair agreement with the previously reported values of

TABLE II. Bond Strengths and Bond Lengths in Magnesium–Oxygen Coordination Spheres.

Compound[a]	Mg–O Bond Distances (Å)	σ_d (Å)	Σ_s[b,c]	Structural Unit	Reference[d]
MgO(g)	[1.672]	–	0.87(–)	MgO^e	Ref. 25
MgO(g)	1.749	–	0.71(–)	MgO^e	*JCP* 1966, *45*, 3226
$MgAl_2O_4$(n)	1.94(4×)	–	1.81(–)	MgO_4^f	*SPC* 1968, *13*, 599
$MgAl_2O_4$(n)	1.917(4×)	–	1.91(–)	MgO_4^f	*AC* 1952, *5*, 684
MgV_2O_4(n)	1.965(4×)	–	1.71(–)	MgO_4^f	*ZaC* 1969, *369*, 306
Mg_2VO_4 (i)	1.98(4×)	0.06	1.65(24)	MgO_4^f	*ZaC* 1947, *253*, 194
K_6MgO_4	1.99, 2.03(3×)	0.02	1.52(2)	MgO_4^f	*AC* 1974, *B30*, 2667
Na_2MgSiO_4	1.924, 1.949, 1.956, 1.960	0.001	1.78(1)	MgO_4^f	Ref. 21
$Mg[PO_2(OC_2H_5)_2]_2$	1.897(2×), 1.905(2×)	0.005	1.98(1)	MgO_4^f	*AC* 1973, *B29*, 1398
(Ca, Na, K)(Mg, Al)Si_2O_7	1.876(4×)	0.015	2.09(8)	MgO_4^f	*AM* 1953, *38*, 643
$[Mg(Me_3PO)_5](ClO_4)_2$	1.94, 2.00, 2.02, 2.04, 2.06	0.02	1.94(2)	MgO_5^g	*AC* 1978, *B34*, 2837
$[Mg(Me_3AsO)_5](ClO_4)_2$	1.920, 2.010, 2.017, 2.030, 2.049	0.010	1.97(1)	MgO_5^g	*IC* 1976, *15*, 303
$(Mg_{0.9}Fe_{0.1})Al_3SiBO_9$	1.970(2×), 2.040, 2.054, 2.176	0.006	1.83(1)	MgO_5^h	*AC* 1968, *B24*, 1518
$Mg_3(PO_4)_2$	1.961, 1.965, 2.012, 2.063, 2.142	0.007	1.88(1)	MgO_5	*ACSc* 1968, *22*, 1466
	2.034(2×), 2.150(2×), 2.179(2×)	0.007	1.85(1)	MgO_6^i	
α-$Mg_2P_2O_7$	2.059, 2.073, 2.084, 2.135, 2.137, 2.142	0.010	1.90(1)	MgO_6^i	*AC* 1967, *23*, 289
	1.985, 2.024, 2.037, 2.054, 2.120, 3.350	0.010	1.81(1)	MgO_5	
α-$Mg_2P_2O_7$	2.00, 2.07, 2.09, 2.11, 2.12, 2.15	0.02	1.97(2)	MgO_6^i	*BAcP* 1967, *15*, 53
	1.94, 2.01, 2.02, 2.06, 2.11	0.02	1.88(2)	MgO_5	
β-$Mg_2P_2O_7$	2.02(2×), 2.05(2×), 2.15(2×)	–	2.04(–)	MgO_6^i	*CJC* 1965, *43*, 1139
	2.02(2×), 2.05(2×), 2.15(2×)	–	2.04(–)	MgO_6^i	
β-$Mg_2P_2O_7$	2.00(2×), 2.03(2×), 2.11(2×)	–	2.16(–)	MgO_6^i	*RC* 1961, *35*, 31
$MgHPO_4 \cdot 3H_2O$	2.015, 2.062, 2.068, 2.106, 2.107, 2.109	0.002	2.01(1)	$MgO_3(OH_2)_3^i$	*AC* 1979, *B35*, 2514
$Mg(PO_2Cl_2)_2(POCl_3)_2$	1.993, 2.003, 2.010, 2.019, 2.122, 2.146	0.013	2.16(1)	MgO_6^i	*ACSc* 1970, *24*, 59
$MgCl_2 \cdot 6H_2O$	2.056(3×), 2.062(3×)	0.001	2.09(1)	$Mg(OH_2)_6^i$	*AC* 1969, *B25*, S118
$MgCl_2 \cdot 12H_2O$	2.059(2×), 2.061(2×), 2.065(2×)	0.007	2.08(1)	$Mg(OH_2)_6^i$	*AC* 1966, *20*, 875
$MgCl_2 \cdot 10H_2O \cdot 2(CH_2)_6N_4$	2.10(6×)	–	1.92(–)	$Mg(OH_2)_6^i$	*RS* 1966, *36*, 466
$MgCl_2 \cdot C_6H_{12}O_6 \cdot 4H_2O$	2.032, 2.038, 2.051, 2.079, 2.094, 2.143	0.004	2.04(1)	$Mg(OH)_2(OH_2)_4^i$	*AC* 1973, *B29*, 1677
$MgCl_2 \cdot C_4H_8O_2 \cdot 6H_2O$	2.057(2×), 2.060(2×), 2.073(2×)	0.004	2.07(1)	$Mg(OH_2)_6^i$	*JSCD* 1976, 1786
$MgCl_2 \cdot 6CH_3OH$	2.07(6×)	0.01	2.04(3)	MgO_6^i	*AC* 1978, *B34*, 432
$MgBr_2 \cdot 6CH_3OH$	2.07(6×)	0.01	2.04(3)	MgO_6^i	*AC* 1978, *B34*, 432
$MgBr_2 \cdot 4THF \cdot 2H_2O$	2.042(2×), 2.117(2×), 2.164(2×)	0.007	1.90(2)	$Mg(OH_2)_6^i$	*JACS* 1977, *99*, 5289
MgO	2.1058(6×)	–	1.89(–)	MgO_6^i	*JACeS* 1966, *49*, 152
$Mg(OH)_2$	2.102(6×)	0.003	1.91(1)	$Mg(OH)_6^i$	*NJB* 1967, 137
$MgCu_2O_3$	2.02(2×), 2.16(2×), 2.17(2×)	–	1.87(–)	MgO_6^i	*ZaC* 1975, *418*, 116
$Mg_2V_2O_7$	1.992, 2.050, 2.062, 2.083, 2.089, 2.246	0.004	2.00(1)	MgO_6^i	*AC* 1974, *B30*, 2491
	2.049, 2.081, 2.095, 2.104, 2.157, 2.221	0.004	1.86(1)	MgO_6^i	

