Table III. Selected Interatomic Distances (Å) and Angles (Deg) for $Na[HCr_2(ms\text{-tart})_2(bpy)_2]\cdot 7H_2O$ with Estimated Standard Deviations

Cr(1)–Cr(2)	4.799 (2)	Cr(1)–O(23)	1.975 (4)
O(11)–O(41)	2.418 (6)	Cr(2)–O(33)	1.946 (4)
O(11)–H(1B)	1.25[a]	Cr(1)–O(13)	1.989 (4)
O(41)–H(1B)	1.22[a]	Cr(2)–O(43)	1.975 (4)
Cr(1)–O(11)	1.954 (4)	Cr(1)–N(1)	2.069 (5)
Cr(2)–O(41)	1.947 (4)	Cr(2)–N(3)	2.057 (5)
Cr(1)–O(21)	1.894 (4)	Cr(1)–N(2)	2.053 (5)
Cr(2)–O(31)	1.932 (4)	Cr(2)–N(4)	2.061 (5)
O(11)–Cr(1)–O(13)	80.7 (1)	N(1)–Cr(1)–N(2)	78.1 (2)
O(41)–Cr(2)–O(43)	81.3 (1)	N(3)–Cr(2)–N(4)	79.0 (1)
O(21)–Cr(1)–O(23)	83.2 (1)	O(11)–H(1B)–O(41)	159[a]
O(31)–Cr(2)–O(33)	83.5 (1)		

[a] Calculated from the difference map peak position for H(1B), the bridging hydrogen atom.

O(11) and O(41), of different tartrate groups and there is very compelling evidence that there exists between these two oxygen atoms a strong and probably symmetric hydrogen bond. This is concluded from considerations of (1) the complex charge, which must be mononegative and therefore requires the presence of a proton, (2) the observation of a difference peak at distances of 1.25 and 1.22 Å from O(11) and O(41), (3) pH titration data[2] which show an unexpectedly low acidity for this complex, (4) the O(11)–O(41) distance which, though not the shortest O–O distance known,[12] is well below the range of 2.50–2.45 Å, which is believed to form the boundary between ordinary and symmetrical hydrogen bonds, [13] and (5) the observation that the Cr–O distances involving the presumably partially protonated hydroxy oxygen atoms (average 1.950 Å) are significantly longer than those involving unprotonated hydroxyl oxygen atoms (average 1.913 Å). An admittedly troubling aspect of this assignment, however, is the absence of any indication of hydrogen bonding in the IR spectra[2] even though other hydrogen-bonded complexes such as oximes with similar short O–O contacts exhibit characteristic O–H–O bending and stretching vibrations.[14]

As found in many other α-hydroxycarboxylate complexes,[10] the coordination distances involving ionized hydroxyl oxygen atoms are significantly shorter than those involving carboxyl oxygen atoms (Table III). The tartrate chain is well staggered with the average dihedral angle of the O–C–C–O fragments containing hydroxyl oxygen and aliphatic carbon atoms being −56.6°. The N–C–C–N torsional angles of 4.0 (5) and 12.2 (5)° for the bipyridyl groups near Cr(1) and Cr(2), respectively, are similar to those found in other bipyridyl complexes.[15]

The low symmetry of the complex, even when idealized, makes possible several interesting comparisons. There are two chemically distinct α-hydroxycarboxylate chelate rings, which can be designated as "O" or "N" depending on whether the coordinated hydroxyl oxygen atom of a ring is trans to an oxygen or a nitrogen atom in the coordination sphere. "N" rings contain hydroxyl oxygen atoms which are apparently involved in hydrogen bonding. The two ring types differ in the O–Cr–O bite angle (averages: "O" rings, 83.4°; "N" rings, 81.0°) and in conformation (average O–C–C–O dihedral angles involving one hydroxyl oxygen atom and one bonded carboxyl oxygen atom: "O" rings, +15.1°; "N" rings, −10.8° for the β-ΛΛ(*RS*,*RS*) enantiomer, where "O" chelate rings contain carbinols of *R* chirality and "N" chelate rings contain carbinols of *S* chirality). Though the UV spectra of the *ms*-tartrate bipyridyl complex has been explained in terms of two chemically distinct pyridyl groups,[2] the crystal structure results do not indicate any significant geometrical differences in the two types of pyridyl groups (trans to a carboxyl oxygen atom or trans to a hydroxyl oxygen atom). Corresponding bond lengths and bond angles and N–Cr coordination distances are the same within experimental error for the two chemically distinct pyridyl fragments.

