

$k_{-1}[\text{Ru}^{3+}] > k_2[\text{H}^+]^2$, the constant k_1k_2/k_{-1} , and hence k_{-1}/k_2 , can be determined. Since $K = k_1/k_{-1}$, we calculate $k_{-1} = 2.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. With $k_{-1}/k_2 = 4.6 \times 10^{-3} \text{ M}$, then $k_2 = 5.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. This acid solvolysis k_2 is in the range of the $2 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$ found from the Pd/C-produced $\text{Mn}^{\text{II}}\text{-TPPS}$ and is in better agreement with a k_2 of $4.5 \times 10^7 \text{ M}^{-2} \text{ s}^{-1}$ found by Neta and Morehouse,²⁸ who generated $\text{Mn}^{\text{II}}\text{-TPPS}$ by pulse radiolysis of aqueous 10% isopropyl alcohol/ N_2O -saturated solutions of $\text{Mn}^{\text{III}}\text{-TPPS}$.

The reduction potential of $\text{Mn}^{\text{III/II}}\text{-TAP}$ is -0.15 V vs. NHE,²⁹ and thus $K = 2.3 \times 10^{-4}$ for the $\text{Ru}(\text{NH}_3)_6^{2+}/\text{Mn}^{\text{III}}\text{-TAP}$ reaction. Since $K = 33 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-1} = 1.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, and with $k_{-1}/k_2 = 5.5 \times 10^3 \text{ M}$, $k_2 = 2.5 \times 10^7 \text{ M}^{-2} \text{ s}^{-1}$. This acid solvolysis k_2 for the formally tetrapositive $\text{Mn}^{\text{III}}\text{-TAP}$ at $I = 0.3$ is similar to that of the formally tetranegative $\text{Mn}^{\text{III}}\text{-TPPS}$. This is expected in that, at $I = 0.5$, zinc porphyrin acid solvolysis reactions of the oppositely charged Zn-TAP^{4+} and Zn-TPPS^{4-} complexes have approximately equal rates.³⁰ As the ionic strength decreases, however, the $\text{Zn-TPPS}^{4-}/\text{H}^+$ solvolysis rates become much faster than those of $\text{Zn-TAP}^{4+}/\text{H}^+$, in line with the Brønsted-Bjerrum equation.

The Marcus equation³¹ can be used to calculate the self-exchange rate constants, k_{22} , for the $\text{Mn}^{\text{III/II}}$ -porphyrin studied. Taking the $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ self-exchange rate constant (k_{11}) as $3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ (25°C , $I = 0.1$),²⁷ we calculate $k_{22} = 3.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Mn}^{\text{III/II}}\text{-TPPS}$ and $2.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Mn}^{\text{III/II}}\text{-TAP}$. A reduction potential of -0.010 V vs. NHE, which is independent of pH between 5 and 10, has been found³² for $\text{Mn}^{\text{III/II}}\text{-TMPyP}(4)$, and the same number is assumed for the protonated manganese(III/II) tetrakis(4-pyridyl)porphyrin in acid.³³ An oxidation potential for the $\text{V}(\text{H}_2\text{O})_6^{2+/3+}$ couple of $+0.230 \text{ V}$ has been reported,²⁷ with a corresponding self-exchange rate constant $k_{22} = 1.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. With use of an average value for k_{22} of $2.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for a $\text{Mn}^{\text{III/II}}$ -porphyrin, the predicted cross reaction (k_{12}) rate constant for the presumed outer-sphere $\text{V}(\text{H}_2\text{O})_6^{2+}/\text{Mn}^{\text{III}}\text{-TPyP}(4)$ reaction is $390 \text{ M}^{-1} \text{ s}^{-1}$. This value is within a factor of 3 of the $145 \text{ M}^{-1} \text{ s}^{-1}$ observed earlier.⁷ Thus, k_{22} appears to be relatively independent of the water-soluble manganese(III/II) porphyrin type, and similar conclusions have been reached for related cobalt(III/II) porphyrins.³⁴

