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The Distortion of the Hexagonal Close Packing of Oxygen Atoms in $Co(OH)_2$ Compared to Isotypic Brucite-Type Structures

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Summary. A refinement of the crystal structure of $Co(OH)_2$ (structure type brucite; $a = 3.186(1)$, $c = 4.653(1)$ Å; space group P$\bar{3}$m1) is the basis for crystal chemical considerations about distortions of the MeO_6 octahedra and deviations of the lattice parameters ratio c/a from the ideal value of $(8/3)^{1/2} \cong 1.633$ for the theoretical model of a hexagonal close packing of oxygen atoms. The MeO_6 octahedra in the structure type brucite are generally compressed parallel to the threefold axis, and the ratio c/a is lowered to values between ~1.35 and ~1.52. The influence on these deviations caused by the hydrogen bonds connecting the layers of edge-sharing MeO_6 octahedra is discussed (donor-acceptor distances: ~3.16 Å).

Keywords. $Co(OH)_2$; Hydrothermal syntheses; Crystal structure; Crystal chemistry; Hexagonal close packing.

Die Verzerrung der hexagonal dichtesten Packung von Sauerstoffatomen in $Co(OH)_2$ verglichen mit isotypen Strukturen des Brucit-Typs

Zusammenfassung. Eine Verfeinerung der Kristallstruktur des $Co(OH)_2$ (Strukturtyp Brucit $a = 3.186(1)$, $c = 4.653(1)$ Å; Raumgruppe P$\bar{3}$m1) wird als Basis für kristallchemische Überlegungen bezüglich der Verzerrung der MeO_6-Oktaeder und Abweichungen des Verhältnisses c/a der Gitterparameter vom idealen Wert von $(8/3)^{1/2} \cong 1.633$ für ein theoretisches Modell einer hexagonal dichtesten Packung der Sauerstoffatome herangezogen. Die MeO_6-Oktaeder sind im Strukturtyp Brucit generell parallel zur dreizähligen Achse gestaucht, und das Verhältnis c/a ist zu Werten zwischen ~1.35 und ~1.52 verringert. Der Einfluß auf diese Abweichungen, hervorgerufen durch Wasserstoffbrücken, welche die aus kantenverknüpften MeO_6-Oktaedern gebildeten Schichten verbinden, wird diskutiert (Donor-Akzeptor-Abstand: ~3.16 Å).

Introduction

Hydrothermal synthesis experiments in the system *Me*-KOH-H_2O (*Me* = divalent transition element) with elementary cobalt yielded excellent tabular crystals of $Co(OH)_2$. The atomic arrangement of $Co(OH)_2$ represents a member of the brucite type structure family (brucite = $Mg(OH)_2$; space group: P$\bar{3}$m1, point symmetry $\bar{3}$2/m, for the Co atom in the CoO_6 octahedron) [1].

There are two remarkable features in this structure type worth to be discussed: a) the compression of the *Me*O_6 octahedra parallel to the threefold axis, and b) the diminuation of the ration c/a (= ratio of the lattice constants) from the ideal value of $(8/3)^{1/2} \cong 1.633$ for a hexagonal close packing arrangement of oxygen atoms. These two points are investigated by comparison of data for $Co(OH)_2$ to data from literature determined in the last three decades for brucite type structures. Further, the compilation of these structures allows a geometrical examination of the unusually long hydrogen bonds between the layers of edge-sharing *Me*O_6 octahedra.

The overall geometry of CoO_x polyhedra with divalent cobalt in inorganic compounds has been analyzed in an extensive study [2]. All investigated CoO_6 octahedra are more or less distorted compared to the highest possible point symmetry $4/m\bar{3}2/m$ for an octahedron, but none is elongated exactly along a fourfold axis as predicted by crystal field theory [3]. One possible point symmetry for these octahedra, $\bar{3}2/m$, has been determined in only two crystal structures out of a number of 72 including 112 CoO_6 octahedra. The two representatives are the structures of γ-Co_2SiO_4 [4] and $K_2Co(SeO_3)_2$ [5]. However, the structure of γ-Co_2SiO_4 is a representative of a spinel type structure with statistic occupations of both the four and the six coordinated atom positions by silicon and cobalt atoms; therefore it was excluded from crystal chemical considerations.

