Synthesis, structure and thermal properties of a new 1D magnesium sulfoacetate coordination polymer

A precursor for MgO

Rajendran Selvakumar · Steven J. Geib ·
Thathan Premkumar · Subbiah Govindarajan

Abstract A new one-dimensional polymeric complex [Mg(SA)(H$_2$O)$_3$], where SA = sulfoacetate, has been synthesised by reaction of Mg(NO$_3$)$_2$·6H$_2$O with sulfoacetic acid in the presence of hydrazine hydrate. The compound was characterized by elemental analysis and FT-IR spectroscopy as well as single-crystal X-ray crystallography. The compound crystallizes in the monoclinic P2$_1$/C space group with $a = 6.5051(5)$ Å, $b = 8.9012(7)$ Å, $c = 13.5724(11)$ Å, $\beta = 90.530(2)°$, and $V = 785.85(11)$ Å^3. The crystal structure shows a one-dimensional chain propagated through bridging and chelating a tridentate sulfoacetate anion. Furthermore, the thermal stability of the compound was investigated by thermogravimetry and differential thermal analysis.

Keywords Chemical synthesis · Crystal structure · Inorganic compounds · Oxides · X-ray diffraction

Introduction

Metal sulfonates are a class of compound with interesting functional properties. The chemistry of metal sulfonates

R. Selvakumar · S. Govindarajan (✉)
Department of Chemistry, Bharathiar University,
Coimbatore 641 046, India
e-mail: drsgovind@yahoo.co.in

S. J. Geib
Department of Chemistry, University of Pittsburgh, Pittsburgh,
PA 15260, USA

T. Premkumar (✉)
Department of Chemistry, The University College,
Sungkyunkwan University, Suwon 440-746, South Korea
e-mail: thathanpremkumar@gmail.com

[1, 2] has not been extensively explored due to the preconception that sulfonates are weakly coordinating ligands [3] unlike metal phosphates, which are well studied. Many research efforts have focused on the chemistry of metal phosphates due to potential applications in the areas of catalysis [4–6], photochemistry, and materials chemistry [7–9], and the strategy of using bifunctional or multifunctional anionic units such as diphosphonates and phosphonocarboxylate have led to a number of 2D and 3D metal phosphonates [10–19].

However, reports on bifunctional or multifunctional sulfonates [20] are still rare. In order to explore the coordination chemistry of sulfonates, as well as the possibility of constructing functional (inorganic–organic hybrid) materials, we have chosen sulfoacetic acid, a bifunctional molecule with both carboxylate and sulfonate coordinating groups, which can act as a bidentate chelating and bridging ligand [21, 22].

We have long been involved in studies on the synthesis and thermal properties of hydrazinium salts with different aliphatic and aromatic carboxylic acids [23–26], as well as their corresponding metal (mostly transition and lanthanide metals) complexes. We are also interested in investigating the coordination ability and thermal stability of different types of carboxylic (aliphatic, aromatic and heteroaromatic) acids with variety of metals. We reported the thermal properties of different simple metal carboxylates, which can be used as precursors for corresponding metal oxides, of heterocyclic carboxylic acids such as 2-pyrazinecarboxylic acid [27], 4,5-imidazoledicarboxylic acid [28] and 3,5-pyrazoledicarboxylic acid [29]. Fortified by laboratory results on the thermal behavior of other metal carboxylate and/or metal hydrazine carboxylate systems [27–36], we extended our study to the coordination ability of sulfoacetic acid with magnesium ion. For the first time, we prepared a

