

**Figure 2.** Schematic diagram of  $H_2$  evolution by 1:12 tungstates. "Org" is an organic reagent that undergoes irreversible oxidation. Hydrogen is produced with and without the Pt catalyst.

of reduced tungstates takes place by  $H^+$ .

Another possible mechanism would be the formation of an alkoxide. However, tungstate ions in HPC are already coordinated to six oxygen atoms, and another oxygen on a seventh coordination site is unlikely.<sup>10</sup>

Table II shows the maximum number of electrons obtained with and without a Pt catalyst, whereas (Table III shows the average rates of hydrogen evolution and HPC reoxidation for all four photochemically reduced tungstates. It should be noted that the extent of reduction and, subsequently, the rate of hydrogen evolution are a function of the intensity of incident light. Extent of reduction is the point at which a steady state is obtained; i.e., the rate of photoreduction of HPC (reactions 1-3) is matched by the rate of reoxidation by  $H^+$  (reaction 4).<sup>11</sup>

- (10) See for instance: Charman, H. B. *J. Chem. Soc. B* 1967, 629 and references therein.
- (11) The calculations of the maximum number of electrons, obtained at the steady-state condition, was made simply from the absorbance and the known molar absorptivities of the reduced species. For instance, if the absorbance indicated that there was a mixture of 1- and 2-electron-reduced products, then if  $C_1$  and  $C_2$  were the corresponding percent concentrations and  $\epsilon_1$  and  $\epsilon_2$  the molar absorptivities,  $C_1\epsilon_1 + C_2\epsilon_2 = 100A/C_i$  and  $C_1(1e) + C_2(2e) = 100 Y_e$ , where  $Y_e$  is the total number of electrons added to the HPC and  $C_i$  is the concentration of HPC.

Apparently HPC also serve as heterogeneous catalysts, in the absence of metallic Pt, but are not as effective. The cycle for  $H_2$  evolution is depicted in Figure 2. The rate of  $H_2$  production is limited by the low quantum yield of HPB production. The quantum yield for the first reduction step (addition of one electron) is of the order of  $\sim 0.15$ , with alcohols, glycols, and glycol acids presenting generally higher quantum yields than carboxylic acids. The quantum yield drops to about  $\sim 0.01$  for the second reduction step of  $PW_{12}^{3-}$ .<sup>12</sup> This is in accordance with the ease of hydrogen abstraction from organic compounds.<sup>13</sup>

Reoxidation of HPBs by  $H^+$  seems to be 100% efficient. The rate of reoxidation of HPB (reaction 4) was followed by the change in absorbance of the HPB bands at  $\sim 750$  nm, after the photolysis lamp was shut off (Table III; Figure 1). This was done by carefully excluding oxygen, first by deaeration and second by repeating cycles of photoreduction and back-reoxidation in which the leftover oxygen was consumed. The total production of hydrogen, measured by gas chromatography, verified reaction 4. About 1 mL of hydrogen was generally produced from 10 mL of HPC ( $5 \times 10^{-4}$  M) and isopropyl alcohol (1 M) in 0.1 M  $HClO_4$ , after 24 h of photolysis with a 150-W Xe lamp. This amounts to an efficiency of the order of one molecule of hydrogen per 100 photons absorbed. The low yield represents the low efficiency of photoreduction of higher reduction products as mentioned before.

Comparing this to other systems, one notes that here one substance, the HPC, functions as sensitizer, relay, and catalyst, as opposed to three components, namely  $Ru(bpy)_3^{2+}$ ,  $MV^{2+}$ , and the platinum catalyst used in the best known system so far. A serious disadvantage, though, is the low absorptivity of HPC in the visible area. However, with appropriate sensitizers, these compounds might be useful as relays and photocatalysts. Work on these matters, is in progress.

**Acknowledgment.** We thank M. Z. Hoffman and N. Rakintzis for useful discussions and comments. Financial support from NATO is gratefully acknowledged.