Acknowledgment. This work was supported by grants from the Minority Biomedical Sciences Program (NIH-DRR 506 RR08139), the National Science Foundation (CH-780921) for purchase of the Syntex P3F and R3 diffractometer and computing systems, and the Research Allocations Committee of the University of New Mexico.

Registry No. $NaH[Cr_2(ms\text{-tart})_2(bpy)_2]\cdot 7H_2O$, 81244-79-3.

Supplementary Material Available: Tables of thermal parameters hydrogen positions, complete interatomic distances and angles, selected least-squares planes, selected torsion angles, and observed and calculated structure factors (48 pages). Ordering information is given on any current masthead page.

---

[12] Bertrand, J. A.; Black, T. D.; Eller, P. G.; Helm, F. T.; Mahmood, R. *Inorg. Chem.* **1976**, *15*, 2965.

[13] Catti, M.; Ferraris, G. *Acta Crystallogr., Sect. B* **1976**, *B32*, 2754.

[14] Chakravorty, A. *Coord. Chem. Rev.* **1974**, *13*, 1.

[15] McKenzie, E. D. *Coord. Chem. Rev.* **1971**, *6*, 187.

Contribution from the Departments of Inorganic and Physical
Chemistry, University of Melbourne,
Parkville, Victoria 3052, Australia

Electronic Spectra of Titanium(II), Vanadium(II), and Chromium(II) in Anhydrous Hydrogen Fluoride

C. G. Barraclough, R. W. Cockman, T. A. O'Donnell,* and Wendy S. J. Schofield

Received August 13, 1981

UV–visible spectra have been recorded for solutions in anhydrous hydrogen fluoride (AHF) of transition-metal, lanthanide, and actinide cations in "normal" oxidation states by treating suspensions in AHF of the appropriate sparingly soluble fluorides with Lewis acids of the HF system such as BF_3,[1] AsF_5,[2] or SbF_5.[3] Treatment of metallic uranium with HF–BF_3 yielded a stable solution containing U^{3+},[3] whereas the corresponding aqueous solution is unstable, with U^{3+} reducing H_2O.

This reaction with uranium has led to an extensive program in which d transition elements and lanthanides in the metallic state have been added to pure AHF or to AHF containing Lewis acids of different strengths. Many stable solutions have been obtained and spectra recorded. Frequently the elements have been in unusually low oxidation states, for which the formally corresponding aqueous spectra cannot be observed because the cations concerned reduce water.

This note reports the results of treating metallic Cr, V, and Ti with AHF acidified with Lewis acids. Stable solutions of Cr^{2+} and V^{2+} were obtained as expected with all the Lewis acids BF_3, AsF_5, and SbF_5. With Ti, an orange solution containing Ti^{2+} was prepared when the strong Lewis acid SbF_5 was used, even though Ti^{3+} might have been expected. Reaction of Ti with less acidic AHF solutions gave evidence of Ti^{3+} formation as will be discussed later. Work is proceeding currently on the characterization of solid residues from all of these solutions.

---

[1] Barraclough, C. G.; Cockman, R. W.; O'Donnell, T. A. *Inorg. Chem.* **1977**, *16*, 673.

[2] Barraclough, C. G.; Cockman, R. W.; O'Donnell, T. A. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 83.

[3] Baluka, M.; Edelstein, N.; O'Donnell, T. A. *Inorg. Chem.* **1981**, *20*, 3279.

