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Kinetic Parameters and Chemical Mechanism for the Solid-State Deaquation–Anation of Salts of Chromium(III) with Mixed Amine Ligands

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The solid-state dehydration–anation of *trans*-[CrF(en)(tn)(H_2O)]X_2 and *trans*-[CrF(chx)(tn)(H_2O)]X_2 (with en = ethylenediamine, tn = 1,3-diaminopropane, and chx = 1,2-diaminocyclohexane; X = Cl^-, Br^-, I^-, and $^1/_2S_2O_6{}^{2-}$) has been studied by isothermal thermogravimetric measurements, previous synthesis, and characterization of the new compounds. The dehydration–anation gives in the majority of the cases the cis isomer, [CrFX(aa)(bb)]X. The activation energies for these processes, compared with those reported for the compounds with only one kind of amine, indicate different trends in the en–tn series with regard to the chx–tn series: (a) in the first series the gradation follows the order en > en–tn > tn as could be expected according to the theory of the free space in the lattice; (b) in the second series, the gradation follows the order chx > chx–tn > tn, indicating that the dehydration and isomerization is expected to be via the rupture of the Cr–N(chx) bond, simultaneously with the rupture of the Cr–OH_2 bond; (c) the I > S_2O_6 > Br > Cl gradation in the series en–tn agrees with a dissociative mechanism controlled by the magnitude of the cation/anion ratio. This gradation does not take place in the chx–tn series due to the different extent of the Cr–N(chx) bond rupture, which depends on the entering anion.

Introduction

In recent years, we have studied systematically the factors that influence the kinetic parameters in the solid-state dehydration–anation reactions in coordination complexes.[1] In a more recent paper,[2] we have specially studied the influence of the size of the amine (ethylenediamine, 1,3-diaminopropane, and 1,2-diaminocyclohexane), the size of the entering anion (Cl, Br, I, S_2O_6), and the trans to cis isomerization that often occurs in the dehydration–anation processes:

$$trans\text{-}[CrF(aa)_2(H_2O)]X_2 \rightarrow cis\text{-}[CrFX(aa)_2]X + H_2O$$

We can summarize our previous conclusions as follows:

(a) Given a particular voluminous complex cation, E_a increases with the size of the anion (Cl < Br < I) due to the existence of less free space in the lattice created by the packing of the ions.

(b) When the coordinated amine is changed, the E_a increases according to tn < en < chx, only when the temperature of the reaction is greater than 160 °C. In this case E_a in the chx series may correspond to two quasi-simultaneous processes, the dehydration and the Cr–N(chx) bond rupture.

(c) When the temperature of the reaction is lower than 160 °C, the E_a increases according to chx < tn < en, following the "free space" theory elaborated by House[3] and repeatedly found by us in a large series of compounds.[1,2] In this case, the E_a value corresponds only to the dehydration process without rupture of the Cr–N(amine)bond. Consequently, E_a must be lower, as is experimentally observed.

The logical following step to corroborate this theory about the importance of the free space and the anomalous behavior of the chx complex, would be the synthesis and the study of the mixed-amine complexes, with en–tn, en–chx and chx–tn, respectively, i.e. *trans*-[CrF(aa)(bb)(H_2O)]X_2, with aa ≠ bb.

Vaughn and co-workers have studied the possibility of synthesizing this kind of complex.[4-6] Recently, following the Vaughn method, we have proposed the synthesis of *trans*-[CrF(en)(tn)(H_2O)]X_2 and *trans*-[CrF(chx)(tn)(H_2O)]X_2 complexes.[7] The series with chx–en has been impossible to obtain with sufficient purity until now.

In this paper we give the results obtained with isothermal measurements on the complexes *trans*-[CrF(aa)(bb)(H_2O)]X_2 (aa = en, chx; bb = tn), and the results confirm the importance of the free-space theory in the lattice and the anomalous behavior of the chx amine, which easily undergoes Cr–N(chx) bond rupture, giving an E_a value greater than that expected.

Experimental Section

Preparation of the Starting Materials. *trans*-[CrF(en)(tn)(H_2O)](ClO_4)$_2$ and *trans*-[CrF(chx)(tn)(H_2O)](ClO_4)$_2$ were prepared by the literature method.[7] Both the elemental analysis and electronic spectral data were in agreement with the values quoted in the literature.

