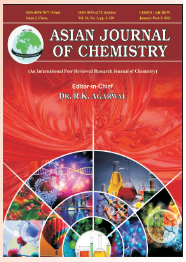
Asian Journal of Chemistry; Vol. 26, No. 24 (2014), 8604-8606

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.18477



Syntheses and Crystal Structure of Ce(IV) Complex Containing 4-Heterocyclic Acylpyrazolone

C.X. Zhao[1], Y.J. Ding[2,*], T.T. Yuan[1], D.Y. Wanyan[1], Y.J. Guo[1], Z.Z. Hu[1] and X. Li[1]

[1]College of Chemistry and Chemical Engineering, Zhoukou Normal University, Zhoukou 466001, P.R. China
[2]Institute of Medicinal Chemistry, College of Chemistry and Chemical Engineering, Zhoukou Normal University, Zhoukou 466001, P.R. China

*Corresponding author: Tel/Fax: +86 394 8178253; E-mail: yongjieding@163.com

Received: 19 July 2014; *Accepted*: 27 August 2014; *Published online*: 1 December 2014; AJC-16414

A novel Ce complex of 4-acylpyrazolones of formula [Ce(CPTP)$_4$] ($C_6H_5CH_3$)$_3$ (HCPTP = 1-(4-chlorophenyl)-3-phenyl-4-thenoyl-1*H*-pyrazol-5-ol) has been synthesized and characterized. It crystallizes in the triclinic space group P-1 with a = 12.9770(12) Å, b = 16.7877(15) Å, c = 21.8362(19) Å; α = 105.5250(10)°, β = 93.389(2)°, γ = 99.209(2)°, V = 4498.4(7) Å^3, $C_{101}H_{72}N_8O_8S_4CeCl_4$, Mr = 1935.87, Z = 2, Dc = 1.429 g/cm^3, m = 0.781 mm^{-1}, F(000) = 1976, R = 0.0312 and wR = 0.0696 for 16643 observed reflections with I > 2σ(I). The complex is mononuclear. In air and solution stable compounds containing an eight-coordinated Ce(IV) center in a distorted dodecahedral configuration, the average Ce-O bond length is 2.3351(14) Å.

Keywords: Acylpyrazolone complex, Cerium, Crystal structure.

INTRODUCTION

Acylpyrazolones are an interesting class of β-diketones compounds and are widely used as solvent extractions of metal ions, laser working materials and NMR shift-reagents[1-3]. Their metal complexes have been found to display catalytic performance, biological activity and enhanced luminescence. HCPTP [1-(4-chlorophenyl)-3-phenyl-4-thenoyl-1*H*-pyrazol-5-ol] is a new 4-heterocyclic acylpyrazolone. In our previous work, the syntheses of some transition metal complexes of HCPTP have been reported[4,5]. In this work, as a continuation of our research, our work focused on synthesizing a novel metal-organic complex of HCPTP with Ce(IV) firstly and then reporting single crystal structure, IR spectra properties and thermal analysis of the synthesized complex.

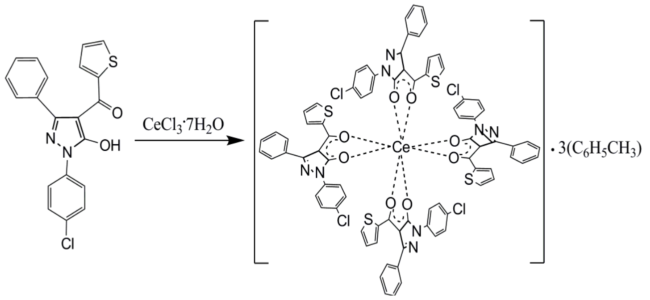
EXPERIMENTAL

All reagents used in the syntheses were analytical grade and used without further purification. Elemental analyses for carbon, hydrogen and nitrogen were performed on an Elementar vario EL III elemental analyzer. The infrared spectra (4000-400 cm^{-1}) were recorded by using KBr pellet on a Nicolet 5700 spectrophotometer. Thermal analysis was performed on a Netzsch STA449F3 TG-DSC thermal analyzer with a heating rate of 10 K/min.

Synthesis of the Ce complex: A solution of $CeCl_3 \cdot 7H_2O$ (1 mmol, 0.37 g) in 5 mL anhydrous ethanol was added to a solution of HCPTP (4 mmol, 1.52 g) and sodium methylate (4 mmol, 0.22 g) in 10 mL methylbenzene. The mixture was placed in a 30 mL Teflon-lined stainless steel vessel, gradually heated to 120 °C for 12 h and then programmed cooled to room temperature over 48 h. Black block crystals suitable for X-ray analysis were obtained, yield: 67 %. The reaction procedure is shown in **Scheme-I**.

