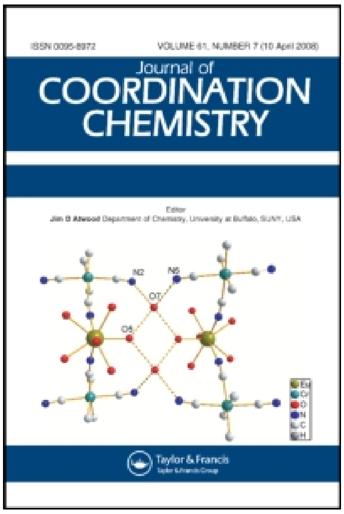

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Crystal structure of a calcium(II) complex with pyrazine-2,3-dicarboxylate, nitrate and water ligands

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Crystal structure of a calcium(II) complex with pyrazine-2,3-dicarboxylate, nitrate and water ligands

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The structure of *catena*-[tris(aquo-*O*)(nitrato-*O*,*O*′)(μ-hydrogen pyrazine-2,3-dicarboxylato-*O*,*N*–*O*′,*N*′)calcium(II)][tetra(aquo-*O*)(μ-hydrogen pyrazine-2,3-dicarboxylato-*O*,*N*–*O*′,*N*′) calcium(I)] nitrate, $\{Ca[H(2,3\text{-}PZDC)](H_3O)_3(NO_3)\}\{Ca[H(2,3\text{-}PZDC)](H_2O)_4\}^+ (NO_3)^-$, is composed of molecular ribbons in which calcium atoms are bridged by both N,O-bonding moieties of singly deprotonated ligand molecules. The hydrogen atom donated by one carboxylic group is linked by a short intramolecular hydrogen bond of 2.37 Å to an oxygen atom of the second carboxylic group of the same ligand. Two crystallographically independent Ca(II) ions exhibit different coordination modes. One is coordinated by two bonding moieties of the bridging ligand molecules, three water oxygen atoms and two oxygen atoms of a nitrate ligand. The other calcium ion is chelated by two bonding moieties donated by the bridging ligand molecules and four water oxygen atoms, forming a positively charged assembly with a nitrate anion located nearby. The coordination polyhedron of the first calcium ion is a strongly deformed bicapped pentagonal bipyramid with nine-coordinated atoms; the second calcium ion is also in a strongly deformed pentagonal bipyramid with one apex on one side of the equatorial plane and two apices on the other. Coordinated water oxygen atoms act as donors in a hydrogen-bond network.

Keywords: Calcium complexes; Pyrazine-2,3-dicarboxylate ligand; Crystal structure

1. Introduction

In the course of our structural studies on calcium(II) coordination compounds with azine and diazine dicarboxylate ligands we have observed that, depending on the type of calcium salt used in the preparation, complexes with different structures are obtained. Two Ca(II) complexes with pyrazine-2,3-dicarboxylate ligands have been synthesized and their crystal structures determined. One of them was obtained by reacting the parent acid with calcium carbonate [1], the other with calcium chloride dissolved in 1 N hydrochloric acid [2]. Both complexes show polymeric molecular patterns. The reaction of pyrazine-2,3-dicarboxylic acid dihydrate with an excess of calcium nitrate yielded

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a compound with a different crystal structure, namely *catena*-[tris(aquo-*O*)(nitrato-*O*,*O*′)(μ-hydrogen pyrazine-2,3-dicarboxylato-*O*,*N*–*O*′,*N*′)calcium(II)] [tetra(aquo-*O*)(μ-hydrogen pyrazine-2,3-dicarboxylato-*O*,*N*–*O*′,*N*′)calcium(I)] nitrate, {Ca[H(2,3-PZDC)]$(H_3O)_3(NO_3)$}{Ca[H(2,3-PZDC)]$(H_2O)_4$}$^+$$(NO_3)^-$, which is described in this article.

