

Bond-Valence–Bond-Length Parameters for Bonds Between Cations and Sulfur

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Abstract

Parameters for calculating bond valences from bond lengths are given for bonds to sulfur from 55 different cations. Most are reported for the first time.

Introduction

Although the correlation between bond valences (bond strengths) and bond lengths has been known for over 30 years (Pauling, 1947) there have been only a few systematic tables of such correlations published (see for example Brown & Shannon, 1973; Allmann, 1975; Brown & Wu, 1976; Zachariassen, 1978) and most of these have been concerned only with bonds to oxygen. The present work reports parameters R_0 and N to be used in calculating the bond valence, S , to sulfur in the expression $S = (R/R_0)^{-N}$ where R is the bond length in Å. The parameters cover the bond types most frequently found.

Procedure

The procedure used was that described by Brown & Shannon (1973). Compounds were chosen whose structures have been published since 1969 and in which the sulfur behaves as an oxygen-ion analogue, *i.e.* we have excluded those structures which contain S–S and metal–metal bonds. Also excluded were structures which were poorly determined or in which there was disorder. As a matter of convenience structures in which the cation also formed bonds with anions other than sulfur were also omitted. The compounds used and the valence sums at each cation are given in the Appendix.†

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Table 1. Parameters for calculating bond valences (S) from bond lengths (R) in the expression $S = (R/R_0)^{-N}$

Cation forming bond to S (oxidation state)	R_0 (Å)	N	Number of cations used (coordination numbers in parentheses)	Remarks			
*C	1.82	5.0					
*N	1.69	5.6					
*Na Mg Al *Si	2.133	5.38	2(4), 5(5), 25(6), 5(7) 2(4) 3(4), 2(5) 14(4)	valence may be too high			
*P					15(4)		
K					9	2(4), 1(5), 9(6), 4(7), 6(8), 1(10)	poor fit
Ca					(5)	1(7), 3(8)	
Sc	2.25	(5.5)	3(6)				
V(5)	2.217	5.6	1(4)				
V(4)					1(6), 7(8)		
V(3)					5(6)		
*Cr(3)	2.10	5.2	20(6) 3(6)				
Cr(2)					1(6)		
Mn(4)	2.19	6.15	3(6)				
Mn(3)					1(3), 5(4), 5(6)		
*Mn(2)					11(3), 3(6)		
*Fe(3)	2.13	5.35	11(3), 3(6)				
*Fe(2)	2.064	5.35	5(3), 12(6)	Hoggins & Steinfink (1976)			
	2.141	6.81					
*Co(3)	1.98	(5)	11(6)				
Ni(2)	1.893	4.4	7(4), 3(5), 1(6), 1(7)				
Cu(2)	2.095	7.15	4(4), 1(6)				
*Cu(1)	1.978	8.2	1(2), 5(3), 37(4)				
Zn(2)	2.08	(5)	7(4)				
Ga(3)	2.18	6.2	9(4), 1(6)				
*Ge(4)	2.205	8	44(4), 2(6)				
As(5)	2.28	4.3	4(4) 50(4), 1(5), 1(6)	N chosen to fit both oxidation states			
*As(3)							
Rb(1)	2.59	7	3(6), 5(7), 2(8), 1(9), 1(10)				
Zr(4)	2.36	5.2	2(6), 1(8)				
Mo(6)	2.320	6.6		Bart and Ragaini (1980)			
Mo(5)	2.224	5.6					
Mo(4)	2.201	5.0					
Mo(3)	2.167	5.8					
*Pd(2)	2.08	(6)	20(4)				
*Ag(1)	2.08	5.8	1(2), 8(3), 37(4), 4(6)				
*Cd(2)	2.27	6	14(4), 1(6)				
*In(3)	2.34	6.2	14(4), 1(5), 28(6)				
*Sn(4)	2.39	5.8	21(4), 3(5), 8(6)				
Sn(2)	2.38	5.8	1(4), 1(5), 3(6)				
Sb(5)	2.45	6	3(4) 19(3), 10(4), 11(5), 6(6), 1(8)				
*Sb(3)							
*Te(4)					4(3), 3(8)		
*Te(2)	2.37	5.7	2(2), 12(4)				
Ba	2.62	6.0	7(6), 4(7), 23(8), 6(9), 1(10)	poor fit			
La(3)	2.541	6	2(7), 12(8), 3(9)				
Yb(3)	2.26	4	3(6), 1(7)				
Lu(3)	2.26	4	5(6), 1(7)				
Ta(5)	2.35	5.8	1(6), 1(7), 2(8)				
Pt(2)	2.06	(6)	11(4)				
Hg(2)	2.23	5	17(4), 1(5)				
*Tl(1)	2.22	5	7(6), 4(7), 2(8), 2(9), 1(10)				
*Pb(2)	2.565	7.9	6(6), 12(7), 9(8), 1(9)				
Bi(3)	2.6	8	1(3), 1(4), 24(6), 21(7), 1(8)				

