

Two New Chromium(III) Complexes with the Pincer-type Pyridine-2,6-dicarboxylate Ligand

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The synthesis and crystal structures of two new salts of chromium(III) with pyridine-2,6-dicarboxylic acid H₂Pda (and 2,2'-bipyridyl, Bpy, as a co-ligand) are reported, (HPyz)[Cr(Pda)₂](H₂Pda)(H₂O)₅ (**1**) and [Cr(Pda)(Bpy)(H₂O)][Cr(Pda)₂](H₂O)₂ (**2**). Both crystal structures contain the octahedral [Cr(Pda)₂][−] anion with the pincer-type *O,N,O*-Pda^{2−} ligand. In **1**, the pyrazole additive does not act as a ligand, rather it is included as a mono-protonated cation. In **2**, both Pda^{2−}, the neutral 2,2'-bipyridyl and water are coordinating Cr³⁺ in the cation [Cr(Pda)(Bpy)(H₂O)]⁺.

Key words: Chromium, Picolinic Acid, Complexes, Crystal Structure

Introduction

The coordination chemistry of chromium(III) is excellently established. Relationships between structures and physical properties such as color and magnetism seem to be very well understood. Nevertheless, the quest for new chromium(III) complexes arises from the endless number of possible ligands and the need to design substances for special needs. Chromium in its oxidation state +3 is essential for plants and animals, and it is ranked second after calcium as a supplement to human diets, apparently playing an essential role in carbohydrate metabolism [1]. An important compound in this connection is *mer*-[Cr(Pic)₃] (Pic = picolinate = pyridine-2-carboxylate) [2] as it has a higher bioavailability than simple inorganic salts.

The picolinate anion can only act as an *N,O*-chelating ligand, as in *mer*-[Cr(Pic)₃], with the possibility to form coordination polymers. The pyridinedicarboxylates have an extended functionality; pyridine-2,6-dicarboxylic acid (H₂Pda; dipicolinic acid) in particular may coordinate as the neutral acid, as a monoanion or as a dianion, and as such it is a pincer-type ligand. Furthermore, two of these anions may coordinate to Cr(III) yielding the octahedral anion [Cr(Pda)₂][−], which has already been observed in a number of salts [3, 4].

As part of our ongoing efforts to study the competition of (multiple) *N*-donor ligands and simple in-

organic anions for coordinating important transition metal ions, such as Hg²⁺ [5], Ag⁺ [6], Cu²⁺ [7], Ni²⁺ [8], or Mn²⁺ [9], we have added Cr³⁺ to the list of our suspects. Here we report on reactions of aqueous chromium(III) chloride with dipicolinic acid as well as pyrazole or 2,2-bipyridyl.

Results and Discussion

Reactions of aqueous/alcoholic solutions of chromium(III) chloride hexahydrate, [CrCl₂(H₂O)₄]-Cl(H₂O)₂, and pyridine-2,6-dicarboxylic acid (H₂Pda) with pyrazole (Pyz) or 2,2-bipyridyl (Bpy), yielded the salts (HPyz)[Cr(Pda)₂](H₂Pda)(H₂O)₅ (**1**) and [Cr(Pda)(Bpy)(H₂O)][Cr(Pda)₂](H₂O)₂ (**2**) as large violet crystals from which small crystals suitable for single-crystal X-ray diffraction structure determinations could be cut. For details and technical results see the Experimental Section.

Both crystal structures contain the anionic complex [Cr(Pda)₂][−], in which two pincer-type *O,N,O*-Pda^{2−} ligands coordinate Cr³⁺ octahedrally, see Fig. 1. Table 1 compares the Cr–N and Cr–O distances for **1** and **2** with those of two structures which were reported in the literature for the salts [Cr(Pda)(Phen)(H₂O)][Cr(Pda)₂](H₂O)₄ (**3**) [3] and (HDpa)-[Cr(Pda)₂](H₂O)₃ (**4**) [4], where Phen is 1,10-phenanthroline and Dpa is dipyridylamine. Judging from distances alone, the CrN₂O₄ octahedra are almost reg-

Table 1. Cr–N and Cr–O distances (pm) in the anionic complexes $[\text{Cr}(\text{Pda})_2]^-$; bold letters for distances indicate averaged values.