For $C_{101}H_{72}N_8O_8S_4CeCl_4$: Anal. Calcd (%) : C, 62.66; H, 3.75; N, 5.79. Found: C, 66.37; H, 3.89; N, 5.67.

X-ray crystallography: Black single crystal of the complex (0.40 mm × 0.15 mm × 0.15 mm) was put on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromated MoK$_\alpha$ radiation (λ = 0.71073 Å) by using a φ/ω scan technique at room temperature. 19860 independent reflections (R_{int} = 0.0190) in the range 1.95 < θ < 27.10 with -12 ≤ h ≤ 16, -20 ≤ k ≤ 21, -27 ≤ l ≤ 24 were collected at 296(2) K. The structure was solved by direct methods with SHELXS-97[6]. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains, while the non-hydrogen atoms were treated with common anisotropic displacement factors and included in the final refinement with geometrical restrains. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97[7]. The final agreement factor values are R = 0.0312 and wR = 0.0696. Crystallographic data and refinement parameters are listed in Table-1. CCDC 1008949 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.



Scheme-I: Synthesis of $[Ce(CPTP)_4]\ (C_6H_5CH_3)_3$

TABLE-1 CRYSTALLOGRAPHIC DATA FOR $[Ce(CPTP)_4]\ (C_6H_5CH_3)_3$	
Compound	$[Ce(CPTP)_4]\ (C_6H_5CH_3)_3$
Color/shape	Black/block
m.f.	$C_{101}H_{72}N_8O_8CeS_4Cl_4$
Formula weight	1935.87
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 12.9770(12) Å, b = 16.7877(15) Å c = 21.8362(19) Å α = 105.525(1)° β = 93.389(2)° γ = 99.209(2)°
Z Volume, $Å^3$	2 4498.4(7)
Calculated density (mg/m^3)	1.429
Absorption coefficient (mm^{-1})	0.781
F(000)	1976
θ range for data collection (°)	1.95-27.10
Reflections collected	28181
Independent reflection	19860 [R_{int} = 0.0190]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	19407/802/1192
Goodness-of-fit on F^2	1.003
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0312, wR2 = 0.0696
R indices (all data)	R1 = 0.0403, wR2 = 0.0737
Largest diff. peak and hole	0.663 and -0.758 $e/Å^3$

RESULTS AND DISCUSSION

Description of the crystal structure: The structure of the title complex is shown in Fig. 1. Single-crystal XRD analysis reveals that crystal $[Ce(CPTP)_4]\ (C_6H_5CH_3)_3$ belongs to Triclinic space group P-1. In the asymmetric unit of the crystal, the exists one crystallographically independent Ce, four bidentate pyrazolonate ligands $CPTP^-$ and three methylbenzene molecules. Eight oxygen atoms [O(1)-O(8)] from four $CPTP^-$ ligands comprise the coordinated sphere of Ce. Each $CPTP^-$ forms a six-membered ring with central ion Ce.

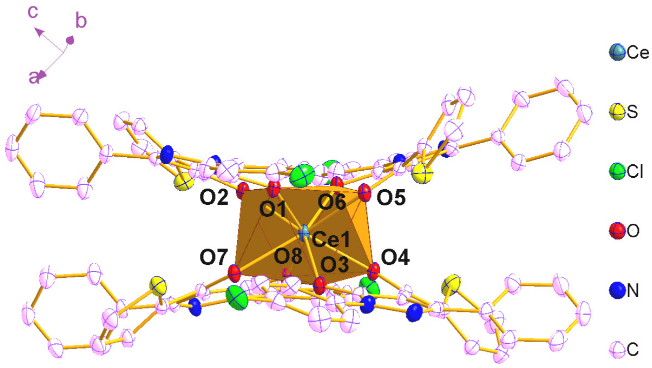


Fig. 1. Molecular structure of $[Ce(CPTP)_4]\ (C_6H_5CH_3)_3$ in the solid state. (30 % probability ellipsoids. The three uncoordinated methylbenzene molecules are omitted for clarity)

The eight-coordinated Ce adopts a distorted triangular dodecahedral coordination geometry. The Ce-O distances are in the range of 2.2592(14)-2.3854(13) Å (Table-2). The calculated bond valence sum of Ce is 4.269, which confirmed that the Ce(III) was oxidized to Ce(IV) in the process of reaction[8,9].

In the complex $[Ce(CPTP)_4]\ (C_6H_5CH_3)_3$, two types of weak intermolecular interactions, $\pi\cdots\pi$ and C-H$\cdots\pi$, are present in the structures results in the formation of a stable 3D network structure (Fig. 2). The packing diagram and the various molecular interactions such as C-H$\cdots\pi$ and $\pi\cdots\pi$ interactions are calculated using the program PLATON-97[10].

