

STRUCTURAL STUDY OF Ca(II) COORDINATION COMPOUND WITH TRIETHANOLAMINE AND 4-NITROBENZOIC ACID

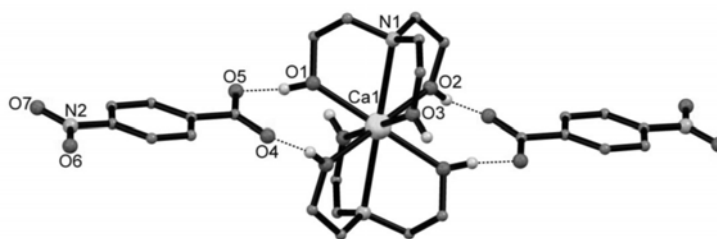
Anastasia GOROBET,^a Manuela CRISAN,^{b,*} Mihaela PETRIC,^b Pavlina BOUROSH^a and Lilia CROITOR^{a,*}

^aInstitute of Applied Physics, Academiei str., 5, MD-2028, Chişinău, Republic of Moldova;

^bInstitute of Chemistry Timişoara of Roumanian Academy, 24 Mihai Viteazul Blvd., 300223 Timişoara, Roumania

Received July 18, 2018

The synthesis of a new calcium complex based on biologically active ligands with N and O donor atoms is an attractive research topic in modern synthetic chemistry. Herein we present the formation of AB₂-type salt [Ca(TEA)₂](4NB)₂ (**1**) by an easy method, starting from CaF₂, 4-nitrobenzoic acid (4NBH) and triethanolamine (TEA). The crystal structure comprises one [Ca(TEA)₂]²⁺ complex cation and two 4NB⁻ anions. In the complex cation, each TEA molecule behaves as an N,O,O',O''-tetradentate ligand,



giving rise to an eight-coordinate Ca(II) ion with a distorted cubic configuration. The complex cation is H-bonded with outer-sphere 4NB⁻ anions by intermolecular O–H...O hydrogen bond interactions. The intermolecular O–H...O hydrogen bonds unite components in well-defined 1D supramolecular chain, which are further assembled in a supramolecular 2D layer *via* π - π stacking interactions.

INTRODUCTION

The development of new calcium complexes is an emerging area of interest in modern synthetic organic chemistry, material science and biochemistry.¹⁻³ Calcium plays a significant role both in biological and structural inorganic chemistry, due to its less toxicity and abundance in the natural world.⁴ Because of large ionic radius, calcium exhibits a high number of coordination sites, preferred being six, seven and eight, which are observed in different binding motifs with protein, organic small molecules and inorganic ions.⁵⁻⁸ A perusal of Cambridge Structural Database (CSD) has revealed a great variety of calcium complexes with biologically active ligands containing N and O donor atoms. We have been interested in triethanolamine (TEA) and 4-nitrobenzoic acid (4NBH) in order to study the complexing ability of

these important biological active ligands with calcium ion.

TEA is a versatile ligand with high electronegativity donor sites which can interact with metal ions in a diversity of coordination modes such as monodentate,⁹ bidentate,¹⁰ tridentate¹¹ and tetradentate.¹² There are also metal complexes where TEA coordinates in bridging mode¹³ and some in which TEA molecules are uncoordinating, situated outside the actual coordination spheres.¹⁴ Much attention has been shown recently for complexes formed by triethanolamine tetradentate ligand, known in some studies as atranes, which have applicative importance in agriculture and medicine.¹⁵

4NBH, used as precursor in the synthesis of benzocaine, folic acid and benzoyl glutamic acid, can function as building blocks/synthons for the synthesis of metal 4-nitrobenzoates complexes

* Corresponding authors: mdorosencu@yahoo.com and croitior.lilia@gmail.com

formation preponderant with transition metals such as Mn, Fe, Co, Ni, Cu, Mo and Rh.¹⁶ In contrast, the structures of alkali and alkaline earth metal 4-nitrobenzoates has been relatively less studied.¹⁷

The interactions between *p*-substituted benzoic acids and alkanolamines and thermal stability were studied in our previous works.¹⁸⁻²¹ The hydrogen bonds O–H...O and N⁺–H...O[–] dominance in crystal packing of alkanolammonium salts and the highest thermal stability of TEA derivatives comparatively with diethanolammonium and ethanolammonium ones were shown. Beside the easy synthesis, alkanolammonium *p*-substituted benzoate salts demonstrate their versatility showing low toxicity on *Hydractinia echinata*^{22, 23} and plant growth regulation activity on *Arabidopsis thaliana*²⁴ and *Cucumis sativus*.²⁵