0020-1669/82/1321-2519$01.25/0

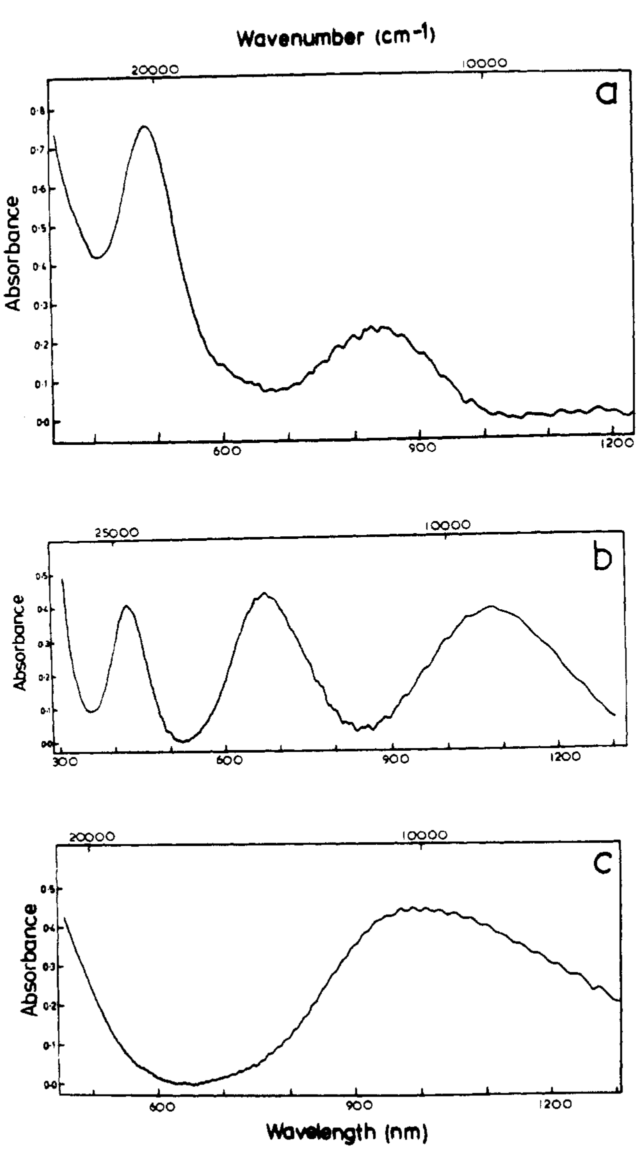

Figure 1. AHF solution spectra: (a) Ti^{2+}, (b) V^{2+}, and (c) Cr^{2+}.

An essential requirement for successful preparation of stable AHF solutions containing metal cations in very low oxidation states is to remove surface oxide coating from the metals. Otherwise oxo–fluoro complexes may be formed. More importantly, a low oxidation state cation produced transiently may be oxidized. It is believed that oxidation can occur in AHF as a result of conversion of chemically bound oxygen to water, which is a strong base in AHF and is protonated. The low oxidation state cations could then reduce protons, releasing water which is again protonated by the solvent. Use of metallic powder or sponge has been avoided because of the large surface available for oxidation. Solid metals, preferably in crystalline form, were used after chemical removal of surface material.

Experimental Section

Reagents. Commercial HF (Matheson 99.8%) was purified by trap-to-trap distillation as described previously.[1] BF_3 (Matheson, 99%) and AsF_5 (Ozark-Mahoning, 99%) were used directly from cylinders as supplied, and SbF_5 (Matheson) was purified by distillation. Metallic chromium (Koch-Light) and vanadium (Johnson, Mathey) were used as high-purity granules and titanium as crystalline rod (Koch-Light, 99.9%).