IR spectra analysis: The infrared spectra of the HCPTP ligand were compared with that of the complex $[Ce(CPTP)_4]$

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR $[Ce(CPTP)_4]\ (C_6H_5CH_3)_3$
WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond	d, Å	Bond	d, Å
Ce(1)-O(1)	2.3033(14)	O(1)-C(14)	1.278(2)
Ce(1)-O(2)	2.3374(13)	O(2)-C(5)	1.280(2)
Ce(1)-O(3)	2.2743(14)	O(3)-C(34)	1.287(2)
Ce(1)-O(4)	2.3854(13)	O(4)-C(25)	1.269(2)
Ce(1)-O(5)	2.3800(14)	O(5)-C(45)	1.268(2)
Ce(1)-O(6)	2.2861(14)	O(6)-C(54)	1.281(2)
Ce(1)-O(7)	2.3792(14)	O(7)-C(65)	1.274(2)
Ce(1)-O(8)	2.2592(14)	O(8)-C(74)	1.284(2)
Angle	ω, (°)	Angle	ω, (°)
O(1)-Ce(1)-O(5)	70.34(5)	O(1)-Ce(1)-O(2)	71.55(5)
O(6)-Ce(1)-O(2)	75.70(5)	O(6)-Ce(1)-O(5)	72.37(5)
O(3)-Ce(1)-O(4)	71.74(5)	O(3)-Ce(1)-O(7)	72.71(5)
O(8)-Ce(1)-O(4)	74.98(5)	O(8)-Ce(1)-O(7)	71.84(5)
O(6)-Ce(1)-O(1)	107.82(5)	O(2)-Ce(1)-O(5)	118.43(5)
O(8)-Ce(1)-O(3)	103.91(5)	O(7)-Ce(1)-O(4)	122.69(5)

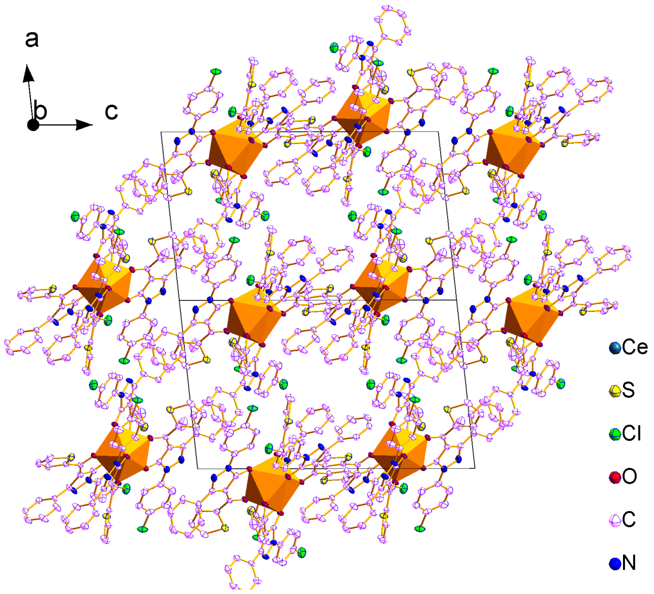


Fig. 2. View of the crystal structure of $[Ce(CPTP)_4]\ (C_6H_5CH_3)_3$. The uncoordinated methylbenzene molecules are omitted for clarity

$(C_6H_5CH_3)_3$ (Fig. 3). In the free ligand, a medium-intensity band at 3072 cm^{-1} is assigned to ν(OH) of β-diketones. The band is absent in the complex. A band at 1591 cm^{-1} in the free ligand allocated as ν(C=O) of the pyrazolone ring is shifted to 1554 cm^{-1} in the complex[11]. The weak band of 430 cm^{-1} is related to a Ce-O stretching vibration. From these observations, it is infered that the enolic proton of the ligand is replaced by Ce(IV) in the complex.