Preparation of *trans*-[CrF(aa)(bb)(H_2O)]X_2 (aa = en, chx; bb = tn; X = Cl, Br). A 2-mmol sample of *trans*-[CrF(aa)(bb)(H_2O)](ClO_4)$_2$ was dissolved in the minimum amount of concentrated HX acid, and the solution was cooled in an ice bath, for 5 min, and 15 mL of ice-cold acetone was added with constant stirring. The pink crystals were collected by filtration, and the product was washed three times with 5-mL portions of acetone and allowed to dry in air. Anal. Calcd for *trans*-[CrF(en)(tn)(H_2O)]Cl_2: C, 20.41; H, 6.80; N, 19.05. Found: C, 20.3; H, 6.7; N, 18.6. Calcd for *trans*-[CrF(en)(tn)(H_2O)]Br_2: C, 15.67; H, 5.22; N, 14.63. Found: C, 15.6; H, 5.1; N, 14.3. Calcd for *trans*-[CrF(chx)(tn)(H_2O)]Cl_2: C, 31.03; H, 7.47; N, 16.09. Found: C, 30.8; H, 7.6; N, 15.9. Calcd for *trans*-[CrF(chx)(tn)(H_2O)]Br_2: C, 24.73; H, 5.95; N, 12.82. Found: C, 24.7; H, 5.8; N, 12.6.

Preparation of *trans*-[CrF(aa)(bb)(H_2O)]I_2. Both compounds (aa = en, bb = tn; aa = chx, bb = tn) were prepared by the literature method.[7] The elemental analysis and electronic spectral data for these compounds were in agreement with the values quoted in the literature.

Preparation of *trans*-[CrF(aa)(bb)(H_2O)]S_2O_6. A 2.5-g sample of $Na_2S_2O_6 \cdot 2H_2O$ was dissolved in the minimum amount of water, and this was passed through an acid-exchange column. In the eluate was dissolved a 1.0-g sample of *trans*-[CrF(aa)(bb)(H_2O)](ClO_4)$_2$, and the solution was cooled in an ice-bath for 5 min. Acetone was added to the solution, and pink crystals of the new product precipitated. These crystals were collected by filtration, and the product was washed three times with 5-mL portions of acetone, and allowed to dry in the air. Anal. Calcd for *trans*-[CrF(en)(tn)(H_2O)]S_2O_6: C, 15.67; H, 5.22; N, 14.63. Found: C, 15.5; H, 5.0; N, 14.4. Calcd for *trans*-[CrF(chx)(tn)(H_2O)]S_2O_6: C, 23.74; H, 6.15; N, 12.31. Found: C, 23.5; H, 6.2; N, 12.2.

Preparation of the Dehydrated Complexes *trans*/*cis*-[CrFX(aa)(bb)]X. All of the dehydrated complexes were prepared in the solid state by heating a weighed sample (100 mg) of the precursor species in an oven, according to the conditions (time and temperature) indicated in Table I. These conditions were obtained from the previous TG diagrams, which will be described below. During the time of heating, the complexes turned from light pink to more or less purple (depending on the entering anion, X), and the reaction was accompanied by a certain loss in water,

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Table I. Best Conditions To Obtain the Dehydrated Complexes with the Analytical Data for the Products

complex	conditions		anal. calcd (found)		
	time	T, °C	% C	% H	% N
trans-$[CrFCl(en)(tn)]Cl$	30 min	110	21.05 (20.9)	6.67 (6.6)	19.65 (19.5)
cis-$[CrFCl(en)(tn)]Cl$	24 h	120	21.74 (21.6)	6.52 (6.4)	20.29 (19.9)
cis-$[CrFBr(en)(tn)]Br$	90 min	115	16.44 (16.5)	4.93 (5.2)	15.34 (15.1)
cis-$[CrFI(en)(tn)]I$	90 min	160	13.08 (13.1)	3.92 (4.0)	12.21 (12.1)
cis-$[CrF(S_2O_6)(en)(tn)]$	20 min	165	16.44 (16.5)	4.93 (4.8)	15.34 (15.3)
cis-$[CrFCl(tn)(chx)]Cl$	3 h	140	31.86 (31.8)	7.37 (7.4)	16.52 (16.4)
cis-$[CrFBr(tn)(chx)]Br$	3 h	140	25.25 (25.3)	5.84 (5.7)	13.09 (12.9)
cis-$[CrFI(tn)(chx)]I$	90 min	175	21.06 (21.1)	4.68 (4.7)	10.92 (10.8)
cis-$[CrF(S_2O_6)(tn)(chx)]$	20 min	165	25.25 (25.3)	5.84 (5.8)	13.09 (12.9)