In the case of Ca²⁺(TEA)(anion) complexes, CSD provides only two single crystal structure analyses, where TEA ligand coordinates with calcium ion, the counteranion being not involved in the coordination sphere,^{26,27} and other two cases where both ligand – TEA and anion coordinate to the calcium ion forming mono- and binuclear complexes.^{28,29} This paper presents the synthesis of [Ca(TEA)₂](4-NB)₂ complex, single crystal X-ray structural analysis and the stereochemistry investigations of the interactions Ca²⁺–TEA–4NBH, beside the role of 4NB[–] in the formation of structural architecture.

RESULTS AND DISCUSSION

Compound **1**, [*bis*(triethanolamine-*N,O,O',O''*) calcium]*bis*[2-(2-oxo-2,3-dihydro-1,3-benzothiazol-3-yl)acetate], crystallizes in triclinic *P*-1 (*N*_o2)

space group (Table 1) and crystal structure of AB₂-type salt consists of a centrosymmetrical [Ca(TEA)₂]²⁺ complex cation and two 4NB[–] anions (Fig. 1a, b). Ca(II) ion is sandwiched between two triethanolamine ligands, each of them coordinating through all four potential donor sites. The coordination polyhedron of the metal is a distorted cubic N₂O₆ geometry (Fig. 1c) originated by two neutral TEA molecules, which act as *N,O,O',O''*-tetradentate ligands as in bis(triethanolamine)calcium 3,5-dinitrobenzoate.²⁶ The TEA molecule is disordered over two positions with almost equal occupations, and the second one is named **1'**. The Ca–N distance is equal to 2.736(2) Å, and Ca–O distances are in the range of 2.347(16)–2.546(14) Å (Table 2). All ethanol groups of each TEA molecule form three five-membered chelate rings CaOCCN in the shape of a chair around the Ca(1) atom with N–Ca–O angles in the range of 64.35(5)–64.97(5)° and O–Ca–O angles are in an interval of 99.6(5) to 111.8(5)°, and angles between planes from rings with O(1) and O(2), O(2) and O(3), O(1) and O(3) atoms are equal 58.9, 58.4, and 117.0°, respectively. The outer-sphere 4NB[–] anions are H-bonded with complex cation by intermolecular O–H...O hydrogen bond interactions generating the supramolecular R²₂(8) synthon (Fig.2a, Table 3).

The intermolecular O–H...O hydrogen bonds unite components in well-defined 1D supramolecular chain (Fig. 2a), which are further assembled in a supramolecular 2D layer *via* π–π stacking interactions between adjacent phenyl rings of 4NB[–] anions (Fig. 2b). The centroid...centroid separation, 3.894 Å, indicates the offset stacking.

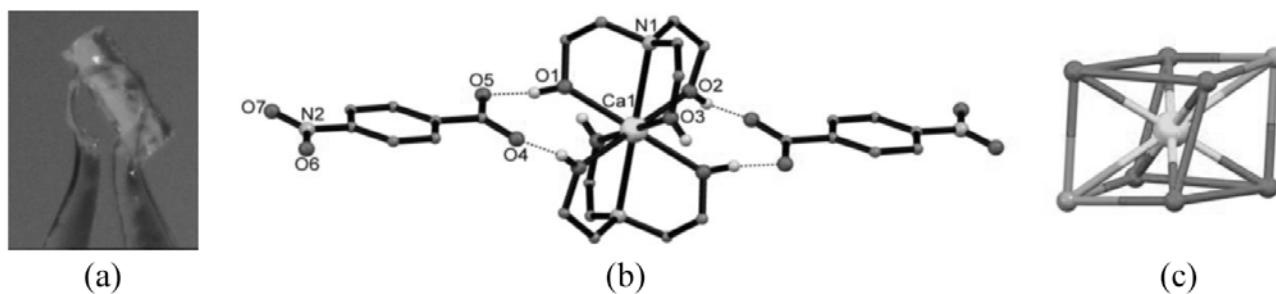


Fig. 1 – Photo of crystal **1** selected for single crystal X-ray experiment (a). View of the AB₂-type salt **1** with the partial numbering scheme (b). The distorted coordination polyhedra of Ca(II) in **1** (c).

Table 1

Crystallographic data and structure refinement details for compounds 1.

