lybdenum compounds containing the MoS_8 core.[34]

Concluding Remarks. The reaction between halogenic acids and $MoO_2(acda)_2$ produced seven-coordinated[12] dihalogeno compounds, $MoOX_2(acda)_2$. The function of acid here is to protonate and hence to labilize one of the oxo groups[35,36] of $MoO_2(acda)_2$. Similar oxo group abstraction due to protonation by ATP is thought to be operative in the functioning of nitrogenase.[37,38] The compound $MoOCl_2(acda)_2$ has a redox potential, $(E_{1/2})_1 = -0.29$V, that is about 650 mV more positive to that of $MoO_2(acda)_2$[5] because of the stabilization of the electron-transfer orbital of the metal ion by more effective π bonding due to chloride ion. To our knowledge, among all molybdenum(VI) complexes reported so far $MoOBr_2(acda)_2$ is undergoing reduction at the least negative potential. The less negative value of the formal potential of $MoOCl_2(acda)_2$ and the relative ease of its preparation have made it a remarkably useful starting material for the preparation of lower valent molybdenum compounds.

Electrochemical features of $MoOX_2(acda)_2$ and MoOL-$(acda)_2$ compounds are grossly similar and can be represented by the following generalized scheme (B = X_2, L):[39]

$$[Mo^{VI}OB(acda)_2] \underset{E_{1/2} \sim -0.3\ V}{\overset{e^-}{\rightleftharpoons}}$$

$$[Mo^{V}OB(acda)_2] \xrightarrow[E_{irrev} \sim -1.25\ V]{e^-} [Mo^{IV}OB(acda)_2]$$

In both cases, the electrochemically generated Mo(IV) species are unstable and undergo post chemical reaction. One interesting observation is the quasi-reversible nature of the reduction of $MoOX_2(acda)_2$, unlike many other Mo(VI) compounds of *cis*-dioxo type where irreversible behavior generally is observed.[40–42]

The voltammetric features of $Mo(acda)_4$ are noteworthy in the sense that it can be used as a possible starting material for the generation of various non-oxo Mo(V) and Mo(III) compounds. Work is now in progress to stabilize these oxidation states by using suitable redox-active reagents.

Acknowledgment. Thanks are due to Dr. K. Nag for helpful discussions and Dr. P. Ghosh for assistance in the electrochemical experiments. I am indebted to Professor A. Chakravorty for providing the facilities for electrochemical measurements and also for some suggestions.

Registry No. **2a**, 92985-00-7; **2b**, 92985-01-8; **2c**, 92985-02-9; **2d**, 92985-03-0; **3a**, 92985-04-1; **3b**, 92985-05-2; **3c**, 92985-06-3; **4**, 89172-34-9; $MoO_2(acda)_2$, 89742-18-7.

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Hydrazinium, Alkali-Metal, and Ammonium Trifluorooxovanadates(IV). Synthesis and Spectroscopic Studies of a New Oxofluorovanadate(IV) Complex, VOF_3^-

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Blue crystalline $N_2H_5VOF_3$ has been synthesized from the reaction of V_2O_5 with 99% hydrazine hydrate in the presence of 40% HF. The alkali-metal and ammonium salts of the complex anion, $AVOF_3$ (A = Na, K, or NH_4), have been prepared by metathesis between $N_2H_5VOF_3$ and alkali-metal or ammonium fluoride, AF, in an aqueous medium. Characterization and assessment of structure were made from the results of chemical analyses, chemical determination of the oxidation state of vanadium, molar conductance and magnetic susceptibility measurements, and infrared, electronic, and ESR spectroscopic studies. The molar conductances of $N_2H_5VOF_3$ and $AVOF_3$ lying between 130 and 135 Ω^{-1} cm^2 mol^{-1} provide evidence for their 1:1 electrolytic nature; their infrared spectra show the multiple nature of the V–O bond and the absence of water. The magnetic moments of the compounds were observed to fall between 1.51 and 1.53 μ_B and the chemically estimated oxidation states of vanadium were found to lie between +3.9 and +4.1. The electronic spectra of the compounds show absorptions at ca. 11 900 and ca. 16 000 cm^{-1} owing to the two d–d transitions characteristic of an oxovanadium(IV) species. The ESR spectrum of $N_2H_5VOF_3$ in a frozen aqueous solution at 100 K indicates that the complex species, VOF_3^-, has a distorted octahedral structure. In the solid state, the complex species VOF_3^- may have a polymeric structure through weak V–O···V and V–F···V interactions.