Table II. Electronic Spectra in Aqueous Solution

complex	λ_{max}, nm (ϵ, M^{-1} cm^{-1})		
trans-$[CrF(tn)(en)(H_2O)]^{2+}$	519 (22.8)	456 (30.1)	368 (42.7)
trans-$[CrF(tn)(chx)(H_2O)]^{2+}$	521 (23.5)	457 (29.2)	370 (41.7)
trans-$[CrFCl(tn)(en)]^+$	542 (21.1)	463 (25.7)	382 (37.8)
cis-$[CrFCl(tn)(en)]^+$	523 (60.3)		385 (42.5)
cis-$[CrFBr(tn)(en)]^+$	515 (62.5)		380 (41.3)
cis-$[CrFI(tn)(en)]^+$	507 (63.8)		365 (40.8)
cis-$[CrF(S_2O_6)(tn)(en)]$	515 (62.7)		378 (41.5)
cis-$[CrFCl(tn)(chx)]^+$	520 (58.5)		380 (41.3)
cis-$[CrFBr(tn)(chx)]^+$	513 (57.7)		380 (42.4)
cis-$[CrFI(tn)(chx)]^+$	500 (55.4)		350 (39.8)
cis-$[CrF(S_2O_6)(tn)(chx)]$	505 (57.5)		372 (40.1)

given in Table I. In all of the cases, except *trans*-$[CrF(en)(tn)(H_2O)]Cl_2$ the dehydration–anation is accompanied by trans to cis isomerization. Only in the *trans*-$[CrF(en)(tn)(H_2O)]Cl_2$ case was there first the dehdyration followed by the isomerization (Table I).

Techniques. Infrared spectra were recorded on a Beckman IR 20-A spectrophotometer purged with dry air. Samples were prepared by using the KBr technique. Electronic absorption spectra were recorded in solution on a Beckman 5230 UV spectrophotometer. Thermogravimetric analyses were carried out on a Perkin-Elmer Model TGS-1 system, under nitrogen (10 cm^3 min^{-1}), the sample size being in the range 4–7 mg. The heating rate for nonisothermal measurements was 5° min^{-1}. In order to test the possible isostructuralism in each series, X-ray powder diffraction patterns were recorded on a Philips PW-1030 diffractometer with graphite monochromatized CuKα radiation.

Results

(a) Characterization of the New Compounds. The new complexes have been characterized mainly by analytical data and electronic spectra, which have been very useful in determining the trans or cis arrangement.

The starting complexes $[CrF(aa)(bb)(H_2O)](ClO_4)_2$ with aa = en and chx and bb = tn have the trans structure with the three characteristic bands in the visible absorption spectrum (Table II).[8,9] On the other hand, the dehydrated complexes show only two symmetrical and perfectly defined bands, with a weak absorptivity, characteristic of the cis structure, as has been pointed out by Vaughn and coworkers in a large series of similar complexes.[4,5,8,10,11] Consequently, there are two simultaneous processes: dehydration and trans to cis isomerization, except in the *trans*-$[CrF(en)(tn)(H_2O)]Cl_2$ complex in which there are two separate steps. The first step is the formation of *trans*-$[CrFCl(en)(tn)]Cl$. The second step is the formation of *cis*-$[CrFCl(en)(tn)]Cl$, as has been indicated by Vaughn.[6]

From the data shown in Table II, we can also deduce the great tendency toward aquation with the Br, I, and dithionato ligands to give the species *cis*-$[CrF(aa)(bb)(H_2O)]^{2+}$, in agreement with the literature data.[8,11,12]