**Registry No.**  $PW_{12}O_{40}^{3-}$ , 12534-77-9;  $SiW_{12}O_{40}^{4-}$ , 12363-31-4;  $FeW_{12}O_{40}^{5-}$ , 12181-27-0;  $H_2W_{12}O_{40}^{6-}$ , 12207-61-3;  $CH_3OH$ , 67-56-1; Pt, 7440-06-4;  $H_2$ , 1333-74-0; isopropyl alcohol, 67-63-0.

- (12) Dimotikali, D.; Papaconstantinou, E. *Inorg. Chim. Acta* 1984, 87, 177.
- (13) See for instance: Swallow, A. J. *Prog. React. Kinet.* 1978, 9, 195.

## Notes

Contribution from the Dipartimento di Chimica, Università di Perugia, 06100 Perugia, Italy

### Kinetics of Stepwise Aquation of the *trans*-Dicyanotetraamminechromium(III) Cation

Pietro Ricciari and Edoardo Zinato\*

Received February 15, 1984

In transition-metal chemistry, cyanide stands out among the acido ligands because of several features of kinetic interest: (i) the exceptional stability of the coordinate bond; (ii) the large trans effect; (iii) the high basicity that enables extensive proton uptake by the coordinate group.<sup>1</sup> As part of a continuing study of the ground-state<sup>2</sup> and excited-state reactivity<sup>3-5</sup> of Cr(III) cyano

ammines, we report here on the aquation kinetics of *trans*-Cr( $NH_3$ )<sub>4</sub>(CN)<sub>2</sub><sup>+</sup> and *trans*-Cr( $NH_3$ )<sub>4</sub>(H<sub>2</sub>O)(CN)<sub>2</sub><sup>+</sup>. The purpose was to characterize the role of protonation, with regard to both its equilibrium and kinetic aspects, made particularly significant by the trans arrangement of the CN<sup>-</sup> ligands.

Besides our previous account on Cr( $NH_3$ )<sub>5</sub>(CN)<sub>2</sub><sup>2+</sup>,<sup>2</sup> other kinetic studies of CN<sup>-</sup> aquation in Cr(III) systems have been reported for some members of the Cr(H<sub>2</sub>O)<sub>6-n</sub>(CN)<sub>n</sub><sup>3-n</sup> series.<sup>6-9</sup>

### Experimental Section

*trans*-[Cr( $NH_3$ )<sub>4</sub>(CN)<sub>2</sub>](ClO<sub>4</sub>) was prepared by a reported procedure.<sup>10</sup> *trans*-Cr( $NH_3$ )<sub>4</sub>(H<sub>2</sub>O)(CN)<sub>2</sub><sup>+</sup> was obtained in situ by acid

- (1) For recent reviews on cyano complexes see: (a) Griffith, W. P. *Coord. Chem. Rev.* 1975, 17, 177. (b) Sharpe, A. G. "The Chemistry of Cyano Complexes of the Transition Metals"; Academic Press: London, 1976.
- (2) Ricciari, P.; Zinato, E. *Inorg. Chem.* 1980, 19, 853.

- (3) Ricciari, P.; Zinato, E. *Inorg. Chem.* 1980, 19, 3279.
- (4) Zinato, E.; Ricciari, P.; Prelati, M. *Inorg. Chem.* 1981, 20, 1432.
- (5) Ricciari, P.; Zinato, E. *Inorg. Chem.* 1983, 22, 2305.
- (6) Birk, J. P.; Espenson, J. H. *Inorg. Chem.* 1968, 7, 991.
- (7) Wakefield, D. K.; Schaap, W. B. *Inorg. Chem.* 1969, 8, 512.
- (8) Wakefield, D. K.; Schaap, W. B. *Inorg. Chem.* 1969, 8, 811.
- (9) Wakefield, D. K.; Schaap, W. B. *Inorg. Chem.* 1971, 10, 306.
- (10) Ricciari, P.; Zinato, E. *Inorg. Chem.* 1981, 20, 3722.

