If the emphasis is put on the heteropolar character of the metal-P bonds, the form of the P polyanion becomes of interest. In $MoFe_2P_{12}$ these polyanions consist of infinite zigzag chains of P(1) and P(2) atoms extending along the *y* direction. Within one chain, adjacent P(1) and P(2) atoms are bridged by a 4-membered sequence of P(6)-P(5)-P(3)-P(4) atoms. In other words, the P polyanions consist of 6-membered rings (all in the boat conformation) formed by the P(1)-P(6)-P(5)-P(3)-P(4)-P(2) atoms linked by bonds from the P(1) atoms of one ring to the P(2) atoms of the next ring: 1,2-poly(hexaphosphacyclohexane) in the terminology of organic chemistry.

The average Fe-P distance of 2.230 Å in $MoFe_2P_{12}$ is slightly shorter than the average Fe-P distances of 2.258 and 2.249 Å in α- and β-FeP_4. On the other hand, the average P-P distance of 2.248 Å in $MoFe_2P_{12}$ is slightly longer than the average P-P distances of 2.227 and 2.225 Å in α- and β-FeP_4. The average Mo-P distance of 2.531 Å in $MoFe_2P_{12}$ cannot be compared with the corresponding distance in MoP_4 because that structure has not been refined.

Acknowledgment. We want to thank Dipl.-Chem. M. H. Möller for the collection of the single-crystal diffractometer data. Cand. chem. Barbara Schunck did careful preparative work in the early stages of this investigation. We also want to acknowledge Dr. G. Heymer (Hoechst-Knapsack AG) for a gift of ultrapure red phosphorus and Dr. G. Höfer (Heraeus Quarzschmelze) for a generous gift of silica tubes. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Registry No. $MoFe_2P_{12}$, 85421-64-3; WFe_2P_{12}, 85421-65-4.

Supplementary Material Available: Listings of structure factor amplitudes and anisotropic thermal parameters of $MoFe_2P_{12}$ (19 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Iowa, Iowa City, Iowa 52242

Synthesis and Molecular Structure Determination of Carboxyl-Bound Nicotinic Acid (Niacin) Complexes of Chromium(III)

JAMES C. CHANG,[1] LARRY E. GERDOM, NORMAN C. BAENZIGER, and HAROLD M. GOFF*

Received July 17, 1982

Suggestions that nicotinic acid may serve as a ligand for a biological chromium(III) complex have prompted systematic preparation of carboxyl-bound derivatives of well-defined structure. The synthetic route involves reaction between nicotinic acid anhydride and a mono- or dihydroxochromium(III) species in dimethylformamide solvent. Compounds prepared include $[Cr(NA)(NH_3)_5](ClO_4)_2$, *cis*-$[Cr(NA)_2(NH_3)_4]ClO_4$, *cis*-$[Cr(NA)_2(NH_3)_4]Br$, *trans*-$[Cr(NA)_2(NH_3)_4]ClO_4$, and *cis*-$[Cr(NA)_2(en)_2]Br$, where NA^- is nicotinate. Characterization by elemental analysis, electronic spectroscopy, and vibrational spectroscopy indicated that carboxylate vs. pyridine nitrogen coordination was preserved. This was unambiguously confirmed through a crystal and molecular structural determination for the pyridyl nitrogen-protonated complex *trans*-$[Cr(NAH)_2(NH_3)_4](ClO_4)_3 \cdot 2H_2O$. Crystal data are as follows: $P2_1/c$; a = 12.881 (6), b = 7.444 (4), c = 28.795 (13) Å; β = 99.36 (4)°; V = 2722.3 Å^3; Z = 4; R_1 = 0.065, and R_2 = 0.065. The molecule is only slightly distorted from octahedral symmetry. Ligand-metal and pyridinium group bond distances are equivalent to those observed for other ammine and carboxylate complexes and protonated pyridyl rings.

Introduction

In 1959 Schwarz and Mertz discovered that a chromium-containing substance in brewers' yeast was required as a dietary agent for the proper maintenance of glucose tolerance in laboratory animals.[2,3] The importance of chromium as a trace element in human nutrition has also been demonstrated.[4-6] Attempts to isolate and characterize the biological chromium complex(es) have been thwarted by only trace occurrence and seeming instability in purified form.[7-11] Analysis of chromium-containing brewers' yeast fractions implied that various amino acids and nicotinic acid (niacin or 3-carboxypyridine) served as structural components of the active complex.[8,9] The possible importance of nicotinic acid in the native structure was also suggested by weak biological activity of synthetic products (of undefined structure) formed between chromium(III), nicotinic acid, and amino acids[8,9] or peptides.[12]

Only recently has the putative role of nicotinic acid as a ligand for chromium(III) been investigated by thermodynamic and structural methods for model compounds. Coordination by either nitrogen or carboxyl groups is possible, but the "bite size" for these two residues precludes simultaneous binding in a monomeric structure. Spectral measurements are consistent with nicotinic acid nitrogen coordination to the Cr(III) salen species in aqueous solution and rearrangement to the carboxyl-bound form in the solid state.[13] Nicotinic acid adducts have reportedly been prepared from parent complexes of a pyridoxal-glycylglycine-chromium(III) Schiff base complex,[15] a glycylglycine complex,[15] and a nitrilotriacetate complex.[16] A trinuclear chromium(III) nicotinic acid complex

