Table V. Wavelength Dependence of Photodissociation Quantum Yields for $(OC)_5W(pyz)W(CO)_5$ in Benzene Containing 0.1 M Pyrazine

irradiation wavelength, nm	quantum yield[a]	irradiation wavelength, nm	quantum yield[a]
395	0.042	465	0.007
430	0.030	514	0.001

[a] Recorded at 293 K.

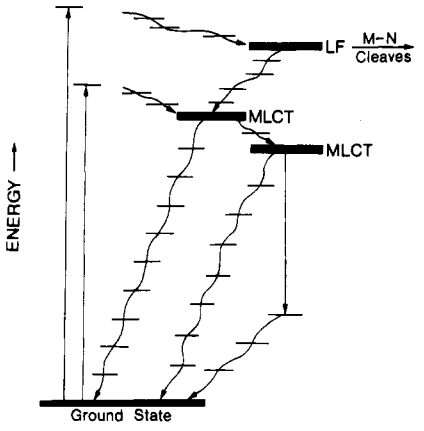

Figure 5. Excited-state scheme for $(OC)_5M(pyz)M'(CO)_5$ complexes, M, M' = Cr, Mo, W. Vertical and wavy lines represent radiative and nonradiative processes, respectively. Heavy horizontal lines depict thermally equilibrated excited states. Light horizontal lines represent successive complex–solvent cage energies as vibrationally excited states relax (only a few of these lines are shown).

lates the LF state, from which photoreaction proceeds with significantly higher quantum efficiency. The relative reaction efficiencies of the LF and W → π*(pyz) excited states of $(OC)_5W(pyz)W(CO)_5$ are characteristic of those obtained from closely related mononuclear metal carbonyl complexes in which the MLCT state lies below the LF state.[4a]

The temperature dependency of the photoreaction efficiency of $(OC)_5W(pyz)W(CO)_5$ was investigated for LF (395 nm) and W → π*(pyz) (514 nm) excitations. For LF excitation photodissociation quantum yields determined at 283, 288, 293, 298, and 303 K are 0.039, 0.043, 0.042, 0.046, and 0.049, respectively. The least-squares line of an Arrhenius type plot ($\ln \phi$ vs. $1/T$) of these data corresponds to an apparent activation energy of 1.9 (±1) kcal mol^{-1}. This low value indicates that the photoreaction of $(OC)_5W(pyz)W(CO)_5$ is not thermally activated to higher energy states and proceeds directly from the LF state. For W → π*(pyz) excitation the quantum yields at the above temperatures are 0.0011, 0.0012, 0.0013, 0.0013, and 0.0014, respectively. Here the least-squares line of an Arrhenius type plot corresponds to an apparent activation energy of 1.9 (±1) kcal mol^{-1}. This result implies that the MLCT state does not significantly thermally populate the LF state and importantly that the MLCT state is intrinsically photoreactive, albeit very inefficiently.

Summary

The experimental observations are summarized in an excited-state scheme for $(OC)_5M(pyz)M'(CO)_5$ (Figure 5). The relative positions of the LF and M → π*(pyz) states identified in the electronic absorption spectra are depicted in the scheme. A $^1A \rightarrow {}^3E$ state is not included in this excited-state scheme; this transition is predicted to be very weak ($\epsilon \approx 500$)[10] and is obscured by the more intense $^1A \rightarrow {}^1E$ and M → π*(pyz) transitions. As a consequence we were unable to populate this excited state to an appreciable extent to characterize its emission and photochemical properties.

Direct excitation into the LF state of each complex yields emission in the 550–850-nm region. For each complex the emission was assigned to the M → π*(pyz) excited state; the vertical line from this state denotes this process. The LF state of $(OC)_5M(pyz)M'(CO)_5$ thus populates the emitting state by nonradiative processes; the wavy line between these states denotes this process. Each complex exhibited a single unstructured emission band; the clear inference is that the low-lying M → π*(pyz) states are in thermal equilibrium with each other. The emission is assigned to the lower energy MLCT component.

