

$\text{Zn} - \text{O} - \text{H}$

(соединения)

$\text{Zn}(\text{OH})_2$

Bp-3684-VI

1956

Venkateswarlu K;
et al.

"Z. phys. Chem"

1956, 212, N3-4, 195-8.

Potential...



$\text{ZnO}_2 \cdot 0,5 \cdot \text{H}_2\text{O}$ Bp-730-V 1959.

Vannerberg N

(Vi; 70...0) Arkiv kemi, 1959,
14, N2, 107-113

И.К. спектры...

^{ZnO}
 $Zn(OH)_4^{2-}$ (vi) ~~Baum~~ 1965-
3144.vi

Fordeyce F. S., Baum R. L.,
J. Chem. Phys., 1965, 43, 43, 843-846 (aun)
Vibrational spectra of solutions of
zinc oxide in potassium hydroxide.

Pub Chem, 1966, 10 6144 W

1987

VI-4050

$\text{Vi}(\text{E-Zn}(\text{OH})_2, -\text{ZnOHCl}, \text{ZnOHF},$
 $\text{Zn}_5(\text{OH})_8\text{Cl}_2, \text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O})$

Stivastova O.K., Secco E.A.

Canad. J. Chem, 1967, 45, N6, 585-88.

Studies on metal hydroxg compounds. II.
Infrared spectra of zinc derivatives
 $\text{E-Zn}(\text{OH})_2, \text{ZnOHCl}, \text{ZnOHF}, \text{Zn}_5(\text{OH})_8\text{Cl}_2$ and
 $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}.$

RX., 1967, 195169

J

$ZnOHF$.
кросс. С;

$ZnOHdeg$. ~~885~~
1015 cm^{-1}

Внекросс. гег. кол.
группировок $F-Zn-OH$
L 885 cm^{-1}

Srinivasan D.K.,
Sesso E.A.

1967.

Canad. J. Chem., 1967, 45,
46, 585-588

Studies on metal
hydroxy compounds.

II Infrared spectra of zinc
derivatives $\beta Zn(OH)_2$, $\beta ZnOHCl$,
 $ZnOHF$, $Zn_5(OH)_8Cl_2$,
and $Zn_5(OH)_8Cl_2 \cdot H_2O$.

$Al(OH)_4^-$; $Zn(OH)_4^{2-}$; $Si(CH_3)_4$; $Ge(CH_3)_4$; $Sn(CH_3)_4$; $Pb(CH_3)_4$; $N(CH_3)_4$; $As(CH_3)_4$; $Sb(CH_3)_4$

(cur.
norm.)

1969

Derig J.R.; Nagarajan G., VI 7278

Monatsh. Chem., 1969, 100(6), 1948-59. (nem.)

Potential energy constants and mean amplitudes of vibration in some XY_4 molecules and ions with tetrahedral symmetry.

NO.

15

CA, 1970, 72, N14, 70815c

$M(H_2O)_6$ (ср. иосм.)

$M = Mg, Zn, Ni, Al$

9 6 15 1970

$\sqrt{17290}$

Ananthanarayanan V.,

J. Chem. Phys., 1970, 52, № 7, 3844-5 (англ.)

Force constants of octahedral $M(H_2O)_6$
complexes: $M = Mg, Zn, Ni, or Al$.

10 10

CA 1970, 72, N22, 1162.7DD

Zn-OH

1972

Opitz Ch., Dürken H.H.

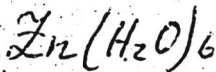
Энерг.
связи
природа
хим. св.

"Z. phys. Chem.", 1972, 249, №3-4,
154-160

● (см. Cu-OH, III)

40213.1847

Ph, Ch, TE



34457

1973

1722

Sanyal Nitish K., Dixit L., Subramanyam B.R. Force constants and mean amplitudes of vibration of some octahedral water complexes of Mg, Al, Ni and Zn.