2. Experimental

Two 50-mL aqueous solutions, one containing 1 mmol of pyrazine-2,3-dicarboxylic acid dihydrate (Aldrich) and the other ca 2 mmol of calcium nitrate tetrahydrate (Aldrich), were mixed and boiled with stirring for 1 h. After keeping the mixture at room temperature for 2 days, several colorless, rectangular single crystals were obtained from the mass of polycrystalline material. The dimensions of a crystal selected for collecting X-ray diffraction data are given in table 1. X-ray reflections were measured at room temperature using a KUMA KM4 four-circle diffractometer operating in the ω–2θ mode. Unit cell parameters were obtained by least-squares fit to 25 reflections ($15^\circ < 2\theta < 30^\circ$). Reflections were processed using profile analysis and corrected for Lorentz factor and polarization effects. Analytical absorption correction was applied. Nonhydrogen atoms were located by the direct method using the SHELXLS

Table 1. Crystal data and structure refinement details for {Ca[H(2,3-PZDC)]$(H_3O)_3(NO_3)$}{Ca[H(2,3-PZDC)]$(H_2O)_4$}$^+$$(NO_3)^-$.

Empirical formula	$C_{12}H_{10}N_6O_{21}Ca_2$
Formula weight	664
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 16.134(3)$ Å
	$b = 6.306(1)$ Å
	$c = 25.360(3)$ Å
	$\beta = 108.06(3)^\circ$
	$V = 2453.03$ Å^3
Z	4
Calculated density	1.799 g cm^{-3}
μ(Mo Kα)	0.58 mm^{-1}
$F(000)$	1368°
Crystal size	$0.10 \times 0.20 \times 0.60$ mm^3
Max 2θ for data collection	60.22°
Index range	$-22 \le h \le 22$, $-8 \le k \le 0$, $-33 \le l \le 0$
No. of measured reflections	7070
No. of unique reflections with $F_o > 4\sigma(F_o)$	4274
R_{int}	0.0466
Method of structure solution	Direct method
Method of structure refinement	Full-matrix least-squares on F^2
No. of parameters refined	450
Goodness-of-fit on F^2	0.978
Absorption correction	Analytical
Min. and max. transmission factors	0.7484; 0.9235
Final $R1$ [$F_o > 4\sigma(F_o)$]	0.0316
Final $wR2$ index	0.0914
Largest diff. peak and hole	0.37 and -0.30 e/Å^3
Weight parameters (A, B)	0.0512, 0.00
Mean shift/esd	0.0001

program [3] and hydrogen atoms then found by successive Fourier syntheses. Final refinement on F^2 by full-matrix least-squares techniques was performed on the positional parameters of all atoms, anisotropic temperature factors of all non-H-atoms and isotropic temperature factors of the hydrogen atoms. The weighting scheme was used in the form: $w=1/[\sigma^2(F_o^2)+(AP)^2+BP]$, where $P=[\max(F_o^2,0)+2F_c^2]/3$. The A and B parameters, as well as other experimental details, are listed in table 1. Calculations were carried out using the SHELXL97 program [4]. Selected bond lengths and angles are given in table 2. Listings of the observed and calculated structure factors,

Table 2. Selected bond distances (Å) and angles (°) for $\{Ca[H(2,3\text{-PZDC})](H_3O)_3(NO_3)\}$ $\{Ca[H(2,3\text{-PZDC})](H_2O)_4\}^+(NO_3)^-$.

