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# Thermal evolution and crystal structures of the 3,5-pyrazole dicarboxylic acid (hydrated form and anhydrous): Ligations with nickel II and barium II

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#### Abstract

A crystalline form of anhydrous 3,5-pyrazole dicarboxylic acid (H<sub>3</sub>pdc), H<sub>3</sub>pdc- $\alpha$ , which is the most stable form at room temperature, has been identified by a variable temperature diffraction study of the commercial form, H<sub>3</sub>pdc,H<sub>2</sub>O. Single crystals of H<sub>3</sub>pdc,H<sub>2</sub>O, anhydrous H<sub>3</sub>pdc- $\beta$ , the high temperature form, as well as Ni(Hpdc),4H<sub>2</sub>O and Ba(H<sub>2</sub>pdc)<sub>2</sub>(H<sub>3</sub>pdc)<sub>2</sub> have been prepared, and their crystal structures determined. The structures of H<sub>3</sub>pdc,H<sub>2</sub>O, and H<sub>3</sub>pdc- $\beta$  consist of a planar central pyrazole ring, with two carboxylic groups slightly twisted from coplanarity, due to a complex hydrogen bonding scheme. The  $\alpha$  form transforms into the  $\beta$  variety upon heating (>240 °C). The mononuclear complex, Ni(Hpdc),4H<sub>2</sub>O, in which deprotonated H<sub>3</sub>pdc serves as a bidentate ligand, has been characterized. The crystal structure of Ba(H<sub>2</sub>pdc)<sub>2</sub>(H<sub>3</sub>pdc)<sub>2</sub> displays a 50% cationic partial occupancy, with double layers of [Ba<sub>0.5</sub>(H<sub>2</sub>pdc)(H<sub>3</sub>pdc)]<sub>∞</sub> planar, polymeric type ribbons along the [010] direction, linked to each other via the Ba coordination scheme along the a axis of the unit cell, with a stacking of Ba(H<sub>2</sub>pdc)<sub>2</sub>(H<sub>3</sub>pdc)<sub>2</sub> layers parallel to (001). © 2006 Elsevier B.V. All rights reserved.

Keywords: Pyrazole; Crystal structures; Thermolysis; Barium complex; Nickel complex

# 1. Introduction

Metal ions complexed by low molecular weight ligands including oxalic acid, citric acid and ethylene-diamine-tetraacetic acid, are often used as starting materials for preparation of metal oxides by low temperature degradation of the complexes [1–8]. Heterocyclic acids or diacids such as picolinic acid, 2,3-pyrazine dicarboxylic acid and 3,6-pyridazine dicarboxylic acid have been used for preparation of various metallic complexes [9–11]. These compounds exhibit usually well-defined structures and stoichiometries depending on the nature of carboxylate chain; they can be designed in order to contain no other heteroelement than carbon, nitrogen, oxygen and hydrogen. Their multidentate structure often favours the formation of polymeric patterns which can help to control the distribution of the active metals on the surface; the thermal decomposition of these ligands into well-defined and finely dispersed powdered samples occurs at moderate temperatures that allow limiting sintering effects. This approach has been previously used for the preparation of ionic conductors [10,11].

They may also be useful in extraction of harmful metals from the environment [12]. 3,5-Pyrazole dicarboxylic acid (H<sub>3</sub>pdc),H<sub>2</sub>O is a commercial product, which has been used for the preparation of coordination complexes with transition metals such as copper(II), in order to investigate their magnetic properties. Oxovanadium(IV), rare earth, cadmium and bismuth complexes were also prepared and their physicochemical properties were characterized [13,14]. Thermal evolution and crystal structure of a polymeric complex of lead have also been reported [15]. In order to

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understand the correlation of physical and structural properties of H<sub>3</sub>pdc and H<sub>3</sub>pdc derivatives with the aim of developing depolution or corrosion inhibition agents [16,17], we have undertaken a study of compounds of this family. We report here the thermal behavior of H<sub>3</sub>pdc,H<sub>2</sub>O as elucidated by thermodiffractometry (HTXRD), the crystal structures of H<sub>3</sub>pdc,H<sub>2</sub>O and H<sub>3</sub>pdc- $\beta$ , and those of complexes of H<sub>3</sub>pdc first with a hazardous metal: Ni(Hpdc),4H<sub>2</sub>O, and secondly with a big size cation: Ba(H<sub>2</sub>pdc)<sub>2</sub>(H<sub>3</sub>pdc)<sub>2</sub>.

