Journal of Coordination Chemistry

Synthesis and characterization of a new strontium(II) coordination polymer based on a μ$_2$-tridentate bridging zwitterionic glycine

S. Natarajan [a] , J. Kalyana Sundar [a] , S. Athimoolam [b] &
Bikshandarkoil R. Srinivasan [c]

[a] School of Physics , Madurai Kamaraj University , Madurai 625
021, India

[b] Department of Physics , University College of Engineering
Nagercoil, Anna University of Technology , Tirunelveli, Nagercoil
629 004, India

[c] Department of Chemistry , Goa University , Goa 403 206, India
Published online: 06 Jul 2011.

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

Synthesis and characterization of a new strontium(II) coordination polymer based on a μ_2-tridentate bridging zwitterionic glycine

S. NATARAJAN*†, J. KALYANA SUNDAR†, S. ATHIMOOLAM‡ and BIKSHANDARKOIL R. SRINIVASAN§

†School of Physics, Madurai Kamaraj University, Madurai 625 021, India
‡Department of Physics, University College of Engineering Nagercoil, Anna University of Technology, Tirunelveli, Nagercoil 629 004, India
§Department of Chemistry, Goa University, Goa 403 206, India

The synthesis and characterization of a new Sr(II) coordination polymer (CP), $[Sr(H_2O)(H\text{-gly})_2Cl_2]_n$ (**1**) (H-gly = glycine), is described. Compound **1** crystallizes in the centrosymmetric orthorhombic space group *Pcnb* and its structure consists of a central Sr(II), a water molecule, a zwitterionic glycine, and a chloride. The central metal is nine coordinate, bonded to six oxygens from four different bridging H-gly ligands, two symmetry-related chlorides, and a terminal water molecule. The μ_2-tridentate bridging zwitterionic glycine results in the formation of a 1-D CP with an Sr···Sr separation of 4.560 Å across the chain. The chloride, H-gly, and coordinated water are involved in five varieties of hydrogen bonding. A comparative study of the structural chemistry of several alkaline-earth glycine compounds is described.

Keywords: Coordination polymer; Strontium; Glycine; Zwitterion

1. Introduction

Coordination polymers (CPs) have attracted much attention because of their topology and applications in catalysis, adsorption (gas storage), separation, and luminescence [1–3]. Compared to the extensive chemistry of CPs based on transition metals, the coordination chemistry of group 1 and 2 metals with organic linkers is relatively less explored. The reluctance to use alkaline-earth cations as building blocks for open framework materials can be attributed to their unpredictable coordination numbers and geometries as no ligand field stabilization effects govern their bonding. Although the closed shell *s*-block metal cations lack useful properties like magnetism or variable oxidation states, alkali and alkaline-earth metals are preferred to transition or lanthanide metal ions because many of the *s*-block cations are non-toxic, cheap, and soluble in aqueous media. Growing interest in the coordination chemistry of *s*-block

*Corresponding author. Email: s_natarajan50@yahoo.com

elements is shown by several recent reports [4–17]. Fromm [18] reviewed the different ligand and polymer types of *s*-block compounds.

Depending on the electronic and steric requirements of the central metal, the flexibility, binding modes, and hydrogen-bonding characteristics of the organic ligand, CPs of differing dimensionalities can be constructed. For oxophilic *s*-block metals, carboxylic-acid-based ligands are useful linkers for the preparation of CPs as metals can be linked into an extended chain with bridging carboxylates or by employing di-, tri-, or multicarboxylic acid ligands. In view of their known affinity for oxygen donors, especially water, *s*-block metal carboxylates are normally synthesized in aqueous media, by reactions between metal carbonate or metal hydroxide or metal chloride and carboxylic acids under ambient conditions [4, 15–17, 19–29]. Many groups employ hydrothermal reactions of metal sources with carboxylic acids for compound synthesis [5–12]. Several CPs based on bivalent alkaline-earth metals have been prepared by employing a variety of carboxylic acids, including aromatic aminobenzoic acids [23–27]. These studies have biological importance for metal–amino acid interactions. In a recent paper, Strasdeit and coworkers [4] have described experiments involving alkaline-earth metals and glycine, pertinent to the prebiotic hot volcanic scenario. Glycine, the simplest achiral amino acid, can exist as a zwitterion (H-gly) or as a negatively charged glycinate (gly)$^-$ or the positively charged glycinium (H$_2$-gly)$^+$ ion depending on the pH of the reaction medium. In continuation of our long-standing research on structural chemistry of *s*-block metal glycine compounds [30–37], we describe herein the synthesis and structural characterization of a new Sr(II) CP based on a μ_2-bridging tridentate zwitterionic glycine ligand.