Mg_3TeO_6	2.022, 2.049, 2.124, 2.130, 2.159, 2.278	0.004	1.84(1)	MgO_6^{i}	*AC* 1971, *B27*, 815
Mg_6MnO_8	2.095(2×), 2.102(4×)	–	1.92(–)	MgO_6^{i}	*AC* 1954, *7*, 246
$MgSO_4$	2.01(2×), 2.09(4×)	–	2.08(–)	MgO_6^{i}	*AC* 1958, *11*, 686
$MgSO_4 \cdot H_2O$	2.024(2×), 2.045(2×), 2.180(2×)	0.005	2.01(1)	$MgO_4(OH_2)_2^{i}$	*BSCF* 1970, 4243
$MgSO_4 \cdot 4H_2O$	2.052, 2.072(2×), 2.082, 2.083, 2.087	0.006	2.02(1)	$MgO_2(OH)_4^{i}$	*AC* 1964, *17*, 863
$MgSO_4 \cdot 6H_2O$	2.044(2×), 2.046(2×), 2.080(2×)	0.003	2.10(1)	$Mg(OH_2)_6^{i}$	*AC* 1964, *17*, 235
	2.054(2×), 2.059(2×), 2.083(2×)	0.003	2.06(1)	$Mg(OH_2)_6^{i}$	
$MgSO_4 \cdot 7H_2O$	2.045, 2.046, 2.054, 2.055, 2.092, 2.099	0.004	2.06(1)	$Mg(OH_2)_6^{i}$	*AC* 1964, *17*, 1361
$Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$	2.051(2×), 2.073(2×), 2.083(2×)	0.005	2.05(1)	$Mg(OH_2)_6^{i}$	*ZK* 1962, *117*, 334
$Mg(NO_3)_2 \cdot 6H_2O$	2.053(2×), 2.061(2×), 2.063(2×)	0.006	2.09(1)	$Mg(OH_2)_6^{i}$	*AC* 1969, *B25*, 354
$MgSO_4 \cdot 1/3Mg(OH)_2 \cdot 1/3H_2O$	2.081(4×), 2.087(2×)	0.002	1.99(1)	$MgO_4(OH)_2^{i}$	*AC* 1981, *B37*, 1001
$[Mg(H_2O)_6][MgC_6H_5O_7(H_2O)]_2 \cdot 2H_2O$	2.019, 2.031, 2.072, 2.077, 2.081, 2.118	0.001	2.06(1)	$MgO_4(OH)(OH)_2^{i}$	*AC* 1965, *18*, 1004
	2.061(2×), 2.080(2×), 2.081(2×)	0.001	2.02(1)	$Mg(OH_2)_6^{i}$	
$Mg(OH_2)_6S_2O_3$	2.068(4×), 2.115(2×)	0.013	1.98(4)	$Mg(OH_2)_6^{i}$	*AC* 1962, *15*, 227
$Cd_2MgCl_6 \cdot 12H_2O$	2.052(4×), 2.081(2×)	0.004	2.07(1)	$Mg(OH_2)_6$	*AC* 1982, *B38*, 237
$MgTh(NO_3)_6 \cdot 8H_2O$	2.09(2×), 2.12(2×), 2.16(2×)	0.05	1.83(18)	$Mg(OH_2)_6^{i}$	*AC* 1965, *18*, 698
$Mg_3Ce_2(NO_3)_{12} \cdot 24H_2O$	2.058(6×)	0.005	2.09(2)	$Mg(OH_2)_6^{i}$	*JCP* 1963, *39*, 2881