# 2. Experimental

The commercial product,  $H_3pdc, H_2O$ , was used as a starting material for the preparation of samples for this investigation.

Characterization of the structural and chemical changes occurring on heating of commercial  $H_3pdc, H_2O$  up to the point of decomposition of the organic framework was carried out with the aid of X-ray thermodiffractometry using a Guinier Lenne camera (heating rate 20 °C h<sup>-1</sup>,  $\lambda$  CuK<sub> $\alpha$ </sub>, gold sample holder). Thermal analysis [1] had already identified the temperatures at which dehydration and phase change occurred.

# 2.1. $H_3pdc, H_2O$

Single crystal samples were obtained from solutions of the commercial material,  $H_3pdc,H_2O$ , in a slightly acidic medium. Depending on crystallization conditions, two different single crystal types could be prepared: crystals of parallelepiped form, shown to be  $H_3pdc,H_2O$  and anhydrous  $H_3pdc$  ( $\beta$  form), were obtained by slow evaporation, respectively, at room temperature and at 100 °C in a drying oven.

# 2.2. Ni(Hpdc),4H<sub>2</sub>O

Solutions of the commercial material,  $H_3pdc, H_2O$ , reacted with nickel chloride solution yielding systematically a blue precipitate which was identified as Ni(H<sub>2</sub>pdc)<sub>2</sub>,4H<sub>2</sub>O [18]. Aiming at preparing heteropolynuclear complexes the addition of NiCl<sub>2</sub>, 6 H<sub>2</sub>O (1.4 g, 6 mmol) to a solution of Cu(H<sub>2</sub>pdc)<sub>2</sub>,4H<sub>2</sub>O (1.34 g, 3 mmol) [19] in 100 ml of 1 M nitric acid led to deep blue needle-shaped crystals which revealed to be Ni(Hpdc),4H<sub>2</sub>O (0.5 g, 1.75 mmol; yield: 29% based on pdc): a TG analysis displayed a two steps evolution, with dehydration occurring first between 120 and 170 °C, followed by ligand decomposition between 240 and 400 °C, and leaving a solid residue identified by X-ray diffraction as NiO, thus corroborating the complex formula.

# 2.3. $Ba(H_2pdc)_2(H_3pdc)_2$

Barium perchlorate (1 g, 3 mmol) dissolved in 20 ml of hot water was added to 3,5-pyrazole dicarboxylic acid monohydrate (0.26 g, 1.5 mmol) dissolved in 10 ml of hot ethanol. The solution was filtered, and allowed to stand at ambient temperature. After 12 h, the colorless compound crystallized. Crystals were washed with water and dried under vacuum (yield: 0.2 g; 73% based on pdc). These crystals were used as isolated from the batch for single crystal X-ray analysis.

Densities were measured by the floatation method.

The TGA of a sampling of these crystals shows a two steps ligand decomposition first occurring abruptly between 250 and 300 °C, of about 37% in weight, and a second identical mass loss occurring smoothly between 300 and 450 °C, which leave a solid residue identified by XRD as BaCO<sub>3</sub>.

Lattice constants were refined from the angular positions of 25 independent reflections randomly. Crystal data of H<sub>3</sub>pdc,H<sub>2</sub>O, H<sub>3</sub>pdc- $\beta$  and Ni(Hpdc),4H<sub>2</sub>O were measured on a Philips PW1100 automated diffractometer, using MoK $\alpha$  radiation, and a graphite monochromator, while data of Ba(H<sub>3</sub>pdc)<sub>4</sub> were recorded on a Bruker Smart CCD 1K with the same radiation.

