Preparation and Properties of Some Chromium(III) Complexes of 1,5,9,13-Tetraazatridecane

D. A. House,[a] J. Eriksen[b] and O. Mønsted[b]

[a]Department of Chemistry, University of Canterbury, Christchurch, New Zealand and [b]Department of Inorganic Chemistry, H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

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Chromium(III) reacts in anhydrous solvents with the title linear tetraamine, 3,3,3-tet or tn tn tn, to give compounds containing species of the general formula *trans*-[Cr(tn tn tn)X_2]. Stoichiometric studies have assigned the (*RS*)-*meso* configuration to the amine. This results in differently coordinated axial ligands, and kinetic studies of chloride ligand aquation in *trans*-[Cr(tn tn tn)Cl_2]$^+$ reveal very different reactivities of the two chloride ligands. This is rationalized in terms of significant differences in steric interactions of the complex and the attacking water molecule.

Inert transition metal complexes with tetraamine ligands have proved to be a rich and fruitful field of investigation. Since the pioneering work on cobalt(III) complexes of linear tetraamine ligands,[1] many such systems have been investigated.[2,3] While most of the early work concentrated on systems with cobalt(III) as the metal center, there has been considerable recent interest in related chromium(III) complexes.[4–8]

These two metal centers often provide contrasting reactivity patterns. Thus, for polyamine ligands with five-membered chelate ring systems, Cr-N bond rupture often competes with aquation of anionic ligands,[9] whereas Co-N bond rupture is rarely observed. However, as the ring size increases, the solvolysis rate for anionic ligands bound to cobalt(III) increases and the propensity for reduction to cobalt(II) also increases.[10] In contrast, the Cr-N bond rupture path is reduced for six-membered ring complexes[11] and the solvolysis rate for anionic ligands is hardly changed.[12]

This sequence of events leads to the situation that cobalt(III) complexes of 1,5,9,13-tetraazatridecane and 1,5,9,13-tetraazacyclohexadecane, ligands which both coordinate to give only six-membered chelate rings, are very unstable with respect to reduction and very labile with respect to ligand solvolysis.[13–16]

The stability of the Cr-N bond in six-membered ring complexes, together with the absence of any reasonable reduction pathway, have earlier motivated an investigation of chromium(III) complexes of the cyclic sixteen-membered tetraamine ring system.[8] This work describes the preparation and some properties of chromium(III) complexes of the linear tetraamine.

Results

1,5,9,13-tetraazatridecane (3,3,3-tet or tn tn tn) reacts with chromium(III) to give *trans*-tetraaminechromium(III) complexes. Green chromic chloride, dehydrated in *N,N*-dimethylformamide, gives a *trans*-dichlorido complex which can be purified as the perchlorate to give olive-green *trans*-[Cr(tn tn tn)Cl_2]ClO_4. Reaction of *trans*-difluoridotetrakis(pyridine)-chromium(III) give a *trans*-difluorido complex which is most conveniently isolated as the red-violet perchlorate salt, *trans*-[Cr(tn tn tn)F_2]ClO_4. This latter compound reacts with hydrochloric or hydrobromic acid to give *trans*-[Cr(tn tn tn)Cl_2]ClO_4 and *trans*-[Cr(tn tn tn)Br_2]ClO_4, respectively.

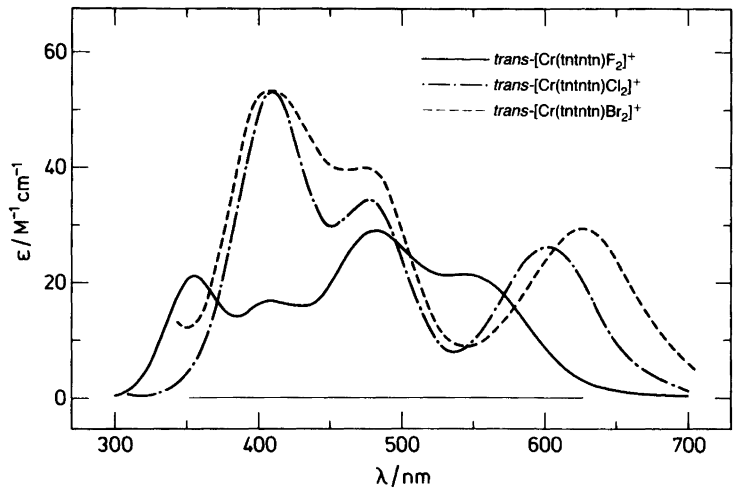

Fig. 1. Visible absorption spectra of *trans*-$[Cr(tn\,tn\,tn)F_2]^+$ (1.0 M $NaClO_4$), *trans*-$[Cr(tn\,tn\,tn)Cl_2]^+$ (1.0 M HCl) and *trans*-$[Cr(tn\,tn\,tn)Br_2]^+$ (1.0 M HCl).

