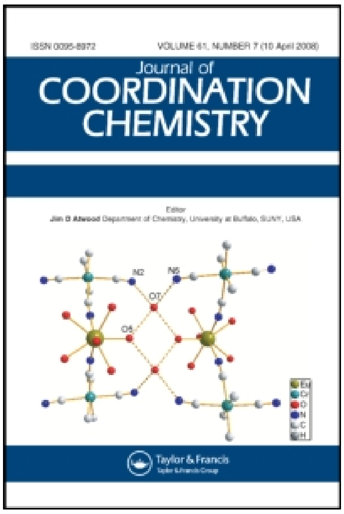

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Synthesis, crystal structure, and characterization of [Nd(tcph)(Htcph)(H_2O)$_5$]

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Synthesis, crystal structure, and characterization of [Nd(tcph)(Htcph)$(H_2O)_5$]

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A lanthanide complex [Nd(tcph)(Htcph)$(H_2O)_5$] (**1**) (H_2tcph = tetrachlorophthalic acid) has been characterized by X-ray single crystal diffraction, elemental analysis, IR, UV-Vis and fluorescence spectra. In the title complex, Nd^{3+} is coordinated by two tetrachlorophthalic acid ligands in a bidentate chelated pattern. Furthermore, the complex contains infinite chains linked by hydrogen bonds.

Keywords: Tetrachlorophthalato; Neodymium(III) complex; Supramolecular structure; Hydrogen bond

1. Introduction

Multidimensional supramolecular systems have attracted interest for their interesting properties and potential in various applications, e.g., host-guest structures, new classes of adsorbent, polar materials, magnetism, semiconductors, conductors, etc. [1]. The rational design of supramolecular structure relies upon exploiting noncovalent forces such as hydrogen bonding and aromatic π–π stacking interactions [1b]. Phthalic acid is a good ligand for transition metal ions and can construct supramolecular structures via strong hydrogen bonds O–H $\cdots$ O and aromatic π–π stacking interactions [2–24]. It can be a hydrogen bond acceptor and also a hydrogen bond donor because of the existence of the protonated carboxyl group which can affect the binding behavior through resonance and/or inductive effects [29]. Although transition metal phthalato complexes have been reported, lanthanide phthalate complexes are limited [25–28]. Based on high coordination numbers, intricate magnetic properties, and special fluorescence of lanthanides, we selected tetrachlorophthalic acid as a ligand and obtained a neodymium complex [Nd(tcph)(Htcph)$(H_2O)_5$] (**1**). Herein, we report the synthesis, crystal structure and fluorescence of **1**.

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2. Experimental

2.1. *Materials and physical techniques*

$Nd(NO_3)_3 \cdot 6H_2O$ was prepared by dissolving neodymium oxide in dilute nitric acid and then dried. Other materials were of analytical grade, obtained from commercial sources and used without further purification. Elemental analyses (C, H) were performed on a Perkin-Elmer 240 analyzer. The FT-IR spectra were measured with a Bruker Tensor 27 spectrometer on KBr disks in the region 4000–400 cm^{-1}. The UV-Vis spectra were measured on a JASCO V-570 spectrophotometer. Fluorescence spectra were measured on a Varian Cary Eclipse Fluorescence spectrophotometer. The magnetic properties were measured on a VSM-9600.

2.2. *Preparation of [Nd(tcph)(Htcph)(H_2O)$_5$]*

A 10 mL water solution of $Nd(NO_3)_3 \cdot 6H_2O$ (0.2 mmol) was added to a suspension of H_2tcph (0.2 mmol) in H_2O (10 mL), then 3 mL water solution of NaOH (0.3 mmol) was added. The mixture was stirred at room temperature for 1 h. After filtration, the filtrate was left undisturbed. Purple crystals were obtained after several days. Anal. Calcd for $C_{16}H_{11}Cl_8O_{13}Nd$: C, 22.88; H, 1.31%; Found: C, 22.95; H, 1.34%.