Ca1 coordination			
Ca1–O1	2.429(2)	O1–Ca1–N1	59.13(4)
Ca1–N1	2.830(1)	O22–Ca1–N22	58.72(4)
Ca1–O22	2.390(2)	N1–Ca1–O17	75.73(5)
Ca1–N22	2.820(1)	O17–Ca1–N22	79.54(5)
Ca1–O15	2.458(2)	N22–Ca1–O15	75.40(6)
Ca1–O16	2.428(2)	O15–Ca1–O16	71.36(7)
Ca1–O17	2399(2)	O16–Ca1–N1	72.90(5)
Ca1–O12	2.638(2)	O12–Ca1–O13	24.32(4)
Ca1–O13	2.560(2)	O1–Ca1–N1	72.92(5)
Pyrazine-2,3-dicarboxylate ligand 1			
N1–C2	1.373(1)	C6–N1–C2	117.1(1)
C2–C3	1.397(2)	N1–C2–C3	121.0(1)
C3–N2	1.397(2)	C2–C3–N2	120.3(1)
N2–C5	1.316(2)	C3–N2–C5	118.1(1)
C5–C6	1.392(2)	N2–C5–C6	121.1(1)
C6–N1	1.318(2)	C5–C6–N1	122.2(1)
C2–C7	1.519(2)		
C7–O1	1.228(2)	O1–C7–O2	122.5(1)
C7–O2	1.275(2)		
C3–C8	1.517(2)		
C8–O3	1.229(2)	O3–C8–O4	121.5(1)
C8–O4	1.284(2)		
O2–H10 ··· O4	2.393(3)	O2–H10–O4	175(4)
Coordinated water molecules			
O15–H151	0.69(3)	H151–O15–H152	110(3)
O15–H152	0.80(4)		
O16–H161	0.92(3)	H161–O16–H162	101(3)
O16–H162	0.76(3)		
O17–H171	0.72(3)	H171–O17–H172	114(3)
O17–H172	0.79(3)		
Coordinated nitrate group			
N11–O11	1.218(2)	O11–N11–O12	121.0(2)
N11–O12	1.248(2)	O12–N11–O13	118.0(2)
N13–O13	1.244(2)	O13–N11–O11	121.0(2)
Ca2 coordination			
Ca2–O3	2.429(1)	O3–Ca2–N2	62.50(5)
Ca2–N2	2.611(1)	O23–Ca2–N21	62.31(4)
Ca2–N21	2.653(1)	O25–Ca2–O26	73.76(6)
Ca2–O23	2.334(1)	O26–Ca2–O28	75.51(6)
Ca2–O25	2.382(2)	O28–Ca2–O27	71.18(6)
Ca2–O26	2.369(2)	O27–Ca2–O3	72.70(4)
Ca2–O27	2.519(1)	O3–Ca2–O25	72.05(5)
Ca2–O28	2.422(2)	N2–Ca2–O27	159.85(4)

(continued)

Table 2. Continued.

Pyrazine-2,3-dicarboxylate ligand 2			
N21–C22	1.337(2)	C26–N21–C22	118.2(1)
C22–C23	1.403(2)	N21–C22–C23	120.2(2)
C23–N22	1.336(2)	C22–C23–N22	120.9(2)
N22–C25	1.317(2)	C23–N22–C25	117.8(2)
C25–C26	1.387(2)	N22–C25–C26	121.6(2)
C26–N21	1.320(2)	C25–C26–N21	121.2(2)
C22–C27	1.517(2)		
C27–O21	1.259(2)	O21–C27–O22	121.7(2)
C27–O22	1.226(1)		
C23–C28	1.527(2)		
C28–O23	1.224(2)	O23–C28–O24	121.6(2)
C28–O24	1.259(2)		
O21–H21···O24	2.374(3)	O21–H21–O24	176(4)
Coordinated water molecules			
O25–H251	0.77(3)	H251–O25–H252	110(3)
O25–H252	0.75(3)		
O26–H261	0.77(3)	H262–O26–H262	113(3)
O26–H262	0.84(3)		
O27–H271	0.77(3)	H271–O27–H272	100(3)
O27–H272	0.85(3)		
O28–H281	0.82(4)	H281–O28–H282	100(3)
O28–H282	0.86(4)		
Nitrate anion			
N31–O31	1.240(2)	O31–N31–O32	121.1(2)
N31–O32	1.282(2)	O32–N31–O33	120.9(2)
N31–O33	1.257(2)	O33–N31–O32	118.0(2)