Results and Discussion

The size and the distortion of the *Me*O_6 octahedra in the structure type under discussion are controlled by the absolute values of the lattice parameters and the z-parameter of the oxygen atom. Whereas, according to the point symmetry of the *Me* atom ($\bar{3}2/m$), the six *Me*-O distances are equidistant with a length according to the absolute values of the lattice constants, the distortion of these octahedra correlate with the above mentioned z-parameter. Three angles are restricted by symmetry to 180°, and six angles between the central *Me* atom and neighbouring O atoms are of equal size. These angles occur between the central *Me* atom and the oxygens with equal z-parameters and between oxygens with parameters z and $-z$, respectively. The symmetry of the central *Me* atom requires a sum of 180° for the acute and obtuse O-*Me*-O’-angles.

The oxygen atoms in the structure type brucite are arranged in a more or less distorted hexagonal close packing (ideal parameters: $c/a = (8/3)^{1/2}$ $z = 0.25$) [6]. The correlation between the ratio c/a and variable z-parameters of the oxygens for ideal undistorted *Me*O_6 octahedra (with O-*Me*-O angles of 180° (3x) and 90° (12x)) is linear. Therefore, the distortion of the *Me*O_6 polyhedra can be characterized by these two parameters. In Fig. 1 this correlation is shown, and the distortion type of the *Me*O_6 octahedra, compressed or elongated, can be deduced directly. This figure enables a clear determination of the deformation of any *Me*O_6 octahedron not only in brucite type structures, but also in the whole structure family with a hexagonal close packing of halogen or chalcogen atoms, mentioned under cadmium iodide-like structures in the literature.

Some characteristic parameters for brucite type compounds are compiled in Table 1. The differences between these parameters recalculated from the individual

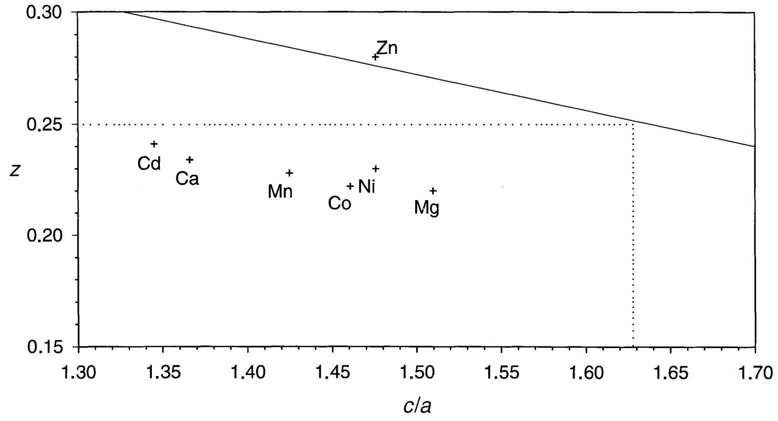

Fig. 1. Ratio *c*/*a* (*c*,*a*: lattice parameters in Å) in correlation with the *z*-parameter (fractional number of the lattice parameter *c*) of the oxygen atom in brucite type structures; the straight line is calculated for undistorted octahedra and indicates the transition from elongated to compressed octahedra; the dots marked with Mg, Ca, Mn, Co, Ni, Zn, and Cd represent the individual values for the different brucite type structures (data in part from literature)

Table 1. Characteristic parameters (min and max value) for the MeO_6 octahedra in brucite type compounds; some of these values are calculated from original data in the literature as well as from data given in Ref. [9]; (*): one structure determination only, (**): this work; MeO_6: six equidistant O atom neighbour distances (Å); bond angle distortion $\sigma^2_{oct} = 1/11\Sigma_i(\Theta_i - 90)^2$; O-Me-O: acute angle in the individual MeO_6 octahedron (°). *c*/*a*: ratio of the lattice parameters