Analytical data and ion exchange fractionation experiments confirm the purity of the compounds, and the visible absorption spectra of solutions of the compounds, shown in Fig. 1, permit unambiguous assignment of a *trans*-tetraamine configuration to the complexes and indicate the presence of the same *trans*-$[Cr(tn\,tn\,tn)Cl_2]^+$ cation in the two differently prepared perchlorate salts.

Base hydrolysis of the dibromido or the dichlorido compound gives solutions of a cation, the acid-base properties, visible absorption spectra (cf. Fig. 2) and elution behaviour of which indicate it to be *trans*-$[Cr(tn\,tn\,tn)(OH)_2]^+$. The corresponding diaqua complex is a divalent acid with acid dissociation constants given by: $-\log(K_1/M) \approx 3.45 \pm 0.02$ and $-\log(K_2/M) \approx 7.44 \pm 0.02$ (1.00 M $NaClO_4$, 25.0 °C), which is in good agreement with values for some similar complex cations in Ref. 8. Mercury(II)-accelerated aquation of the halide ligands in acidic solution, however, gives a mixture of tetraamine-diaqua complexes with the previously characterized *trans* complex as main constituent. Ion exchange fractionation of the band of trivalent cations indicates, however, another species in this band which is eluted with greater difficulty (cf. Fig. 2). Visible absorption spectra in acidic and basic solution, and titrations with base suggest that this may be *cis*-$[Cr(tn\,tn\,tn)(OH_2)_2]^{3+}$.

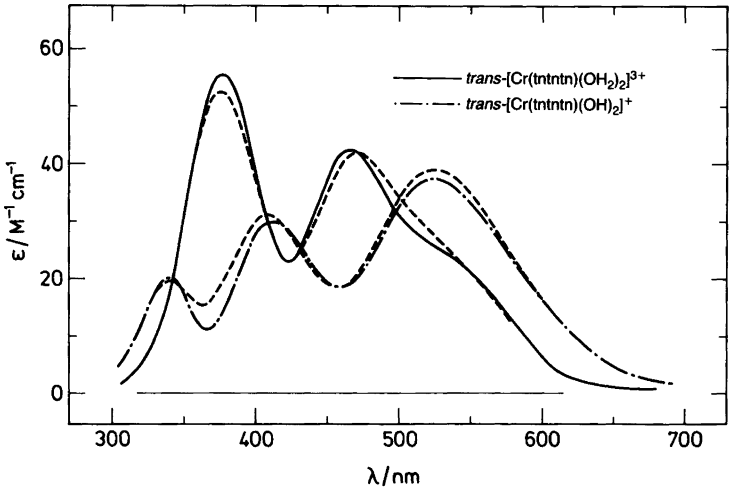

Fig. 2. Visible absorption spectra of *trans*-$[Cr(tn\,tn\,tn)(OH_2)_2]^{3+}$ (0.1 M $HClO_4$ + 0.9 M $NaClO_4$) and *trans*-$[Cr(tn\,tn\,tn)(OH)_2]^+$ (0.1 M NaOH + 0.9 M $NaClO_4$). Dashed curves are spectra of mixtures supposed to contain *cis*-Cr(tn tn tn) complexes.

