Synthesis and characterization of μ-carboxylato-O,O-μ-hydroxo chromium(III) complexes containing amino acids, acetate and nicotinate as bridging ligands. Crystal structure of $K_2[Cr(nta)(OH)(acetate\text{-}O,O)Cr(nta)]\cdot 4H_2O$

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Abstract

A series of μ-carboxylato-μ-hydroxo chromium(III) complexes containing amino acids, acetate and nicotinate as bridging ligands has been synthesized and characterized by ^2H NMR and electronic absorption spectroscopy: $[Cr(en)_2(OH)(Hamino\ acid\text{-}O,O)Cr(en)_2]^{5+}$ (en = ethylenediamine; Hamino acid-O,O = glycine (previously reported), alanine, serine and threonine); $[Cr(en)_2(OH)(acetate\text{-}O,O)Cr(en)_2]^{4+}$ (previously reported); $[Cr(nta)(OH)(acetate\text{-}O,O)Cr(nta)]^{2-}$ (nta = nitrilotriacetate). The crystal structure of $K_2[Cr(nta)(OH)(acetate\text{-}O,O)Cr(nta)]\cdot 4H_2O$ was determined. This complex crystallizes in the space group $P\bar{1}$ of the triclinic crystal system with $a = 9.678(3)$, $b = 11.182(2)$, $c = 13.137(4)$ Å, $\alpha = 97.57(2)$, $\beta = 102.26(2)$, $\gamma = 108.96(2)°$ and $Z = 2$. Magnetic susceptibility data were also collected for this complex (80 to 280 K) and show a J/k value of -19.5 K. The ^2H NMR spectra of these di-Cr(III) complexes, with deuterium labeled (2-carbon) bridging ligands, show isotropic shifts which are distinctly different from the shifts observed for the mononuclear Cr(III) complexes containing these ligands: amino acids, +72 to +81 ppm; acetate, +58 ppm (bis(en)) and +41 ppm (nta); nicotinic acid, +3.6 ppm.

Introduction

Chromium(III) complexes have a tendency to form dimers, with oxygen containing ligands serving as bridges between the metal ions. Water and hydroxide are commonly involved in dimer formation, and ligands containing carboxylate groups are also encountered. Bis(ethylenediamine)chromium(III) complexes containing a hydroxo and a carboxylato bridging ligand have been reported previously [1]. The characterization of these complexes was based on infrared spectra an on the reactivity of the complexes. We have been investigating the coordination mode of ligands containing carboxylate groups to Cr(III), including nicotinic acid [2, 3] and amino acids [4]. Deuterium NMR spectroscopy has been found to be particularly helpful in differentiating modes of ligand coordination. Since the di-Cr(III) complexes provide a unique coordination mode for these ligands, several complexes were synthesized with deuterium labeled ligands. Two complexes with bridging acetate, a bis(bis(ethylenediamine)Cr(III)) complex (previously reported) [1] and a bis((nitrilotriacetate)Cr(III)) complex, were investigated. The crystal structure of $K_2[Cr(nta)(OH)(acetate\text{-}O,O)Cr(nta)]\cdot 4H_2O$ (where nta = nitrilotriacetate and acetate-O,O = bridging carboxylate coordinated acetate) was determined. The synthesis and characterization of $[Cr(en)_2(OH)(Hamino\ acid\text{-}O,O)Cr(en)_2]^{5-}$ and $[Cr(en)_2(OH)(Hnic\text{-}O,O)Cr(en)_2]^{5-}$ (where en = ethylenediamine; Hamino acid-O,O = bridging carboxylate coordinated alanine, glycine (previously reported) [1], serine and threonine; and Hnic-O,O = bridging carboxylate coordinated nicotinic acid) are also reported.

