Contribution from the Department of Chemistry,
University of Detroit, Detroit, Michigan 48221

Syntheses and Kinetics of the First-Stage Aquation of *cis*-Dichlorobis(iso-, *meso*-, and *dl*-butylenediamine)chromium(III) Cations[1]

C. P. MADHUSUDHAN and JOHN A. McLEAN, Jr.*

Received March 8, 1974

AIC40160Y

The syntheses and characterization of *cis*-$[Cr(i\text{-bn})_2Cl_2]ClO_4$, *cis*-$[Cr(ms\text{-bn})_2Cl_2]ClO_4 \cdot 0.5H_2O$, and *cis*-$[Cr(dl\text{-bn})_2Cl_2]ClO_4 \cdot H_2O$ are described. The kinetics and steric course of first-stage aquation of these complexes have been studied in 0.1 *N* $HClO_4$ at 15.0, 25.0, and 35.0°. The replacement of chloride by H_2O occurs with essentially complete retention of configuration. In 0.1 *N* $HClO_4$ at 25.0 ± 0.05° the first-order rate constants for the aquation reactions, activation energies, and entropies of activation are $k_a = (1.54 \pm 0.11) \times 10^{-4}$ sec^{-1}, $E_a = 21.9 \pm 0.8$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -4.5 \pm 2.8$ cal deg^{-1} mol^{-1} for *cis*-$Cr(i\text{-bn})_2Cl_2^+$; $k_a = (3.55 \pm 0.27) \times 10^{-4}$ sec^{-1}, $E_a = 20.2 \pm 1.2$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -8.6 \pm 4.2$ cal deg^{-1} mol^{-1} for *cis*-$Cr(ms\text{-bn})_2Cl_2^+$; $k_a = (3.91 \pm 0.34) \times 10^{-4}$ sec^{-1}, $E_a = 19.0 \pm 0.4$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -12.3 \pm 1.5$ cal deg^{-1} mol^{-1} for *cis*-$Cr(dl\text{-bn})_2Cl_2^+$. The corresponding *cis*-chloroaquo cations for each of the above *cis*-dichloro species have been isolated.

Introduction

It is generally agreed that the aquation of dihalobis(diamine)cobalt(III) cations proceeds by a dissociative mechanism.[2] This mechanism is supported by many studies involving entering, leaving, and nonleaving group effects, charge effects, and steric effects. Until recently, a sufficient number of model Cr(III) compounds did not exist to permit mechanistic tests for aquation in terms of the above effects. Recently, we synthesized several propylenediamine complexes and examined the influence of the *C*-methyl group on the rates and steric course of aquation of *cis*- and *trans*-dihalo- and haloaquochromium(III) complexes.[3,4] Steric crowding affected the rates much less than had been reported for the Co(III) analogs. This observation suggested the need for synthesizing Cr(III) complexes with increased C-alkylation so that the influence of steric crowding would be more pronounced. We report here the synthesis, spectra, kinetics and steric course for the aquation of *cis*-$Cr(i\text{-bn})_2Cl_2^+$, *cis*-$Cr(ms\text{-bn})_2Cl_2^+$, and *cis*-$Cr(dl\text{-bn})_2Cl_2^+$. The mechanistic implications of the steric influence of four *C*-methyl groups in each of these complexes are discussed.

Experimental Section

Materials. 2-Methyl-1,2-propanediamine (isobutylenediamine) was obtained from K & K Laboratories Inc. and used without further purification. *dl*- and *meso*-butylenediamine were obtained by the reduction of dimethylglyoxime by Raney nickel in aqueous NaOH according to the method of Dickey, *et al.*[5] All other chemicals were reagent grade. Water used in preparing solutions was doubly distilled. All chromatographic separations were performed on jacketed columns containing a prewashed cation-exchange resin (Dowex AG50W-X8, 100–200 mesh, H^+ form, 40 × 9 mm). These columns were maintained at 0° and protected from light with Al foil except when opened quickly to check the progress of elution. The details of these chromatographic procedures are identical with those previously reported.[3,4]

