Contribution from the Department of Chemistry,
Illinois Institute of Technology, Chicago, Illinois 60616

Carbon-13 Nuclear Magnetic Resonance Studies of *trans*-Diacido(tetraamine)cobalt(III) Complexes[1]

GEORGE R. BRUBAKER* and DAVID W. JOHNSON

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Carbon-13 nuclear magnetic resonance spectra of a series of *trans*-diacido(1,10-diamino-4,7-diazadecane)cobalt(III) complexes (*trans*-Co(3,2,3-tet)X_2, X = Br^-, Cl^-, N_3^-, NH_3, NO_2^-, OAc) and *trans*-diacido(1,9-diamino-3,7-diazanonane)cobalt(III) complexes (*trans*-Co(2,3,2-tet)X_2, X = Cl^-, GlyH, ^-OAc, NH_3, NO_2^-) will be discussed. The ^{13}C chemical shift is found to be linearly dependent on the ligand field strength (estimated from the electronic spectrum) of the axial ligands (X). The shielding of selected carbon atoms within the tetraamine ligand, which has been attributed to the central metal ion, increases with increasing axial ligand field strength.

Introduction

In the course of our continuing study of the stereochemistry of six-coordinate transition-metal complexes, we have reported carbon-13[2] and proton NMR and strain energy minimization studies of some cobalt(III) complexes with the unsymmetrical tetradentate ligand 1,9-diamino-3,6-diazanonane (2,2,3-tet).[3] In this report, we offer details of a systematic carbon-13 nuclear magnetic resonance study of some *trans*-diacidocobalt(III) complexes with flexible tetraamine ligands.

We have found[2] that the chemical shift of carbon in traditional diamagnetic "Werner" complexes is dependent on the micro environment of each carbon atom, i.e., details of bond lengths and bond angles, as previously shown for hydrocarbons.[4] We have referred to this effect as the "steric effect".

In addition, the electron density of first-row transition-metal ions introduces significant shielding of the carbon atoms in simple hydrocarbon chelate rings (e.g., polymethylene chains). We have refered to this as the "electronic effect". In this report, we correlate selected carbon-13 chemical shifts in some *trans*-diacido(tetraamine)cobalt(III) complexes with the apparent ligand field strength of the "axial" liands.

Experimental Section

Physical Methods. NMR Spectra. Carbon-13 NMR spectra were measured with a Varian CFT-20 spectrometer in the deuterium-locked, noise-decoupled mode. Samples were dissolved in a minimum of Me_2SO-d_6 (99.5 atom %, Aldrich Chemical), placed in 10-mm NMR tubes (Wilmad), and spun in a jet of air. Transients were collected until an acceptable signal to noise ratio was achieved (400–30 000 transients). Tetramethylsilane was used as an internal standard throughout this work.

Electronic Spectra. Electronic spectra were measured on a Cary Model 14 spectrophotometer. The solutions were typically 10^{-3} M complex in water.

Elemental Analyses. Cobalt analyses were performed with a Varian Model 1200 atomic absorption spectrophotometer. All other analyses (C, H, N) were performed by Guelph Chemical Laboratories, Guelph, Ontario.

Syntheses. *trans*-Diammine(1,10-diamino-4,7-diazadecane)cobalt(III) Chloride, *trans*-(Co(3,2,3-tet)$(NH_3)_2$)Cl_3. To 50 mL of ethanol saturated with NH_3 was added a solution of 1 g of *trans*-(Co(3,2,3-tet)Cl_2)Cl in 50 mL of ethanol. The product precipitated immediately and was filtered and recrystallized from an ethanol–water (1:1, v/v) mixture. Anal. Calcd: C, 25.70; H, 7.49; N, 22.49; Co, 15.77. Found: C, 24.87; N, 7.68; N, 21.94; Co, 14.96.