The crystal structures of  $H_3pdc,H_2O$ ,  $H_3pdc-\beta$  and Ni(Hpdc),4H<sub>2</sub>O were solved and refined using JANA2000 [20]. In the nickel complex, the nickel atomic position was determined from a Patterson synthesis. Non-hydrogen atoms were located from a difference Fourier synthesis and refined with anisotropic thermal parameters. Hydrogen atoms were located from a final Fourier difference synthesis. Structures drawings were prepared with the Diamond package [21].

The structure of the Ba complex was solved from direct methods; one barium location was identified in a general 2i crystallographic site, thus generating a too short Ba–Ba distance: the subsequent refinement of the occupancy factor converged to 0.5. The other non-hydrogen atoms were identified and refined with anisotropic thermal parameters. Two hydrogen atoms related to the central carbon atom of the pyrazole ring were located from Fourier difference syntheses and refined isotropically. The remaining H atoms were not found, probably in relation with the statistic disorder on the Ba cation, which bears residual electronic density in its surroundings; their theoretical positions were calculated and included in the drawings for clarity, but were not included in the last refinement cycles since they were not significant.



Fig. 1. High temperature X-ray diffraction of H<sub>3</sub>pdc,H<sub>2</sub>O.

# 3. Results and discussion

#### 3.1. Thermal behaviour

The X-ray diffraction pattern of H<sub>3</sub>pdc, H<sub>2</sub>O (Fig. 1) evidences the stability of this compound between room temperature and 150 °C, where a structural modification occurs. The new pattern is observed through the temperature range 150–240 °C. The reflections of the powder pattern observed between 150 and 240 °C were indexed (diffraction data recorded with a Siemens D5000 diffractometer) in the orthorhombic system using TREOR [22,23] (a = 17.877(8),

Table 1 X-ray pattern of anhydrous  $H_3pdc-\alpha$ 

hkl	$d_{\rm obs.}$	$d_{\text{calc.}}$	$I/I_{\rm o}$	hkl	$d_{\rm obs.}$	$d_{\text{calc.}}$	$I/I_{\rm o}$
110	8.2926	8.2861	6.93	610	2.8362	2.8389	31.52
210	6.4643	6.4615	29.75	221	2.7297	2.7304	9.95
310	5.0322	5.0254	19.54	321	2.5858	2.5839	4.52
020	4.6744	4.6756	25.18	700	2.5548	2.5539	5.49
120	4.5220	4.5235	12.91	511	2.4596	2.4578	3.44
220	4.1407	4.1430	29.05	131	2.3468	2.3445	7.59
410	4.0332	4.0324	9.55	231	2.2867	2.2863	5.04
101	3.5508	3.5578	6.58	521	2.2364	2.2370	16.56
011	3.3848	3.3843	100.0	810	2.1742	2.1734	5.44
111	3.3265	3.3258	41.44	630	2.1529	2.1534	5.48
420	3.2297	3.2307	11.85	621	2.0655	2.0661	4.09
600	2.9791	2.9795	34.31	341	1.8662	1.8666	3.63
311	2.9421	2.9428	12.59				

Table 2

Crystallographic data for H<sub>3</sub>pdc,H<sub>2</sub>O, anhydrous H<sub>3</sub>pdc-β, Ni(Hpdc),4H<sub>2</sub>O and Ba(H<sub>2</sub>pdc)<sub>2</sub>(H<sub>3</sub>pdc)<sub>2</sub>