Synthesis of Complexes. *cis*-$[Cr(i\text{-bn})_2Cl_2]ClO_4$ was prepared by a modification of the method used by Pedersen[6] for the en analog. $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (2.665 g, 0.01 mol) was dissolved in 20 ml of DMF and the solution heated to boiling (*ca.* 153°). Boiling was maintained for 10 min to remove all water from the starting material. The solution was allowed to cool to 110° and dry *i*-bn (1.76 g, 0.02 mol) was added dropwise with stirring. The reaction mixture was heated in an oil bath at 140° for 1 hr and allowed to cool to room temperature. Crystallization of the resulting viscous oil was induced by grinding with 200 ml of acetone. The product was filtered, washed with acetone and ether, and dried under vacuum for 3 hr (yield 2.51 g). The product is thought to be impure *cis*-$[Cr(i\text{-bn})_2Cl_2]Cl$. After all attempts to purify this chloride met with failure, the following procedure was used to obtain the perchlorate salt. Eight milliliters of 60% $HClO_4$ was added dropwise to 2 g of crude product with occassional stirring. The mixture was stirred an additional 15 min and filtered. The filtrate was kept at −18° for 3 days and filtered, and the resulting pink violet crystals were washed with 2-propanol and ether and dried under vacuum for 3 hr (yield 1.91 g, 60%). *Anal.* Calcd for $[Cr(i\text{-bn})_2Cl_2]ClO_4$: C, 24.09; H, 6.02; N, 14.05; Cr, 13.05; ligand Cl, 17.82. Found: C, 23.83; H, 5.85; N, 13.85; Cr, 12.89; ligand Cl, 17.76.

The following two dichlorobis(diamine) compounds were obtained as crude chloride salts by substituting *ms*-bn and *dl*-bn for *i*-bn in the procedure outlined above with the modifications indicated.

***cis*-$[Cr(ms\text{-bn})_2Cl_2]ClO_4 \cdot 0.5H_2O$.** Excess *ms*-bn (0.33 g, 0.0038 mol) was added after the initial 140° 1-hr heating period and heating was continued at this temperature for 30 additional min. The reaction mixture was allowed to cool to room temperature; the crude chloride complex was extracted with acetone and precipitated from the acetone solution with ether. This salt was converted to the perchlorate by the procedure used in the *i*-bn case above (yield 0.26 g, 7%). *Anal.* Calcd for $[Cr(ms\text{-bn})_2Cl_2]ClO_4 \cdot 0.5H_2O$: C, 23.56; H, 6.14; N, 13.74; Cr, 12.76; ligand Cl, 17.42. Found: C, 23.76; H, 6.38; N, 13.24; Cr, 12.68; ligand Cl, 17.39.

***cis*-$[Cr(dl\text{-bn})_2Cl_2]ClO_4 \cdot H_2O$.** The 140° heating period was initially extended to 2 hr, excess *dl*-bn (0.35 g, 0.004 mol) was added, and the reaction temperature was maintained at 140° for 45 min. The acetone treatment of the reaction mixture was identical with the *i*-bn case; however, an additional crop of crude chloride was obtained here by combining all the acetone extracts, adding ether, and filtering. Conversion to the perchlorate salt was the same as before (yield 0.3 g, 7%). *Anal.* Calcd for $[Cr(dl\text{-bn})_2Cl_2]ClO_4 \cdot H_2O$: C, 23.05; H, 6.24; N, 13.45; Cr, 12.49; ligand Cl, 17.05. Found: C, 22.99; H, 6.63; N, 13.04; Cr, 12.46; ligand Cl, 16.98.

Caution! Although no difficulties were encountered with the perchlorate salts of the above complexes, they should be treated as potentially explosive and handled with care.