Table 1 Crystal structure data for the Mg complex

Empirical formula	$C_4H_{16}Mg_2O_{16}S_2$
Formula weight	432.91
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	$a = 6.5051(5)$ Å
	$b = 8.9012(7)$ Å
	$c = 13.5724(11)$ Å
	$\alpha = 90°$
	$\beta = 90.530(2)°$
	$\gamma = 90°$
Volume	785.85(11) Å^3
Z	2
Density (calculated)	1.830 Mg/m^3
Absorption coefficient	0.501 mm^{-1}
F(000)	448
Crystal size	$0.29 \times 0.23 \times 0.19$ mm^3
Theta range for data collection	2.74–32.62°
Index ranges	$-9 \leq h \leq 9$, $-13 \leq k \leq 13$, $-9 \leq l \leq 20$
Reflections collected	9911
Independent reflections	2781 [R(int) = 0.0273]
Completeness to theta = 32.62°	96.5 %
Absorption correction	None
Maximum and minimum transmission	0.9108 and 0.8682
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2781/0/141
Goodness-of-fit on F^2	0.968
Final R indices [I > 2sigma(I)]	R1 = 0.0390, wR2 = 0.1047
R indices (all data)	R1 = 0.0522, wR2 = 0.1141
Largest difference peak and hole	0.666 and −0.299 e.Å−3

one-dimensional coordination polymer of magnesium ion with sulfoacetic acid and studied the coordination ability of the acid and thermal properties of metal complex.

Experimental

Materials and methods

All of the chemicals used for the preparation of the ligand and complexes were of analytical grade and were used without further purification. Elemental analyses were carried out with a Perkin Elmer-240B CHN analyzer. IR spectra were recorded on a Shimadzu FTIR 8000 spectrometer with samples prepared as KBr pellets. Simultaneous TG–DTA

$$[Mg(NO_3)_2] \cdot 6H_2O + HOOC\text{-}CH_2\text{-}SO_3H \xrightarrow[\text{pH} \sim 4\text{-}5]{N_2H_4 \cdot H_2O} [Mg(OOC\text{-}CH_2\text{-}SO_3)(H_2O)_3]$$
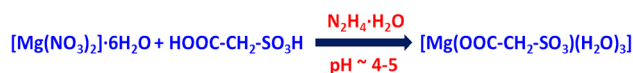
Scheme 1 A simple synthetic scheme showing the preparation of magnesium sulfoacetate in the presence of hydrazine hydrate
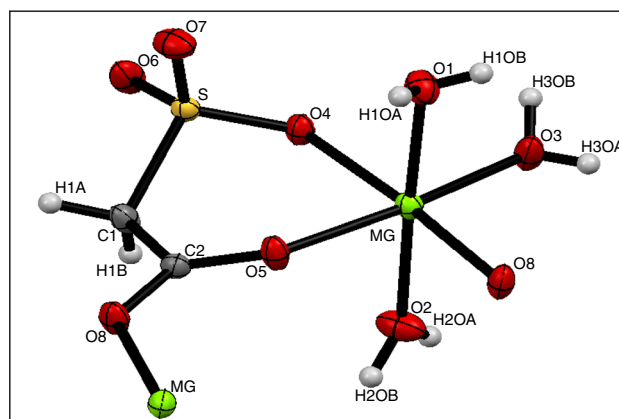

Fig. 1 View of the coordination environment of the Mg ion with 50 % thermal ellipsoids

curves were recorded on a Perkin Elmer Pyris Diamond instrument at a heating rate of 10 °C min^{-1} in air. The powder X-ray diffraction was recorded on a Rigaku diffractometer with a copper radiation ($\lambda = 0.154\ 06$ nm) at 40 kV and 40 mA.

Preparation of [Mg(SA)(H$_2$O)$_3$]

The compound was prepared by dissolving magnesium nitrate hexahydrate (0.085 g; 0.33 mmol) in an aqueous solution containing sulfoacetic acid (0.093 g; 0.66 mmol) and hydrazine hydrate (0.66 mL of 10 % solution; 1.3 mmol). Room temperature evaporation of the resulting solution gave a colorless polycrystalline compound. Crystals suitable for X-ray analysis were obtained by recrystallization from a 1:1 water–ethanol mixture. CHN analysis for $C_4H_{16}Mg_2O_{16}S_2$ (**1**), calculated (%): C, 11.08 and H, 3.69. Found: C, 12.02 and H 3.57.