Hydrogen bonds

Intrachain

D–H···A	d(D–H···A)	d(D–H)	d(H···A)	D–H–A
O2–H10···O4	2.393(2)	1.18(3)	1.21(3)	175(3)
O21–H21···$\mathrm{O24}^{\mathrm{I}}$	2.374(2)	1.13(4)	1.24(5)	176(4)
O15–H152···O16	2.850(3)	0.80(4)	2.51(3)	107(3)
O16–H161···O22	2.973(3)	0.70(3)	2.89(4)	89(3)
O17–H171···O13	2.999(2)	0.72(3)	2.88(3)	93(2)
O25–H252···O26	2.851(2)	0.75(3)	2.88(3)	80(3)
O26–H261···O25	2.851(2)	0.77(3)	2.63(3)	99(2)
O26–H262···O28	2.991(3)	0.84(3)	2.86(3)	86(2)
O28–H281···O27	2.876(3)	0.86(3)	2.69(4)	94(3)
O17–H172···O1	2.819(2)	0.79(3)	2.58(3)	100(2)
O25–H251···O3	2.819(2)	0.77(3)	2.67(3)	94(2)
O27–H272···O3	2.933(2)	0.85(3)	2.76(3)	92(2)
Coordinated water molecules as donors				
O15–H151···$\mathrm{O13}^{\mathrm{II}}$	2.962(2)	0.70(3)	2.28(3)	170(3)
O16–H162···O33	2.868(3)	0.92(4)	1.98(4)	164(3)
O17–H171···$\mathrm{O22}^{\mathrm{III}}$	2.798(2)	0.72(3)	2.12(3)	157(4)
O17–O172···$\mathrm{O3}^{\mathrm{IV}}$	2.962(2)	0.80(3)	2.21(3)	159(3)
O25–H251···$\mathrm{O1}^{\mathrm{IV}}$	2.872(2)	0.77(3)	2.11(3)	173(3)
O26–H261···$\mathrm{O27}^{\mathrm{III}}$	2.788(2)	0.77(3)	2.04(3)	167(3)
O26–H262···$\mathrm{O33}^{\mathrm{V}}$	2.769(2)	0.84(3)	1.98(3)	155(3)
O27–H271···O31	2.740(2)	0.77(3)	1.97(3)	175(3)
O27–H272···$\mathrm{O2}^{\mathrm{VI}}$	2.891(2)	0.85(3)	2.10(3)	156(3)
O28–H282···$\mathrm{O12}^{\mathrm{V}}$	2.990(3)	0.82(4)	2.21(4)	160(4)

Symmetry codes: (I): $x+1$, y, z; (II): $-x+1$, $-y+2$, $-z+1$; (III): x, $y+1$, z; (IV): $-x$, $y+1/2$, $-z+1/2$; (V): $-x$, $-y+2$, $-z+1$; (VI): $-x$, $y-1/2$, $-z+1/2$.

final atomic coordinates and anisotropic thermal parameters can be obtained on request from the authors. Detailed data on the structure of the title compound have also been deposited with Cambridge Crystallographic Data Centre, CCDC No. 238303.

3. Discussion

The structure of the title compound is composed of molecular ribbons in which Ca(II) ions are bridged by singly deprotonated H(2,3-PZDC) ligands through their N,O-bonding moieties. The mode of bridging is illustrated in figure 1 and the atom-numbering scheme is shown in figure 2. The ribbons are aligned along the *a* axis and contain two symmetry-independent Ca ions, two H(2,3-PZDC) and two nitrate molecules. The molecular pattern observed shows two unusual features that were not encountered earlier in the structures of Ca(II) complexes with diazine dicarboxylate ligands: the occurrence of Ca ions with different coordination modes and numbers and the existence of a local polarization caused by the positive charge on one Ca ion and the localization of a nitrate anion near it. One of the calcium ions (Ca1) coordinates nine atoms: two N,O-bonding moieties, each donated by different 2,3-PZDC ligands (N1, O1 and N22, O22), three water oxygen atoms (O15, O16, O17) and two oxygen atoms from a nitrate ligand (O12, O13). The coordination polyhedron is a bicapped pentagonal bipyramid with a strongly distorted pentagonal equatorial plane composed of Ca1, N1, N22, O15, O16 and O17 atoms. Maximum and minimum shifts from the average plane are +0.794 Å (O15) and −0.654 Å (O16) respectively, and the mean deviation from the plane is 0.383 Å. The double apices on both sides of the equatorial plane are formed by the nitrate oxygen atoms (O12 and O13) and two carboxylate oxygen atoms (O1 and O22). The other calcium ion (Ca2) is also coordinated by two bonding moieties of adjacent ligands (N2, O3 and N21, O23) and four water oxygen atoms (O25, O26, O27, O28). The coordination polyhedron is a pentagonal bipyramid with two apices (N21, O23) on one side of the equatorial plane and one apex (N2) on the other side. The strongly distorted equatorial plane is composed of Ca2, O3, O25, O26, O27 and O28 atoms. Maximum deviation from the average plane is shown by the O26 atom (+0.629 Å), and the minimum deviation by the O25 atom