	Cr–N	$\langle \text{Cr–N} \rangle$	Cr–O	$\langle \text{Cr–O} \rangle$
1	197.2(4), 197.9(4)	197.5(4)	198.3(4)–199.4(4)	198.7(4)
2	196.8(7), 197.3(7)	197.1(7)	197.2(7)–200.3(7)	198.2(7)
3	197.5(2), 197.7(2)	197.6(2)	196.1(2)–199.1(2)	198.3(2)
4	197.1(2), 197.7(2)	197.4(2)	196.8(2)–200.7(2)	199.0(2)

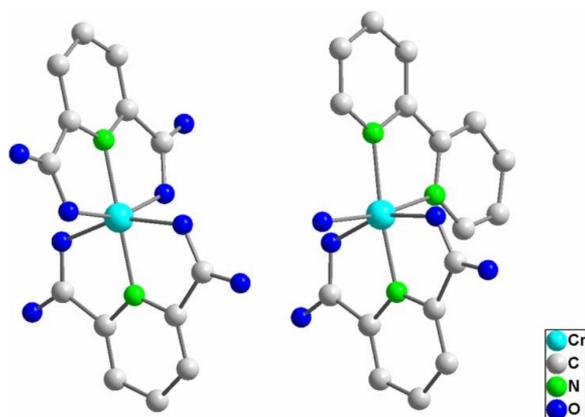
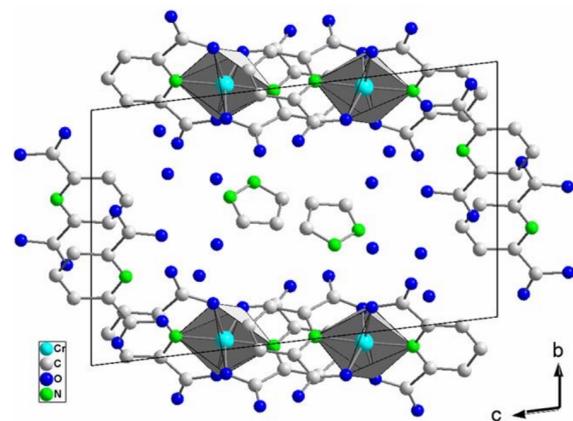


Fig. 1 (color online). Perspective view of the anion $[\text{Cr}(\text{Pda})_2]^-$ as observed in **1** and **2** (left) and the cation $[\text{Cr}(\text{Pda})(\text{Bpy})(\text{H}_2\text{O})]^+$ in **2** (right).

ular with Cr–N and Cr–O distances around 198 pm. However, the angles deviate considerably from 90° and 180° , with the N–Cr–N angle at $177.4(2)^\circ$ and O–Cr–O angles of $90.9(2)$, $91.2(2)$ and $93.5(2)^\circ$ closest to ideal. The N–Cr–O angles deviate most, ranging from $78.6(2)$ to $103.6(2)^\circ$ (data refer to **1**).

The crystal structure of $(\text{HPyz})[\text{Cr}(\text{Pda})_2](\text{H}_2\text{Pda})(\text{H}_2\text{O})_5$ (**1**) contains non-coordinating dipicolinic acid



as well as five water molecules per formula unit. The cation is a protonated pyrazole (1,2-diazole) molecule, HPyz. Fig. 2 shows a projection of the crystal structure of **1**.

The crystal structure of $[\text{Cr}(\text{Pda})(\text{Bpy})(\text{H}_2\text{O})][\text{Cr}(\text{Pda})_2](\text{H}_2\text{O})_2$ (**2**) contains the heteroleptic cation $[\text{Cr}(\text{Pda})(\text{Bpy})(\text{H}_2\text{O})]^+$, see Fig. 1. Again, Cr^{3+} is octahedrally coordinated, this time by the pincer-type ligand Pda^{2-} , the chelating ligand Bpy and one water molecule. Hence, the octahedron is constituted by the ligating atoms $\text{Cr}(\text{ONO})(\text{O})(\text{NN})$ with distances of 193.6(7), 196.3(7), 198.8(8), 197.7(7), 204.4(9), and 204.6(8) pm. The Cr(ONO) distances are slightly shorter than in the $[\text{Cr}(\text{Pda})_2]^-$ anions, compare with Table 1. The Cr–N distances of 204.5 pm (av.) to the Bpy ligand are considerably larger than to the Pda^{2-} ligand. However, they are very close to those found in **3** with the cation $[\text{Cr}(\text{Pda})(\text{Phen})(\text{H}_2\text{O})]^+$ containing 1,10-phenanthroline instead of 2,2'-bipyridyl, 206.4(2) and 207.0(2) pm [3]. Fig. 2 shows the arrangement of the cations and anions in the crystal structure of **2**. The cation/anion pairs are arranged in layers parallel (001) and stacked in the [001] direction.