Crystal structure determination

An X-ray crystal structure for $C_4H_{16}Mg_2O_{16}S_2$ using a single crystal was determined on a Bruker Smart apex CCD diffractometer with graphite-monochromated MoKα ($\lambda = 0.71073$ Å) radiation. The parameters used during the collection of diffraction data are summarized in Table 1. The crystal was mounted in fluorolube on a glass loop, and data were collected at 173 K under nitrogen. **1** was assigned to centrosymmetric P2$_1$/c based on unit cell parameters and systematic absences. Unit cell dimensions were derived from the least-squares fit of the angular
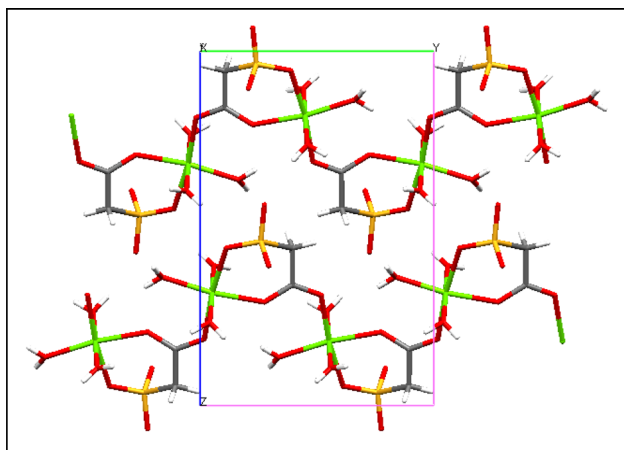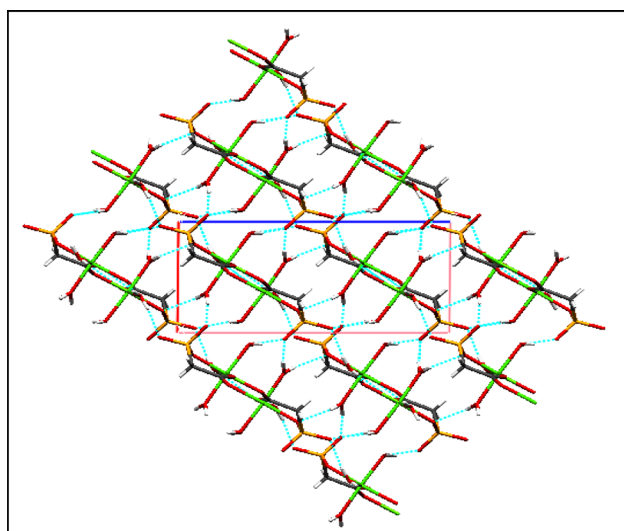
Fig. 2 1D zig-zag chain–viewed down *a*