For the $\text{Ru}(\text{NH}_3)_6^{2+}/\text{Co}^{\text{III/II}}\text{-TMPyP}(4)$ reaction, Pasternack and co-workers^{13,14} found a k_{22} for $\text{Co}^{\text{III/II}}\text{-TMPyP}(4)$ of $20 \text{ M}^{-1} \text{ s}^{-1}$, close to the value of $21 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Co}(\text{phen})_3^{2+/3+}$. From the $\text{Ru}(\text{NH}_3)_6^{2+}/\text{Fe}^{\text{III/II}}\text{-TMPyP}(4)$ reaction,¹⁵ $k_{22} = 1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for high-spin $\text{H}_2\text{O-Fe}^{\text{III/II}}\text{-TMPyP}(4)$, $>10^7 \text{ M}^{-1} \text{ s}^{-1}$ for low-spin bis(imidazole)- $\text{Fe}^{\text{III/II}}\text{-TMPyP}(4)$, and $\geq 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the low-spin $\text{HO-Fe}^{\text{III/II}}\text{-TMPyP}(4)$. The last two $\text{Fe}^{\text{III/II}}$ -porphyrin low-spin values were noted¹⁵ to be in the range of $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Fe}(\text{phen})_3^{2+/3+}$, suggesting that electron transfer in low-spin porphyrin derivatives proceeds through the porphyrin π system.³⁶ $k_{11} = 3 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Mn}(\text{H}_2\text{O})_6^{2+/3+}$,³⁷ $7.7 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Co}(\text{en})_3^{2+/3+}$,³⁵ and $1.1 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Fe}(\text{H}_2\text{O})_6^{2+/3+}$.³⁵ The ratios of the self-exchange rate constants for the $\text{M}^{\text{III/II}}$ porphyrins to those of the saturated ligand complexes are 1×10^7 for manganese, 3×10^5 for cobalt, and 1×10^6 for iron. One thus sees an increase in exchange rates of ca. 10^6 when the metal ion moves from a hard environment into the soft porphyrin center.

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Acknowledgment. This work was supported in part by Howard University NIH Biomedical Research Grant 5-SO-6-RR-08016-9 and PHS Grant No. GM-07799-05. We thank Dr. David Lavalley and Dr. P. Neta for helpful discussions.

Registry No. $\text{Mn}^{\text{III}}\text{-TPPS}$, 88992-32-9; $\text{Mn}^{\text{III}}\text{-TAP}$, 84177-73-1; $\text{Ru}(\text{NH}_3)_6^{3+}$, 19052-44-9.

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Deuterium-Substitution Effects on Relaxation Times and Interligand Nuclear Overhauser Effects for Assignment of Ligand Resonances and Isomer Identification in Cobalt(III) Complexes

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Received July 5, 1984

The assignment of proton resonances in heterocyclic ligands in coordination compounds is complicated by the variety of effects the metal ion can have on the ligand chemical shifts. Also, the assignment of closely related structural isomers by other than X-ray structure determinations is uncertain, at best. In this report we demonstrate the use of specific deuterium substitution effects on T_1 's of ligand protons and interligand nuclear Overhauser effects (NOE) in making resonance and isomer assignments.

Proton resonances in nitrogen-containing heterocyclic ligands in metal complexes may be affected by a number of factors, including changes in electron density in the ligand due to σ -bond or π -bond interactions, specific solvent-substrate interactions, changes in ligand magnetic anisotropy upon complex formation, paramagnetic anisotropy resulting from the temperature-independent paramagnetic moment of the metal ion, anisotropic effects of the metal-ligand bond, and ligand proton-metal ion nucleus spin-spin interactions. The likely relative importance of these different factors has been discussed by Foust and Ford.¹

Imidazole complexes of $(\text{NH}_3)_5\text{Co}^{3+}$ (A_5Co^{3+}) have been studied as models for histidine complexes in biological systems,^{2,3} and complexes of substituted imidazole have been prepared and characterized.⁴ The assignment of resonances and isomers in these complexes is ambiguous, unless a specific isotopic substitution is made or an X-ray structure is available. We report here T_1 and NOE results for nine imidazole complexes and one histidine complex from which unequivocal resonance and isomer assignments can be made.

Experimental Section

^1H NMR spectra were obtained at 200.068 MHz on a Nicolet NT-200 spectrometer. T_1 's were measured by using a standard inversion recovery sequence, $180^\circ\text{-}\tau\text{-}90^\circ\text{-acquire}$.⁵ The T_1 's were first estimated by obtaining a null point and τ values chosen to obtain an appropriate range of data points. The data were fit by a nonlinear least-squares program from the Nicolet 1180 software (DR- T_1 -IR).

Nuclear Overhauser effects were obtained by comparing spectra with an F_2 frequency off-resonance to one with an ammine resonance of interest irradiated. Sufficient power was used to saturate the ammine resonance. The integrated areas of the peaks were compared or difference spectra obtained.