	Mg [10–17]		Ca [18–21]		Mn [22, 23]	
	min	max	min	max	min	max
MeO_6	2.062	2.099	2.363	2.370	2.196	2.208
σ^2_{oct}	50.592	63.508	77.709	82.002	62.845	74.791
O-Me-O	81.65	84.78	81.33	81.56	81.72	82.41
c/*a*	1.502	1.518	1.363	1.368	1.425	1.425

	Co [24]		Ni [25–27]		Zn [7]	Cd [28]
	min	max (**)	min	max	(*)	(*)
MeO_6	2.097	2.116	2.073	2.136	2.268	2.315
σ^2_{oct}	64.680	75.515	13.904	28.152	0.241	71.222
O-Me-O	81.68	82.30	82.13	86.43	89.53	81.92
c/*a*	1.460	1.462	1.469	1.483	1.476	1.345

structure determinations are more or less within the limiting e.s.d. values. Therefore, only the mean values for the ratio *c*/*a* and the *z*-parameter (oxygen atom) are given in Fig. 1, marked with the individual atomic symbol. For the given structure of $Co(OH)_2$ with a *c*/*a* ratio of ~1.46045 the theoretical value for the *z*-parameter of the oxygen atom leading to an undistorted CoO_6 octahedron will be 0.27955.

It is common to brucite type structures that the MeO_6 octahedra are compressed parallel to the threefold axis. An exception is respresented by the structure of $Zn(OH)_2$ calculated from X-ray diffraction powder data with an elongated ZnO_6 octahedron [7]. At the author's opinion, this structure needs a reinvestigation, for there is no plausible explanation for this unusual elongation of the ZnO_6 octahedron (*e.g. Jahn-Teller* distortion).

In the special case of the $Co(OH)_2$ structure, the six Co-O distances with 2.116(1) Å compare well to the mean value of 2.1115(621) Å calculated for 672 individual Co–O distances in octahedral coordination [2], and the value $\sigma^2_{oct} = 64.68$ for the CoO_6 octahedra compressed parallel to the threefold axis (bond angle distortion $\sigma^2_{oct} = 1/11\Sigma_i(\theta_i - 90)^2$) [8] is within the common range from 0.4 to 221.0 (the mean value calculated for the already mentioned 112 octahedra is 53.2 [2]).

Whereas the CoO_6 octahedron in $Co(OH)_2$ is compressed parallel to the threefold axis, in $K_2Co(SeO_3)_2$ [5] this octahedron (same point symmetry) is elongated parallel to this axis, the six Co–O distances are 2.142(1) Å, the distortion parameter is 45.5, and the O–Co–O angles measure 96.46° (6x) and 83.54° (6x). The different deformation of the octahedra under discussion seems to be induced by the special structure type and not by an uneven electron distribution in the 3d orbitals of the cobalt atom.

The compression of the MeO_6 octahedra in brucite type structures effects an enlargement of the distance between the oxygen atoms at positions (1/3, 2/3, z) and (2/3, 1/3, $-z$). In $Co(OH)_2$, the distance between these above mentioned oxygen atoms, each of them donor and acceptor atom of a hydrogen bond, measures 3.155(3) Å (cf. Table 3). On one side, this donor-acceptor distance is rather long compared to distances in normal hydrogen bonds in the range from 2.5 to 3.0 Å. On the other side, the shortest H–H distance in an ordered arrangement measures