The photochemical findings are expressed in the excited-state scheme. Chemical reaction (M–N dissociation) was observed to occur relatively efficiently from the higher energy LF state, whereas the low-energy M → π*(pyz) excited states are, in contrast, virtually unreactive.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the University Awards Program of the Research Foundation of SUNY for support of this research. We thank the Research Corp. for the argon ion laser used in this study.

Registry No. THF, 109-99-9; $(OC)_5Cr(pyz)Cr(CO)_5$, 70772-41-7; $(OC)_5Cr(pyz)Mo(CO)_5$, 90914-25-3; $(OC)_5Mo(pyz)Mo(CO)_5$, 69456-73-1; $(OC)_5Mo(pyz)W(CO)_5$, 90914-26-4; $(OC)_5W(pyz)Cr(CO)_5$, 90914-27-5; $(OC)_5W(pyz)W(CO)_5$, 70738-71-5; pyz, 290-37-9; C_6H_6, 71-43-2; dimethyl sulfoxide, 67-68-5; dimethylformamide, 68-12-2; acetone, 67-64-1; cyclohexanone, 108-94-1; methanol, 67-56-1; cyclohexanol, 108-93-0; piperidine, 110-89-4; methylene chloride, 75-09-2; triethylamine, 121-44-8; mesitylene, 108-67-8; carbon tetrachloride, 56-23-5; tetrachloroethylene, 127-18-4; isooctane, 540-84-1.

Contribution from the Department of Chemistry and Program in Biochemistry, Washington State University, Pullman, Washington 99164-4630

Characterization of a Stable Chromium(III)–Nicotinic Acid Complex by Deuteron NMR

CHARLES A. GREEN, ROBERT J. BIANCHINI, and J. IVAN LEGG*

Received April 18, 1984

The first carboxyl-bound nicotinic acid complex of chromium(III), *trans*-$[Cr(1,3\text{-pn})_2(nic\text{-}O)_2]Cl$, which is stable in aqueous solution at physiological pH has been synthesized. The stability and the identity of the complex have been established by deuteron NMR obtained for this complex with deuterium-labeled nicotinic acid. The deuteron NMR spectral data are also provided for previously reported chromium(III) nicotinate complexes having both carboxyl and pyridyl nitrogen coordination to chromium(III). The variation in chemical shifts with these different modes of coordination provides a direct method for determining coordination to chromium(III) in solution.

Nicotinic acid (niacin) complexes of chromium(III) are of current interest since chromium has been shown to be an essential trace element associated with glucose metabolism.[1] Nicotinic acid has been found with chromium in natural

0020-1669/84/1323-2713$01.50/0

Table I. Visible-Ultraviolet Spectra in Aqueous Solution

complex	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})		
trans-[Cr(1,3-pn)$_2$(nic-*O*)$_2$]Cl·4H$_2$O	263 (11 800)	373 (45.9)	512 (46.7)
trans-[Cr(1,3-pn)$_2$(OAc)$_2$]Cl[a]		370 (38.5)	508 (39.5)
trans-[Cr(NH$_3$)$_4$(Hnic-*O*)$_2$](ClO$_4$)$_3$·2H$_2$O[b]	260 (11 700)	374 (40.7)	513 (47.6)

[a] Reference 6. [b] Reference 4b; spectrum obtained in aqueous 0.01 M HClO$_4$; complex stable in acid solution only.

products that show biological activity, and it has been suggested that a chromium(III)–nicotinic acid complex may be involved.[2] Although stable cobalt(III)–nicotinic acid complexes have been characterized,[3] nicotinic acid complexes of chromium(III) have shown low solubility or limited stability in aqueous solution.[4] These studies have not recognized that the stability of chromium(III) nicotinic acid complexes may be a function of the ligand complement. In addition, previous investigations have not benefited from a method for directly identifying chromium(III)–ligand coordination in solution. We report the first chromium(III)–nicotinic acid complex that is stable at physiological pH. The complex, *trans*-[Cr(1,3-pn)$_2$(nic-O)$_2$]Cl·4H$_2$O (1,3-pn = 1,3-propanediamine; nic-O = nicotinate), has nicotinic acid coordinated through the carboxyl group to chromium(III). The stability of the complex is apparently due to the six-membered chelate rings formed by the complementary ligands. Both the identity and the stability of the complex have been established by a deuteron NMR technique recently developed in our laboratory.[5] This technique is a sensitive monitor of ligand coordination and has been used to define the stereochemistry of paramagnetic chromium(III) complexes in solution.