	2.056(2×), 2.058(4×)	0.005	2.10(2)	$Mg(OH_2)_6^{i}$	
$[Mg(OH_2)_6][H_3IO_6]$	2.06(2×), 2.08, 2.11, 2.13, 2.15	0.05	1.93(8)	$Mg(OH_2)_6^{i}$	*AC* 1970, *B26*, 1075
MgOMPA	2.061(6×)	0.002	2.08(1)	MgO_6^{i}	*IC* 1970, *9*, 151
$Mg[B_3O_3(OH)_5](H_2O)_4 \cdot H_2O$	2.007, 2.023, 2.080, 2.083, 2.113, 2.137	0.002	2.04(1)	$Mg(OH)_2(OH_2)_4^{i}$	*AC* 1974, *B30*, 2194
$MgZnEDTA \cdot 6H_2O$	⟨2.08⟩(6×)	0.05	2.00(18)	$Mg(OH_2)_6^{i}$	*ZSK* 1972, *13*, 738
$Mg_2EDTA \cdot 9H_2O$	2.047(2×), 2.051(2×), 2.087(2×)	0.001	2.08(1)	$Mg(OH_2)_6^{i}$	*ICA* 1977, *24*, 13
$MgH_2EDTA \cdot 6H_2O$	2.053(2×), 2.087(4×)	0.001	2.02(1)	$Mg(OH_2)_6^{i}$	*IC* 1973, *12*, 1754
$[Mg(POCl_3)_6][Ti_2Cl_{10}] \cdot 2POCl_3$	2.005(2×), 2.049(2×), 2.056(2×)	0.009	2.19(2)	MgO_6^{i}	Ref. 36
$[Mg(POCl_3)_6][TiCl_6]$	2.011(2×), 2.019(2×), 2.028(2×)	0.009	2.28(2)	MgO_6^{i}	Ref. 36
$[Mg(POCl_2C_6H_5)_6][TiCl_5POCl_2C_6H_5]_2$	2.012(2×), 2.053(2×), 2.073(2×)	0.008	2.15(2)	MgO_6^{i}	Ref. 36
	2.026(2×), 2.063(2×), 2.077(2×)	0.008	2.11(2)	MgO_6^{i}	
$[Mg(Me_3PO)_5H_2O](ClO_4)_2$	2.05(2×), 2.08, 2.09, 2.11, 2.15	0.03	1.95(2)	$MgO_5(OH_2)^{i}$	*AC* 1978, *B34*, 2835
$MgNH_4PO_4 \cdot 6H_2O$	2.046(2×), 2.069(2×), 2.094, 2.108	0.003	2.03(1)	$Mg(OH_2)_6^{i}$	*AC* 1970, *B26*, 1429
$[Mg(OH_2)_4(OPO_2OH)_2][NH_4]_2$	2.05(2×), 2.08, 2.09, 2.11, 2.15	0.03	1.97(5)	$MgO_2(OH_2)_4^{i}$	*AC* 1972, *B28*, 683
$Mg(C_{11}H_{12}ON_2)_6(ClO_4)_2$	2.059(6×)	0.006	2.09(3)	MgO_6^{i}	*AC* 1967, *23*, 1000
$Mg(C_6H_5SO_3)_2 \cdot 6H_2O$	⟨2.04⟩(6×)	–	2.18(–)	$Mg(OH_2)_6^{i}$	*AC* 1948, *1*, 88
$Mg(C_5H_7O_2)_2 \cdot 2H_2O$	2.027(2×), 2.040(2×), 2.148(2×)	0.004	2.05(1)	$MgO_4(OH_2)_2^{i}$	*AC* 1967, *22*, 316
$Mg_3Al_2(SiO_4)_3$	2.198(4×), 2.343(4×)	–	1.83(–)	MgO_8^{j}	*AM* 1965, *50*, 2023

