multiple influences of the metal center, altered hybridization upon coordination, and any TIP influence moderates the substituent influence relative to an H substituent on C(4).

The trends for the ^1H NMR chemical shift differences are similar to those of the ^{13}C NMR experiments. The hydrogens at the remote 5-position and the 2-position are shifted downfield as a result of σ-electron polarization without effective π-backbonding. The protons at the adjacent position are subject to the same considerations as a methyl group substituted at C(4). Lavallee et al.[1] attribute the upfield shifts of α-protons in substituted pyridines complexed to CoA_5^{3+}, RhA_5^{3+}, and RuA_5^{2+} to a TIP effect ($A = NH_3$). Work with other 6-membered azines with RuA_5^{2+} and RhA_5^{3+} has been likewise interpreted.[11] These effects apparently are not applicable here since hydrogens at the 2-position, also adjacent to the cobalt center, are shifted downfield.

The trend at H(4) upon coordination of an imidazole can be rationalized by assuming that there are π bond order changes within the heterocycle and that these changes occur with rehybridization of the ring carbons. The substituents on the ring will then exhibit subsequent changes in electron density, leading to small upfield shifts at the 4-position and downfield shifts at the 5-position. The upfield shift in the adjacent position is apparently of small magnitude and does not cancel the downfield effect of σ-polarization.

Acknowledgment. R.E.S. and W.W.H. gratefully acknowledge NSF Grant CHE 8417751 for support. The X-ray diffraction system was supported in part by the NIH (Grant 1-S10-RR0238-01). Preliminary efforts toward synthesis of a suitable crystal for analysis by M. F. Hoq and structural work by G. Mott are acknowledged. Crystal data were collected by J. Mandel. Dr. F.-T. Lin assisted with the ^1H saturation–^{13}C decoupling studies.

Registry No. $[Co(NH_3)_5(4\text{-Meim})]Cl_3\cdot 2H_2O$, 103203-21-0; $[Co(NH_3)_5(2\text{-Meim})]^{3+}$, 89955-97-5; $[Co(NH_3)_5(4\text{-meim})]^{3+}$, 89955-98-6; $[Co(NH_3)_5(5\text{-Meim})]^{3+}$, 103302-00-7; $[Co(NH_3)_5(1\text{-Meim})]^{3+}$, 91209-43-7; $[Co(NH_3)_5(1,2\text{-Me}_2im)]^{3+}$, 91209-45-9; $[Co(NH_3)_5(1,4\text{-Me}_2im)]^{3+}$, 103203-22-1; $[Co(NH_3)_5(1,5\text{-Me}_2im)]^{3+}$, 103203-23-2; $[Co(NH_3)_5(2,5\text{-Me}_2im)]^{3+}$, 103203-24-3; imidazole, 288-32-4; 2-methylimidazole, 693-98-1; 4-methylimidazole, 822-36-6; 1-methylimidazole, 616-47-7; 1,2-dimethylimidazole, 1739-84-0; 1,4-dimethylimidazole, 6338-45-0; 1,5-dimethylimidazole, 10447-93-5; 2,4-dimethylimidazole, 930-62-1.

Supplementary Material Available: Table of anisotropic temperature factors (1 page). Ordering information is given on any current masthead page.

Contribution from the Department of Structural Studies, Research Laboratory for Inorganic Chemistry,
Hungarian Academy of Sciences, Budapest, H-1431 Hungary

Molecular Structures of Zinc Dichloride, Zinc Dibromide, and Zinc Diiodide from Electron Diffraction Reinvestigation

Magdolna Hargittai,* J. Tremmel, and I. Hargittai

Received November 13, 1985

The molecular structures of zinc dichloride, zinc dibromide, and zinc diiodide have been determined at approximately 656, 614, and 580 K, respectively, by gas-phase electron diffraction. The analysis was paralleled by spectroscopic calculations. When the consequences of perpendicular vibrations are accounted for, all molecules display linear configurations with the following bond lengths (r_g): Zn–Cl = 2.072 ± 0.004 Å, Zn–Br = 2.204 ± 0.005 Å, and Zn–I = 2.401 ± 0.005 Å.