---

(1) On leave from the University of Northern Iowa, Cedar Falls, IA.
(2) Mertz, W.; Schwarz, K. *Am. J. Physiol.* **1959**, *196*, 614.
(3) Mertz, W. *Physiol. Rev.* **1969**, *49*, 163.
(4) Jeejeebhoy, K. N.; Chu, R. C.; Marliss, E. B.; Greenberg, G. R.; Bruce-Robertson, A. *Am. J. Clin. Nutr.* **1977**, *30*, 531.
(5) Offenbacher, E. G.; Pi-Sunyer, F. X. *Diabetes* **1980**, *29*, 919.
(6) Anderson, R. A. *Sci. Total Environ.* **1981**, *17*, 13.
(7) Votava, H. J.; Hahn, C. J.; Evans, G. W. *Biochem. Biophys. Res. Commun.* **1973**, *55*, 312.
(8) Mertz, W.; Toepfer, E. W.; Roginski, E. E.; Polansky, M. M. *Fed. Proc. Fed. Am. Soc. Exp. Biol.* **1974**, *33*, 2275.
(9) Toepfer, E. W.; Mertz, W.; Polansky, M. M.; Roginski, E. E.; Wolf, W. R. *J. Agric. Food Chem.* **1977**, *25*, 162.
(10) Kumpulainen, J.; Koivistoinen, P. *Bioinorg. Chem.* **1978**, *8*, 419.
(11) Mirsky, N.; Weiss, A.; Dori, Z. *J. Inorg. Biochem.* **1980**, *13*, 11.
(12) Anderson, R. A.; Brantner, J. H.; Polansky, M. M. *J. Agric. Food Chem.* **1978**, *26*, 1219.
(13) Gerdom, L. E.; Goff, H. M. *Inorg. Chem.* **1982**, *21*, 3847. Note that nitrogen coordination in the solid state is claimed in ref 14 for the [Cr(salen)(NA)] complex prepared by a different route.
(14) Prasad, D. R.; Ramasami, T.; Ramaswamy, D.; Santappa, M. *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 431.
(15) Gonzalez-Vergara, E.; DeGonzalez, B. C.; Hegenauer, J.; Saltman, P. *Isr. J. Chem.* **1981**, *21*, 18.

0020-1669/83/1322-1739$01.50/0

Table I. Analytical Results for Nicotinic Acid Complexes

compd prepared	% yield[a]	% Cr calcd	% Cr found	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found	% Br calcd	% Br found
$[Cr(NA)(NH_3)_5](ClO_4)_2\cdot 0.67DMF$	29	10.3	10.5	19.0	19.4	4.71	4.70	18.4	19.9		
cis-$[Cr(NA)_2(NH_3)_4]ClO_4\cdot 0.37DMF$	9	10.6	10.3	32.1	31.9	4.64	4.43	18.2	16.9		
trans-$[Cr(NAH)_2(NH_3)_4](ClO_4)_3\cdot 2H_2O$[b]	81	7.42	7.48	20.6	20.1	3.74	3.45	12.0	12.4		
trans-$[Cr(NA)_2(NH_3)_4]ClO_4$[c]	81	11.2	10.8	31.1	29.5	4.35	4.25	18.1	18.7		
cis-$[Cr(NA)_2(en)_2]Br\cdot 0.03DMF$[d]	95	10.4	10.2	38.8	37.6	4.90	4.97	18.9	16.3	16.0	14.2
cis-$[Cr(NA)_2(en)_2]Br\cdot 0.03DMF$[e]	81	10.4	9.7	38.8	37.4	4.90	4.68	18.9	16.1	16.0	16.5

[a] Percentage yield of crude product, based on the parent aqua complex. [b] Precipitated by 70% $HClO_4$ from 0.001 M $HClO_4$ solution. [c] Precipitated by 5 M $NaClO_4$ from 0.001 M $HClO_4$ solution. [d] Prepared from *cis*-$[CrBr(H_2O)(en)_2](Br)_2\cdot H_2O$. [e] Prepared from *cis*-$[Cr(H_2O)_2(en)_2](Br)_3\cdot 2H_2O$.

analogous to known transition-metal trinuclear carboxylic acid derivatives has also been structurally characterized.[17]

Herein are reported syntheses of chromium(III) ammine and ethylenediamine complexes containing the nicotinic acid anion (nicotinate, NA^-). A systematic approach has been utilized that dictates carboxylate binding to the chromium(III) center of parent complexes of well-defined structure. The method is based on that reported by Jackman et al.[18] in which a hydroxo–transition-metal complex is allowed to react with an acid anhydride species. Further development of the synthetic scheme as described here should provide strategy for other desired nicotinic acid or carboxylate-based chromium(III) complexes. The X-ray crystal structure of the doubly protonated *trans*-tetraamminebis(nicotinato)chromium(III) perchlorate complex, $[Cr(NAH)_2(NH_3)_4](ClO_4)_3\cdot 2H_2O$, confirms retention of the carboxyl oxygen binding in the solid state. Solution spectroscopic and hydrolysis properties are discussed with regard to the question of nicotinic acid as a structural component in biologically active chromium complexes.

Experimental Section

Preparation of Aqua–Chromium(III) Complexes. The aquachromium(III) complexes used in this work, listed below, were prepared by literature methods. Compounds include pentaammineaquachromium(III) perchlorate,[18–20] *cis*-tetraamminediaquachromium(III) perchlorate,[21] *trans*-tetraamminediaquachromium(III) perchlorate,[22] *cis*-aquachlorobis(ethylenediamine)chromium(III) bromide monohydrate,[23] *cis*-aquabromobis(ethylenediamine)chromium(III) bromide monohydrate,[24] *cis*-diaquabis(ethylenediamine)chromium(III) bromide dihydrate,[25,26] and *cis*-tetraamminediaquachromium(III) bromide.[21]

Preparation of Chromium(III)–Nicotinate Complexes. This synthetic procedure was accomplished by separate in situ generation of the nicotinic acid anhydride and deprotonated chromium(III) aqua species, followed by mixing the two components. In a typical preparation, 1.23 g (0.01 mol) of nicotinic acid in 15 mL of dimethylformamide (DMF) and 1.03 g (0.005 mmol) of dicyclohexylcarbodiimide (DCC) in 5 mL of DMF were mixed and stirred for 30 min at room temperature. The dicyclohexylurea formed was removed by filtration, and the filtrate containing nicotinic acid anhydride was added to a freshly prepared solution of 0.0015 mol of an aqua–chromium(III) complex and 0.75 mL of dimethylbenzylamine in 5–10 mL of DMF. When a diaqua complex was used, the amounts of all other starting materials were doubled. After the mixture was stirred for 10–20 min at room temperature, it was cooled in ice, and 50 mL of 95% ethanol was added. Three hundred milliliters of diethyl ether was added slowly, with constant stirring, to precipitate the nicotinic acid complex, which was collected by filtration, washed with ether, and air-dried. The crude product was vacuum dried at room temperature (for the perchlorates) or 40 °C for several hours, then washed with absolute ethanol and ether, and again vacuum dried for at least 8 h. The bromide complexes were heated to 80 °C during this second vacuum drying step. This second washing step served to remove occluded amine and at least part of the DMF retained in the crystals. Only *trans*-tetraamminebis(nicotinato)chromium(III) perchlorate was not vacuum dried but was reprecipitated from 0.001 M $HClO_4$ by either 70% $HClO_4$ or 5 M $NaClO_4$. *Caution!* Any perchlorate compound is potentially hazardous with regard to detonation. Detonation of one of the ammine complexes did occur during microanalysis, and caution is urged during preparation and manipulation.