"Indian J. Phys.", 1973, 47, N 10, 577-582

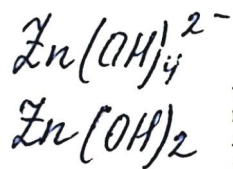
(см. $\text{Mg}(\text{H}_2\text{O})_6$; (англ.) III)

0044 БМК

024 025

ВИНИТИ

1980



8 Б46. Неэмпирическое исследование стереоэлектронных эффектов в модельных комплексах $\text{Zn}(\text{OH})_4^{2-}$ и $\text{Zn}(\text{OH})_2$. Lehn J. M., Wipff G., Demuynck J. An ab initio study of stereoelectronic effects in $\text{Zn}(\text{OH})_4^{2-}$ and $\text{Zn}(\text{OH})_2$ model complexes. «Chem. Phys. Lett.», 1980, 76, № 2, 344—346 (англ.)

Методом ССП МО ЛКАО с использованием базиса сгруппированных гауссовых орбиталей Zn (12s8p5d/5s-4p2d), O(8s4p/3s2p) и H(4s/2s) рассчитано электронное строение модельных комплексов $\text{Zn}(\text{OH})_4^{2-}$ (I) и $\text{Zn}(\text{OH})_2$ (II). Комплексы I и II рассматривались в конформациях с различными, фиксированными ориентациями связей OH. Для сравнения методом ССП МО ЛКАО проведены также расчеты стерео-электронных эффектов в комплексе $\text{Al}(\text{OH})_4^-$ и молекуле $\text{C}(\text{OH})_4$ в той же конформации, что и I. Оптимизация длин связей в $\text{Al}(\text{OH})_4^-$ и $\text{C}(\text{OH})_4$ проведена в миним. базисе ОСТ—3ГФ. Вычисленная энергия стабилизации I и II по отношению к разделенным фрагментам составила 1017 и 882 ккал/моль соотв. Хелатный эффект в I (энергия, требуемая для переориентации 4 лигандов

кв. мек.
расчет

X. 1981 n 8

ОН⁻ в правильную геометрию комплекса) составил 626 ккал/моль. Оптимизированные длины связей Zп—О в I и II показывают слабую конформац. зависимость. На основании данных проведенных расчетов сделан вывод, что стереоэлектронные эффекты, обусловленные ориентацией лигандов, слабы в соединениях X(ОН)₄ⁿ⁻

(X=Zп²⁺, Al³⁺), где связи являются ионными и длинными, по сравнению со стереоэлектронными эффектами в ковалентной тетраэдрич. молекуле С(ОН)₄.

И. А. Тополь

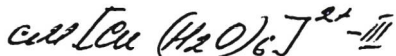


1980

Sano Mitsuru, et al.

Chem. Lett. 1980, (12),
1496-6.

кв. мех.
рас.
потенц.
ор-изм



Zn(OH)₂-ионы

1982

Mohan S.

Коричнев.
постоян.,
сильн. пост.

Indian J. Phys.,
1982, B56, N1, 23-28.

(сер. Ti O₄-ионы, III)

$Zn(H_2O)^{2+}$ Sano Mitsuru, 1983
Yamatera Hideo.

Ions and Mol. Solut Col-
lect. Invit. Pap. Sess. Lect.
металлов. and Microsymp. 6 Int.
период. Symp. Solute-Solute-Sol-
vent Interact. Linco, 4-10
July, 1982. Amsterdam
e.a., 1983, 109-116.
(cur. $Be(H_2O)^{2+}$; III)

$Zn(H_2O)_6^{2+}$ Sano Mitsuru, 1983
Yamatera Hidéo.

Trans. and Mol. Solut. Collect.
Invit. Pap. Sess. Lect. and
Microsymp. 6 Int. Symp.
Solute-Solute-Solvent Inte-
ract. Minoo, 4-10 July, 1982.
Amsterdam e.a., 1983,
109-116.

(c.c. Be $\bullet$ $(H_2O)_6^{2+}$; III)

$Zn^{n+} - OH_2 \dots OH_2$

1984

Барановский В.И.,
Сизова О.В. и др.

расчёт эк. общ. железа, 1984,
электр. 54, N 3, 507 - 511.
срукт.

(см. $M^{n+} - OH_2 \dots OH_2$; III)

$H_2O \cdots Zn^{2+}$. [om. 19654]

1984

Sauer J., Hobza P.,

Theor. chim. acta,
1984, 65, N4, 291-
- 302.