2. Experimental

2.1. *Materials and methods*

All chemicals were of reagent grade and used as received. The starting materials and reaction products are air stable and hence were prepared under normal laboratory conditions. Infrared (IR) spectra of solid samples diluted with KBr were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer from 4000 to 400 cm^{-1}. UV-Vis spectra of aqueous solutions were recorded using matched quartz cells on a Shimadzu UV-2450 double beam spectrophotometer.

2.2. *Preparation of [Sr(H$_2$O)(H-gly)$_2$Cl$_2$]$_n$ (1)*

Glycine and strontium chloride were taken in distilled water in equimolar ratio (1 : 1). The reaction mixture was filtered and left undisturbed for crystallization. Slow evaporation at room temperature (27°C) resulted in the formation of transparent crystals in a week in ∼25% yield. Anal. Calcd for SrC$_4$H$_{12}$Cl$_2$N$_2$O$_5$ (326.68) **1** (%): C, 14.71; H, 3.70; N, 8.58. Found (%): C, 14.52; H, 3.63; N, 8.71.

2.3. *X-ray crystal structure determination*

Intensity data for **1** were collected on a Nonius MACH3/CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. An absorption correction was applied to

Table 1.   Selected refinement data for $[Sr(H_2O)(H\text{-gly})_2Cl_2]_n$ (1).

Empirical formula	$[Sr(H_2O)(H\text{-gly})_2Cl_2]_n$
Formula weight (g mol^{-1})	326.68
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pcnb*
Unit cell dimensions (Å)	
a	8.177(3)
b	9.056(4)
c	14.411(3)
Volume (Å^3), *Z*	1067.1(7), 4
Calculated density, D_{Calcd} (Mg m^{-3})	2.033
Absorption coefficient (mm^{-1})	5.552
F(000)	648
θ range for data collection ($^\circ$)	2.83–24.97
Index ranges	$0 \le h \le 9$; $0 \le k \le 10$; $-1 \le l \le 17$
Reflections collected	1023
Independent reflections (R_{int})	945 (0.0215)
Completeness to θ	100.0%
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	945/0/67
Goodness-of-fit on F^2	1.114
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0333$, $wR_2 = 0.0787$
R indices (all data)	$R_1 = 0.0398$, $wR_2 = 0.0812$
Extinction coefficient	0.064(3)
Largest difference peak and hole (e Å^{-3})	0.653 and -1.589

the collected reflections. The structure was solved with direct methods using SHELXS-97 [38] and refinement was done against F^2 using SHELXL-97 [38]. All non-hydrogen atoms were refined anisotropically. The hydrogens of coordinated water and amine of glycine were located in the difference Fourier map, but were positioned with idealized geometry and refined using a riding model. Selected crystal refinement results for **1** are listed in table 1.

3. Results and discussion

3.1. *Synthetic aspects and spectral characteristics*

The synthesis of **1** involves crystallization of product from an aqueous reaction mixture of metal salt and glycine. The methodology is very similar to the one employed earlier for the synthesis of several other alkali and alkaline-earth glycine compounds [30–37]. Recent work of Strasdeit *et al.* [4] demonstrates the rich chemistry of alkaline-earth metal–glycine compounds especially of Ca. A variety of Ca–glycine products can be isolated by changing the metal : glycine stoichiometry [4]. Aqueous reaction of SrCl$_2$ with glycine in equimolar ratio resulted in the formation of $[Sr(H\text{-gly})_2(H_2O)Cl_2]$ (**1**) in low yield containing Sr : H-gly : water in a 1 : 2 : 1 mole ratio. The use of two moles of glycine per Sr(II) in the reaction has been reported to result in $[Sr(H\text{-gly})_2(H_2O)_3]Cl_2$ [39]

containing Sr : glycine : water in $1:2:3$ mole ratio. In $SrCl_2$–glycine systems, **1** can be isolated by using less glycine, while use of $1:2$ or an excess glycine favors the formation of $[Sr(H\text{-}gly)_2(H_2O)_3]Cl_2$. The metal : glycine ratio in the final product is dependent on the reaction stoichiometry of the metal salt and glycine, the nature of counter anion, and the conditions employed for crystallization. It has been observed by us that complete evaporation of solvent leads to the formation of a mixture of products. The formation of **1** was confirmed by analytical and spectral data and single-crystal X-ray structure determination. As expected, **1** does not show an absorption in the UV-Vis spectrum; the spectrum is identical to that of free glycine. The IR spectrum of **1** exhibits several signals in the mid-IR region, indicating the presence of the organic moiety. A comparison of the IR spectra of pure glycine and the title compound shows a broad and strong band between 3500 and 2500 cm^{-1}, which can be attributed to the presence of water in **1**. In the carboxylate region the band at 1665 cm^{-1} in free glycine is shifted to 1612 cm^{-1} in **1**. Although the absorptions indicate the presence of organic moiety, the exact nature of the binding of glycine cannot be inferred from IR data alone.