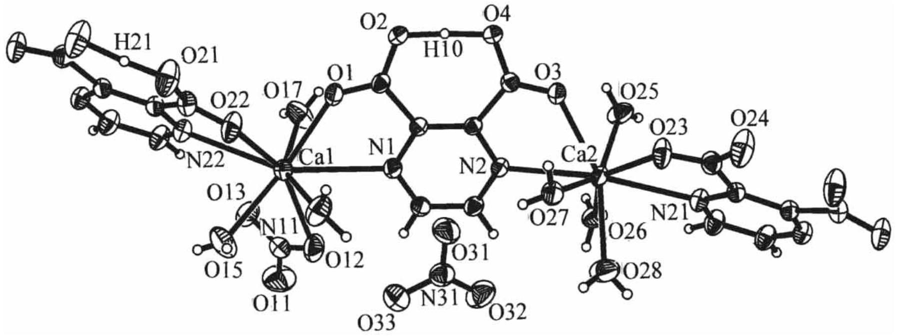

Figure 1. $\{Ca[H(2,3\text{-}PZDC)](H_3O)_3(NO_3)\}\{Ca[H(2,3\text{-}PZDC)](H_2O)_4\}^+(NO_3)^-$ molecular assembly with atom-labeling scheme. The nonhydrogen atoms are shown at the 50% probability level. For clarity, the pyrazine ring carbon atoms are not marked.

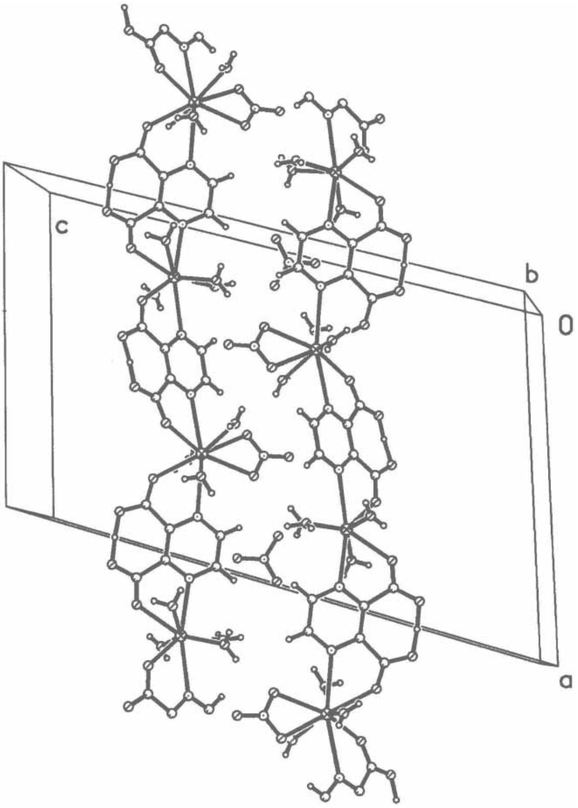

Figure 2. The alignment of molecular chains with respect to the unit cell in the structure of {Ca[H(2,3-PZDC)](H_3O)$_3$(NO_3)}{Ca[H(2,3-PZDC)](H_2O)$_4$}$^+$(NO_3)$^-$. For clarity, only two chains are shown.

(−0.447 Å). The mean shift is 0.351 Å. The pyrazine rings of crystallographically independent ligands are planar, with mean deviations from the plane amounting to 0.014 and 0.0011 Å for ligands 1 and 2, respectively. The planes of the carboxylate groups make dihedral angles with the plane of the ligand 1 pyrazine ring of 18.3° (C7, O1, O2) and 18.4° (C8, O3, O4). The relevant angles in the case of ligand 2 are 18.40° (C27, O21, O22) and 8.0° (C28, O23, O24). The bond lengths and angles determined for both ligands agree reasonably well with those reported for the parent acid [5]. However, one carboxylate group in the molecule of the acid is coplanar with the pyrazine ring, the other makes an angle of 90°. Both pyrazine-2,3-dicarboxylate ligands in the title compound are singly deprotonated. Hydrogen atoms attached to carboxylate oxygen atoms form short, almost straight intrachain hydrogen bonds O2–H10 ··· O4 with $d = 2.393(3)$ Å and O21–H21 ··· O24^{I} with $d = 2.374(3)$ Å (for further details, see table 2).

