



Crystal structure and properties of L-tryptophanium hydrogen selenite

José António Paixão^a, Manuela Ramos Silva^{a,*}, Ana Matos Beja^a, Ermelinda Eusébio^b

^a CEMDRX, Departamento de Física, FCT, Universidade de Coimbra, 3004-516 Coimbra, Portugal

^b Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal

Received 27 September 2005; accepted 20 December 2005

Available online 28 February 2006

Abstract

L-Tryptophanium hydrogen selenite was synthesised and structurally characterised at room and low temperature. The amino acid is positively charged with the amine and carboxylic group protonated. It adopts a staggered conformation with the N1 *gauche* to C4 that is *gauche* to C1. The anion displays a pyramidal conformation with three different Se–O bond lengths, one characteristic of a double bond, another of a single bond and the third with an intermediate character. At room temperature there is a disordered hydrogen atom between the carboxylic group of the cation and the O atom of the anion with the intermediate Se–O bond length. At low temperature this hydrogen atom orders and attaches to the carboxylic group. This ordering is most likely related to the transition seen in DSC measurements occurring at $-82.5\text{ }^{\circ}\text{C}$.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Phase transition; Hydrogen bonds; DSC measurements; Optical properties

1. Introduction

The title compound belongs to a series of new selenite compounds of organic moieties synthesised as part of a project to study new materials with potentially interesting optical and dielectric properties [1–4]. Ferro- and antiferroelectric properties have been observed in alkali trihydrogen selenites [5–10]. Sodium trihydrogen selenite, $\text{NaH}_3(\text{SeO}_3)_2$, for instance, is ferroelectric below $-79\text{ }^{\circ}\text{C}$ [5] while the corresponding lithium salt is ferroelectric [6] at room-temperature. Potassium trihydrogen selenite undergoes a phase transition involving a change in the dielectric properties at $-61.6\text{ }^{\circ}\text{C}$ [7] and $\text{CsH}_3(\text{SeO}_3)_2$ becomes anti-ferroelectric below $-128\text{ }^{\circ}\text{C}$ [8]. Rubidium trihydrogen selenite is an improper ferroelectric [9] which has also an incommensurate phase at low temperature between $-120\text{ }^{\circ}\text{C}$ and $-118\text{ }^{\circ}\text{C}$ [10].

The onset of the polar phases has been explained, in this family of compounds, by the ordering of H-atoms strongly shared by two oxygen atoms belonging to HSeO_3^- ions/ H_2SeO_3 molecules [11].

A new approach to obtain new non-linear optical, piezoelectric and ferroelectric materials is the supramolecular engineering of inorganic–organic hybrids [12]. An example of success is bis(nicotinato)zinc whose second-harmonic-generation signal is a thousand times larger than that of α -quartz [13]. L-Argininium hydrogen selenite is one of the new inorganic/organic compounds with non-linear optical and possible dielectric properties [4]. Benzyltrimethylammonium trihydrogen selenite is also a promising material where three transitions at -78.6 , -25.8 and $-1.7\text{ }^{\circ}\text{C}$ were observed in DSC measurements [1].

L-Tryptophan is a naturally occurring amino acid, with a non-polar chain and no net charge at physiological pH. L-Tryptophan has been used as a fluorescence probe to monitor protein conformation and dynamics and consequently many spectroscopic studies of the electronic properties of L-tryptophan and its derivatives have been performed [14,15]. L-Tryptophan exhibits a non-exponential

* Corresponding author. Tel. +351 239 410600/410648; fax: +351 239 829158.

E-mail address: manuela@pollux.fis.uc.pt (M.R. Silva).

fluorescence decay in aqueous solutions and that has been explained by the emission from non-interconverting rotamers which have different lifetimes due to different rates of intramolecular charge transfer [16].

DSC measurements on a L-tryptophanium hydrogen selenite powdered sample revealed the existence of a second-order transition at $-82.5\text{ }^{\circ}\text{C}$.

We report here these DSC measurements and a thorough single-crystal X-ray diffraction study performed at room and low temperature to unravel the nature of the phase transition.

2. Experimental

2.1. Preparation of L-tryptophanium hydrogen selenite

A few drops of selenious acid were added to an aqueous solution of L-tryptophan. Within a few months transparent light brown crystals of prismatic shape grew from the solution.