Compound	$H_3pdc, H_2O$	H <sub>3</sub> pdc-β	$N_1(Hpdc), 4H_2O$	$Ba(H_2pdc)_2 (H_3pdc)_2$
Formula	$C_5N_2O_5H_6$	$C_5N_2O_4H_4$	$C_5N_2O_8H_{10}Ni$	$(C_5N_2O_4H_3)_2 (C_5N_2O_4H_4)_2Ba$
Mol. wt	174.11	156.11	284.80	761.78
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	Pl	Pl
$a(\mathbf{A})$	14.369(3)	6.06(2)	10.683(3)	7.614(3)
b (Å)	3.750(1)	28.26(9)	7.663(5)	9.106(2)
<i>c</i> (Å)	13.415(3)	3.66(1)	6.075(5)	9.696(2)
α (°)	90	90	78.02(2)	80.44(1)
β (°)	101.75(3)	91.78(3)	80.54(3)	77.24(1)
γ (°)	90	90	87.18(3)	75.48(1)
$V(\text{\AA}^3)$	707.70(3)	627.07(3)	479.88(4)	630.31(3)
Ζ	4	4	2	2
$D_{\rm obs} ({\rm g}{\rm cm}^{-3})$	1.72(5)	1.67(4)	2.02(4)	1.99(2)
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.63(3)	1.65(2)	1.97(1)	2.00(2)
F(000)	364	320	292	364
Temperature (K)	298	298	298	298
Diffractomer	Philips PW1100	Philips PW1100	Philips PW1100	Bruker Smart CCD 1K
$\theta$ range (°)	2.33-29.47	2.88-30.97	2.72-29.98	2.17-31.02
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	ω
No. of data collected	2301	2332	3030	6502
No. of unique data	1437	1296	2276	3438
hkl range	-18:18; -5:5; 0:18	0:8; -39:39; -5:5	-15:15; -10:10; 0:8	-10:10; -13:12; -13:13
R <sub>merge</sub>	0.020	0.038	0.023	0.031
Standard reflections	$(21\bar{1}); (11\bar{1}); (10\bar{2})$	$(03\bar{1}); (0\bar{2}\bar{1}); (\bar{1}10)$	$(011); (\bar{4}00); (11\bar{2})$	NA
No. of data used $(I \ge 3\sigma(I))$	852	813	1798	2773
No. of parameters	128	112	145	216
Final R (obs., all)	0.0510, 0.1213	0.0504, 0.1007	0.0421, 0.0597	0.0485, 0.0596
Weighting scheme	$w = 1/(\sigma^2(F))$	$w = 1/(\sigma^2(F) + 0.00001F^2)$	$w = 1/(\sigma^2(F))$	$w = 1/(\sigma^2(F) + 0.0009F^2)$
Final $R_w$ (obs., all)	0.0488, 0.0699	0.0445, 0.0560	0.0439, 0.0507	0.0666, 0.0701
Residual densities	0.44, -0.45	0.41, -0.38	0.48, -0.60	1.56, -0.37

b = 9.351(5), c = 3.630(2) Å;  $M_{11} = 24$ ,  $F_{11} = 25$ (0.0133;34)). The measured density,  $D_{obs} = 1.707(1)$  g cm<sup>-3</sup>, is in good agreement with the calculated one  $D_{calc.} = 1.71(5)$  g cm<sup>-3</sup>, Z = 4, for anhydrous H<sub>3</sub>pdc, thus labelled  $\alpha$ . The X-ray pattern of H<sub>3</sub>pdc- $\alpha$  is shown in Table 1.

A careful examination of the powder diffraction pattern shows that the modification occurring at 240 °C corresponds to the disappearance of a number of the diffraction peaks. The transformation, which occurs without weight loss, can be considered as a polymorphic transition  $\alpha \rightarrow \beta$ . The set of diffraction lines observed at temperatures above 240 °C can be indexed completely according to the cell dimensions obtained from the single crystals prepared at 100 °C. The structure of these crystals was solved and that compound clearly identified as H<sub>3</sub>pdc- $\beta$ , the anhydrous high temperature variety.