Empirical formula	C ₂₆ H ₃₈ CaN ₄ O ₁₄
Formula weight	670.68
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1 (No. 2)
Z	1
<i>a</i> (Å)	7.2948(5)
<i>b</i> (Å)	8.9531(7)
<i>c</i> (Å)	12.6963(9)
α (deg)	101.911(6)
β (deg)	100.041(6)
γ (deg)	97.548(6)
<i>V</i> (Å ³)	786.79(10)
<i>D_c</i> (g/cm ⁻³)	1.415
μ (mm ⁻¹)	0.273
F(000)	354
Crystal size (mm ³)	0.5 x 0.22 x 0.04
Reflections collected/unique	4804/2765 [R(int) = 0.0250]
Reflections with [<i>I</i> >2 σ (<i>I</i>)]	1961
Data/restraints/parameters	2765 / 155 / 296
GOF on <i>F</i> ²	1.005
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> >2 σ (<i>I</i>)]	0.0523, 0.1215
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0772, 0.1350

Table 2

Selected bond distances (Å) and angles (°) in metal coordination cores in 1 and 1'.

	1	1'
Ca(1)–O(1)	2.35(2)	2.51(2)
Ca(1)–O(2)	2.35(1)	2.50(2)
Ca(1)–O(3)	2.54(1)	2.22(2)
Ca(1)–N(1)	2.736(2)	–
O(1)–Ca(1)–N(1)	64.97(5)	64.34(5)
O(2)–Ca(1)–N(1)	64.79(5)	64.76(5)
O(3)–Ca(1)–N(1)	64.61(5)	64.65(5)
O(2)–Ca(1)–O(1)	110.9(5)	101.7(6)
O(2)–Ca(1)–O(1) ⁱ	69.1(5)	78.3(6)
O(2)–Ca(1)–O(3)	100.3(4)	101.0(6)
O(1)–Ca(1)–O(3)	97.8(5)	106.0(6)
O(2)–Ca(1)–O(3) ⁱ	79.7(4)	79.0(6)
O(1)–Ca(1)–O(3) ⁱ	82.2(5)	74.0(6)

Symmetry transformations used to generate equivalent atoms: ⁱ –*x*, *y*+1, –*z*+1

Table 3

Hydrogen bond distances (Å) and angles (°) in 1 and 1'.

<i>D</i> – <i>H</i> ⋯ <i>A</i>	<i>d</i> (<i>H</i> ⋯ <i>A</i>)	<i>d</i> (<i>D</i> ⋯ <i>A</i>)	\angle (<i>DHA</i>)	Symmetry transformations for acceptor
O(1)–H⋯O(5)	1.96	2.67(2)	138	<i>x</i> , <i>y</i> –1, <i>z</i>
O(2)–H⋯O(4)	1.80	2.65(1)	167	– <i>x</i> , – <i>y</i> +2, – <i>z</i> +1
O(3)–H⋯O(5)	1.76	2.61(1)	178	<i>x</i> –1, <i>y</i> –1, <i>z</i>
O(1')–H⋯O(5)	1.98	2.75(2)	146	<i>x</i> , <i>y</i> –1, <i>z</i>
O(2')–H⋯O(4)	1.74	2.60(2)	177	– <i>x</i> , – <i>y</i> +2, – <i>z</i> +1
O(3')–H⋯O(5)	1.97	2.73(2)	148	<i>x</i> –1, <i>y</i> –1, <i>z</i>