Introduction

The present investigation of the molecular structure of zinc dihalides was initiated in order to augment our electron diffraction studies of first-row transition-metal dihalides, viz. VCl_2,[1] $CrCl_2$,[1] $MnCl_2$,[2] $MnBr_2$,[3] $FeCl_2$,[4,5] $FeBr_2$,[4] $CoCl_2$,[6] $CoBr_2$,[7] and $NiBr_2$.[8] The structure of $NiCl_2$ was determined in Professor Hedberg's laboratory.[9] Another investigation[10] is under way concerning the molecular structure of $CaCl_2$, $CaBr_2$, and CaI_2. While calcium is not a transition metal, this work is an extension of the above studies.

Determination of the structures of these apparently simple symmetric molecules is not always easy. The temperatures required for their volatilization (800–1300 K)[1-8] may lead to reaction with nozzle material or to the formation of dimers.[1,3,4,7] Also, these high temperatures excite large-amplitude bending vibrations that make determination of the equilibrium symmetries difficult. Mass spectrometric control and optimization of the electron diffraction experimental conditions have considerably facilitated these studies.[11]

The structures of $ZnCl_2$, $ZnBr_2$, and ZnI_2 were studied[12] by electron diffraction nearly 30 years ago, but the authors were not able to determine with certainty whether or not the equilibrium configuration of the molecules was linear. Improvements in the method, which include use of spectroscopic data, now permit more accurate analyses of such structures. Since the equilibrium configuration of the molecules is an important question, the structures have been reinvestigated by making use of spectroscopic data that have become available in the meantime.[13,14]

Experimental Section

For all three compounds commercial samples were used. The electron diffraction patterns were recorded in our modified EG-100A apparatus[15] with a nozzle[16] of stainless steel. Quadrupole mass spectrometric measurements under the conditions of the electron diffraction experiments revealed no detectable amounts of dimeric species. Some of the electron diffraction experimental conditions are summarized in Table I. Other experimental conditions and data processing were the same as in the other studies of the series. Listings of total electron diffraction intensities are available as supplementary material. The electron scattering factors for

---

(1) Hargittai, M.; Dorofeeva, O. V.; Tremmel, J. *Inorg. Chem.* **1985**, *24*, 3963.
(2) Hargittai, I.; Tremmel, J.; Schultz, Gy. *J. Mol. Struct.* **1975**, *26*, 116.
(3) Hargittai, M.; Hargittai, I.; Tremmel, J. *Chem. Phys. Lett.* **1981**, *83*, 207.
(4) Vajda, E.; Tremmel, J.; Hargittai, I. *J. Mol. Struct.* **1978**, *44*, 101.
(5) Hargittai, M.; Hargittai, I. *J. Mol. Spectrosc.* **1984**, *108*, 155.
(6) Tremmel, J.; Ivanov, A. A.; Schultz, Gy.; Hargittai, I.; Cyvin, S. J.; Eriksson, A. *Chem. Phys. Lett.* **1973**, *23*, 533.
(7) Hargittai, M.; Dorofeeva, O. V.; Tremmel, J. *Inorg. Chem.* **1985**, *24*, 245.
(8) Molnár, Zs.; Schultz, Gy.; Tremmel, J.; Hargittai, I. *Acta Chim. Acad. Sci. Hung.* **1975**, *86*, 223.
(9) Eddy, L. Dissertation, Oregon State University, Corvallis, OR, 1973.
(10) Hargittai, M.; Vajda, E.; Brunvoll, J.; Tremmel, J.; Hargittai, I., to be submitted for publication in *Inorg. Chem.*
(11) Hargittai, I.; Bohátka, S.; Tremmel, J.; Berecz, I. *HSI, Hung. Sci. Instrum.* **1980**, *50*, 51.
(12) Akishin, A. P.; Spiridonov, V. P. *Kristallografiya* **1957**, *2*, 475.
(13) Loewenschuss, A.; Givan, A. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, *82*, 69.
(14) Givan, A.; Loewenschuss, A. *J. Mol. Struct.* **1978**, *48*, 325.
(15) Hargittai, I.; Tremmel, J.; Kolonits, M. *HSI, Hung. Sci. Instrum.* **1980**, *50*, 31.
(16) Tremmel, J.; Hargittai, I. *J. Phys. E* **1985**, *18*, 148.

