

## A Novel Proton Transfer Compound Obtained from Pyridine-2,6-dicarboxylic Acid and Phenyl hydrazine and Its Cerium Complex: Synthesis and Crystal Structure

Mohammad Ghadermazi<sup>1,\*</sup>, Fariba Feizi<sup>1</sup>, Shabnam Sheshmani<sup>2</sup> and Hossein Aghabozorg<sup>3</sup>

1- Department of Chemistry, Faculty of Science, University of Kurdistan, Sanandaj, Iran.

2- Department of Chemistry, Islamic Azad University, Shahr-e Rey Branch, Tehran, Iran.

3- Department of Chemistry, Islamic Azad University, North Tehran Branch, Tehran, Iran.

Received: April 2011, Revised: June 2011, Accepted: July 2011

**Abstract:** A novel proton transfer compound, (phenhzH)<sub>2</sub>(pydc), and its complex, [Ce(pydc)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>.4H<sub>2</sub>O, in which pydcH<sub>2</sub> is pyridine-2,6-dicarboxylic acid and phenhz is phenyl hydrazine were obtained in aqueous solution. Characterizations were performed by IR, and X-ray crystallography. The [Ce(pydc)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>.4H<sub>2</sub>O complex crystallizes in the monoclinic system and space group P21/c with four formula in the unit cell. The unit cell dimensions are: a=14.0016(6)Å, b=11.2249(5)Å, c=12.9539(6)Å, and β=102.1930(10)°.

**Keywords:** Proton transfer, Pyridine-2,6-dicarboxylic acid, Phenyl hydrazine, Ce(IV) complex, Synthesis, Crystal structure.

### Introduction

There are now many self-assembled supramolecular systems in which metal ions play an important, if not essential role in the assembly process. The process of self-assembly involves the noncovalent interactions of two or more molecular subunits to form a

supramolecular arrangement whose novel structure and properties are determined by the nature and positioning of the components [1]. Various types of interactions may be distinguished, that present different degrees of strength, directionality, dependence on distances and angles [2], such as hydrogen bonding, ion pairing, hydropho-

\*Corresponding Autor E mail: mghadermazi@yahoo.com

bic or hydrophilic, host-guest,  $\pi$ - $\pi$  stacking and donor-acceptor interactions. Hydrogen bonding is one of the several types of non-covalent interactions in many organic and inorganic species, by which self-association and self-organization can be achieved to form discrete assemblies and extended lattices. Since some of the organic systems have the ability of metal ion complexation and to form hydrogen bonding, it is interesting to coordinate them to metals and then have an inorganic self-assembled system. The approach we have applied in the preparation of such systems is using the proton transfer compounds obtained from processes between appropriate carboxylic acids and amines. Functionalized carboxylic acids and amines can enhance the intermolecular forces between the obtained cationic and anionic fragments and interactions described above can provide a large part of the stabilization energy of the resulting self-assembly system [3]. A structural investigation of a number of metal complexes synthesized from different proton transfer compounds has described in the literatures [4–18]. The potential for constructing novel metal-containing systems that bridge the gap between classical coordination and organic supramolecular chemistry seems virtually unlimited [19]. In all of these proton transfer compounds and the related metal complexes, we noticed the very significant contribution of hydrogen bonding to the

stabilization of the resulting 3D networks in the crystal structures. In continuation of our research we were interested in studying the complexation behavior of cerium with other proton-transfer compound.

### Experimental

For preparation of proton transfer compound, an aqueous solution of pyridine-2,6-dicarboxylic acid (1.67 g, 10 mmol) in THF (50 ml) was added to a solution of phenyl hydrazine (2.16 g, 20 mmol) in THF (5 ml). White powder was obtained by slow evaporation of the solvent. Yield: 93%, mp = 218 °C.

The reaction of proton transfer compound (phenhzH)<sub>2</sub>(pydc), where phenhz is phenyl hydrazine and pydcH<sub>2</sub> is pyridine-2,6-dicarboxylic acid, with cerium ammonium nitrate in 3:1 molar ratio was carried out. Therefore, to a solution of (phenhzH)<sub>2</sub>(pydc) (0.5 g, 3 mmol) in water (10 ml) was added to solution of cerium ammonium nitrate (0.21 g, 1 mmol) in water (10 ml). Yellow crystalline [Ce(pydc)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>.4H<sub>2</sub>O complex was obtained by the slow evaporation of the solvent at room temperature after four weeks.