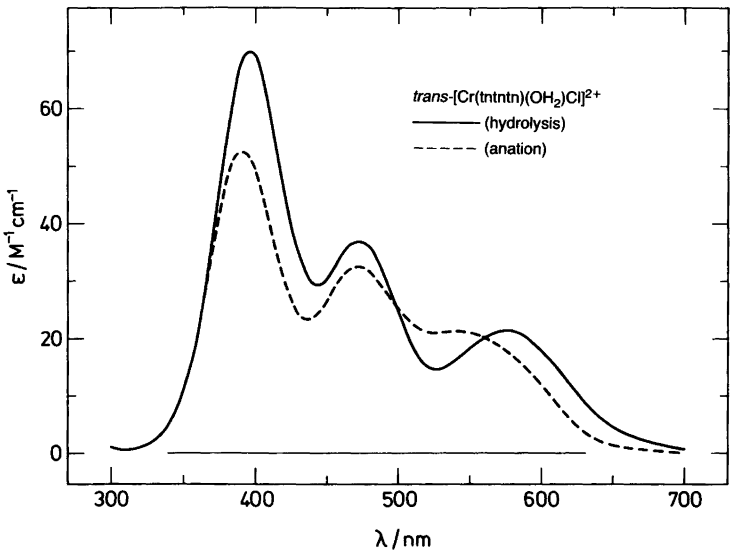

Fig. 3. Visible absorption spectra of two *trans*-$[Cr(tn\,tn\,tn)(OH_2)Cl]^{2+}$ isomers (0.1 M $HClO_4$ + 0.9 M $NaClO_4$).

Acid hydrolysis of *trans*-$[Cr(tn\,tn\,tn)Cl_2]^+$ gives the same *trans*-$[Cr(tn\,tn\,tn)(OH_2)_2]^{3+}$ isomer as that obtained by acidifying base-hydrolyzed solutions of the dibromido or dichlorido compounds. Aquation of chloride ligands in acidic solution is a two-stage process, and loss of the first chloride ligand is significantly faster than loss of the second. *trans*-$[Cr(tn\,tn\,tn)(OH_2)Cl]^{2+}$ can be isolated by ion exchange chromatography from partly hydrolyzed solutions, and fractionation experiments on the band of dipositive species indicate only one product. Anation with chloride of *trans*-$[Cr(tn\,tn\,tn)(OH_2)_2]^{3+}$, however, gives mixtures of dipositive cations. Ion exchange fractionation experiments on such solutions indicate the presence of two isomers, of which that eluted with greater difficulty is identical to that obtained by acid hydrolysis of the dichlorido compound. Both isomers regenerate *trans*-$[Cr(tn\,tn\,tn)(OH_2)_2]^{3+}$ on treatment with mercury(II), but at significantly different rates, with the isomer formed by hydrolysis reacting more slowly than that formed by anation. Visible absorption spectra of the two isomers are given in Fig. 3.

The rate of hydrolysis of the first chloride ligand in *trans*-$[Cr(tn\,tn\,tn)Cl_2]^+$ has been measured in trifluoromethanesulfonic acid and in nitric acid at a series of temperatures and hydrogen ion concentrations. Differently prepared isomers react at the same rate, and rate constants and activation parameters are given in Table 1.

Discussion

For octahedral complexes of the linear tetraamine 1,5,9,13-tetraazatridecane, three *cis* and two *trans* configurations are possible. The solid compounds isolated here undoubtedly have a *trans* configuration, as evidenced by the similarity of the visible absorption spectra with those of re-

Table 1. Summary of kinetic data for *trans*-$[Cr(tn\,tn\,tn)Cl_2]^+ \rightarrow$ *trans*-$[Cr(tn\,tn\,tn)Cl(OH_2)]^{2+} + Cl^-$.

Medium	Temperature range/°C	$10^3 \cdot k(70\,°C)/s^{-1}$	E_a/kJ mol^{-1}
0.1 M HNO_3	25–70	1.87 ±0.05	104.6±2.7
0.1 M CF_3SO_3H	25–70	1.817±0.017	108.3±1.2
1.0 M (Na, H) CF_3SO_3[a]	50–80	1.63 ±0.03	104.9±2.1
1.0 M HNO_3	70	1.62 ±0.05	–

[a] 0.25 M $\lesssim [H^+] \lesssim$ 1.00 M.

Table 2. Kinetic parameters for chloride ligand aquation of some *trans*-tetraaminedichloridochromium(III) complexes in acidic aqueous solution.