2.2. Physical measurements

Single-crystal X-ray diffraction data for the title compound were collected both with a Mach3 diffractometer, equipped with a conventional detector at room temperature and another similar diffractometer equipped with an area detector at 80 K. The room temperature data were collected using ω - 2θ scans and $\text{CuK}\alpha$ radiation ($\lambda = 1.5408\text{ \AA}$). The unit cell parameters were determined by least-squares refinement of diffractometer angles ($21^{\circ} < \theta < 37^{\circ}$) for 25 automatically centered reflections.

The low temperature data were collected using φ and ω scans and $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The unit cell

parameters were determined by least-squares refinement of diffractometer angles ($2.60^{\circ} < \theta < 36.11^{\circ}$) for 9018 automatically centered reflections.

For both temperatures the structure was solved by direct methods using SHELXS-97 [17] and refined anisotropically (non-H atoms) by full-matrix least-squares on F^2 using the SHELXL-97 program [17]. All the hydrogen atoms with the exception of that involved in the strong $\text{O1-H1}\cdots\text{O3}$ hydrogen bond were allowed to ride on their parent atoms using SHELXL-97 defaults. H1 was freely refined with an isotropic displacement parameter multiple of the parent atom. The crystallographic details and selected interatomic distances and angles are given in Tables 1–4.

Thermal behaviour was studied using a power compensation differential scanning calorimeter DSC Pyris1, from Perkin–Elmer, equipped with a liquid nitrogen Cryofill

Table 2
Selected bond lengths (\AA) and angles ($^{\circ}$) at room and low temperatures

	293 K	80 K
Se–O5	1.625(3)	1.6342(14)
Se–O3	1.711(3)	1.7224(16)
Se–O4	1.765(3)	1.7637(16)
N1–C2	1.498(4)	1.497(3)
O5–Se–O3	103.52(14)	102.96(8)
O5–Se–O4	97.84(13)	97.28(7)
O3–Se–O4	97.82(15)	98.83(8)
O2–C1–O1	126.1(3)	126.09(18)
C5–C4–C3–C2	$-102.5(4)$	$-100.6(2)$
O1–C1–C2–N1	167.7(3)	167.11(17)
O2–C1–C2–N1	$-15.5(4)$	$-15.8(3)$
O2–C1–C2–C3	107.4(3)	107.1(2)
O1–C1–C2–C3	$-69.5(3)$	$-70.0(2)$
C4–C3–C2–N1	55.8(4)	55.2(2)
C4–C3–C2–C1	$-65.8(4)$	$-66.3(2)$

Table 1
Crystal data and structure refinement parameters

	293(2)	80(2)
Temperature (K)	293(2)	80(2)
Empirical formula	$\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_5\text{Se}$	$\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_5\text{Se}$
Formula weight	333.20	333.20
Wavelength (\AA)	1.5408	0.71073
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a (\AA)	5.4406(6)	5.3910(3)
b (\AA)	8.2436(6)	8.2097(4)
c (\AA)	27.539(3)	27.3216(14)
Volume (\AA^3)	1235.1(2)	1209.21(11)
Z	4	4
Calculated density (g/cm^3)	1.792	1.830
Absorption coefficient (mm^{-1})	4.328	3.125
$F(000)$	672	672
Crystal size (mm^3)	$0.37 \times 0.24 \times 0.15$	$0.40 \times 0.40 \times 0.15$
θ Range for data collection ($^{\circ}$)	3.21–72.16	1.49–30.56
Index ranges	$-6 < h < 6, -10 < k < 10, 0 < l < 34$	$-7 < h < 7, -11 < k < 11, -21 < l < 38$
Reflections collected/unique (R_{int})	4955/2439 (0.0335)	8551/3640 (0.0247)
Completeness to $\theta = 72.16$	100%	99%
Data/restraints/parameters	2439/0/179	3640/0/177
Goodness-of-fit on F^2	1.111	1.036
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0346, wR_2 = 0.0938$	$R_1 = 0.0250, wR_2 = 0.0583$
R indices (all data)	$R_1 = 0.0348, wR_2 = 0.0940$	$R_1 = 0.0273, wR_2 = 0.0619$
Largest difference in peak and hole ($e\text{ \AA}^{-3}$)	0.846 and -1.271	0.490 and -0.383