### Results and Discussion

The IR spectroscopy has been widely used as a diagnostically useful tool for investigation of the proton transfer compounds and their complexes. The most definitive features in the IR spectrum of (phenhzH)<sub>2</sub>(pydc) are the characteristic loss of the broad carboxyl

O–H stretching frequency (2500–3300  $\text{cm}^{-1}$ ) together with the presence of asymmetric and symmetric carboxylate stretching frequencies at 1580 and 1371  $\text{cm}^{-1}$ . The IR spectrum of the complex shows also some vibrations due to the water molecules existing in the lattice. Lattice water normally appears in the 3200–3550  $\text{cm}^{-1}$  (antisymmetric and symmetric OH stretching) and 1600–1630  $\text{cm}^{-1}$  regions (HOH bending). The vibration frequencies depict the uncoordinative mode of water fragments. The two bands at 1615 and 1660  $\text{cm}^{-1}$  caused by water molecules overlap the absorption band of  $\text{CO}_3^{2-}$ . The stretching vibrations of  $\text{CO}_3^{2-}$  illustrate the corresponding bands at 1380 and 1660  $\text{cm}^{-1}$ .

The crystallographic and experimental data, selected bond distances, bond angles, and intermolecular hydrogen bonds are listed in Tables 1, 2 and 3, respectively. The ORTEP diagram and crystal packing of the complex are presented in Figures 1 and 2, respectively.

The molecular structure of Ce(IV) complex shows a polymeric complex in which the two central atoms are connected together via carboxylate groups. This connectinome is formed by  $(\text{pydc})^{2-}$  fragments which act as bridge ligands. Each cerium atom is coordinated by four oxygen and two nitrogen atoms of two  $(\text{pydc})^{2-}$  ligands as well as two oxygen atoms from water molecules. There are also four uncoordinated water molecules in the crystal structure. The  $(\text{pydc})^{2-}$  fragments are linked to the cerium atom via three donor atoms, and act as tridentate ligands. The complex is not accompanied by counter ions.

The non-covalent interactions in the crystal packing of the complex is hydrogen bonding. A number of O–H...O hydrogen bonds with D...A distances ranging from 2.640(3) to 2.993(3) Å are observed in the crystal packing. The uncoordinated water molecules increase the number of hydrogen bonds in the whole crystal lattice.

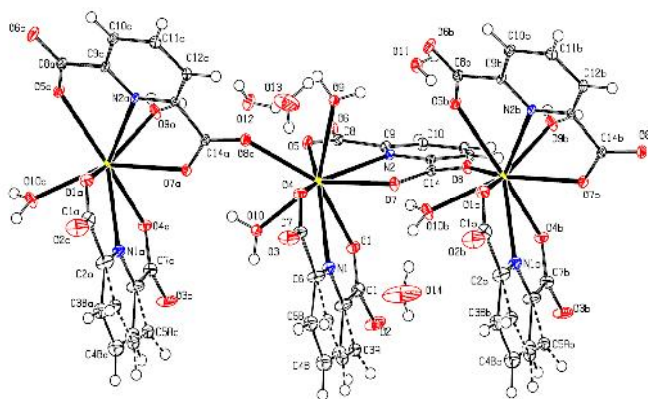


Figure 1 The molecular structure (ORTEP) of the Ce(IV) complex with atom labeling. Displacement ellipsoids are drawn at the 50% probability level.

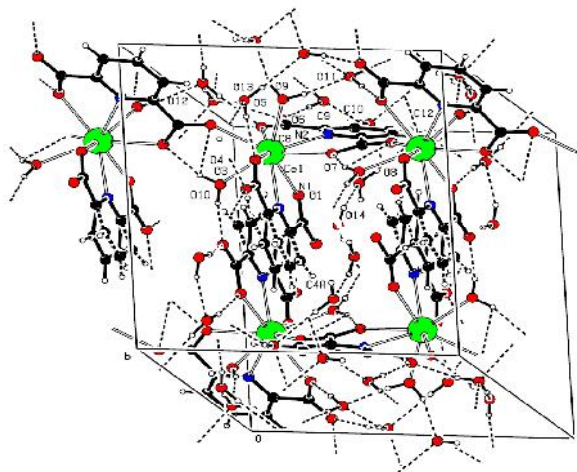


Figure 2 The packing diagram of the Ce(IV) complex, dashed lines represent the hydrogen bonding between species.