Preparation of Solutions. So that contamination by surface oxides could be eliminated, a single piece of metal (usually less than 200 mg) was added to a Kel-F trap fitted with a Teflon-coated magnetic stirrer bar and the metal was washed with AHF or with AHF containing a Lewis acid or an oxidant such as fluorine or ClF_3, depending on the circumstances, to remove some surface metal and, with it, any oxide. The washing liquids were decanted from the trap, and the metal was washed finally with pure AHF. Then 5–10 mL of HF was added, containing SbF_5 when that was the Lewis acid used. The gases BF_3 and AsF_5 were applied at a pressure of 1–2 atm in excess of the HF vapor pressure. When solutions contained suspended solids, they were filtered with Teflon filter paper (Millipore, type LC, 10 μm) contained in a Kel-F cartridge which was a modification of a Büchner funnel.

Table I. Positions (cm^{-1}) of Band Maxima for Metals in Oxidation State II in Different Octahedral Environments

M	M-$(OH_2)_6{}^{2+}$ [a]	M-$(FH)_6{}^{2+}$ [b]	$MCl_6{}^{4-}$ in molten $AlCl_3$ [c]	1% M^{2+} doped into NaCl crystals[d]	assignt
Cr	14 100	9 900	8 400		
V	27 930	23 590	20 300	20 200	${}^4A_{2g} \rightarrow {}^4T_{2g}$
	18 490	14 840	12 100	12 600	${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$
	12 300	9 210	8 000	8 130	${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$
Ti		20 830	14 500	15 870	${}^3T_{1g} \rightarrow {}^3T_{1g}$
		11 910	7 600	8 810	${}^3T_{1g} \rightarrow {}^3T_{2g}$

[a] References 12 and 13. [b] This work. [c] Reference 10. [d] Reference 11.

Cr and V gave solutions suitable for spectroscopy even with the weak Lewis acid BF_3 and gave solutions with moderate concentrations of the stronger acids AsF_5 and SbF_5. However, very concentrated solutions of AsF_5 and SbF_5 tended to give precipitates containing Cr(III) and V(III). Cleaned crystalline Ti showed no reaction with BF_3–HF. AsF_5–HF gave blue or green solutions with complex spectra, suggesting the presence of Ti(III). Within about 30 min, 3 M SbF_5 in AHF caused evolution of H_2 and gave a stable orange solution, the spectrum of which indicated the presence of $Ti(FH)_6{}^{2+}$. High concentrations of AsF_5 or SbF_5, in which significant concentrations of the molecular pentafluorides have been shown to exist in equilibrium with fluoroarsenates or fluoroantimonates,[4] gave blue solutions or precipitates, indicating oxidation of Ti(II) to Ti(III).

Recording of Spectra. The Kel-F-bodied spectral cells with synthetic sapphire windows were as previously described,[1] and spectra were recorded as before on a Cary 17 spectrophotometer. The small-scale undulations in the spectra should be ignored. They are due to interference fringes resulting from the configuration of the cell.

Results and Discussion

$CrF_2{}^{5a}$ and $VF_2{}^{5b,6}$ have been prepared by high-temperature reactions, as has TiF_3.[5c] However, there is no reported preparation of TiF_2.[7] Aqueous Cr^{2+} solutions are easily prepared and are stable, providing air and other oxidants are excluded.[8] V^{2+} solutions can be prepared by electrolytic reduction, but V^{2+} slowly reduces H_2O.[9] Anhydrous $TiCl_2$ can be prepared at high temperature, but it is reported to react violently with water with the evolution of hydrogen,[5d] indicating that there is no possibility of obtaining stable aqueous solutions containing Ti(II). Gruen has studied $CrCl_2$, VCl_2, and $TiCl_2$, as well as several other dihalides, in molten $AlCl_3$ and recorded spectra at 227 °C.[10] Smith and co-workers[11] doped Ti^{2+} and V^{2+} at the 1% level into NaCl crystals and recorded electronic spectra at 10 K and, in the case of Ti^{2+}, investigated temperature dependence of the spectra. Aqueous spectra for Cr^{2+} [12] and V^{2+} [13] have been reported.

---

(4) Davies, P. B.S. (Honors) Report, University of Melbourne, 1980.