Experimental

The previously reported complexes [1], $[Cr(en)_2(OH)(acetate\text{-}O,O)Cr(en)_2](ZnCl_4)_2\cdot H_2O$

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TABLE 1. Visible spectra[a]

Complex	λ_{max} (nm)	(ϵ (μ mol^{-1} cm^{-1}))	
$[Cr(en)_2(OH)(Hala\text{-}O,O)Cr(en)_2](ZnCl_4)_2Cl \cdot H_2O$	374(78)	504(192)	
$[Cr(en)_2(OH)(Hser\text{-}O,O)Cr(en)_2](ZnCl_4)_2Cl \cdot 2H_2O$	374(80)	504(192)	
$[Cr(en)_2(OH)(Hthr\text{-}O,O)Cr(en)_2](ZnCl_4)_2Cl$	374(80)	504(202)	
$[Cr(en)_2(OH)(Hnic\text{-}O,O)Cr(en)_2](ZnCl_4)_2Cl \cdot H_2O$	374(96)	504(215)	
$K_2[Cr(nta)(OH)(acetate\text{-}O,O)Cr(nta)] \cdot 4H_2O$	414(206)	532(133)	591(163)

[a]In 0.01 M HCl.

TABLE 2. Deuterium NMR spectra[a]

Complex	δ (ppm)[b]
$[Cr(en)_2(OH)(Hgly\text{-}O,O)Cr(en)_2]^{5+}$ [c]	+81
$[Cr(en)_2(OH)(Hala\text{-}O,O)Cr(en)_2]^{5+}$ [c]	+74
$[Cr(en)_2(OH)(Hser\text{-}O,O)Cr(en)_2]^{5+}$ [c]	+75
$[Cr(en)_2(OH)(Hthr\text{-}O,O)Cr(en)_2]^{5+}$ [c]	+72
$[Cr(en)_2(OH)(Hnic\text{-}O,O)Cr(en)_2]^{5+}$ [c]	+3.6
$[Cr(en)_2(OH)(acetate\text{-}O,O)Cr(en)_2]^{4+}$ [c]	+58
$[Cr(nta)(OH)(acetate\text{-}O,O)Cr(nta)]^{2-}$ [d]	+41, (+52)[e]
trans-$[Cr(1,3\text{-pn})_2(OAc)_2]^{+}$ [f]	+21

[a]Deuterium label on the 2-carbon of the amino acid, on the methyl group of the acetate, or on the 2-carbon of the nicotinic acid. [b]Shift relative to $CDCl_3$ assigned as +7.26 ppm. [c]In 0.01 M HCl. [d]In 0.001 M HCl. [e]Approximately 15% of the coordinate acetate. [f]In H_2O.

and $[Cr(en)_2(OH)(Hgly\text{-}O,O)Cr(en)_2](ZnCl_4)_2Cl \cdot 4H_2O$, were prepared as reported but with acetic acid-d_4 (Aldrich) and glycine-d_2 [4]* (deuterium labeled on the 2-carbon). The synthesis of *trans*-$[Cr(1,3\text{-pn})_2(OAc)_2]Cl$ [6] (where 1,3-pn = 1,3-propanediamine and OAc = acetate) was repeated using acetic acid-d_4. The following preparations were also done with deuterium labeled (2-carbon) amino acids [4, 5], deuterium labeled (2-carbon) nicotinic acid [7] and acetic acid-d_4.

$[Cr(en)_2(OH)(Hala\text{-}O,O)Cr(en)_2](ZnCl_4)_2Cl \cdot H_2O$

This complex was prepared by a procedure similar to that reported for the corresponding complex containing glycine [1]. Alanine (1.0 g, 1.1 mmol) was dissolved in 2 ml of 1 M HCl at 55 °C. $[Cr(en)_2OH]_2Cl_4 \cdot 2H_2O$ [8] (0.37 g, 0.67 mmol) was added and the mixture was stirred and heated at 55 °C for 30 min. The mixture was then cooled in an ice bath, and 4 M Li_2ZnCl_4 (1 ml) was slowly added dropwise to precipitate the product. After standing for 30 min at ice temperature, the red precipitate was filtered, washed with 95% ethanol, ethanol and ether, and then air dried; yield 0.17 g (28%). *Anal.* Calc. for $[Cr(NH_2(CH_2)_2NH_2)_2(OH)(OCOCH(CH_3)NH_3)Cr(NH_2(CH_2)_2(NH_2)_2](ZnCl_4)_2Cl \cdot H_2O$: C, 14.4; H, 4.61; N, 13.7. Found: C, 14.4; H, 4.53; N, 13.7%.