Although several oxofluorovanadate(IV) complexes are known,[1] the species of the formula VOF_3^- does not seem to have any reported evidence in the literature. The corresponding trichlorooxovanadate(IV), $VOCl_3^-$, has, however, been reported.[2] The salts of the $VOCl_3^-$ anion were synthesized by the reduction of V^{5+}, in the presence of an excess of Cl^- ions, with ethanol followed by precipitation of the salts from aqueous ethanolic media.[2] Similar reactions of V^{5+} in the presence of an excess of F^- ions, however, did not lead to the synthesis of the VOF_3^- complex.[3] As an extension of our studies of oxo fluoro[3] and heteroligand peroxo[4] compounds of

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Table I. Amounts of Reactants Used and Yield of $AVOF_3$ ($A = NH_4$, Na, or K)

compd	yield/g (%)	amt of $N_2H_5VOF_3$/g (mmol)	amt of AF/g (mmol)
NH_4VOF_3	0.8 (89)	1.0 (6.4)	0.71 (19.2)
$NaVOF_3$	0.5 (53)	1.0 (6.4)	0.81 (19.2)
$KVOF_3$	0.9 (90)	1.0 (6.4)	1.12 (19.2)

vanadium, we undertook the synthesis of bis(acetylacetonato)fluorovanadium(III), $VF(acac)_2$, and in the course of its synthesis[5] the complex species VOF_3^- was isolated as $N_2H_5VOF_3$ as an intermediate that generated considerable interest.[6] Thus it is imperative and incumbent on us to provide information in regard to the synthesis of various salts of the trifluorooxovanadate(IV) anion, VOF_3^-, and to make an assessment of the structure of the complex species. In this report we present an account of the syntheses of different salts and a structural assessment of VOF_3^-.

Experimental Section

The chemicals used were all reagent grade products. Infrared spectra were recorded on a Perkin-Elmer Model 125 spectrophotometer. Molar conductance measurements were made with a Philips PR 9500 conductivity bridge. Magnetic susceptibility measurements were made by the Gouy method using $Hg[Co(NCS)_4]$ as the standard. Electronic spectra were recorded on a Beckman Model UV-26 spectrophotometer. An ESR spectrum of a frozen aqueous solution of $N_2H_5VOF_3$ was recorded on a Varian E109 X-band ESR spectrometer with a 100-kHz field modulator.

Synthesis of Hydrazinium Trifluorooxovanadate(IV), $N_2H_5VOF_3$. A 4.0-g amount (22 mmol) of V_2O_5, taken as a suspension in about 15–20 cm^3 of water, was treated with 4.4 cm^3 (88 mmol) of 40% hydrofluoric acid. The mixture was warmed at ca. 100 °C for 15 min and then cooled at room temperature. The solution was filtered to remove any undissolved material. The clear solution was cooled in an ice bath, and 99% hydrazine hydrate solution was added drop by drop with stirring, while the solution turned blue. Hydrazine hydrate (99% solution) addition was continued until the blue crystalline hydrazinium trifluorooxovanadate(IV), $N_2H_5VOF_3$, ceased to appear, with the mother liquor becoming practically colorless. The compound was separated by filtration, dried on a filter paper, and finally dried in vacuo over diphosphorus pentoxide. The yield of $N_2H_5VOF_3$ was 3.2 g (92%).

Preparation of Alkali-Metal and Ammonium Trifluorooxovanadates(IV), $AVOF_3$ (A = Na, K, or NH_4). Since the methods of preparation of $AVOF_3$ compounds are similar, only a representative method is described.

To a saturated solution of freshly synthesized hydrazinium trifluorooxovanadate(IV), $N_2H_5VOF_3$, was directly added with slow stirring a very concentrated solution of alkali-metal or ammonium fluoride, AF (A = Na, K, or NH_4), with maintenance of the molar ratio of $N_2H_5VOF_3$ to AF at 1:3. A blue crystalline product was obtained immediately, which was separated by filtration, dried by being placed between folds of a filter paper, and then dried in vacuo over diphosphorus pentoxide. Specific amounts of reactants used and the yields of various $AVOF_3$ compounds are reported in Table I.