Table I. Electronic Spectral Data for Some *trans*-Diacido(tetraamine)cobalt(III) Complexes

complex	band IA	band IB	band II	D_t'
uns-cis-Co(3,2,3-tet)(en)$^{3+}$ [a]	20.92		29.27	
trans-Co(3,2,3-tet)Br_2^+ [a]	14.83	masked	masked	696
trans-Co(3,2,3-tet)Cl_2^+ [a]	15.67	masked	22.59	600
trans-Co(3,2,3-tet)$(N_3)_2^+$	17.4	masked	masked	378
trans-Co(3,2,3-tet)$(OAc)_2^+$ [b]	18.19	21.52	27.24	312
trans-Co(3,2,3-tet)$(NH_3)_2^{3+}$	20.7		29.46	26
trans-Co(3,2,3-tet)$(NO_2)_2^+$ [d]	21.9		masked	−112
uns-cis-Co(2,3,2-tet)(en)$^{3+}$ [a]	21.09		29.16	
trans-Co(2,3,2-tet)Cl_2^+ [a]	16.1	masked	23.4	570
trans-Co(2,3,2-tet)$(OAc)_2^+$ [b]	18.43	22.57	27.72	304
trans-Co(2,3,2-tet)$(GlyH)_2^+$ [b]	18.19	22.89	27.92	331
trans-Co(2,3,2-tet)$(NH_3)_2^{3+}$	21.05		27.77	6
trans-Co(2,3,2-tet)$(NO_2)_2^+$ [c]	22.5		masked	−160

[a] Reference 5a. [b] Reference 5b. [c] Reference 5c. [d] Reference 5d.

***trans*-Diammine(1,9-diamino-3,7-diazanonane)cobalt(III) Chloride, *trans*-(Co(2,3,2-tet)$(NH_3)_2$)Cl_3.** To 50 mL of ethanol saturated with NH_3 was added a solution of 1 g of *trans*-(Co(2,3,2-tet)Cl_2)Cl in 50 mL of ethanol. The product precipitated immediately and was filtered and recrystallized from an ethanol water (1:1, v/v) mixture. Anal. Calcd: C, 23.37; H, 7.23; N, 23.37; Co, 16.38. Found: C, 22.97; H, 7.39; N, 22.97; Co, 15.97.

***trans*-Diazido(1,10-diamino-4,7-diazadecane)cobalt(III) Tetrafluoroborate, *trans*-(Co(3,2,3-tet)$(N_3)_2$)BF_4.** To a solution of 1.9 g of sodium azide in 25 mL of water was added 5 g of *trans*-(Co(3,2,3-tet)Cl_2)Cl dissolved in 50 mL of water. A fourfold excess (6.5 g) of sodium tetrafluoroborate was added, and the solution was allowed to stand at room temperature. The product crystallized after several days standing and was recrystallized from water. Anal. Calcd: C, 23.76; H, 5.45; N, 34.65; Co, 14.58. Found: C, 24.19; H, 5.87; N, 35.90; Co, 15.00. All of the remaining complexes discussed herein were prepared by previously published procedures.[5]

Results

A. Apparent Axial Ligand Field Strength in *trans*-Diacido(tetraamine)cobalt(III) Complexes. Electronic spectra for some *trans*-diacido(tetraamine)cobalt(II) complexes are given in Table I. The most significant feature of each spectrum is the splitting of the low-energy "octahedral" transition into two components, one of which is observed at about 21 × 10^3 cm^{-1} and the other in the range 16–22 × 10^3 cm^{-1}. The interpretation of these spectra under the point-charge model proposed by Piper and Wentworth[6] has been reported elsewhere.[7] Briefly, the band observed at about 21

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$\times 10^3$ cm^{-1} is relatively insensitive to the nature of axial ligands (less than 2% variation within this series) and is assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition in D_{4h} microsymmetry. The band which is more important on the axial ligand is assigned to the $^1A_{1g} \rightarrow {}^1E_g$ transition. We have used the energy of this transition W (vide infra) to calculate the empirical tetragonal crystal field parameter, D_t', from the relationship $D_t' = 4/35(W - (10Dq - C))$ ($10Dq$ is the energy of the lowest energy electronic transition observed in the spectra of "octahedral" *uns-cis*-ethylenediamine(tetraamine)cobalt(III) cations and C is the interelectron repulsion parameter observed to be about 3800 cm^{-1}).

The remaining band observed in these spectra is assigned to the octahedral $^1A_{1g} \rightarrow {}^1T_{2g}$ transition. We have found no reports of splitting of this band in the electronic spectra of *trans*-diacido(tetraamine)cobalt(III) complexes.