Fig. 3 A part of the 3D polymer in [Mg(SA)(H$_2$O)$_3$]- viewed down *b*

Table 2 Bond lengths/Å and angles/° for the Mg complex

Mg–O(5)	2.0319(12)	O(5)–Mg–O(3)	172.21(5)
Mg–O(3)	2.0356(13)	O(5)–Mg–O(2)	88.87(6)
Mg–O(2)	2.0463(14)	O(3)–Mg–O(2)	89.42(6)
Mg–O(1)	2.0776(14)	O(5)–Mg–O(1)	91.25(6)
Mg–O(8)#1	2.0811(11)	O(3)–Mg–O(1)	90.80(6)
Mg–O(4)	2.1201(11)	O(2)–Mg–O(1)	177.37(6)
S–O(7)	1.4467(12)	O(5)–Mg–O(8)#1	87.13(5)
S–O(6)	1.4516(11)	O(3)–Mg–O(8)#1	100.47(5)
S–O(4)	1.4655(11)	O(2)–Mg–O(8)#1	89.95(6)
S–C(1)	1.7684(15)	O(1)–Mg–O(8)#1	87.43(5)
O(1)–H(1OA)	0.77(3)	O(5)–Mg–O(4)	86.42(4)
O(1)–H(1OB)	0.76(3)	O(3)–Mg–O(4)	86.04(5)
C(1)–C(2)	1.522(2)	O(2)–Mg–O(4)	92.11(5)
C(1)–H(1B)	0.83(2)	O(1)–Mg–O(4)	90.51(5)
C(1)–H(1A)	0.95(2)	O(8)#1–Mg–O(4)	173.19(5)
O(2)–H(2OA)	0.77(3)	O(7)–S–O(6)	113.20(8)
O(2)–H(2OB)	0.82(3)	O(7)–S–O(4)	112.16(7)
C(2)–O(8)	1.2484(16)	O(6)–S–O(4)	111.19(7)
C(2)–O(5)	1.2545(18)	O(7)–S–C(1)	106.98(8)
O(3)–H(3OA)	0.75(2)	O(6)–S–C(1)	105.98(7)
O(3)–H(3OB)	0.84(2)	O(4)–S–C(1)	106.85(7)
O(8)–Mg#2	2.0811(11)	Mg–O(1)–H(1OA)	114(2)
		Mg–O(1)–H(1OB)	112(2)
		H(1OA)–O(1)–H(1OB)	103(3)
		C(2)–C(1)–S	114.70(10)
		C(2)–C(1)–H(1B)	110.8(17)
		S–C(1)–H(1B)	104.7(17)
		C(2)–C(1)–H(1A)	111.6(12)
		S–C(1)–H(1A)	104.8(12)
		H(1B)–C(1)–H(1A)	110(2)
		Mg–O(2)–H(2OA)	129.5(19)
		Mg–O(2)–H(2OB)	127(2)
		H(2OA)–O(2)–H(2OB)	103(2)
		O(8)–C(2)–O(5)	124.59(13)
		O(8)–C(2)–C(1)	116.02(12)
		O(5)–C(2)–C(1)	119.36(12)
		Mg–O(3)–H(3OA)	124.5(17)
		Mg–O(3)–H(3OB)	125.6(16)
		H(3OA)–O(3)–H(3OB)	102(2)
		S–O(4)–Mg	125.54(6)
		C(2)–O(5)–Mg	137.74(10)
		C(2)–O(8)–Mg#2	125.61(9)

setting of 2454 reflections. Data were corrected for absorption using the Bruker program Sadabs.

The structure was solved via direct methods that located all non-hydrogen atoms, which were refined anisotropically. Hydrogen atoms were located from difference Fourier maps and were refined isotropically. The final Fourier map showed no significant electron density.

All computer programs used in the data collection and refinements are contained in the Bruker program packages SMART (vers. 5.625), SAINT (vers. 6.22), and SHELXTL (vers. 6.14).

Results and discussion

Treatment of sulfoacetic acid with hydrazine hydrate and magnesium nitrate resulted in a simple metal carboxylate. Preparation of the metal carboxylate in the absence of

hydrazine was unsuccessful. It is worth mentioning that hydrazine hydrate plays an important role in the preparation of magnesium sulfoacetate (Scheme 1) in suitable crystalline form and acts as base reacting with sulfoacetic acid. The formed sulfoacetate anion then reacts with magnesium ion resulting in precipitation of magnesium sulfoacetate trihydrate.