**Table I.** Pseudo-First-Order Rate Constants<sup>a</sup> for Aquation of Cyano Ammine Complexes of Chromium(III)<sup>b</sup>

[H <sup>+</sup> ], M	<i>trans</i> -Cr(NH <sub>3</sub> ) <sub>4</sub> (CN) <sub>2</sub> <sup>+</sup> 10 <sup>3</sup> <i>k</i> <sub>obsd</sub> , s <sup>-1</sup>			<i>trans</i> -Cr(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O)(CN) <sub>2</sub> <sup>2+</sup> 10 <sup>3</sup> <i>k</i> <sub>obsd</sub> , s <sup>-1</sup>		
	15.0 °C	25.0 °C	35.0 °C	35.0 °C	45.0 °C	55.0 °C
0.00100			1.23			
0.00250			3.04			
0.00350			4.12			0.250
0.00500			5.98			0.270
0.0100	1.62	4.76	11.8		0.090	0.300
0.0500	7.04	18.9	49.3		0.240	0.630
0.100	12.1	33.1	82.4	0.128	0.350	1.05
0.200	18.9	48.1	133	0.230	0.630	1.73
0.400	23.9	67.2	178	0.435	1.24	3.22
0.600	28.7	76.6	208	0.650	1.80	4.65
0.800	29.5	83.0	215	0.848	2.36	6.37
1.00	31.3	87.5	220	1.02	2.90	7.82
1.20	32.3	88.0	223	1.30	3.55	8.97
1.40	32.6	91.5	228	1.48	4.06	11.0
1.60	32.8	92.7	233	1.67	4.56	12.6
1.80	33.0	94.1	236	1.83	5.11	13.9
2.00	33.3	96.3	238	2.07	5.61	14.4

<sup>a</sup> Each entry is the average of at least three kinetic experiments. Precision is ±3%. <sup>b</sup> Ionic strength maintained constant at 2.0 M by added sodium perchlorate.

hydrolysis of the parent *trans*-dicyano complex,<sup>10</sup> in the course of the kinetic measurements.

The rates of CN<sup>-</sup> aquation were determined spectrophotometrically, as already described,<sup>2</sup> by following the decrease of the charge-transfer band at 230 nm. Here, the extinction coefficients of the two cyano complexes ( $\epsilon$  1330 and 470, respectively), as well as their difference, are fairly large, while the final aquation product absorbs much less ( $\epsilon$  70). Complex concentrations were (2–3 × 10<sup>-4</sup> M; the acidity ranged between 1 × 10<sup>-3</sup> and 2.00 M HClO<sub>4</sub>, and the ionic strength was kept constant at 2.00 M by addition of NaClO<sub>4</sub>. Buffers were avoided, since previous experience with Cr(NH<sub>3</sub>)<sub>2</sub>(CN)<sub>2</sub><sup>2+</sup> yielded evidence of anation by acetate and phosphate ions.<sup>2</sup> Reactions were usually followed for 3–4 half-lives. At 35 °C both aquation stages were studied in sequence. At 15 and 25 °C only the first step was monitored, whereas at 45 and 55 °C only the second stage was measurable, as most of the dicyano complex disappeared within a few seconds.

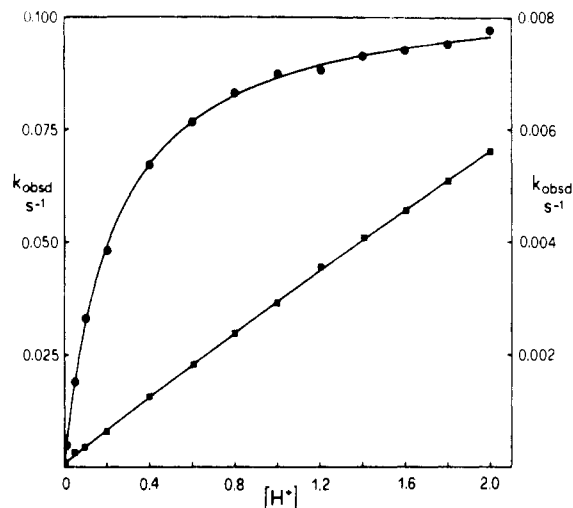
Absorption decay traces were digitized by use of a plotter, connected with an HP 9825 B desk computer. For aquation of *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub><sup>+</sup> it was not possible to measure  $A_{\infty}$ , since the product, *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)(CN)<sub>2</sub><sup>2+</sup>, undergoes further reaction. The experimental  $A_t$  values were then treated according to eq 1, where  $\Delta$  is a constant and