2.3. *X-ray crystallography*

Determination of the unit cell and data collection were performed on a BRUKER SMART 1000 diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K with crystal size $0.26 \times 0.20 \times 0.14$ mm^3. A total of 14008 [$R_{int} = 0.0191$] independent reflections were collected by the ω–ϕ scan technique in the range $2.06 \sim 25.02°$ with index ranges $-13 \leq h \leq 13$, $-22 \leq k \leq 22$, $-11 \leq l \leq 14$. Semiempirical absorption corrections were applied using the SADABS program. The structure was solved by direct methods and successive Fourier difference syntheses (SHELX-97) and refined by full-matrix least-squares procedure on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [30]. Hydrogen atoms were generated geometrically and refined isotropically.

3. Results and discussion

3.1. *Structure description*

As illustrated in figure 1 Nd(1) is surrounded by nine oxygen atoms, four of which are from two carboxylate groups of a tcph and a Htcph, both 1,3 chelates, while the other oxygen atoms are from five water molecules. In Sm tetrachlorophthalato complexes [27], tcph anions are monochelating and bidentate chelating. While in Pr tetrachlorophthalato complex [28], tcph anions are only monochelating ligands. The difference of the coordination modes of tcph anions is due to more deprotonation of tetrachlorophthalic acid in **1**. The Nd–O distances range from 2.446 to 2.646 Å. Crystal data and structure refinement for **1** are given in table 1. Selected bond lengths and

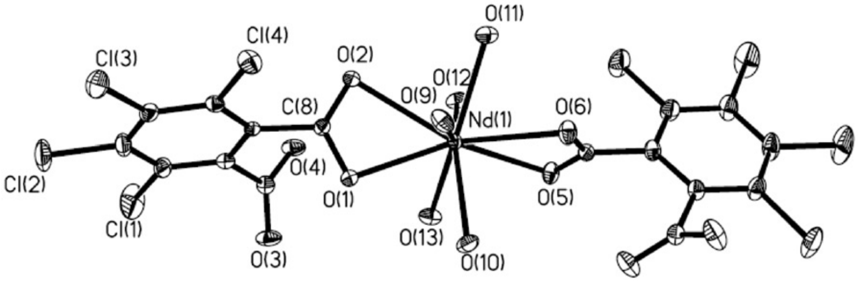

Figure 1. An ORTEP view of **1** with H atoms omitted for clarity. The displacement ellipsoids are drawn at 30% probability level.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{16}H_{11}Cl_8O_{13}Nd$
Formula weight	839.09
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pca2(1)*
Unit cell dimensions (Å, °)	
a	11.6518(6)
b	18.7527(9)
c	12.3626(6)
α	90
β	90
γ	90
V (Å^3)	2701.3(2)
Z	4
Calculated density (g cm^{-3})	2.063
Absorption coefficient (mm^{-1})	2.775
F(000)	1628
Crystal size (mm^3)	0.26 × 0.20 × 0.14
θ range for data collection	2.06–25.02
Limiting indices	$-13 \leq h \leq 13$, $-22 \leq k \leq 22$, $-11 \leq l \leq 14$
Reflections collected/unique	14008/4172 [$R_{\text{int}} = 0.0191$]
Max. and min. transmission	1.000000 and 0.678292
Data/restraints/parameters	4172/16/344
Goodness of fit on F^2	1.065
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0175$, $wR_2 = 0.0399$
R indices (all data)	$R_1 = 0.0193$, $wR_2 = 0.0404$
Absolute structure parameter	−0.010(8)
Largest diff. peak and hole (e Å^{-3})	0.329 and −0.415