Table III. Temperature Interval (ΔT) for DSC and TG Diagrams, ΔH from DSC Diagrams, and Geometry of the Final Product Obtained by Both Methods (TG and DSC)

complex	ΔT, °C		ΔH, kJ/mol	final product
	DSC	TG		
trans-$[CrF_2(en)(tn)]Br$	25–250			trans
trans-$[CrF_2(tn)(chx)]Br$	25–250			trans
trans-$[CrF(en)(tn)(H_2O)]Cl_2$	80–95 95–100	85–120	11.9 26.9	trans cis
trans-$[CrF(en)(tn)(H_2O)]Br_2$	125–185	90–140	74.0	cis
trans-$[CrF(en)(tn)(H_2O)]I_2$	25–250	145–205		cis
trans-$[CrF(en)(tn)(H_2O)]S_2O_6$	*a*	135–180	*a*	cis
trans-$[CrF(tn)(chx)(H_2O)]Cl_2$	55–260	75–205	48.1	cis
trans-$[CrF(tn)(chx)(H_2O)]Br_2$	110–170	85–225	17.0	cis
trans-$[CrF(tn)(chx)(H_2O)]I_2$	25–250	100–200		cis
trans-$[CrF(tn)(chx)(H_2O)]S_2O_6$	*a*	85–205	*a*	cis

[a] In the DSC of $S_2O_6^{2-}$ complexes there is an overlap between the dehydration and the decomposition ($S_2O_6^{2-} \rightarrow SO_4^{2-}$). For this reason is not possible to calculate accurately the ΔH of the dehydration process.

(b) DSC and TG Measurements. DSC. We have recorded all the DSC diagrams for the corresponding *trans*-$[CrF(aa)(bb)(H_2O)]X_2$ complexes in order to calculate the ΔH of the dehydration-anation reaction. These values are given in Table III, together with the temperature interval and the trans or cis geometry of the final product. Surprisingly, both *trans*-$[CrF(aa)(bb)(H_2O)]I_2$ complexes do not present any evaluable peak in the 50–250 °C interval, although the final product is *cis*-$[CrFI(aa)(bb)]I$. Perhaps this due to a very low value of ΔH in a very long temperature interval, and consequently, the peak would be masked by the deviation of the base line.

We have also recorded the DSC of both *trans*-$[CrF_2$ $(aa)(bb)]Br$ complexes. Between 50 and 250 °C there is no evaluable ΔH, and the final products have the same trans geometry. We have to remember [2] that in *trans*-$[CrF_2(chx)_2]Br$, there is a trans to cis isomerization, with a ΔH of 55.5 kJ/mol.

TG. In order to evaluate the kinetic parameters, we have recorded one nonisothermal TG run for all of the substances (Figure 1). The temperature intervals for the dehydration–anation reactions are given in Table III. Also in this table are indicated the new species formed. In all cases, the analytical data are in agreement with the formula proposed and the electronic spectra clearly indicate the trans or cis geometry.

The kinetic parameters were determined from the isothermal TG runs in the same manner described in our previous paper.[2] For brevity, in Table IV are given only the chosen results for the kinetic parameters for all the dehydration–anation reactions studied here.[13]

Discussion

The complexes studied in this work are soluble only in water, but their instability with respect to the hydrolysis prevented us from obtaining single crystals suitable for X-ray structural determination. Lacking the X-ray structural data, we are forced to neglect the very important structural aspects of the solidstate reactions. On the other hand, the X-ray powder pattern of all the products indicates that there is no isostructuralism in the halide

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(13) The computational results and details can be requested from the authors.