$[Cr(en)_2(OH)(Hser\text{-}O,O)Cr(en)_2](ZnCl_4)_2Cl \cdot 2H_2O$

This complex was prepared as described above with serine (0.10 g, 1.0 mmol), 1.6 ml of 1 M HCl, and $[Cr(en)_2OH]_2Cl_4 \cdot 2H_2O$ (0.31 g, 0.56 mmol); yield 0.18 g (34%). *Anal.* Calc. for $[Cr(NH_2(CH_2)_2NH_2)_2(OH)(OCOCH(CH_2OH)NH_3)Cr(NH_2(CH_2)_2NH_2)_2](ZnCl_4)_2Cl \cdot 2H_2O$: C, 13.9; H, 4.66; N, 13.2. Found: C, 14.0; H, 4.27; N, 13.2%.

$[Cr(en)_2(OH)(Hthr\text{-}O,O)Cr(en)_2](ZnCl_4)_2Cl$

This complex was prepared as described above with threonine (0.15 g, 1.3 mmol), 1.8 ml of 1 M HCl and $[Cr(en)_2OH]_2Cl_4 \cdot 2H_2O$ (0.35 g, 0.63 mmol); yield 0.20 g (34%). *Anal.* Calc. for $[Cr(NH_2(CH_2)_2NH_2)_2(OH)(OCOCH(CH(CH_3)OH)NH_3)Cr(NH_2(CH_2)_2NH_2)_2](ZnCl_4)_2Cl$: C, 15.5; H, 4.55; N, 13.6. Found: C, 15.5; H, 4.52; N, 13.4%.

$[Cr(en)_2(OH)(Hnic\text{-}O,O)Cr(en)_2](ZnCl_4)_2Cl \cdot H_2O$

This complex was prepared as described above with nicotinic acid (0.080 g, 0.064 mmol), 1 ml of 1 M HCl and $[Cr(en)_2OH]_2Cl_4 \cdot 2H_2O$ (0.21 g, 0.38 mmol); yield 0.13 g (36%). *Anal.* Calc. for $[Cr(NH_2(CH_2)_2NH_2)_2(OH)(OCOC_5H_4NH)Cr(NH_2(CH_2)_2NH_2)_2](ZnCl_4)_2Cl \cdot H_2O$: C, 17.7; H, 4.23; N, 13.2. Found: C, 17.7; H, 4.08; N, 13.3%.

$K_2[Cr(nta)(OH)(acetate\text{-}O,O)Cr(nta)] \cdot 4H_2O$

$K_2[Cr(nta)OH]_2 \cdot 4H_2O$ [9] (0.5 g, 0.75 mmol) was suspended in 4 ml of H_2O. Acetic acid (0.15 ml, 2.4 mmol) was added and the mixture was stirred for 20 min at 45 °C to form a dark blue–green solution. Methanol was added to cloud the warm solution and the mixture was allowed to stand for 20 min. The dark green crystals which formed were collected on a filter, and then recrystallized from a small volume of warm H_2O (40–50 °C) by the addition of methanol; yield 0.35 g (66%). *Anal.* Calc. for $K_2[Cr(N(CH_2COO)_3)(OH)(OCOCH_3)Cr(N(CH_2-$

*For preparing unresolved, deuterium labeled (2-carbon) amino acids, a rather direct method is described in ref. 5.