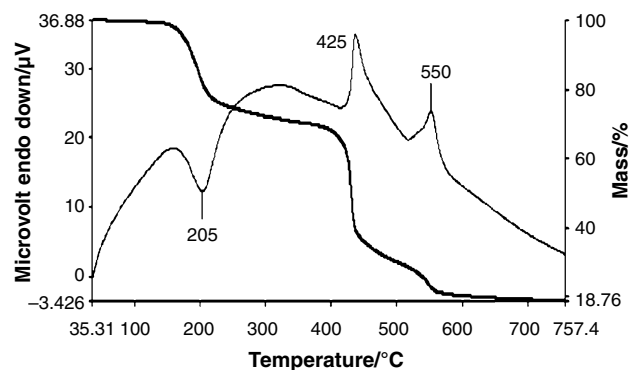**Table 3** Hydrogen bond lengths/Å and angles/° for the Mg complex

D–H⋯A	d(D–H)	d(H⋯A)	d(D⋯A)	(DHA)
O1–H1OA⋯O6(v)	0.77	2.10	2.8590	167
O1–H1OB⋯O7(iv)	0.76	2.09	2.8413	167
O2–H2OA⋯O4(ii)	0.77	2.12	2.8646	165
O2–H2OB⋯O7(vi)	0.82	2.05	2.8645	172
O3–H3OA⋯O8(vii)	0.75	2.33	3.0379	158
O3–H3OA⋯O5(i)	0.75	2.29	2.7912	125
O3–H3OB⋯\O6(iii)	0.84	1.93	2.7672	173

Symmetry codes: (i) $1 - x$, $1/2 + y$, $½ - z$ (ii) $1 - x$, $1 - y$, $-z$ (ii) $- x$, $1 - y$, $-z$ (iv) $-x$, $1/2 + y$, $½ - z$ (v) x, $½ - y$, $1/2 + z$, (vi) $1 + x$, y, z (vii) x, $1 + y$, z

Fig. 5 Simultaneous TG–DTA of $[Mg(SA)(H_2O)_3]$

Fig. 4 IR spectra of **a** $[Mg(SA)(H_2O)_3]$ and **b** sulfoacetic acid

Crystal structure of $[Mg(SA)(H_2O)_3]$

The asymmetric unit consists of Mg^{2+} ion, a sulfoacetate group, and three water molecules. The environment around Mg ion is best described as a distorted octahedron (Fig. 1) with Mg ion coordinated to a sulfonate oxygen O(4), carboxylate oxygen O(5), carboxylate oxygen O(8) from a different sulfoacetate group, and three water oxygens [O(1), O(2), and O(3)]. Water oxygens O(1) and O(2) are *trans* disposed, O(3) is *trans* to O(5), and O(4) is *trans* to O(8)$_{adjacent}$. The Mg–O distances, which range from 2.0319(12) to 2.1201(11) Å and the Mg-O4 bond distance [2.1201(11) Å arising from the sulfonate oxygen] are longer than other reported distances [13] (2.045–2.063). The structure consists of a one-dimensional polymeric chain (Fig. 2) with Mg ions bridged by carboxylate groups such as O–C–O–Mg–O–C–O–Mg. The sulfoacetate ligand acts as both a bidentate chelator [through coordination with O(4) and O(5)] and a bridging ligand [using O(8)–C(2)–O(5)]. Additionally, the three water molecules are involved in a three-dimensional hydrogen-bonded network (Fig. 3), with O(1) H-bonded to sulfonate oxygens O(6) and O(7), O(2) H-bonded to O(4) and O(7), O(5), O(6), and O(8). The crystal structure data including experimental details, bond lengths, bond angles, and hydrogen bonding parameters are given in Tables 1–3.

Infrared (IR) spectroscopic analysis

The IR spectrum of the complex (Fig. 4a) shows broad bands at 3489 and 1640 cm^{-1} corresponding to the O–H stretching frequency of coordinated water molecules [37]. As seen in the free acid (Fig. 4b), the C–H stretching of CH$_2$ is clearly seen at 2920 cm^{-1}. The carboxylate asymmetric stretching mode is observed at 1589 cm^{-1}, and the symmetric stretch occurs at 1419 and 1388 cm^{-1}. Unlike the free acid, the absence of a band in the 1734–1620 cm^{-1} region indicates complete deprotonation of the carboxyl group. The characteristic peak at approximately 1197 cm^{-1} is attributed to the sulfonate group. These features were further confirmed by the single-crystal X-ray diffraction study.