Hydrogen bonding plays, if any, only a minor role in both structures, as an analysis of the possible donor-acceptor distances shows. In **1**, space appears to be filled very well (Fig. 2), with small cations and large anions producing the major part of the lattice energy, and non-coordinating dipicolinic acid and water filling empty space. In **2**, the packing is dominated by complex cations and anions of similar size and shape, forming layers roughly parallel (001) (Fig. 3).

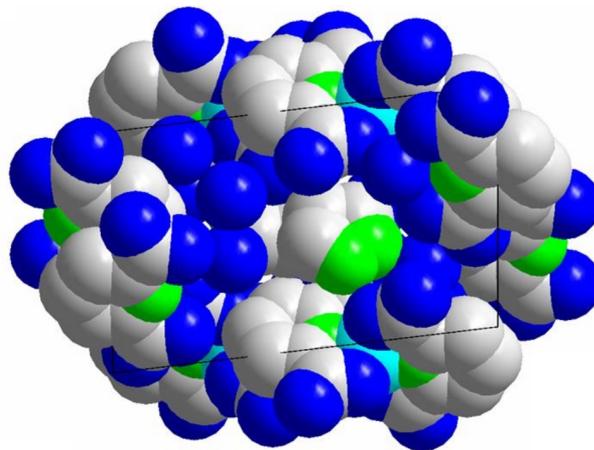


Fig. 2 (color online). Perspective projection of the crystal structure of $(\text{HPyz})[\text{Cr}(\text{Pda})_2](\text{H}_2\text{Pda})(\text{H}_2\text{O})_5$ (**1**) onto (100), ball-and-stick and space-filling models.

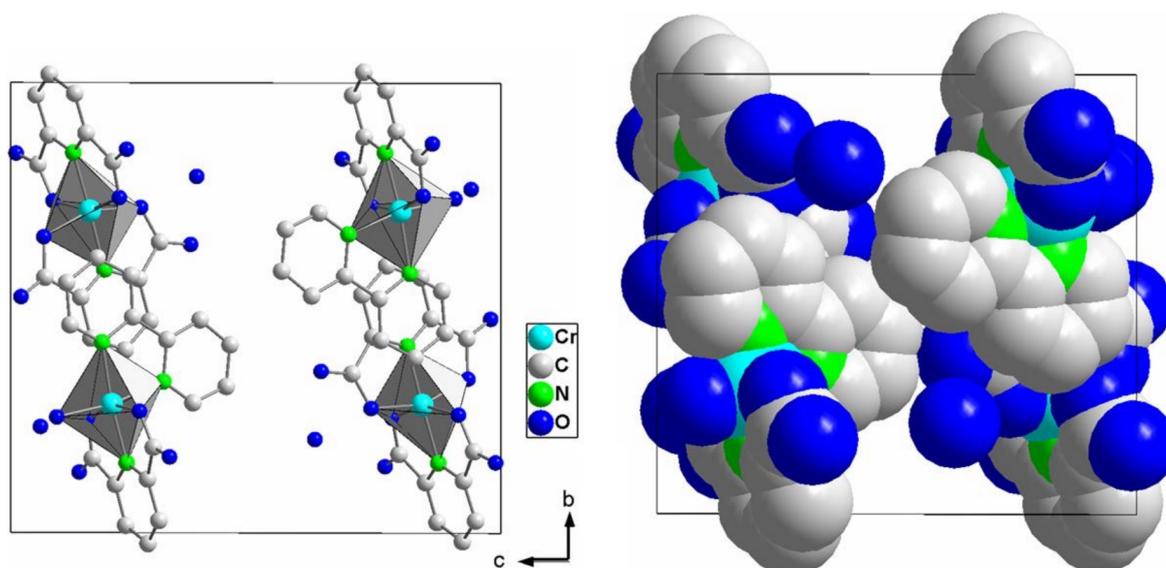


Fig. 3 (color online). Perspective projection of the crystal structure of $[\text{Cr}(\text{Pda})(\text{Bpy})(\text{H}_2\text{O})][\text{Cr}(\text{Pda})_2](\text{H}_2\text{O})_2$ (**2**) onto (100), ball-and-stick and space-filling models.