Table 3
Hydrogen bond geometry (Å, °) at 293(2) K

	D–H	H···A	D···A	Angle	Acceptor site symmetry
O1–H1···O3	1.22(6)	1.27(6)	2.482(3)	172(5)	
O4–H4···O2	0.82	2.20	2.789(4)	128.9	$x - 1, y, z$
O4–H4···O3	0.82	2.53	3.220(4)	143.0	$x - 1, y, z$
N1–H1A···O3	0.89	2.26	2.981(4)	138.3	$-x, y + 0.5,$ $-z + 1.5$
N1–H1A···O4	0.89	2.56	3.290(4)	140.0	$-x, y + 0.5,$ $-z + 1.5$
N1–H1A···O2	0.89	2.68	3.367(4)	135.3	$-x + 1, y + 0.5,$ $-z + 1.5$
N1–H1B···O5	0.89	1.93	2.806(4)	168.1	$x + 1, y + 1, z$
N1–H1B···O4	0.89	2.55	3.128(4)	123.7	$x + 1, y + 1, z$
N1–H1C···O1	0.89	2.15	2.945(4)	149.1	$x + 1, y, z$

Table 4
Hydrogen bond geometry (Å, °) at 80(2) K

	D–H	H···A	D···A	Angle	Acceptor site symmetry
O1–H1···O3	0.71(3)	1.82(3)	2.473(2)	154(3)	
O4–H4···O2	0.82	2.22	2.800(2)	127.5	$x - 1, y, z$
O4–H4···O3	0.82	2.47	3.169(2)	143.8	$x - 1, y, z$
N1–H1A···O3	0.89	2.28	2.980(3)	135.4	$-x, y + 0.5,$ $-z + 1.5$
N1–H1A···O4	0.89	2.63	3.314(3)	134.8	$-x, y + 0.5,$ $-z + 1.5$
N1–H1A···O2	0.89	2.55	3.278(2)	139.7	$-x + 1, y + 0.5,$ $-z + 1.5$
N1–H1B···O5	0.89	1.89	2.776(2)	172.5	$x + 1, y + 1, z$
N1–H1B···O4	0.89	2.54	3.070(2)	118.9	$x + 1, y + 1, z$
N1–H1C···O1	0.89	2.10	2.911(2)	150.7	$x + 1, y, z$

cooling unit. Purge was performed with a helium flux (20 mL/min). The crystalline product was powdered to obtain the sample and aluminum pans recommended for non-volatile substances were used for the sample and for the reference. An empty pan was used as the reference. Temperature calibration was performed with cyclohexane (Merck, GC, $x > 99.7\%$) and cyclopentane (Merck, GC, $x > 99.7\%$) [18]. DSC cooling and heating curves were traced at 10, 20 and 50 °C min⁻¹ scanning rates, in the temperature range $-170\text{ °C} \leq T \leq 25\text{ °C}$.

3. Results and discussion

3.1. Structural properties

Tryptophan molecules can be divided in two parts: the hydrophobic ring and the hydrophilic amino-carboxylate tail. In cationic form the tail is positively charged with both the amine and carboxylic group protonated. The indole ring is practically planar, the five-membered ring has an

average torsion angle of 0.36(14)° [0.96(9)° at 80 K] and the six-membered ring has an average torsion angle of 1.1(2)° [0.83(2)° at 80 K]. The least-squares plane of the indole ring makes an angle of 51.51(15)° [50.66(10)° at 80 K] with the carboxylic plane.

The stereographic projection about C_α–C_β (C2–C3) shows that the cation adopts a staggered conformation with N1 *gauche* to C4 that is *gauche* to C1. This conformation has been named the G+ conformer, according to Cao and Fisher [19]. This latter study, using ab initio molecular orbital calculations with a non-aqueous self-consistent reaction field (SCRFF), identified three possible conformers of the zwitterionic aminoacid. The dominant conformer was found to be the one with N1 *gauche* to C4 that is *trans* to C1, determined by comparison of the predicted fundamental vibrational frequencies and intensities with the experimental IR spectra.

In the title compound the conformation of the positively charged aminoacid molecules practically does not change with the lowering of the temperature, as seen by the value of the torsion angles: N1–C2–C3–C4, 55.8(4)° and C1–C2–C3–C4 –65.8(4)° at room temperature and 55.2(2)° and –66.3(2)°, respectively, at low temperature.

The differences between the structure at room and low temperature are found in the geometry of the carboxylic group. While the length of the C–O double bond does not change significantly with temperature [1.232(4) Å and 1.237(2) Å for 80 K], the single C–O bond elongates from 1.278(4) Å to 1.288(3) Å as the temperature decreases. This suggests that the hydrogen atom in this group is closer to O1 at lower temperatures.