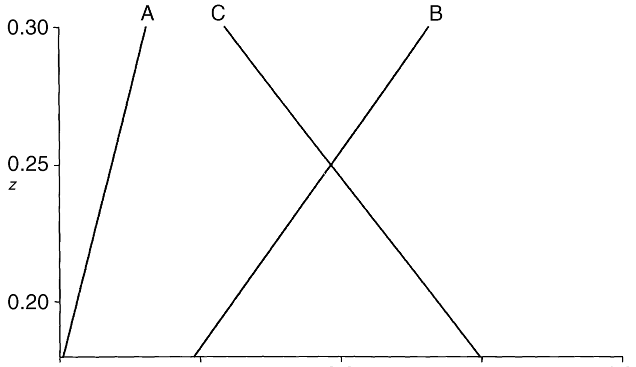

Fig. 2. Variations of bond distances (in Å) as a function of the z-parameter of the oxygen atom calculated for the title compound (lattice parameters: $a = 3.186$, $c = 4.653$ Å); A: Co–O, B: O–O distances in the CoO_6 octahedron inclined to the threefold axis, C: O–O distance between the layers formed by the edge-sharing CoO_6 octahedra (possible hydrogen bridges); the O–O distances parallel to (001) are identical to the lattice parameter a (3.186 Å)

1.95(6) Å. This is the distance between hydrogen atoms bonded to opposite CoO_6 layers.

The dependency of three characteristic distances in the structure of $Co(OH)_2$ are given in Fig. 2. The theoretical variation of the six Co–O distances as well as the effects of these variations upon the intra- and inter octahedral O–O distances are shown. It can be seen that a small enlargement of the six Co–O distances causes a pronounced shortening of the distance between the donor and acceptor oxygen atoms involved in the formation of the hydrogen bond.

Conclusions

To the author's opinion, the resumé of the crystal chemical considerations with regard to the structure type brucite is that the hydrogen bond system between the layers of edge-sharing MeO_6 octahedra is the predominant reason for the compression of the mentioned octrahedra and the diminuation of the ratio c/a. A compilation of halogen and chalcogen compounds crystallizing in the same structure type [29] exhibits less deviations of both above mentioned parameters from the ideal values. The distances between the atoms forming the hexagonal close packing arrangement in these compounds are more or less the results of the (covalent?) atomic radii. The results are a ratio c/a near to 1.63 and a z-parameter of ~0.25 for the atoms in the hexagonal close packing arrangement.

Experimental

Crystals of $Co(OH)_2$ were prepared by hydrothermal reactions of elementary cobalt and concentrated aqueous KOH solutions in ‚Teflon' coated steel vessels at 200°C. The capacity of the vessels was ~50 cm^3 and the reaction time one week followed by a cooling period of 12 h. $Co(OH)_2$ forms deep red hexagonal crystals up to 0.2×1.0 mm. A selected single crystal was chosen for X-ray data collection at room temperature. Crystal data, structure refinement parameters, and results are compiled in Tables 2 and 3.

Table 2. Summary of crystal data, X-ray data collection, and structure refinement of $Co(OH)_2$

$a = 3.186(1)$ Å	Crystal size: 0.20 ×0.20×0.04 mm^3
$b = 4.653(1)$ Å	μ: 96.4 cm^{-1}
$c/a = 1.460$	2 ϑ/ω- scan mode, scan width 1.50^0 + (α_1–α_2 dispersion)
$V = 40.91$ Å^3	3 standard reflections, interval 120 min
$Z = 1$	Range of data: $2^0 < 2\vartheta < 100^0$
$F(000) = 45$	Measured reflections: 923 ($\pm h,k,\pm l$)
$\rho_{(calc)} = 3.773\ g \cdot cm^{-3}$	Unique reflections: 189; $R_{int} = 0.059$
Space group: P$\bar{3}$m1 (No 164)	Reflections with $F_o > 2\sigma(F_o)$: 189
$R(F)$, $F_o > 2\sigma(F_o) = 0.029$	Empirical absorption correction: ψ- scan data
$R(F)$, all data $= 0.033$	Transmission factors from 0.19 to 0.51
$R_w = 0.030$; $w = (\sigma(F_o))-2$	Final difference *Fourier* summation: 1.35 to −1.13 e/Å^3
Variable parameters: 8	Stoe AED 2 four cicle diffractometer
Max $\Delta/\sigma < 0.001$	Mo X-ray tube, graphite monochromator