For NOE's and T_1 's of protonated forms, the complexes were dissolved in 1 M DCl. Under this condition the N-H exchange is slow. For T_1 's of deuterated forms, the complex was dissolved in D_2O and allowed to stand until all of the N-H had exchanged. Then, sufficient concentrated DCl was added to make the solution 1 M. No attempt was made to exclude air or to purify D_2O or other reagents.

Chemical shifts are reported on the δ scale relative to internal 3-(trimethylsilyl)propionate. T_1 values on duplicate measurements were reproducible to $\pm 0.1 \text{ s}$.

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Table I. Structures of the Compounds Studied

compd ^{a,b}	R ₁	R ₂	R ₃	R ₄	R ₅
1	(NH ₃) ₅ Co ³⁺	H	H	H	H
2	(NH ₃) ₅ Co ³⁺	H	CH ₃	H	H
3	(NH ₃) ₅ Co ³⁺	CH ₃	H	H	H
4	(NH ₃) ₅ Co ³⁺	H	H	CH ₃	H
5	(NH ₃) ₅ Co ³⁺	H	H	H	CH ₃
6	(NH ₃) ₅ Co ³⁺	CH ₃	CH ₃	H	H
7 ^c	<i>cis</i> -(en) ₂ ClCo ²⁺	H	H	H	H
8	<i>cis</i> -(en) ₂ ClCo ²⁺	H	CH ₃	H	H
9	<i>cis</i> -(en) ₂ ClCo ²⁺	H	H	CH ₃	H
10 ^d	enCl(His)Co ⁺	H	H	H	CH ₂ CH-

a



^b In the following tables the a series of numbers will refer to N-H, the b series of numbers to N-D, exchanged in solvent D₂O at neutral pH and adjusted to 1 M DCl. ^c en = ethylenediamine.

^d His = histidine; see ref 6 for structure.

Table II. T₁ Values for Ligand Protons in Imidazole and Histidine Complexes

compd ^a	R ₂ ^b	R ₃	R ₄	R ₅
1a	2.62	NR ^c	5.55	1.96
1b	9.02	NR	5.56	4.73
2a	1.69	1.21	3.64	1.79
2b	3.51	1.32	3.29	3.85
3a	1.08	NR	4.48	1.13
3b	1.32	NR	4.06	3.13
4a	2.10	NR	1.15	1.58
4b	6.35	NR	1.22	3.93
5a	1.37	NR	5.37	0.94
5b	5.43	NR	5.04	1.08
6a	0.88	0.78 ^d	2.46	1.01
6b	1.13	1.00	2.58	3.04
7a	1.86	NR	4.34	1.12
7b	5.75	NR	4.53	3.05
8a	1.33	1.03	2.86	1.12
8b	2.54	1.03	2.72	2.52
9a	1.57	NR	0.87	0.99
9b	3.01	NR	0.89	2.03
10a	1.57	NR	4.48	0.41 (A), 0.32 (B), 0.78 (X)
10b	3.75	NR	4.69	0.40 (A), 0.35 (B), 1.65 (X)

^a See Table I for structures. ^b T₁ values in s. ^c NR = no resonance. ^d Uncertain due to overlap with the trans ammine resonance.

The A₅Co³⁺ imidazole complexes were prepared by the method of Harrowfield et al.^{2,4} and crystallized as either the chloride or perchlorate salt. The Co(en)₂Cl(Im)²⁺ and Co(en)₂Cl(His) complexes were prepared by the method of Brodsky et al.⁶

Results

Table I gives the structures of the compounds studied. In all cases the nitrogen coordinated to the metal ion is designated N-1; thus, protons or substituents at positions 2 and 5 are adjacent to the ammine ligands in the octahedral coordination sphere of the Co(III).

In Table II we present the T₁ values for the ligand protons in the complexes with protonated ammine ligands (a series) and the parallel series with deuterated ammine ligands (b series). Note

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Table III. Nuclear Overhauser Effects Observed on Imidazole Ligand Protons from Irradiation of Ammine Protons

compd ^a	R ₂ ^b	R ₃	R ₄	R ₅	freq irradiated ^c
1	+	NR	0	+	3.79
2	+	0	0	+	3.77
3	+	NR	0	+	3.89
4	+	NR	0	+	3.77
5	+	NR	0	+	3.92
6	+	0	0	+	3.86
7	+	NR	0	+	4.31
	+	NR	0	+	4.66
	+	NR	0	+	4.95
	+	NR	0	+	5.84
8	+	0	0	+	4.30
	0	0	0	0	4.66
	0	0	0	0	4.90
	+	0	0	+	5.82
9	+	NR	0	+	4.24
	0	NR	0	0	4.62
	0	NR	0	0	4.92
	0	NR	0	0	5.78
10	+	NR	0	0,0, ^d	5.54
	+	NR	0	0,0, ^d	6.04
	+	NR	0	0,0, ^d	6.46

^a See Table I for structures. ^b + = positive NOE; 0 = no NOE; NR = no resonance. ^c Chemical shift in δ of irradiated NH.