The complex, *trans*-[Cr(1,3-pn)$_2$(nic-O)$_2$]Cl·4H$_2$O, was synthesized by a procedure similar to that used by Vaughn et al. to produce *trans*-[Cr(1,3-pn)$_2$(OAc)$_2$]Cl.[6] Nicotinic acid (4.9 g, 0.04 mol), CrCl$_3$·6H$_2$O (2.0 g, 0.008 mol), and 10 mL of distilled water were mixed in a 50-mL beaker. After it was stirred at room temperature for 15 min, the resulting suspension was placed in an ice bath. The mixture was continuously stirred as 1,3-propanediamine (7.2 g, 0.1 mol) was slowly added over 1 h. The blue-gray mixture was then removed from the ice bath and stirred at room temperature for 2 h. The resulting dark purple mixture was transferred to a steam bath and heated at 65–75 °C. After the volume was reduced to about 14 mL, the purple-red paste was cooled to room temperature, mixed with 8 mL water, and stirred for 30 min. The product formed as fine orange crystals, which were filtered from the mixture. Recrystallization was carried out by dissolving the crystals in about 5 mL of water at 60–70 °C and then cooling the solution slowly to 4 °C; yield 0.84 g (20%). Anal. Calcd for *trans*-[Cr(NH$_2$(CH$_2$)$_3$NH$_2$)$_2$(OCOC$_5$H$_3$N)$_2$]Cl·4H$_2$O: C, 39.17; H, 6.57; N, 15.22. Found: C, 39.20; H, 6.84; N, 15.20.

Table I shows the electronic spectra of *trans*-[Cr(1,3-pn)$_2$(nic-O)$_2$]Cl and similar, previously characterized, carboxyl-bound complexes. The similarity of band maxima and

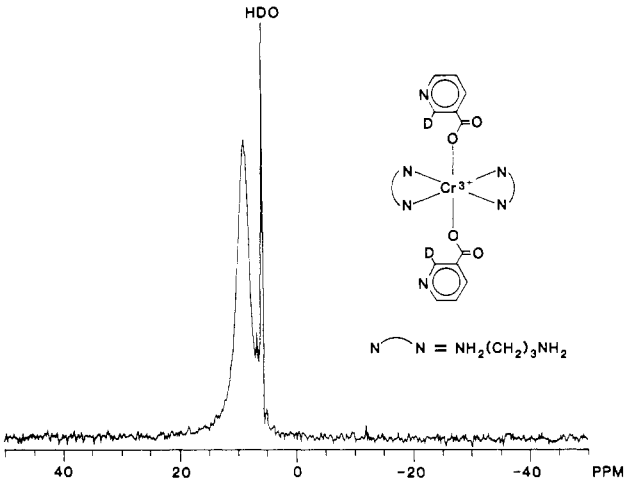

Figure 1. Deuteron NMR spectrum of *trans*-[Cr(1,3-pn)$_2$(nic-O)$_2$]$^+$ (31-MHz ^{2}H NMR spectrum; spectrometer field 4.7 T; 12-mm bore sample tube; 8 K block size; 7000 scans; 40-min acquisition time for spectrum; external standard of CDCl$_3$ assigned to +7.2 ppm). The HDO signal comes from natural-abundance deuterium in water.