#### 3.2. Crystal structures

Crystallographic data and final refinement results for  $H_3pdc, H_2O$ ,  $H_3pdc-\beta$ , Ni(Hpdc),  $4H_2O$  and  $[Ba(H_2pdc)_2 (H_3pdc)_2]$  are summarized in Table 2.

# 3.2.1. $H_{3}pdc, H_{2}O$ and the anhydrous high temperature form, $H_{3}pdc-\beta$ of 3,5-pyrazole dicarboxylic acid

Projection views of  $H_3pdc, H_2O$  and the anhydrous high temperature form,  $H_3pdc-\beta$ , based on the final atomic

coordinates and equivalent isotropic thermal parameters of Tables 3 and 4 are presented in Figs. 2 and 3, respectively.

In H<sub>3</sub>pdc,H<sub>2</sub>O, the two carboxylic functions are distorted from coplanarity with the aromatic ring. The plane of C(2), O(1) and O(3) subtends an angle of 1.87° with the aromatic ring. The plane of C(5), O(2) and O(4) subtends an angle of  $3.44^{\circ}$ . H<sub>3</sub>pdc molecules are hydrogen bonded in pairs to their centrosymmetric equivalents. These dimers further hydrogen bond together, head to tail, forming a chain-like polymer parallel to the **a** axis (Fig. 2). Hydrogen bonding to water molecules located between the polymeric chains further stabilizes the solid.

In the anhydrous and high temperature form,  $H_3pdc-\beta$ , the  $H_3pdc$  molecule displays no internal symmetry element. The aromatic pyrazole central ring is planar. The C(1), C(2), O(1) and O(2) atoms are coplanar, as are C(4), C(5), O(3) and O(4). Both planes are twisted from coplanarity with the plane of the pyrazole ring (1.84° and 1.56°, respectively). The stability of the crystal structure results

Table 3 Atomic coordinates and isotropic thermal parameters for  $H_3pdc, H_2O$ 

Atom	X	У	Ζ	$U(eq)[\text{\AA}^2]$
01	0.55290(16)	0.2673(7)	0.11522(19)	0.0511(10)
O2	0.08200(17)	0.2047(8)	0.9556(2)	0.0585(10)
O3	0.50888(17)	-0.0409(7)	0.2403(2)	0.0505(10)
O4	0.10374(17)	-0.0708(8)	0.1065(2)	0.0567(10)
N1	0.27196(18)	0.3332(8)	0.9832(2)	0.0398(10)
N2	0.36531(18)	0.3350(8)	0.0185(2)	0.0378(10)
C1	0.3903(2)	0.1767(9)	0.1101(3)	0.0336(11)
C2	0.4924(2)	0.1406(10)	0.1560(3)	0.0374(11)
C3	0.2364(2)	0.1634(9)	0.0552(3)	0.0349(11)
C4	0.3081(2)	0.0603(10)	0.1366(3)	0.0365(11)
C5	0.1325(2)	0.1012(10)	0.0349(3)	0.0406(11)
05	0.6916(2)	-0.1327(10)	0.2951(2)	0.0704(13)
HO3	0.571(3)	-0.085(11)	0.256(3)	0.0608
HO4	0.043(3)	-0.109(11)	0.088(3)	0.0682
HN2	0.401(2)	0.438(9)	0.983(3)	0.0453
HC4	0.301(2)	-0.063(9)	0.193(3)	0.0440
HO51	0.713(3)	-0.058(12)	0.361(4)	0.0846
HO52	0.724(4)	-0.280(14)	0.278(4)	0.0846