Tetraamine[a]	Medium	$10^6 \cdot k(25\,°C)/s^{-1}$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/JK^{-1} mol^{-1}	Ref.
$(NH_3)_4$	1 M (Na, H) ClO_4	45±3	88.9±1.2	−29±4	17, 18
(en)(tn)	0.4 M HNO_3	19.3±0.9	95±2	−15±7	19
$(Me_2\,tn)_2$	0.1 M HNO_3	22.0±0.5	100.9±1.3	+5±4	20
$(tn)_2$	0.1 M HNO_3	20.7±0.6	99.8±1.4	+1±5	12
$(tn)_2$	1 M (Na, H) ClO_4	9.9±1.0	107±2	+19±6	21
meso-2,3,2-tet	Dilute HNO_3	3.2±0.3	104±2	+4±6	22
rac-3,2,3-tet	0.1 M HNO_3	1.06±0.08	91.9±1.3	−50±4	6
cyclam	0.01 M HNO_3	0.026±0.012	113±3	−9±10	23
meso-3,3,3-tet	0.1 M HNO_3	7.4±0.9	102±3	−2±8	This work
meso-3,3,3-tet	1 M (Na, H) CF_3SO_3	6.3±0.8	102±2	−2±6	This work

[a]Abbreviations for ligand names are: en = 1,2-ethanediamine, tn = 1,3-propanediamine, Me_2 tn = 2,2-dimethyl-1,3-propanediamine, 2,3,2-tet = 1,4, 8, 11-tetraazaundecane, 3,2,3-tet = 1,5,8,12-tetraazadodecane, cyclam = 1,4,8,11-tetraazacyclotetradecane.

lated tetraaminechromium(III) systems. The two possible *trans* configurations are characterized by the conformation of the central chelate ring, which can have either a twist conformation, giving the *(RR,SS)-rac-trans* form with equivalent axial ligands, or have a chair conformation, giving the *(RS)-meso-trans* form with inequivalent axial ligands.

Characterization of only one isomer of those complexes with the general formula *trans*-[Cr(tn tn tn)X_2]$^+$, of two *trans*-[Cr(tn tn tn)(OH_2)Cl]$^{2+}$ isomers, and the ease of transformation between these *trans* complexes suggest that all the isolated components are isomerically pure and have the *meso-trans* amine configuration with inequivalent axial ligands.

The presence of only one of the *trans*-[Cr(tn tn tn)Cl(OH_2)]$^{2+}$ isomers in solutions obtained by acid chloride ligand hydrolysis of *trans*-[Cr(tn tn tn)Cl_2]$^+$ indicates a significant difference in reaction rates for aquation of the two different chloride ligands. Table 2 shows kinetic data for some other *trans*-tetraaminedichloridochromium (III) systems. Rate constants at 25 °C span more than three orders of magnitude, with *trans*-[Cr(cyclam)Cl_2]$^+$ reacting slowest. Coordinated 'cyclam' has both six-membered chelate rings in chair conformations, and this apparently protects the coordinated chloride ligands from replacement by an associative attack of an incoming water molecule. This rationalization applies to the "slow" chloride ligand in the present complex (cf. Fig. 4) and explains the significant rate difference.

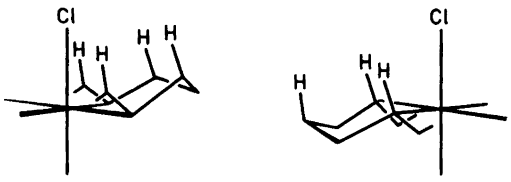

Fig. 4. Axial hydrogen atoms in the direction of the two differently coordinated chloride ligands in *(RS)-meso-trans*-[Cr(tn tn tn)Cl_2]$^+$.

Experimental

Caution! Although we have experienced no difficulties with the perchlorate salts described here, they should all be regarded as potentially explosive and handled accordingly.

Chemicals. The ligand, 1,5,9,13-tetraazatridecane (3,3,3-tet or tn tn tn), was either purchased from Eastman Organic Chemicals or was prepared by the method in Ref. 24. *trans*-[Cr$(py)_4F_2$]ClO_4 and *trans*-[Cr$(py)_4F_2$]I (py = pyridine) were prepared according to the procedure in Ref. 25. All other chemicals were of the best reagent grade commercially available and were purified as necessary.

1.trans-*[Cr(tn tn tn)Cl_2]ClO_4*. 4.25 g of hydrated chromium(III) chloride is boiled in 30 ml of *N,N*-dimethylformamide until the volume is reduced to about 20 ml and a deep purple colour develops. The resulting solution is cooled to about 100 °C and a solution of 3 g of tn tn tn in 20 ml of *N,N*-dimethylformamide is added with vigorous stirring. A green precipitate deposits and the mixture is digested at about 120 °C for 15 min. The product is collected from the ice-cooled solution by filtration, washed with 2-propanol and ether, and air dried. The perchlorate salt is obtained by dissolving the crude chloride in 60 ml of 3 M HCl at 40 °C and adding 10 ml of 60 % $HClO_4$. Olive green crystals deposit from the ice-cooled solution. They are isolated by filtration, and washed and dried as above. Yield 5 g (76 %). Anal. $CrC_9H_{24}N_4O_4Cl_3$: C, H, N.