Table II. Deuteron NMR Spectral Data

complex	δ (ω)[a]	pH
trans-[Cr(1,3-pn)$_2$(nic-*O*)$_2$]$^+$	9.1 (70)	7.2[b]
trans-[Cr(1,3-pn)$_2$(Hnic-*O*)$_2$]$^{3+}$ [c]	8.8 (68)	1.0[d]
trans-[Cr(NH$_3$)$_4$(Hnic-*O*)$_2$]$^{3+}$ [e]	9.0 (66)	1.3[f]
[Cr$_3$O(nicH)$_6$(H$_2$O)$_3$]$^{8+}$ [e,g]	6.7 (155)	0.2[h]
trans-[Cr(Me-nic)$_2$(H$_2$O)Cl$_2$][e,i]	−70 (1,650)	*j*
trans-[Cr(mal)$_2$(py-2-*d*)$_2$]$^-$ [k]	−70 (500)	*l*

[a] δ = chemical shift with respect to CDCl$_3$ assigned as +7.2; ω = band width at half-height in Hz. [b] Aqueous solution buffered with MOPS. [c] The pyridyl nitrogen is protonated at this pH. [d] 0.1 M HCl. [e] Structure determined crystallographically. [f] 0.1 M HClO$_4$. Complex is stable in acid solution only.[4b] [g] nicH indicates that the pyridyl nitrogen is protonated and carboxyl group is bridging two chromium(III) atoms.[4a] [h] 1 M HClO$_4$. [i] Me-nic = methylnicotinate. Coordination is through the pyridyl nitrogen.[8] [j] In EtOH. [k] mal = malonate; py-2-*d* = pyridine with deuterium on 2-carbon.[5] [l] In MeOH.

molar absorptivities supports the assignment of a trans oxygen-coordinated nicotinate structure for this complex.

Conclusive evidence for nicotinic acid coordination and for coordination through the carboxyl group was obtained by deuteron NMR. Nicotinic acid was deuterated at the 2-carbon as previously reported[7] and used in the synthesis described above. The deuterated complex (80 mg) was dissolved in 3.5 mL of water and then analyzed by using a Nicolet NT-200WB spectrometer. The deuteron NMR spectrum obtained is shown in Figure 1. Related complexes, which have been previously reported,[4a,b,5,8] were also synthesized with a deuterium label. The deuteron NMR spectra of these complexes are summarized in Table II. The data obtained show that coordination to the chromium(III) through the pyridyl nitrogen induces (for the deuterium on the 2-carbon) a dramatic shift to ca. −70 ppm. Carboxylate coordination causes a much smaller shift to ca. +9.1 ppm. In all cases broadening of the signal is observed as expected.[5]

At physiological pH, *trans*-[Cr(1,3-pn)$_2$(nic-O)$_2$]$^+$ is quite stable as compared to the nicotinic acid complexes previously reported.[4b,c] A 0.04 M solution of the deuterated complex, buffered at pH 7.2 with morpholinopropanesulfonic acid (MOPS), was monitored via deuteron NMR. Free nicotinic acid appeared in the spectrum as a spike at +9.9 ppm. After

(1) Anderson, R. A. *Sci. Total Environ.* **1981**, *17*, 13.
(2) Mertz, W.; Schwarz, K. *Am. J. Physiol.* **1959**, *196*, 614. Anderson, R. A.; Brantner, J. H.; Polansky, M. M. *J. Agric. Food Chem.* **1978**, *26*, 1219.
(3) Wierenga, T. J.; Legg, J. I. *Inorg. Chem.* **1982**, *21*, 2881.
(4) (a) Gonzalez-Vergara, E.; Hegenauer, J.; Saltman, P.; Sabat, M.; Ibers, J. A. *Inorg. Chim. Acta* **1983**, *66*, 115. (b) Chang, J. C.; Gerdom, L. E.; Baenziger, N. C.; Goff, H. M. *Inorg. Chem.* **1983**, *22*, 1739. (c) Gerdom, L. E.; Goff, H. M. *Ibid.* **1982**, *21*, 3847.
(5) Wheeler, D. W.; Kaizaki, S.; Legg, J. I. *Inorg. Chem.* **1982**, *21*, 3248. Wheeler, D. W.; Legg, J. I. *Ibid.*, in press.
(6) Vaughn, J. W.; Seiler, G. J.; Johnson, M. W.; Traister, G. L. *Inorg. Chem.* **1970**, *9*, 2786.
(7) Mauzerall, D.; Westheimer, F. H. *J. Am. Chem. Soc.* **1955**, *77*, 2261.
(8) McArdle, J. V.; de Laubenfels, E.; Shorter, A. L.; Ammon, H. L. *Polyhedron* **1982**, *1*, 471.