3.2. *Crystal structure description of $[Sr(H_2O)(H\text{-}gly)_2Cl_2]_n$ (1)*

Compound **1** crystallizes in the centrosymmetric orthorhombic space group *Pcnb* with Sr(II) and the oxygen of water situated in special positions (mirror plane). The crystal structure of **1** consists of a central Sr(II), a terminal water molecule, a crystallographically unique H-gly ligand, and a chloride (figure 1). Geometric parameters of the glycines are in the normal range. The Sr(II) is nine coordinate, bonded to oxygen (O3) from water, six oxygens from four different H-gly ligands, and two symmetry-related chlorides resulting in a distorted tricapped trigonal prismatic $\{SrO_7Cl_2\}$ polyhedron around Sr (figure 1). The Sr–O bond distances in **1** vary between 2.593(4) and 2.775(2) Å, while the two identical Sr–Cl bond lengths are 3.0876(10) Å (table 2). The long Sr–Cl distances indicate significant ionic character. The O–Sr–O angles $(47.25(7)–170.27(11)°)$ are in a very wide range.

The unique H-gly ligand functions as a μ_2-tridentate bridging ligand (figure 2) and is coordinated to Sr through O1 and O2 at Sr–O distances of 2.730(2) and 2.775(2) Å, respectively, and O2 is bonded to a symmetry related Sr at an Sr^{ii}–O2 distance of 2.594(2) Å with an $Sr \cdots Sr^{ii}$ separation of 4.560(2) Å. The μ_2–η^2:η^1 binding mode of H-gly results in the formation of a 1-D CP. The polymeric structure of **1** can be visualized as follows: a pair of μ_2-bridging H-gly ligands link a pair of $\{Sr(H_2O)(Cl)_2)\}$ units resulting in the formation of a tricyclic distrontium–diglycine block with an $Sr \cdots Sr$ separation of 4.560(2) Å in **1** (figure 2). This tricyclic unit can be considered as the basic building block of the 1-D polymer. The net result of the bridging binding mode of H-gly in **1** is the formation of a 1-D polymeric chain extending along the *b*-axis with a terminal water (O3) and two symmetry-related chlorides (Cl1, Cl1^{iii}), accounting for three of the nine binding sites of each Sr(II) (figure 3). The remaining six binding sites for Sr(II) are provided by six oxygens of four symmetry-related μ_2-bridging H-gly ligands. The structure reveals that the molecular surface has several H-donors and H-acceptors. Hydrogens of coordinated water, amine of glycine and methylene function as donors and are involved in several short contacts. Oxygens of carboxylate of glycine, water, and the chloride function as H-acceptors resulting in the formation of five
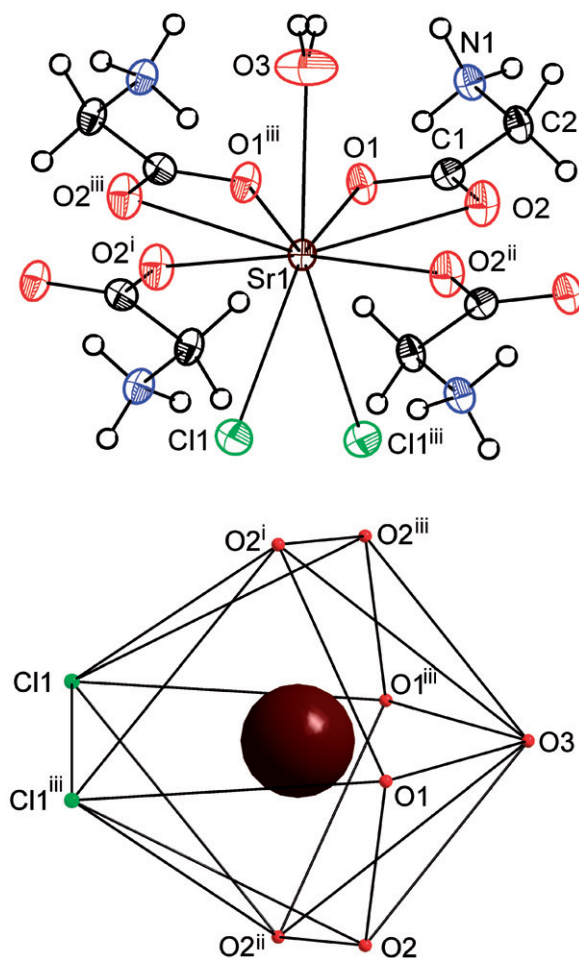
Figure 1. A view of the coordination sphere of Sr(II) in **1** showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level except for hydrogens, which are shown as circles of arbitrary radius (top). The distorted tricapped trigonal prismatic coordination polyhedron around Sr(II) in **1** (bottom). Symmetry codes: (^{i}) $x, y - 1/2, -z + 2$; (^{ii}) $-x, -y + 2, -z + 2$; (^{iii}) $-x, -y + 3/2, z$.