2. trans-*[Cr(tn tn tn)F_2]ClO_4*. 15.1 g of *trans*-[Cr(py)$_4F_2$]ClO_4 is dissolved in 30 ml of warm 2-methoxyethanol. 5.6 g of tn tn tn is added to this solution, which is then heated under reflux for 1 h. During this treatment a red violet precipitate is gradually formed. The resulting mixture is cooled in ice, after which the precipitate is filtered off and washed twice with acetone. Yield 8.6 g (76 %). Anal. $CrC_9H_{24}N_4O_4F_2Cl$: C, H, N, Cr, Cl. The compound is difficult to recrystallize in good yield. The crude product is analytically pure, however, and can be used directly for subsequent synthetic work.

3. trans-*[Cr(tn tn tn)F_2]I* is prepared analogously to the perchlorate salt, but from *trans*-[Cr(py)$_4F_2$]I. The yield is slightly higher (83 %). Anal. $CrC_9H_{24}N_4F_2I$: C, H, N, Cr, I. This compound is also difficult to recrystallize in good yield and is a less satisfactory starting material for the following preparations than the perchlorate salt.

4. trans-*[Cr(tn tn tn)Cl_2]ClO_4*. 2.0 g of *trans*-[Cr(tn tn tn)F_2]ClO_4 is dissolved in 5 ml of conc. (37 %) hydrochloric acid and the solution kept in a Teflon flask at 100 °C for 1 h. The mixture is then left overnight at 0 °C. The dark green precipitate is filtered off and washed twice with a 1:1 acetone-ether mixture. Yield of crude material 1.6 g. The crude product is dissolved in 50 ml of a 1:1 acetone-water mixture at room temperature, the solution filtered, and the perchlorate precipitated by slowly adding 15 ml of conc. aqueous sodium perchlorate solution and cooling to 0 °C. The olive-green compound is filtered off and washed twice with ice-cold water. Yield 1.1 g (51 %) of the anhydrous compound. Anal. $CrC_9H_{24}N_4O_4Cl_3$: C, H, N, Cr, Cl.

5. trans-*[Cr(tn tn tn)Br_2]ClO_4*. This compound is prepared analogously to *trans*-[Cr(tn tn tn)Cl_2]ClO_4 (preparation No. 4), using 2.0 g of *trans*-[Cr(tn tn tn)F_2]ClO_4 and 5 ml of conc. (48 %) hydrobromic acid. Yield of crude green product 2.1 g. This is dissolved in 100 ml of 1:1 acetone-water mixture and reprecipitated and washed as in preparation No. 4. Yield 1.3 g (50 %). Anal. $CrC_9H_{24}N_4O_4Br_2Cl$: C, H, N, Cr, Br, Cl.

6. trans-*[Cr(tn tn tn)$(OH_2)_2$]$^{3+}$*. The *trans*-diaqua complex is generated in solution by acidifying solutions obtained by base hydrolysis of *trans*-[Cr(tn tn tn)Cl_2]$^+$ or *trans*-[Cr(tn tn tn)Br_2]$^+$ as follows: 100 mg of *trans*-[Cr(tn tn tn)Cl_2]ClO_4 (prep. No. 4) is treated with 10 ml of 0.1 M NaOH at room temperature for 30 min. The resulting mixture is filtered and acidified by addition of perchloric acid. Ion exchange fractionation experiments show identical spectral characteristics for all fractions of the 3+ charged eluate (cf. Fig. 2). Analogous treatment of *trans*-[Cr(tn tn tn)Cl_2]ClO_4 (prep. No. 1) or *trans*-[Cr(tn tn tn)Br_2]ClO_4 (prep. No. 5) gives a cation with identical elution behaviour and identical spectral characteristics.

Mercury(II) induced aquation of the halide ligands gives a mixture of triply-charged cations which are partially separated by ion exchange chromatography. Pure *trans*-[Cr(tn tn tn)$(OH_2)_2$]$^{3+}$ is eluted prior to fractions which according to their elution behaviour and spectral characteristics also contain some *cis*-[Cr(tn tn tn)$(OH_2)_2$]$^{3+}$ isomer (cf. Fig. 2).

