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Crystal structure of poly[triaqua-(di(2,2'-bipyridine- κ^2N,N')- μ_4 -silanetetrayltetrakis(benzene-4,1-diyl)tetrakis (hydrogen phosphonato)- $\kappa^4O:O':O'':O'''$) dicadmium(II)], $C_{44}H_{42}N_4O_{15}P_4Cd_2Si$

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.50 × 0.40 × 0.30 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.10 mm ⁻¹
Diffractometer, scan mode:	Bruker D8 QUEST, φ and ω
$\theta_{\max}$, completeness:	26.1°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	15498, 9617, 0.034
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 7610
$N(\text{param})_{\text{refined}}$:	643
Programs:	Bruker [1], SHELX [2, 3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1	0.4668(3)	−0.2011(3)	1.1643(3)	0.0144(9)
C2	0.5800(4)	−0.2208(4)	1.1481(3)	0.0261(11)
H2	0.6234	−0.2254	1.0865	0.031*
C3	0.6306(4)	−0.2340(4)	1.2205(3)	0.0251(11)
H3	0.7084	−0.2481	1.2080	0.030*
C4	0.5696(3)	−0.2270(3)	1.3108(3)	0.0148(9)
C5	0.4577(4)	−0.2108(4)	1.3286(3)	0.0238(10)
H5	0.4148	−0.2078	1.3905	0.029*
C6	0.4074(4)	−0.1990(4)	1.2557(3)	0.0219(10)
H6	0.3305	−0.1894	1.2693	0.026*
C7	0.8206(5)	0.0278(4)	1.2278(3)	0.0345(13)
H7	0.7902	−0.0160	1.2174	0.041*
C8	0.8642(5)	0.0930(5)	1.1503(4)	0.0435(16)
H8	0.8655	0.0933	1.0875	0.052*
C9	0.9061(5)	0.1581(5)	1.1651(4)	0.0391(14)
H9A	0.9363	0.2045	1.1127	0.047*
C10	0.9036(4)	0.1549(4)	1.2570(4)	0.0295(11)
H10	0.9320	0.1994	1.2687	0.035*
C11	0.8595(4)	0.0865(3)	1.3326(3)	0.0186(9)
C12	0.8542(3)	0.0794(3)	1.4341(3)	0.0183(9)
C13	0.9024(4)	0.1348(3)	1.4586(3)	0.0232(10)
H13A	0.9365	0.1814	1.4105	0.028*
C14	0.8994(4)	0.1205(4)	1.5539(4)	0.0269(11)
H14A	0.9309	0.1578	1.5722	0.032*
C15	0.8499(4)	0.0515(4)	1.6223(3)	0.0260(11)
H15A	0.8487	0.0389	1.6880	0.031*
C16	0.8024(4)	0.0015(4)	1.5930(3)	0.0232(10)
H16	0.7666	−0.0444	1.6400	0.028*
C17	0.3003(3)	−0.0155(3)	1.0484(3)	0.0164(9)
C18	0.3027(4)	0.0489(3)	1.0981(3)	0.0187(9)
H18	0.3519	0.0186	1.1423	0.022*
C19	0.2350(4)	0.1563(4)	1.0845(3)	0.0191(10)

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Abstract

$C_{44}H_{42}N_4O_{15}P_4Cd_2Si$, triclinic, $P\bar{1}$ (no. 2), $a = 13.4778(9)$ Å, $b = 14.2036(9)$ Å, $c = 15.2206(10)$ Å, $\alpha = 69.637(1)^\circ$, $\beta = 72.355(1)^\circ$, $\gamma = 64.861(1)^\circ$, $V = 2431.1(3)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0428$, $wR_{\text{ref}}(F^2) = 0.0987$, $T = 120(2)$ K.

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A part of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