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[a] H_4EDTA, ethylenediamine-tetracetic acid; OMPA, octamethylpyrophosphoramide. THF, tetrahydrofuran; (i) inverse spinel; (n) normal spinel. [b] Calculated with the parameter set $s = (d/1.62)^{-4.40}$. [c] In valence units. Standard deviations were estimated for the shortest d-value of the set. [d] Notation as in ref. 37. Additional abbreviations: *BAcP*, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*; *CJC*, *Can. J. Chem.*; *JCSD*, *J. Chem. Soc. Dalton*: *RC*, *Roczn. Chem.*: *RCM*, *Rev. Chim. Minér.* [e] Linear. [f] Tetrahedral. [g] Square pyramidal. [h] Intermediate between trigonal bipyramid and tetragonal pyramid. [i] Octahedral. [j] Dodecahedral.

2.085 Å [22] and 2.058 Å (for hexaquocations) [23] or the range of mean Mg–$(OH_2)_6$ distances in octahedral environments, namely 2.062–2.083 Å [24]. While the large spread of the mean values is surprising, we have noticed only a small difference in the dimensions of MgO_6 and $Mg(OH_2)_6$ coordinations, with average Mg–O bond length differences not exceeding 0.004 Å.

Other reference points for the Mg–O bond strength–bond length curve are eventually MgO(*g*) with quoted bond distances of 1.672 and 1.749 Å [25, 26] for s = 2.0 v.u. and the dodecahedral environment in $Mg_3Al_2(SiO_4)_3$ (d, 2.270 Å, s = 0.25 v.u.). Although magnesium also occasionally adopts a seven coordination, as in $Na_2[(H_2O)MgEDTA]\cdot 5H_2O$ [27] and $Mg_2EDTA\cdot 9H_2O$ [28], the available data are beyond the scope of the present paper.

After considerable trial-and-error, giving high weight to the atypical coordinations we have adopted (d_1, N) values of (1.62, 4.40) as being most appropriate to describe Mg–O bond lengths of 1.896, 2.079 and 2.220 Å with bond strengths of 0.5, 0.33 and 0.25 v.u., respectively. For reasons outlined above, this parameter set does not minimize the overall discrepancy with the ideal valence sums. As may be noticed, our parameters are close to those established by B & S using a less extensive data set.

Bond strength–bond length relations may be used in a simple way to calculate the degree of inversion of spinel structures thus being complementary to other methods [29–31]. Apart from some spinel structures (with inaccurately determined degrees of inversion), the most remarkable deviation from the expected Mg–O valence sum is observed for K_6MgO_4 [20]. This structure contains an unusual antiprismatic unit composed of K atoms. Our analysis casts further doubt on the correctness of one of the proposed oxomagnesium environments in α-$Mg_2P_2O_7$ [32] with an anomalous Mg–O distance of 3.35 Å. The oxygen atom concerned shows the highest mean-square vibrations of the set of oxygen atoms and may be erroneously located. Apart from the discrepancies in valence sums mentioned above, the average variation amounts to 4% with a maximum of 7%.

As may be seen from the data presented (Tables I and II) Mg–O bond distances vary over a wide range, namely from 1.87–2.42 Å with bond strengths of 0.53–0.17 v.u., respectively. The cation is usually found in a (highly distorted) octahedral coordination (*cf.* also ref. 33) and only occasionally in a different environment up to eightfold. The existence of four-coordinated magnesium ions is strongly limited for all-oxygen coordinations and is almost inexistent for all-chlorine environments. This limits the accuracy in the derivation of bond strength – bond length relationships.

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