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
trans-Cr(NH$_3$)$_4$(CN)$_2$$^+$	15.0	<1	5.1 ± 0.7	3.7 ± 0.1^c	190 ± 30	a
	25.0	<2	4.2 ± 0.7	10.7 ± 0.2^c	450 ± 50	a
	35.0	<6	5.1 ± 0.7	26.2 ± 1.0^c	1340 ± 130	a
trans-Cr(NH$_3$)$_4$(H$_2$O)(CN)$^{2+}$	25.0^b	0.48 ± 0.14	0.028 ± 0.010	1.3 ± 0.5	0.350 ± 0.006	a
	35.0	1.7 ± 0.5^d	0.032 ± 0.010	3.3 ± 0.7^e	1.06 ± 0.01	a
	45.0	6 ± 2^d	0.036 ± 0.010	8.4 ± 1.7^e	2.98 ± 0.03	a
	55.0	18 ± 5^d	0.041 ± 0.012	19.4 ± 2.9^e	7.98 ± 0.15	a
Cr(NH$_3$)$_5$(CN)$^{2+}$	25.0	<0.01	0.28 ± 0.01	1.47 ± 0.04	4.10 ± 0.01	2
fac-Cr(H$_2$O)$_3$(CN)$_3$	25.0	<0.3	1.1 ± 0.4	0.058 ± 0.023	0.66 ± 0.02	9
cis-Cr(H$_2$O)$_4$(CN)$_2$$^+$	25.0	<0.6	0.55 ± 0.22	0.15 ± 0.06	0.84 ± 0.02	9
Cr(H$_2$O)$_5$(CN)$^{2+}$	25.0	1.1 ± 0.1	0.19 ± 0.01	0.32 ± 0.01	0.590 ± 0.005	7

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

(H$_2$O)$_{6-n}$(CN)$_n$$^{3-n}$ species.[6-9] 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 σ bonding of CN$^-$, further stabilized by the π back-donation. As discussed previously,[2] the magnitude of k_0 fits the expectations based on the combination of σ and π effects that, within homogeneous groups of complexes, determines a familiar sequence of leaving ability, placing CN$^-$ at the lower end of the series of the most common monodentate ligands.[20,21]

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 ammines, indicating that other effects, besides the electrostatic ones, are operative in the latter. Specifically, despite similar extents of proton uptake by Cr(NH$_3$)$_5$(CN)$^{2+}$ and Cr(H$_2$O)$_5$(CN)$^{2+}$, on passing to the respective dicyano complexes the increase of K is much larger for *trans*-Cr(NH$_3$)$_4$(CN)$_2$$^+$ than for *cis*-Cr(H$_2$O)$_4$-(CN)$_2$$^+$. This is a definite example of thermodynamic trans effect,[22] ascribable to the high electron donor power of CN$^-$. Even the neutral *fac*-Cr(H$_2$O)$_3$(CN)$_3$ species, where the CN$^-$ 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$_3$)$_5$(CN)$^{2+}$ and *trans*-Cr(NH$_3$)$_4$(H$_2$O)(CN)$^{2+}$ ions that may be explained by the larger electronegativity of oxygen, relative to nitrogen. Thus, the strength of the *trans*-Cr-(NH$_3$)$_4$X(CNH)$^{i+}$ acids increases in the order X = CN < NH$_3$ < H$_2$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$_3$)$_4$(CN)$_2$$^+$, k_H is exceptionally high with respect to the other cyano ammines, which are both 2+ ions. Such an inversion is accounted for by the large trans labilizing influence of cyanide.[20-22] 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 ammines. 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$^-$ 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 ammines give rise to a much wider range of reactivities.

Registry No. *trans*-Cr(NH$_3$)$_4$(CN)$_2$$^+$, 76299-50-8; *trans*-Cr(NH$_3$)$_4$-(H$_2$O)(CN)$^{2+}$, 74523-68-5.

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Ligand Field Spectra of the 3d Transition Metals in Molten Cesium Trifluoroacetate–Sodium Trifluoroacetate–Potassium Trifluoroacetate[†]

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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$_2$CO$_3$–Na$_2$CO$_3$–K$_2$CO$_3$ (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

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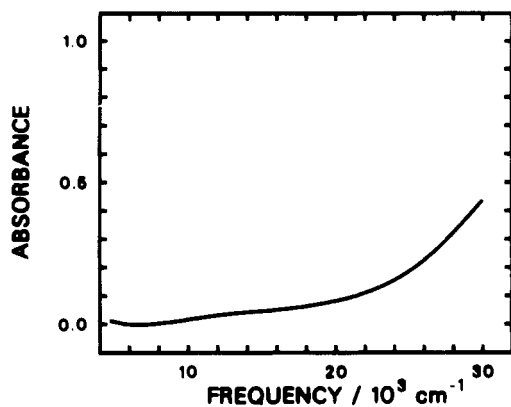(22) Pratt, J. M.; Thorp, R. G. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 375.