^d A, B, X values.

Table IV. Chemical Shifts of Ligand Protons in Cobalt(III) Imidazole and Histidine Complexes

compd ^a	R ₂ ^b	R ₃	R ₄	R ₅	NH
1	8.14	NR ^c	7.46	7.14	3.79
2	8.02	3.86	7.38	7.08	3.77
3	2.48	NR	7.31	6.84	<i>cis</i> 3.89, <i>trans</i> 3.70
4	7.97	NR	2.31	6.80	3.77
5	7.90	NR	7.11	2.21	<i>cis</i> 3.92, <i>trans</i> 3.70
6	2.43	3.71 ^d	7.30	6.79	<i>cis</i> 3.86, <i>trans</i> 3.71
7	8.29	NR	7.41	7.30	5.84, 4.95, 4.66, 4.31
8	8.19	3.85	7.34	7.24	5.82, 4.90, 4.66, 4.30
9	8.12	NR	2.31	6.97	5.78, 4.92, 4.62, 4.24
10	8.14	NR	7.23	3.25 (A) ^e , 3.68 (B), 4.08 (X)	6.46, 6.04, 5.54

^a See Table I for structures. ^b Chemical shift in δ. ^c NR = no resonance. ^d Overlaps with *trans* NH. ^e J_{AB} = -17.6 Hz, J_{AX} = 5.28 Hz, J_{BX} = 2.64 Hz.

that in each pair there are imidazole ligand resonances that have much longer T₁'s when the adjacent ammine ligands are deuterated.

In Table III we summarize the results of the NOE's observed on imidazole ligand protons resulting from irradiating the ammine protons. Note that positive NOE's are obtained for those resonances that show large changes in T₁'s when the ammine protons are exchanged for deuterium. The NOE's obtained ranged from 8% to 35%. As the solutions were not degassed and no attempt was made to exclude any adventitious metal ion contamination, no attempt is made to interpret the NOE's quantitatively. The NOE's are simply reported as positive (+) or zero (0).

In Table IV the chemical shift assignments are given for the 10 complexes studied in this report. The assignments are based on the T₁ and NOE effects reported in Tables II and III.

Discussion

The substitution of deuterium for a hydrogen removes a dipolar relaxation source for other nearby protons and leads to longer T₁'s for those nearby protons in the substituted molecule.⁷ The deuterium-substitution effect on relaxation times (DESERT) has

been used to determine intranuclear distances and molecular conformations.⁸

We have previously assigned the resonances in the A_2CoImH^{3+} complex³ based on the magnitude of the $\Delta\delta$ excursion on deprotonation of the coordinated imidazole. In comparison of the C-4 and C-5 H excursions, the site closest to the protonation (C-4 H) undergoes the largest excursion. The C-2 H is at lowest field by a considerable amount, and its assignment can be easily confirmed by deuterium exchange prior to complex synthesis.³

The T_1 values reported in Table I for compounds 1-6 confirm and extend our previous assignment. An isolated proton in the C-2 position (compounds 1, 4, and 5) has a longer T_1 in the deuterium-exchanged complex by a factor of 3-4. With an adjacent methyl group (compound 2) to provide a competitive relaxation source, the T_1 at C-2 H still lengthens by a factor of 2 in the deuterated ammine complex. The same trend follows for the T_1 values of protons at the C-5 position (compounds 1-4, and 6). When the adjacent ammine ligands are exchanged for deuterium, the T_1 values are much longer. A similar pattern is also reflected in the T_1 values of methyl (compound 3, 5, and 6) adjacent to ammine ligands. In addition to the dipolar interaction with the ammine protons, other relaxation pathways are available to the protons of the methyl groups. Thus, the effect is not nearly as dramatic as in the more isolated aromatic protons.

The chemical shifts in compounds 4 and 5 have been assigned by Shepard et al.⁴ based on an X-ray structure. Our assignments are of the same order, although the chemical shifts are slightly different due to pH and ionic strength effects.