TABLE 3. Data collection and structure determination

Compound name	K_2[Cr(nta)(OH)(acetate-*O*,*O*)Cr(nta)]·4H_2O
Empirical formula	$C_{14}H_{16}Cr_2K_2N_2O_{15}$·4$H_2O$
Molecular weight	706.6
Diffractometer system	Nicolet R3m/E
Radiation	Mo Kα (0.71069 Å) with graphite monochromator
Crystal class	triclinic
Space group	$P\bar{1}$
Systematic absences	none
Lattice constants (based on 23 reflections in the range $29° < 2\theta < 31°$)	
a	9.678(3) Å
b	11.182(2) Å
c	13.137(4) Å
α	97.57(2)°
β	102.26(2)°
γ	108.96(2)°
Volume	1282.61 Å^3
Calculated density, ρ	1.83 g/cm^3 ($Z=2$)
Crystal size	approximately 0.32×0.10×0.10 mm, needle shape
Absorption coefficient	12.32 cm^{-1}
F(000)	720
Type of absorption correction	empirical psi scan assuming ellipsoidal shape
Maximum transmission	0.641
Minimum transmission	0.394
Data collection technique	omega scan[a]
Scan range	1.0°
Scan speed	5°/min (min), 30°/min (max)
Temperature	22 °C
Check reflections (monitored every 100 scans)	1,−4,3; 2,−1,4; 3,−3,2
Total reflections	2648 (2θ (max) 40°)
Data collected for $h>0$, $k>0$, and all l	
Unique reflections	2383 (2112 with $I>3\sigma$)
R for equivalent reflections	0.0237
Structure solution package	Nicolet SHELXTL[b]
Scattering factors[c]	
Structure solution technique	direct methods
Least-squares full matrix refinement minimizing $\Sigma_w(\|F_o\|-\|F_c\|)^2$	$R=\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|=0.0557$ $R_w=[\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}=0.0596$ with $w=1/[\sigma^2(F)+g(F)^2]$, $g=0.00276$
Total parameters refined	377
Thermal parameters	anisotropic on all non-hydrogen atoms
Hydrogen atoms	constrained to C–H=0.960 Å, thermal parameters fixed at 1.2 times isotropic heavy atom parameters
Largest peak on final difference map	0.517 e$^-$/Å^3 near O(11)
Extinction corrections	none

[a]Ref. 11. [b]Ref. 12. [c]Ref. 13.

COO)$_3$)]·4H_2O: C, 23.8; H, 3.42; N, 3.96. Found: C, 24.4; H, 3.25; N, 3.98%.

Physical measurements

Elemental analyses were performed by Galbraith Laboratories, TN. Visible spectra for the complexes were recorded on a Varian/Cary 219 and are summarized in Table 1. Deuterium NMR spectra were obtained using a Nicolet NT-200 and the data are presented in Table 2. The conditions used to obtain the NMR data have previously been reported [10].

The crystal structure was determined using a crystal of K_2[Cr(nta)(OH)(acetate-*O*,*O*)Cr(nta)]·4H_2O grown by the addition of methanol to an aqueous solution of the complex. The parameters for the data collection [11] and structure determination are given in Table 3. A view of K_2[Cr(nta)(OH)-(acetate-*O*,*O*)Cr(nta)] is shown in Fig. 1. The atom positions are given in Table 4, and the bond lengths and bond angles are given in Table 5 [12, 13].

Magnetic susceptibility data were measured for K_2[Cr(nta)(OH)(acetate-*O*,*O*)Cr(nta)]·4H_2O using a vibrating-sample magnetometer. The data (collec-

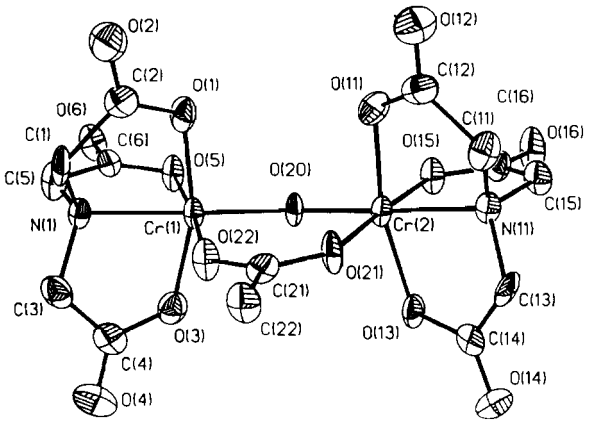

Fig. 1. An illustration of the dimeric unit in $K_2[Cr(nta)(OH)(acetato\text{-}O,O)Cr(nta)]\cdot 4H_2O$.

ted from 80 to 280 K) were fitted to susceptibilities calculated from the isotropic Hamiltonians for two exchange coupled $S=3/2$ chromium(III) ions. The model used assumes both a quadratic and biquadratic interaction, $\mathscr{H} = -2JS_1S_2 - 2j(S_1S_2)^2$ [15, 16]. The data gave values of $J/k = -19.5(5)$ K, $j/k = -2.8(5)$ K, and $g = 2.016(5)$, as shown in Fig. 2.