$$A_t = A_{\infty}(1 - \exp(-k\Delta)) + A_{t+\Delta} \exp(-k\Delta) \quad (1)$$

arbitrary time increment.<sup>11,12</sup> For a given run, the result was independent of the  $\Delta$  value, in the 0.5–2 half-life range. For the second aquation stage, final optical densities were often measured after 8–10 half-lives. The calculated and experimental  $A_{\infty}$  values always agreed within 1% of the total absorption changes occurring during reaction. The reported rate constants are the average of three or more independent determinations. The reproducibility was generally ±3%. Activation parameters were obtained from least-squares analyses of  $\log(k/T)$  vs.  $1/T$ .

## Results and Discussion

While neutral or basic solutions of *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub><sup>+</sup> are highly inert,<sup>10</sup> acidic samples undergo rapid CN<sup>-</sup> aquation. The terminal product, exclusively *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)(CN)<sub>2</sub><sup>2+</sup> (as authenticated by spectral comparison with an independently synthesized sample), warrants substitution of both cyanides to proceed with total stereoretention, in line with the customary ground-state, aqueous behavior of Cr(III) amines.<sup>13,14</sup> Aquation is accompanied by a bathochromic shift of the ligand field maxima, consistent with coordination of the spectrochemically weaker H<sub>2</sub>O ligand. In addition, the intense and structured charge-transfer band, typical of coordinated CN<sup>-</sup>,<sup>10</sup> progressively drops, to dis-



**Figure 1.** Dependence of the pseudo-first-order rate constants on the hydrogen ion concentration at a constant ionic strength of 2.0 M: circles, aquation of *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub><sup>+</sup> at 25.0 °C (left scale); squares, aquation of *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)(CN)<sub>2</sub><sup>2+</sup> at 45.0 °C (right scale).

appear upon complete cyanide loss. The general spectrophotometric changes alone provide evidence that aquation occurs in two successive steps, separated by at least 2 orders of magnitude. Isobestic points are, in fact, maintained at 449, 387, and 357 nm up to at least 95% removal of one CN<sup>-</sup> group. Subsequently, new crossing points persist at 511, 412, and 361 nm until cyanide solvation is complete.

Such an evolution allowed an independent kinetic study for each stage. For both stages, plots of eq 1 were linear ( $r > 0.999$ ) up to 70–90% conversion.<sup>15</sup> The pseudo-first-order rate constants,  $k_{\text{obsd}}$ , given in Table I, show a large acid dependence. However, the patterns for the first and the second step are different, as illustrated in Figure 1. Both aquation stages can be described in terms of an acid-independent pathway ( $k_0$ ) and an acid-dependent one ( $k_H$ ), the latter consequent to instantaneous and reversible ( $K$ ) protonation of a fraction of the reactant. According to this scheme

$$k_{\text{obsd}} = (k_0 + k_H K [H^+]) / (1 + K [H^+]) \quad (2)$$

The  $k_0$ ,  $k_H$ , and  $K$  parameters were determined by fitting the  $k_{\text{obsd}}$  data to eq 2 by means of a nonlinear least-squares treatment, involving iterative calculations. For *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub><sup>+</sup> the intercepts of eq 2 are very close to zero, so that only upper limits were established for  $k_0$ . Also, for *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)(CN)<sub>2</sub><sup>2+</sup>, the scarce curvature in the plots of Figure 1, denoting small extents of protonation, allowed only the  $k_H K$  products to be determined with sufficient precision, and a larger uncertainty remained on the individual contributions of  $k_H$  and  $K$ . The kinetic and equilibrium parameters are collected in Table II.