Table 4

Atomic	coordinates	and	isotropic	thermal	parameters	for	$H_3pdc-\beta$

Atom	x	У	Ζ	$U(eq)[Å^2]$
01	0.5374(4)	0.05758(7)	0.4705(6)	0.0483(8)
O2	0.2508(4)	0.01999(7)	0.7402(7)	0.0546(9)
O3	-0.2971(3)	0.17643(7)	1.2326(6)	0.0453(8)
O4	-0.0869(4)	0.23662(7)	1.0337(6)	0.0486(9)
N1	0.2194(4)	0.18019(7)	0.7558(6)	0.0294(7)
N2	0.3436(4)	0.14366(8)	0.6499(6)	0.0294(8)
C1	0.3588(5)	0.05754(10)	0.6372(8)	0.0364(10)
C2	0.2471(5)	0.10195(8)	0.7376(8)	0.0290(8)
C3	0.0490(5)	0.11169(9)	0.9095(8)	0.0300(9)
C4	0.0397(5)	0.16105(9)	0.9167(7)	0.0263(9)
C5	-0.1345(5)	0.19182(10)	1.0791(8)	0.0301(9)
HO2	0.312(6)	-0.0043(11)	0.666(9)	0.0655
HO4	-0.190(6)	0.2543(11)	1.125(9)	0.0583
HN2	0.475(5)	0.1487(10)	0.533(8)	0.0353
HC3	-0.061(5)	0.0901(10)	1.002(7)	0.0359



Fig. 2. Hydrogen bonds in H<sub>3</sub>pdc,H<sub>2</sub>O.



Fig. 3. Hydrogen bonds in H<sub>3</sub>pdc-β.

from the three-dimensional hydrogen bonding scheme (Fig. 3), which includes dimers of carboxylic functional groups, (linked via CO-HO), and organized in herringbone head to tail fashion, in a 12-membered ring utilizing N-H donor and N acceptor moieties.

# 3.2.2. Nickel complex

Good quality single crystals of Ni(Hpdc),4H<sub>2</sub>O allowed complete structural characterization. Atomic positions of

Ni(Hpdc), $4H_2O$  are presented in Table 5. The structure exists as a mononuclear complex in which Hpdc serves as a bidentate ligand, contributing one nitrogen atom from the pyrazole ring and one oxygen atom from a deprotonated carboxylic acid functional group to nickel.

The octahedral coordination sphere of Ni is completed by four oxygen atoms, from four independent water molecules. Thermal gravimetric analysis of a sample made of crushed crystals shows that dehydration occurs in a single step.

The Ni atom is involved in a five-membered ring with four atoms from Hpdc: N(1) and O(1), plus C(4) and C(2). There is no significant difference in ligand geometry (bond distances and angles) as seen in the Ni complex, in H<sub>3</sub>pdc,H<sub>2</sub>O and in anhydrous H<sub>3</sub>pdc- $\beta$ ; nevertheless, deprotonation results in modification of the hydrogen bonding pattern, making the ligand Hpdc more planar.

The crystal structure of Ni(Hpdc), $4H_2O$  shows a hydrogen bonding network as seen in Fig. 4. Four water molecules are involved in hydrogen bonds with the nonchelated oxygen atoms of carboxylato groups of three neighbouring ligands and with the pyrazole ring proton. Bond lengths and angles, specific details of hydrogen bonding and structure data for all four structures are available from CCDC upon request.

#### 3.2.3. Barium complex

Single crystals of the barium complex were grown and their structural investigation yielded an interesting feature as described by atomic positions presented in Table 6: one Ba is found in a general position with a 50% occupancy

Table	e 5
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Atomic coordinates and isotropic thermal parameters for Ni(Hpdc),4H2O