теор.
расч. и
геометр.
и
энергии

ZnDH.

22327

1985

Kauffman J. W.,
Mauje R. H., et al. Margrave

структур
в

J. Phys. Chem., 1985,

магнетизм 89, N 16, 3541-3547.

(ср. CuOH; III)

$Zn^{2+} - OH_2$

1986

11 Л224. Теоретические исследования интенсивностей ИК-полос в $Zn^{2+}OH_2$ и $Mg^{2+}OH_2$. Theoretical studies of I. R. intensities in $Zn^{2+}OH_2$ and $Mg^{2+}OH_2$. Her-
man-son Kersti, Lindgren Jan, Ågren Hans. «Mol. Phys.», 1986, 57, № 4, 857—863 (англ.)

Методами одно- и многоконфигурационного самосо-
гласованных полей рассчитаны интенсивности ИК-полос
валентных колебаний связей $O-H$ в комплексах
 $Mg^{2+}OH_2$ и $Zn^{2+}OH_2$, а также в изолированных молеку-
лах H_2O . В гармонич. приближении определены сило-
вые постоянные связей и ф-ции дипольного момента в
гидратированных ионах. Обнаружено увеличение равно-
весной длины связи $O-H$ молекул H_2O при их коорди-
нации с ионами Mg^{2+} и Zn^{2+} . Изложена модель гидра-
тирования этих ионов. Показано, что в комплексах
 Mg^{2+} орбитали иона и молекул H_2O не перекрываются,
тогда как в комплексах Zn^{2+} обобщенные орбитали
приобретают характер $3d-\sigma$. Сделан вывод о возмож-
ности образования водородных связей с участием этих
комплексов и 2 молекул H_2O в жидкой фазе. Библ. 21.

И. В. А.

(М.П.)

⊗(H)

ф. 1986, Л8, № 11

$Zn(OH)H^+$

[om. 31286]

1988

$Zn(OH)_2 H^+$ Tran Q., Kabellas N.S., et al.,

присут-
ствие
в

пламени,
масс-
спектр.

Can. J. Chem. 1988, 66, n 9,
2216-2218.

Ion chemistry of transition
metals in hydrocarbon
flates. ● I Cations of Fe,

Co, Ni, Cu and Zn.



ZnH⁺

[om. 3/286]

1988

присут-
ствие в
пламени,
масс-
спектр.

Tran Q., Kavelas N.S., et al.,

Can. J. Chem. 1988, 66, n 9,
2216-2218.

Ion chemistry of transition
metals in hydrocarbon
flates. I ● Cations of Fe, Co,

Ni, Cu and Zn.



$Zn(H_2O)_n^{+}$

(OM 33941)

1990

Rosi M., Bauschlicher ChW.,
72.

D_0 , γ . Chem. Phys., 1990, 92,
 ΔH_f . N3, 1876-1878.

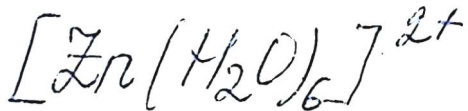
The binding energies of
one or two water molecules to the first transi-

transition metal positive ions
II.



$[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ 1992
Axelsson R., Peterson
L.F.M. et al;

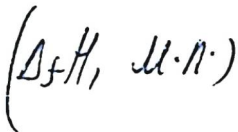
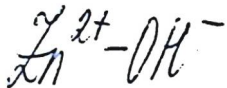
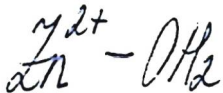
$2(\text{Zn}-\text{O})$, γ . Phys. Chem. 1992,
ab initio 96 (26), 10773-9
param
(calc. $[\text{Ca} \bullet (\text{H}_2\text{O})_6]^{2+}$, III)



1992

Waizumi Kenji,
сорука. и Ohtaki Hitoshi
первый
свдзет, et al.
Chem. Lett. 1992,
мор. (8), 1489-92.
раерит. (сц. $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$; III)

1992



10 Д118. Параметризация полуэмпирического квантовохимического метода MINDO/3 для цинксодержащих соединений / Жанпеисов Н. У., Жидомиров Г. М. // Ж. структур. химии.— 1992.— 33, № 1.— С. 151—153

Предложена параметризация метода МЧПДП/3 для изучения геометрии и энергетики Zn-содержащих молекул. Получены значения энтальпии образования и потенциалы ионизации. Рассмотрена реакция образования комплексов катиона Zn^{2+} с рядом электронодонорных молекул и оценена энергия связи в комплексах $\text{Zn}^{2+} - \text{X}$, где $\text{X} = \text{OH}_2, \text{CO}_2, \text{SH}_2, \text{OH}^-, \text{SH}^-$.