B. General Features of the Carbon-13 NMR Spectra of *trans*-Diacido(tetraamine)cobalt(III) Complexes. The carbon-13 NMR spectra of these complexes are characterized by excellent signal to noise ratios (20:1) and narrow lines (5 Hz). The spectra do not suffer significantly from broadening due to coupling with either cobalt or nitrogen, which often makes the proton NMR spectra of cobalt(III) amine complexes difficult to interpret.[8]

Our ^{13}C NMR spectra sometimes exhibit a heptet arising from the solvent, centered at 39.55 ppm. The narrow line widths associated with the spectra of the subject complexes normally minimize the problem of solvent masking. All of the expected resonance signals can usually be identified, though occasionally one line appears at the same shift as the solvent peak and must be found by comparing the solvent peak intensities.

The 1,10-Diamino-4,7-diazadecane (3,2,3-tet) System. The carbon-13 NMR of the free ligand was assigned with use of criteria established for other organic amines.[9] The resonance signal at lowest chemical shift results from the atoms bonded only to carbon. The carbon atoms bonded to the primary amine nitrogen atoms appear at 40.02 ppm. The atoms bonded to secondary amine nitrogen appear at considerably larger chemical shift, 49.30 and 47.31, for the two different groups of atoms bonded to secondary amine nitrogen (vide supra).

Resonance of the carbon atoms in five-membered chelate rings always appears at lower field than does that of carbon in six-membered chelate rings. The bond lengths and angles in five-membered chelate rings are very close to the "ideal" values (i.e., tetrahedral bond angles, C–C bond lengths of 0.154 nm, and C–N bond lengths of 0.147 nm).[10] This is reflected in ^{13}C NMR spectra which show the carbon atoms associated with these rings affected primarily by the shielding of the metal ion (i.e., the "electronic effect").

Carbon-13 resonance signals of the atoms in the six-membered chelate rings appear at equal or higher field (lower chemical shift) than those of the free ligand, indicating a significant steric perturbation. The carbon atom bonded only to carbon, which is also the farthest from the metal atom, is expected to show the smallest metal ion shielding compared with the free ligand. Accordingly, the chemical shift of this carbon atom is significantly smaller than the corresponding shift in the free ligand spectrum. The other carbon atoms of the six-membered chelate rings appear at approximately the same chemical shift as in the free ligand.

Table II. ^{13}C Nuclear Magnetic Resonance Data for Some *trans*-Diacido(3,2,3-tet)cobalt(III) Complexes

complex	A	B	C	D
trans-Co(3,2,3-tet)Br$_2^+$	52.86	49.08	39.30	26.70
trans-Co(3,2,3-tet)Cl$_2^+$	52.55	48.21	38.24	25.26
trans-Co(3,2,3-tet)(N$_3$)$_2^+$	52.09	47.91	38.53	26.43
trans-Co(3,2,3-tet)(OAc)$_2^+$	51.89	47.36	37.75	26.25
trans-Co(3,2,3-tet)(NH$_3$)$_2^{3+}$	51.44	46.75	37.95	25.26
trans-Co(3,2,3-tet)(NO$_2$)$^+$	50.77	48.87	38.56	25.71

Table III. ^{13}C Nuclear Magnetic Resonance Data for Some *trans*-Diacido(2,3,2-tet)cobalt(III) Complexes

complex	A	B	C	D
trans-Co(2,3,2-tet)Cl$_2^+$	54.67	47.87	42.41	28.04
trans-Co(2,3,2-tet)(Gly)$_2^+$	54.32	47.19	42.18	27.77
trans-Co(2,3,2-tet)(OAc)$_2^+$	54.39	47.08	41.69	27.60
trans-Co(2,3,2-tet)(NH$_3$)$_2^{3+}$	53.89	47.84	41.74	27.69
trans-Co(2,3,2-tet)(NO$_2$)$_2^+$	53.53	47.56	42.41	27.26

