

## Mononuclear and Binuclear Chromium(III) Picolinate Complexes

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Received June 5, 1991

The chromium(III) picolinate complexes [Cr(pic)<sub>3</sub>] (1) and [Cr(pic)<sub>2</sub>OH]<sub>2</sub> (2) (where pic = 2-carboxypyridine) have been isolated from the reaction of chromium(III) chloride and picolinic acid in aqueous solution. The monomeric complex 1·H<sub>2</sub>O (CrC<sub>18</sub>H<sub>14</sub>N<sub>3</sub>O<sub>7</sub>) crystallizes in the monoclinic space group C2/c with *a* = 30.219 (3) Å, *b* = 8.529 (1) Å, *c* = 13.942 (2) Å, β = 95.141 (1)°, *V* = 3579 (2) Å<sup>3</sup>, *Z* = 4, *R* = 0.032, and *R<sub>w</sub>* = 0.043 for 1815 reflections (*I* > 3σ(*I*)). The binuclear complex 2·5H<sub>2</sub>O (Cr<sub>2</sub>C<sub>24</sub>H<sub>28</sub>N<sub>4</sub>O<sub>15</sub>) crystallizes in the monoclinic space group P2<sub>1</sub>/*n* with *a* = 12.569 (2) Å, *b* = 18.839 (3) Å, *c* = 13.000 (4) Å, β = 105.823 (3)°, *V* = 2962 (2) Å<sup>3</sup>, *Z* = 8, *R* = 0.046, *R<sub>w</sub>* = 0.067 for 3250 reflections (*I* > 3σ(*I*)). The mononuclear complex 1 is the meridional isomer, not the facial isomer as previously assumed. For 2 the bridging geometry is as follows: Cr–Cr = 2.999 (1) Å; Cr–O(bridge) range = 1.934 (3)–1.980 (3) Å; Cr–O–Cr = 99.0 (1), 101.6(1)°, O–Cr–O = 79.4 (1), 79.9 (1)°. Magnetic susceptibility data for 2 were measured from 280 to 6 K and can be fit using an isotropic spin-exchange Hamiltonian,  $\mathcal{H} = -2J\hat{S}_1\hat{S}_2$ , with a weak antiferromagnetic interaction (*J* = –8.02 (4) cm<sup>–1</sup>), *g* = 1.844, and a 2.23 (4) mol % paramagnetic impurity. The extent of magnetic coupling in 2 is compared to predictions made by the Glerup–Hodgson–Pedersen (GHP) equation. Compounds 1 and 2 are discussed in the general context of biologically active chromium.

## Introduction

Among the motivating factors for studying chromium(III) picolinate coordination chemistry, two that we are concerned with are (i) the clarification of misconceptions in the literature regarding the prevalent isomer for [Cr(pic)<sub>3</sub>] and (ii) the evaluation of these complexes as potential bioavailable sources of chromium, an essential trace element.<sup>2a–c</sup> While claims have been made regarding the biological efficacy of chromium tris(picolinate),<sup>3a,b</sup> the issue is by no means settled (vide infra).

Prior to the work described herein, the only structurally characterized chromium picolinate complex was the hexakis(picolinato) μ<sub>3</sub>-oxo trinuclear species [Cr<sub>3</sub>O(Hpic)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](ClO<sub>4</sub>)<sub>7</sub>·6NaClO<sub>4</sub>·3H<sub>2</sub>O<sup>4,5</sup> which bears resemblance to other compounds that contain the {Cr<sub>3</sub>O}<sup>n+</sup> core.<sup>6a,b</sup> We report here the spectroscopic, structural and magnetic properties of [Cr(pic)<sub>3</sub>] (1), and [Cr(pic)<sub>2</sub>(OH)]<sub>2</sub> (2). Since the Cr(III) ion (d<sup>3</sup>) is relatively substitutionally inert, an understanding of the structures of these complexes may ultimately be useful in rationalizing the uptake and function (or lack thereof) of chromium–picolinate complexes as biologically active sources of chromium.

As implied above, chromium complexes of picolinic acid have been previously described in the literature.<sup>7–10</sup> In cases where

the geometrical isomerism was mentioned, the red [Cr(pic)<sub>3</sub>] complex was assigned as the facial isomer<sup>7,9</sup> based on comparison of its color to similar complexes such as [Co(gly)<sub>3</sub>],<sup>11</sup> [Co(pic)<sub>3</sub>],<sup>12</sup> and [Cr(gly)<sub>3</sub>].<sup>13</sup> Yuen et al.<sup>9</sup> included the red [Cr(pic)<sub>3</sub>] in a spectrochemical series of CrN<sub>3</sub>O<sub>3</sub> complexes with tris(amino carboxylate) ligands, assuming [Cr(pic)<sub>3</sub>] to be the facial isomer. Oki and Yoneda<sup>14</sup> isolated a purple complex from the reaction of [Cr(NH<sub>3</sub>)<sub>6</sub>](NO<sub>3</sub>)<sub>3</sub> with L-proline, which they demonstrated to be the bis(μ-hydroxo)tetrakis(L-prolinato)dichromium(III) dimer using X-ray crystallography. Prior to the structure solution they assumed the purple complex to be either the meridional monomer or the bis(μ-hydroxo) dimer since "all facial isomers of tris(aminoacidato)chromium(III) complexes are reported to be either pink or red in color."<sup>14</sup>

The crystal structure of the red [Cr(pic)<sub>3</sub>] complex has been solved, and we find it to be the meridional isomer. There are at least two common assumptions in the literature that have been disproven by the characterization of the complexes described here. The first is that meridional isomers of CrL<sub>3</sub> (where L = a bidentate amino carboxylate ligand) are purple and that only facial isomers are red;<sup>7,14</sup> the second, that the facial isomers are generally more stable than the meridional ones.<sup>7,15,16</sup>

The magnetic exchange interaction in 2 is discussed in relation to the Glerup–Hodgson–Pedersen (GHP) model<sup>17</sup> which corre-

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$$J = e^{-a(r-1.8)} \left[ \frac{b \cos^4 \theta}{\{(1 - \sin^2 \theta)/\tan^2(\phi/2)\}^2} - \frac{c \sin^2 \phi}{(1 - \cos \phi)^2} \right]$$

where *r* = Cr–O bond length (Å), φ = Cr–O–Cr angle (deg), θ = angle of O–H bond out of the Cr<sub>2</sub>O<sub>2</sub> plane (deg), *a* = 19 Å<sup>–1</sup>, *b* = 611 cm<sup>–1</sup>, and *c* = 172 cm<sup>–1</sup>.