□ (43)

Ф. 1992, N 10

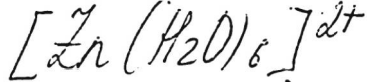
Zn-H-OH

1993

119: 234388k Nascent rotational and vibrational distributions in both products of the reaction zinc + water $\rightarrow$ zinc hydride + hydroxyl ($\text{Zn}(4^1\text{P}_1) + \text{H}_2\text{O} \rightarrow \text{ZnH}(\text{X } ^2\Sigma^+) + \text{OH}(\text{X } ^2\Pi)$). Kuwahara, Kazuya; Ikeda, Hiroyuki; Misaizu, Fuminori; Fuke, Kiyokazu (Dep. Energy Sci., Tokyo Inst. Technol., Tokyo, Japan 152). *J. Chem. Phys.* 1993, 99(4), 2715-22 (Eng). The reaction $\text{Zn}(4^1\text{P}_1) + \text{H}_2\text{O} \rightarrow \text{ZnH}(\text{X } ^2\Sigma^+) + \text{OH}(\text{X } ^2\Pi)$ was studied under thermal equil. conditions at 700 K. The nascent internal state distributions of both products ZnH and OH were detd. by using a pump-and-probe technique. The rotational distributions of ZnH and OH were both Boltzmann-like for their $v'' = 0$ vibrational levels. However, the rotational temperatures were significantly different-12,000 K for ZnH and 900 K for OH. ZnH was also vibrationally excited. The nascent vibrational distribution of ZnH was detd. to be obsd. such a nonstatistical energy partitioning is explained by considering a short-lived Zn-H-OH. intermediate in a nonlinear geometry.

Описана -
реакция
реакция.

C. A. 1993, 119, N22

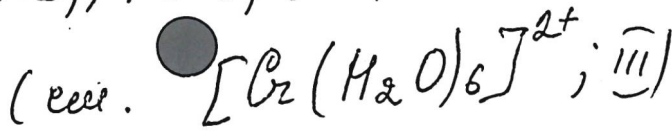


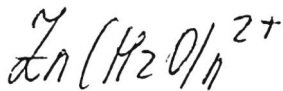
1993.

Waiizumi K., Ohtaki H. et al.

теорет.
расчет
высульты,
До

Comput. Aided Innovation
New Mater. 2 Proc. Int. Conf.
Exhib. Comput. Appl. Mater.
Mol. Sci. Eng, 2nd 1992 (Pub.
1993), Pt 1, 861-4.





1994

$n=1,2$

Akesson, Lalf; Pettersson, Lars E.M.

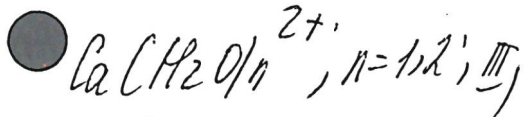
структур.
параметр., Chem. Phys., 1994, 184 (1-3),

жесткие
связи,

теорет.

расчет.

(all:



KZnOH

[Om. 38046.]

1995

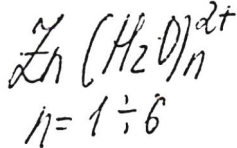
Greene T.M., Andrews L., et al.,
J. Am. Chem. Soc., 1995,

117, 8180 - 8187.

uk

8

sample



структур.,
термод. гут.
характер.,
спектр.,
теор. расчет.

