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Preparation, Physical Properties, and Crystal Structure of $MoFe_2P_{12}$ and WFe_2P_{12}

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The new compounds $MoFe_2P_{12}$ and WFe_2P_{12} were prepared by reaction of the elemental components in a tin flux. They have isotypic crystal structures of space group *Pbcn*, $Z = 4$, and the following lattice constants: $MoFe_2P_{12}$, $a = 13.725$ (9) Å, $b = 5.672$ (3) Å, $c = 11.092$ (3) Å; WFe_2P_{12}, $a = 13.732$ (6) Å, $b = 5.673$ (1) Å, $c = 11.088$ (3) Å. Their structure was determined from diffractometer data of a $MoFe_2P_{12}$ single crystal and refined to a residual of $R = 0.042$ for 2852 F values and 70 variable parameters. The Mo atoms have eight P neighbors which form a slightly distorted square antiprism, and the Fe atoms are in an approximately octahedral P coordination. All P atoms are four-coordinated either to one metal and three P atoms or to two metal and two P atoms. All near-neighbor interactions can be rationalized by classical two-electron bonds. This agrees with the diamagnetism and the semimetallic behavior of the electrical conductivity of both compounds.

Introduction

Almost 20 pnictides with the general composition MPn_4 (M = metal, Pn = P or As) are known. They crystallize with 10 different structure types,[1] which can be classified according to several common building principles.[2] These principles allow one to envision many more compounds with related structures. We have therefore started to investigate the pseudobinary sections MP_4–$M'P_4$, where M and M′ are two different transition metals. In all structure types with composition MPn_4 including MoP_4[3] and the two modifications of FeP_4,[4,5] the metal atoms are octahedrally coordinated to the pnicogen atoms. In $MoP_4{\cdot}2FeP_4 = MoFe_2P_{12}$ and the isotypic compound WFe_2P_{12} reported here, however, the Mo (W) atoms have coordination number 8 and thus the structure is of an entirely new type and has no close relationship to the known MPn_4 structures. Like these, however, it can completely be rationalized by classical two-electron bonds.

Preparation

Both compounds were prepared well crystallized by reaction of the elemental components in a tin flux. Starting materials were powders of Mo and W (Ventron, 99.9%), Fe (Merck, "reinst"), red P (Knapsack, "ultrapure"), Sn (Riedel, "rein"). They were mixed in the atomic ratio Fe:Mo (W):P:Sn = 2:1:12:20 and sealed with Ar into silica tubes that had been previously annealed to get rid of the absorbed water. The tube volumes were about 5 cm^3, and the P contents were 100 mg. After the samples were annealed for 1 week at 970 K, the samples were quenched and the tin-rich matrices were dissolved in hot 6 N hydrochloric acid. The resulting crystals of $MoFe_2P_{12}$ and WFe_2P_{12} had prismatic shapes with rectangular cross sections and typical dimensions varying between about 0.1 × 0.05 × 0.02 and 0.2 × 0.1 × 0.05 mm. Guinier powder patterns of samples prepared under a variety of differing starting compositions did not show significant homogeneity ranges. X-ray fluorescence analyses of the crystals in a scanning electron microscope gave no indications for a tin or silicon content. The limits for the detectability of both elements were less than 0.5 atom %.

The thermodynamic stability range for WFe_2P_{12} was not established. For $MoFe_2P_{12}$, however, many samples were prepared under a variety of differing conditions. With starting compositions as given above, samples annealed at 1170 K for 1 week resulted in MoP_2[6] and FeP_2.[7] Annealing at 870 K gave MoP_2 and α-FeP_4.[4] Thus $MoFe_2P_{12}$ seems to be thermodynamically stable only within a limited temperature range.

Properties

Powders and crystals of $MoFe_2P_{12}$ and WFe_2P_{12} are black with a metallic luster. They are stable in air and resistant to hot solutions of NaOH, HCl, and HNO_3 as well as aqua regia.

Magnetic susceptibility measurements were carried out at room temperature with a Faraday balance. Both compounds are diamagnetic with molar susceptibilities of $\chi = -62.1 \times 10^{-6}$ cm^3·mol^{-1} for $MoFe_2P_{12}$ and $\chi = -106.3 \times 10^{-6}$ cm^3·mol^{-1} for WFe_2P_{12} and error limits for the measurements of $\pm 3.0 \times 10^{-6}$ cm^3·mol^{-1}.