Experimental Section

Syntheses

$(\text{HPyz})[\text{Cr}(\text{Pda})_2](\text{H}_2\text{Pda})(\text{H}_2\text{O})_5$ (**1**)

20 mL of a 0.01 M aqueous solution of chromium(III) chloride, $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}(\text{H}_2\text{O})_2$, 40 mL of a 0.01 M ethanolic solution of pyrazole ($\text{C}_3\text{H}_4\text{N}_2$), and 40 mL of a 0.01 M aqueous solution of pyridine-2,6-dicarboxylic acid ($\text{C}_7\text{H}_5\text{NO}_4$) were mixed and stirred continuously with moderate heating at 50–55 °C for 10 to 13 h. The purple solution was covered with perforated Parafilm™ and kept at r. t. until a violet crystalline solid was obtained.

$[\text{Cr}(\text{Pda})(\text{Bpy})(\text{H}_2\text{O})][\text{Cr}(\text{Pda})_2](\text{H}_2\text{O})_2$ (**2**)

20 mL of a 0.02 M ethanolic solution of chromium(III) chloride, $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}(\text{H}_2\text{O})_2$, 20 mL of a 0.02 M methanolic solution of pyridine-2,6-dicarboxylic acid ($\text{C}_7\text{H}_5\text{NO}_4$) and 40 mL of a methanolic solution of 2,2'-bipyridyl, $\text{C}_{10}\text{H}_8\text{N}_2$, were mixed in a beaker, and the resulting purple solution was stirred continuously for 5 h at 30 °C. This solution was kept at r. t.; after one week, violet prismatic crystals were isolated.

Crystal structure determinations

Single crystals of $(\text{HPyz})[\text{Cr}(\text{Pda})_2](\text{H}_2\text{Pda})(\text{H}_2\text{O})_5$ (**1**) and of $[\text{Cr}(\text{Pda})(\text{Bpy})(\text{H}_2\text{O})][\text{Cr}(\text{Pda})_2](\text{H}_2\text{O})_2$ (**2**) were selected directly from the mother liquors under a microscope and sealed in thin-walled glass capillaries. Their quality was checked on a single-crystal X-ray diffractometer

(Stoe Image Plate Diffraction System, IPDS I), and complete intensity data sets were collected at ambient temperature using graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 71.073$ pm). The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on crystal shape optimization was applied for all data. The structures were solved by Direct Methods and completed by difference Fourier maps. Hydrogen atoms were placed in idealized positions and constrained to ride on their respective parent atom. The H_2O molecules were refined without H atoms. The last refinement cycles included atomic positions for all atoms, with anisotropic displacement parameters for all non-hydrogen atoms and isotropic displacement parameters for all hydrogen atoms. The programs used in this work are Stoe's X-AREA [10], including X-RED [11] and X-SHAPE [12] for data reduction and absorption correction, respectively, and the WINGX suite of programs [13], including SIR-92 [14] and SHELXL-97 [15] for structure solution and refinement.

CCDC 818705 (**1**) and 818706 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data

$(\text{HPyz})[\text{Cr}(\text{Pda})_2](\text{H}_2\text{Pda})(\text{H}_2\text{O})_5$ (**1**): $\text{C}_{24}\text{H}_{26}\text{N}_5\text{O}_{17}\text{Cr}$, 708.50 g mol^{-1} ; $T = 293(2)$ K; triclinic, $P\bar{1}$ (no. 2), $a = 913.4(2)$, $b = 1022.4(2)$, $c = 1666.8(3)$ pm, $\alpha = 96.67(2)$, $\beta = 102.83(2)$, $\gamma = 90.32(2)^\circ$, $V = 1506.5(5) \times 10^6$ pm³,

$Z = 2$; $\rho_{\text{calc}} = 1.56 \text{ g cm}^{-3}$; $F(000) = 730 \text{ e}$; $\mu(\text{MoK}\alpha) = 0.5 \text{ mm}^{-1}$; $2\theta_{\text{max}} = 56.3^\circ$; $0^\circ \leq \varphi \leq 250^\circ$, $\Delta\varphi = 2^\circ$, 125 images; hkl range: $-9 \leq h \leq 9$, $-12 \leq k \leq 12$, $-19 \leq l \leq 19$; 13304 measured reflections of which 4975 were symmetrically independent; $R_{\text{int}} = 0.0538$; 425 refined parameters; R values: R_1/wR_2 for 3136 reflections with $[I_0 \geq 2\sigma(I_0)]$: 0.0700 / 0.1833, for all data: 0.1076 / 0.1970; $S_{\text{all}} = 1.132$; $\Delta\rho_{\text{fin}}$ (max / min): $0.58 / -0.44 \times 10^6 \text{ e pm}^{-3}$.