Two main features, both related to the atypical electronic and bonding properties of CN<sup>-</sup>, characterize the aquation behavior of these complexes: very low  $k_0$  values and, by contrast, remarkably high  $k_H$  values. The large predominance of acid-assisted aquation is evidently due to protonation of the departing ligand, as has already been observed in Cr(NH<sub>3</sub>)<sub>3</sub>X<sup>2+</sup> ions with X = CN,<sup>2</sup> F,<sup>16</sup> N<sub>3</sub>,<sup>17</sup> ONO,<sup>18</sup> and OCOCCl<sub>3</sub>,<sup>19</sup> as well as in some Cr-

(11) Kezdy, F. J.; Jaz, J.; Bruylants, A. *Bull. Soc. Chim. Belg.* **1958**, *67*, 687.

(12) Swinbourne, E. S. *J. Chem. Soc. A* **1960**, 2371.

(13) Garner, C. S.; House, D. A. *Transition Met. Chem. (N.Y.)* **1970**, *6*, 59.

(14) Archer, R. D. *Coord. Chem. Rev.* **1969**, *4*, 243.

(15) Only for  $[H^+] > \text{ca. } 0.5 \text{ M}$ , the first stage showed an initial upward curvature. This may be ascribed in part to improper instrumental response for very fast conversions, but possibly also to a nonaquation process of a Cr–NC linkage isomer, instantaneously formed in neutral solution, i.e., before acid addition, and converting back to the Cr–CN form upon acidification, with a fast, but finite rate. Evidence for such a complexity has been obtained for Cr(NH<sub>3</sub>)<sub>3</sub>(CN)<sub>2</sub><sup>2+</sup> in approximately the same pH range: Huchital, D.; Adamson, A. W., private communication.

(16) Jones, T. P.; Phillips, J. K. *J. Chem. Soc. A* **1968**, 674.

(17) Staples, P. J. *J. Chem. Soc. A* **1968**, 2731.

(18) Matts, T. C.; Moore, P. *J. Chem. Soc. A* **1969**, 219.

Table II. Kinetic and Equilibrium Data for Cyanide Aquation of Cyano Ammine and Cyano Aquo Complexes of Chromium(III) at  $\mu = 2.0$  M

complex	temp, °C	$10^5 k_0, s^{-1}$	$K, M^{-1}$	$10^2 k_H, s^{-1}$	$10^3 k_H K, M^{-1} s^{-1}$	ref
<i>trans</i> -Cr(NH <sub>3</sub> ) <sub>4</sub> (CN) <sub>2</sub> <sup>+</sup>	15.0	<1	5.1 ± 0.7	3.7 ± 0.1 <sup>c</sup>	190 ± 30	a
	25.0	<2	4.2 ± 0.7	10.7 ± 0.2 <sup>c</sup>	450 ± 50	a
	35.0	<6	5.1 ± 0.7	26.2 ± 1.0 <sup>c</sup>	1340 ± 130	a
<i>trans</i> -Cr(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O)(CN) <sub>2</sub> <sup>+</sup>	25.0 <sup>b</sup>	0.48 ± 0.14	0.028 ± 0.010	1.3 ± 0.5	0.350 ± 0.006	a
	35.0	1.7 ± 0.5 <sup>d</sup>	0.032 ± 0.010	3.3 ± 0.7 <sup>e</sup>	1.06 ± 0.01	a
	45.0	6 ± 2 <sup>d</sup>	0.036 ± 0.010	8.4 ± 1.7 <sup>e</sup>	2.98 ± 0.03	a
	55.0	18 ± 5 <sup>d</sup>	0.041 ± 0.012	19.4 ± 2.9 <sup>e</sup>	7.98 ± 0.15	a
Cr(NH <sub>3</sub> ) <sub>5</sub> (CN) <sub>2</sub> <sup>+</sup>	25.0	<0.01	0.28 ± 0.01	1.47 ± 0.04	4.10 ± 0.01	2
<i>fac</i> -Cr(H <sub>2</sub> O) <sub>3</sub> (CN) <sub>3</sub>	25.0	<0.3	1.1 ± 0.4	0.058 ± 0.023	0.66 ± 0.02	9
<i>cis</i> -Cr(H <sub>2</sub> O) <sub>4</sub> (CN) <sub>2</sub> <sup>+</sup>	25.0	<0.6	0.55 ± 0.22	0.15 ± 0.06	0.84 ± 0.02	9
Cr(H <sub>2</sub> O) <sub>5</sub> (CN) <sub>2</sub> <sup>+</sup>	25.0	1.1 ± 0.1	0.19 ± 0.01	0.32 ± 0.01	0.590 ± 0.005	7