The bond-valence parameters are listed in Table 1. Not all are equally reliable. The best sets are those marked with an asterisk, those that are uncertain are enclosed in parentheses. The value of N is not easy to determine accurately and in cases where the cation only occurs with a narrow range of bond lengths it can hardly be determined at all. However, since the value of R_0 , which in principle can be much more accurately determined, depends critically on the particular value of N used, any attempts to use a different value of N must be accompanied by a corresponding change in R_0 [see for example the two values given for Fe(2)].

For completeness Table 1 includes values for sulfur bonds that have been reported by other workers in addition to the 51 reported here for the first time.

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Etude Structurale des Hydroxysulfates de Cadmium. IV. Structure Cristalline de $\text{Cd}_8(\text{OH})_{12}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$

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Abstract

$\text{Cd}_8(\text{OH})_{12}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ is monoclinic, space group $C2/c$, with $a = 27.180$ (4), $b = 5.855$ (2), $c = 14.825$ (3) Å, $\beta = 124.96$ (3)°, $V = 1934$ Å³, $Z = 4$, $d_m = 4.51$, $d_x = 4.512$ Mg m⁻³. The structure has been solved from single-crystal data collected on a four-circle diffractometer by Patterson and Fourier syntheses. With anisotropic temperature factors, the final R value is 0.051 for 2174 independent observed reflexions; H atoms have not been located. The structure is constructed from CdO_6 octahedra, CdO_5 pyramids and sulphate tetrahedra sharing edges and corners. A discussion of the chemical formula is presented and the relation between cadmium hydroxysulfates and the brucite-type structure is reported.

Introduction

Les hydroxysels de métaux bivalents cristallisent fréquemment avec une structure en couche dérivant du type structural brucite. Une revue systématique de la chimie structurale des hydroxyhalogénures a été récemment décrite par Hulliger (1976). Dans un travail

précédent, Louër, Louër & Grandjean (1973) ont également montré qu'une substitution partielle des ions hydroxyle par un groupement plan oxygéné, tel que l'ion nitrate, est possible. Il a ainsi été proposé une classification cristallographique des hydroxynitrates de métaux bivalents présentant une structure en couche. Cette classification permet de prévoir les structures cristallines ainsi que les formulations chimiques dérivant du type brucite; de nombreux exemples confirment cette classification prévisionnelle. Après l'étude de la déformation du type structural brucite provoquée par la substitution des ions hydroxyle par des ions simples (halogènes), puis par des groupements plans (nitrate), il nous a semblé intéressant de procéder à la même analyse avec le groupement tridimensionnel SO_4 . Pour cela notre choix s'est porté sur la famille des hydroxysulfates de cadmium pour deux raisons: la structure de $\text{Cd}(\text{OH})_2 \cdot \beta$ est de type CdI_2 et quatre hydroxysulfates polycristallins sont mentionnés dans la littérature (Walter-Lévy, Groult & Visser, 1974a). Nous avons synthétisé des monocristaux de trois variétés α , β et γ de $\text{Cd}_2(\text{OH})_2\text{SO}_4$ et déterminé leur structure cristalline (Labarre, Louër, Louër & Grandjean, 1976a,b; Louër, Louër & Grandjean, 1982). L'objet de cet article est de décrire la structure cristalline de la quatrième phase qui