$[\text{Cr}(\text{Pda})(\text{Bpy})(\text{H}_2\text{O})][\text{Cr}(\text{Pda})_2](\text{H}_2\text{O})_2$ (**2**): $\text{C}_{31}\text{H}_{23}\text{N}_5\text{O}_{15}\text{Cr}_2$, 809.54 g mol^{-1} ; $T = 293(2) \text{ K}$; triclinic, $P\bar{1}$ (no. 2), $a = 837.0(1)$, $b = 1491.4(3)$, $c = 1589.4(4) \text{ pm}$, $\alpha = 88.24(2)$, $\beta = 82.11(2)$, $\gamma = 78.18(1)^\circ$, $V = 1923.6(6) \times 10^6 \text{ pm}^3$, $Z = 2$; $\rho_{\text{calc}} = 1.40 \text{ g cm}^{-3}$; $F(000) = 824 \text{ e}$;

$\mu(\text{MoK}\alpha) = 0.6 \text{ mm}^{-1}$; $2\theta_{\text{max}} = 56.3^\circ$; $0^\circ \leq \varphi \leq 250^\circ$, $\Delta\varphi = 2^\circ$, 125 images; hkl range: $-9 \leq h \leq 9$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$; 10423 measured reflections of which 5139 were symmetrically independent; $R_{\text{int}} = 0.0526$; 479 refined parameters; R values: R_1/wR_2 for 2431 reflections with $[I_0 \geq 2\sigma(I_0)]$: 0.0739 / 0.1996, for all data: 0.1499 / 0.2280; $S_{\text{all}} = 1.046$; $\Delta\rho_{\text{fin}}$ (max / min): $1.29 / -0.34 \times 10^6 \text{ e pm}^{-3}$.

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- [1] a) F. Mirasol, *Chem. Mark. Rep.* **2000**, 257, 26; b) W. Mertz, K. Schwarz, *Am. J. Physiol.* **1959**, 196, 614; c) W. Mertz, K. Schwarz, *Am. J. Physiol.* **1959**, 196, 614.
- [2] D. M. Staerns, W. H. Armstrong, *Inorg. Chem.* **1992**, 31, 5178–5184.
- [3] M. Rafizadeh, V. Amani, B. Neumüller, *Z. Anorg. Allg. Chem.* **2006**, 632, 2190–2192.
- [4] V. C. R. Payne, O. St. C. Headley, R. T. Stibrany, P. T. Maragh, T. P. Dasgupta, A. M. Newton, A. A. Holder, *J. Chem. Crystallogr.* **2007**, 37, 309–314.
- [5] a) G. Meyer, P. Nockemann, *Z. Anorg. Allg. Chem.* **2003**, 629, 1447–1461; b) M. Nolte, Dissertation, Universität zu Köln, Köln **2005**.
- [6] a) G. Meyer, M. Sehabi, I. Pantenburg in *Design and Construction of Coordination Polymers* (Eds.: M.-C. Hong, L. Chen), John Wiley, **2009**, chapter 1, pp. 1–23; b) C. Link, Dissertation, Universität zu Köln, Köln **2010**.
- [7] I. Pinkert, Dissertation, Universität zu Köln, Köln **2011**.
- [8] V. Abramov, Dissertation, Universität zu Köln, Köln **2011**.
- [9] N. Cesur, Dissertation, Universität zu Köln, Köln **2006**.
- [10] X-Area (version 1.15), Stoe & Cie GmbH, Darmstadt (Germany) **2005**.
- [11] X-RED (version 1.22), Stoe & Cie GmbH, Darmstadt (Germany) **2005**.
- [12] X-SHAPE (version 1.06), Stoe & Cie GmbH, Darmstadt (Germany) **1999**.
- [13] L. J. Farrugia, WINGX, A MS-Windows System of Programs for Solving, Refining and Analysing Single X-ray Diffraction Data for Small Molecules, University of Glasgow, Glasgow, Scotland (U. K.) **2005**. See also: L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, 32, 837–838.
- [14] A. Altomare, G. Cascarano, C. Giacovazzo, A. Gualardi, SIR92, A Program for Automatic Solution of Crystal Structures by Direct Methods; see: *J. Appl. Crystallogr.* **1993**, 26, 343–350.
- [15] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, A64, 112–122.