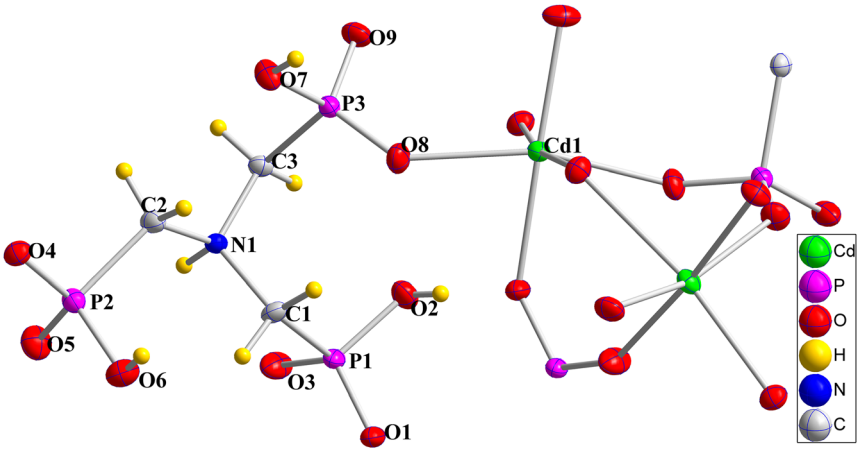
Si N. Gu, Zhi Y. Ou, Ting T. Wu, Ting Y. Nie and Yang Liu*

# Crystal structure of poly [($\mu_6$-ammoniotris(methylene))tris(hydrogen phosphonato)cadmium(II)], $C_3H_{10}CdNO_9P_3$




https://doi.org/10.1515/ncrs-2023-0332
Received July 18, 2023; accepted August 20, 2023;
published online September 26, 2023

**Abstract**

$C_3H_{10}CdNO_9P_3$, monoclinic, $P2_1/c$ (no. 14), $a$ = 9.1770(5) Å, $b$ = 8.3742(4) Å, $c$ = 15.4660(6) Å, $\beta$ = 119.657(2)°, $V$ = 1032.86(9) Å$^3$, $Z$ = 4, $R_{gt}(F)$ = 0.0202, w$R_{ref}(F^2)$ = 0.0515, T = 296 K.

**CCDC no.:** 2281782

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Colourless block |
| Size: | 0.20 × 0.20 × 0.20 mm |
| Wavelength: | Mo *Kα* radiation (0.71073 Å) |
| $\mu$: | 2.62 mm$^{-1}$ |
| Diffractometer, scan mode: | Bruker SMART CCD 6000, |
| $\theta_{max}$, completeness: | 27.6°, >99 % |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 12229, 2370, 0.020 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 2322 |
| $N(param)_{refined}$: | 157 |
| Programs: | Bruker [1], OLEX2 [2], SHELX [3] |

## 1 Source of materials

$Cd(NO_3)_2{\cdot}4H_2O$ (0.3 mmol, 0.093) was dissolved in 8 mL water, followed by the addition of a 50 % solution of nitrilo-*tris*(methylenephosphonic acid) (0.3 mL). Then the mixture was transferred into a 25 mL Teflon-lined stainless-steel vessel, which was followed by heated at 140 °C under autogenous pressure for 2 days. After the mixture was cooled to room temperature, colorless block crystals were obtained, washed with ethanol, and dried at room temperature.

## 2 Experimental details

The structures were solved by Direct Methods using the SHELX-97 program incorporated into OLEX2. Empirical absorption corrections were applied with SADABS. The

***Corresponding author: Yang Liu**, Key Laboratory of Functional Organometallic Materials, College of Chemistry and Materials Science, Hengyang Normal University, Hengyang City, 421008, Hunan Province, People's Republic of China, E-mail: liuyang@hynu.edu.cn. https://orcid.org/0000-0002-1142-1674
**Si N. Gu, Zhi Y. Ou, Ting T. Wu and Ting Y. Nie,** College of Chemistry and Materials Science, Hengyang Normal University, Hengyang City, 421008, Hunan Province, People's Republic of China

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)

| Atom | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cd1 | −0.47676 (2) | −0.05304 (2) | −0.75041 (2) | 0.01582 (6) |
| P1 | −0.42787 (8) | −0.29929 (7) | −0.55102 (4) | 0.01415 (12) |
| P2 | −0.17571 (8) | 0.20844 (8) | −0.58821 (5) | 0.01633 (13) |
| P3 | −0.18609 (7) | −0.32297 (7) | −0.73982 (4) | 0.01392 (12) |
| O3 | −0.4420 (3) | −0.1548 (2) | −0.61112 (14) | 0.0264 (4) |
| O1 | −0.4689 (2) | −0.4616 (2) | −0.59943 (13) | 0.0194 (4) |
| O2 | −0.5359 (2) | −0.2676 (2) | −0.49969 (14) | 0.0227 (4) |
| H2 | −0.5391 | −0.3488 | −0.4710 | 0.034* |
| O4 | −0.3566 (2) | 0.1922 (2) | −0.67055 (13) | 0.0187 (4) |
| O5 | −0.1146 (3) | 0.1155 (3) | −0.49404 (14) | 0.0271 (4) |
| O6 | −0.1328 (3) | 0.3857 (2) | −0.55129 (14) | 0.0260 (4) |
| H6 | −0.1710 | 0.4459 | −0.5994 | 0.039* |
| O8 | −0.2608 (2) | −0.1596 (2) | −0.76055 (14) | 0.0221 (4) |
| O7 | 0.0076 (2) | −0.3163 (3) | −0.66683 (14) | 0.0235 (4) |
| H7 | 0.0277 | −0.2524 | −0.6221 | 0.035* |
| O9 | −0.7324 (2) | 0.0571 (2) | −0.79548 (14) | 0.0222 (4) |
| N1 | −0.1298 (2) | −0.1569 (2) | −0.40785 (14) | 0.0131 (4) |
| H1 | −0.1546 | −0.0853 | −0.4636 | 0.016* |
| C1 | −0.2094 (3) | −0.3143 (3) | −0.45269 (18) | 0.0177 (5) |
| H1A | −0.2034 | −0.3829 | −0.4005 | 0.021* |
| H1B | −0.1453 | −0.3648 | −0.4797 | 0.021* |
| C2 | −0.0584 (3) | 0.1673 (3) | −0.65317 (18) | 0.0179 (5) |
| H2A | −0.0992 | 0.0672 | −0.6886 | 0.021* |
| H2B | −0.0858 | 0.2502 | −0.7027 | 0.021* |
| C3 | −0.2027 (3) | −0.4205 (3) | −0.84996 (17) | 0.0145 (4) |
| H3A | −0.1515 | −0.5250 | −0.8295 | 0.017* |
| H3B | −0.3210 | −0.4379 | −0.8958 | 0.017* |