cis-$Cr(i\text{-bn})_2(OH_2)Cl^{2+}$ was prepared in solution by dissolving *ca.* 80 mg of *cis*-$[Cr(i\text{-bn})_2Cl_2]ClO_4$ in 80 ml of 0.1 *N* HNO_3 and allowing the solution to aquate in the dark at 25° for 80 min. The reaction solution was then adsorbed on the cation-exchange column at 0°. Unreacted *cis*-$Cr(i\text{-bn})_2Cl_2^+$ was eluted with *ca.* 125 ml of 0.6 *N* HNO_3. The second band containing the chloroaquo complex was eluted with 95 ml of 3 *N* HNO_3. The isolated chloroaquo species had a Cr:Cl atom ratio of 1.01 and its elution behavior is very similar to its en and pn analogs.[3,7]

cis-$Cr(ms\text{-bn})_2Cl(OH_2)^{2+}$ and *cis*-$Cr(dl\text{-bn})_2Cl(OH_2)^{2+}$ were prepared from their corresponding dichloro cations and isolated chromatographically in solution by the procedure outlined above for the *i*-bn analog. The Cr:Cl atom ratios are 1.03 and 0.99 for the *ms*-bn and *dl*-bn chloroaquo cations, respectively.

Kinetic Measurements. We have employed three methods—spectrophotometric, chromatographic, and potentiometric—in our kinetic studies. Rate data for the disappearance of the dichloro complexes, the formation of the chloroaquo species, and chloride release were obtained by chromatographic and potentiometric titration techniques reported earlier.[3]

In all spectrophotometric runs solutions were prepared by dissolving a sufficient quantity of complex in 0.1 *N* $HClO_4$ to give a concen-

Table I. Absorption Maxima and Minima (in nm) of *cis*-$Cr(AA)_2XB^{n+}$ Complexes in Acidic Media[a]

Complex	Acid	λ_{max}	λ_{min}	λ_{max}
cis-$Cr(en)_2Cl_2^+$ [b]	0.1 *N* HCl	402 (68.5)	456 (20.7)	528 (70.6)
cis-$Cr(pn)_2Cl_2^+$ [c]	0.1 *N* $HClO_4$	400 (77.0)	455 (23.0)	530 (80.6)
cis-$Cr(i\text{-bn})_2Cl_2^+$ [d]	0.1 *N* $HClO_4$	403 (74.0)	458 (25.1)	534 (89.7)
cis-$Cr(ms\text{-bn})_2Cl_2^+$ [d]	0.1 *N* $HClO_4$	406 (74.1)	460 (26.1)	534 (87.7)
cis-$Cr(dl\text{-bn})_2Cl_2^+$ [d]	0.1 *N* $HClO_4$	402 (75.9)	455 (23.1)	527 (81.1)
cis-$Cr(en)_2(OH_2)Cl^{2+}$ [b]	0.2 *N* HCl	385 (55.7)	438 (20.3)	510 (71.4)
cis-$Cr(pn)_2(OH_2)Cl^{2+}$ [c]	2.0 *N* $HClO_4$	387 (59.1)	440 (20.4)	511 (74.7)
cis-$Cr(i\text{-bn})_2(OH_2)Cl^{2+}$ [d]	3.0 *N* HNO_3	388 (60.2)	442 (22.4)	515 (78.6)
cis-$Cr(ms\text{-bn})_2(OH_2)Cl^{2+}$ [d]	3.0 *N* HNO_3	390 (64.3)	443 (23.3)	514 (80.7)
cis-$Cr(dl\text{-bn})_2(OH_2)Cl^{2+}$ [d]	3.0 *N* HNO_3	386 (60.3)	438 (21.5)	508 (74.4)

[a] Values inside parentheses are the molar absorbancy indices a_m defined by $A = \log (I_0/I) = a_m cd$, in M^{-1} cm^{-1}. [b] D. J. MacDonald and C. S. Garner, *J. Amer. Chem. Soc.*, **83**, 4152 (1961). [c] Reference 7. [d] This work.

Table II. First-Order Rate Constants for the Aquation of *cis*-$Cr(AA)_2Cl_2^+$ in 0.1 *N* $HClO_4$[a]