Atom	X	у	Ζ	$U(eq)[\text{\AA}^2]$
Nil	0.85831(5)	0.73945(7)	-0.22131(9)	0.0163(1)
01	0.7655(2)	0.2094(4)	0.0468(5)	0.0226(8)
O2	0.8273(2)	0.6382(4)	0.1266(5)	0.0215(8)
03	0.6653(3)	1.0361(4)	0.3534(5)	0.0342(10)
O4	0.6743(3)	0.5367(5)	0.4109(5)	0.0379(10)
05	0.8376(3)	0.4954(4)	-0.2913(5)	0.0249(8)
O6	0.9021(3)	0.9839(4)	-0.1879(6)	0.0388(10)
O7	0.8772(2)	0.8467(4)	-0.5695(5)	0.0229(8)
O8	0.9538(3)	0.3135(4)	0.2562(6)	0.0289(10)
N1	0.6649(3)	0.7746(4)	-0.1417(6)	0.0203(9)
N2	0.5657(3)	0.8370(4)	-0.2400(6)	0.0216(9)
C1	0.4565(3)	0.7947(5)	-0.0994(6)	0.0191(10)
C2	0.6674(3)	1.1461(5)	0.1725(7)	0.0189(10)
C3	0.4861(3)	0.7012(5)	0.1031(7)	0.0205(10)
C4	0.7111(4)	0.6130(5)	0.2164(7)	0.0219(11)
C5	0.6178(3)	0.6925(5)	0.0686(6)	0.0180(10)
HO51	0.80475	0.41821	-0.17793	0.0299
HO52	0.78747	0.49010	-0.37713	0.0299
HO61	0.96328	1.02873	-0.25803	0.0463
HO62	0.85487	1.05828	-0.12825	0.0463
HO71	0.88099	0.78005	-0.66278	0.0275
HO72	0.82400	0.91958	-0.60761	0.0275
HO81	1.06807	0.57925	-0.23997	0.0347
HO82	1.08627	0.73786	-0.22845	0.0347
HN2	0.57962	0.92225	-0.39196	0.0260
HC3	0.43269	0.66151	0.25304	0.0247



Fig. 4. Packing in Ni(Hpdc),4H<sub>2</sub>O complex.

factor, and two independent ligands, hereafter A and B, complete the structure: A displays a planar pyrazole central ring and two regular carboxylic ending groups:

Table 6

Atomic coordinates and isotropic thermal parameters for  $Ba(H_2pdc)_2$  ( $H_3pdc)_2$ 

Atom	X	У	Ζ	U(eq)[Å <sup>2</sup> ]
Ba1	0.45450(5)	-0.00129(4)	0.37716(4)	0.0253(1)
Ola	0.5439(4)	0.7418(3)	0.2220(3)	0.0420(9)
O1b	0.3216(4)	-0.7247(3)	0.4891(3)	0.0379(8)
O2a	0.7458(5)	0.7306(3)	0.0143(3)	0.0512(10)
O2b	0.0756(4)	-0.7032(3)	0.6674(3)	0.0383(8)
O3a	0.6795(4)	0.0188(3)	0.0711(3)	0.0483(10)
O3b	0.1511(4)	0.0034(3)	0.6205(3)	0.0432(9)
O4a	0.8550(5)	0.1348(3)	-0.1082(3)	0.0535(10)
O4b	-0.1052(4)	-0.0703(3)	0.7382(3)	0.0382(8)
N1a	0.5694(4)	0.2914(3)	0.1984(3)	0.0323(9)
N1b	0.2603(4)	-0.2655(3)	0.4897(3)	0.0310(8)
N2a	0.5413(4)	0.4359(3)	0.2257(3)	0.0318(8)
N2b	0.2983(4)	-0.4123(3)	0.4683(3)	0.0309(8)
Cla	0.6456(5)	0.5092(4)	0.1204(4)	0.0292(9)
Clb	0.1808(5)	-0.4823(4)	0.5659(4)	0.0275(9)
C2a	0.7443(5)	0.4101(4)	0.0221(4)	0.0315(10)
C2b	0.0623(5)	-0.3777(4)	0.6526(4)	0.0279(9)
C3a	0.6914(5)	0.2738(4)	0.0757(4)	0.0294(9)
C3b	0.1188(4)	-0.2417(3)	0.6011(3)	0.0258(8)
C4a	0.6402(5)	0.6715(4)	0.1243(4)	0.0308(9)
C4b	0.2003(5)	-0.6483(4)	0.5690(3)	0.0271(9)
C5a	0.7424(5)	0.1297(4)	0.0136(4)	0.0320(10)
C5b	0.0507(5)	-0.0909(3)	0.6565(3)	0.0278(9)
H1a	0.835(5)	0.424(4)	-0.058(4)	0.025(9)
H1b	-0.035(6)	-0.397(4)	0.740(4)	0.032(10)