The geometry of the anion does not change much with the temperature as seen in Table 2. The HSeO₃⁻ is pyramidal with one short Se–O bond, one long and another of intermediate length [Se–O3, 1.711(3) Å (at 293 K), 1.7224(16) Å (at 80 K)].

There is a hydrogen atom (H1) strongly shared between the anion (O3) and the cation (O1), in a strong H-bond

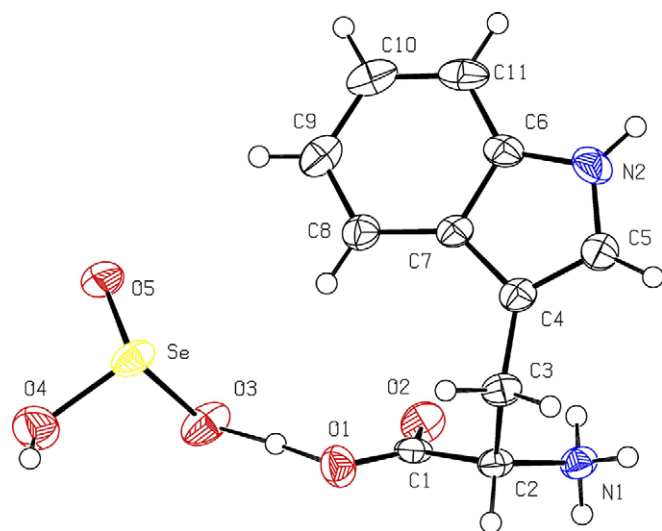


Fig. 1. ORTEP plot of the title compound. Displacement ellipsoids are drawn at the 50% level.

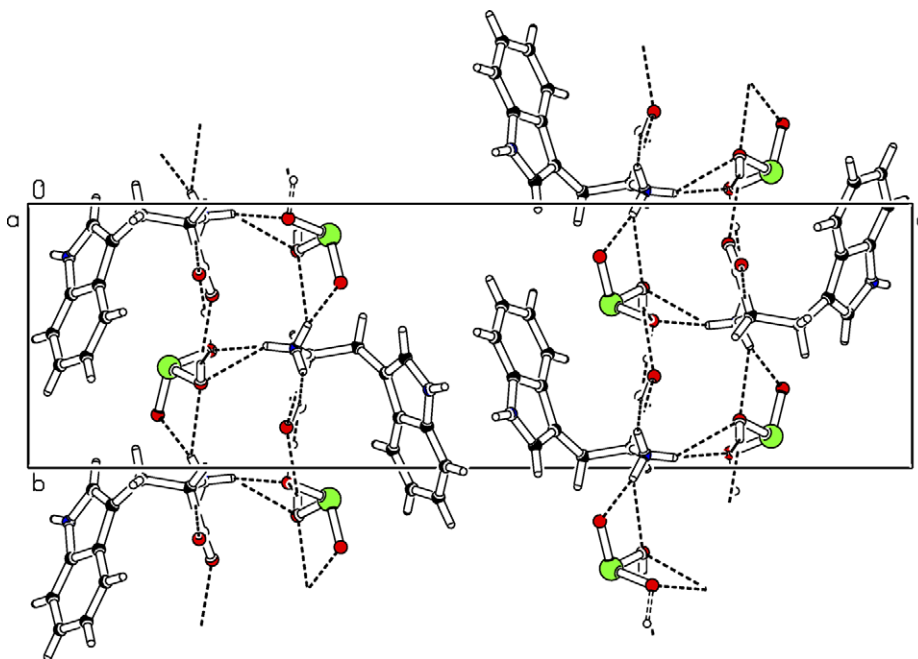


Fig. 2. Conventional hydrogen bond pattern viewed along the *a* axis.

(Fig. 1). The free refinement of this atom has shown that at room temperature H1 locates halfway between O1 and O3 as seen by the distances O1–H1 1.23(5) Å and O3–H1 1.26(5) Å. Difference electron density shows that the most likely explanation for such unusual O–H distances is that the proton is disordered between the O atoms. At low temperature O1–H1 decreases to 0.71(3) Å and O3–H1 increases to 1.82(3) Å, showing an ordering of the proton involved into an O1–H···O3 bond.

In the crystal, anions and cations assemble forming a vast 3-dimensional network of hydrogen bonds. The bond O4–H4···O3ⁱ (*i*: $x-1,y,z$) links the selenite ions in chains along the *a*-axis. Also along the *a*-axis, the bond N1–H1C···O1ⁱⁱ (*ii*: $x+1,y,z$) joins the cations in chains. Those chains are connected by other H-bonds between the anions and cations as described in Tables 3 and 4, where one can find bifurcated and trifurcated bonds.