Analytical Results. The compounds prepared and respective analytical results are summarized in Table I. Chromium was analyzed by the alkaline-peroxide method.[27] Initially poor microanalytical results demanded a search for possible solvent, urea, or free nicotinic acid contaminants. This was accomplished by dissolution of the complex in 0.01 M DCl/D_2O followed by proton NMR spectral examination. Proton signals for coordinated ligand are expected to be very broad, whereas those for contaminants should remain relatively sharp. Variable and nonstoichiometric amounts of DMF of solvation were detected and quantitated by NMR integrations using an internal standard of *tert*-butyl alcohol. Calculated elemental percentages in Table I reflect the DMF content.

Physical Measurements. Proton NMR spectra were recorded with a 90-MHz JEOL FX90Q pulsed Fourier transform spectrometer. Infrared spectra were obtained from KBr pellets by a Beckman IR-20A instrument. Cary Model 219 and Beckman Model 25 spectrophotometers were employed for visible and ultraviolet spectroscopy. Aqueous solutions 0.01 or 0.1 M in $HClO_4$ were sufficient to prevent hydrolysis during spectral measurements.

Crystal Structure Analysis. Pink crystals of $[Cr(C_6H_5NO_2)_2(NH_3)_4](ClO_4)_3\cdot 2H_2O$ grown from a concentrated solution of 0.01 M $HClO_4$ heated with steam and cooled to room temperature were examined with precession photographs. Systematic absences define the space group ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) as $P2_1/c$. Unit cell parameters were obtained from a least-squares fit of the 2θ values for 10 reflections (2θ values were greater than 40°) hand centered on a Picker FACS-1 diffractometer. The crystal used for data collection was elongated along c with dimensions 1.4 × 0.2 × 0.07 mm.

Crystal data for $[Cr(NH_3)_4(C_6H_5NO_2)_2](ClO_4)_3\cdot 2H_2O$ follow: $M_r = 700.73$; $a = 12.881$ (6), $b = 7.444$ (4), $c = 28.795$ (13) Å; $\beta = 99.36$ (4)°; $V = 2722.3$ Å^3; $Z = 4$; $D_c = 1.71$ g cm^{-3}; $D_o = 1.71$ g cm^{-3}; $F(000) = 1436$; $\mu(\text{Mo } K\bar{\alpha}) = 4.8$ cm^{-1}; $\lambda(K\bar{\alpha}) = 0.7107$ Å; all at 25 °C. The density was determined by using an n-butyl bromide and 1,4-dibromobutane mixture.

Intensity data in the range $3° < \theta < 40°$ were collected with a Picker FACS-1 diffractometer as described previously.[28,29] The intensities of three standard reflections ($0\bar{2}1$; 500; 0,0,12), which were measured

---

(16) Sharma, C. L.; Jain, P. K.; De, T. K. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1681.

(17) Gonzalez-Vergara, E.; Hegenauer, J.; Saltman, P.; Sabat, M.; Ibers, J. A. *Inorg. Chim. Acta* **1982**, *66*, 115.

(18) Jackman, L. M.; Scott, R. M.; Portman, R. H.; Dormish, J. F. *Inorg. Chem.* **1979**, *18*, 1497.

(19) Mori, M. *Inorg. Synth.* **1957**, *5*, 131.

(20) Schlessinger, G. G. "Inorganic Laboratory Preparations"; Chemical Publishing Co.: New York, 1962; pp 199–200.

(21) Springborg, J.; Schäffer, C. E. *Inorg. Synth.* **1978**, *18*, 75.

(22) Hoppenjans, D. W.; Hunt, J. B. *Inorg. Chem.* **1969**, *8*, 505.

(23) House, D. A.; Garner, C. S. *J. Inorg. Nucl. Chem.* **1966**, *28*, 904.

(24) Reference 20, p 229.

(25) Woldbye, F. *Acta Chem. Scand.* **1958**, *12*, 1079.

(26) Reference 21, p 85.

(27) Chang, J. C. *J. Inorg. Nucl. Chem.* **1968**, *30*, 945.

(28) Baenziger, N. C.; Foster, B. A.; Howells, M.; Howells, R.; Vander Valk, P.; Burton, D. J. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2329.

(29) Baenziger, N. C.; Dittemore, K. M.; Doyle, J. R. *Inorg. Chem.* **1974**, *13*, 805.