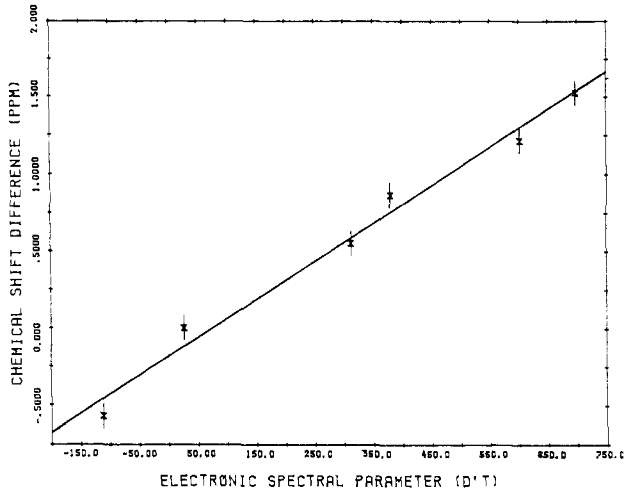

Figure 1. Plot of the difference in chemical shift (ppm) between the *trans*-diamino(1,10-diamino-4,7-diazadecane)cobalt(III) cation and some *trans*-diacido(1,10-diamino-4,7-diazadecane)cobalt(III) cations vs. the apparent tetragonal crystal field strength, D_t'.

The 1,9-Diamino-3,7-diazanonane (2,3,2-tet) System. The ^{13}C NMR spectrum of *trans*-diacido(2,3,2-tet)cobalt(III) complexes exhibit four signals with relative intensity 2:2:2:1. These spectra systematically reflect the several different steric environments of the carbon atoms.[2,11] The ^{13}C NMR spectrum of *trans*-diacido(2,3,2-tet)cobalt(III) complexes reflect the steric effects described above.

Effect of Apparent Axial Ligand Field Strength on ^{13}C Chemical Shifts. The effect of apparent axial ligand field strength on ^{13}C chemical shifts is most pronounced for carbon atoms 5 and 6 of 1,10 diamino-4,7-diazadecane in *trans*-diacido(3,2,3-tet)cobalt(III) complexes. The chemical shift of these equivalent carbon atoms varies from 52.86 ppm (from Me$_4$Si as an internal standard) for the *trans*-dibromo(3,2,3-tet)cobalt(III) cation ($D_t' = 696$ cm^{-1}) to 50.77 ppm for the *trans*-dinitro(3,2,3-tet)cobalt(III) cation ($D_t' = -112$ cm^{-1}). The chemical shifts for *trans*-diacido complexes with intermediate values of D_t' vary linearly within ±5% (Table II, Figure 1). The chemical shifts of the remaining carbon atoms vary independently of the apparent axial ligand field strength.

Similarly, the chemical shift of carbon atoms 2 and 8 of 1,9-diamino-3,7-diazanonane in *trans*-diacido(2,3,2-tet)cobalt(III) cations vary from 54.67 ppm for the *trans*-dichloro complex ($D_t' = 570$ cm^{-1}) to 53.54 ppm for the *trans*-dinitro complex ($D_t' = -160$ cm^{-1}). The chemical shift differences of the remaining carbon atoms are either insignificant (carbon

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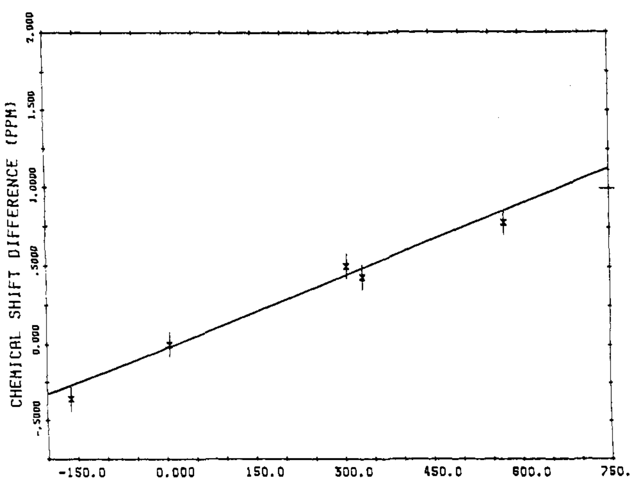

Figure 2. Plot of the difference in chemical shift (ppm) between the *trans*-diamino(1,9-diamino-3,7-diazanonane)cobalt(III) cation and some *trans*-diazido(1,9-diamino-3,7-diazanonane)cobalt(III) cations vs. the apparent tetragonal crystal field strength, D_t'.

atoms 1 and 9) or varies independently of the apparent axial ligand field strength (carbon atoms 4–6) (Table III, Figure 2).