<sup>a</sup> This work. <sup>b</sup> Values at 25.0 °C are obtained from the activation parameters. <sup>c</sup>  $\Delta H^\ddagger = 16.7 \pm 0.5$  kcal mol<sup>-1</sup>;  $\Delta S^\ddagger = -7 \pm 2$  eu mol<sup>-1</sup>. <sup>d</sup>  $\Delta H^\ddagger = 23 \pm 3$  kcal mol<sup>-1</sup>;  $\Delta S^\ddagger = -6 \pm 9$  eu mol<sup>-1</sup>. <sup>e</sup>  $\Delta H^\ddagger = 17 \pm 3$  kcal mol<sup>-1</sup>;  $\Delta S^\ddagger = -10 \pm 7$  eu mol<sup>-1</sup>.

(H<sub>2</sub>O)<sub>6-n</sub>(CN)<sub>n</sub><sup>3-n</sup> species.<sup>6-9</sup> Table II includes the data at 25 °C for other Cr(III) cyano ammine and cyano aquo complexes and shows some interesting regularities and exceptions.

All the  $k_0$  parameters are smaller than the corresponding  $k_H$  values by 2-5 orders of magnitude. This reflects the strong  $\sigma$  bonding of CN<sup>-</sup>, further stabilized by the  $\pi$  back-donation. As discussed previously,<sup>2</sup> the magnitude of  $k_0$  fits the expectations based on the combination of  $\sigma$  and  $\pi$  effects that, within homogeneous groups of complexes, determines a familiar sequence of leaving ability, placing CN<sup>-</sup> at the lower end of the series of the most common monodentate ligands.<sup>20,21</sup>

The protonation constants,  $K$ , tend, in general, to increase with decreasing complex charge. However, while in the cyano aquo systems the  $K$  values differ by a nearly constant and relatively small factor, less uniformity is apparent in the cyano amines, indicating that other effects, besides the electrostatic ones, are operative in the latter. Specifically, despite similar extents of proton uptake by Cr(NH<sub>3</sub>)<sub>5</sub>(CN)<sub>2</sub><sup>+</sup> and Cr(H<sub>2</sub>O)<sub>5</sub>(CN)<sub>2</sub><sup>+</sup>, on passing to the respective dicyano complexes the increase of  $K$  is much larger for *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub><sup>+</sup> than for *cis*-Cr(H<sub>2</sub>O)<sub>4</sub>(CN)<sub>2</sub><sup>+</sup>. This is a definite example of thermodynamic trans effect,<sup>22</sup> ascribable to the high electron donor power of CN<sup>-</sup>. Even the neutral *fac*-Cr(H<sub>2</sub>O)<sub>3</sub>(CN)<sub>3</sub> species, where the CN<sup>-</sup> groups are cis to one another, is much less protonated. Noteworthy is the considerable difference between the  $K$  values of the equally charged Cr(NH<sub>3</sub>)<sub>5</sub>(CN)<sub>2</sub><sup>+</sup> and *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)(CN)<sub>2</sub><sup>+</sup> ions that may be explained by the larger electronegativity of oxygen, relative to nitrogen. Thus, the strength of the *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>X(CNH)<sub>2</sub><sup>+</sup> acids increases in the order X = CN < NH<sub>3</sub> < H<sub>2</sub>O; i.e., it consistently parallels the electron-withdrawing ability of the X ligand.

