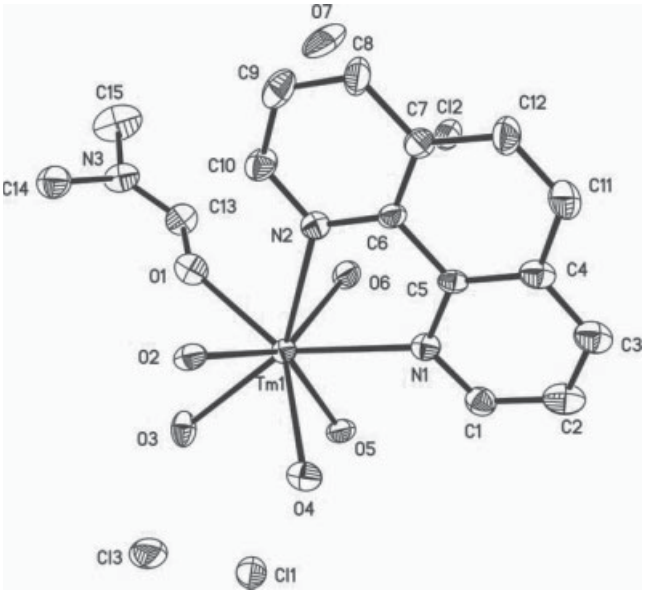
Crystal structure of (1,10-phenanthroline-κ^2*N*,*N*')-dimethyl- formamide-pentaaqua-thulium(III) trichloride monohydrate, $[Tm(C_{12}H_8N_2)((CH_3)_2NCHO)(H_2O)_5]Cl_3{\cdot}H_2O$, $C_{15}H_{27}Cl_3N_3O_7Tm$

Yong-Sheng Yang[I], Min Liu[II], Xin Wang[I], Jian-Bao Li[I] and Qiong-Hua Jin[*, I]

[I] Department of Chemistry, Capital Normal University, Beijing 100048, P. R. China
[II] The College of Materials Scienceand Engineering, Beijing University of Technology, Beijing 100022, P. R. China

Received March 20, 2013, accepted June 17, 2013, available online July 29, 2013, CCDC no. 1267/3999



Abstract

$C_{15}H_{27}Cl_3N_3O_7Tm$, monoclinic, $P2_1/c$ (no. 14), a = 17.492(2) Å, b = 9.6752(5) Å, c = 14.972(1) Å, β = 110.986(2)°, V = 2365.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.0409, $wR_{ref}(F^2)$ = 0.1023, T = 298 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.14×0.27×0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	41.27 cm^{-1}
Diffractometer, scan mode:	Bruker Smart CCD area detector, φ and ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8419, 4166
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3281
$N(param)_{refined}$:	264
Programs:	SHELX [8]

Source of material

A mixture of $TmCl_3{\cdot}6H_2O$ (0.0804 g, 0.21 mmol) and phenanthroline (*phen*, 0.0398 g, 0.20 mmol) was dissolved in 10 ml acetonitrile, then *L* ligand (methylenediphosphonate, 0.20 mmol) and DMF (*N,N*-dimethylformamide, 3 drops) were added under stirring at room temperature. The clear colourless solution was stirred for 6.5 hours at room temperature. The insoluble residues were removed by filtration, and the filtrate was allowed to be evaporated slowly at room temperature for two weeks to yield colourless crystals.

* Correspondence author (e-mail: jinqh@mail.cnu.edu.cn)