Complex	Temp, °C	10^4k, sec^{-1}	Method
cis-$Cr(i\text{-bn})_2Cl_2^+$	15.0	0.52 ± 0.40	Cl^- release
	25.0[b]	1.51 ± 0.02	Spectro
	25.0[c]	1.55 ± 0.02	
	25.0	1.57 ± 0.09	Cl^- release
	25.0[d]	1.49 ± 0.21	Chromatogr
	25.0[e]	1.57 ± 0.10	
	35.0	5.78 ± 0.23	Cl^- release
cis-$Cr(ms\text{-bn})_2Cl_2^+$	15.0[f]	1.13 ± 0.02	Spectro
	15.0[c]	1.10 ± 0.04	
	25.0[f]	3.51 ± 0.15	
	25.0[c]	3.58 ± 0.11	
	25.0	3.21 ± 0.24	Cl^- release
	25.0[d]	3.33 ± 0.15	Chromatogr
	25.0[e]	3.37 ± 0.19	
	35.0[f]	11.55 ± 0.03	Spectro
	35.0[c]	10.72 ± 0.13	
cis-$Cr(dl\text{-bn})_2Cl_2^+$	15.0[g]	1.07 ± 0.02	Spectro
	15.0[h]	1.08 ± 0.02	
	25.0[g]	4.01 ± 0.06	
	25.0[h]	3.82 ± 0.11	
	25.0	4.10 ± 0.12	Cl^- release
	25.0[d]	3.81 ± 0.3	Chromatogr
	25.0[e]	4.10 ± 0.3	
	35.0[g]	9.51 ± 0.28	Spectro
	35.0[h]	9.35 ± 0.30	

[a] Errors are estimated as three standard deviations. [b] 403 nm. [c] 534 nm. [d] Rate of disappearance of dichloro complex. [e] Rate of formation of chloroaquo complex. [f] 406 nm. [g] 402 nm. [h] 527 nm.

tration of *ca.* 8 × 10^{-4} *M* and quickly transferring it to a 10-cm cell. The spectrum was quickly scanned repeatedly at known times from 570 to 360 nm to search for isosbestic points and provide absorbancy data for kinetic analysis. Rate constants were calculated at two different wavelengths corresponding to the maxima of each dichloro cation. The temperature was maintained at the required temperature ±0.05° with a thermostatically controlled water bath.

Analytical Methods. Chromium analyses on solid samples as well as chromatographic fractions were performed by methods previously described.[3,8] The remaining elements were determined by microanalyses.[9] Visible absorption spectra were obtained with a Cary Model 41 spectrophotometer using matched quartz cells.

Results

Three complexes *cis*-$[Cr(i\text{-bn})_2Cl_2]ClO_4$, *cis*-$[Cr(ms\text{-bn})_2Cl_2]ClO_4 \cdot 0.5H_2O$, and *cis*-$[Cr(dl\text{-bn})_2Cl_2]ClO_4 \cdot H_2O$ have been prepared as crystalline solids. Aquation rates and activation parameters have been determined for these complexes. In addition, their corresponding chloroaquo species have been prepared and characterized in solution.

Characterization of Complexes. The stoichiometry of the solid perchlorate salts of the *cis*-dichloro complexes was confirmed by microanalysis and that of the chloroaquo cations by determination of the Cr:Cl ratio. We were able to assign the configuration of these complexes using their visible absorption spectra and cation-exchange behavior. Table I compares the spectra of cis *i*-, *ms*-, and *dl*-bn complexes with their cis en and pn analogs. The fact that no tetragonal splitting is observed for the low-energy bands of the new complexes is typical of cis geometry.

The isomeric purity of the dichloro complexes was also checked by cation-exchange chromatography. Identical chromatographic behavior was observed in all three cases. The solid salts were dissolved in 0.1 *N* $HClO_4$ at 0° and adsorbed on the cation-exchange column (see Experimental Section). When 50 ml of 0.3 *N* $HClO_4$ (which would be expected to elute any *trans*-dichloro isomer) was passed through the column, the eluates in all cases contained 0% Cr. The next two eluates resulting from 200 ml of 0.6 *N* $HClO_4$ (which would be expected to elute the *cis*-dichloro isomers)[7] and 75 ml of 1.0 *N* $HClO_4$ contained all the original Cr and both solutions had spectra identical with those of the original complexes.

Aquation Rates of *cis*-Dichloro bn Cations. In some spectrophotometric runs the spectrum was repeatedly scanned from 570 to 360 nm. However, the majority of the data were obtained at fixed wavelengths corresponding to the maxima of each dichloro cation as indicated in Table I. In all cases spectrophotometric data were analyzed with the equation

$$\ln [(A_t - A_\infty)/(A_0 - A_\infty)] = kt$$

where A_t, A_0, and A_∞ are the absorbancies (at a given wavelength) at time *t*, at zero time, and of the product, respectively.