(5) (a) Colton, R.; Canterford, J. H. "Halides of the First Row Transition Metals"; Wiley-Interscience: New York, 1969; p 181. (b) *Ibid.*, p 134. (c) *Ibid.*, p 57. (d) *Ibid.*, p 66.

(6) Cros, C.; Ferurer, R.; Buchard, M. *J. Fluorine Chem.* **1975**, *5*, 457.

(7) Clark, R. J. H. In "Comprehensive Inorganic Chemistry"; Bailar, J. C., Emeleus, H. J., Nyholm, R. S., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, 1973; Vol. 3, p 363.

(8) Muetterties, E. L., Ed. "Inorganic Syntheses"; McGraw-Hill: New York, 1967; Vol. X, p 26.

(9) Baes, C. F.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley: New York, 1976; p 198.

(10) Øye, H. A.; Gruen, D. M. *Inorg. Chem.* **1964**, *3*, 836.

(11) Brown, D. H.; Hunter, A.; Smith, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 79.

(12) Fackler, J. P.; Holah, D. G. *Inorg. Chem.* **1965**, *4*, 954.

(13) Jørgensen, C. K. *Adv. Chem. Phys.* **1963**, *5*, 33.

Table II. Octahedral Crystal Field Parameters (cm^{-1}) for V(II) and Ti(II) with Various Ligands[a]

		H_2O[b]	HF	Cl^- in molten $AlCl_3$	Cl^- in crystalline NaCl[c]
V(II)	*Dq*	1235	930	800	813
	B	690	720	560	565
Ti(II)	*Dq*		1300	750	850
	B		685	615	615

[a] Free ion values of *B*: V(II) = 766 cm^{-1}, Ti(II) = 718 cm^{-1}. [b] Reference 13. [c] Calculated from the band positions given in Table I.

These available spectra are compared in Table I with those observed in AHF in the present work. The previously reported[1] shift of absorption peaks to lower energy is observed in passing from aqueous to AHF solutions, and the AHF spectra correlate well with those in molten $AlCl_3$, where an octahedral environment was assumed, and with those in NaCl, where octahedral coordination is expected. There are some limits to the possible comparisons because, as stated above, Ti^{2+} cannot exist in water and there is no report of doping of NaCl with Cr^{2+}. An extinction coefficient of about 4.5 mol^{-1} dm^3 cm^{-1} for the 480-nm band of the Ti^{2+} spectrum, the most novel of the spectra reported here, is typical of the magnitude expected for a d transition metal.

Comparison of the AHF spectra with those in aqueous or chloride media indicates that these divalent cations are in an octahedral environment in AHF; and on this basis the absorption peaks in AHF may be assigned as shown in Table I. With standard crystal field theory,[14] the crystal field parameters *Dq* and *B* have been calculated for Ti(II) and V(II) and are given in Table II. Cr(II) gives only one broad band in all the media given in Table I, so it is not possible to derive any crystal field parameters. All that can be said is that the absorption maximum for Cr(II) in AHF is intermediate in energy between that in water and that in molten $AlCl_3$. This is consistent with the results for V(II) where the *Dq* value for HF lies between the values for H_2O and Cl^-. In our previous paper[1] it was suggested that HF had very similar crystal field parameters to those of F^-. Unfortunately no data are available for Cr(II), V(II), or Ti(II) ions in a fluoride environment. The electronic repulsion parameter *B* does show the trend expected for a fluorine containing ligand; i.e., with HF ligands, *B* is much closer to the free ion value than for H_2O or Cl^- ligands.

The crystal field parameters of Table II will reproduce the experimental absorption peaks within a few hundred wavenumbers in each case. This is strong support for our interpretation of the spectra in AHF as being due to octahedral coordination of Cr(II), V(II), and Ti(II) by HF. However, some consideration should be given to other interpretations of the results. If HF and F^- produce rather similar crystal fields, one or, less likely, more ligands could be F^- with the remainder HF molecules. In principle the peaks in the spectrum should be split but the peaks are already broad and small splittings would not be seen. Perhaps, much less likely still, some coordination positions may be occupied by fluorines from the anions BF_4^-, AsF_6^-, or SbF_6^-.