Discussion

Lanthanide complexes have attracted attention due to their potential applications in fluorescence materials, electroluminescent devices, bioassays, luminescent probes, catalytic and ion exchange fields [1, 2]. Phosphoryl(methylenediphosphonate) has been confirmed to be a very efficient ligand, it can form stable complexes with lanthanide ions. In recent years, many lanthanide complexes containing methylenediphosphonate (*L*), such as $[Nd(OTf)_2(L)_2(OH)_2](OTf)$, $[La(L)_4](OTf)_3(CH_3CN)_3$, $[Ln(NO_3)_3(L)_2](CH_3CN)_2$, were reported [3]. Phenanthroline is a very valid bidentate ligand, so it was chosen as an auxiliary ligand to form mixed-ligand lanthanide complexes, such as $[CeCl_3(phen)_2DMF]{\cdot}DMF$ [4]. Since the lanthanide cations are very oxophilic, they are expected to interact strongly with highly polarized oxygen-bearing functional groups. We are interested in the reactions of lanthanide chloride with phosphoryl and *phen*, becauce it can always produce diverse compounds. In our previous work, some lanthanide complexes with (*L*) or *phen* have been synthesized and structurally characterized, such as $[CeCl_3(phen)_2DMF]{\cdot}DMF$ [4] and $[Ce(NO_3)_3(L)_2]$ [5]. In this paper, we report a complex $[Tm(phen)(DMF)(H_2O)_5]Cl_3{\cdot}H_2O$ which is obtained by the similar reaction. Single-crystal X-ray diffraction study revealed that the mononuclear complex $[Tm(phen)(DMF)(H_2O)_5]Cl_3{\cdot}H_2O$ was obtained despite the presence of tetrakis(*O*-isopropyl)methylenediphosphonate. The presence of methylenediphosphonate may have subtle effects on the coordination of *phen* ligand with lanthanide atom, just as in our previous work [4]. In the title complex, the *phen*, water and even the solvent DMF molecules are coordinated to the central Tm atom. The phenomenon that the DMF molecule was coordinated to the lanthanide atom through the oxygen atom also happened in preparing the complex ($[CeCl_3(phen)_2DMF]{\cdot}DMF$ [4]). The thulium atom is coordinated by two nitrogen atoms from one *phen* ligand, one oxygen atom from DMF, and five oxygen atoms from five water molecules with the total coordination number of 8. There are also three chloride ions and one free water molecule out of the coordination sphere. The average Tm–N(*phen*) bond distance of 2.489 Å is shorter than the average Tm–N(*phen*) bond distance of 2.536 Å in the complex $[Tm_2(phen)_4(H_2O)_2(OH)_2]{\cdot}(phen)_2(NO_3)_4$ [6]. The Tm–O(DMF) bond distance is 2.249 Å, which is larger than Tm–O(DMF) bond distance of 2.332 Å in the complex $[Tm(DMF)_4(H_2O)_3(\mu\text{-}CN)Fe(CN)_5]{\cdot}1.25H_2O$ [7]. The ions and molecules of the title structure form a two-dimensional network through the hydrogen bonds O–H···Cl and O-H···O. The hydrogen bonds O–H···Cl are formed between O–H donors of water molecules and chloride ions (O···Cl = 3.029-3.204 Å, O–H···Cl = 173.19-176.91°); while the hydrogen bond O2–H2···O7 is formed between O2–H2 group of the coordinated

water molecule and O7 atom of the free water molecule (O2···O7 = 2.637 Å, O2–H2D···O7 = 175.75°).

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2C)	4*e*	0.7820	0.4443	0.7332	0.047
H(2D)	4*e*	0.7782	0.3243	0.6820	0.047
H(3C)	4*e*	0.9155	0.6966	0.7106	0.053
H(3D)	4*e*	0.9485	0.5674	0.7094	0.053
H(4C)	4*e*	0.7600	0.6477	0.7400	0.051
H(4D)	4*e*	0.7175	0.7626	0.6936	0.051
H(5C)	4*e*	0.8458	0.8505	0.6144	0.056
H(5D)	4*e*	0.8108	0.8568	0.5160	0.056
H(6C)	4*e*	0.7425	0.603	0.3621	0.054
H(6D)	4*e*	0.7858	0.7166	0.4095	0.054
H(7C)	4*e*	0.7478	0.4048	0.1903	0.106
H(7D)	4*e*	0.8289	0.4106	0.1992	0.106
H(1)	4*e*	0.6563	0.8655	0.5234	0.050
H(2)	4*e*	0.5256	0.9472	0.4443	0.066
H(3)	4*e*	0.4245	0.7978	0.3616	0.062
H(8)	4*e*	0.5244	0.1466	0.3316	0.061
H(9)	4*e*	0.6594	0.0884	0.4037	0.068
H(10)	4*e*	0.7530	0.2488	0.4923	0.056
H(11)	4*e*	0.3813	0.5538	0.3043	0.067
H(12)	4*e*	0.4170	0.3309	0.2946	0.062
H(13)	4*e*	0.8937	0.4513	0.4366	0.056
H(14A)	4*e*	0.9331	0.2178	0.6173	0.088
H(14B)	4*e*	1.0066	0.1531	0.5951	0.088
H(14C)	4*e*	0.9175	0.0969	0.5431	0.088
H(15A)	4*e*	0.9597	0.3129	0.3724	0.124
H(15B)	4*e*	0.9488	0.1555	0.3899	0.124
H(15C)	4*e*	1.0303	0.2314	0.4494	0.124