varieties of H-bonds (table 3). The geometric details of a total of seven hydrogen bonds comprising three N–H$\cdots$Cl interactions and one each of N–H$\cdots$O, O–H$\cdots$Cl, C–H$\cdots$Cl, and C–H$\cdots$O are listed in table 3. The H-bonds can be classified as inter-chain and intra-chain. The C–H$\cdots$Cl interaction involving methylene hydrogen as a donor is within the CP chain and thus is an intra-chain interaction (figure 3) while all others are inter-chain interactions, linking adjacent chains. Of the inter-chain interactions, the O–H$\cdots$Cl interaction between a coordinated water molecule in one chain and a chloride on an adjacent chain extends the network along the *c*-axis resulting in a layer along the *bc* plane (figure 3). The N–H$\cdots$O, N–H$\cdots$Cl, and C–H$\cdots$O interactions link adjacent layers resulting in the formation of an intricate 3-D H-bonded network.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Sr(1)–O(2)^i	2.594(2)	Sr(1)–O(2)	2.775(2)
Sr(1)–O(2)^{ii}	2.594(2)	Sr(1)–O(2)^{iii}	2.775(2)
Sr(1)–O(3)	2.593(4)	Sr(1)–Cl(1)^{iii}	3.0876(10)
Sr(1)–O(1)^{iii}	2.730(2)	Sr(1)–Cl(1)	3.0876(10)
Sr(1)–O(1)	2.730(2)	Sr(1)$\cdots$Sr(1)^{ii}	4.560(2)
O(2)^i–Sr(1)–O(2)^{ii}	170.27(11)	O(1)^{iii}–Sr(1)–O(2)^{iii}	47.25(7)
O(2)^i–Sr(1)–O(3)	94.86(5)	O(1)–Sr(1)–O(2)^{iii}	118.71(7)
O(2)^{ii}–Sr(1)–O(3)	94.86(5)	O(2)–Sr(1)–O(2)^{iii}	148.23(10)
O(2)^i–Sr(1)–O(1)^{iii}	111.02(7)	O(2)^i–Sr(1)–Cl(1)^{iii}	81.23(6)
O(2)^{ii}–Sr(1)–O(1)^{iii}	72.71(7)	O(2)^{ii}–Sr(1)–Cl(1)^{iii}	90.71(6)
O(3)–Sr(1)–O(1)^{iii}	68.74(5)	O(3)–Sr(1)–Cl(1)^{iii}	145.610(17)
O(2)^i–Sr(1)–O(1)	72.71(7)	O(1)^{iii}–Sr(1)–Cl(1)^{iii}	144.45(5)
O(2)^{ii}–Sr(1)–O(1)	111.02(7)	O(1)–Sr(1)–Cl(1)^{iii}	77.57(5)
O(3)–Sr(1)–O(1)	68.74(5)	O(2)–Sr(1)–Cl(1)^{iii}	78.15(6)
O(1)^{iii}–Sr(1)–O(1)	137.49(10)	O(2)^{iii}–Sr(1)–Cl(1)^{iii}	131.08(5)
O(2)^i–Sr(1)–O(2)	119.23(10)	O(2)^i–Sr(1)–Cl(1)	90.71(6)
O(2)^{ii}–Sr(1)–O(2)	63.77(9)	O(2)^{ii}–Sr(1)–Cl(1)	81.23(6)
O(3)–Sr(1)–O(2)	74.12(5)	O(3)–Sr(1)–Cl(1)	145.610(17)
O(1)^{iii}–Sr(1)–O(2)	118.71(7)	O(1)^{iii}–Sr(1)–Cl(1)	77.57(5)
O(1)–Sr(1)–O(2)	47.25(7)	O(1)–Sr(1)–Cl(1)	144.45(5)
O(2)^i–Sr(1)–O(2)^{iii}	63.77(9)	O(2)–Sr(1)–Cl(1)	131.08(5)
O(2)^{ii}–Sr(1)–O(2)^{iii}	119.23(10)	O(2)^{iii}–Sr(1)–Cl(1)	78.15(6)
O(3)–Sr(1)–O(2)^{iii}	74.12(5)	Cl(1)^{iii}–Sr(1)–Cl(1)	68.78(3)