To determine the electrical conductivities, selected single crystals of both compounds were squeezed between flat tungsten contacts. The voltage difference was determined at constant current with a compensator at temperatures between 75 and 500 K. The contacting areas of the crystals could not be determined accurately, and therefore the absolute values of the conductivities are estimated to be correct only within a factor of 3. The relative values for one crystal at different temperatures are much more reliable (Figure 1). The resistivities were independent of the current direction, and the current–voltage relations were found to be linear. Thus the behavior of the conductivities seems not to be determined by surface barriers. The specific resistivities have flat minima at intermediate temperatures for both compounds as is typical for semimetals (zero band gap semiconductors): at low temperatures the materials behave more like semiconductors while at high temperatures the metallic character of the conductivities becomes dominant.

Structure Determination

Single crystals of $MoFe_2P_{12}$ were investigated with a Buerger precession camera. They have Laue symmetry *mmm* and a primitive orthorhombic lattice with the following systematic extinctions: $hk0$ only observed with $h + k = 2n$, $h0l$ only with $l = 2n$, and $0kl$ only with $k = 2n$. This is characteristic for the space group *Pbcn*-D_{2h}^{14}. The lattice constants were refined from Guinier powder data (Table I) with use of α-quartz ($a = 4.9130$ Å, $c = 5.4046$ Å) as a standard: $a = 13.725$ (9) Å, $b = 5.672$ (3) Å, $c = 11.092$ (3) Å, $V = 863.5$ (7) Å^3. With $Z = 4$ formula units per cell, the X-ray density is 4.45 g·cm^{-3}. For isotypic WFe_2P_{12} the lattice constants are $a = 13.732$ (6) Å, $b = 5.673$ (1) Å, $c = 11.088$ (3) Å, $V = 863.8$ (5) Å^3.

X-ray data were recorded for a single crystal of $MoFe_2P_{12}$ of dimensions 45 × 87 × 155 μm^3 in a four-circle diffractometer using Mo Kα radiation, a graphite monochromator, a scintillation counter, and a pulse-height discriminator. ω–2θ scans were taken with varying scan rate which was optimized by a fast prescan. The scan widths were 1.4° (2θ) plus the angular separation of the Kα doublet. Background counts were taken at both ends of each scan. A total of 4002 reflections were recorded within one octant of the reciprocal space up to $(\sin\theta)/\lambda = 1$. After omission of the reflections with intensities smaller than 3 standard deviations, 2873 reflections remained, which were used for the structure determination. An empirical

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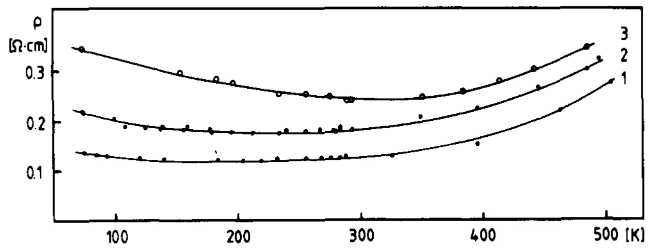

Figure 1. Specific resistivities of MoFe$_2$P$_{12}$ and WFe$_2$P$_{12}$. The crystals were cycled repeatedly between 75 and 500 K. Curves 1 and 2 summarize the measurements for two crystals of MoFe$_2$P$_{12}$, and curve 3 shows the results for a WFe$_2$P$_{12}$ crystal.

Table I. Powder Patterns of MoFe$_2$P$_{12}$ and WFe$_2$P$_{12}$[a]