Table II. Final Fractional Coordinates for $[Cr(NH_3)_4(C_6H_5NO_2)_2](ClO_4)_3 \cdot 2H_2O$ ($\times 10^4$) with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
Cr	5224 (1)	7825 (2)	3853 (1)
O1	4091 (5)	6237 (8)	3561 (2)
O2	6475 (4)	9222 (8)	4091 (2)
N1	5899 (6)	7490 (10)	3254 (3)
N2	4418 (6)	10095 (11)	3582 (3)
N3	6015 (6)	5579 (10)	4153 (3)
N4	4535 (6)	8150 (11)	4444 (3)
C1	3097 (8)	6392 (15)	3493 (4)
C2	1505 (8)	4469 (16)	3259 (4)
C3	2549 (8)	4829 (14)	3226 (3)
C4	3046 (7)	3668 (14)	2964 (3)
C5	2414 (9)	2260 (15)	2730 (4)
C6	1500 (10)	1982 (17)	2777 (4)
N5	1030 (6)	3068 (15)	3045 (3)
C7	6609 (8)	10629 (14)	4350 (4)
C8	8481 (9)	10596 (14)	4238 (4)
C9	7738 (7)	11211 (13)	4485 (3)
C10	8047 (8)	12341 (14)	4859 (4)
C11	9073 (10)	12823 (15)	4978 (4)
C12	9787 (9)	12168 (17)	4725 (5)
N6	9481 (7)	11086 (13)	4354 (4)
O3	2595 (6)	7622 (11)	3617 (3)
O4	5916 (6)	11488 (10)	4493 (3)
O17	722 (7)	5768 (16)	2024 (5)
O18	1092 (7)	73 (14)	3905 (4)
Cl1	3713 (2)	7275 (3)	2113 (1)
O5	2897 (5)	6100 (11)	1924 (3)
O6	4588 (6)	6189 (10)	2311 (2)
O7	4014 (7)	8319 (13)	1754 (3)
O8	3409 (7)	8335 (12)	2472 (3)
Cl2	7007 (2)	8149 (4)	449 (1)
O9	7272 (14)	7399 (25)	86 (4)
O10	7819 (11)	9263 (23)	621 (5)
O11	6930 (9)	7042 (17)	823 (4)
O12	6101 (8)	9205 (14)	311 (4)
Cl3	8949 (2)	9112 (4)	8665 (1)
O13	8417 (17)	7862 (26)	8416 (5)
O14	9811 (9)	8466 (30)	8865 (6)
O15	8312 (15)	9406 (26)	8975 (8)
O16	9163 (10)	10509 (18)	8402 (7)

after each block of 58 reflections, did not change significantly during data collection.

A total of 10 280 data were collected and corrected for Lorentz, polarization, and absorption effects,[30] the maximum and minimum values of the transmission coefficients being 1.120 and 1.046, respectively, with an average value of 1.071. Of the 2829 unique reflections, the 2025 reflections with $I > 3\sigma(I)$ were used for all subsequent calculations. The coordinates of the cation and all three chlorine atoms were located from a MULTAN[31] analysis of the crystal. The remaining non-hydrogen atoms were located from subsequent Fourier syntheses. Atomic scattering factors and dispersion corrections were taken from ref 32. Hydrogens on amine nitrogens and water oxygens were located from electron density maps ($R_2 = 0.097$) and each was assigned an isotropic thermal parameter equal to the atom to which the hydrogen is bonded. Pyridinium hydrogen positions were calculated at 0.95 Å and assigned thermal parameters equal to those of the ring atoms. Refinement on non-hydrogen atoms converged to final residual values $R_1 = \sum \Delta F / \sum F_o = 0.065$ and $R_2 = [\sum w(\Delta F)^2 / \sum F_o^2]^{1/2} = 0.065$, where $w = 1/(S_F^2 + C_o^2 + F_o^2)$ as described in ref 29. In the final cycle, the maximum coordinate shift/error ratio was 0.04 for the *x* coordinate of C6, and there were no significant features in the final difference map.

Final fractional coordinates for the non-hydrogen atoms are in Table II, and details of molecular dimensions are given in Table III. A view of the molecule with the crystallographic numbering scheme is presented in Figure 1.[33] A figure depicting molecular packing with hydrogen bonding and lists of anisotropic thermal parameters, calculated hydrogen coordinates and isotropic thermal parameters,

Table III. Selected Distances (Å) and Angles (deg) with Their Estimated Standard Deviations for $[Cr(NH_3)_4(C_6H_5NO_2)_2](ClO_4)_3 \cdot 2H_2O$

Cr–O1	1.958 (6)	C1–O1	1.268 (11)
Cr–O2	1.947 (6)	C1–O3	1.208 (11)
Cr–N1	2.068 (7)	C1–C3	1.506 (14)
Cr–N2	2.068 (8)	C7–O2	1.281 (11)
Cr–N3	2.072 (8)	C7–O4	1.223 (11)
Cr–N4	2.059 (7)	C7–C9	1.507 (13)
O1–Cr–O2	172.0 (4)	N2–Cr–N3	177.4 (5)
O1–Cr–N1	87.4 (3)	N2–Cr–N4	87.6 (4)
O1–Cr–N2	92.2 (3)	N3–Cr–N4	89.9 (4)
O1–Cr–N3	88.5 (3)	Cr–O1–C1	132.4 (6)
O1–Cr–N4	92.0 (3)	Cr–O2–C7	131.9 (5)
O2–Cr–N1	85.6 (3)	O1–C1–O3	126.8 (8)
O2–Cr–N2	91.9 (3)	O1–C1–C3	112.8 (7)
O2–Cr–N3	87.8 (3)	O3–C1–O3	120.5 (9)
O2–Cr–N4	95.1 (3)	O2–C7–O4	125.9 (7)
N1–Cr–N2	92.1 (4)	O2–C7–C9	114.7 (7)
N1–Cr–N3	90.4 (4)	O4–C7–C9	119.3 (9)
N1–Cr–N4	179.4 (4)		

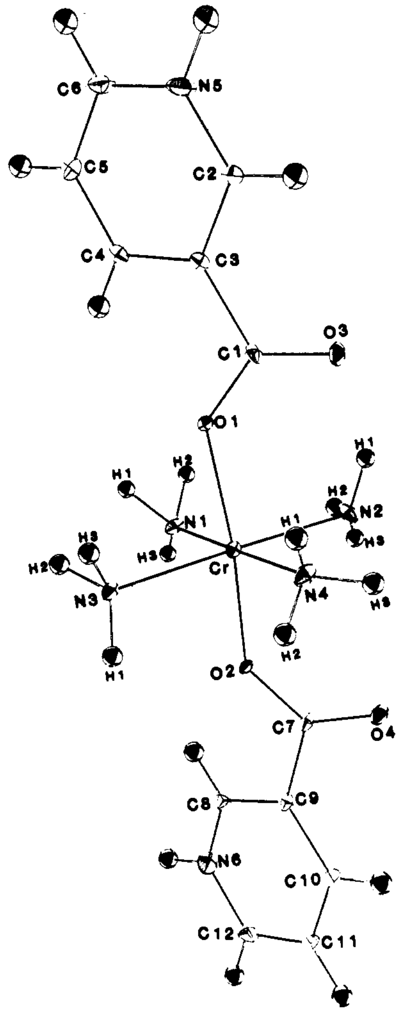

Figure 1. Drawing of a molecule of *trans*-$[Cr(NAH)_2(NH_3)_4](ClO_4)_3 \cdot 2H_2O$ (ORTEP diagram; 10% probability). Hydrogens on the pyridinium rings are designated by the atom to which they are bound, i.e., H(C2).