Fig. 5. Ba coordination scheme in [Ba<sub>0.5</sub>(H<sub>2</sub>pdc)(H<sub>3</sub>pdc)].

(C4a-O1a = 1.22 Å; C4a-O2a = 1.31 Å and C5a-O3a = 1.23 Å; C5a-O4a = 1.30 Å) while in **B** only one ending carboxylic group displays such a geometry: C4b-

O1b = 1.21 Å; C4b–O2b = 1.31 Å; the second one showing two nearly identical bond lengths: C5b–O3b = 1.260 Å; C5b–O4b = 1.266 Å. Thus **A** and **B** can be identified as (H<sub>3</sub>pdc) and (H<sub>2</sub>pdc), respectively, and the barium complex can be given the composition  $Ba(H_2pdc)_2$  (H<sub>3</sub>pdc)<sub>2</sub>, in good agreement with the T.G. analysis.

Each one of the disordered Ba position is 9th coordinated to 7 ligands: firstly through a bonding scheme implying 4 oxygen and two nitrogen atoms from 4 ligands organized in a planar, slightly distorted hexagonal ring: one A and one B entities are involved as bidendate ligands via one terminal O atom and one nitrogen of their central ring, while the two others (one A and one B) are acting as monodendate ligands, thus developing a planar, polymeric type ribbon  $[Ba_{0.5}(H_2pdc)(H_3pdc)]_{\infty}$  along the [010] direction. The Ba 9th fold coordination is completed on one side of the mean plane by two atoms O1b and O3b from carboxylic groups belonging to two **B**-type H<sub>2</sub>pdc, from the equivalent centrosymmetric ribbon, and finally on the opposite side of the mean plane, by a single O4b atom from a **B**-type  $H_2pdc$ , as the apex of a slightly distorted hexagonal pyramid on this side. The centrosymmetric equivalent Ba position, with a 50% occupancy, displays an equivalent centrosymmetric coordination scheme, obtained through the center of symmetry located midway between the two Ba disordered atomic positions. The structure is organized in double  $[Ba_{0.5}(H_2pdc)(H_3pdc)]_{\infty}$  planar ribbons stacked parallel to



Fig. 6. Stacking of  $[Ba(H_2pdc)_2(H_3pdc)_2]_{\infty}$  layers parallel to (001).

(101), building  $[Ba(H_2pdc)_2(H_3pdc)_2]$  entities linked to each others via the Ba coordination scheme (i.e., through the Ba–O4b link described previously) along the a axis of the unit cell, and designing an overall stacking of  $Ba(H_2pdc)_2(H_3pdc)_2$  layers parallel to (001) (Figs. 5 and 6).

#### 4. Conclusion

 $H_3$ pdc is a versatile ligand that can be useful in metal sequestering processes.  $H_3$ pdc is also potentially a tetrachelating ligand; the rigidity of the N—N bonding, and the positioning of the two carboxyl groups may allow simultaneous complexation to two metal atoms leading to polynuclear complexes. The use of pdc complexes as corrosion inhibiting agent and as anticorrosive coating agents is under investigation.

The crystallographic data have been deposited and can be obtained through the CCDC data bank, under the reference CCDC 286900, CCDC 286901, CCDC 286902 and CCDC 286903 for  $Ba(H_2pdc)_2(H_3pdc)_2$ ,  $H_3pdc-\beta$ ,  $H_3pdc,H_2O$  and Ni(Hpdc),4H<sub>2</sub>O, respectively.

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