Table IV. Average Kinetic Parameters[a]

entering X^-	solid-state mechanism (order)	E_a, kJ/mol	log k_0	r^2	$\Delta H^\ddagger$, kJ/mol	$\Delta S^\ddagger \pm \sigma$, J/(mol K)	$\Delta G^\ddagger$, kJ/mol
	Series with the *trans*-$[CrF(en)(tn)(H_2O)]^{2+}$ Cation						
Cl^-	nucl growth (n = 3)	51.5	4.76	0.9953	48.4	−39.1 ± 0.4	109.2
Br^-	growth (n = 0.2)	95.0	10.10	0.9920	91.7	−14.8 ± 0.9	116.3
I^-	nucleation (n = 1)	114.1	12.72	0.9884	108.7	−12.1 ± 0.6	131.3
$S_2O_6^{2-}$	nucl growth (n = 2)	125.8	12.54	0.9979	122.1	−3.9 ± 0.8	129.3
	Series with the *trans*-$[CrF(tn)(chx)(H_2O)]^{2+}$ Cation						
Cl^-	nucleation (n = 0.75)	71.5	5.60	0.9942	68.2	−35.4 ± 1.4	128.1
Br^-	nucleation (n = 0.3)	140.3	13.27	0.9978	136.6	−0.5 ± 2.8	137.0
I^-	nucleation (n = 0.5)	108.6	9.60	0.9875	104.9	−17.4 ± 1.1	137.8
$S_2O_6^{2-}$	nucleation (n = 0.5)	175.3	17.96	0.9894	168.2	−19.0 ± 0.7	155.0

[a] The solid-state mechanism must be considered with precaution, taking into account the low correlation coefficients. This fact does not influence the validity of the kinetic parameters, which are almost independent of the rate law in the isothermal TG measurements.

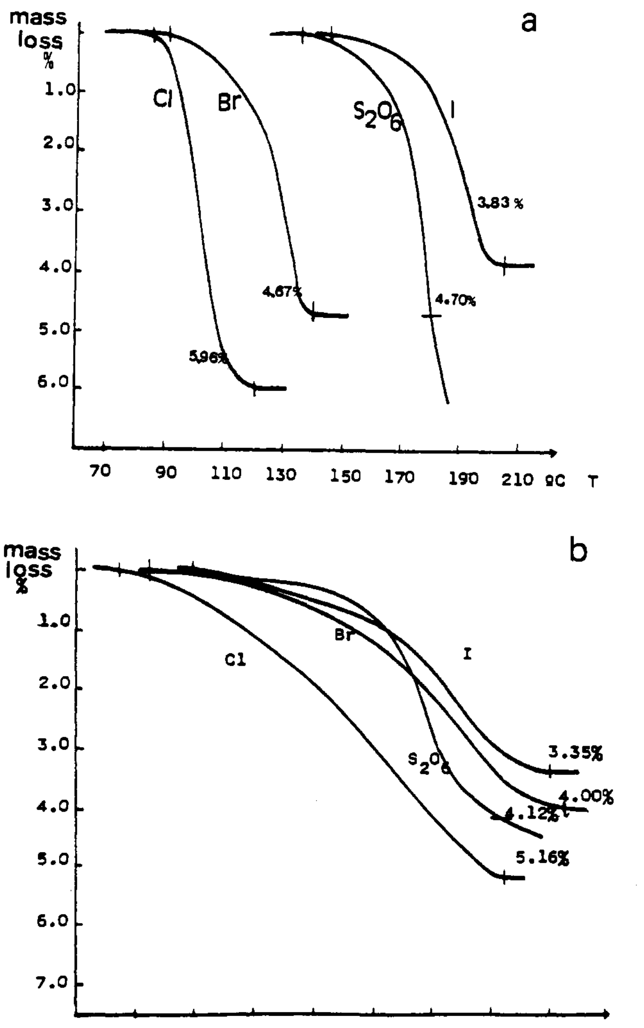

Figure 1. Nonisothermal TG runs for *trans*-$[CrF(en)(tn)(H_2O)]X_2$ (a) and *trans*-$[CrF(tn)(chx)(H_2O)]X_2$ (b).

complexes of each series. Consequently, with regard to the free-space theory, we are restricted in the interpretation of the facts. From the E_a values (Table IV) and those previously reported by us[2] for similar compounds with only one type of amine, we can construct the diagram shown in Figure 2.