0020-1669/86/1325-3163$01.50/0

Table I. Experimental Conditions

	$ZnCl_2$		$ZnBr_2$		ZnI_2	
nozzle temp, K	656	656	614	614	580	580
camera ranges, cm	50	19	50	19	50	19
no. of plates[a] used in anal.	4	5	4	4	5	5
data intervals, $Å^{-1}$	2.50–14.00	9.50–32.50	2.25–14.00	9.25–32.25	2.50–14.00	9.75–33.00
data steps, $Å^{-1}$	0.125	0.25	0.125	0.25	0.125	0.25

[a] Kodak electron image plates.

Table II. Molecular Parameters of ZnX_2 (X = Cl, Br, I) from Electron Diffraction Least-Squares Analysis (Estimated Total Errors[a] Given as Error Limits)

parameter[b]	$ZnCl_2$	$ZnBr_2$	ZnI_2
r_g(Zn–X), Å	2.072 ± 0.004	2.204 ± 0.005	2.401 ± 0.005
l(Zn–X), Å	0.062 ± 0.001	0.061 ± 0.002	0.074 ± 0.002
$\varkappa$(Zn–X), $Å^3$[c]	$9.4 \times 10^{-6} \pm 1.8 \times 10^{-6}$	$5.5 \times 10^{-6} \pm 2.2 \times 10^{-6}$	$2.09 \times 10^{-5} \pm 4.9 \times 10^{-6}$
r_g(X···X), Å	4.115 ± 0.010	4.370 ± 0.010	4.753 ± 0.010
l(X···X), Å	0.088 ± 0.003	0.094 ± 0.003	0.109 ± 0.004
$\varkappa$(X···X), Å[c]	$2.55 \times 10^{-5} \pm 2.79 \times 10^{-5}$	$1.66 \times 10^{-5} \pm 2.66 \times 10^{-5}$	$1.83 \times 10^{-5} \pm 3.35 \times 10^{-5}$
δ_g, Å[d]	0.029 ± 0.006	0.038 ± 0.006	0.049 ± 0.006
r(Zn–X), Å[e]	2.05 ± 0.02	2.21 ± 0.02	2.38 ± 0.02

[a] They include an experimental systematic error estimated to be 0.2%. See: Hargittai, M.; Hargittai, I. *J. Chem. Phys.* **1973**, *63*, 2335. [b] The parameter r_g is related to r_a, directly determined in the analysis, by the expression $r_g \approx r_a + l^2/r_a$. [c] $\varkappa$ is an asymmetry parameter in the expression of electron-scattering molecular intensities and can be related to l and the Morse constant a as $\varkappa = al^4/6$. [d] δ is the shrinkage, viz. $2r$(Zn–X) – r(X···X). [e] From earlier work.[12]

Table III. Vibrational Frequencies[a] and Valence Force Constants of Zinc Dihalides after Loewenschuss and Givan[13]

parameter	$ZnCl_2$	$ZnBr_2$	ZnI_2
ν_1, cm^{-1}	355.5	223.4	163.1
ν_2, cm^{-1}	100.3	71.0	61.0
ν_3, cm^{-1}	503.5	400.3	342.5
f_r, mdyn $Å^{-1}$	2.59	2.27	1.893[b]
f_{rr}, mdyn $Å^{-1}$	0.05	0.08	0.096[b]
f_α, mdyn $Å^{-1}$	0.0504	0.0344	0.0285[b]

[a] The frequencies given here correspond to the natural isotope abundances and were calculated by us from the frequencies measured by Loewenschuss and Givan.[13] [b] The valence force constants for ZnI_2 are from our normal-coordinate analysis for a linear model. Those given in ref 13 refer to a bent model with C_{2v} point group.

zinc were taken from the same sources[17] as those for the other elements.