Symmetry transformations used to generate equivalent atoms: $^{(i)}$ $x, y - 1/2, -z + 2$; $^{(ii)}$ $-x, -y + 2, -z + 2$; $^{(iii)}$ $-x, -y + 3/2, z$.
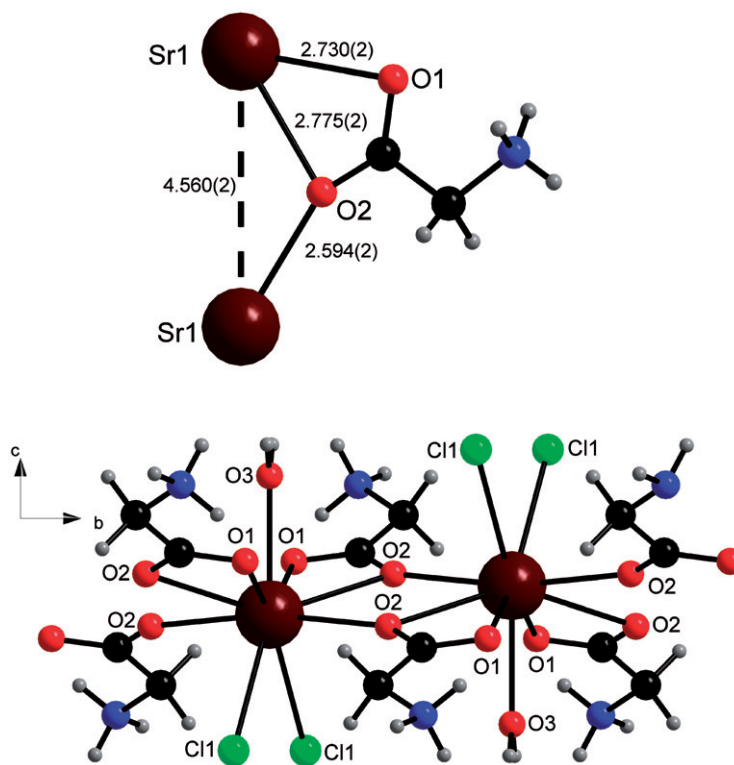

Figure 2. The μ_2-tridentate binding mode of glycine which leads to formation of a 1-D polymer extending along the *b*-axis (top) and the tricyclic distrontium–diglycine unit (building block) of the polymer (bottom).
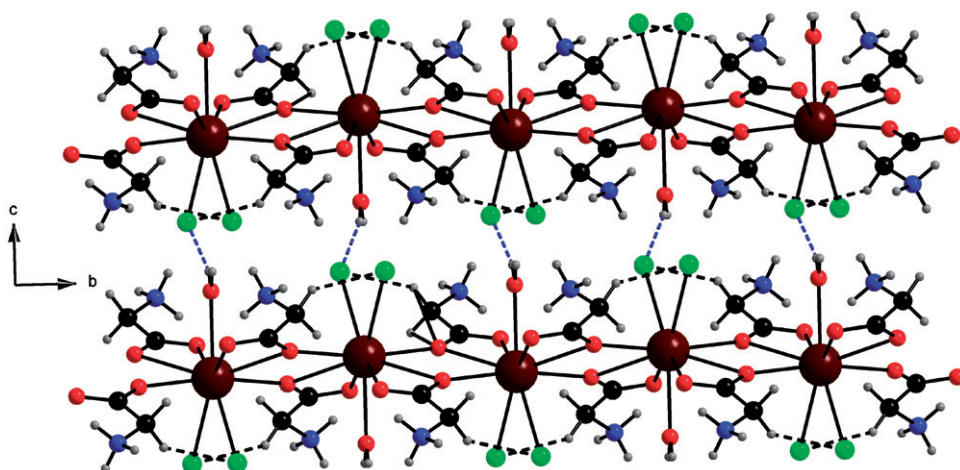
Figure 3. A view of the packing diagram showing a portion of the CP extending along the *b*-axis. The intra-chain C–H · · · Cl interactions are shown as broken lines (black) while the O–H · · · Cl interactions (blue) serve to link adjacent chains and extend the H-bonding network along the *c*-axis resulting in layers. For clarity, only the C–H · · · Cl and O–H · · · Cl interactions are shown.