Elemental Analyses. Determinations of vanadium, fluoride, nitrogen, and alkali metals were accomplished by the methods described in our previous papers.[4]

Chemical Determination of the Oxidation State of Vanadium in $AVOF_3$ Compounds. The oxidation state of vanadium in each of the alkali-metal and ammonium trifluorooxovanadates(IV), $AVOF_3$ (A = Na, K, or NH_4), was estimated by dissolving an accurately weighed amount of the compound in water followed by direct titration with a standard potassium permanganate solution.

Analytical data, chemically estimated oxidation states of vanadium, molar conductance and magnetic moment values, structurally important IR bands, and electronic spectral band positions and their assignments are summarized in Table II.

Results and Discussion

The electron-transfer reaction between quinquevalent vanadium and an excess of hydrazine hydrate in the presence of aqueous hydrofluoric acid affords hydrazinium trifluorooxovanadate(IV), $N_2H_5VOF_3$, directly in a very high yield. The role of hydrazine hydrate, in the present case, was not only to act as a reducing agent but also to provide the $N_2H_5^+$ cation, which facilitated precipitation of the complex ion VOF_3^- formed in the medium. In order to show the existence of the novel complex species in the presence of other countercations, a series of alkali-metal and ammonium salts of trifluorooxovanadate(IV) were prepared by metathesis between $N_2H_5VOF_3$ and AF (A = Na, K, or NH_4). The formation of $AVOF_3$ compounds thus proves the existence as well as the stability of the complex VOF_3^- ion in the presence of various countercations. It may be noted that the complex ion VOF_3^-, unlike the corresponding $VOCl_3^-$ ion, is not sensitive to rapid hydrolysis. The enhanced stability of the new species is believed to be due to the coordination of F^- ions to the vanadium(IV) center. Indeed it is known from some other studies[7] that the stabilities of fluoro complexes of VO^{2+} are generally much higher than those of the corresponding chloro complexes. The yield of $NaVOF_3$ was low, relative to any other $AVOF_3$ compound, owing to the comparatively high dilution of the reaction solution maintained in order to avoid contamination of the end product by the relatively less soluble NaF. To study the effect of relatively larger amounts of F^- ions on the reaction product, we carried out similar hydrazine hydrate reduction of V^{5+} in the presence of higher amounts of F^- ions, e.g. a V:F ratio of 1:5 or 1:6. Here again, however, the product obtained was nothing other than $N_2H_5VOF_3$. This result and those obtained from the metathesis between $N_2H_5VOF_3$ and AF thus suggest that a higher concentration of fluoride ions does not have any net effect on the VOF_3^- species and also does not yield the already known[7] VOF_4^{2-} or VOF_5^{3-} ion, at least within the limits specified.

Characterization and Assessment of Structure. The trifluorooxovanadate(IV) complexes $N_2H_5VOF_3$ and $AVOF_3$ (A = Na, K, or NH_4) are all blue crystalline compounds, are stable for prolonged periods, and can be stored in sealed polyethylene capsules. The compounds are soluble in water but insoluble in common organic solvents. The molar conductance of the compounds lies in the range 130–135 Ω^{-1} cm^2 mol^{-1}, suggesting a uni-univalent electrolytic nature of each of them, in agreement with their formulas. The oxidation states of vanadium, estimated chemically, in the alkali-metal and ammonium salts of the newly synthesized complex anion were found to be between +3.9 and +4.1, lending strong support to the contention that vanadium in each of the compounds has an oxidation state of +4. Further support to this is adduced from the results of the magnetic susceptibility measurements at room temperature. The room-temperature magnetic moments of $N_2H_5VOF_3$ and $AVOF_3$ compounds were found to fall between 1.51 and 1.53 μ_B ($\mu_B = 0.927 \times 10^{-23}$ A m^2), suggesting the occurrence of V^{4+} in the complexes. The somewhat lower moments must be attributed to the existence of a weak antiferromagnetic exchange interaction between the contiguous V^{4+} units in the solid state, presumably through a weak V–F···V or a weak V–O···V interaction.