The molecular intensities and radial distributions are shown in Figures 1 and 2.

Structure Analysis

The first and second distinct peaks on each of the experimental radial distributions in Figure 2 can be identified with the contributions of Zn–X and X···X interactions of ZnX_2 molecules, respectively. The corresponding apparent bond angles are about 164–167°. The refinement of structural parameters was carried out by a least-squares technique based on molecular intensities.[18] The results are summarized in Table II. The standard deviations from the least-squares refinement were very small as the parameters are well determined, and the estimated total errors originate mainly from the 0.2% experimental systematic error.

Normal-coordinate analysis and calculation of mean amplitudes of vibration accompanied the electron diffraction analysis. Experimental vibrational frequencies and force constants from Loewenschuss and Givan[13] were utilized (Table III). The calculations were done for both linear and bent molecular models, in two approximations.[19,20] The results are compared in Table IV together with results of similar calculations for l(X···X) of other metal dihalides. Note that for two of the molecules, viz. VCl_2 and $CrCl_2$, highly bent geometries were determined by electron diffraction.[1] It is seen that the calculated amplitudes are more sensitive to the assumption of molecular shape (linear vs. bent) than to the choice of the approximation used in the computation. Comparison of the experimental values with the calculated ones suggests linearity for the zinc dihalide molecules. However, in view of the results of the electron diffraction analysis presented in Table II, we have to address ourselves in more detail to the question of molecular shapes of these molecules. The *apparent* bond angles of about 165° would seem to be in good agreement with the intervals for angles given by Loewenschuss and Givan[13,14] as between 148 and 180°. Even when their actual calculations yielded bent

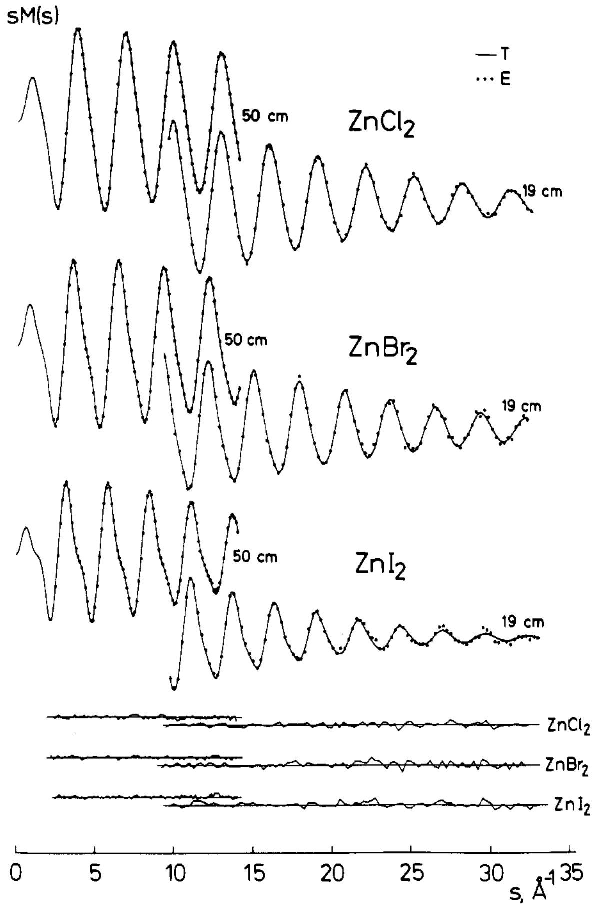

Figure 1. Experimental (E) and theoretical (T) molecular intensities and their differences for zinc dihalides.

---

(17) Bonham, R. A.; Schäfer, L. "International Tables for X-ray Crystallography"; Kynoch: Birmingham, England, 1974; Vol. IV, p 176 (coherent scattering factors). Tavard, C.; Nicolas, D.; Rouault, M. *J. Chim. Phys. Phys.-Chim. Biol.* **1967**, *64*, 540 (incoherent scattering factors).