Results and discussion

In an earlier study it was shown that ^2H NMR can readily distinguish monodentate from bidentate amino acid coordination to Cr(III) [4]. Isotropic shifts for the complexes containing bidentate coordinated amino acids ranged from -26 to -61 ppm, whereas the complexes containing monodentate, carboxylate coordinated amino acids showed shifts in the range of $+19$ to $+37$ ppm. In the present study, the bridging, carboxylate coordinated amino acid complexes show isotropic shifts in the range of $+72$ to $+81$ ppm (Table 2). Thus, bridging carboxylate coordination can also be distinguished by ^2H NMR spectroscopy.

The crystal structure of $K_2[Cr(nta)(OH)(acetate\text{-}O,O)Cr(nta)]\cdot 4H_2O$ confirms the formation of a μ-carboxylato-O,O-μ-hydroxo complex. The dimer, lacking any crystallographic symmetry, has effective C_{2v} symmetry. Both bridges are symmetric (average Cr–OH = 1.928 Å, average Cr–O (acetate) = 1.968 Å). The Cr–OH–Cr bridging angle is 129.6° while the Cr–O–C angles average 136.0°. The C–O distances within the bridging acetate group are equal within experimental error (1.261 Å average). The nta ligands span two adjacent faces of each Cr coordination octahedron. The Cr–N distances (2.068 Å average) are significantly longer than those to the oxygen atoms on the acetate anions (1.964 Å average). The Cr–O distances to the acetate anions on the common edge of the two faces spanned are shorter by 0.025 Å than the Cr–O distances to the outer acetate anions.

TABLE 4. Atomic coordinates ($\times 10^4$) for $K_2[Cr(nta)(OH)(acetate\text{-}O,O)Cr(nta)]\cdot 4H_2O$

Atom	x	y	z
Cr(1)	4085(1)	3267(1)	6994(1)
Cr(2)	6376(1)	6548(1)	7645(1)
K(1)	7123(2)	2191(2)	5767(1)
K(2)	10541(2)	6359(2)	6434(2)
N(1)	2229(5)	1610(5)	6864(4)
N(11)	7075(6)	8520(5)	8209(4)
O(1)	2505(5)	3683(4)	6068(4)
O(2)	46(5)	3371(5)	5686(4)
O(3)	5134(5)	2412(4)	7947(4)
O(4)	4728(6)	1076(5)	9061(4)
O(5)	4358(4)	2268(4)	5771(3)
O(6)	3435(5)	358(4)	4634(3)
O(11)	4797(5)	6883(4)	6641(3)
O(12)	3469(5)	8188(5)	6492(4)
O(13)	8093(5)	6744(4)	8868(3)
O(14)	9569(6)	8051(5)	10433(4)
O(15)	7793(5)	7016(4)	6777(3)
O(16)	9527(5)	8629(4)	6442(4)
O(20)	5829(4)	4747(4)	7013(3)
O(21)	5015(5)	6237(4)	8586(3)
O(22)	3651(5)	4116(4)	8235(3)
O(31)	7068(5)	4585(4)	5318(3)
O(32)	8190(7)	2459(6)	8052(5)
O(33)	12157(15)	8281(10)	8811(10)
O(34)	9619(8)	5182(8)	8004(6)
C(1)	918(7)	2012(6)	6706(6)
C(2)	1136(7)	3099(7)	6090(5)
C(3)	2588(8)	1162(7)	7869(5)
C(4)	4256(8)	1544(7)	8348(5)
C(5)	2143(8)	663(6)	5917(5)
C(6)	3378(7)	1089(6)	5378(5)
C(11)	5704(7)	8862(7)	7941(5)
C(12)	4568(7)	7938(7)	6939(5)
C(13)	7790(8)	8754(7)	9368(5)
C(14)	8578(7)	7810(7)	9597(5)
C(15)	8192(8)	9159(7)	7630(5)
C(16)	8550(7)	8218(6)	6884(5)
C(21)	4016(7)	5273(6)	8727(5)
C(22)	3180(8)	5492(7)	9543(5)