125: 151552g Ab Initio Study of the Structures, Energetics, and Spectra of Aquazinc(II). Lee, Sik; Kim, Jongseob; Park, Jong Keun; Kim, Kwang S. (Department of Chemistry and Center for Biofunctional Molecules, Pohang University of Science and Technology, Pohang, 790-784 S. Korea). *J. Phys. Chem.* 1996, 100(34), 14329-14338 (Eng). Using extensive ab initio calcns. including electron correlation, the authors have studied the structures, thermodyn. quantities, and spectra of hydrated zinc ions $[\text{Zn}(\text{H}_2\text{O})_n]^{2+}$ ($n = 1-6$). Various conformers for $n = n_1 + n_2$ (where n_1 and n_2 are the nos. of water mols. in the first and second hydration shells, resp.) were investigated along with their thermodyn. quantities. The entropy effect was found to be important for the stabilities. At 0 K, the most stable structures for $n = 5$ and 6 are $5 + 0$ and $6 + 0$, resp. However, at room temp., both $4 + 1$ and $5 + 0$ seem to be almost equally populated in the case of $n = 5$, while $6 + 0$ is the most populated in the case of $n = 6$. The predicted successive binding energies for the addn. of each water mol. to the zinc ion are reported. The vibrational frequency shifts, depending on the no. of water mols., were investigated along with the frequency characteristics, depending on the presence/absence of outer-shell water mols.

C. A. 1996, 125, N 12

1383
√F: ZnOH

P: 3

131:149998 Thermochemistry of ZnCl(g).
Hildenbrand, D. L.; Lau, K. H.; Ro J. W. (SRI
International, Menlo Park, CA 94025, USA). J. Chem.
Phys., 11 1337-1338 (English) 1999 The gaseous
species Zn, ZnCl, and ZnCl₂ were generated in an
effusion cell by reaction of Cl₂(g) with ZnO(s) near 1400
K, and were identified and monitored by mass spectrometry.
Equilibrium constants were evaluated for the gaseous reaction
ZnCl₂ = 2ZnCl from ion intensities measured over the

range 1336-1436 K used to derive the third law enthalpy change $\Delta H_{298}^{\circ} = 176 \text{ kJ mol}^{-1}$ and the dissociation energy $D_0^{\circ}(\text{ZnCl}) = 229 \pm 8 \text{ kJ mol}^{-1}$.

This result is in good agreement with an earlier value derived from equilibrium measurements made by monitoring the electronic spectrum of ZnCl(g) in equilibrium with gaseous Zn and ZnCl_2 . The results are useful in estimating the thermochemical properties of gaseous ZnOH and Zn(OH)_2 for chemical modeling applications.

Y999

J F: Zn(OH)_2

P: 3

131:149998 Thermochemistry of ZnCl(g) .
 Hildenbrand, D. L.; Lau, K. H.; Ro J. W. (SRI
International, Menlo Park, CA 94025, USA). J. Chem.
Phys., 11 1337-1338 (English) 1999 The gaseous
species Zn , ZnCl , and ZnCl_2 were generated in an
effusion cell by reaction of $\text{Cl}_2(\text{g})$ with ZnO(s) near 1400
K, and were identified and measured by mass spectrometry.
Equil. constants. were evaluated for the gaseous reaction +

$\text{ZnCl}_2 = 2\text{ZnCl}$ from ion intensities measured over the range 1336-1436 K used to derive the third law enthalpy change $\Delta H_{298}^\circ = 176 \text{ kJ mol}^{-1}$ and the dissocn. energy $D_0^\circ(\text{ZnCl}) = 229 \pm 8 \text{ kJ mol}^{-1}$.

This result is in good agreement with an earlier value derived from equil. measurements made by monitoring the electronic spectrum of ZnCl(g) in equ with gaseous Zn and ZnCl_2 . The results are useful in estg. the thermoche properties of gaseous ZnOH and Zn(OH)_2 for chem. modeling applications.

Zn-H₂O

(om. 40880)

2001

computer,
pressure
curve.

Grant D. Smith[†],
Richard Bell et al.,

J. Phys. Chem. 2001,

A105, 6806 - 6812.

A Density



Functional

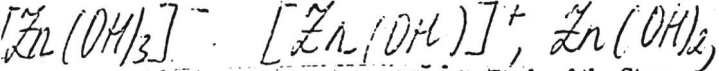
Theory Study of the Structure
and Energetics of Zincate
Complexes.