Chloride release data were plotted as $\ln [a/(a - x)]$ *vs. t*, where *a* is half of the total coordinated chloride concentration and *x* is the concentration of the chloride released at time *t*.

The first-order rate constants for the disappearance of the *cis*-dichloro species were obtained from linear plots of $\ln (C_0/C_t)$ *vs. t*, where C_0 and C_t are the complex concentrations at zero time and time *t*, respectively. The rate constants for the formation of products of first-stage aquation were obtained from the initial-slope method previously described.[3]

All rate plots were linear over >50% reaction. The effect of temperature on the observed aquation rates was studied and the results are presented in Table II. The energies of activation, E_a, were obtained by plotting log *k vs.* 1000/*T*°K and the entropies of activation, $\Delta S^{\ddagger}_{298}$, were calculated using the equation

$$\frac{\Delta S^{\ddagger}_{298}}{4.576} = \log k - 10.753 - \log(298) + \frac{E_a(1000)}{4.576(298)}$$

where *k* (in sec^{-1}) is the first-order rate constant at 25°. These data are presented in Table III.

Table III shows that in general the addition of one or two *C*-methyl groups per chelate ring has no noticeable effect on the aquation rates of analogous *cis*-dihalodiaminechromium(III) complexes. It is difficult to explain the relative aquation rate of the one exception, *cis*-$Cr(i\text{-bn})_2Cl_2^+$, in terms

Table III. Rate Constants and Activation Parameters for *cis*-$Cr(AA)_2X_2^+$

Complex	Acid	$10^4k(25°)$, sec^{-1}	E_a, kcal mol^{-1}	$\Delta S^{\ddagger}_{298}$, cal deg^{-1} mol^{-1}
cis-$Cr(en)_2Cl_2^{+\,a}$	0.1 *N* HNO_3	3.3	21.1	−5.72
cis-$Cr(pn)_2Cl_2^{+\,b}$	0.1 *N* $HClO_4$	3.5 ± 0.3		
cis-Cr(*i*-bn)$_2Cl_2^{+\,c}$	0.1 *N* $HClO_4$	1.54 ± 0.11	21.9 ± 0.8	−4.5 ± 2.8
cis-Cr(*ms*-bn)$_2Cl_2^{+\,c}$	0.1 *N* $HClO_4$	3.55 ± 0.27	20.2 ± 1.2	−8.6 ± 4.2
cis-Cr(*dl*-bn)$_2Cl_2^{+\,c}$	0.1 *N* $HClO_4$	3.91 ± 0.34	19.0 ± 0.4	−12.3 ± 1.5
cis-$Cr(en)_2Br_2^{+\,d}$	0.01 *N* HNO_3	23.0 ± 3.0	19.2 ± 0.9	−8.3 ± 3.0
cis-$Cr(pn)_2Br_2^{+\,d}$	0.1 *N* HNO_3	25.7 ± 1.5	19.4 ± 1.2	−7.4 ± 3.6

[a] J. Selbin and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, 79, 4285 (1957). [b] Reference 7. [c] This work. [d] Reference 4.

Table IV. Theoretical and Experimental Isosbestic Points[a] for the Aquation of *cis*-$Cr(AA)_2Cl_2^+$ in 0.1 *N* $HClO_4$ at 25°

AA		
i-bn	*ms*-bn	*dl*-bn
	Theoretical	
515 (78.6)	516 (80.0)	509 (74.0)
455 (25.0)	456 (26.8)	448 (23.9)
389 (60.1)	390 (64.3)	383 (60.0)
	Experimental	
517 (78.5)	515 (79.9)	510 (74.1)
456 (25.4)	455 (26.9)	449 (24.1)
390 (60.1)	391 (64.4)	384 (60.2)

[a] The first numbers are wavelengths in nm and the numbers in parentheses are molar absorbancy indices in M^{-1} cm^{-1}.

of the activation energies and entropies listed because of the relatively large experimental errors.