Adjacent molecular ribbons are linked by a network of hydrogen bonds operating between coordinated water molecules acting as donors and carboxylate oxygen atoms as well as coordinated nitrate oxygen atoms acting as acceptors. The lengths of these bonds fall in the range 2.79–3.00 Å (table 2). It is interesting to note that the oxygen atoms of the nitrate anion (O31 and O33) are acceptors of hydrogen bonds donated by coordinated water molecules: d(O27–H271 ··· O31) = 2.740(3) Å and d(O16–H161 ··· O33) = 2.868(3) Å. The other distances to the oxygen atoms of the nitrate anion are longer than 3.2 Å.

The other interesting feature is the presence of intrachain hydrogen bonds operating between coordinated water molecules with O–H–O bond angles close to 90° [as, for example, O26–H262 ··· O28; d = 2.9333(2) Å, bond angle = 86°] and coordinated water molecules and carboxylate oxygen atoms [as, for example, O27–H272 ··· O3; d = 2.993(2) Å, bond angle = 92(2)°]. The other bonds of this type are listed in table 2.

The "neutral" complex Ca[(2,3-PZDC)(H_3O)$_2$] dihydrate obtained when calcium carbonate was used for its preparation exhibits a two-dimensional layered molecular pattern [1]. The structure of the title compound may be viewed as the result of accommodation of fairly large nitrate groups, partly coordinated to Ca(II) ions and partly appearing as separate anions, leading to the collapse of the two-dimensional network and formation of a catenated pattern composed of polycationic ribbons and nitrate anions. A similar mechanism was observed when calcium chloride dissolved in 1 N hydrochloric acid was used for chemical synthesis. The structure of the resulting complex contains $\{Ca[H(2,3\text{-}PZDC)](H_2O)_4\}^+$ polycationic ribbons and Cl^- anions located between the ribbons [2].

The structure of the title compound provides evidence for a tendency observed in divalent ion complexes with 2,3-PZDC ligand to form catenated molecular patterns. Two general structural classes can be distinguished. In the first, metal ions bridged by 2,3-PZDC ligands form single chains, with the bridging path aligned along the propagation direction of the chain. In the second, metal ions form either single or double chains, but with the bridging 2,3-PZDC molecules aligned normal to the propagation direction of the chains. The first class comprises four structure types:

- M(2,3-PZDC)(H_2O)$_2$ · 2H_2O (M = Co, Ni, Cu [6], Co [7], Cu [8, 9]. Metal ions form single chains bridged by the ligands, which use both N,O-bonding moieties. Octahedral coordination around the metal ion is completed by two water oxygen atoms in axial positions.
- Cu[H(2,3-PZD)$_2$] · 2H_2O [6]. Cu(II) ions are bridged by two ligands oriented *trans*. Each ligand uses one N,O-bonding moiety and one oxygen atom donated by the second carboxylic group.
- (H_3O)$_2$M(2,3-PZDC)$_2$ (M = Mn, Cd [10], Zn [11]). Metal ions are bridged by two ligands in *cis*-configuration, each contributing one N,O-bonding moiety and one oxygen atom of the second carboxylic group. Electrical neutrality is maintained by hydronium cations located in the lattice.
- Ca[H(2,3-PZD)(H_2O)$_4$]Cl [2] and the title compound. In both structures the ligand bridges the Ca(II) ions using both its bonding moieties.

In the second class two structure types can be distinguished:

- M(2,3-PZDC)(H_2O)$_3$ · H_2O (M = Cd [10], Mg [12], Zn [13]). Metal ions are bridged by one N,O-bonding moiety and one oxygen atom of the second carboxylate group, giving rise to a zigzag molecular ribbon in which the plane of the bridging ligand is normal to the direction of the chain.
- M(2,3-PZDC)(H_2O)$_2$ · H_2O (M = Mn, Cd [10], Zn [14]). The metal ions form double chains cross-linked by the ligands, which use their N,O-bonding moieties and both oxygen atoms of the second carboxylate group for bridging. A "ladder"-type

molecular ribbon is thus formed, extending in the direction perpendicular to the ligand planes.

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