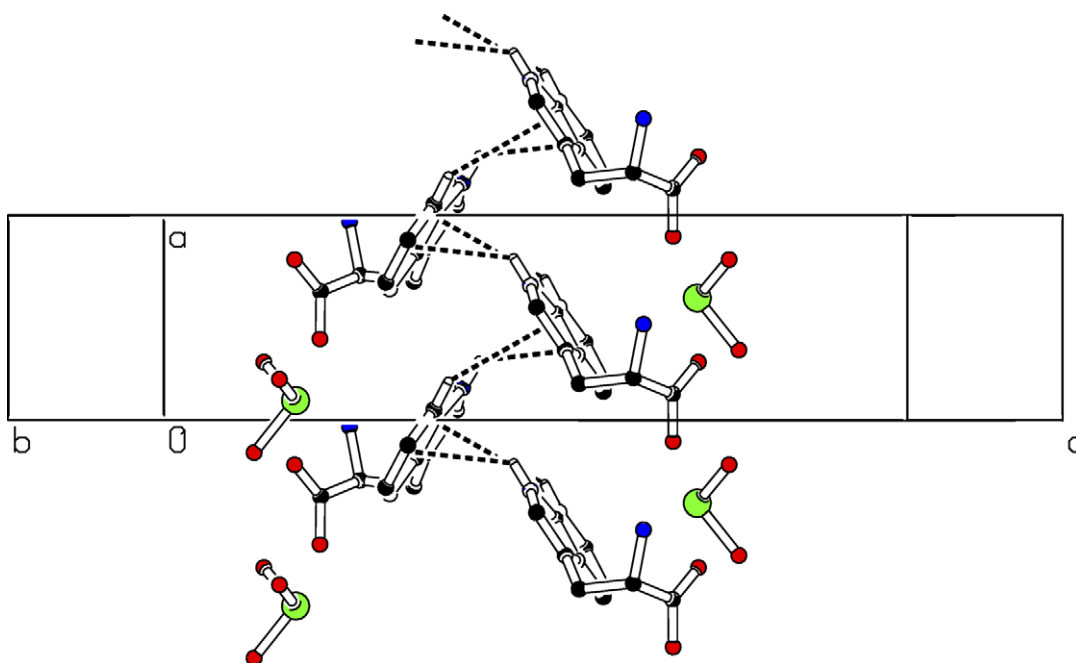


Fig. 3. X–H···π interactions shown as dashed lines. All hydrogen atoms not involved in these bonds were omitted for clarity.

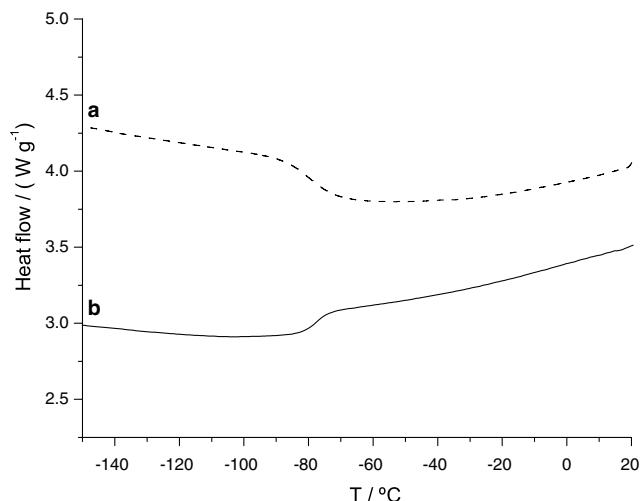


Fig. 4. Typical DSC L-tryptophanium hydrogen selenite (a) cooling curve and (b) heating curve, for the temperature range investigated.

Projecting the crystal packing down the *a*-axis one sees double layers of aminoacid tails and pyramidal anions strongly linked by hydrogen bonds (Fig. 2). Between those layers there are double layers of indole rings connected by N–H··· π and C–H··· π bonds, with the π electron system of the aromatic rings acting as the acceptor. The N2–H2 bond points towards the edge of the C6–C11 ring of a neighbouring molecule with the shared hydrogen situated above the centre ring. The H2-centroid distance is 2.681 Å, the interaction angle N2–H2···centroid is 127.83°, and the angle between the H2-centroid line and the ring perpendicular is 25.80°. This geometry is described as type III by Malone et al. [20]. The same geometry is seen in the intermolecular interaction, C11–H11···(N2–C6 centroid), with a slightly larger distance, 3.184 Å, and angle, 131.40°. Fig. 3 shows these intermolecular interactions joining the cations.