angles are presented in table 2. Nonlinear Nd^{3+} ions in the supramolecular structure may be due to steric hindrance of ligands. The arrangement of Nd^{3+} ions with uncoordinated atoms omitted is shown in figure 2. There are infinite chains linked by hydrogen bonds between the oxygen atoms of coordinated water and the oxygen atoms of carboxylate groups of the ligands. The lengths of short hydrogen bonds range from 2.583 to 2.810 nm and the angles range from 133.31 to 179.18° resembling those in the Sm tetrachlorophthalato complex [27]. The presence of deprotonated carboxylate groups and a significant number of water molecules result in plentiful hydrogen bonds.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Nd(1)–O(11)	2.4459(19)	Nd(1)–O(13)	2.519(3)
Nd(1)–O(9)	2.446(2)	Nd(1)–O(6)	2.640(2)
Nd(1)–O(5)	2.4571(18)	Nd(1)–O(2)	2.646(2)
Nd(1)–O(12)	2.461(2)	Nd(1)–C(16)	2.903(3)
Nd(1)–O(1)	2.464(2)	Nd(1)–C(8)	2.925(3)
Nd(1)–O(10)	2.466(3)		
O(11)–Nd(1)–O(9)	77.70(9)	O(12)–Nd(1)–O(6)	108.22(8)
O(11)–Nd(1)–O(5)	92.77(7)	O(1)–Nd(1)–O(6)	141.96(8)
O(9)–Nd(1)–O(5)	120.90(9)	O(10)–Nd(1)–O(6)	77.37(9)
O(11)–Nd(1)–O(12)	72.03(9)	O(13)–Nd(1)–O(6)	121.99(8)
O(9)–Nd(1)–O(12)	146.69(8)	O(11)–Nd(1)–O(2)	75.08(7)
O(5)–Nd(1)–O(12)	74.81(9)	O(9)–Nd(1)–O(2)	76.54(8)
O(11)–Nd(1)–O(1)	123.52(7)	O(5)–Nd(1)–O(2)	156.68(8)
O(9)–Nd(1)–O(1)	75.86(8)	O(12)–Nd(1)–O(2)	82.45(8)
O(5)–Nd(1)–O(1)	143.45(7)	O(1)–Nd(1)–O(2)	50.65(7)
O(12)–Nd(1)–O(1)	109.82(8)	O(10)–Nd(1)–O(2)	121.90(7)
O(11)–Nd(1)–O(10)	140.68(11)	O(13)–Nd(1)–O(2)	101.79(8)
O(9)–Nd(1)–O(10)	73.43(9)	O(6)–Nd(1)–O(2)	135.98(8)
O(5)–Nd(1)–O(10)	80.06(8)	O(11)–Nd(1)–C(16)	77.94(8)
O(12)–Nd(1)–O(10)	139.85(9)	O(9)–Nd(1)–C(16)	97.01(9)
O(1)–Nd(1)–O(10)	74.18(8)	O(5)–Nd(1)–C(16)	25.60(9)
O(11)–Nd(1)–O(13)	139.97(10)	O(12)–Nd(1)–C(16)	90.08(9)
O(9)–Nd(1)–O(13)	141.40(8)	O(1)–Nd(1)–C(16)	153.87(8)
O(5)–Nd(1)–O(13)	74.60(8)	O(10)–Nd(1)–C(16)	79.69(9)
O(12)–Nd(1)–O(13)	68.03(9)	O(13)–Nd(1)–C(16)	99.31(9)
(1)–Nd(1)–O(13)	74.13(8)	O(6)–Nd(1)–C(16)	25.29(8)
O(10)–Nd(1)–O(13)	75.45(7)	O(2)–Nd(1)–C(16)	153.00(8)
O(11)–Nd(1)–O(6)	68.66(9)	O(11)–Nd(1)–C(8)	99.60(8)
O(9)–Nd(1)–O(6)	72.16(7)	O(9)–Nd(1)–C(8)	75.36(8)
O(5)–Nd(1)–O(6)	50.71(8)	O(5)–Nd(1)–C(8)	161.63(9)
O(12)–Nd(1)–C(8)	96.07(9)	O(6)–Nd(1)–C(8)	147.11(8)
O(1)–Nd(1)–C(8)	25.30(8)	O(2)–Nd(1)–C(8)	25.37(8)
O(10)–Nd(1)–C(8)	98.32(8)	C(16)–Nd(1)–C(8)	172.36(9)
O(13)–Nd(1)–C(8)	87.24(8)		

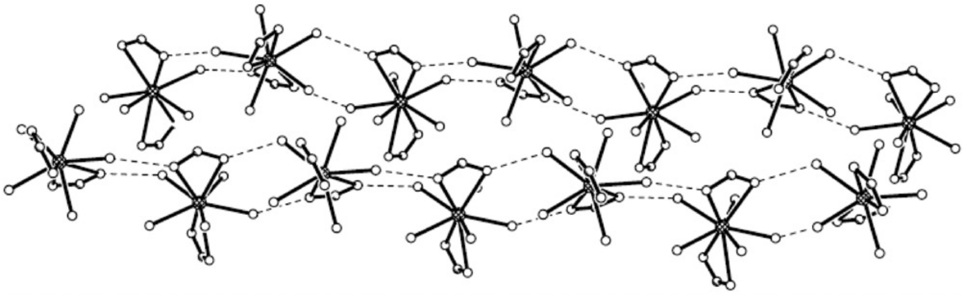

Figure 2. The chains of **1** linked by H bonds without uncoordinated atoms.