Discussion

Chemical shift phenomena are often described in terms of a diamagnetic contribution arising from the bonding and core electrons of a test nucleus, a paramagnetic contribution arising from mixing of excited states of the test nucleus, and a "catchall" contribution which includes electronic currents on all other atoms and interatomic currents which can not be localized, steric and nonbonded effects, etc. Karplus and Pople[12] have described these effects as

$$\sigma = \sigma^d + \sigma^p + \sigma'$$

In the chemistry of carbon, chemical shifts of about 100 ppm distinguish tetrahedral from trigonal-planar carbon atoms, for example.[13] Shifts of similar magnitude have been ascribed to charge effects.[14] These shifts are included in the diamagnetic term and reflect differences in bonding among the test atoms.

In the chemistry of carbon these terms obey straightforward empirical additivity rules since the atomic number of the bonded atoms is usually 9 or less, and contributions from heavier atoms such as sulfur, phosphorus, and halogens are predictable.

It is more difficult to unambiguously assign contributions to the ^{13}C chemical shift from the paramagnetic term:

$$\sigma^p = -(e^2h/2\pi)_2)/2m^2e^2(\Delta E)\langle r^{-3}\rangle(Q_{nn} + \Sigma Q_{nn})$$

The magnitude of the paramagnetic term is inversely proportional to the energy difference which separates the ground state from an excited state which is mixed under the influence of an external magnetic field, for example. The sign of the paramagnetic term is such that an increase in the energy difference between the mixed states leads to increased shielding of the test nucleus.

In contrast, ^{59}Co NMR spectra have been reported for a series of octahedral cobalt(III) complexes which show the expected dependence of the ^{59}Co chemical shift on the magnitude of the crystal field parameter, $10Dq$, a measure of the energy separation of the ground and first excited electronic states.[15] The chemical shift was observed to decrease linearly over a wide range of some 6000 ppm as $10Dq$ varied from 16.4 ($K_3(Co(C_2O_4)_3)$) to 32.1×10^3 cm^{-1} ($K_3(Co(CN)_6)$) and to fit the expression

$$\sigma = A - B_0/10Dq$$

which is analogous to the expression given by Karplus and Pople[10] among others.

The "catchall" term

$$\sigma' = \tfrac{1}{3}(R_{nb})^{-3}(\Delta\chi_b)(1 - \cos^2 \phi_b)$$

has been applied indirectly to describe steric effects (such as the effects of bond length and angle deformation on chemical shifts: vide supra), sometimes leading to useful empirical additivity rules, etc. These effects have the same sign and approximately the same magnitude in proton and carbon NMR experiments.

For diamagnetic transition metal complexes, $\Delta\chi_b$ arises from the temperature-independent paramagnetism of the metal ion

$$\chi_{TIP} = 2N\beta^2 8/10Dq$$

which exhibits an inverse dependence on the energy difference between the diamagnetic ground state and paramagnetic excited states.

In the case of classical or Werner complexes, the dominant diamagnetic and paramagnetic effects most often occur not at the test atom (carbon in this study) but at the central metal ion where most of the electrons are found and where the energy separating states participating in the paramagnetic term is usually small. Thus, both the diamagnetic and paramagnetic contributions of the metal ion are reflected in relatively small perturbations observed in ^{13}C NMR spectra.

It is apparent that the expresions applied to diamagnetic and paramagnetic chemical shifts cannot be directly applied in this case since the energy difference is observed in the electronic spectrum of the central cobalt(III) ion and the chemical shift is observed for a remote carbon atom. In the Karplus model, these effects arise from the σ' term. The inverse dependence of the chemical shift of the apparent ligand field strength of the axial ligands is analogous to the paramagnetic term, however, and may arise via a long range coupling between the central ion and the test carbon nucleus. This interpretation is consistent with the small magnitude of the observed effect. Furthermore, since no similar correlation was observed in the proton spectra,[3] we conclude that the present observations do not arise from temperature-independent paramagnetism, alone.

Grutzner[16] has suggested that this effect may arise from coupling of orbital angular momenta through the σ^* system of the chelate ring. Grutzner's model involves an extension of the paramagnetic term, σ^p, throughout the molecule under study. This interpretation is consistent with the observations that the effect is only manifested in rings with odd numbers of atoms (vide supra) and that the diamagnetic term does not change significantly between the *trans*-dichloro and *trans*-dibromo complexes (*trans*-$Co(3,2,3\text{-tet})Br_2^+$) in C_2 symmetry.