Table 3. H-bonding geometry (Å, °) for **1**.

D–H · · · A	d(D–H) (Å)	d(H · · · A) (Å)	∠DHA (°)	d(D · · · A) (Å)	Symmetry code
Intra-chain interactions					
C2–H2A · · · Cl1	0.969	2.641	144	3.468	$-x$, $2-y$, $2-z$
Inter-chain interactions					
O3–H1O3 · · · Cl1	0.813	2.500	166	3.294	$-x+1/2$, y, $z+1/2$
N1–H1N1 · · · Cl1	0.890	2.228	165	3.097	$x-1$, $y+1/2$, $-z+2$
N1–H2N1 · · · Cl1	0.890	2.350	152	3.162	$x-1/2$, $-y+3/2$, $z+1/2$
N1–H2N1 · · · Cl1	0.890	2.868	124	3.446	$-x-1/2$, y, $z+1/2$
N1–H3N1 · · · O1	0.890	1.964	161	2.820	$-x-1$, $-y+3/2$, z
C2–H2B · · · O1	0.970	2.686	156	3.594	$-x-1$, $2-y$, $2-z$

3.3. *Comparative study of alkaline-earth metal–glycine compounds*

Several compounds containing coordinated glycine or glycinate [28] bonded to transition metals [40–44] as well as *s*-block metals [4, 31–37, 45, 46] are known. Metal–glycine compounds crystallize in both centrosymmetric and non-centrosymmetric space groups. Of the structurally characterized compounds, a representative list of metal–glycine compounds based on alkaline-earth metals is shown in table 4. The Be and Mg compounds show a coordination number of four and six, respectively, while higher coordination number is preferred by Ca, Sr, and Ba, with Sr and Ba favoring coordination number nine. The oxophilic nature of the bivalent alkaline-earths can be seen, as most of the compounds prefer exclusively oxygen donors or in a few cases like in **1** a mixed ligand donor set. One interesting feature of glycine in all these compounds is its ability to adopt a bridging mode of ligation leading to the formation of a chain polymer. In [BeF$_4$(H-gly)$_3$], the glycine functions as a free ligand as the Be is bonded

Table 4. Comparative structural features of alkaline-earth glycine compounds.

Compound	Space group	Coordination sphere	Binding mode	D	Ref.
$[BeF_4(H\text{-gly})_3]$	$P2_1$	BeF_4	Free	0	[45]
$[Mg_2(H_2O)_{10}(gly)_2](SO_4)_2$	$P\text{-}1$	MgO_6	Monodentate	0	[42]
$[[Mg\,(H_2O)_2(\mu_2\text{-gly})_2]Br_2]_n$	$P2_1/a$	MgO_6	μ_2-bridging bidentate	1	[31]
$[Mg(NO_3)_2(\mu_2\text{-H-gly})(H_2O)_4]_n$	$P2_1/n$	MgO_6	μ_2-bridging bidentate	1	[40]
$[MgCl_2(\mu_2\text{-H-gly})(H_2O)_4]_n$	$Pnma$	MgO_6	μ_2-bridging bidentate	1	[46]
$[Ca(NO_3)_2(H\text{-gly})(H_2O)_2]$	$P2_12_12_1$	CaO_8	μ_3-bridging tridentate	1	[32]
$[CaCl_2(H\text{-gly})_3]$	$Pb2_1/a$	CaO_6	μ_2-bridging bidentate;	2	[33]
		CaO_7	μ_2-bridging tridentate; monodentate		
$[CaCl_2(H\text{-gly})_2(H_2O)_4]$	$P2_1/c$	CaO_8	μ_2-bridging bidentate monodentate	1	[34]
$[CaBr_2(H\text{-gly})_3]$	$Pbc2_1$	CaO_6Br	μ_2-bridging bidentate;	2	[35]
		CaO_6Br	μ_2-bridging tridentate; monodentate		
$[CaCl_2(\mu_3\text{-H-gly})_3(H_2O)_3]_n$	$P2_1/c$	CaO_7Cl	μ_3-bridging tetradentate	1	[4]
$[CaI_2(H\text{-gly})_3(H_2O)]$	$P2_1/c$	CaO_7	μ_2-bridging bidentate; monodentate	1	[36]
$[Ca_2I_4(\mu_2\text{-H-gly})_4(H_2O)_6]_n$	$Pca2_1$	CaO_7	μ_2-bridging bidentate	1	[37]
		CaO_7			
$[Sr(H\text{-gly})_2(H_2O)_3]Cl_2$	$Pbcn$	SrO_9	μ_2-bridging tridentate	1	[39]
$[Sr(H_2O)(H\text{-gly})_2Cl_2]_n$	$Pcnb$	SrO_7Cl_2	μ_2-bridging tridentate	1	This work
$[BaCl_2(H\text{-gly})_2(H_2O)]_n$	$Pbcn$	BaO_7Cl_2	μ_2-bridging tridentate	1	[39]