3.2. *Spectroscopic properties*

In IR spectra of **1**, a broad band (2700–3700 $\mathrm{cm^{-1}}$) of the $\nu(\mathrm{H_2O})$ centered at 3346 $\mathrm{cm^{-1}}$ was observed. A very strong band for the antisymmetry stretching of carboxylic group appears at 1581 $\mathrm{cm^{-1}}$, and the symmetrical stretching band is at 1451 $\mathrm{cm^{-1}}$ [31].

The UV-Vis spectra of **1** were measured in the solid state. The hypersensitive transition observed for Nd^{3+} ions at 580 nm can be assigned to the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transitions and the band at 743 nm corresponds to the $^4I_{9/2} \rightarrow {}^4F_{7/2}$ transition [32].

The luminescence spectra of **1** were measured in the solid state. The luminescence spectrum corresponds to $^4F_{3/2} \rightarrow {}^4I_{9/2}$ at 825 nm blue shifts compared to the former report, suggesting energy transfer from tcph anions to Nd^{3+} center. We did not observe fluorescence emission bands in the near-infrared region for **1** [32–34], indicating that tcph cannot sensitize the NIR luminescence of Nd^{3+} ions.

3.3. *Magnetic properties*

The μ_{eff} at room temperature, 3.54 B.M., is close to that expected (3.62 B.M.) for insulated Nd(III) ion in the $^4I_{9/2}$ ground state ($g = 8/11$).

Supplementary data

CCDC 609797 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: +44 1223 336 033, Email: deposit@ccdc.cam.ac.uk

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References

[1] (a) D. Braga, F. Grepioni. *Chem. Rev.*, **98**, 1375 (1998); (b) B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001).

[2] Z.H. Jiang, S.L. Ma, D.Z. Liao, S.P. Yan, G.L. Wang, X.K. Yao, R.J. Wang. *J. Chem. Soc., Chem. Commun.*, 745 (1993).

[3] K. Kobayashi, H. Izawa, K. Yamaguchi, E. Horn, N. Furukawa. *J. Chem. Soc., Chem. Commun.*, 1428 (2001).

[4] E.G. Bakalbassis, D.G. Paschalidis, C.P. Raptopoulou, V. Tangouis. *Inorg. Chem.*, **37**, 4735 (1998).

[5] J. Lewinski, J. Zachara, I. Justyniak. *Inorg. Chem.*, **37**, 2575 (1998).

[6] Z.N. Chen, H.X. Zhang, K.B. Yu, B.S. Kang, H. Cai, C.Y. Su, T.W. Wang, Z.L. Lu. *Inorg. Chem.*, **37**, 4775 (1998).

[7] E. Suresh, K. Boopalan, R.V. Jasra, M.M. Bhadbhade. *Inorg. Chem.*, **40**, 4078 (2001).

[8] S.G. Baca, Y.A. Simonov, N.V. Gerbeleu, M. Gdaniec, P.N. Bourosh, G.A. Timco. *Polyhedron*, **20**, 831 (2001).

[9] S.G. Baca, Y.A. Simonov, M. Gdaniec, N.V. Gerbeleu, I.G. Filloppova, G.A. Timco. *Inorg. Chem. Commun.*, **6**, 685 (2003).

[10] S.G. Baca, I.G. Filloppova, N.V. Gerbeleu, Y.A. Simonov, M. Gdaniec, G.A. Timco, O.A. Gherco, Y.L. Malaestean. *Inorg. Chim. Acta*, **344**, 109 (2003).

[11] S.B. Raj, P.T. Muthiah, G. Bocelli, A. Cantoni. *Inorg. Chem. Commun.*, **6**, 748 (2003).