MoFe$_2$P$_{12}$					WFe$_2$P$_{12}$				
hkl	Q_c	Q_o	I_c	I_o	hkl	Q_c	Q_o	I_c	I_o
200	212	212	25	m	200	212	208	12	m
002	325	-	0	-	002	325	326	3	w
110	364	-	2	-	110	364	-	0	-
102	378	-	4	-	102	379	-	5	-
111	445	445	12	w	111	445	444	5	w
202	537	538	46	s	202	538	538	36	s
211	604	605	16	m	211	604	605	20	s
112	689	689	100	vvs	112	689	689	92	vs
310	789	788	44	s	310	788	788	42	s
302	803	-	0	-	302	803	-	0	-
212	848	850	7	w	212	848	849	8	w
400	849		6		400	849		2	
311	870	870	47	s	311	870	869	45	s
113	1095	1095	30	s	113	1096	1096	29	s
312	1114	1114	12	w	312	1114	1114	8	m
402	1174	1174	51	s	402	1174	1174	50	s
411	1241	1242	28	m	411	1241	1242	36	s
020	1243		13		020	1243		15	
213	1255	-	0	-	213	1255	-	0	-
004	1300	1300	39	s	004	1302	1303	40	s
021	1325	1325	43	s	021	1324	1324	44	s
104	1353	1353	53	s	104	1355	1355	66	vs
121	1378	1379	37	s	121	1377	1377	47	s
220	1456	1455	33	s	220	1455	1455	45	s
412	1485	1485	58	vs	412	1485	1485	73	vs
204	1513	1514	17	m	204	1514	1519	28	s
313	1520	1520	53	s	313	1520		58	
221	1537	-	3	-	221	1536	1538	1	vw
022	1568	1569	9	vw	022	1568	1571	10	w
122	1621	1622	16	w	122	1621	1620	20	m
510	1638	1638	54	s	510	1637	1636	59	s
502	1652	-	1	-	502	1652	-	1	-
114	1664	1661	35	s	114	1666	1666	34	s
511	1719	1721	11	vw	511	1718	1718	19	m
304	1778	1780	29	vs	304	1779	1780	35	s
222	1781		29		222	1781		33	
321	1802	1804	20	m	321	1802	1802	24	m
214	1823	-	2	-	214	1825	-	2	-
413	1891	1895	13	w	413	1892	1892	16	m
600	1911	1911	39	s	600	1910	1910	44	s
512	1963	-	1		512	1962	-	0	-
023	1975	1974	8	vw	023	1975	1975	6	vw
123	2028	-	0	-	123	2028	-	0	-
322	2046	2045	19	m	322	2046	2046	23	m
314	2089	2090	21	m	314	2090	2091	20	m
420	2093	-	2	-	420	2092		3	
404	2149	-	2	-	404	2151	2153	1	vw
421	2174	2171	20	m	421	2173	2173	18	m
223	2187	2186	16	m	223	2187	2188	14	m
602	2236	2233	11	w	602	2235	2236	10	w
611	2303	-	0	-	611	2302	-	0	-
513	2369	2368	37	s	513	2369	2369	42	s
115	2396	-	3	-	115	2398	2399	2	vw

[a] The diagrams were recorded with Cu Kα_1 radiation in a Guinier camera. The calculated patterns were computed[8] with the positional parameters as determined in the MoFe$_2$P$_{12}$ structure refinement. The Q values are defined by $Q = 10^4/d^2$ (Å^{-2}). Because of their large number only the first halves of the patterns are listed.

absorption correction was made ($\mu_{\text{Mo K}\alpha}$ = 68.8 cm^{-1}) from four azimuthal scans. The ratio of the maximal and minimal transmission was 1.25.

The structure was determined by a program system supplied by Enraf-Nonius. The positions of the metal atoms were deduced from a Patterson map, and the P atoms were located through a difference Fourier synthesis. Full-matrix least-squares refinements were carried out with atomic scattering factors[9] corrected for anomalous dispersion.[10] Weights accounted for counting statistics. An isotropic secondary extinction parameter was refined and applied to the F_c values. An inspection of the F_o–F_c table revealed that most of the strong reflections were overcorrected by this procedure. Therefore the 21 highest F values were given zero weight in the final least-squares cycles. The final conventional R value is 0.042 for a refinement with anisotropic thermal parameters, 2852 F values, and a total of 70 variables. A final difference Fourier map showed the electron densities of 4.8 and 2.7 e·Å^{-3} as highest peaks. These are close to the metal positions and most likely result from inaccuracies in the absorption correction. Positional and equivalent isotropic thermal parameters are listed in Table II and interatomic distances in Table III. Structure factors and ellipsoidal thermal parameters are available as supplementary material. The structure and near-neighbor environments of the metal atoms are shown in Figures 2–4.

Table II. Atomic Parameters of MoFe$_2$P$_{12}$[a]

	x	y	z	B, Å^2
Mo	0	0.10045 (7)	$^1/_4$	0.257 (4)
Fe	0.34992 (3)	0.10336 (8)	0.45918 (4)	0.268 (5)
P(1)	0.16817 (6)	0.9838 (2)	0.19588 (8)	0.39 (1)
P(2)	0.31018 (7)	0.1192 (2)	0.27026 (7)	0.39 (1)
P(3)	0.49228 (7)	0.2560 (2)	0.39814 (8)	0.40 (1)
P(4)	0.08663 (7)	0.4390 (2)	0.14551 (8)	0.39 (1)
P(5)	0.09128 (7)	0.2328 (2)	0.43888 (8)	0.39 (1)
P(6)	0.29766 (6)	0.4684 (2)	0.50039 (8)	0.37 (1)

[a] The Mo atoms are in position 4*c* and all other atoms in the general position of space group *Pbcn*. Standard deviations in the least significant digits are given in parentheses. The last column contains equivalent isotropic thermal parameters computed from the anisotropic ones.