The infrared spectra of the four compounds were found to be similar, except for the additional cation bands for hydrazinium and ammonium ions in the cases of the $N_2H_5VOF_3$ and

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Table II. Analytical Data, Magnetic Moments, Estimated Oxidation States, Molar Conductance Values, and Structurally Significant IR and Electronic Spectral Bands of $N_2H_5VOF_3$ and $AVOF_3$ ($A = NH_4$, Na, or K)

compd	μ_{eff}/μ_B at 299 K	estd oxidation state of V	molar conductance/ Ω^{-1} cm^2 mol^{-1}	% found (% calcd)			IR/cm^{-1}	assignt	electronic spectral bands/cm^{-1}	transitions
				A or N	V	F				
$N_2H_5VOF_3$	1.51		130	17.41	32.63	36.87	970 (s)	ν_{V-O}	12000	$e \leftarrow b_2$
				(17.85)	(32.47)	(36.31)	930 (w, br)	$\nu_{V-O\cdots V}$	16000	$b_1 \leftarrow b_2$
							500 (s, br)	$\nu_{V-F\cdots V}$		
NH_4VOF_3	1.53	3.9	130	9.52	35.68	40.72	975 (s)	ν_{V-O}	11900	$e \leftarrow b_2$
				(9.87)	(35.89)	(40.15)	935 (w, br)	$\nu_{V-O\cdots V}$	15800	$b_1 \leftarrow b_2$
							510 (s, br)	$\nu_{V-F\cdots V}$		
$NaVOF_3$	1.53	4.1	135	15.88	34.23	38.22	980 (s)	ν_{V-O}		
				(15.65)	(34.68)	(38.79)	930 (w, br)	$\nu_{V-O\cdots V}$		
							500 (s, br)	$\nu_{V-F\cdots V}$		
$KVOF_3$	1.51	4.1	130	24.34	31.72	34.87	970 (s)	ν_{V-O}	12000	$e \leftarrow b_2$
				(23.98)	(31.25)	(34.96)	930 (w, br)	$\nu_{V-O\cdots V}$	16000	$b_1 \leftarrow b_2$
							505 (s, br)	$\nu_{V-F\cdots V}$		

NH_4VOF_3 compounds, respectively, indicating that the compounds are similar both structurally and stoichiometrically. The strong and sharp band at 970–980 cm^{-1} has been assigned to the ν_{V-O} mode arising from the presence of a terminally bonded V=O group.[8] The appearance of this band enables us to infer that the compounds contain terminally bonded V–O multiple bonds. The observance of a weak but broad band around 930 cm^{-1} indicates a fair possibility of a weak V=O$\cdots$V=O interaction[2] in the compounds, and in the solid state the complex may have a polymeric structure through a weak V–O–V–O chain. It is interesting to note that the ν_{V-O} frequencies for $VOCl_3^-$ (ref 2) and VOF_3^- compare very well, suggesting thereby that the enhanced electronegativity of the coordinated halide ligands in going from $VOCl_3^-$ to VOF_3^- does not alter the V–O bonding to any appreciable extent. The absorption at ca. 500 cm^{-1}, observed in the spectrum of each of the newly synthesized compounds, has been assigned to the V–F stretching mode originating from the coordination of fluoride to the vanadium(IV) center. Its position and slightly broad nature indicate the possibility of a weak V–F$\cdots$V interaction in the compounds. In order to confirm the absence of water, coordinated or otherwise, we carefully examined the IR spectra of the $NaVOF_3$ and $KVOF_3$ compounds, since in these two cases there is no interference from the cation modes, by recording their spectra in both KBr and mull media. No indication of the presence of water was obtained in any of these cases. This result in conjunction with those of chemical analyses render it certain that there is no water present in the compounds. The IR spectrum of $N_2H_5VOF_3$ shows the bands typical for the $N_2H_5^+$ ion,[9] while that of NH_4VOF_3 shows the absorptions characteristic of the NH_4^+ ion.[4,10]