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Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H19	0.2382	0.1985	1.1194	0.023*
C20	0.1627(3)	0.2030(3)	1.0206(3)	0.0174(9)
C21	0.1609(4)	0.1401(4)	0.9687(3)	0.0230(10)
H21	0.1130	0.1709	0.9235	0.028*
C22	0.2288(4)	0.0332(4)	0.9831(3)	0.0220(10)
H22	0.2267	−0.0086	0.9471	0.026*
C23	0.2830(3)	−0.2358(3)	1.1210(3)	0.0156(9)
C24	0.3185(4)	−0.3464(4)	1.1536(3)	0.0250(11)
H24	0.3959	−0.3873	1.1425	0.030*
C25	0.2441(4)	−0.3993(4)	1.2022(3)	0.0253(11)
H25	0.2712	−0.4755	1.2241	0.030*
C26	0.1304(3)	−0.3417(3)	1.2191(3)	0.0155(9)
C27	0.0935(4)	−0.2311(4)	1.1869(4)	0.0276(11)
H27	0.0160	−0.1903	1.1982	0.033*
C28	0.1692(4)	−0.1790(4)	1.1379(3)	0.0258(11)
H28	0.1422	−0.1028	1.1156	0.031*
C29	0.4789(4)	−0.1921(3)	0.9552(3)	0.0162(9)
C30	0.5577(4)	−0.2933(3)	0.9488(3)	0.0211(10)
H30	0.5663	−0.3506	1.0050	0.025*
C31	0.6239(4)	−0.3128(4)	0.8630(3)	0.0218(10)
H31	0.6776	−0.3824	0.8610	0.026*
C32	0.6117(3)	−0.2301(3)	0.7794(3)	0.0156(9)
C33	0.5370(4)	−0.1287(4)	0.7847(3)	0.0220(10)
H33	0.5292	−0.0714	0.7285	0.026*
C34	0.4734(4)	−0.1098(4)	0.8711(3)	0.0223(10)
H34	0.4244	−0.0387	0.8735	0.027*
C35	0.2608(4)	0.5739(4)	0.8784(3)	0.0309(12)
H35	0.2143	0.5546	0.9371	0.037*
C36	0.3456(5)	0.6031(5)	0.8789(4)	0.0448(15)
H36	0.3581	0.6033	0.9370	0.054*
C37	0.4122(5)	0.6321(6)	0.7933(4)	0.0546(18)
H37	0.4697	0.6549	0.7917	0.065*
C38	0.3949(5)	0.6277(5)	0.7100(4)	0.0467(16)
H38	0.4417	0.6453	0.6509	0.056*
C39	0.3081(4)	0.5971(4)	0.7139(3)	0.0275(11)
C40	0.2825(4)	0.5908(4)	0.6288(3)	0.0241(10)
C41	0.1611(4)	0.5688(4)	0.5646(3)	0.0258(11)
H41	0.0940	0.5573	0.5730	0.031*
C42	0.2252(4)	0.5815(4)	0.4744(3)	0.0317(12)
H42	0.2027	0.5790	0.4221	0.038*
C43	0.3229(4)	0.5978(4)	0.4623(3)	0.0344(12)
H43	0.3702	0.6046	0.4016	0.041*
C44	0.3508(4)	0.6040(4)	0.5394(3)	0.0316(12)
H44	0.4168	0.6173	0.5317	0.038*
Cd1	0.73028(2)	−0.07422(2)	1.44706(2)	0.01366(8)
Cd2	0.08702(3)	0.53987(3)	0.79651(2)	0.01772(9)
H7A	−0.090(3)	0.705(4)	0.699(3)	0.032(15)*
H7B	−0.073(5)	0.722(5)	0.776(5)	0.07(2)*
N1	0.8045(3)	0.0146(3)	1.5012(2)	0.0165(8)
N2	0.8190(3)	0.0233(3)	1.3174(3)	0.0193(8)
N3	0.2413(3)	0.5717(3)	0.7983(3)	0.0261(9)
N4	0.1885(3)	0.5718(3)	0.6406(3)	0.0220(8)
O1	0.5709(2)	0.0764(3)	1.4316(2)	0.0250(7)
H1A	0.5482	0.1258	1.4620	0.038*
H1B	0.5101	0.0770	1.4222	0.038*
O2	0.8981(2)	−0.2259(2)	1.4616(2)	0.0213(7)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H2A	0.9110	−0.2599	1.4193	0.032*
H2B	0.8889	−0.2717	1.5161	0.032*
O3	0.6632(2)	−0.1350(2)	1.3723(2)	0.0186(7)
O4	0.5531(2)	−0.2500(2)	1.49598(19)	0.0182(6)
O5	0.0411(3)	0.3686(2)	1.0959(2)	0.0296(8)
O6	0.1418(2)	0.4047(2)	0.9214(2)	0.0227(7)
O7	−0.0447(3)	0.7146(3)	0.7212(3)	0.0255(8)
O8	0.6554(2)	−0.1430(2)	0.59366(19)	0.0175(6)
O9	0.6317(2)	−0.3243(2)	0.6481(2)	0.0182(6)
H9	0.6071	−0.2952	0.5969	0.027*
O10	0.8064(2)	−0.3139(2)	0.6611(2)	0.0214(7)
O11	0.0118(2)	−0.4517(2)	1.2162(2)	0.0205(7)
O12	−0.0712(3)	−0.3240(2)	1.3244(2)	0.0257(7)
O13	0.0822(2)	−0.4976(2)	1.3671(2)	0.0208(7)
H13	0.1163	−0.5551	1.3498	0.031*
O14	−0.0284(2)	0.3540(2)	0.9683(2)	0.0228(7)
H14	−0.0255	0.3847	0.9099	0.034*
O15	0.7389(2)	−0.3380(2)	1.4079(2)	0.0233(7)
H15	0.7955	−0.3222	1.3777	0.035*
P1	0.02951(9)	−0.40560(9)	1.28371(8)	0.0165(2)
P2	0.07746(10)	0.34409(9)	1.00062(8)	0.0192(3)
P3	0.68338(9)	−0.25233(9)	0.66279(7)	0.0144(2)
P4	0.63298(9)	−0.23372(9)	1.40194(8)	0.0153(2)
Si1	0.38576(10)	−0.16328(9)	1.06988(8)	0.0142(2)