From this figure we can deduce that the complexes of the series with en–tn amines have the E_a values intermediate between the series with bis(ethylenediamine) and bis(1,3–diaminopropane). These results agree perfectly with the free–space theory; i.e., the more compact the packing in the lattice, the greater is E_a. For a given entering anion, X, the packing is due to the size of the amine. Consequently, the observed order in the E_a, tn < en–tn < en, is that previously expected. The order Cl < Br < I < S_2O_6 is also what would be expected as has been explained in the case of *trans*-$[CrF(aa)_2(H_2O)]X_2$.[2]

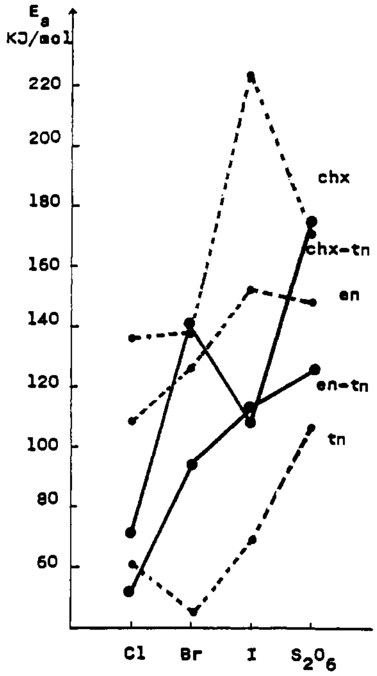

Figure 2. Variation of E_a with the entering anion, X, for each series with different amine ligands.

According to the free-space theory, in the chx–tn series, two voluminous amines in the cations create a less compact structure and consequently, the E_a must be lowest. That is, the expected order would be chx–tn < tn. The experimental results are opposite (Figure 2) because, as we pointed out in our previous work,[2] the chx complexes can produce a greater value of E_a due to the possibility of the Cr(III)–N(chx) bond rupture. The average order obtained is chx > chx–tn > en > en–tn > tn. This fact can be interpreted as a consequence of the rupture of the Cr–N(chx) bond. Tsuchiya and Uehara[14,15] have found a similar behavior in analogous complexes with Cl^- or Br^-, instead of F^-, as ligands.

Consequently, there is a question about which amine undergoes this rupture, chx or tn. Taking into account that with the *trans*-$[CrF_2(aa)_2]Br_2$ series there is only the rupture of this Cr–N(amine) bond when aa = chx and that with the *trans*-$[CrX_2(aa)(bb)]X$ (X = Cl,Br) this rupture is given at lower temperature when aa = bb = chx, we can propose that the monodentate amine in the pentacoordinate intermediate is only the 1,2-diaminocyclohexane.

There is an aspect that corroborates this theory. The *trans*-$[CrF(en)(tn)(H_2O)]Cl_2$ may first convert to *trans*-$[CrFCl(en)(tn)]Cl$ in a very definite process. To convert it to *cis*-

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[CrFCl(en)(tn)]Cl it is necessary to heat the complex a very long time (24 h at 130 °C). Following the Tsuchiya theory,[14,15] this isomerization undoubtedly takes place with the Cr–N(amine) bond rupture to give a pentacoordinate species, because there is no water in the coordination of Cr(III). Taking into account the absence of the chx ligand, this rupture is very difficult and it needs either high temperature or a long time (as is the experimental fact).

On the other hand, in the chx–tn series, the variation of the E_a values is not linear with the size of the entering anion (as occurs in the other series) (Figure 2). The possible explanation is to suppose, specifically, that the Cr–N(chx) bond rupture has a different extent depending on the entering anion.

The other kinetic parameters follow the same variation as E_a (Table IV). ΔS^* is a measurement of the distortion in the lattice in forming the activated complex.[3] If we suppose the Cr–N(chx) bond rupture, the monodentate chx amine creates more distortion by free rotation and increases the ΔS^*. The frequency factor, k_0, indicates, according to the literature,[16,17] the rigidity of the activated complex. Greater k_0 indicates greater mobility in the activated complex. The *trans*-[CrF(en)(tn)(H_2O)]Cl_2, which does not show isomerization, has a very small value of k_0. The activated complex is, consequently, very rigid, and the anion entrance in the same position from which the water molecule is lost would be very easy.