Stable Cr(II) and V(II) solutions can be produced in AHF solutions that are only weakly acidic, i.e., where BF_3 is the Lewis acid. However, Ti(II) is not stable in these solutions or even in those in which the much stronger Lewis acid AsF_5 is used; it appears that there is an equilibrium between Ti(II) and Ti(III) in HF–AsF_5, depending on the AsF_5 concentration. A molarity of about 3 for the stronger Lewis acid SbF_5 is needed to provide stable Ti(II) solutions. It is likely that in weakly acidic HF there will be small but significant concentrations of TiF^+. This species will have a more negative reduction potential than HF-solvated Ti^{2+} and will reduce H_2F^+ to H_2, thereby being oxidized to Ti(III).

On the other hand, as the absolute concentrations of AsF_5 and SbF_5 in AHF increase, the concentrations of the uncharged pentafluorides will increase relative to the concentrations of the fluoro anions[4] which are weaker oxidants than the pentafluorides. It is postulated that, in concentrated solutions of AsF_5 and SbF_5 in AHF, Ti(II) is oxidized to Ti(III) by the pentafluorides, as reported in the Experimental Section. The oxidation of V(II) and Cr(II) by very concentrated pentafluoride solutions is believed to be of similar origin.

It is of particular interest to note that AHF as a solvent appears able to provide stable solutions containing both unusually high oxidation states, e.g., Ni(IV) as NiF_6^{2-},[15] and unusually low oxidation states, e.g., Ti(II). This can be rationalized by recognizing that it has been demonstrated voltammetrically that the useable potential range in AHF is at least 4.5 V[16,17] between H_2 and F_2 evolution compared with an aqueous range of about 2 V for water reduction and oxidation.

Acknowledgment. We acknowledge financial support from the Australian Research Grants Committee, especially for the award of a Graduate Research Assistantship (R.W.C.).

Registry No. Cr, 7440-47-3; V, 7440-62-2; Ti, 7440-32-6; AHF, 7664-39-3.

---

(14) Lever, A. B. P. "Inorganic Electronic Spectroscopy"; Elsevier: Amsterdam, 1968.

(15) Stein, L.; Neil, J.; Almo, G. *Inorg. Chem.* **1969**, *8*, 2472.

(16) Doughty, A. G.; Fleischmann, M.; Pletcher, D. *J. Electroanal. Chem. Interfacial Electrochem.* **1974**, *51*, 456.

(17) Irvine, I. Ph.D. Thesis, University of Melbourne, 1975, pp 28–29.

Contribution from the Laboratory of Inorganic Chemistry,
College of General Education,
and the Department of Chemistry, Faculty of Science,
Nagoya University, Nagoya 464, Japan

^{15}N Chemical Shifts and ^{13}C–^{15}N Coupling Constants of Cyanide Complexes

Mitsuru Sano,* Yuzo Yoshikawa, and Hideo Yamatera

Received November 20, 1981

The nuclear magnetic resonance (NMR) technique has been applied to the study of the structure and dynamic processes of molecules in solution.[1] Especially, the use of ^{13}C magnetic resonances has become extensive as a spectroscopic tool for the investigation of metal complexes with carbon-containing ligands. We have already reported the electronic structures of octahedral, hexacyano complexes as well as other types of cyanide complexes.[2-5] It is of interest to study the relationship between the NMR spectra and the electronic structures of cyanide complexes. The ^{13}C NMR spectra of cyanide complexes have been reported by Hirota et al.[6] and Pesek et al.[7] However, no reports have been found concerning ^{15}N resonances and C–N nuclear-spin coupling constants, J_{C-N}, for cyano complexes. The data for J_{C-N} and ^{15}N and ^{13}C resonances may be useful in interpreting the NMR spectra of cyano complexes.

---

* To whom correspondence should be addressed at the Laboratory of Inorganic Chemistry.