48 h at room temperature, about 95% of the nicotinate was still bound to chromium(III) (based on curve-fitting analysis). Assuming formation of a trans aqua nicotinate complex, 90% of the *trans*-$[Cr(1,3\text{-pn})_2(nic\text{-}O)_2]^+$ was still present. In addition, the visible spectrum obtained after 48 h showed ca. 5% decrease in absorption at 373 and 512 nm and ca. 3% increase at 423 nm (λ_{min}). Since a trans aqua nicotinate complex is not expected to have a markedly different visible spectrum, it is difficult to estimate the amount of decomposition by visible spectroscopy. However, it is apparent from the NMR and visible spectral data that approximately 90% of the original complex was still present.

The stability of this complex appears to be due to the chelation of 1,3-pn to chromium(III). Unlike bis(ethylenediamine) complexes of chromium(III), $(1,3\text{-pn})_2$ complexes prefer a trans arrangement and do not show any evidence for partial dissociation of the chelate rings.[9] Since substitution of octahedral chromium(III) complexes proceeds by an associative mechanism,[10] the bulkiness of the 1,3-pn chelate rings probably inhibits substitution. If there is a biologically active form of the chromium(III)–nicotinic acid complex, it may be stabilized by the ligand complement. For example, chromium(III)-bound nicotinic acid may be stabilized within a peptide or protein matrix.

Acknowledgment. We thank Donald Appel for his assistance in using the Nicolet NT-200. The Nicolet 200-MHz spectrometer was acquired with the aid of the Boeing Co. Partial support of this study by the USDA (Grant No. 82-CRCR-1-1005) is gratefully acknowledged.

Registry No. *trans*-$[Cr(1,3\text{-pn})_2(nic\text{-}O)_2]Cl$, 91084-62-7; *trans*-$[Cr(1,3\text{-pn})_2(nic\text{-}O)_2]^+$ (deuterated), 91110-51-9; *trans*-$[Cr(mal)_2(py\text{-}2\text{-}d)_2]^-$, 91084-66-1; deuterium, 7782-39-0.

(9) Couldwell, M. C.; House, D. A. *Inorg. Chem.* **1972**, *11*, 2024. Vaughn, J. W. *Ibid.* **1981**, *20*, 2397. DeJovine, J. M.; Mason, W. R.; Vaughn, J. W. *Ibid.* **1974**, *13*, 66.

(10) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217.

Notes

Contribution from the Department of Inorganic Chemistry, University of Groningen, 9747 AG Groningen, The Netherlands, and Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

Identification of the Zinc Reduction Product of $VCl_3 \cdot 3THF$ as $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$

Reinder J. Bouma,† Jan H. Teuben,*† W. R. Beukema,† Rick L. Bansemer,‡ John C. Huffman,‡ and Kenneth G. Caulton*‡

Received November 2, 1983

Anhydrous vanadium trichloride is reduced by zinc in tetrahydrofuran (THF) to a material claimed first to be a mixture of $VCl_2(THF)_2$ and $ZnCl_2 \cdot x$THF[1] and then later (exclusively on the basis of elemental analysis for Cl, C, H, and V) to be $VCl_2(THF)_2$.[2] This material is of substantial synthetic utility, leading to Cp_2V,[1] to $V_2(fulvalene)_2$,[3] to a polynuclear vanadium carboxylate,[4] and to $Cp_2V_2C_8H_8$.[5] Our work[6] with low-valent vanadium complexes led us to question the accuracy of this[2] characterization, and yet microscopic visual inspection of the crystalline material and visual observation of its reaction with O_2 (all crystals oxidize, suggesting the absence of $ZnCl_2 \cdot x$THF crystals) suggested that it was homogeneous. We report here on the true identity of this material.