From all the results obtained with the TG and DSC measurements we can deduce that the activation parameters (over all the low values of E_a) (Table IV) are in agreement with a dissociative mechanism for all these reactions,[1,2] with the formation of a pentacoordinate intermediate. In the en–tn series, this pentacoordinate intermediate is due to the loss of the water molecule. The external anion can enter in the cis or trans position depending on the mobility of this activated complex. In the chx–tn series, instead, the mechanism (although dissociative) is somewhat different. There are two possible pentacoordinate intermediates: one created by the loss of the water molecule and the other created by the Cr–N(chx) bond rupture.

Conclusion

The results reported here confirm, once more, the importance of the ratio of anion/cation volume and the importance of the compacity in the packing, which is the so-called "free-space theory". On the other hand, the low values of E_a in all the complexes support the dissociative mechanism in this kind of solid-state reactions, as was previously predicted by House and LeMay.[3,20]

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Registry No. *trans*-[CrFCl(en)(tn)]Cl, 96482-47-2; [CrFCl(en)(tn)]Cl, 96554-58-4; [CrFBr(en)(tn)]Br, 96554-55-1; [CrFI(en)(tn)]I, 109864-08-6; [CrF(S_2O_6)(en)(tn)], 109889-32-9; [CrFCl(tn)(chx)]Cl, 109864-09-7; [CrFBr(tn)(chx)]Br, 109864-10-0; [CrFI(tn)(chx)]I, 109864-11-1; [CrF(S_2O_6)(tn)(chx)], 109864-12-2; *trans*-[CrF(en)(tn)(H_2O)]Cl_2, 96482-40-5; *trans*-[CrF(en)(tn)(H_2O)]Br_2, 96482-41-6; *trans*-[CrF(en)(tn)(H_2O)]I_2, 96482-39-2; *trans*-[CrF(en)(tn)(H_2O)]S_2O_6, 109864-13-3; *trans*-[CrF(tn)(chx)(H_2O)]Cl_2, 109864-14-4; *trans*-[CrF(tn)(chx)(H_2O)]Br_2, 109864-15-5; *trans*-[CrF(tn)(chx)(H_2O)]I_2, 109864-16-6; *trans*-[CrF(tn)(chx)(H_2O)]S_2O_6, 109864-17-7; *trans*-[CrF_2(en)(tn)]Br, 97107-81-8; *trans*-[CrF_2(tn)(chx)]Br, 109864-18-8; *trans*-[CrF(en)(tn)(H_2O)](ClO_4)$_2$, 96482-38-1; *trans*-[CrF(chx)(tn)(H_2O)](ClO_4)$_2$, 106676-16-8.

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Electronic Structure and Ligand Field States of $NpO_2Cl_4^{2-}$ and $NpO_2(NO_3)_3^-$: A Relativistic MS–Xα Study

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Relativistic MS–Xα calculations are reported for two neptunyl complexes: $NpO_2Cl_4^{2-}$ and $NpO_2(NO_3)_3^-$. From the MS–Xα results a perturbation method is used to set up simultaneous ligand field + spin–orbit coupling matrices for the f^1 system. The predicted symmetries and energies of the f–f transitions are in good agreement with experiment. The ligand field parameters obtained in this work for $NpO_2Cl_4^{2-}$ are compared with those of UCl_6^- and $PaCl_6^{2-}$ derived from other Xα calculations.

Introduction

The quasi-relativistic MS–Xα method (RXα) has been applied successfully to many molecules,[1–5] since the work of Boring et al. on the uranyl ion,[6] UO_2^{2+}. The development of the method to include the mass-velocity and Darwin terms necessary for treating molecules containing heavy atoms is due to Wood and Boring.[7] Their approach is based on the scheme described by Cowan and Griffin[8] for the solution of the Dirac–Hartree–Fock equation.

In this work the relativistic Xα spin–orbit coupling free Hamiltonian was used to obtain the SCF ground-state electronic structures of $NpO_2Cl_4^{2-}$ and $NpO_2(NO_3)_3^-$ ions.

Many attempts[9–11] have been elaborated in order to combine the Xα method with ligand field theory to obtain a proper description of the electronic d–d transitions of metal complexes. Good results have been obtained recently[12] for $CrCl_6^{3-}$ and CrF_6^{3-} ions from a direct evaluation of the Griffith electron repulsion parameters necessary for describing the energies of the ligand field

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