Table 1 Crystallographic data, details of data collection and structure determination.

Empirical formula	$C_{14}H_{18}CeN_2O_{14}$
Formula weight	578.42
Temperature (T, K)	100(2)
Wavelength ( , Å)	0.71073 (Mo K )
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimension	a=14.0016(6)Å b= 11.2249(5)Å c =12.9539(6)Å = 102.1930(10)°
Volume (Å <sup>3</sup> )	1989.99(15)
Z	4
Goodness of fit	1.004
Absorption coefficient (μ, mm <sup>-1</sup> )	2.365
F (000)	1144
Crystal size (mm <sup>3</sup> )	0.18 × 0.11 × 0.07
Theta ( ) range for data collection (°)	2.42-34.20
Index ranges	-19=< h <= 19, -15 = <k <= 15, -18 =< l <= 18
Refinement method	Full-Matrix Least- Squares on F <sup>2</sup>
Final R indices	R <sub>1</sub> = 0.0263 wR <sub>2</sub> =0.0779
R indices (all data)	R <sub>1</sub> = 0.0295 wR <sub>2</sub> =0.0809
Largest diff. peak and hole (e <sup>-</sup> Å <sup>-3</sup> )	0.006 and 0.001

Table 2 Selected bond lengths / Å, and bond angles / °

Ce1–N1	2.638(2)	Ce1–O5	2.5325(15)
Ce1–N2	2.6375(18)	Ce1–O7	2.5530(17)
Ce1–O1	2.5648(16)	Ce1–O9	2.4589(16)
Ce1–O4	2.4983(16)	Ce1–O10	2.4909(16)
O1–Ce1–O4	122.48(6)	O4–Ce1–N1	61.68(5)
O5–Ce1–O8	78.44(5)	O5–Ce1–N2	61.14(5)
O9–Ce1–O10	141.65(5)	O7–Ce1–N2	61.08(5)
O1–Ce1–N1	61.09(5)	-	-

Table 3 Selected hydrogen bonds in the complex.

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	<DHA (°)
O9–H1...O11	0.85	1.879	2.722(2)	171
O9–H2...O12	0.85	1.894	2.709(2)	160
O10–H3...O7	0.85	1.902	2.708(2)	158
O10–H4...O3	0.85	1.869	2.704(2)	167
O11–H5...O5	0.85	2.032	2.860(2)	164
O11–H6...O6	0.85	1.991	2.836(2)	173
O12–H7...O11	0.85	2.099	2.853(2)	148
O12–H8...O6	0.85	1.859	2.698(2)	169
O13–H9...O12	0.85	2.144	2.993(3)	177
O13–H10...O4	0.85	2.102	2.945(3)	171
O14–H11...O13	0.85	1.994	2.763(4)	150
O14–H12...O3	0.85	1.801	2.640(3)	168

## References

1. Lehn, J. M.; Supramolecular Chemistry, Steed, J. W. and Atwood, J. L.; Eds. Wiley: Chichester, 2000.
2. Lehn, J. M.; Supramolecular Chemistry, VCH, 1995.
3. Aakeröy, C. B. Beatty, A. M. and Helfrich, B.; A. Angew. Chem. Int. Ed.; 40, 3240; 2001.
4. Moghimi, A. Alizadeh, R. Shokrollahi, A. Aghabozorg, H. Shamsipur, M. and Shockravi, A.; Inorg. Chem.; 42, 1616; 2003.
5. Ranjbar, M. Moghimi, A. Aghabozorg, H. and Yap, G. P. A.; Anal. Sci.; 18, 219; 2002.
6. Aghabozorg, H. Dalir Khairollahi, P. Moghimi, A. and Sadr-Khanlou, E.; Anal. Sci.; 21, x79; 2005.
7. Aghabozorg, H. Akbari Saei, A. Sadr-Khanlou, E. and Moghimi, A.; Anal. Sci.; 21, x207; 2005.
8. Moghimi, A. Sheshmani, S. Shokrollahi, A. Aghabozorg, H. Shamsipur, M. Kickelbick, G. Aragoni, M. C. and Lippolis, V.; Z. Anorg. Allg. Chem.; 630, 617; 2004.