The nta, acetate complex and the corresponding bis(ethylenediamine) complex have resonances at $+41$ and $+58$ ppm, respectively (Table 2). The spectrum of the complex containing nta-d_6 has resonances at -9, -25 and -30 ppm with relative integration ratios of 1:1:1. These are somewhat shifted from the resonances observed for $[Cr(nta\text{-}d_6)OH]_2^{2-}$ (which occur at -7, -13 and -26 ppm; [7]). The weak resonance at $+52$ ppm may be due to another isomer (three are possible), but attempts to isolate isomers were unsuccessful. The magnetic susceptibility data for $K_2[Cr(nta)(OH)(acetate\text{-}$

TABLE 5. Bond lengths and bond angles for $K_2[Cr(nta)(OH)(acetate\text{-}O,O)Cr(nta)]\cdot 4H_2O$

Atoms	Distance (Å)	Atoms	Distance (Å)
Cr(1)–N(1)	2.077(5)	Cr(1)–O(1)	1.964(5)
Cr(1)–O(3)	1.980(5)	Cr(1)–O(5)	1.949(5)
Cr(1)–O(20)	1.936(4)	Cr(1)–O(22)	1.969(5)
Cr(2)–N(11)	2.060(5)	Cr(2)–O(11)	1.966(5)
Cr(2)–O(13)	1.982(4)	Cr(2)–O(15)	1.951(5)
Cr(2)–O(20)	1.925(4)	Cr(2)–O(21)	1.972(5)
N(1)–C(1)	1.461(10)	N(1)–C(3)	1.486(9)
N(1)–C(5)	1.489(9)	N(11)–C(11)	1.482(10)
N(11)–C(13)	1.480(8)	N(11)–C(15)	1.500(9)
O(1)–C(2)	1.281(8)	O(2)–C(2)	1.225(10)
O(3)–C(4)	1.316(9)	O(4)–C(4)	1.211(10)
O(5)–C(6)	1.305(7)	O(6)–C(6)	1.208(9)
O(11)–C(12)	1.293(10)	O(12)–C(12)	1.235(10)
O(13)–C(14)	1.302(7)	O(14)–C(14)	1.226(7)
O(15)–C(16)	1.276(7)	O(16)–C(16)	1.210(9)
O(21)–C(21)	1.259(7)	O(22)–C(21)	1.263(8)
C(1)–C(2)	1.532(11)	C(3)–C(4)	1.495(10)
C(5)–C(6)	1.495(11)	C(11)–C(12)	1.514(8)
C(13)–C(14)	1.514(12)	C(15)–C(16)	1.511(11)
C(21)–C(22)	1.510(11)		