---

(30) Programs for the IBM computer used in this analysis were developed at the University of Iowa.

(31) Main, P.; Woolfson, M. M.; Germain, G. "Multan: A Computer Program for the Automatic Solution of Crystal Structures"; University of York: York, England, 1971.

(32) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1959; Vol. III, p 201.

(33) Johnson, C. K. "ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

Scheme I

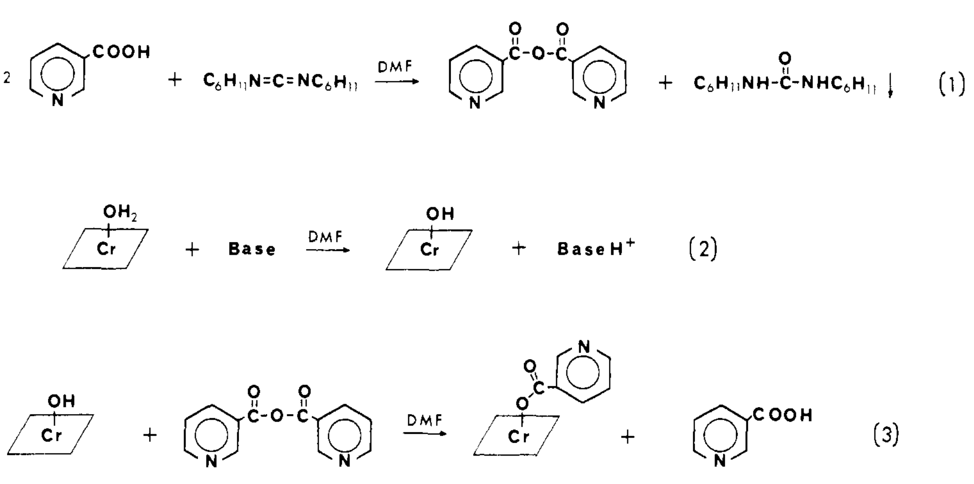

Table IV. Visible-Ultraviolet Spectra of Nicotinic Acid Complexes of Cr(III)[a]

compd	λ, nm (ε, L mol⁻¹ cm⁻¹)					10*Dq*, cm⁻¹ × 10³
	λ_{max}	λ_{min}	λ_{max}	λ_{min}	λ_{max}	
$[Cr(NA)(NH_3)_5](ClO_4)_2$	261 (5830)	322 (20.9)	361 (38.6)	416 (17.4)	485 (54.3)	20.6
$[Cr(NH_3)_5(H_2O)](ClO_4)_3$			357 (30.4)	405 (8.95)	477 (35.5)	21.0
cis-$[Cr(NA)_2(NH_3)_4]ClO_4$	261 (11 500)	340 (38.8)	377 (54.0)	432 (31.4)	510 (73.3)	19.6
cis-$[Cr(NH_3)_4(H_2O)_2]Br_3$			365 (26.4)	418 (8.13)	495 (35.9)	20.2
trans-$[Cr(NAH)_2(NH_3)_4](ClO_4)_3{\cdot}2H_2O$[b]	260.5 (11 700)	334 (17.5)	374 (40.7)	429 (13.7)	513 (47.6)	19.5
trans-$[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$			367 (29.5)	417 (10.9)	470 (20.2) 550 sh (13.4)	21.3[c]
cis-$[Cr(NA)_2(en)_2]Br$	261 (11 500)	331 (29.3)	370 (67.1)	418 (24.5)	490 (107)	20.4
cis-$[Cr(H_2O)_2(en)_2]Br_3{\cdot}2H_2O$			368 (40.4)	415 (17.1)	486 (62.6)	20.6

[a] Solvent: aqueous 0.1 M $HClO_4$, except as noted. [b] Solvent: aqueous 0.01 M $HClO_4$. [c] For major band.

least-squares planes, hydrogen bonds and angles between molecules, perchlorate group and pyridinium ring bond distances and angles, and observed and calculated structure factors are available in the supplementary material.

Results and Discussion

Preparation of Complexes. Initial efforts to prepare nicotinic acid adducts by anation of amine–aqua complexes in aqueous solution were unsuccessful due to the rather low affinity for the monodentate ligand and competing base hydrolysis. Use of a polar, nonaqueous solvent system thus appears desirable. Furthermore, the ambidentate character of nicotinic acid dictates that a synthetic route be chosen that will yield one predominant isomer. The acid anhydride method of Jackman et al.[18] has proven successful in this regard. Reactions 1–3 in Scheme I describe generation of the acid anhydride, formation of a hydroxo complex, and nucleophilic attack of the anhydride by the hydroxo ligand. The basic requirement for preparation of a nicotinate complex is availability of a parent aqua species that has adequate solubility in an aprotic solvent such as DMF. Favorable solubility is generally the case for previously described perchlorate and bromide salts of ammine- and ethylenediamine–aqua complexes of chromium(III).