135: 171003p A Density Functional Theory Study of the Structure and Energetics of Zincate Complexes. Smith, Grant D.; Bell, Richard; Borodin, Oleg; Jaffe, Richard L. (Department of Materials Science and Engineering and Department of Chemical and Fuels Engineering, University of Utah, Salt Lake City, UT 84112 USA). *J. Phys. Chem. A* 2001, 105(26), 6506-6512 (Eng), American Chemical Society. The accuracy of the DFT/B3LYP method and the adequacy of the at. basis sets employed were established through investigation of the ionization potentials of Zn, the geometry and bond energy of ZnO, and the geometries and energies of selected Zn-OH and Zn-H₂O complexes. Our investigation revealed that the [Zn(OH)]⁺, Zn(OH)₂, and [Zn(OH)₃]⁻ zincate complexes are stable in the gas phase. However, we found that dissoed. [Zn(OH)₃]⁻ + OH⁻ is more stable than [Zn(OH)₄]²⁻ in the gas phase and that the gas-phase geometry of [Zn(OH)₄]²⁻ differs significantly from that gleaned from exptl. studies of aq. KOH/zincate solns. We also investigated zincate complexes involving mol. water and K⁺



(cmp-pa
u Hemevike)

cations in order to better understand the influence of condensed phase effects in aq. KOH solns. on the stability and geometry of the zincate complexes. We found that water does not significantly influence complex binding energies or the geometries of the underlying $[\text{Zn}(\text{OH})_n]^{2-n}$ complexes for $n = 1, 2$, and 3 . In contrast, for $[\text{Zn}(\text{OH})_4]^{2-}$ the introduction of water strongly stabilizes the complex relative to the gas phase and results in a structure close to that obsd. exptl. We were unable to find a stable $[\text{Zn}(\text{OH})_4(\text{H}_2\text{O})_2]^{2-}$ complex with a planar $\text{Zn}(\text{OH})_4$ arrangement and close $\text{Zn}-\text{H}_2\text{O}$ coordination, corresponding to a $\text{Zn}-\text{O}$ coordination of no. of six, as has been suggested in some interpretations of expts. We found through investigation of the $\text{K}_2\text{Zn}(\text{OH})_4$ complex that K^+ cations are also effective in engendering a structure that is very close to expt. and that K^+ ions are even more strongly bound to the $[\text{Zn}(\text{OH})_4]^{2-}$ complex than water. Finally, we detd. the structure and stability of $[\text{ZnO}(\text{OH})_2]^{2-}$ (oxodihydroxozincate), a species that has been hypothesized to be important in water-poor zincates solns.

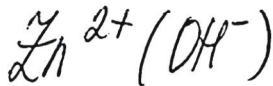


2001

135: 171003p A Density Functional Theory Study of the Structure and Energetics of Zincate Complexes. Smith, Grant D.; Bell, Richard; Borodin, Oleg; Jaffe, Richard L. (Department of Materials Science and Engineering and Department of Chemical and Fuels Engineering, University of Utah, Salt Lake City, UT 84112 USA). *J. Phys. Chem. A* 2001, 105(26), 6506-6512 (Eng), American Chemical Society. The accuracy of the DFT/B3LYP method and the adequacy of the at. basis sets employed were established through investigation of the ionization potentials of Zn, the geometry and bond energy of ZnO, and the geometries and energies of selected Zn-OH and Zn-H₂O complexes. Our investigation revealed that the [Zn(OH)]⁺, Zn(OH)₂, and [Zn(OH)₃]⁻ zincate complexes are stable in the gas phase. However, we found that dissoc. [Zn(OH)₃]⁻ + OH⁻ is more stable than [Zn(OH)₄]²⁻ in the gas phase and that the gas-phase geometry of [Zn(OH)₄]²⁻ differs significantly from that gleaned from exptl. studies of aq. KOH/zincate solns. We also investigated zincate complexes involving mol. water and K⁺