The same pattern continues in the bis(ethylenediamine) complexes (compounds 7-9), with imidazole protons adjacent to exchangeable ethylenediamine protons having much longer T_1 's in the deuterium-exchanged complexes.

In the tridentate histidine complex (compound 10) only the proton at C-2 and the proton at the α -carbon of the amino acid show a large T_1 change when the ethylenediamine and histidine amino protons are exchanged for solvent deuterium. This is consistent with the previously reported X-ray structure.⁶

Protons that are spatially close and interact by a dipolar relaxation mechanism show an enhancement of intensity in one peak when the other is saturated; the nuclear Overhauser effect.⁸ The NOE's presented in Table III follow the T_1 trends in Table II. In each case where a T_1 lengthened on deuterium exchange of the ammine ligand protons, a NOE is observed on irradiation of the ammine ligand protons. A comparison of the tables shows that either method can be used to assign resonances or isomers.

The NOE results for the ethylenediamine complexes (compounds 7-9) are surprisingly different. Although the NH resonances have quite similar chemical shifts, substantiating that these are all cis complexes, the NOE's to ligand imidazole protons are quite selective. One possible explanation is that the methyl imidazoles have different conformational rotamer populations than unsubstituted imidazole. The details of NOE's in these complexes will be the subject of a future study.

Conclusion

The T_1 's and NOE's reported here result in unambiguous assignments of proton resonances and linkage isomers in Co(III) complexes. The methods should be general and apply to other ligands such as pyrazines, tetrazoles, and pyridines and other diamagnetic, exchange-inert metal centers such as Ru(II), Os(II), Pt(II), Pt(IV), Pd(II), and Pd(IV). Two-dimensional NMR techniques relying on the NOE (NOSEY)¹⁰ can also be used to make the assignments. ^{13}C assignments can be made from the proton assignments by using single-frequency off-resonance decoupling or a two-dimensional heteroscalar-correlated $^{13}C\{^1H\}$ NMR spectra.¹⁰ The method should also have potential for ligand assignment and NH resonance assignment in metalloproteins.

Acknowledgment. This work was supported by University of California—Los Alamos National Laboratory subcontract 9-X33-L0152-1 and by National Science Foundation Grant PCM-78-13235.

Registry No. 1, 38716-02-8; 2, 91209-43-7; 3, 89955-97-5; 4, 89922-05-4; 5, 89955-98-6; 6, 91209-45-9; 7, 60314-38-7; 8, 60314-39-8; 9, 95250-94-5; 10, 88657-78-7; deuterium, 7782-39-0.

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Gas-Phase Structure of Pentacarbonyl(trifluoromethyl isocyanide)chromium, $(CF_3NC)Cr(CO)_5$

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Received July 30, 1984

Although alkyl and aryl isocyanides and their transition-metal complexes have been known for a long time and have been studied extensively,² very little is known about isocyanides bearing strong electron-withdrawing groups, especially perfluoroalkyl or -aryl groups. The availability of an efficient method for preparing trifluoromethyl isocyanide³ has led to studies of this molecule,⁴ including its ligand behavior. The IR spectra of the complexes $(CF_3NC)M(CO)_5$ ($M = Cr, W$)⁵ indicate that CF_3NC is a strong π acceptor ligand. The PE spectra⁶ and XPS spectra⁷ of $(CF_3NC)Cr(CO)_5$ confirm this result. Since the structure of the CF_3NC ligand provides direct information on the π acceptor properties of this ligand,⁸ we have studied the gas-phase structure of the chromium complex by electron diffraction. Our prime interest in this study is the geometry of the CF_3NC group.

The scattering intensities have been recorded with the Balzers gas diffractograph KD-G2⁹ at two camera distances (25 and 50 cm) and an accelerating voltage of about 60 kV. The sample was kept at 35 °C during the experiment (mp 26 °C), and the inlet system and nozzle were kept at 40 °C. The pressure in the diffraction camera was about 10^{-6} torr. Two plates for each camera distance were evaluated by the usual procedures,¹⁰ and the averaged molecular intensities are presented in Figure 1.

A preliminary structural model was derived from the analysis of the radial distribution function (Figure 2). For a linear $CNCF_3$ ligand a strong peak around 5.1 Å, corresponding to the three Cr...F distances, is expected. Such a strong peak, however, is not observed in this distance range, indicating a bent $CNCF_3$ structure.

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