Discussion

When the three *cis*-dichlorobutylenediamine cations were investigated spectrophotometrically under aquation conditions, it was found that A_∞ could not be observed experimentally due to second-stage aquation. Therefore, A_∞ (at a given wavelength) was calculated assuming 100% aquation to the corresponding *cis*-chloroaquo species. Rate data plotted from absorbancies at the two absorption peaks of each *cis*-dichloro complex were linear over 55% reaction and the three sharp isosbestic points which were observed over the same period are compared with the theoretical values in Table IV. It is seen that both sets of data agree within experimental error.

The agreement of theoretical and experimental isosbestics and the agreement of (1) rate data calculated at two different wavelengths, (2) rate data for disappearance of complex and product formation, and (3) rate data for chromatographic, spectrophotometric, and halide release support the conclusion that first-stage aquation for all three *cis*-dichlorobutylenediamine cations proceeds as

$$cis\text{-}Cr(AA)_2Cl_2^+ + H_2O \rightarrow cis\text{-}Cr(AA)_2(OH_2)Cl^{2+} + Cl^-$$

Esparza and Garner[7] noted that supporting data similar to the above could not rule out two additional possible pathways involving *trans*-dichloro or *trans*-chloroaquo intermediates in the aquation of *cis*-$Cr(pn)_2Cl_2^+$. The results we obtained[3] in a subsequent study of *trans*-$Cr(pn)_2Cl_2^+$ eliminated these two paths for the *cis*-dichloropropylenediamine system. Since the corresponding trans cations are presently unknown for *i*-bn, *dl*-bn, and *ms*-bn, we must use analogy to rule out these additional pathways in the study reported here.

Comparison of Co(III) and Cr(III) Systems. First-stage aquation rate studies which have been carried out on *cis*- and *trans*-$Co(en)_2Cl_2^+$,[10] $Co(pn)_2Cl_2^+$,[11] and *trans*-Co(*i*-bn)$_2Cl_2^+$ cations[12] show that the cis pn:en, trans pn:en, and trans *i*-bn:en ratios[13] are 1.7, 1.8, and 68, respectively. Second, it is generally found that cis isomers aquate with retention of configuration whereas most trans isomers aquate with steric change. The results of Co(III) studies are consistent with a unimolecular dissociative mechanism where (1) faster rates arise from steric crowding of the *C*-methyl group and (2) a square-pyramidal intermediate (D) or transition state (I_d) is postulated in stereoretentive aquations and a trigonal-bipyramidal geometry (D or I_d) for aquations where change in configuration is observed.

In earlier studies of Cr(III) complexes we found the pn:en ratios of *trans*-dibromo[4] and *trans*-dichloro[3] compounds to be 1.2 and 1.4, respectively. These differences, even though small when compared to the Co(III) ratios, are within limits of experimental detectability. On the other hand, identical en and pn rates are observed for the cis Cr(III) systems which have been examined to date, *viz.*, dichloro,[7] dibromo,[4] and bromoaquo.[4] We previously rationalized these data in terms of an interchange mechanism which is more dissociative than associative in character. Therefore, in Cr^{III}–pn complexes the steric crowding of the *C*-methyl group has a smaller effect on k_{aq} than in corresponding Co^{III}–pn complexes which are largely dissociative.

The above mechanism is consistent with the stereoretentive character of the aquation of the three *cis*-dichlorobutylenediamine cations found in the present study. No trans products or Cr–N bond rupture products were detected spectrophotometrically or by chromatographic techniques.

Steric Effects of *C*-Methyl Groups. The interchange mechanism above seems to account satisfactorily for the equal aquation rates of *cis*-$Cr(AA)_2Cl_2^+$ cations (where AA = en, pn, *ms*-bn, or *dl*-bn). However, the question remains as to why *cis*-Cr(*i*-bn)$_2Cl_2^+$ aquates at a slower rate. The slower rate is possibly related to the unique structural feature of the *i*-bn complex, *viz.*, two *gem*-dimethyl chelate rings. There are three possible conformations of these rings.[14] Liehr[15] labeled these as δδ, λλ, and δλ. If one assumes that the bulky *gem*-dimethyl groups in this complex restrict the inversions of the rings, there would be a preferred conformation in solution.[16] This more stable form could aquate more slowly than the corresponding cis en, pn, *ms*-bn, and *dl*-bn complexes where inversions would occur more rapidly. An alternative explanative is simply that the bulky *gem*-dimethyl groups reflect the associative character of the interchange mechanism.