A simple, graphical interpretation is suggested to us by the interaction of the filled cobalt(III) π orbitals with the test nucleus. In the point-charge model, as the apparent axial ligand field increases, interelectron repulsions force the cobalt π electrons into the region in space occupied by the test carbon nuclei, resulting in increased shielding. This model ascribes the effect to the σ' term involving steric and delocalized electronic effects.

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Registry No. *trans*-[Co(3,2,3-tet)$(NH_3)_2$]Cl_3, 81120-92-5; *trans*-[Co(2,3,2-tet)$(NH_3)_2$]Cl_3, 81120-93-6; *trans*-[Co(3,2,3-tet)$(N_3)_2$]BF_4, 81120-95-8; *trans*-[Co(3,2,3-tet)Cl_2]Cl, 31842-33-8; *trans*-[Co(2,3,2-tet)Cl_2]Cl, 15041-27-7; *trans*-[Co(3,2,3-tet)Br_2]$^+$, 55722-17-3; *trans*-[Co(3,2,3-tet)$(OAc)_2$]$^+$, 47100-49-2; *trans*-[Co(3,2,3-tet)$(NO_2)_2$]$^+$, 55722-18-4; *trans*-[Co(2,3,2-tet)$(gly)_2$]$^+$, 81244-25-9; *trans*-[Co(2,3,2-tet)$(OAc)_2$]$^+$, 57022-13-9; *trans*-[Co(2,3,2-tet)$(NO_2)_2$1$^+$, 46845-89-0.

Contribution from the Departments of Chemistry, Texas A&M University,
College Station, Texas 77843, and University of Antwerp (U.I.A.), B-2610 Wilrijk, Belgium

Synthesis and Spectroscopic Properties of Divalent and Trivalent Tris(2,2′-bipyridine)iron Complexes in Zeolite Y

WILLIAM H. QUAYLE,[1] GUIDO PEETERS,[2] GILBERT L. DE ROY,[2] ETIENNE F. VANSANT,[2]
and JACK H. LUNSFORD*[1]

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Mössbauer, EPR, and visible-region diffuse-reflectance techniques were used to characterize divalent and trivalent tris(2,2′-bipyridine)iron complexes which had been synthesized within the large cavities of Y-type zeolites at low and high loadings. Exposure of samples containing the divalent Fe complex to chlorine gas produced the supported trivalent complex. The spectroscopic data for the low-loading iron complexes in the zeolite were similar to data obtained for $Fe(bpy)_3$ complexes in other matrices; i.e., for $[Fe^{II}(bpy)_3]$–Y(5.3) λ_{max} = 528, 495, and 353 nm, IS = 0.626, and QS = 0.339 mm/s and for $[Fe^{III}(bpy)_3]$–Y(5.3) λ_{max} = 612 nm, $g_\perp = -2.60 \pm 0.02$, and $g_\parallel = 1.66 \pm 0.01$. Differences were attributed to the probable higher negative charge density within the zeolite. The bipyridine ligand complexed 88% of the iron specifically in the tris form, and chlorine gas oxidized 89% of this divalent complex. With the high-loading sample, only 55% of the total iron was complexed by bipyridine since the iron content exceeded that necessary for one large tris complex per supercage. Excess Fe(II) was apparently close enough that it exerted an electron–withdrawing influence on the bpy ligands. Only 33% of the bpy complexes were effectively oxidized by chlorine gas, presumably due to exclusion of Cl_2 or Cl^- from certain cation sites.

Introduction

Well-characterized transition-metal complexes such as $[Cu(en)_2]^{2+}$[3] synthesized within a zeolite, either by direct ion exchange of the complex or sorption of the ligand within the support, serve as models of complex-support interactions which may occur during photochemical or catalytic reactions. We recently examined the spectroscopic and redox properties of large tris(2,2′-bipyridine)ruthenium(II) and -(III) complexes located in supercages of Y-type zeolites.[4,5] The photophysical behavior of the ruthenium(II) complex in the zeolite was altered from that commonly observed for the solution phase complex in ways that could be rationalized in terms of synergistic complex-support interplay.[4] Since the zeolite offered a regular, characterizable medium in which potential nonaqueous, aqueous, or gas-phase photochemistry could be conducted, we initiated studies designed to test the thermal and photo activities for reactions of small molecules within these materials. As part of that study the chlorine oxidation of $[Ru^{II}(bpy)_3]^{2+}$ ions in a Y-type zeolite was undertaken in order to evaluate the thermal reaction of the respective trivalent complex with water.[5]