(18) Andersen, B.; Seip, H. M.; Strand, T. G.; Stølevik, R. *Acta Chem. Scand.* **1969**, *23*, 3224.

(19) Cyvin, S. J. *Molecular Vibrations and Mean Square Amplitudes*; Elsevier: Amsterdam, 1968.

(20) Spiridonov, V. P.; Gershikov, A. G. *Chem. Phys. Lett.* **1981**, *77*, 36. Gershikov, A. G.; Spiridonov, V. P. *J. Mol. Struct.* **1981**, *75*, 291.

Table IV. Observed and Calculated l(X···X) Values (Å)

molecule	T, K	l_{exptl}	l_{calcd} for linear model[a] (1)[b]	l_{calcd} for linear model[a] (2)[c]	l_{calcd} for bent model[a] (1)[b]	l_{calcd} for bent model[a] (2)[c]
$CaCl_2$	1433	0.238 (14)	0.184	0.248	0.361	0.304
VCl_2	1333	0.230 (12)	0.120	0.146	0.241	0.273
$CrCl_2$	1168	0.256 (48)	0.121	0.140	0.280	0.307
$FeCl_2$	898	0.119 (8)	0.108	0.124	0.150	0.140
$ZnCl_2$	656	0.088 (2)	0.085	0.091	0.099	0.098
$CaBr_2$	1383	0.241 (7)	0.193	0.239	0.289	0.250
$ZnBr_2$	614	0.094 (2)	0.086	0.097	0.108	0.105
CaI_2	1183	0.262 (13)	0.195	0.267	0.319	0.293
ZnI_2	580	0.109 (2)	0.090	0.105	0.122	0.114

[a] In two approximations (see text). [b] Cf. ref 19. [c] Cf. ref 20.

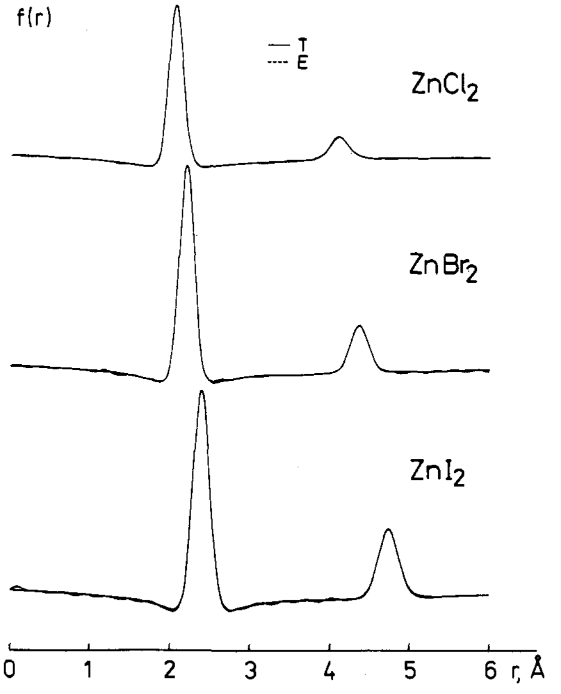

Figure 2. Experimental (E) and theoretical (T) radial distributions for zinc dihalides. The first and second peaks correspond to the Zn–X and X···X contributions, respectively.