3.2. Thermal behaviour

The thermal behaviour of L-tryptophanium hydrogen selenite between $T = 25$ °C and $T = -170$ °C is illustrated in Fig. 4. For all scan rates investigated a second-order transition is observed on cooling. The behaviour is reversible on heating, with a transition temperature $T = -82.5$ °C. These observations are compatible with the existence of the hydrogen disorder at room temperature found in the X-ray experiments.

4. Conclusion

A new selenite compound has been synthesised and characterised by DSC and X-ray single crystal diffraction. The crystal structure of the L-tryptophanium hydrogen selenite has been solved at room and low temperature. An ordering of a hydrogen atom shared between the anion

and the cation is seen and that is the probable cause of the DSC observed anomaly at -82.5 °C.

Acknowledgement

This work was supported by Fundação para a Ciência e a Tecnologia under project POCI/FIS/57876/2004.

Appendix A. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 284629 for the room temperature phase and 284630 for the low temperature phase. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2005.12.028.

References

- [1] E. de Matos Gomes, A. Matos Beja, J.A. Paixão, L. Alte da Veiga, M. Ramos Silva, J. Martín-Gil, F.J. Martín-Gil, Z. Kristallogr. 210 (1995) 929.
- [2] J.A. Paixão, M. Ramos Silva, A. Matos Beja, E. Matos Gomes, L. Alte da Veiga, J. Martín-Gil, F.J. Martín-Gil, Z. Kristallogr. 212 (1997) 51.
- [3] J.A. Paixão, A. Matos Beja, M. Ramos Silva, E. Matos Gomes, L. Alte da Veiga, J. Martín-Gil, F.J. Martín-Gil, Acta Cryst. C 53 (1997) 1113.
- [4] E. de Matos Gomes, E. Nogueira, I. Fernandes, M. Belsley, J.A. Paixão, A. Matos Beja, M. Ramos Silva, J. Martín-Gil, F. Martín-Gil, J.F. Mano, Acta Cryst. B 57 (2001) 828.
- [5] R. Pepinsky, K. Vedam, Phys. Rev. 114 (1959) 1217.
- [6] K. Vedam, Y. Okaya, R. Pepsinsky, Phys. Rev. 119 (1960) 1252.
- [7] L.A. Shuvalov, N.R. Ivanov, T.K. Sitnik, Sov. Phys. – Crystallogr. 12 (1967) 315.
- [8] Y. Makita, J. Phys. Soc. Jap. 20 (1965) 1567.
- [9] L.A. Sannikov, N.R. Ivanov, T.K. Stinik, Sov. Phys. Crystallogr. 12 (1967) 315.
- [10] V.V. Gladkii, V.A. Krikov, V.K. Magataev, L.A. Shuvalov, Sov. Phys. – Solid State 19 (1977) 167.
- [11] M. Vijayan, Acta Cryst. B 24 (1968) 1237.
- [12] O.R. Evans, W. Lin, Chem. Mater. 13 (2001) 3009.
- [13] W. Lin, O.R. Evans, R.-G. Xiang, Z. Wang, J. Am. Chem. Soc. 120 (1998) 13272.
- [14] A.P. Demchenko, Luminescence 17 (2002) 19.
- [15] A.H.A. Clayton, W.H. Sawyer, Eur. Biophys. J. 31 (2002) 9.
- [16] J.W. Pietrich, M.C. Chang, D.B. McDonald, G.R. Fleming, J. Am. Chem. Soc. 105 (1983) 3824.
- [17] G.M. Sheldrick, SHELXS-97 and SHELXL-97, University of Gottingen, Germany, 1997.
- [18] R. Sabbah, X.W. An, J.S. Chickos, M.L.P. Leitão, M.V. Roux, L.A. Torres, Thermochim. Acta 331 (1999) 93.
- [19] X. Cao, G. Fischer, Phys. Chem. A 103 (1999) 9995.
- [20] J.F. Malone, C.M. Murray, M.H. Charlton, R. Docherty, A.J. Lavery, J. Chem. Soc., Faraday Trans. 93 (1997) 3429.