Table 3. Atomic coordinates, anisotropic displacement parameters (hydrogen isotropic) defined as $\exp(-2\pi^2\Sigma_i\Sigma_j U_{ij}h_ih_j\mathbf{a}_i^*\mathbf{a}_j^*)(\text{Å}^2 \times 10^4)$, selected interatomic distances (Å), and bond angles (^{0}) for $Co(OH)_2$. e.s.d. values in parentheses

	z	U_{11}/U_{iso}	U_{33}
Co on 1(a); (0, 0, 0; *etc.*)	–	75(1)	116(2)
O on 2(d); (1/3, 2/3, z; etc.)	0.2246(4)	110(3)	108(6)
H on 2(d); (1/3, 2/3, *z*; *etc.*)	0.429(19)	399(280)	–
	CoO_6 octahedron	H coordination	
Co–O: 2.116(1); 6x	O–Co–O': 97.70(5); 6x	H–O: 0.95(9)	O–H–O': 131.2(27)
O–O': 3.186(3); 6x	82.30(5); 6x	H–O': 2.45(6)	
2.785(3); 6x	180.0(−); 3x	O–O': 3.155(3)	

References

[1] Pertlik F (1999) Z Kristallogr [Suppl] **16**: 53

[2] Wildner M (1992) Z Kristallogr **202**: 51

[3] Burns RG (1970) Mineralogical Applications of Crystal Field Theory. University Press, London Cambridge

[4] Morimoto N, Tokonami M, Watanabe M, Koto K (1974) Amer Mineral **59**: 475

[5] Wildner M (1992) Acta Cryst **C48**: 410

[6] Zemann J (1966) Kristallchemie. de Gruyter, Berlin

[7] Baneeva MI, Popova SV (1969) Geokhimiya 1014

[8] Fleet ME (1976) Min Mag **40**: 531

[9] ICSD / Retrieve (1997) Gmelin Institute, FIZ Karlsruhe

[10] Isetti G (1965) Period Mineral **34**: 327

[11] Zigan F, Rothbauer R (1967) N Jb Miner Mh 137

[12] Parise JB, Leinenweber K, Weidner DJ, Tan K, Von Dreele RB (1994) Amer Mineral **79**: 193

[13] Partin DE, O'Keeffe M, von Dreele RB (1994) Journ Appl Cryst **27**: 581

[14] Catti M, Ferraris G, Hull S, Pavese A (1995) Phys Chem Mineral **22**: 200

[15] Winkler B, Milman V, Hennion B, Payne MC, Lee MH, Lin JS (1995) Phys Chem Mineral **22**: 461

[16] Cerny R, Valvoda V, Chládek M (1995) Journ Appl Cryst **28**: 247

[17] Desgranges L, Calvarin G, Chevrier G (1996) Acta Cryst **B52**: 82

[18] Busing WR, Levy HA (1957) Journ Chem Phys **26**: 563

[19] Petch HE (1961) Acta Cryst **14**: 950

[20] Chaix-Pluchery O, Pannetier J, Bouillot J, Niepce JC (1987) Journ Solid State Chem **67**: 225

[21] Desgranges L, Grebille D, Calvarin G, Chevrier G, Floquet N, Niepce JC (1993) Acta Cryst **B49**: 812

[22] Noerlund-Christensen A (1965) Acta Chem Scand **19**: 1765

[23] Christensen AN, Ollivier G (1972) Solid State Comm **10**: 609

[24] Lotmar W, Feitknecht W (1936) Z Kristallogr **93**: 368

[25] Cairns RW, Ott E (1933) Journ Amer Chem Soc **55**: 527

[26] Szytula A, Murasik A, Balanda M (1971) Phys Stat Sol **B43**: 125

[27] Greaves C, Thomas MA (1986) Acta Cryst **B42**: 51

[28] Bertrand G, Dusausoy Y (1970) Compt Rend Acad Sci C **270**: 612

[29] Wyckoff RWG (1963) Crystal Structures, vol 1. Wiley, New York London Sydney

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