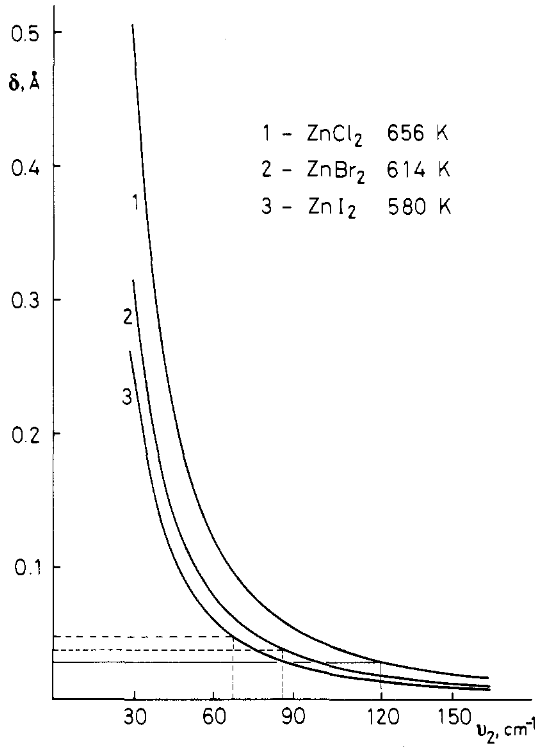

Figure 3. Calculated shrinkages (δ) as a function of the ν_2 bending frequencies of $ZnCl_2$, $ZnBr_2$, and ZnI_2. The experimental shrinkages and corresponding frequencies are indicated.

geometries of 162.5° for ZnI_2[13] and 162–169° for $ZnBr_2$,[14] the authors emphasized that the linear geometry was never outside the acceptable range of parameters for these molecules. At the same time, the electron diffraction results must be considered in conjunction with the spectroscopic data, especially with the bending vibrational frequency ν_2.

The electron diffraction results for molecular geometry is a set of average internuclear distances where averaging is over all molecular vibrations.[21] The symmetric triatomic molecules with low-frequency bending vibrations will appear to be bent in their effective electron diffraction structure, especially from high-temperature experiments, even if their equilibrium configuration is strictly linear. Lacking additional spectroscopic information, it would not even be possible to decide between a bent and a linear structure on the basis of the electron diffraction information alone. Supposing linearity for the equilibrium configuration, however, vibrational frequencies and, in particular, the bending frequency ν_2 may be estimated from electron diffraction data.[22] As illustrated in Figure 3, the following ν_2 values were obtained for zinc dihalide molecules with estimated uncertainties in parentheses:

	$ZnCl_2$	$ZnBr_2$	ZnI_2
ν_2, cm^{-1}	120 (15)	86 (8)	67 (4)

The uncertainties here reflect the uncertainties of the observed shrinkages, $\delta_g = 2r_g(\text{Zn–X}) - r_g(\text{X···X})$, and not the error of the (harmonic) approximations used. It has been noted[22] that the δ_g/ν_2 relationship is most suitable for estimating bending frequencies from electron diffraction shrinkages from high-temperature data and for very low ν_2 values where the relationship becomes especially steep. Among the above estimates, there is gradual improvement from $ZnCl_2$ toward ZnI_2, as regards agreement with the spectroscopic data.[13,14] The spectroscopic values from a matrix also have uncertainties. Sjøgren et al.[23] recently noted for metal trihalides that out-of-plane fundamentals are consistently at higher frequencies in the vapor than in Ar-matrix spectra. Agreement between our estimated and experimental ν_2 values within about 10–20 cm^{-1} is satisfactory. Noteworthy is that all electron diffraction ν_2 values for zinc halides are higher than the spectroscopic ones, making the assumption of linearity secure: even somewhat higher frequency bending vibrations would lead to the observed deviation from linearity in the apparent structures.

Examining the electron diffraction and spectroscopic information from the point of view of molecular shape, it is also instructive to convert the r_g thermal average distance into r_α distances,[21] which refer to the thermal average nuclear positions. The geometry in terms of r_α distances does not suffer from the consequences of perpendicular vibrations and should display linearity. The perpendicular vibrational corrections,[21] $K_{ij} = (\langle(\Delta x_{ij})^2\rangle + \langle(\Delta y_{ij})^2\rangle)/2r_{ij}$, where x_{ij} and y_{ij} are the perpendicular displacements and r_{ij} is the internuclear distance, were calculated[19] and are given here together with the calculated mean parallel vibrational amplitudes:

---

(21) See e.g.: Kuchitsu, K. In *Diffraction Studies on Non-Crystalline Substances*; Hargittai, I., Orville-Thomas, W. J., Eds.; Elsevier: Amsterdam, New York, 1981.

(22) Hargittai, I.; Tremmel, J. *Coord. Chem. Rev.* **1976**, *18*, 257.