This report describes the spectroscopic properties of divalent and trivalent iron tris(bipyridine) complexes in zeolite Y. Since the diameter of the $[Fe^{II}(bpy)_3]^{2+}$ complexes was too large (~1 nm) to exchange directly through the zeolite lattice free apertures (~0.74 nm),[6] a procedure for in situ synthesis of the complex was adopted.

Experimental Section

$[Fe^{II}(bpy)_3]$–Y. A $[Fe^{II}(bpy)_3]$–Y(5.3) sample which contained 1.7 wt % Fe or 5.3 Fe ions per unit cell was prepared by exchange of 8.00 g of Na–Y zeolite (Linde) with 1.00 g of $Fe^{II}SO_4\cdot 7H_2O$ (Fisher) in an aqueous solution, pH 4, under flowing N_2. The Fe^{II}–Y zeolite was then washed and dried at room temperature. A 4.00-g sample of the Fe^{II}–Y zeolite was mixed with 1.00 g of 2,2′-bipyridine, degassed for 4 h at 25 °C, and then heated at 200 °C overnight in a closed system. The preparative mole ratio of Fe to bpy was about 1:3.5. The reddish pink product was subsequently degassed at 200 °C to 5 × 10^{-4} torr.

A Fe^{II}–Y sample used for the synthesis of the higher loading $[Fe^{II}(bpy)_3]$–Y(13) sample which contained 4.0 wt % Fe or 13 Fe ions per unit cell was prepared after the method of Delgass et al.[7] by exchange of 5 g of Na–Y with an excess (12.2 g) of $Fe^{II}SO_4\cdot 7H_2O$ in a pH 4 solution under N_2. The reaction with bpy was analogous to the low-loading preparation except that 0.33 g of bpy/g of zeolite was used to produce the deep red product.

An impregnated $[Fe^{II}(bpy)_3]$–Y sample was prepared by addition of bpy in about a 3:1 bpy:Fe mole ratio to an Fe^{II}(aq) solution. This produced $[Fe^{II}(bpy)_3]^{2+}$, to which some Na–Y was added with stirring. Filtration and drying at room temperature yielded a light pink material.

$[Fe^{III}(bpy)_3]$–Y. A 1-g sample of $[Fe^{II}(bpy)_3]$–Y(5.3) was placed in a sample tube equipped with a 0.5-cm fused quartz curvette, for diffuse-reflectance studies, and a 4-mm o.d. quartz sidearm, for EPR studies. The sample was degassed typically for 4 h at 25 °C and then for 20 h at 180 °C (pressure 4 × 10^{-4} torr). The samples prepared for the Mössbauer study were degassed at 200 °C to 5 × 10^{-4} torr. For one EPR study a sample was degassed at 300 °C for 4 h, and the results showed that the higher degassing temperature did not significantly alter the spectrum. Following spectroscopic examination the samples were exposed to about 400 torr Cl_2 (Matheson) for 13 h at 25 °C. Excess Cl_2 was then removed from the light gray-blue zeolite by evacuation at 25 °C for 3 h (pressure = 7 × 10^{-5} torr).

The $[Fe^{II}(bpy)_3]$–Y(13) zeolite was treated in the same manner as the $[Fe^{II}(bpy)_3]$–Y(5.3) samples except that the temperature was maintained at 50 °C during the exposure to chlorine. In addition, the sample prepared for the Mössbauer study was treated with only 20 torr Cl_2 for 5 h.

X-ray Diffraction and Spectroscopic Methods. X-ray diffraction (XRD) patterns were recorded with a Seifert-Scintag PAD II diffractometer using Ni-filtered Cu radiation. The samples were allowed to equilibrate with atmospheric moisture for at least 24 h prior to recording their patterns.

X-Band EPR spectra were obtained with a Varian E-6S spectrometer. Samples were allowed to thermally equilibrate for at least

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(2) University of Antwerp (U.I.A.).
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