Registry No. *cis*-[Cr(*i*-bn)$_2Cl_2$]ClO_4, 53042-38-9; *cis*-[Cr(*ms*-bn)$_2Cl_2$]ClO_4, 53042-40-3; *cis*-[Cr(*dl*-bn)$_2Cl_2$]ClO_4, 53109-05-0; *cis*-Cr(*i*-bn)$_2(OH_2)Cl^{2+}$, 53042-35-6; *cis*-Cr(*ms*-bn)$_2(OH_2)Cl^{2+}$, 53042-36-7; *cis*-Cr(*dl*-bn)$_2(OH_2)Cl^{2+}$, 53109-03-8.

References and Notes

(1) Abbreviations used: en, ethylenediamine; pn, 1,2-propanediamine (propylenediamine); *i*-bn, 2-methyl-1,2-propanediamine (isobutylenediamine); *ms*-bn, 2,3-butanediamine (*meso*-butylenediamine); *dl*-bn, 2,3-butanediamine (*dl*-butylenediamine); tn, 1,3-propanediamine (trimethylenediamine); dan, 2,2-dimethyl-1,3-propanediamine; DMF, *N,N*-dimethylformamide.

(2) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y. 1965, p 90.

(3) R. R. Barona and J. A. McLean, Jr., *Inorg. Chem.*, **10**, 286 (1971).

(4) N. A. Maes, M. S. Nozari, and J. A. McLean, Jr., *Inorg. Chem.*, **12**, 750 (1973).

(5) F. H. Dickey, W. Fickett, and H. J. Lucas, *J. Amer. Chem. Soc.*, **74**, 944 (1952).

(6) E. Pedersen, *Acta Chem. Scand.*, **24**, 3362 (1970).

(7) M. Esparza and C. S. Garner, *J. Inorg. Nucl. Chem.*, **29**, 2377 (1967).

(8) J. A. McLean, Jr., and R. R. Barona, *Inorg. Nucl. Chem. Lett.*, **5**, 385 (1969).

(9) Microanalysis by M-H-W Microanalytical Laboratories, Garden City, Mich.

(10) M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4736 (1961).

(11) R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Amer. Chem. Soc.*, **78**, 2673 (1956).

(12) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Amer. Chem. Soc.*, **75**, 3089 (1953).

(13) pn:en or *i*-bn:en are ratios of specific rate constants at 25° for first-stage aquation of the analogous diamine systems indicated.

(14) E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

(15) A. D. Liehr, *J. Phys. Chem.*, **68**, 3629 (1964).

(16) It has been suggested [M. C. Couldwell and D. A. House, *Inorg. Chem.*, **11**, 2024 (1972)] that similar reasoning can explain the threefold decrease in the aquation rate of *trans*-$Co(dan)_2Cl_2^+$ relative to *trans*-$Co(tn)_2Cl_2^+$, where the *gem*-dimethyl groups restrict the distortion from the favored chair six-membered ring configuration.

Contribution from Chemistry Department I (Inorganic Chemistry),
H. C. Orsted Institute, DK-2100 Copenhagen O, Denmark

Electron Spin Resonance Spectra of Tetragonal Chromium(III) Complexes. II.[1] Frozen-Solution and Powder Spectra of $[Cr(NH_3)_5X]^{n+}$. A Correlation with Zero-Field Splittings and *g* Factors Obtained from Complete d^3-Configuration Calculations.