Figure 1. Absorption spectrum of CsTFAc–NaTFAc–K(TFAc) (50–25–25 mol %) at 100 °C taken in a 1-mm path length quartz spectrophotometer cell.

sample. The samples to be equilibrated were transferred to the vacuum line in a Pyrex tube capped off with a stopcock joint and melted under vacuum in a silicone fluid bath that was heated gradually to ~100 °C by using a heating tape. The samples were left under vacuum at a temperature of ~100 °C for 1–2 days to ensure removal of any residual moisture. Following equilibration, the samples were removed from the silicone bath, allowed to cool, and returned to the glovebox, where the sample tubes were cut just above the top surface of the solidified sample and stored upright in capped bottles.

^{13}C and ^{1}H NMR spectra of the neat molten TFAc salt were recorded on a Varian FT-80 Fourier transform NMR spectrometer equipped with a variable-temperature probe. The procedures used in these measurements were the same as those described in a previous publication.[1] The ^{13}C spectra were fully consistent with published ^{13}C NMR data for the TFAc anion in neat trifluoroacetic acid.[2] There was no evidence in either the ^{13}C or ^{1}H spectra of the presence of water, hydrocarbons, or fluorocarbon species other than the trifluoroacetate anion.

Electronic absorption spectra were recorded on a Cary 17H absorption spectrophotometer coupled with specially designed furnace for elevated-temperature spectrophotometric measurements. The equilibration sample tube containing the sample to be studied was inverted and loaded into an optical assembly consisting of a 1-mm path length, UV-grade quartz cell (12.5 mm wide and 45 mm high, from J&S Scientific) fused to the end of a 15-mm diameter quartz tube (~200 mm long) that terminated at the opposite end with a ground joint. After loading in the glovebox, the cell assembly was capped off with a stopcock joint, transferred to a Marshall furnace, connected to the glass vacuum line, evacuated, and heated to ~100 °C. When the sample had completely melted and flowed out of the inverted tube, the cell assembly was back-filled with dry helium, forcing the melted salt to fill the optical path of the cell if it had not already done so. The cell assembly was then rapidly transferred to the preheated spectrophotometer furnace before the sample had a chance to solidify. The absorbance vs. wavelength data for each sample were loaded into a computer data file (from which the background spectrum of the molten TFAc salt was subtracted), converted to a molar absorptivity vs. wavenumber data set, and plotted by a computer graphics routine.

Results and Discussion

Attempts were made to obtain ligand field spectra of at least one oxidation state of the 3d transition metals Ti through Cu in the molten TFAc salt. Typically, spectra were recorded at 100 °C; however, in the case of Co^{2+} a more extensive study was made as a function of temperature (120–40 °C) because of the observation that the Co^{2+} solutions changed color from blue at higher temperatures to pink at room temperature (prior to crystallization of the TFAc salt). The results of the absorption spectrophotometric studies are described below:

The absorption spectrum of the molten TFAc salt at 100 °C is shown in Figure 1. The transmission throughout the 5000–30000-cm^{-1} range is very good, and unlike molten acetates,[1] there are no observable absorption features due to vibrational overtones
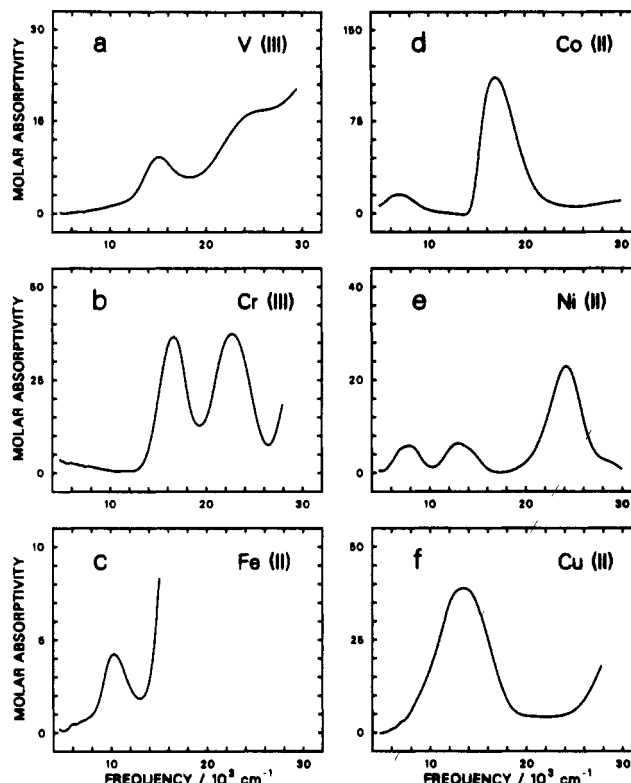
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Figure 2. Absorption spectra of (a) V^{3+}, (b) Cr^{3+}, (c) Fe^{2+}, (d) Co^{2+}, (e) Ni^{2+}, and (f) Cu^{2+} in molten CsTFAc–NaTFAc–K(TFAc) (50–25–25 mol %) at 100 °C.