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tm(1)	4*e*	0.77785(2)	0.58172(3)	0.56890(2)	0.0314(2)	0.0257(2)	0.0290(2)	0.0016(1)	0.0131(1)	–0.0006(1)
Cl(1)	4*e*	0.9366(1)	0.9301(2)	0.7526(2)	0.048(1)	0.041(1)	0.064(1)	–0.0060(9)	0.005(1)	–0.0064(8)
Cl(2)	4*e*	0.6544(1)	0.5476(2)	0.2209(1)	0.055(1)	0.044(1)	0.050(1)	–0.014(1)	0.017(1)	–0.0021(8)
Cl(3)	4*e*	0.8038(2)	0.5483(2)	0.8811(1)	0.114(2)	0.050(1)	0.038(1)	0.019(1)	0.032(1)	0.0023(8)
N(1)	4*e*	0.6372(4)	0.6723(5)	0.4866(3)	0.042(4)	0.027(3)	0.034(3)	0.006(3)	0.016(3)	–0.002(2)
N(2)	4*e*	0.6788(4)	0.4058(5)	0.4708(4)	0.033(4)	0.032(3)	0.038(3)	0.005(3)	0.015(3)	0.001(2)
N(3)	4*e*	0.9375(4)	0.2772(6)	0.4925(4)	0.056(5)	0.040(4)	0.055(4)	0.014(3)	0.035(3)	0.003(3)
O(1)	4*e*	0.8638(3)	0.4251(5)	0.5453(3)	0.046(4)	0.049(3)	0.042(3)	0.014(2)	0.023(3)	–0.004(2)
O(2)	4*e*	0.7737(3)	0.4118(4)	0.6777(3)	0.062(4)	0.028(2)	0.036(2)	0.002(2)	0.026(3)	–0.000(2)
O(3)	4*e*	0.9041(3)	0.6130(5)	0.6936(3)	0.027(3)	0.040(3)	0.059(3)	0.001(2)	0.008(2)	–0.012(2)
O(4)	4*e*	0.7419(3)	0.6898(5)	0.6866(3)	0.058(4)	0.037(3)	0.036(2)	0.012(2)	0.022(2)	–0.002(2)
O(5)	4*e*	0.8100(3)	0.8144(5)	0.5654(3)	0.073(4)	0.034(3)	0.033(2)	–0.011(3)	0.019(3)	0.002(2)
O(6)	4*e*	0.7767(3)	0.6313(5)	0.4152(3)	0.062(4)	0.040(3)	0.037(2)	–0.011(3)	0.021(3)	–0.006(2)
O(7)	4*e*	0.7863(5)	0.3599(6)	0.1815(5)	0.089(6)	0.037(3)	0.150(6)	–0.009(3)	0.056(5)	–0.024(4)
C(1)	4*e*	0.6161(5)	0.8033(7)	0.4886(5)	0.044(5)	0.039(4)	0.038(4)	0.006(4)	0.012(4)	0.001(3)
C(2)	4*e*	0.5370(6)	0.8537(9)	0.4416(5)	0.062(7)	0.054(5)	0.057(5)	0.023(5)	0.031(5)	0.013(4)
C(3)	4*e*	0.4776(5)	0.7657(9)	0.3924(5)	0.041(5)	0.064(5)	0.053(4)	0.015(4)	0.021(4)	0.014(4)
C(4)	4*e*	0.4953(5)	0.6257(8)	0.3874(5)	0.039(5)	0.051(4)	0.043(4)	0.011(4)	0.020(4)	0.012(3)
C(5)	4*e*	0.5770(4)	0.5844(6)	0.4334(4)	0.033(4)	0.035(4)	0.027(3)	0.005(3)	0.016(3)	0.007(3)
C(6)	4*e*	0.5995(5)	0.4411(6)	0.4267(4)	0.042(5)	0.030(3)	0.028(3)	–0.004(3)	0.015(3)	0.003(3)
C(7)	4*e*	0.5386(5)	0.3504(8)	0.3722(5)	0.035(5)	0.049(4)	0.038(4)	–0.007(4)	0.018(4)	0.007(3)
C(8)	4*e*	0.5626(6)	0.2123(8)	0.3654(5)	0.048(6)	0.048(5)	0.050(4)	–0.019(4)	0.011(4)	–0.011(3)
C(9)	4*e*	0.6422(6)	0.1780(8)	0.4090(6)	0.074(7)	0.033(4)	0.068(5)	–0.012(4)	0.032(5)	–0.016(4)
C(10)	4*e*	0.6988(5)	0.2759(7)	0.4619(5)	0.046(5)	0.030(4)	0.062(4)	0.005(4)	0.017(4)	–0.001(3)
C(11)	4*e*	0.4355(5)	0.527(1)	0.3346(5)	0.021(5)	0.075(6)	0.066(5)	0.000(4)	0.010(4)	0.009(5)
C(12)	4*e*	0.4569(5)	0.3943(9)	0.3284(5)	0.038(5)	0.064(6)	0.050(5)	–0.018(4)	0.012(4)	–0.002(4)
C(13)	4*e*	0.8977(5)	0.3911(8)	0.4865(5)	0.044(5)	0.052(5)	0.053(4)	0.001(4)	0.027(4)	0.000(4)
C(14)	4*e*	0.9497(6)	0.1779(8)	0.5683(5)	0.079(7)	0.046(5)	0.053(4)	0.005(5)	0.027(5)	–0.004(4)
C(15)	4*e*	0.9720(7)	0.241(1)	0.4198(7)	0.108(9)	0.070(6)	0.104(7)	0.028(6)	0.080(7)	0.011(5)