The electronic spectrum of trifluorooxovanadate(IV) consists of three absorption bands between 10000 and 28000 cm^{-1}, the region in which vanadyl complexes generally absorb. The frequencies fall at 12000, 16000, and >22000 cm^{-1}, with the third one being obscured by strong charge-transfer transitions. We assign the first and the second bands to $e \leftarrow b_2$ and $b_1 \leftarrow b_2$ transitions,[7] respectively. The spectral pattern points to a C_{4v} symmetry of the complex ion, in solution. It is possible that the complex species VOF_3^- might have achieved essentially C_{4v} symmetry by gaining an F^- ligand at the vacant site in the equatorial plane through fluoride exchange between two contiguous VOF_3^- ions. A comparison of the optical spectra of the trichlorooxovanadates(IV)[2] with those of the trifluorooxovanadates(IV) (present work) reveals that though the spectral pattern is generally similar, there is a difference in the band positions. The $e \leftarrow b_2$ and $b_1 \leftarrow b_2$ transitions in the latter case have been found to shift to relatively lower frequencies, leading us to believe that the complex species may have a pseudooctahedral structure, which it might have attained through a weak F bridging, probably in a manner somewhat similar to that of VOF_4^- species.[11]

The ESR spectrum of a frozen aqueous solution of hydrazinium trifluorooxovanadate(IV), $N_2H_5VOF_3$, was found to be analogous to those of various tetravalent vanadium complexes.[12] The experimentally obtained magnetic parameters of the complex VOF_3^- are $g_\parallel = 1.937$, $g_\perp = 1.978$, $A_\parallel(^{51}V) = 530.8$ MHz, and $A_\perp(^{51}V) = 205.1$ MHz. The values of spin-Hamiltonian parameters agree very well with those reported for V^{4+} (d^1) complexes.[12] The fact that an ESR spectrum appears with normal line widths at 100 K suggests that the unpaired electron finds itself in an orbitally nondegenerate ground state. Further, the observed g values and ^{51}V hyperfine couplings indicate that the ligand field is axially symmetric, and the complex species may have an axially distorted octahedral (or pseudooctahedral) structure, which also agrees very well with the results of electronic spectroscopic studies, as discussed above. In an attempt to study the effect of an excess of F^- ions on the ESR spectrum, we recorded the spectrum in the presence of a 100-fold excess F^- ion concentration. However, we did not observe any significant change in the g values as well as in the hyperfine tensors. The optical spectrum of a similar solution also did not show any notable change. The results, therefore, support the view that an excess of F^- ions does not bring about any effective change in the complex. Similar inference was also made from our synthetic studies, wherein, under the specified conditions, the use of a higher V:F ratio did not alter the composition of the complex. The absence of any fluorine hyperfine coupling leads us to believe that the orbital of the unpaired electron is not involved in the bond formation. Accordingly, the unpaired electron can be assigned to be in the d_{xy} orbital by selecting a coordinate system with V=O being in the z axis and equatorial V–F directions as x and y axes. The approximate ordering of the energy levels may be written as $d_{xy} < d_{xz} < d_{yz} < d_{x^2-y^2} < d_{z^2}$. The g values, to the first order, are given by[13]

$$g_\parallel = g_e - 2\xi k_1/\Delta \tag{1}$$

$$g_\perp = g_e - 8\xi k_2/\delta \tag{2}$$

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where g_e is the free-electron g value, k_1 and k_2 are the orbital reduction factors, ξ is the spin-orbit coupling constant of the free ion, and

$$\Delta = |E_{xy} - E_{x^2-y^2}|$$

$$\delta = |E_{xy} - E_{yz}| \quad \text{or} \quad |E_{xy} - E_{xz}|$$

where E_{xy} etc. are the one-electron orbital energies.

The d-d bands observed in the electronic spectrum of $N_2H_5VOF_3$ at 16 000 cm^{-1} ($\epsilon = 3.6$) and at 12 000 cm^{-1} ($\epsilon = 0.85$) can be correlated to the transitions $(xy) \leftrightarrow (x^2 - y^2)$, Δ, and to $(xy) \leftrightarrow (xz)$ or (yz), δ, respectively. In order to get an idea regarding the extent of covalency involved in different planes, we calculated the ratio $\xi k_1/\xi k_2$ by making use of the experimentally observed values for Δ and δ. The value of the ratio was found to be 0.89, indicating that the covalency involved in the xy plane is comparatively more than that in the xz plane.