(23) Sjøgren, C. E.; Klaeboe, P.; Rytter, E. *Spectrochim. Acta, Part A* **1984**, *40A*, 457.

	$ZnCl_2$	$ZnBr_2$	ZnI_2
l(Zn-X), Å	0.061	0.063	0.066
K(Zn-X), Å	0.022	0.028	0.029

On the basis of these K values, the r_α bond angles for all three molecules are 180°, well within experimental error, viz. 179.7, 179.6, and 179.8° for $ZnCl_2$, $ZnBr_2$, and ZnI_2 with estimated total errors, 2.0, 1.4, and 1.4°, respectively.

Discussion

The molecular parameters of zinc dihalides, ZnX_2, X = Cl, Br, I, are well determined. It is noteworthy that the early results of Akishin and Spiridonov[12] are in good agreement with the present work if error limits are considered (Table II).

Our electron diffraction data in conjunction with available spectroscopic information from Loewenschuss and Givan[13,14] reveal the unambiguously linear configuration of $ZnCl_2$, $ZnBr_2$, and ZnI_2 molecules. This is not surprising in view of the $[Ar]3d^{10}4s^2$ electronic configuration of zinc and is also in agreement with the discussion of MX_2 structures including ZnX_2 molecules by Drake and Rosenblatt[24] and by Coulson.[25]

The present results and those on analogous calcium derivatives[10] well augment structural information on bond lengths of first-row transition-metal dichlorides and dibromides. The mean chloride/bromide difference is 0.140 Å with a standard deviation of 0.015 Å.

Registry No. $ZnCl_2$, 7646-85-7; $ZnBr_2$, 7699-45-8; ZnI_2, 10139-47-6.

Supplementary Material Available: Listings of total electron diffraction intensities for two camera ranges (50 and 19 cm) for all three compounds (6 pages). Ordering information is given on any current masthead page.

(24) Drake, M. C.; Rosenblatt, G. M. *J. Electrochem. Soc.* **1979**, *126*, 1387.
(25) Coulson, C. A. *Isr. J. Chem.* **1973**, *11*, 683.

Contribution from the Departament de Química Inorgànica, Universitat Autònoma de Barcelona, Bellaterra (Barcelona), Spain, and Departament de Química Inorgànica, Universitat de Barcelona, Barcelona, Spain

Solid-State Kinetic Parameters for the Deaquation-Anation of the Double-Complex Salts $[CoH_2O(NH_3)_5][CoX(CN)_5]$ (X = CN, Cl, Br, I, NO_2, N_3) and the Preparation of Dinuclear Derivatives with μ-Cyano Bridges

J. Casabó,[*†] T. Flor,[†] F. Teixidor,[†] and J. Ribas[‡]

Received December 26, 1985

Double-complex salts of formula $[CoH_2O(NH_3)_5][Co(CN)_5X]$ (X = CN, Cl, Br, I, NO_2, N_3) have been synthesized and characterized. Dinuclear μ-CN compounds $[(NH_3)_5CoNCCo(CN)_4X]$ (X = CN, Cl, Br, I, NO_2, N_3) have been prepared by controlled heating of the aforementioned double-complex salts. These dinuclear compounds have been characterized by methods such as ^{59}Co NMR spectrometry and IR and UV-visible spectrophotometry. The double-complex salts have been proven by X-ray powder diffraction techniques to be isostructural with $[Co(NH_3)_6][Co(CN)_6]$. Several unit cell parameters have been calculated and discussed. The solid-phase thermal deaquation-anation of the double-complex salts has been studied by nonisothermal methods, and several kinetics parameters have been calculated. The activation energy values of these processes have been related to the unit cell parameters.