Problems and unexpected results were noted for attempted preparation of the *cis*-halo(nicotinato)bis(ethylenediamine) complexes. When *cis*-aquachlorobis(ethylenediamine)chromium(III) bromide was used as the starting aqua complex, an oil (rather than crystalline solid) was obtained from the reaction mixture. A hygroscopic solid product could be obtained by triturating the oily material several times with ether. Nonstoichiometric halide analysis indicated the product was likely heterogeneous, and this preparation was not examined further. Partial base hydrolysis for the chloro complex is suggested by the observation that *cis*-$[CrBr(H_2O)(en)_2]Br_2{\cdot}H_2O$ yielded only *cis*-$[Cr(NA)_2(en)_2]Br$ and not *cis*-$[CrBr(NA)(en)_2]Br$ as expected. The rate of hydrolysis of *cis*-$[CrBr(H_2O)(en)_2]^{2+}$ is sufficiently fast ($k = 5.7 \times 10^{-2}$ s^{-1} at pH 6.9 and 25 °C[34]) that the species present for reaction with nicotinic anhydride may well have been *cis*-$[Cr(OH)_2(en)_2]^+$. A somewhat slower rate of hydrolysis expected for the chloro complex would then dictate reactions between aqua–chloro and diaqua adducts to give a mixture of products.

Crude products examined by NMR spectroscopy were found to be contaminated with DMF and dimethylbenzylamine. After the products were washed with absolute ethanol, only DMF remained, and most of it was removed by vacuum drying at 40–80 °C. The perchlorate compounds, however, were not heated during vacuum drying and contained relatively high mole percentages of DMF. Attempts to reprecipitate the complexes of cis configuration either from ethanol solution with ether or from dilute $HClO_4$ solution with 70% $HClO_4$ were unsuccessful. Only *trans*-$[Cr(NA)_2(NH_3)_4]ClO_4$ could be precipitated from aqueous solution. Elemental analysis and X-ray diffraction showed that this compound, when precipitated by 70% $HClO_4$, contains two water molecules and, effectively, two molecules of $HClO_4$ through protonation of pyridyl nitrogen atoms.

Hydrolytic stability of the nicotinate complexes in aqueous solution is highly pH dependent. In dilute acid media no color changes are noted for a period of hours at room temperature and brief heating to 80 °C caused no decomposition, as is evident in the material utilized for X-ray crystal structure determination. Complexes described here are susceptible to base hydrolysis at neutral pH. Within a few minutes of dissolution at neutral pH, characteristic gray coloration is observed and precipitates are formed. Examination by proton NMR spectroscopy reveals release of free nicotinic acid during hydrolysis.

Spectroscopic Characterization. Electronic spectra were of value in confirming the desired nicotinic acid stoichiometry and in demonstrating preservation of the primary structure

---

(34) Randolph, L.; Linck, R. G. *Inorg. Chem.* **1977**, *16*, 2653.

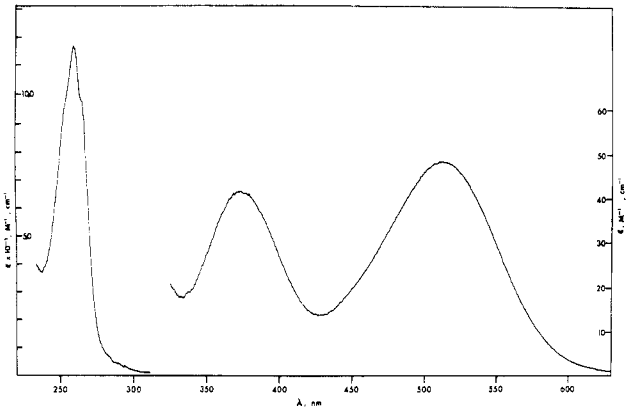

Figure 2. Electronic spectrum of *trans*-$[Cr(NAH)_2(NH_3)_4](ClO_4)_3 \cdot 2H_2O$ dissolved in 0.01 M aqueous $HClO_4$.

of the parent complex. In Table IV the visible–UV spectra of the compounds are compared to the visible spectra of the corresponding aqua complexes. The visible spectra of the aqua complexes prepared in this work agreed well with those reported in the literature for $[Cr(NH_3)_5(H_2O)](ClO_4)_3$,[35] *cis*-$[Cr(NH_3)_4(H_2O)_2]Br_3$,[36] and *cis*-$[Cr(H_2O)_2(en)_2]Br_3 \cdot 2H_2O$.[25] (The spectrum of *trans*-$[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$ was similar to that reported by Hoppenjans and Hunt[22] except for the shoulder at 550 nm that we have observed). It can be seen from Table IV and Figure 2 that the UV spectra of all the nicotinic acid complexes show a maximum near 261 nm with molar absorptivities higher than that of free nicotinic acid in acidic solution (λ = 260.5 nm, ϵ = 5140 L mol^{-1} cm^{-1}). The bis(nicotinato) complexes all have molar absorptivities more than twice that of free nicotinic acid. This criterion was also of value in demonstrating that the bis(nicotinato) adduct was formed when the parent $[CrBr(H_2O)(en)_2]Br_2 \cdot H_2O$ was used. It is assumed that pyridyl nitrogen groups of coordinated nicotinic acid are protonated in acidic media (0.01–0.1 M $HClO_4$). Rapid hydrolysis at neutral pH precluded reliable spectral examination of the deprotonated complex.

Visible spectra of the nicotinic acid complexes exhibited d–d λ_{max} at lower energies than the corresponding aqua complexes. The crystal field parameter, 10*Dq*, is readily obtained for d^3 octahedral complexes, as this energy separation matches the lowest energy d–d transition.[37] Values of 10*Dq* are listed in Table IV. Nicotinic acid complexes consistently exhibit a 10*Dq* value smaller than that for the parent aqua species. Consideration of all the complexes in Table IV leads to a spectrochemical ordering, NA–COO$^-$ < H_2O < NH_3 < en, consistent with the general spectrochemical series.[37] Smaller 10*Dq* values for nicotinic acid complexes provide reassurance that carboxylate rather than pyridyl nitrogen binding is preserved.