[12] C.B. Ma, C.N. Chen, Q.T. Liu, D.Z. Liao, L.C. Li, L.C. Sun. *New J. Chem.*, **27**, 890 (2003).

[13] S.L. Ma, D.Z. Liao, Z.H. Jiang, S.P. Yan, F.C. Xue, G.L. Wang. *Synth. React. Inorg. Met. -Org. Chem.*, **24**, 1683 (1994).

[14] L.C. Li, D.Z. Liao, Z.H. Jiang, S.P. Yan. *Polyhedron*, **19**, 2529 (2000).

[15] Y. Zhang, J. Li, Q. Su, Q. Wang, X. Wu. *J. Mol. Struct.*, **516**, 231 (2000).

[16] C. Chen, H. Zhu, D. Huang, T. Wen, Q. Liu, D.Z. Liao, J.Z. Cui. *Inorg. Chim. Acta*, **320**, 159 (2001).

[17] C. Ma, W. Wang, H. Zhu, C. Chen, Q. Liu. *Inorg. Chem. Commun.*, **4**, 720 (2001).

[18] H.X. Zhang, B.S. Kang, A.W. Xu, Z.N. Chen, Z.Y. Zhou, A.S.C. Chan, K.B. Yu, C. Ren. *J. Chem. Soc., Dalton Trans.*, 2559 (2001).

[19] J.C. Yao, W. Huang, B. Li, S.H. Gou, Y. Xu. *Inorg. Chem. Commun.*, **5**, 711 (2002).

[20] S.Y. Yang, L.S. Long, Z.Y. Wu, M.X. Zhan, R.B. Huang, L.S. Zheng. *Trans. Met. Chem.*, **27**, 546 (2002).

[21] X.R. Sun, P. Cheng, J.Z. Cui, D.Z. Liao, Z.H. Jiang, S.P. Yan, G.L. Wang. *Trans. Met. Chem.*, **22**, 65 (1997).

[22] Y.Q. Qi, M.M. Miao, X.R. Sun, Z.H. Jiang, D.Z. Liao, G.L. Wang. *Trans. Met. Chem.*, **20**, 270 (1995).

[23] X.R. Sun, M.M. Miao, Y.Q. Qi, D.Z. Liao, Z.H. Jiang, G.L. Wang. *Synth. React. Inorg. Met.-Org. Chem.*, **25**, 481 (1995).

[24] S.G. Baca, M.T. Reetz, R. Goddard, I.G. Filippova, Y.A. Simonov, M. Gdaniec, N. Gerbeleu. *Polyhedron*, **25**, 1215 (2006).

[25] Y.H. Wang, L.P. Jin, K.Z. Wang, L.P. Zhang, X.J. Zheng, S.Z. Lu. *New J. Chem.*, **26**, 1590 (2002).

[26] Y.H. Wan, L.P. Zhang, L.P. Jin, S. Gao, S.Z. Lu. *Inorg. Chem.*, **42**, 4985 (2003).

[27] M. Liang, Y.Q. Sun, D.Z. Liao, Z.H. Jiang, S.P. Yan, P. Cheng. *J. Coord. Chem.*, **57**, 275 (2004).

[28] N. Xu, Y. Ou-Yang, D.Z. Liao, Z.H. Jiang. *Acta Cryst. E*, **61**, m1272 (2005).

[29] B. Yan, Y.Y. Bai, Z.X. Chen. *J. Mol. Struct.*, **741**, 141 (2005).

[30] G.M. Sheldrick. *SHELXS-97 and SHELXL-97, Software for Crystal Structure Analysis*, Siemens Analytical X-ray Instruments Inc, Madison, WI (1997).

[31] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn, Wiley Press, New York (1986).

[32] A.T. Baker, A.M. Hamer, S.E. Livingstone. *Trans. Met. Chem.*, **9**, 423 (1984).

[33] W.K. Wong, X.P. Yang, R.A. Jones, J.H. Rivers, V. Lynch, W.K. Lo, D. Xiao, M.M. Oye, A.L. Holmes. *Inorg. Chem.*, **45**, 4340 (2006).

[34] G.A. Hebbink, L. Grave, L.A. Woldering, D.N. Reinhoudt, F.C.J.M.V. Veggel. *J. Phys. Chem. A*, **107**, 2483 (2003).