Atoms	Angle (°)	Atoms	Angle (°)
N(1)–Cr(1)–O(1)	81.0(2)	N(1)–Cr(1)–O(3)	81.8(2)
N(1)–Cr(1)–O(5)	85.1(2)	N(1)–Cr(1)–O(22)	89.3(2)
O(1)–Cr(1)–O(5)	91.4(2)	O(1)–Cr(1)–O(20)	98.5(2)
O(1)–Cr(1)–O(22)	88.4(2)	O(3)–Cr(1)–O(5)	89.6(2)
O(3)–Cr(1)–O(20)	98.8(2)	O(3)–Cr(1)–O(22)	88.9(2)
O(5)–Cr(1)–O(20)	90.6(2)	O(20)–Cr(1)–O(22)	95.1(2)
(N1)–Cr(1)–O(20)	175.6(2)	O(1)–Cr(1)–O(3)	162.6(2)
O(5)–Cr(1)–O(22)	174.3(2)	N(11)–Cr(2)–O(11)	81.4(2)
N(11)–Cr(2)–O(13)	81.9(2)	N(11)–Cr(2)–O(15)	84.6(2)
N(11)–Cr(2)–O(21)	90.4(2)	O(11)–Cr(2)–O(15)	92.1(2)
O(11)–Cr(2)–O(20)	97.8(2)	O(11)–Cr(2)–O(21)	87.8(2)
O(13)–Cr(2)–O(15)	89.5(2)	O(13)–Cr(2)–O(20)	99.1(2)
O(13)–Cr(2)–O(21)	89.2(2)	O(15)–Cr(2)–O(20)	89.8(2)
O(20)–Cr(2)–O(21)	95.1(2)	N(11)–Cr(2)–O(20)	174.4(2)
O(11)–Cr(2)–O(13)	163.0(2)	O(15)–Cr(2)–O(21)	175.0(2)
Cr(1)–N(1)–C(1)	105.6(4)	Cr(1)–N(1)–C(3)	105.5(3)
Cr(1)–N(1)–C(5)	105.9(4)	C(1)–N(1)–C(3)	115.1(6)
C(1)–N(1)–C(5)	112.2(5)	C(3)–N(1)–C(5)	111.6(6)
Cr(2)–N(11)–C(11)	106.6(3)	Cr(2)–N(11)–C(13)	105.5(4)
Cr(2)–N(11)–C(15)	107.1(4)	C(11)–N(11)–C(13)	114.6(6)
C(11)–N(11)–C(15)	110.5(6)	C(13)–N(11)–C(15)	111.9(4)
Cr(1)–O(1)–C(2)	116.5(5)	Cr(1)–O(3)–C(4)	115.5(5)
Cr(1)–O(5)–C(6)	117.3(4)	Cr(2)–O(11)–O(12)	116.3(4)
Cr(2)–O(13)–C(14)	115.8(5)	Cr(2)–O(15)–C(16)	117.7(5)
Cr(1)–O(22)–C(21)	135.4(4)	Cr(2)–O(21)–C(21)	136.5(4)
Cr(1)–O(20)–Cr(2)	129.6(3)	N(1)–C(1)–C(2)	110.6(6)
N(1)–C(3)–C(4)	112.8(6)	N(1)–C(5)–C(6)	116.1(5)
O(1)–C(2)–C(1)	115.2(6)	O(1)–C(2)–O(2)	125.0(7)
O(2)–C(2)–C(1)	119.8(6)	O(3)–C(4)–C(3)	115.2(6)
O(3)–C(4)–O(4)	123.9(7)	O(4)–C(4)–C(3)	120.7(7)
O(5)–C(6)–C(5)	115.6(6)	O(5)–C(6)–O(6)	123.9(7)
O(6)–C(6)–C(5)	120.4(5)	N(11)–C(11)–C(12)	110.5(6)
N(11)–C(13)–C(14)	110.9(6)	N(11)–C(15)–C(16)	113.9(5)
O(11)–C(12)–C(11)	115.8(6)	O(11)–C(12)–O(12)	124.2(5)
O(12)–C(12)–C(11)	119.9(7)	O(13)–C(14)–C(13)	115.2(5)
O(13)–C(14)–O(14)	124.1(7)	O(14)–C(14)–C(13)	120.7(6)
O(15)–C(16)–C(15)	116.5(6)	O(15)–C(16)–O(16)	124.1(7)
O(16)–C(16)–C(15)	119.4(6)	O(21)–C(21)–C(22)	118.6(6)
O(21)–C(21)–O(22)	124.8(7)	O(22)–C(21)–C(22)	116.7(6)