Table III. Interatomic Distances (Å) in MoFe$_2$P$_{12}$[a]

Mo:	P(1)	2.475 (2×)	P(3):	Mo	2.555
	P(4)	2.538 (2×)		Fe	2.242
	P(5)	2.555 (2×)		P(5)	2.262
	P(3)	2.555 (2×)		P(4)	2.268
Fe:	P(2)	2.167	P(4):	Mo	2.538
	P(6)	2.213		Fe	2.256
	P(6)	2.238		P(2)	2.228
	P(3)	2.242		P(3)	2.268
	P(4)	2.256	P(5):	Mo	2.555
	P(5)	2.263		Fe	2.263
P(1):	Mo	2.475		P(6)	2.245
	P(6)	2.235		P(3)	2.262
	P(2)	2.246	P(6):	Fe	2.213
	P(2)	2.252		Fe	2.238
P(2):	Fe	2.167		P(1)	2.235
	P(4)	2.228		P(5)	2.245
	P(1)	2.246			
	P(1)	2.252			

[a] All metal–P distances shorter than 3 Å are listed. The shortest metal–metal distance is an Fe–Fe distance of 3.95 Å. The shortest nonbonding P–P interactions are all greater than 2.86 Å. Standard deviations are 0.002 Å for metal–P and 0.003 Å for P–P distances.

Discussion

MoFe$_2$P$_{12}$ and isotypic WFe$_2$P$_{12}$ can formally be considered as tetraphosphides (M,M′)P$_4$. As do all binary tetraphosphides,[1,2] they belong to those transition-metal polyphosphides that have low-coordination structures, where all near-neighbor interactions can be rationalized on the basis of classical two-electron bonds.[11] In order to establish formal oxidation numbers for MoFe$_2$P$_{12}$, the electrons of the (certainly essentially covalent) metal–P bonds are counted as belonging to the P atoms, and the P–P bonds are split homolytically. In this way the P(1) and P(2) atoms with one metal and three P neighbors attain oxidation number 0, while for the other P atoms with two metal and two P neighbors, the oxidation

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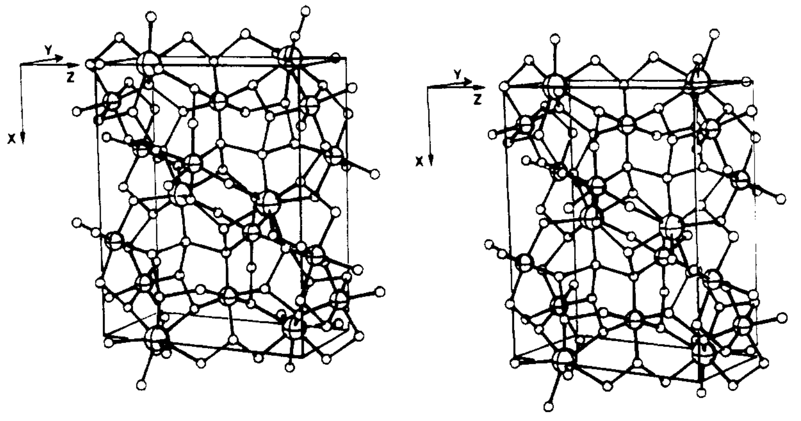

Figure 2. Stereoplot of the structure of $MoFe_2P_{12}$: large spheres, Mo; medium spheres, Fe; small spheres, P.

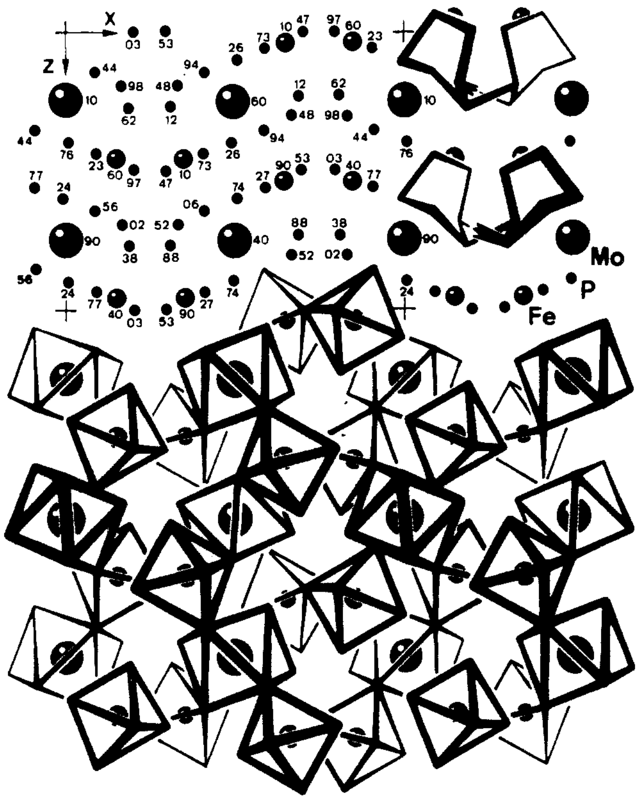

Figure 3. Crystal structure of $MoFe_2P_{12}$. The heights of the atoms are indicated in hundredths of the y coordinate. The MoP_8 square antiprisms and FeP_6 octahedra are linked only by common corners. In the upper right-hand part of the drawing two of the P poly-"anions" with infinite extension along the projection direction are shown.