In the absence of extraneous effects, the  $k_H$  rate constants are expected to increase regularly with the positive charge of the complex because of increasing ligand repulsion, as is true in the cyano aquo series. For *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub><sup>+</sup>,  $k_H$  is exceptionally high with respect to the other cyano amines, which are both 2+ ions. Such an inversion is accounted for by the large trans labilizing influence of cyanide.<sup>20-22</sup> The strikingly high reactivity of the *trans*-dicyano complex (described almost totally by the  $k_H K$  term) is therefore due to the combination of thermodynamic and kinetic trans effects.

The separation of equilibrium from rate contributions allows a further comparison between the two dipositive cyano amines. Since the intrinsic reactivity of the protonated form is nearly the same for both these ions, the difference between the overall aquation rates is exclusively determined by the different extents of protonation. In conclusion, while in the cyano aquo family (whose known members have adjacent CN<sup>-</sup> groups) the balancing of the opposing trends of  $k_H$  and  $K$  levels off the  $k_H K$  products,

the trans effects operating in the cyano amines give rise to a much wider range of reactivities.

**Acknowledgment.** Financial support of the National Research Council of Italy (CNR) is gratefully acknowledged.

**Registry No.** *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub><sup>+</sup>, 76299-50-8; *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)(CN)<sub>2</sub><sup>+</sup>, 74523-68-5.

Contribution from Argonne National Laboratory, Argonne, Illinois 60439

### Ligand Field Spectra of the 3d Transition Metals in Molten Cesium Trifluoroacetate-Sodium Trifluoroacetate-Potassium Trifluoroacetate<sup>†</sup>

C. E. Philbin<sup>‡</sup> and V. A. Maroni\*

Received June 4, 1984

This paper reports the results of electronic absorption spectroscopic studies that were carried out to investigate the ligand field properties of 3d transition metals in molten alkali-metal trifluoroacetates. The purpose of these studies was to examine the nature of transition-metal trifluoroacetate complexes in a medium free of other ligands and to explore the solvent properties of molten trifluoroacetates relative to other glassy and molten salts and to water.

### Experimental Section

The trifluoroacetate (TFAc) salt used in these studies had the composition 50 mol % CsTFAc-25 mol % K(TFAc)-25 mol % NaTFAc. Its preparation was carried out as follows: A concentrated aqueous solution of Cs<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> (50-25-25 mol %) was neutralized to pH 5 with 5 N trifluoroacetic acid and then evaporated to near dryness on a rotary evaporator, with the bath operated at ~70 °C. The product was further dried by vacuum evaporation on a glass vacuum line at ~70 °C. Following this, the molten salt was cooled to room temperature (~22 °C, where it was initially an extremely viscous liquid) and then placed in a helium atmosphere glovebox. After a period of several days, the viscous liquid crystallized. The crystalline salt was then broken free from its glass enclosure and stored in a capped bottle inside the glovebox. All subsequent weighings and transfers of this salt (i.e., into spectrophotometer tubes) were done in the helium atmosphere glovebox. A differential scanning calorimetry (DSC) measurement (40 → 150 → 40 °C) showed the melting point of the crystallized TFAc salt to be in the 75-80 °C range. No exothermic peak was observed in the DSC cooling curve down to 40 °C.

The transition-metal (TM) solutions were prepared by adding small measured quantities of the TM acetate, chloride, or fluoride (commercial high-purity grades) to the TFAc salt. Equilibration experiments were performed in Pyrex sample tubes with sealed-off bottoms that were ~5-mm I.D. and ~130-mm length of which ~25 mm was taken up by the

(19) Zinato, E.; Furlani, C.; Lanna, G.; Riccieri, P. *Inorg. Chem.* 1972, 11, 1746.

(20) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; Chapter 3.

(21) Langford, C. H.; Gray, H. B. "Ligand Substitution Processes"; W. A. Benjamin: New York, 1965.

(22) Pratt, J. M.; Thorp, R. G. *Adv. Inorg. Chem. Radiochem.* 1969, 12, 375.

<sup>†</sup> Work performed under the auspices of the U.S. Department of Energy.

<sup>‡</sup> Present address: Department of Chemistry, Columbia University, New York, NY 10027.