Table 4 Thermal data

Compound	DTA peak temp./°C	Thermogravimetry			Possible intermediate/end product
		Temp. range/°C	Mass loss/%		
			Found	Calculated	
[Mg(SA)(H$_2$O)$_3$]	205(+)	150–300	24.00	24.95	[Mg(SA)]
	425(−)	300–600	81.50	81.38	MgO
	550(−)				
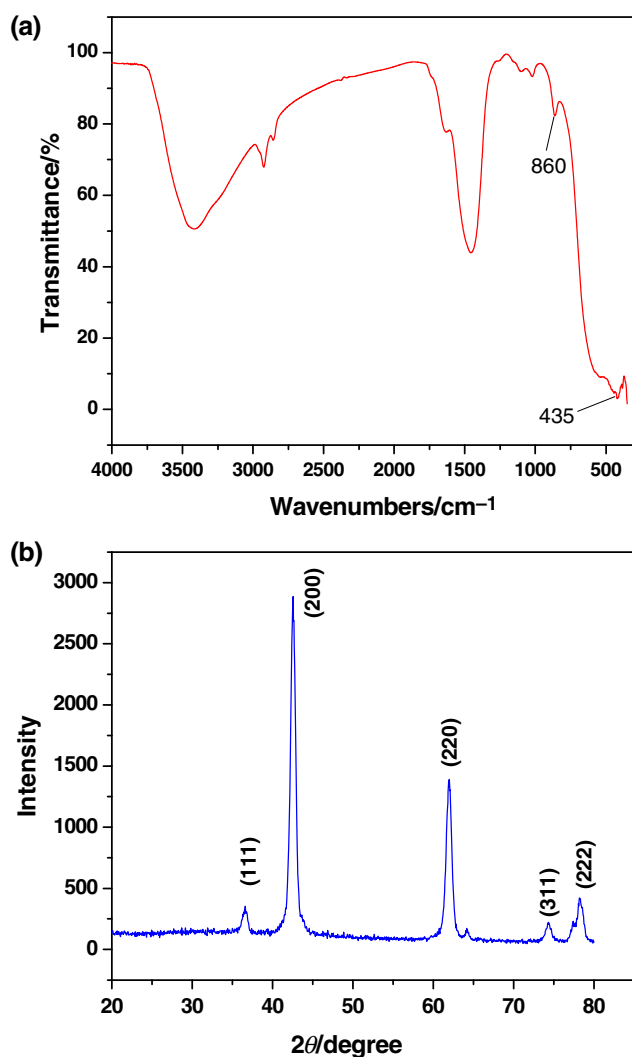
Fig. 6 a IR spectrum of MgO and **b** the powder XRD pattern of MgO obtained from thermal decomposition of [Mg(SA)(H$_2$O)$_3$]

Thermal analyses

Simultaneous TG–DTA of the complex (Fig. 5) shows two distinct steps of decomposition. In the TG curve, the first mass loss (found: 24.0 %; calculated: 24.95 %) corresponds to loss of three water molecules, which is seen as an endotherm (205 °C). This suggests that the water molecules are coordinated to the magnesium ion. Further, the anhydrous complex decomposes exothermically between 425 and 550 °C resulting in magnesium oxide as the end product. TG also shows continuous decomposition in accordance with the DTA results.

Our effort to separate the intermediate was unsuccessful due to its continuous decomposition, as evident in the TG curve. Hence, we have tried to assign the likely intermediate (anhydrous magnesium sulfoacetate) as observed from the TG mass losses (Table 4), which are consistent with the calculated mass losses. However, the final decomposition product of the magnesium complex was identified as MgO, which was further confirmed by its IR spectroscopic and powder X-ray diffraction data.