Source of material

A mixture of silanetetrayltetrakis(benzene-4,1-diyl)tetrakis phosphonic acid (0.2 mmol), 2,2'-bipyridine (0.2 mmol), Cd(NO₃)₂ · 4(H₂O) (0.2 mmol), H₂O (8 mL) was stirred for ten minutes. The mixture was transferred in a 25 mL stainless steel reactor with a Teflon liner and heated from 298 to 453 K in 5 h and a constant temperature was maintained at 453 K for 72 h. After cooling to room temperature, colorless block crystals were collected in 55.3% yield based on the amounts of Cd.

Experimental details

Coordinates of hydrogen atoms were calculated. Their U_{iso} values were set to 1.2 U_{eq} of the parent atoms.

Comment

Coordination polymers (CPs) composed of metal nodes and bridging linkers have attracted much attention over the past decades due to their enormous variety of intriguing structural topologies and great potential applications [4, 5]. Compared with carboxylates and pyrazolate counterparts, phosphonate groups have a stronger interaction with metal ions, and consequently higher chemical and thermal stability [6–8]. The excellent robustness of metal phosphonates represents

remarkable added value and should promote their investigation, regardless of the challenges relating to their synthesis and characterization, in order to develop a new generation of robust CPs able to overcome the typical weaknesses of classical CPs.

The asymmetric unit of the title structure contains two crystallographically independent cadmium(II) ions, one silanetetrayltetrakis (benzene-4,1-diyl)tetrakis(hydrogen phosphonato) ligand, two 2,2'-bipyridine and three coordinated water molecules. Cd1 is six-coordinated by four O atoms from two silanetetrayltetrakis(benzene-4,1-diyl)tetrakis(hydrogen phosphonato) ligands and two water molecules, two N atoms from one 2,2'-bipyridine, forming a distorted octahedral geometry. Cd2 is also six-coordinated by four O atoms from three silanetetrayltetrakis(benzene-4,1-diyl)tetrakis(hydrogen phosphonato) ligands and one water molecule, two N atoms from one 2,2'-bipyridine, also forming a distorted octahedral geometry. The distances between Cd and the coordinated atoms are: $d(Cd1 \cdots O1) = 2.302(3) \text{ \AA}$, $d(Cd1 \cdots O2) = 2.375(3) \text{ \AA}$, $d(Cd1 \cdots O3) = 2.199(3) \text{ \AA}$, $d(Cd1 \cdots O8) = 2.215(3) \text{ \AA}$, $d(Cd1 \cdots N1) = 2.360(3) \text{ \AA}$, $d(Cd1 \cdots N2) = 2.360(3) \text{ \AA}$, $d(Cd2 \cdots O5) = 2.284(3) \text{ \AA}$, $d(Cd2 \cdots O6) = 2.224(3) \text{ \AA}$, $d(Cd2 \cdots O7) = 2.477(3) \text{ \AA}$, $d(Cd2 \cdots O11) = 2.264(3) \text{ \AA}$, $d(Cd2 \cdots N3) = 2.317(4) \text{ \AA}$, and $d(Cd2 \cdots N4) = 2.349(4) \text{ \AA}$, respectively. The Cd1 coordination angles are from $70.93(12)^\circ$ to $178.12(10)^\circ$, and Cd2 coordination angles are from $66.81(12)^\circ$ to $158.45(12)^\circ$. These above mentioned bond distances and angles are all in their normal ranges. They can be compared with those previously reported compounds [9]. The Cd1 ion links its symmetry-related atoms to form a dinuclear secondary building unit (SBU) bridged by two silanetetrayltetrakis(benzene-4,1-diyl)tetrakis (hydrogen phosphonato) ligands. Cd2 ion is mononuclear linked by two silanetetrayltetrakis (benzene-4,1-diyl)tetrakis(hydrogen phosphonato) ligands. The Cd1 dinuclear SBUs and Cd2 mononuclear are linked by silanetetrayltetrakis(benzene-4,1-diyl)tetrakis (hydrogen phosphonato) ligands to form two-dimensional (2D) layer framework parallel to the *bc* plane. These 2D layers are packed together to form 3D framework structures through the π - π interactions between neighboring benzene rings from parallel 2,2'-bipyridine. There are related structures that have been reported with the same ligand [10]. For example, three-dimensional compound $Cd_4(H_4L)_2(phen)_2(H_2O)_4$ which is characterized as a 3,4,6-connected network with the vertex

symbol of $\{4 \cdot 6^4 \cdot 8\}^2\{4^2 \cdot 6^4 \cdot 8^9\}\{6^2 \cdot 8\}^2$ and the compound $Cu_2H_4STPPA \cdot 2H_2O$ with three dimensional porous framework were synthesized using hydrothermal reaction method [11, 12].

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