The chemistry of V(II), especially of V(II) dimers, is relevant to the efficient reduction of N_2 in alkaline protic media.[7] Vanadium(II), both in aqueous solution[8] and in THF,[9] is a useful reagent for reduction of a variety of organic compounds.

Experimental Section

General Procedures and Materials. All experiments were carried out under nitrogen, by using Schlenk and drybox techniques and dried solvents. Temperature-dependent magnetic susceptibility measurements were performed on a Faraday system (Oxford Instruments) equipped with a Mettler ME 21 electronic vacuum microbalance. Vanadium was analyzed coulometrically[10] as metavanadate after digestion with perchloric acid at 180 °C.[11] Zinc was analyzed by using atomic absorption spectrophotometry after digestion with concentrated H_2SO_4/HNO_3.[11]

Table I. Magnetic Susceptibilities of $[V_2Cl_6(THF)_6]_2[Zn_2Cl_6]$ at Various Temperatures[a]

T, K	$10^{-6}\chi_{mol}$, cgsu	T, K	$10^{-6}\chi_{mol}$, cgsu
32.3	469	106.4	2659
38.2	633	120.3	2944
44.8	831	140.2	3267
52.3	1073	160.2	3527
61.0	1372	180.6	3741
70.1	1668	200.1	3914
80.1	2000	225.0	4107
92.1	2337	250.1	4272

[a] Susceptibilities are corrected for diamagnetism ($\chi_{mol,dia} = 520 \times 10^{-6}$ cgsu) and a paramagnetic impurity (2% based on V^{2+}).

Synthesis of $[V_2(\mu\text{-}Cl)_3(THF)_6]_2[Zn_2Cl_6]$. A suspension of 1.70 g (26 mmol) of zinc powder and 4.16 g of $VCl_3 \cdot 3THF$ (11.1 mmol) in 35 mL of THF was stirred for 18 h at 25 °C. After the supernatant was decanted, the green product was dissolved in 30 mL of CH_2Cl_2. The solution was filtered and the solvent partly removed under vacuum. The product was precipitated with pentane. The resulting green powder was filtered, washed with pentane, and dried under vacuum; yield 4.10 g (2.52 mmol, 91%). Anal. Calcd for $C_{48}H_{96}Cl_{12}O_{12}V_4Zn_2$: C, 35.47; H, 5.95; Cl, 26.18; V, 12.54; Zn, 8.04. Found: C, 35.79, 35.59; H, 6.08, 5.98; Cl, 26.57, 26.46; V, 12.60, 12.61, 12.52; Zn, 7.92, 8.03. IR (Nujol, cm^{-1}): THF frequencies at 1343 (m), 1294

† University of Groningen.
‡ Indiana University.

(1) Köhler, F. H.; Prössdorf, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 1026.
(2) Hall, V. M.; Schmulbach, C. D.; Soby, W. N. *J. Organomet. Chem.* **1981**, *209*, 69.
(3) Smart, J. C.; Pinsky, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 1009.
(4) Cotton, F. A.; Lewis, G. E.; Mott, G. M. *Inorg. Chem.* **1982**, *21*, 3316.
(5) Elschenbroich, C.; Heck, J.; Massa, W.; Nun, E.; Schmidt, R. *J. Am. Chem. Soc.* **1983**, *105*, 2905.
(6) Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 6163.
(7) Shilov, A. E. *Russ. Chem. Rev. (Engl. Transl.)* **1974**, *43*, 378.
(8) Ho, T.-L. *Synthesis* **1979**, 1.
(9) Ho, T.-L.; Olah, G. A. *Synthesis* **1977**, 170.
(10) Lingane, J. J. "Electroanalytical Chemistry", 3rd ed.; Interscience: New York, 1966; p 58.
(11) Ingram, G. "Organic Elemental Micro Analysis"; Chapman and Hall: London, 1962; p 272.

0020-1669/84/1323-2715$01.50/0