(смысл и значение)

cations in order to better understand the influence of condensed phase effects in aq. KOH solns. on the stability and geometry of the zincate complexes. We found that water does not significantly influence complex binding energies or the geometries of the underlying $[\text{Zn}(\text{OH})_n]^{2-n}$ complexes for $n = 1, 2$, and 3 . In contrast, for $[\text{Zn}(\text{OH})_4]^{2-}$ the introduction of water strongly stabilizes the complex relative to the gas phase and results in a structure close to that obsd. exptl. We were unable to find a stable $[\text{Zn}(\text{OH})_4(\text{H}_2\text{O})_2]^{2-}$ complex with a planar $\text{Zn}(\text{OH})_4$ arrangement and close $\text{Zn}-\text{H}_2\text{O}$ coordination, corresponding to a $\text{Zn}-\text{O}$ coordination of no. of six, as has been suggested in some interpretations of expts. We found through investigation of the $\text{K}_2\text{Zn}(\text{OH})_4$ complex that K^+ cations are also effective in engendering a structure that is very close to expt. and that K^+ ions are even more strongly bound to the $[\text{Zn}(\text{OH})_4]^{2-}$ complex than water. Finally, we detd. the structure and stability of $[\text{ZnO}(\text{OH})_2]^{2-}$ (oxodihydroxozincate), a species that has been hypothesized to be important in water-poor zincates solns.



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135: 247458p Interactions of Metal Ions with Water: Ab Initio Molecular Orbital Studies of Structure, Vibrational Frequencies, Charge Distributions, Bonding Enthalpies, and Deprotonation Enthalpies. 2. Monohydroxides. Trachtman, Mendel; Markham, George D.; Glusker, Jenny P.; George, Philip; Bock, Charles W. (Department of Chemistry, Philadelphia University, Philadelphia, PA 19144 USA). *Inorg. Chem.* 2001, 40(17), 4230-4241 (Eng), American Chemical Society. The formation and properties of a wide range of metal ion monohydroxides, $\text{M}^{n+}[\text{OH}^-]$, where $n = 1$ and 2, have been studied by ab initio MO calcs. at the MP2(FULL)/6-311++G**//MP2(FULL)/6-311++G** and CCSD(T)(FULL)/6-311++G**//MP2(FULL)/6-311++G** computational levels. The ions M^{n+} are from groups 1A, 2A, 3A, and 4A in the second, third, and fourth periods of the Periodic Table and from the first transition series. Geometrical parameters, vibrational frequencies, at. charge distributions, orbital occupancies, and bonding enthalpies are reported. The $\text{M}^{n+}-\text{O}$ distances are shorter in the hydroxides, than in the corresponding hydrates (published previously as Part 1, *Inorg. Chem.* 1998, 37, 4421-4431) due to a greater electrostatic interac-

α-βa, смпухм,
Di, ΔH₂₉₈,
неоп. рачем

(17)

tion in the hydroxides. The natural bond orbitals for most of the first-row transition metal ion hydroxides do not contain a formal metal-oxygen bonding orbital; nevertheless the at. charge distributions show that for both $n = 1$ and 2 a significant amt. of electron d. is consistently transferred from the hydroxide ion to the bound metal ion. Deprotonation enthalpies for the hydrates have been evaluated according to the simple dissocn. process, $M^{n+}[\text{OH}_2] \rightarrow M^{n+}[\text{OH}^-] + \text{H}^+$, and also via proton transfer to another water mol., $M^{n+}[\text{OH}_2] + \text{H}_2\text{O} \rightarrow M^{n+}[\text{OH}^-] + \text{H}_3\text{O}^+$. The drastic redn. in these deprotonation enthalpies as H_2O mols. are sequentially bonded in the first coordination shell of the metal ion (amounting to 71, 64, 85, and 91 kcal/mol for the bonding of six water mols. to Mg^{2+} , Ca^{2+} , Mn^{2+} , and Zn^{2+} , resp.) is found to be due to the greater decrease in the bonding enthalpies for the hydroxides relative to the hydrates. Proton transfer to bases other than water, for example side chain groups of certain amino acids, could more than offset the decrease in deprotonation energy due to the filling of the first coordination shell. Linear relationships have been found between the pK_a values for ionization of the Mg^{2+} ; Ca^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} .