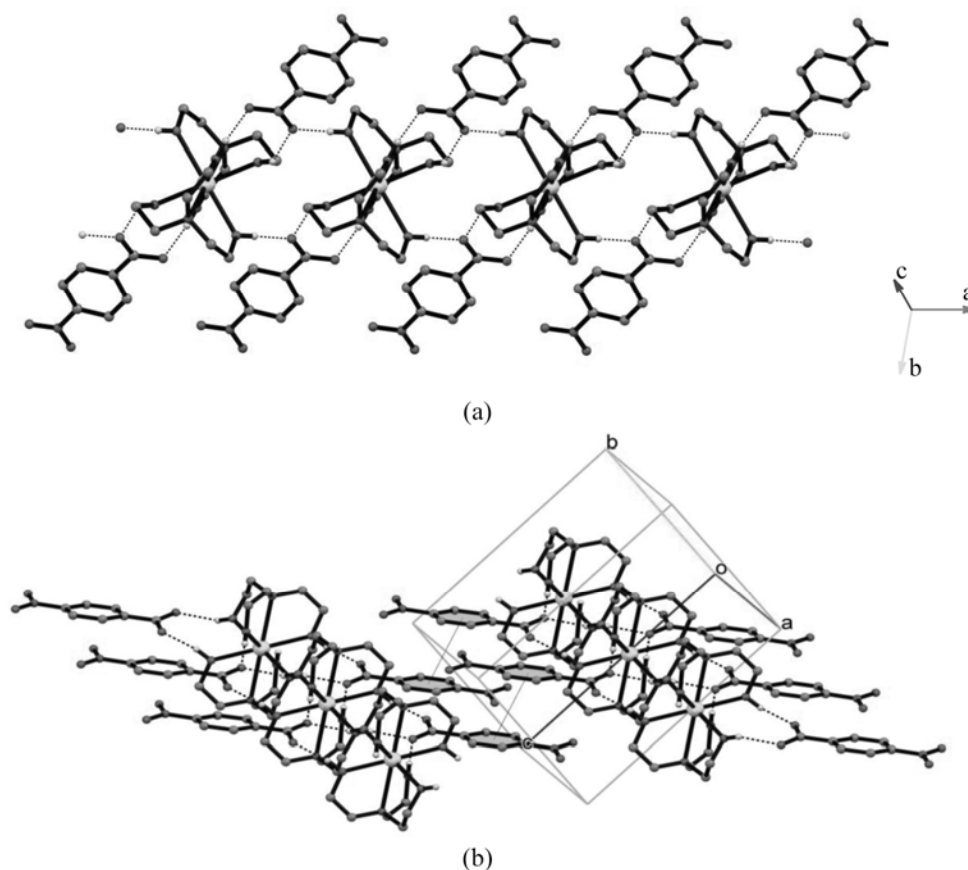


Fig. 2 – The fragment of 1D hydrogen-bonding chain (a) and supramolecular 2D layer (b) in **1**.

EXPERIMENTAL

All reagents and solvents were obtained from commercial sources and were used without further purification.

Synthesis of $[\text{Ca}(\text{TEA})_2](4\text{NB})_2$ (1**):** TEA (0.04 mg, 0.3 mmol) was added dropwise to a mixture acetone:H₂O (1:1.6 mL), containing CaF₂ (11.71 mg, 0.15 mmol) and 4NBH (50.14 mg, 0.3 mmol), until pH~6.2 has been reached. The reaction mixture was stirred at room temperature for ~5 min, filtered off and then slowly cooled to room temperature giving a white precipitate. The obtained powder was dissolved in the mixture acetone:H₂O (2.5:1, 3.5 mL). From transparent solution colorless crystals of prism habitus precipitated after 3 weeks. Yield: ~78% (based on Ca).

X-ray structure determination: Diffraction measurement for **1** was carried out at room temperature on a Xcalibur “Oxford Diffraction” diffractometer equipped with CCD area detector and a graphite monochromator utilizing MoK α radiation. Final unit cell dimensions were obtained and refined on an entire data set. All calculations to solve the structures and to refine the proposed models were carried out with the SHELXS2014 program package.³⁰ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon and oxygen atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters with Uiso(H)=1.2Ueq(O). The TEA molecule is disordered over two positions (58/42% occupancy). The second position is named **1'**. The disordered TEA molecule has been well treated by restraining it to be the SAME as the well resolved TEA molecule and was refined anisotropically. The Figures

were produced using the Mercury program.³¹ Crystallographic data of the new structure reported herein were deposited with the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 1856507.

CONCLUSIONS

A new Ca(II) salt namely $[\text{Ca}(\text{TEA})_2](4\text{NB})_2$ was prepared in soft condition and its structure was determined by single-crystal X-ray diffraction. Crystal packing reveals supramolecular 2D layers governed by combination of O–H \cdots O hydrogen bonds and π - π stacking interactions between adjacent phenyl rings of 4NB⁻ anions.

Acknowledgements. This project was financially supported by Project 2.1 of the Institute of Chemistry of Romanian Academy.

REFERENCES

1. K. M. Fromm and E. D. Gueneau, *Polyhedron*, **2004**, *23*, 1479-1504.
2. G. C. R. Ellis-Davies, *Chem. Rev.*, **2008**, *108*, 1603-1613.
3. K. L. Haas and K. J. Franz, *Chem. Rev.*, **2009**, *109*, 4921-4960.