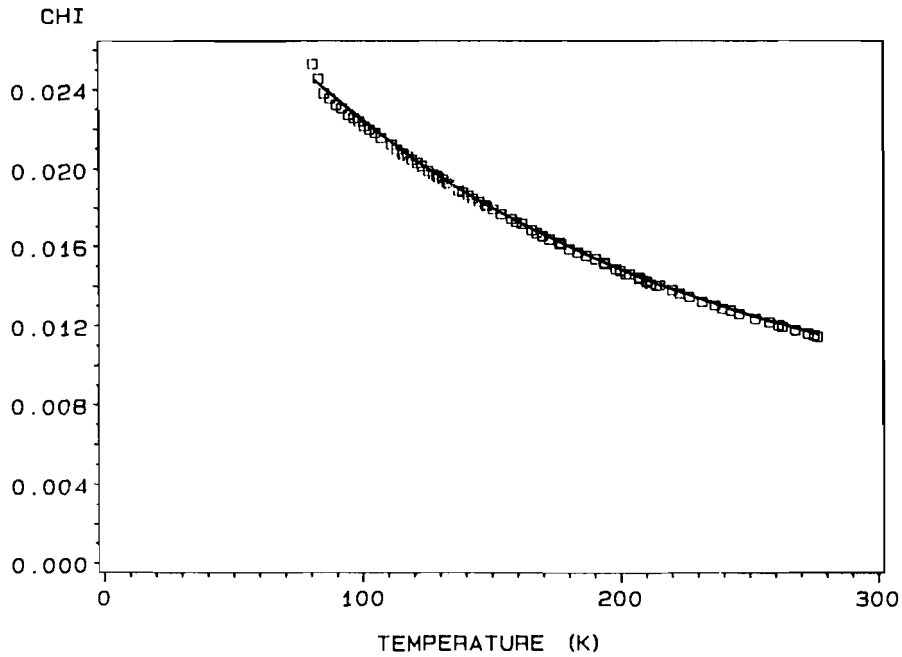

Fig. 2. Plot of measured and calculated magnetic susceptibility for $K_2[Cr(nta)(OH)(acetato\text{-}O,O)Cr(nta)]\cdot 4H_2O$.

O,O)Cr(nta)]·$4H_2O$ shows this complex to be slightly antiferromagnetic with a J/k value of -19.5 K (-13.6 cm^{-1}). This value is in the range of values observed for mono-μ-hydroxo complexes [14, 15]. Although crystal structures of two complexes containing an unsymmetrical bridge, $[Cr(en)_2(OH)(SO_4)Cr(en)_2](S_2O_6)_3\cdot 2H_2O$ [16] and $[Cr(en)_2(OH)$-(trifluoroacetate-*O,O*)$Cr(en)_2](ClO_4)_3Br\cdot H_2O$ [17], have been published, magnetic data were not reported. Exchange coupling in di-Cr(III) complexes has been correlated with the Cr(III)–OH–Cr(III) bridging angle and the orientation of the O–H bond in the bridging hydroxide [14]. The inability to locate the hydrogen atom of the μ-hydroxide in the structure reported here prevents comparison with this data.

The ^2H NMR spectrum of $[Cr(en)_2(OH)(Hnic\text{-}O,O)Cr(en)_2]^{5+}$ shows a single resonance at +3.6 ppm (Table 2). This is close to the resonances observed for other carboxylate coordinated nicotinic acid complexes (+6.7 to +9.1 ppm) [3], and distinct from the resonances observed for the pyridyl nitrogen coordinated nicotinic acid complexes (*c.* −70 ppm) [2].

The relative order of the isotropic shifts observed for the complexes containing monodentate coordinated acetate (Table 2) and amino acids [16, 17] is similar to the order observed for the complexes which contain bridging carboxylate coordinated acetate and amino acids (Table 2). As observed for the bidentate and monodentate amino acid complexes, the bridging carboxylato complex containing glycine shows a resonance which is distinctly shifted from the resonances observed for the other complexes. The amino acid sidechain is expected to have considerably greater influence on the shifts observed for the bidentate coordinated amino acids since the conformation of the chelate ring is directly related to the nature of the substituent on the 2-carbon [4]. The range of shifts observed for both the monodentate carboxyl bound amino acid complexes (the monodentate complexes, $[Cr(en)_2(Hgly\text{-}O)(OH)]^{2+}$, $[Cr(en)_2$-$(Hala\text{-}O)$-$(OH)]^{2+}$, $[Cr(en)_2(Hser\text{-}O)(OH)]^{2+}$ and $[Cr(en)_2(Hthr\text{-}O)(OH)]^{2+}$, have shifts of +37, +32, +30 and +27, respectively [5]) and the bridging carboxylate coordinated amino acid complexes (+19 to +37 and +72 to +81 ppm, respectively) is less than that observed for the complexes containing bidentate coordinated amino acids (−26 to −61 ppm). Thus, the electronic effects directly associated with the sidechain are perhaps of secondary importance, relative to the steric effects, in determining the isotropic shifts observed for the complexes containing deuterium labeled (2-carbon) amino acids.

In summary, it is evident that it is possible to establish the coordination mode of amino acids to Cr(III) in solution, and to monitor changes in coordination. Since the solvent used in these studies is often water, Cr(III)–amino acid coordination can be directly determined in crude mixtures during synthesis. Also, complexes which are difficult to isolate in a solid form (a situation frequently encountered

in Cr(III) chemistry) can be conveniently studied following purification by chromatography.

Supplementary material

Listings of anisotropic thermal parameters and structure factors, a packing diagram, and a stereoview are available from the authors on request.

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