7. trans-*[Cr(tn tn tn)Cl(OH_2)]$^{2+}$*. Acid hydrolysis of *trans*-[Cr(tn tn tn)Cl_2]$^+$ gives solutions which according to the mode of formation, the elution behaviour and the spectral characteristics contain *trans*-[Cr(tn tn tn)Cl(OH_2)]$^{2+}$. Ion exchange fractionation of the band of divalent cations shows only one component. This contrasts with the behaviour of solutions prepared by chloride ion anation of *trans*-[Cr(tn tn tn)$(OH_2)_2$]$^+$, where the band of dipositive ions contains two *trans*-[Cr

(tn tn tn)Cl(OH$_2$)]$^{2+}$ isomers. The species eluted with greater difficulty is identical to that obtained by hydrolysis of the dichlorido complex ion, and they both give the same *trans*-[Cr(tn tn tn)(OH$_2$)$_2$]$^{3+}$ ion on treatment with mercury(II), as judged from absorption spectra. The experimental conditions for formation of solutions of the aquachlorido complex ion are as follows:

Aquation: 100 mg of *trans*-[Cr(tn tn tn)Cl$_2$]ClO$_4$ is dissolved in 10 ml of 0.1 M HClO$_4$ at 80 °C and the solution kept at this temperature for 15 min. This gives a greyish green solution.

Anation: 150 mg of *trans*-[Cr(tn tn tn)Cl$_2$]ClO$_4$ is treated with 5 ml of 2 M NaOH at 25 °C for 15 min and the solution is then filtered into a mixture of 1 ml of 2 M HCl and 2 ml of 4 M NaCl. The resulting solution is kept at 80 °C for 30 min. This gives a greyish green solution.

8. cis-*[Cr(tn tn tn)(ox)]*$^+$. A mixture of 150 mg of *trans*-[Cr(tn tn tn)Br$_2$]ClO$_4$, 100 mg of Na$_2$(ox) and 150 mg H$_2$(ox) [(ox) ≡ oxalate dianion] in 15 ml of water is kept at 100 °C for 5 min. This gives a red to reddish-violet solution. Ion exchange fractionation experiments suggest the presence of small amounts of [Cr(ox)$_3$]$^{3+}$ and [Cr(tn tn tn H$_2$)(ox)$_2$]$^+$ in addition to the desired *cis*-[Cr(tn tn tn)(ox)]$^+$ ion. Fractions of this latter complex have visible absorption spectra with maxima around 375 nm and 498 nm, which is typical for *cis*-tetraamineoxalatochromium(III) ions. The molar absorption coefficients are not constant for individual fractions, however, and are also slightly different in acidic and basic solution. This suggests the presence of several *cis*-isomers and possibly also some [Cr(tn tn tn)(oxH)$_2$]$^+$.

Ion exchange chromatography. Cation fractionation experiments were performed using 2×20 cm Sephadex SP-C-25 filled columns and aqueous 0.25 − 0.50 M NaClO$_4$ + 0.001 M HClO$_4$ as eluent. Further details may be found in Ref. 8.

Kinetic measurements. The rate of loss of the first chloride ligand from *trans*-[Cr(tn tn tn)Cl$_2$]$^+$ in acidic solution was measured spectrophotometrically using either a Varian DMS-100 or a Cary 118 C spectrophotometer. Solutions of the reaction medium were allowed to reach thermal equilibrium in a thermostatted cell housing, and small samples of the solid salt were then added. *Method of calculation.* Pseudo first-order rate constants, k_{obs}, were calculated from the absorbance vs. time data: $A(t)_{obs}$. In order to minimize possible interference from aquation of the second chloride ligand, $A(t)_{obs}$ was approximated by

$$A(t)_{obs} \approx A(t)_{calc} = a_o + a_1 \cdot e^{-k_{obs}t} + a_2 t$$

and the four parameters k_{obs}, a_o, a_1 and a_2 were determined by minimization of

$$\sum_t [A(t)_{obs} - A(t)_{calc}]^2/\sigma^2[A(t)_{obs}]$$

where $\sigma[A(t)_{obs}]$ is the estimated uncertainty in the measured absorbances.

Activation parameters were calculated from the variation of k_{obs} with temperature.[26,27]

Potentiometric titrations and the processing of the data to give acid dissociation constants were performed as previously described.[28]

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