hydrogen atoms bonded to nitrogen and oxygen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached [1–3].

# 3 Comment

Organophosphonate-based complexes have received continuous attention owing to their structural diversity and potential applications in catalysis, absorption, separation, and so on [4–9]. Nitrilo-*tris*(methylenephosphonic acid) (NTMP) is known as a functionalized flexible triphosphonate ligand with a promising ligation ability due to the large number and steric availability of donor oxygen atoms.

Crystal structure analysis reveals that the asymmetric unit contains one central Cd(II) atom and one ligand. Each Cd atom is octahedrally coordinated by six phosphonate oxygen atoms from six different ligands. The Cd–O distances range from 2.1882(18) to 2.5562(18) Å, which are comparable with those of the reported Cd organotriphosphonate analogues [10, 11]. Three phosphonate and the amine groups are uniformly 1H-protonated, guaranteeing electric neutrality of the full moiety. The ligand adopts a $m_6$-hexadentate coordination mode. Two neighboring Cd atoms are triply bridged by two $\{PO_3\}$ groups and the $\mu_2$–O atom (O4) of another $\{PO_3\}$ group, leading to a densely compact 3D framework.

**Author contributions:** All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
**Research funding:** Foundation of Key Laboratory of Functional Metal-Organic Compounds of Hunan Province (2022HSKFJJ027).
**Conflict of interest statement:** The authors declare no conflicts of interest regarding this article.

# References

1. Bruker. *SAINT and SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2000.
2. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a Complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3.
4. Wang G. M., Li J. H., Pan J., Xue Z. Z., Wei L., Han S. D., Bao Z. Z., Wang Z. H. Two hybrid transition metal triphosphonates decorated with a tripodal imidazole ligand: synthesis, structures and properties. *Dalton Trans*. 2017, *46*, 808–813.
5. Xu Q., Xu B., Kong H., He P., Wang J., Kannan T., Ma P., Wang J., Niu J. Synthesis and characterization of a crown-shaped 36-molybdate cluster and application in catalyzing knoevenagel condensation. *Inorg. Chem.* 2020, *59*, 10665–10672.
6. Chausov F. F., Lomova N. V., Somov N. V., Kazantseva I. S., Kholzakov A. V., Sapozhnikov G. V., Zakirova R. M. Competitive formation of crystalline phases and its structural properties within the system $[Cu_xNi_{(1-x)}\{N(CH_2PO_3)_3\}]Na_4{\cdot}nH_2O$ ($x$= 0…1). *J. Cryst. Growth* 2019, *4*, 125187.
7. Mao J. G., Wang Z., Clearfield A. Hydrothermal synthesis, characterization and crystal structures of two new zinc (ii) phosphonates: $Zn_2[(O_3PCH_2)_2NHCH_2CO_2]$ and $Zn_2[HO_3PCH_2NH(CH_2PO_3)_2]$. *New J. Chem.* 2002, *26*, 1010–1014.
8. Fu R., Hu S., Wu X. Syntheses, structures, thermal stabilities and luminescence of two new 3D zinc phosphonates. *J. Solid State Chem.* 2011, *184*, 159–163.
9. Silva P., Vieira F., Gomes A. C., Ananias D., Fernandes J. A., Bruno S. M., Soares R., Valente A. A., Rocha J., Paz F. A. A. Thermal transformation of a layered multifunctional network into a metal–organic framework based on a polymeric organic linker. *J. Am. Chem. Soc.* 2011, *133*, 15120–15138.

10. Chausov F. F., Kazantseva I. S., Reshetnikov S. M., Lomova N. V., Maratkanova A. N., Somov N. V. Zinc and cadmium nitrilotris (methylenephosphonate) s: a comparative study of different coordination Structures for corrosion inhibition of steels in neutral aqueous media. *ChemistrySelect* 2020, *5*, 13711–13719.

11. Wang B., Man X. Crystal structure of poly[triaqua-(di(2,2′-bipyridine-κ2N,N′)-$\mu_4$-silanetetrayltetrakis(benzene-4,1-diyl)tetrakis (hydrogen phosphonato)-$\kappa_4$O:O′:O″:O‴) dicadmium(II)], $C_{44}H_{42}N_4O_{15}P_4Cd_2Si$. *Z. Kristallogr. N. Cryst. Struct*. 2020, *235*, 1361–1363.