Acknowledgments. This work has been supported by National Natural Science Foundation of China (No.21171119),the National High Technology Research and development Program 863 of China (2012AA063201), Beijing Personnel Bureau, the National Keystone Basic Research Program (973 Program) under grant no. 2007CB310408, no. 2006CB302901 and the Committee of Education of the Beijing Foundation of China (grant No. KM201210028020).

References

1. Li, X.; Zhang, Y, B.; Zou Y, Q.: Hydrothermal synthesis, crystal structure, and luminescence of lanthanide(III)coordination polymers with tetrafluorosuccinate and 1,10-phenanthroline. J. Mol. Struct. **919** (2009) 277-283.
2. Fawcett, J.; Platt, A. W. G.; Russell, D. R.:Structures and catalytic properties of triphenylphosphine oxide complexes of scandium and lanthanide triflates. Polyhedron **21** (2002) 287-293.
3. Jin, Q. H.; Ricard, L.; Nief, F.: Lanthanide complexes with a chelating methylenedihosphonate. Polyhedron **24** (2005) 549-555.
4. Jin, Q. H.; Deng, S. F.; Dong, J. C.; Gao H. W.; Li, P. Z.: Crystal structure of trichloro-bis(*N,N'*-1,10-phenanthroline)-dimethylformamide-cerium(III) dimethylformamide solvate, $Ce(C_{12}H_8N_2)_2((CH_3)_2NCHO)Cl_3 \cdot (CH3)_2NCHO$. Z. Kristallogr. NCS **222** (2007) 98-100.
5. Wang, R.; Mu, K. J.; Deng, S. F.; Jin, Q. H.; Zhang, C. L.: Crystal structure of bis(*O,O'*-tetraisopropylmethylenediphosphonate)-cerium(III)trinitrate, $Ce(NO_3)_3[CH_2P_2O_2(C_3H_7O)_4]_2$. Z. Kristallogr. NCS **225** (2010) 613-615.
6. Wei, D. Y.; Zhang, Y. Q.; Lin, J. L.: Two Hydroxo Bridged Dinuclear Lanthanide *Phen* Complexes: $[Ln_2(phen)_4(H_2O)_4(OH)_2](phen)_2(NO_3)_4$ with Ln = Tm, Yb. Z. Naturforsch. **57b** (2002)625-630.
7. Figuerola, A.; Diaz, C.; Ribas, J.; Tangoulis, V.; Granell, J.; Lloret, F.; Mahia, J.; Maestro, M.:Synthesis and Characterization of Heterodinuclear Ln^{3+}-Fe^{3+} and Ln^{3+}-Co^{3+} Complexes, Bridged by Cyanide Ligand (Ln^{3+} = Lanthanide Ions). Nature of the Magnetic Interaction in the Ln^{3+}-Fe^{3+} Complexes. Inorg. Chem. **42** (2003) 641-649.
8. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.