Table I. Ligand Field Transition Energies (cm^{-1} × 10^{3}) and Molar Absorptivities for 3d TM Cations in CsTFAc–NaTFAc–K(TFAc) and in Aqueous Solution

3d TM cation	ligand medium	ligand field transn energies^a	max molar absorp^b
V^{3+}	TFAc	(32.8)/25.2/15.2*	8
	H_2O^c	(36.0)/25.6/17.2*	7
Cr^{3+}	TFAc	(36.0)/22.4*/16.6	37
	H_2O^c	(36.0)/24.0*/17.0	16
Fe^{2+}	TFAc	10.2*	4
	H_2O^c	10.0*	3
Co^{2+}	TFAc	16.8*/6.9	109
	H_2O^c	21.6/19.6*/8.0	5
Ni^{2+}	TFAc	23.9*/13.4/7.7	23
	H_2O^c	25.3*/14.5/8.7	5
Cu^{2+}	TFAc	13.4*	39
	H_2O^c	12.0*	11

^{a} Transition energies in parentheses were not observed. They were estimated from Tanabe–Sugano diagrams for octahedral complexes.[3] ^{b} Molar absorptivity at the peak marked with an asterisk in the column to the left. ^{c} Data taken from ref 3.

of the anion. Thus, the TFAc salt is well suited for absorption spectrophotometric studies of 3d transition-metal cations. The metastable nature of the molten phase permits measurements to be made at progressively descending temperatures to at least as low as room temperature, i.e., prior to the onset of crystallization.

The cations V^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} formed stable solutions in the TFAc melt up to at least 120 °C. The colors of most of these solutions are quite vivid: V^{3+} is a bright green color, Cr^{3+} is dark green, Mn^{2+} is colorless, Co^{2+} is blue, Ni^{2+} is yellow-green, and Cu^{2+} is blue. Solutions of Ti^{3+} in the TFAc salt were initially purple in color but developed a brown colloidal precipitate within a few hours. Fe^{3+} was also unstable in the molten TFAc salt, leaving the melt a cloudy yellow-brown color. The ligand field spectra of V^{3+}, Cr^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} are shown in Figure 2 (a–f, respectively). Ligand field parameters derived from these spectra are summarized in Table I. No distinguishable features were observed in spectra of Mn^{2+}

solutions in the TFAc melt up to $\sim$1 M; hence, no spectrum for Mn^{2+} is shown in Figure 2.

On the basis of a comparison of the values of the ligand field parameters, the general character of the spectra, and the observed molar absorptivities in Figure 2 and Table I with corresponding data for these same transition metals in aqueous media[3] and in related glassy and molten salts (e.g., nitrates, acetates, sulfates),[4-8] we make the following observations. In appearance, the spectra of the 3d transition metals in the TFAc melt shown in Figure 2 are much like the corresponding spectra of these same transition-metal cations in water where octahedral $M(H_2O)_6^{n+}$ complexes (M^{n+} = transition-metal cation) are known to exist; however, the molar absorptivities in the TFAc melt are roughly twice as high as in aqueous media for V^{3+}, Cr^{3+}, and Fe^{2+} and 4–20 times higher for Co^{2+}, Ni^{2+}, and Cu^{2+}. Also, there is other evidence for oxyanion ligands such as CF_3COO^-, CH_3COO^-, and NO_3^- that complexes of the type MA_4^{n-4} (A = monovalent anion) can exist in both the solid and solution state.[4,9-12] Similar complexes involving the sulfate anion have been reported[5] for Co^{2+} in molten alkali-metal bisulfates, i.e., $Co(O_2SO_2)_4^{6-}$. In these complexes, each oxyanion ligand coordinates to the central metal cation through two of its oxygen atoms, with one of the metal-oxygen (M–O) bonds being shorter than the other. The four oxygen atoms associated with the short M–O bonds and the four associated with the longer M–O bonds form two sets of interpenetrating (somewhat distorted) tetrahedra about the central metal cation. The resulting array of atoms produces an eight-coordinated structure that is approximately dodecahedral.[9-12]