Infrared spectra further demonstrate the carboxyl ligation mode in the solid state. Monodentate carboxyl ligation is generally associated with conversion of the approximately 1600-cm^{-1} $\nu_a(CO_2^-)$ band of the free ion to a higher energy ν(C=O) mode and conversion of the approximately 1420-cm^{-1} $\nu_s(CO_2^-)$ band to a lower energy ν(C—O) mode.[38] Solid sodium nicotinate thus exhibits major carboxylate IR bands at 1620 and 1418 cm^{-1}. Other nicotinate ring stretches in these regions and the presence of DMF complicated the IR spectral analysis for certain products. However, in all spectra of nicotinate complexes, the very strong band for free sodium nicotinate at 1418 cm^{-1} was replaced by a very strong band(s) in the region 1350–1390 cm^{-1}. The complexes obtained as bromide salts were isolated essentially free of DMF, and hence the carboxyl bands can be reliably identified. For *cis*-$[Cr(NA)_2(en)_2]Br$ very strong absorptions were observed at 1635, 1380, and 1355 cm^{-1}, and likewise very strong, broad absorptions at 1640 and 1365 cm^{-1} were observed for *cis*-$[Cr(NA)_2(NH_3)_4]Br$. Appearance of the ν(C–O) stretch in the 1355–1380-cm^{-1} region is reminiscent of the 1372-cm^{-1} value for [Cr(glycinate)$_3$][39] and the 1372-cm^{-1} value for nicotinate and benzoate complexes of Cr^{III} salen.[13]

Crystal and Molecular Structure. The structural study reveals that the geometry around the chromium atom is very nearly octahedral. Average chromium–nitrogen bond lengths of 2.066 Å and chromium–oxygen bond lengths of 1.952 Å are in agreement with those reported in the literature for ammine ligands[40–42] and monocoordinated carboxylic acids,[43,44] respectively. The bond angles have an average deviation of only 2.2° from 90°, which means that there is a minimum of distortion around the chromium center.

Carboxylic acid groups are planar. However, they do not lie in the plane of the pyridinium ring to which they are bound. Angles between carboxylic planes and planar pyridinium rings are approximately 20°. The planes of trans-carboxylic groups are staggered by 10°. Upon coordination to chromium the carbon–oxygen bonds take on double- and single-bond character with bond lengths differing by 0.06 Å. The lengthening of the C1–O1 and C7–O2 bonds and shortening of the C1–O3 and C7–O4 bonds are identical with the results of similar structures.[43,44] The nitrogen of the pyridine ring is protonated as evidenced by the need for three perchlorate counterions in the chemical formula. Protonation of the ring nitrogen forms a pyridinium ring, which is known to be distorted with respect to the pyridine ring structure. These distortions are usually manifested in a shortening of C–N bond lengths in the ring and slight deviations of these rings from planarity. The bond distances and bond angles found here are in accord with comparable reports where the pyridine nitrogen is known to be protonated,[45,46] but the ring cannot be described as significantly different from planar.

The crystal structure is defined by an extensive hydrogen-bonding network. At least 21 hydrogen bonds per molecular unit are recognized (supplementary material). The chlorine–oxygen bond lengths in the perchlorate groups are shortened due to the disorder in the crystal lattice and high thermal motion of the oxygen atoms.[47] Disorder is at a minimum for the perchlorate ion associated with chlorine 1. This reasonably reflects the fact that nine hydrogen bonds (six N–H–O, one O–H–O, and two C–H–O) are formed with the oxygen atoms of this group. The perchlorate ion containing chlorine 3 has the greatest amount of disorder; however, bond distances and bond angles are in agreement for those reported for a diperchlorate structure where disorder was reported.[48]

---

(35) Jorgensen, E.; Bjerrum, J. *Acta Chem. Scand.* **1958**, *12*, 1047.
(36) Springberg, J.; Schaffer, C. E. *Acta Chem. Scand.* **1958**, *12*, 76.
(37) Purcell, K. F.; Kotz, J. C. "Inorganic Chemistry"; W. B. Saunders: Philadelphia, 1977; pp 567–577.
(38) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; p 232.
(39) Nakamoto, K.; Morimoto, Y.; Martell, A. E. *J. Am. Chem. Soc.* **1961**, *83*, 4528.
(40) Goldfield, S. A.; Raymond, K. N. *Inorg. Chem.* **1971**, *10*, 2604.
(41) Wieghardt, V. K.; Weiss, J. *Acta Crystallogr., Sect. B* **1972**, *B29*, 529.
(42) Clegg, W.; Greenhalgh, D. A.; Straughn, B. P. *J. Chem. Soc., Dalton Trans.* **1975**, 2591.
(43) Gerdom, L. E.; Baenziger, N. C.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 1606.
(44) Bryan, R. F.; Greene, P. T.; Stokely, P. F.; Wilson, E. W., Jr. *Inorg. Chem.* **1971**, *10*, 1468.
(45) Minshall, P. C.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1978**, *B34*, 1378.
(46) Weiss, R.; Mitschler, A.; Carpentier, M. *Acta Crystallogr., Sect. B* **1972**, *B28*, 1288.
(47) Camerman, A.; Balaban, A. T.; Jensen, L. H. *Acta Crystallogr.*, **1969**, *B25*, 2623.
(48) Kepert, D. L.; Taylor, D.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1973**, 893.

Interestingly, only four hydrogen bonds (three C–H–O and one N–H–O) are associated with this group.

Relevance to Biological Chromium. This study represents the first systematic effort to prepare nicotinic acid complexes of chromium(III) with defined, controlled structure. Resulting species are highly water soluble but have limited stability with respect to hydrolysis at neutral pH. Although the poor kinetic stability will preclude in vivo biological assay, in vitro methods that measure the rapid cellular uptake of an appropriate sugar may be feasible. Such bioassay work is in progress.

Spectroscopic work described here should be compared with that reported previously for synthetic complexes (of undefined structure and homogeneity) and for chromium-containing fractions obtained from brewers' yeast.[9] Biologically active yeast fractions reportedly have a UV absorption band at 262 nm reminiscent of that for nicotinic acid.[9] This absorption could well be due to free nicotinic acid or other heterocyclic compounds. However, it must be acknowledged that, on the basis of our model study, a carboxyl-coordinated nicotinic acid complex is expected to have a UV band near 262 nm (with two shoulders as in the free-ligand spectrum). Infrared spectra recorded in the earlier study lack major bands in the 1635- and 1355–1380-cm^{-1} regions, indicating the presence of free nicotinic acid or possibly a nitrogen-coordinated complex. In this regard, further attempts should be made to prepare and examine nitrogen-coordinated species.