ERIK PEDERSEN* and SOLVEIG KALLESOE

Received March 11, 1974 AIC40165V

The X-band esr spectra have been recorded for complexes of the type $[Cr(NH_3)_5X]^{n+}$ where X = F^-, Cl^-, Br^-, I^-, H_2O, and OH^-. The complexes were in frozen solutions or diluted in the corresponding cobalt(III) complexes. All halide complexes showed tetragonal symmetry in frozen solutions. Small rhombic distortions were found in the hydroxo complex and in some halide complexes in polycrystalline powders. The zero-field splittings are in the range 0.06–0.94 cm^{-1}. The *g* factors are close to 1.99 and almost isotropic. These values have been compared with theoretical calculations based on all 120 states of the d^3 configuration, ligand field and interelectronic repulsion parameters obtained from vis–uv spectra, and the free-ion spin–orbit coupling constant. The zero-field splittings calculated in this way are very different from those obtained *via* simple second-order perturbation calculations including the lowest quartet and doublet states. The *g* factors calculated by the two methods differ only slightly. Thereby much better agreement with the experimental zero-field splittings has been obtained for the complexes with nonheavy ligands. Evidence for increased spin–orbit coupling constants in iodo and bromo complexes is found as also predicted by simple molecular orbital calculations. The experimental *g* factors, however, can only be explained by assuming all complexes to have spin–orbit coupling constants reduced to approximately 70% of the free-ion values.

Introduction

In a current investigation of the esr spectra of tetragonal chromium(III) complexes we have previously discussed the two series *trans*-$[Cr(NH_3)_4XY]^{n+}$ and *trans*-$[Cr(py)_4XY]^{n+}$ where X and Y are halide, water, or hydroxo ligands.[1] All these complexes showed essencially tetragonal symmetry, only slightly distorted by rhombic fields introduced by water and hydroxo ligands or in some cases by lattice effects in the polycrystalline powders. The tetragonal zero-field splittings were found to be in good agreement with complete d^3-configuration calculations based on parameters obtained from vis–uv absorption spectra. The free-ion value of the spin–orbit coupling constant was found satisfactory except for bromo and iodo complexes, for which increased values were required.

The present work extends this investigation to the pentaamminechromium(III) complexes and thereby exhausts the present sources of complexes having ideal symmetries and sufficiently well-determined ligand field and interelectronic repulsion parameters. During the preparation of this article another paper dealing with the esr spectra of the same series of complexes has appeared.[2] This investigation included the aqua-, chloro-, and bromopentaamminechromium(III) complexes in the microcrystalline state and agreed with our results for the chloro and bromo complexes.

Previous investigations of the kind discussed here have been made on systems exhibiting lower symmetry;[3-6] in the theoretical calculations most of the excited states have generally been neglected.[3,4,7-12] One of the exceptions is the calculation of the zero-field splitting of the ground states in ruby.[13-15] In this system the chromium(III) ions are in a trigonal environment. The breakdown of Van Vleck's theory[7] of zero-field splittings in axial symmetry is therefore obvious because of configuration interaction *via* the ligand field between the ground states and some of the excited states. In tetragonal symmetry all the interactions between the ground states and the excited states take place *via* spin–orbit coupling as assumed by Van Vleck.[7] A more detailed discussion of the results of these earlier papers is found in part I of this series.[1]

Experimental Section

Preparations. All complexes were prepared according to literature methods.[16-25] The chromium complexes were syncrystallized with the corresponding cobalt complexes from aqueous solutions containing 0.5% of chromium relative to cobalt. The chromium contents in the precipitates were not analyzed. Chlorides, bromides, perchlorates, and dithionates were investigated. Change of anions was generally found to have only small influence on the esr spectra. Due to the rapid hydrolysis of the iodopentaamminechromium(III) ion, even in acid solution, all spectra of this complex showed varying contamination with aquapentaammine complex. Frozen-solution spectra were measured on 10^{-2}–10^{-4} *M* solutions in a mixture of dimethylformamide, water, and methanol in the volume ratios 1:1:2. Solutions of aqua and hydroxo complexes were 10^{-2} *M* in H^+ and OH^-, respectively.

Esr Spectra. The spectra were recorded on a JEOL JES-ME-1X spectrometer, operating at the X band. The frequency was measured with a resonant cavity wavemeter with an accuracy of 1 MHz. The standard magnet pole gap was reduced by application of extra pole caps. The magnetic field thus obtained was 20–9000 G (2×10^{-3}–0.9 T). The field calibration below 2000 G was performed with a Hall probe gaussmeter with an accuracy of 1 G. Above 2000 G a sample of oxygen at 0.7 Torr was used as a reference having very narrow peaks at small intervals throughout the field range. Their positions and frequency dependencies have been carefully measured by Tinkham and Strandberg.[26] The accuracy of the field measurements in this