Cotton and Bergman[9] have proposed a principle to account for the quasi-bidentate coordination exhibited by some oxyanions, which is based on the premise that a polyatomic ligand having two or more chemically equivalent coordinating atoms (CECAs) will often tend to interact with the central metal atom through two of the CECAs. Although one of the two "coordinated" oxygen atoms of a given ligand is usually found to lie closer to the central metal cation than the other in the solid state, it is reasonable to suppose that in solution, the two CECAs will, on the average, be equidistant from the central metal cation, leading to a somewhat more symmetrical overall coordination environment than that for the dodecahedral MA_4^{n-4} complexes in the solid state.[9-12]

The implications of the quasi-bidentate MA_4^{n-4} structure with regard to ligand field spectral properties have been reviewed in detail by Johnson and Dickinson.[4] Without repeating their discussion, it is clear that the results in Figure 2 and Table I reflect the same characteristics as those observed for NO_3^- and CH_3COO^- complexes of Co^{2+} and Ni^{2+} under conditions where the MA_4^{n-4} dodecahedral structure was determined to exist. In the case of Co^{2+} in the TFAc melt, we observe the same type spectral behavior by varying temperature (40–120 °C) that was reported by Ingram et al.[6] when alkali acetates were added to Co^{2+} in lead acetate, namely a shift from a pink solution of relatively low molar absorptivity to a blue solution of considerably higher molar absorptivity. Here again, the interpretation was in terms of transformation from a distorted octahedral CoA_6^{4-} complex to the dodecahedral CoA_4^{2-} complex. The existence of the dodecahedral structure in the case of the Co^{2+}–TFAc complex in the TFAc melt is best supported by the X-ray diffraction study of Bergman and Cotton,[10] which showed that the $Co(O_2CCF_3)_4^{2-}$ structure in $[(C_6H_5)_4As]_2[Co(O_2CCF_3)_4]$ is intermediate between tetrahedral and dodecahedral. Johnson and Dickinson[4] observe

that the molar absorptivities for Co^{2+} complexes generally decrease as one goes from CoA_4^{2-} (tetrahedral) to CoA_4^{2-} (dodecahedral) to CoA_6^{4-} (octahedral). The peak molar absorptivity for the Co^{2+}–TFAc complex of Figure 2d ($\epsilon \simeq$ 109 at 16 800 cm^{-1}) is intermediate between the value reported by Cotton and Bergman[10] for $Co(O_2CCF_3)_2^{2-}$ in acetonitrile ($\epsilon \simeq$ 200 at 17 400 cm^{-1}) and the value, e.g., for $Co(H_2O)_6^{2+}$ in aqueous media[3] ($\epsilon \simeq$ 5 at 19 600 cm^{-1}) or for Co^{2+} at octahedral sites in $Pb(O_2CCH_3)_2$ glass ($\epsilon \simeq$ 35 at 18 400 cm^{-1}).[6]

The body of information from this study, taken in the context of prior work on related systems,[7] suggests that the V^{3+} and Cr^{3+} cations most probably exist in an octahedral ligand field in the TFAc melt, with some slight distortion causing the twofold increase in molar absorptivity relative to that observed in aqueous media. The absence of any observable features in the spectra of concentrated Mn^{2+} solutions in the TFAc melt shows rather conclusively that Mn^{2+} is in a weak, high-spin ligand field (as expected); nothing more definitive can be said concerning its coordination environment. The Fe^{2+} results in TFAc media are most consistent with octahedral coordination (probably somewhat distorted). Those for Cu^{2+} are interpreted as being due to the MA_4^{n-4} dodecahedral structure based on the relatively high value of the molar absorptivity.

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Formation of a New 1:1 Addition Compound of Borane with Aminoarsine

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Several articles have appeared in the literature describing the synthesis and characterization of the addition compounds formed by the interactions of BX_3 (X = F, Cl, Br, I) and B_2H_6 Lewis acids with phosphines,[1-7] arsines,[2,3,8-11] and stibines.[2,3,9] However,

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