Questions have been raised concerning the viability of nicotinic acid as a stable chromium(III) ligand at physiological pH.[13,49] With regard to base hydrolysis, nicotinate confers no particular stability to the ammine and ethylenediamine complexes examined here, and the residue is displaced as a chromium(III) ligand at neutral pH. This is not surprising, in view of the enhanced ligand substitution rates reported for chromium(III) complexes of carboxylates and other oxyanions.[50] Problems with hydrolysis of complexes and protonation of free nicotinic acid precluded quantitative kinetic and thermodynamic evaluations of nicotinic acid coordination. However, the qualitative observations made here offer no support for a carboxyl-bound form of nicotinic acid in physiological chromium(III) complexes.

Acknowledgment. This work was supported by the U.S. Department of Agriculture, Competitive Research Grants Office, Grant No. 79-59-2192-1-1-281-1. C. Potini began the initial preparation of the ammine complexes in this laboratory.

Registry No. $[Cr(NA)(NH_3)_5](ClO_4)_2$, 85454-43-9; *cis*-$[Cr(NA)_2(NH_3)_4]ClO_4$, 85454-45-1; *trans*-$[Cr(NAH)_2(NH_3)_4](ClO_4)_3 \cdot 2H_2O$, 85454-48-4; *trans*-$[Cr(NA)_2(NH_3)_4]ClO_4$, 85610-71-5; *cis*-$[Cr(NA)_2(en)_2]Br$, 85454-49-5; $[Cr(NH_3)_5(H_2O)](ClO_4)_3$, 32700-25-7; *trans*-$[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$, 21034-95-7; *cis*-$[CrBr(H_2O)(en)_2]Br_2$, 30172-32-8; *cis*-$[Cr(H_2O)_2(en)_2]Br_3$, 15040-49-0; *cis*-$[Cr(NH_3)_4(H_2O)_2]Br_3$, 85454-41-7; *cis*-tetraamminediaquachromium(III) perchlorate, 41733-15-7; *cis*-aquachlorobis(ethylenediamine)chromium(III) bromide, 13966-43-3; nicotinic acid anhydride, 16837-38-0.

Supplementary Material Available: A figure showing molecular packing with hydrogen bonding and listings of anisotropic thermal parameters, calculated hydrogen coordinates and isotropic thermal parameters, least-squares planes, hydrogen bond distances and angles, perchlorate group and pyridinium ring bond distances and angles, and observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

---

(49) Gonzalez-Vergara, E.; Hegenauer, J.; Saltman, P. *Fed. Proc., Fed. Am. Soc. Exp. Biol.* **1982**, *41*, 286 (abstract).

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

Contribution from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47405

New Nitrene Complexes of Niobium and Tantalum of the Type $M(NR)(S_2CNR'_2)_3$

L. SENG TAN, GARY V. GOEDEN, and BARRY L. HAYMORE*[1]

Received July 19, 1982

Niobium and tantalum nitrene complexes having the formula $M(NR)(S_2CNR'_2)_3$ ($R' = CH_3, CH_2CH_3$) have been prepared from $NbCl_5$ or $TaCl_5$ and $(CH_3)_2SiS_2CNR'_2$ in the presence of excess amine (RNH_2) or hydrazine (R_2NNH_2). A wide variety of aliphatic ($R = CH_3, CH_2CH_2CH_3, CH(CH_3)_2, C(CH_3)_3$) and aromatic amines was used. The structure of one complex ($M = Nb$; $R = p\text{-}CH_3C_6H_4$; $R' = C_2H_5$) was determined at −145 °C by using X-ray diffraction techniques. The complex is monomeric and seven-coordinate and has a distorted pentagonal-bipyramidal geometry. Two dithiocarbamate groups occupy four equatorial coordination sites, and the third group spans an axial and an equatorial site. The Nb atom is displaced 0.30 Å out of plane of the five equatorial sulfur atoms toward the nitrene, which occupies the remaining axial site. The nitrene ligand is only slightly bent at the nitrogen atom (Nb–N(4)–C(41) = 167.4 (3)°) with a typical Nb≡N(4) distance of 1.783 (3) Å. The NR ligand exerts little, if any, trans influence. The title complex crystallizes in space group *Pbca* with $a = 23.468$ (7) Å, $b = 15.485$ (5) Å, $c = 16.326$ (5) Å, and $Z = 8$. On the basis of 4701 unique reflections with $F_o^2 > 3\sigma(F_o^2)$, the structure was refined by using full-matrix, least-squares methods to $R(F) = 0.038$ and $R_w(F) = 0.048$.

Introduction

Owing to their formal similarity to carbene ligands and their potential synthetic uses, coordinated nitrenes have been studied more intensely in recent years.[2] Electron-rich nitrene complexes of the sort $OsO_2(NR)_2$,[3] $Mo(NR)_2(S_2CNR'_2)_2$,[4] and $TaCl(NR)(PR_3)_4$[8] have been shown to possess reactive NR groups, which are readily removed from the metal under mild conditions; in contrast, most other coordinated nitrenes are tightly bound to the metal and are not readily displaced. Among the first nitrene complexes to be reported are those containing Nb and Ta, $M(NR)(NR_2)_3$ (M = Nb, Ta), which were first prepared from lithium dialkylamides and the metal pentahalides.[5] Improved syntheses and the structure of $Ta(NR)(NMe_2)_3$ have recently appeared.[6]

---

[1] To whom correspondence should be addressed at Corporate Research Laboratories, Monsanto Co., St. Louis, MO 63167.

(2) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

(3) Ching, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420.

(4) Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063. Maatta, E. A.; Haymore, B. L.; Wentworth, R. A. D. *Inorg. Chem.* **1980**, *19*, 1055.

(5) Bradley, D. C.; Thomas, I. M. *Can. J. Chem.* **1962**, *40*, 1355.

(6) Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1978**, 579.

0020-1669/83/1322-1744$01.50/0