9. Ranjbar, M. Taghaviipur, M. Aghabozorg, H. Moghimi, A. Jalali, F. and Shamsipur, M.; Polish J. Chem.; 76, 785; 2002.
10. Aghabozorg, H. Ghadermazi, M. Manteghi, F. and Nakhjavan, B.; Z. Anorg. Allg. Chem.; 632, 2058; 2006.
11. Aghabozorg, H. Mohammad Panah, F. and Sadr-Khanlou, E.; Acta Crystallogr.; E62, m2509; 2006.
12. Moghimi, A. Sharif, M. A. Shokrollahi, A. Shamsipur, M. and Aghabozorg, H.; Z. Anorg. Allg. Chem.; 631, 902; 2005.
13. Moghimi, A. Sheshmani, S. Shokrollahi, A. Shamsipur, M. Kickelbick, G. and Aghabozorg, H.; Z. Anorg. Allg. Chem.; 631, 160; 2005.
14. Aghajani, Z. Sharif, M. A. Aghabozorg, H. and Naderpour, A.; Acta Crystallogr.; E 62, m830; 2006.
15. Aghabozorg H. and Sadr-Khanlou, E.; Acta Crystallogr. E63, m1753 2007.
16. Aghabozorg, H. Ghasemikhah, P. Ghadermazi, M and Sheshmani, S.; Acta Crystallogr.; E62, m2835; 2006.
17. Aghabozorg, H. Zabihi, F. Ghadermazi, M Attar Gharamaleki, J. and Sheshmani, S.; Acta Crystallogr.; E62, m2091; 2006.
18. Aghabozorg, H. Ghadermazi, M. and Attar Gharamaleki, J.; Acta Crystallogr.; E62, o3174; 2006.
19. Lindoy L. F. and Atkinson, I. M.; Self Assembly in Supramolecular Systems, Royal Society of Chemistry, R. S. C., 2000.

## یک ترکیب انتقال پروتون جدید به دست آمده از پیریدین-۲،۶-دی کربوکسیلیک اسید و فنیل هیدرازین و کمپلکس آن با سریم: تهیه و ساختار بلوری

\*<sup>1</sup>، فریبا فیضی<sup>1</sup> و حسین آقابزرگ<sup>2</sup>

- 1- دانشکده علوم، گروه شیمی، دانشگاه کردستان، سنندج، ایران.
- 2- دانشکده شیمی، دانشگاه آزاد اسلامی واحد شهرری، تهران، ایران.
- 3- دانشکده شیمی، دانشگاه آزاد اسلامی واحد تهران شمال، تهران، ایران.

دریافت: خرداد 1390، بازنگری: تیر 1390، پذیرش: شهریور 1390

**چکیده:** یک ترکیب انتقال پروتون جدید،  $(\text{phenhzH})_2(\text{pydc})$  و کمپلکس آن  $[\text{Ce}(\text{pydc})_2(\text{H}_2\text{O})_2]_n \cdot 4\text{H}_2\text{O}$  که در آن  $\text{pydcH}_2$  پیریدین-2،6-دی کربوکسیلیک اسید و  $\text{phenhz}$  فنیل هیدرازین است، در محلول آبی به دست آمد. شناسایی به وسیله X IR انجام شد. کمپلکس  $[\text{Ce}(\text{pydc})_2(\text{H}_2\text{O})_2]_n \cdot 4\text{H}_2\text{O}$  در سیستم بلوری مونوکلینیک و گروه فضایی P21/c با چهار مولکول در سلول واحد متبلور می شود. ابعاد سلول واحد عبارت اند از:  $a=14.0016(6)\text{\AA}$   $b=11.2249(5)\text{\AA}$   $c=12.9539(6)\text{\AA}$   $\beta=102.1930(10)^\circ$

**واژه های کلیدی:** انتقال پروتون، پیریدین-2،6-دی کربوکسیلیک اسید، فنیل هیدرازین، کمپلکس سریم (IV)، تهیه، ساختار بلوری.