Thus it is evident that, under suitable conditions, trifluorooxovanadate(IV) complexes can be synthesized from aqueous solutions. The complex may have a polymeric distorted octahedral or pseudooctahedral structure through weak V-F···V and V-O···V interactions.

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Registry No. $N_2H_5VOF_3$, 93254-05-8; V_2O_5, 1314-62-1; $NaVOF_3$, 93254-06-9; $KVOF_3$, 93254-07-0; NH_4VOF_3, 93254-08-1; hydrazine hydrate, 7803-57-8.

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Thermodynamic Equilibria in the System Zinc(II)-Pyridoxal 5′-Phosphate-2-Amino-3-phosphonopropionic Acid in Aqueous Solution

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The equilibria in D_2O and H_2O between pyridoxal 5′-phosphate (PLP), 2-amino-3-phosphonopropionic acid (APP), the PLP-APP Schiff base (SB), zinc(II), and the secondary ligand 2,6-pyridinedicarboxylic acid (PDA) have been investigated by potentiometric $[H^+]$ or $[D^+]$ determination, proton magnetic resonance, and ^{31}P magnetic resonance. The protonation and Zn(II) formation constants of the individual components and of the mixed-ligand, SB-PDA-Zn(II), complex are reported. The logarithms of the protonation constants of the mixed-ligand complex Zn(II)-SB-PDA were found to be 8.38, 6.66, and 5.75, corresponding respectively to protonation of the phosphonate group, the phosphate group, and the pyridine nitrogen. The species distribution curves were calculated for the pH range 2-12. The ^{31}P magnetic resonance of the Zn(II)-SB-PDA complex and the Zn(II)-SB′-PDA complex, where SB′ is the Schiff base formed by 2-(aminoethyl)phosphonic acid (2-AEP) and PLP, showed that at pD values <8.50 zinc(II) is coordinated to the carboxylate group of the amino acid moiety of the SB, while at pD values >8.50 the phosphonate group is coordinated to the Zn(II) ion. Evidence is reported for hydrogen bonding involving the phosphate and phosphonate groups of the monoprotonated Zn(II)-SB-PDA complex.

Introduction

The purpose of this research is to determine the concentrations of zinc-Schiff base species present under varying conditions in equilibrium systems containing Zn(II), pyridoxal 5′-phosphate (PLP), and 2-amino-3-phosphonopropionic acid (APP). In order to avoid hydrolysis of the metal ions[1,2] and precipitation of neutral complexes and to maintain if possible a 1:1 molar ratio of the PLP-APP Schiff base to Zn(II), a terdentate secondary ligand, 2,6-pyridinedicarboxylic acid (PDA), was added in a nearly equimolar ratio (1:1:1:1.2 = Zn(II):PLP:APP:PDA). The measurement of the equilibrium constants in this mixed-ligand system and the determination of the composition and concentrations of the Zn(II) complexes formed are essential for the planning and interpretation of the rates and mechanisms of metal and vitamin B_6-catalyzed reactions of 2-amino-3-phosphonopropionic acid.

Preliminary studies of Schiff base formation between pyridoxal (PL) and (aminomethyl)phosphonic acid,[3] β-(aminoethyl)phosphonic acid,[3] and 2-amino-3-phosphonopropionic acid (APP) have been reported.[3,4] It has also been demonstrated by spectrophotometric measurements that the PL-APP system undergoes metal ion catalyzed transamination and dephosphonylation.[5-7] The aminophosphonic acid, APP, is of considerable interest because it is found in nature[7-10] and is analogous to aspartic acid, and the reaction pathway suggested for its dephosphonylation reaction[5] appears to resemble the mechanism proposed for the pyridoxal-catalyzed β-decarboxylation of aspartic acid.[11]

Potentiometric data have been employed by Leussing et al.[12,13] and Martell et al.[14] to determine stability constants for the metal ion-vitamin B_6-amino acid Schiff base systems, but

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[†] Abstracted in part from a dissertation submitted by Bruno Szpoganicz to the faculty of Texas A&M University in partial fulfillment of the requirements of the degree of Doctor of Philosophy, 1984.

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