Abbreviation used: D – dimensionality.

to four fluorides. In many compounds zwitterionic glycine exhibits a symmetrical μ_2-bridging bidentate mode although other modes like a μ_2-bridging tridentate mode, as in **1**, is also observed. In a few compounds, glycine exhibits monodentate binding; more than one binding mode of glycine is observed in a few compounds which contain more than one unique glycine in the crystal structure. The structure of **1** is closely related to the earlier reported nine-coordinate $[Sr(H\text{-gly})_2(H_2O)_3]Cl_2$ which shows a $\{SrO_9\}$ coordination sphere; **1** has a $\{SrCl_2O_7\}$ coordination sphere containing a single terminal water molecule and two terminal chlorides instead of three terminal water molecules as in $[Sr(H\text{-gly})_2(H_2O)_3]Cl_2$ and crystallizes when less glycine (excess chloride) is present. However, in both the Sr–glycine compounds the binding mode of glycine is the same.

4. Conclusion

In this work, we have described the synthesis under ambient conditions and structural characterization of a new Sr(II) CP, based on a bridging tridentate glycine. Compound **1** is a new example to the growing list of structurally characterized polymeric alkaline-earth coordination compounds.

Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as

supplementary publication no. CCDC 812391 (**1**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (Fax: +44-(0)1223-336033 or E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