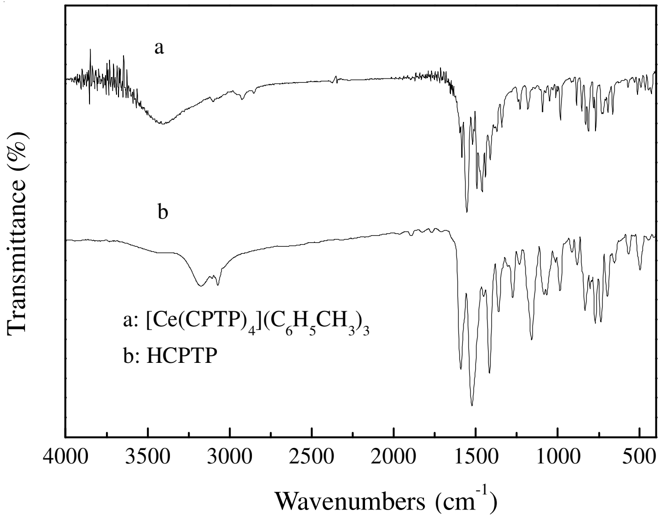


Fig. 3. FT-IR spectra of HCPTP and $[Ce(CPTP)_4]\ (C_6H_5CH_3)_3$

Thermal analysis: The TG and DSC analyses were carried out over the temperature range from 30 to 950 °C under a nitrogen atmosphere. The TG-DSC curves of the $[Ce(CPTP)_4]\ (C_6H_5CH_3)_3$ shows decomposition of the complex in two regions (Fig. 4). The first region at about 30-350 °C with a mass loss of 13 % (calcd. 14.3 %) is due to the evolution of three solvate methylbenzene molecules. The second step occurs at 350-950 °C, accompanied by many exothermic peaks in the DSC curve due to the decomposition of the organic residues. Besides, The ligand HCPTP began to decompose[4] at 168 °C. So compare to ligand HCPTP, the thermal stability of the $[Ce(CPTP)_4]\ (C_6H_5CH_3)_3$ is improved obviously.

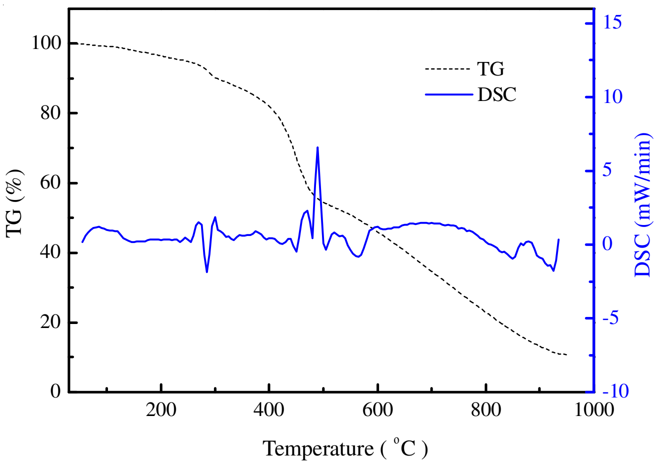


Fig. 4. TG-DSC curves of $[Ce(CPTP)_4]\ (C_6H_5CH_3)_3$

Conclusion

In summary, A novel 4-heterocyclic acylpyrazolone cerium(IV) complex $[Ce(CPTP)_4]\ (C_6H_5CH_3)_3$ has been synthesized. The eight-coordinated Ce(IV) adopts a distorted triangular dodecahedral coordinationg geometry. The complex forms a stable 3D network structure through weak intermolecular interactions.

ACKNOWLEDGEMENTS

The work was supported by the Henan Province Foundation and Advanced Technology Research Program (No. 122300410387), Scientific Research Starting Foundation for Doctor of Zhoukou Normal University (No. zksybscx201106), Innovation Fund project of Zhoukou Normal University (No. zksykycx201304), The Key Scientific and Technological Research Project of Education Department of Henan Province (No. 14B530008) and The opening laboratory project of Zhoukou Normal University (No. K201428).

REFERENCES

1. S. Yamazaki, M. Hanada, Y. Yanase, C. Fukumori, K. Ogura, T. Saeki and S. Umetani, *J. Chem. Soc. Perkin Trans. I*, 693 (1999).
2. C. Pettinari, F. Marchetti, and A. Drozdov, Comprehensive Coordination Chemistry II, Elsevier, Camerino (2003).
3. G.X. Zheng, Q.F. Wang and S.G. Luo, *J. Radioanal. Nucl. Chem.*, **258**, 693 (2003).
4. Y.J. Ding, C.X. Zhao, C.Y. Pei and G.X. Wen, *Z. Naturforsch.*, **67b**, 204 (2012).
5. Y.J. Ding and C.X. Zhao, *Asian J. Chem.*, **26**, 3036 (2014).
6. G.M. Sheldrick, SHELXS 97, Program for the Solution of Crystal Structures, University of Gottingen, Germany (1997).
7. G.M. Sheldrick, SHELXL 97, Program for the Refinement of Crystal Structures, University of Gottingen, Germany (1997).
8. R.M. Wood and G.J. Palenik, *Inorg. Chem.*, **37**, 4149 (1998).
9. S.Y. Mao, Y.X. Huang, Z.B. Wei, J.X. Mi, Z.L. Huang and J.T. Zhao, *J. Solid State Chem.*, **149**, 292 (2000).
10. A.L. Spek, PLATON-97, Molecular Geometry and Plotting Program, University of Utrecht, Netherlands (1997).
11. E.C. Okafor, *Spectrochim. Acta A*, **37**, 945 (1981).