Introduction

The solid-phase thermal reaction of the double-complex salts $[MH_2O(NH_3)_5][M'(CN)_6]$ (M, M' = Co(III), Cr(III)) has been largely studied since Haim et al. prepared the dinuclear compound $[(NH_3)_5CoNCCo(CN)_5]$ from $[CoH_2O(NH_3)_5][Co(CN)_6]$.[1,2] House[3] proposed general mechanisms for the solid-state dehydration-aquation of coordination compounds. In these, the generation of a Schottky or Frenkel type of point defect is considered in the formation of the transition state. The dehydration of $[M(H_2O)(NH_3)_5]X_3$ complexes as well as several double-complex salts such as $[MH_2O(NH_3)_5][M'(CN)_6]$ has been shown to be consistent with an S_N1 dissociative mechanism with a Frenkel type defect generation.[4,5]

If the process takes place by an SN_1 pathway, the rate-determining step is the loss of the water from the cation $[MH_2O(NH_3)_5]^{3+}$ and its location in an interstitial position in the lattice. The activation energy should be largely influenced by a crystal field component due to formation of a pentacoordinated transition state but almost invariant to the nature of the entering anion.

Several papers have been written pointing out the influence of the crystal field component in the activation energy.[5] Our aim is to show the influence of the different entering anions in the lattice energy component of the activation energy favoring or hindering the diffusion of the water molecule through the lattice.

We have chosen a family of *isostructural double-complex salts*, $[CoH_2O(NH_3)_5][Co(CN)_5X]$ (X = CN, Cl, Br, I, NO_2, N_3), to prove this point. The unit cell parameters will be modified by the different X groups; consequently, varying the lattice free spaces allows a study of their influence in the activation energy of the solid-state process.

Experimental Section

Preparation of Starting Materials. $K_3[Co(CN)_5X]$ (X = Cl, Br, I, NO_2) complexes were prepared from $K_3[Co(CN)_5N_3]$ by a procedure already described by the authors.[6] $K_3[Co(CN)_5N_3]$,[7] $K_3[Co(CN)_6]$,[8] and $[CoH_2O(NH_3)_5](ClO_4)_3$[9] were prepared by procedures reported in the literature and identified by elemental analyses and spectrophotometric methods.

Preparation of the New Compounds $[CoH_2O(NH_3)_5][Co(CN)_5X]$ (X = Cl, Br, I, NO_2, N_3). In a typical experiment, $K_3[Co(CN)_5Cl]$ (1.2 g) was dissolved in a H_2O/glacial acetic acid (5:1) mixture. $NaClO_4$ (2 g)

[†] Universitat Autònoma de Barcelona.
[‡] Universitat de Barcelona.

(1) Castelló, R. A.; Piriz, C.; Egen, E.; Haim, A. *Inorg. Chem.* **1969**, *8*, 700.
(2) Jepsen, C. A.; House, J. E. *J. Inorg. Nucl. Chem.* **1981**, *43*, 953.
(3) House, J. E., Jr. *Thermochim. Acta* **1980**, *38*, 59.
(4) LeMay, M. E.; Babich, M. W. *Thermochim. Acta* **1981**, *48*, 147.
(5) (a) Serra, M.; Escuer, A.; Ribas, J.; Barô, M. D.; Casabó, J. *Thermochim. Acta* **1982**, *56*, 183. (b) Corbella, M.; Serra, M.; Martinez, M. L.; Ribas, J. *Thermochim. Acta* **1982**, *57*, 283. (c) Serra, M.; Escuer, A.; Ribas, J.; Barô, M. D. *Thermochim. Acta* **1983**, *64*, 237. (d) Monfort, M.; Serra, M.; Escuer, A.; Ribas, J. *Thermochim. Acta* **1983**, *69*, 397. (e) Corbella, M.; Diaz, C.; Escuer, A.; Seguí, A.; Ribas, J. *Thermochim. Acta* **1984**, *74*, 23.
(6) Casabó, J.; Flor, T. *Synth. React. Inorg. Met.-Org. Chem.*, in press.
(7) Linhard, M.; Flygare, H. *Z. Anorg. Chem.* **1950**, *262*, 340.
(8) *Inorg. Synth.* **1946**, *2*, 225.
(9) Schlessinger, G. C. *Preparación de Compuestos Inorgânicos en el Laboratorio*; CECSA: México, 1965; p 214.