References

[1] C. Janiak, J.K. Vieth. *New J. Chem.*, **34**, 2366 (2010); S.R. Batten, S.M. Neville, D.R. Turner. *Coordination Polymers: Design, Analysis and Application*, RSC Publishing, Cambridge UK (2009).
[2] D.J. Tranchemontagne, J.L. Mendoza-Cortes, M. O'Keeffe, O.M. Yaghi. *Chem. Soc. Rev.*, **38**, 1257 (2009); S. Natarajan, P. Mahata. *Chem. Soc. Rev.*, **38**, 2304 (2009).
[3] K. Biradha, A. Ramanan, J.J. Vittal. *Cryst. Growth Des.*, **9**, 2969 (2009).
[4] K. Yusenko, S. Fox, P. Guni, H. Strasdeit. *Z. Anorg. Allg. Chem.*, **634**, 2347 (2008).
[5] Z. Guo, G. Li, L. Zhou, S. Su, Y. Lei, S. Dang, H. Zhang. *Inorg. Chem.*, **48**, 8069 (2009).
[6] M.C. Das, S.K. Ghosh, E.C. Sanudo, P.K. Bharadwaj. *Dalton Trans.*, 1644 (2009).
[7] C.A. Williams, A.J. Blake, C. Wilson, P. Hubberstey, M. Schroder. *Cryst. Growth Des.*, **8**, 911 (2008).
[8] C. Volkringer, J. Marrot, G. Ferey, T. Loiseau. *Cryst. Growth Des.*, **8**, 685 (2008).
[9] P.C. Dietzel, R. Blom, H. Fjellvag. *Z. Anorg. Allg. Chem.*, **635**, 1953 (2009).
[10] A. Rossin, A. Ienco, F. Costantino, T. Montini, B.D. Credico, M. Caporali, L. Gonsalvi, P. Fornasiero, M. Peruzzini. *Cryst. Growth Des.*, **8**, 3302 (2008).
[11] L.N. Appelhans, M. Kosa, A.V. Radha, P. Simoncic, A. Navrotsky, M. Parrinello, A.K. Cheetham. *J. Am. Chem. Soc.*, **131**, 15375 (2009).
[12] D.T. Tran, D. Chu, A.J. Oliver, S.R.J. Oliver. *Inorg. Chem. Commun.*, **12**, 351 (2009).
[13] B.R. Srinivasan, S.Y. Shetgaonkar, J.V. Sawant, P. Raghavaiah. *Polyhedron*, **27**, 3299 (2008).
[14] B.R. Srinivasan, S.Y. Shetgaonkar, C. Näther, W. Bensch. *Polyhedron*, **28**, 534 (2009).
[15] B.R. Srinivasan, S.Y. Shetgaonkar. *J. Coord. Chem.*, **63**, 3403 (2010).
[16] B.R. Srinivasan, S.Y. Shetgaonkar, P. Raghavaiah. *Polyhedron*, **28**, 2879 (2009).
[17] B.R. Srinivasan, S.Y. Shetgaonkar, C. Näther. *Z. Anorg. Allg. Chem.*, **637**, 130 (2011).
[18] K.M. Fromm. *Coord. Chem. Rev.*, **252**, 856 (2008).
[19] M. Dan, A.K. Cheetham, C.N.R. Rao. *Inorg. Chem.*, **45**, 8227 (2006).
[20] H.-F. Zhu, Z.-H. Zhang, W.-Y. Sun, T. Okamura, N. Ueyama. *Cryst. Growth Des.*, **5**, 177 (2005).
[21] Z. Fei, T.J. Geldbach, R. Scopelliti, P.J. Dyson. *Inorg. Chem.*, **45**, 6331 (2005).
[22] R.K.B. Nielsen, K.O. Kongshaug, H. Fjellvåg. *Solid State Sci.*, **8**, 1237 (2006).
[23] F. Wiesbrock, H. Schimdbaur. *Inorg. Chem.*, **42**, 7283 (2003).
[24] R. Murugavel, P. Kumar, M.G. Walawalkar, R. Mathialagan. *Inorg. Chem.*, **46**, 6828 (2007).
[25] R. Murugavel, S. Banerjee. *Inorg. Chem. Commun.*, **6**, 810 (2003).
[26] R. Murugavel, V.V. Karambelkar, G. Anantharaman, M.G. Walawalkar. *Inorg. Chem.*, **39**, 1381 (2000).
[27] R. Murugavel, V.V. Karambelkar, G. Anantharaman. *Indian J. Chem.*, **39A**, 843 (2000).
[28] S. Fox, I. Büsching, W. Barklage, H. Strasdeit. *Inorg. Chem.*, **46**, 818 (2007).
[29] A. Grirrane, A. Pastor, E. Álvarez, R. Moyano, A. Galindo. *Inorg. Chem. Commun.*, **10**, 1125 (2007).
[30] R.V. Krishnakumar, M.S. Nandhini, S. Natarajan, K. Sivakumar, B. Varghese. *Acta Crystallogr.*, **57E**, 1149 (2001).
[31] R.V. Krishnakumar, S. Natarajan. *Indian J. Phys.*, **69A**, 223 (1995).
[32] S. Natarajan, K. Ravikumar, S.S. Rajan. *Z. Kristallogr.*, **168**, 75 (1984).
[33] K. Ravikumar, S.S. Rajan, S. Natarajan, M.N. Ponnuswamy, J. Trotter. *Z. Kristallogr.*, **175**, 217 (1986).
[34] S. Natarajan, J.K.M. Rao. *Z. Kristallogr.*, **152**, 179 (1980).
[35] J.K.M. Rao, S. Natarajan. *Acta Crystallogr.*, **36B**, 1058 (1980).
[36] S. Natarajan, J.K.M. Rao. *J. Inorg. Nucl. Chem.*, **43**, 1693 (1981).
[37] S. Natarajan, G. Shanmugam, S.A.M.B. Dhas, S. Athimoolam. *Acta Crystallogr.*, **63E**, m2897 (2007).
[38] G.M. Sheldrick. *Acta Crystallogr.*, **64A**, 112 (2008).
[39] P. Narayanan, S. Venkataraman. *Z. Kristallogr.*, **142**, 52 (1975).

[40] M. Fleck, L. Bohaty. *Acta Crystallogr.*, **61E**, m1887 (2005).
[41] M. Fleck, L. Bohaty. *Acta Crystallogr.*, **62C**, m22 (2006).
[42] K. Elayaraja, S.P. Parthiban, S. Ramalingom, G. Bocelli, S.N. Kalkura. *Acta Crystallogr.*, **63E**, m2901 (2007).
[43] S.M.N. Priya, B. Varghese, J.M. Linet, G. Bhagavannarayana, C.J. Raj, S. Krishnan, S. Dinakaran, S.J. Das. *Cryst. Growth Des.*, **8**, 1663 (2008).
[44] C.D. Ch'ng, S.G. Teoh, S. Chantrapromma, H.-K. Fun, S.M. Goh. *Acta Crystallogr.*, **64E**, m865 (2008).
[45] A. Waskowska, S. Olejnik, K. Lukaszewicz, M. Ciechanowicz-Rutkowska. *Ferroelectrics*, **22**, 855 (1979).
[46] M. Fleck, L. Bohaty. *Acta Crystallogr.*, **61C**, m412 (2005).