4. F. A. Cotton, G. Wilkinson, P. L. Gaus, „Basic Inorganic Chemistry”, 3rd edition, Wiley: New York, 1995.
5. W. Yi and H. Ma, *Inorg. Chem.*, **2013**, *52*, 11821-11835.
6. F. Dankert, K. Reuter, C. Donsbach and C. von Hänisch, *Dalton Trans.*, **2017**, *46*, 8727-8735.
7. M. Kalinowska, L. Mazur, E. Regulska, A. Korczak, G. Świdorski and W. Lewandowski, *J. Coord. Chem.*, **2016**, doi: 10.1080/00958972.2016.1197389
8. S. Natarajan, B. R. Srinivasan, J. K. Sundar, K. Ravikumar, R. V. Krishnakumar and J. Suresh, *J. Chem. Sci.*, **2012**, *124(4)*, 781–790.
9. R. Kumar, S. Obrai, A. Kaur, M. S. Hundal, H. Meehnid and A. K. Jana, *New J. Chem.*, **2014**, *38*, 1186–1198.
10. G. M. Kapteijn, P. J. Baesjou, P. L. Alsters, D. M. Grove, G. V. Koten, W. J. J. Smeets, H. Kooijman and A. L. Spek, *Chem. Ber. Recl.*, **1997**, *130*, 35–44.
11. A. N. Mirskova, S. N. Adamovich, R. G. Mirskov and U. Schilde, *Chem. Cent. J.*, **2013**, *7*, 34–38.
12. S. K. Langley, L. Ungur, N. F. Chilton, B. Moubaraki, L. F. Chibotaru and K. S. Murray, *Chem. Eur. J.*, **2011**, *17*, 9209–9218.
13. D. Yang, Y. Liang, P. Ma, S. Li, J. Wang and J. Niu, *CrystEngComm*, **2014**, *16*, 8041–8046.
14. A. B. Ilyukhin, P. S. Koroteev, M. A. Kiskin, Z. V. Dobrokhotova and V. M. Novotortsev, *J. Mol. Struct.*, **2013**, *1033*, 187–199.
15. M. Voronkov and V. Baryshok, *Herald Russ. Acad. Sci.*, **2010**, *80*, 514-521.
16. S. M. Roy, M. R. Sudarsanakumar, V. S. Dhanya, S. Suma and M. R. Prathapachandra Kurup, *J. Korean Chem. Soc.*, **2014**, *58*, 258-266.
17. G. Smith, *Acta Cryst. C*, 2015, *71*, 499-505.
18. M. Crisan, G. Vlase, N. Plesu, M. Petric, L. Croitor, V. Kravtsov, Y. Chumakov, P. Bourosh and T. Vlase, *J. Therm. Anal. Calorim.*, **2018**, doi: 10.1007/s10973-018-7465-7.
19. M. Crisan, G. Vlase, E. I. Szerb and T. Vlase, *J. Therm. Anal. Calorim.*, **2018**, *132*, 1409-1418.
20. M. Crisan, P. Bourosh, Yu. Chumakov, M. Petric and G. Ilia, *Cryst. Growth Des.*, **2013**, *13*, 143-154.
21. Y. M. Chumakov, Y. A. Smirnov, M. Grozav, M. Crisan, G. Bocelli, A. A. Yakovenko and D. Lyubetsky, *Cent. Eur. J. Chem.*, **2006**, *4*, 458-475.
22. S. A. Chicu, M. Grozav, L. Kurunczi and M. Crisan, *Rev. Chim. (Bucharest)*, **2008**, *59*, 582-587.
23. M. Crisan, L. Halip, P. Bourosh, S.A. Chicu and Y. Chumakov, *Chem. Cent. J.*, **2017**, *11*, 129-139.
24. M. Crisan, M. Grozav and C. Berteau, *J. Plant Interact.*, **2009**, *4*, 271-277.
25. M. Crisan, M. Grozav, L. Kurunczi, Gh. Ilia and C. Berteau, *J. Plant Interact.*, **2007**, *2*, 53-61.
26. G. Hundal, M. Martinez-Ripoll, M. S. Hundal and N. S. Poonia, *Acta Crystallogr. C*, **1996**, *52*, 789-792.
27. A. Taeb, H. Krischner and C. Kratky, *Z. Kristallogr.*, **1986**, *177*, 263-269.
28. G. Hundal and M. Martinez-Ripoll, *Acta Crystallogr. C*, **1995**, *51*, 1788-1791.
29. G. Hundal, M. Martinez-Ripoll, M. S. Hundal and N. S. Poonia, *Acta Crystallogr. C*, **1996**, *52*, 786-789.
30. G.M. Sheldrick, *Acta Crystallogr. C*, **2015**, *71*, 3-8.
31. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, T. Mowler and J. van de Streek, *J. Appl. Crystallogr.*, **2006**, *39*, 453-457.