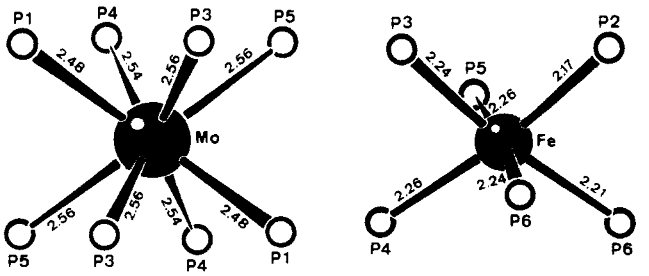

Figure 4. Near-neighbor environment of the Mo and Fe atoms in $MoFe_2P_{12}$. Interatomic distances are indicated in units of angstroms.

number −1 can be ascribed to. The resulting oxidation numbers of the metal atoms are Mo^{4+} (d^2 system) and Fe^{2+} (d^6 system). Other assignments (Mo^0 and Fe^{4+} or Mo^{2+} and Fe^{3+}) are incompatible with the diamagnetism of $MoFe_2P_{12}$ (and WFe_2P_{12}). They are also less likely considering the related compounds α- and β-FeP_4[4,5,12] and $LnFe_4P_{12}$ (Ln = lanthanoids),[13] where the Fe atoms also have a low-spin d^6 system in a distorted-octahedral P environment. The other two d orbitals (usually designated e_g for perfect octahedral symmetry) participate in the formation of the six Fe–P bonds ("d^2sp^3 hybrid").

In all tetra(poly)phosphides MP_4, including MoP_4,[3] the metal atoms are octahedrally surrounded by P atoms. $MoFe_2P_{12}$ is the first compound where the Mo atoms have an approximately square-antiprismatic P coordination. In a simple molecular orbital rationalization four of the d orbitals are utilized to form the eight Mo–P bonds (d^4sp^3 hybrid) while the fifth (d_{z^2}) is filled with a pair of nonbonding electrons.[14] In contrast in MoP_4 with a CrP_4 type structure,[3] the Mo atoms have oxidation number +2 (d^4 system) and are approximately octahedrally coordinated to P, utilizing only two d orbitals for the six Mo–P bonds (d^2sp^3 hybrid). The other three d orbitals of Mo in MoP_4 are needed to hold two nonbonding electrons and to form two Mo–Mo bonds across the shared edges of adjacent MoP_6 octahedra. Thus, even though the oxidation numbers and coordination polyhedra of the Mo atoms in $MoFe_2P_{12}$ and MoP_4 are different, the coordination number (if the Mo–Mo bonds in MoP_4 are counted also) is 8 for the Mo atoms of both compounds. Both compounds also make optimal use of all d orbitals, which form bonds to neighboring atoms or are filled with nonbonding electrons. In this respect $MoFe_2P_{12}$ and WFe_2P_{12} are similar to most transition-metal polyphosphides. Unfilled or partially filled (valence) d orbitals are rare in thermodynamically stable transition-metal polyphosphides.[15] In the preceding bonding description of the $MoFe_2P_{12}$ structure, which accounts for all electrons, all spins are compensated. It is therefore strongly supported by the diamagnetism of both compounds. The semimetallic character of the electrical conductivitites is also compatible with this rationalization of chemical bonding.

In Figure 3 the structure of $MoFe_2P_{12}$ is viewed as a packing of corner-shared MoP_8 square antiprisms and FeP_6 octahedra. In stressing the two-electron bond description, one may also consider the structure as a three-dimensional network of condensed and puckered 5- and 6-membered rings. All rings contain one or two metal atoms. There is also one 4-membered ring (occurring eight times in one cell, near the edges and not visible in Figure 2) formed by the atoms Fe–P(4)–P(3)–P(5). Such 5- and 6-membered rings are very common in polyphosphides, while 4-membered rings occur less frequently.[2,16]

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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.

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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.

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

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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; $\beta = 99.36$ (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

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