The IR spectrum (Fig. 6a) of the MgO registers a characteristic absorption band at around 435 cm^{-1} was ascribed to the Mg–O stretching vibration [38, 39]. Further, it can be observed that the characteristic vibration of cubic MgO occurs in the band ranging from 1000 to 420 cm^{-1} with the clear absorption peak at 860 cm^{-1}, revealing the formation of cubic MgO [40]. As can be seen in the IR spectrum of MgO, the characteristic bands obtained from the sulfoacetate moieties in the complex (Fig. 4a) completely disappear after the thermal decomposition at around 600 °C, which indicated the decomposition of [Mg(SA)(H$_2$O)$_3$] to MgO.

Further, the final residue of the thermal decomposition of magnesium complex was confirmed as MgO by using powder XRD data. The XRD lines of the final decomposition products, MgO, are very sharp and intense indicating its pure and crystalline nature. According to the JCPDS data (JCPDS No. 45-0946), the phase of the MgO (Fig. 6b) obtained from thermal decomposition of as-prepared magnesium complex precursor can be indexed to be cubic MgO structure which is in good agreement with the results reported in the literatures [38–40].

Conclusions

A new magnesium sulfoacetate coordination polymer has been synthesized at room temperature and was characterized

structurally. Mg ion was coordinated to sulfonate oxygen O(4), carboxylate oxygen O(5), carboxylate oxygen O(8) from a different sulfoacetate group, and three water oxygens [O(1), O(2), and O(3)]. A relatively low-temperature thermal decomposition of the complex resulted in magnesium oxide as the end product. Hence, this complex may be used as a precursor to fine magnesium oxide particles due to the low temperature of decomposition [40].

Supplementary material

Crystallographic data for structural analysis reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC number 1032143. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail:deposit@ccdc.cam.ac.uk).

References

1. Kobayashi S, Wakabayashi T. Scandium trisdodecylsulfate (STDS). A new type of lewis acid that forms stable dispersion systems with organic substrates in water and accelerates aldol reactions much faster in water than in organic solvents. Tetrahedron Lett. 1998;39:5389–92.
2. Zhou JS, Cui J, Wang L, Ng SW. Reversible and selective amine interactions of $[Cd(\mu_2\text{-}N, O\text{-}p\text{-}NH_2C_6H_4SO_3)_2(H_2O)_2]n$. Dalton Trans. 2004;9:1493–7.
3. Husgen NS, Luinstra GA, Schaper F, Schmidt K. Variation in the mode of coordination of aryl sulfonates to zirconocene in the solid state. Inorg Chem. 1998;37:3471–4.
4. Mller M, Hermes S, Khler K, van den Berg MWE, Muhler M, Fischer RA. Loading of MOF-5 with Cu and ZnO nanoparticles by gas-phase infiltration with organometallic precursors: properties of Cu/ZnO@MOF-5 as catalyst for methanol synthesis. Chem Mater. 2008;20:4576–87.
5. Perles J, Iglesias M, Martín-Luengo M-A, Monge MA, Ruiz-Valero C, Snejko N. Metal-organic scandium framework: useful material for hydrogen storage and catalysis. Chem Mater. 2005;17:5837–42.
6. Alaerts L, Seguin E, Poelman H, Thibault-Stazyk F, Jacobs PA, De Vos DE. Probing the Lewis acidity and catalytic activity of the metal–organic framework $[Cu_3(btc)_2]$ (BTC = Benzene-1,3,5-tricarboxylate). Chem Eur J. 2006;12:7353–63.
7. Clearfield A. Metal phosphonate chemistry. In: Karlin KD, editor. Progress in inorganic chemistry. New York: Wiley; 1998. p. 371–510.
8. Maeda K. Metal phosphonate open-framework materials. Micro Meso Mater. 2004;73:47–55.
9. Mao J-G. Structures and luminescent properties of lanthanide phosphonates. Coord Chem Rev. 2007;251:1493–520.
10. Distlern A, Sevov SC. Synthesis and characterization of $Co_3(\text{-}O_2CCH_2CH_2PO_3)_2\cdot6H_2O$, a metal carboxylate–phosphonate with a framework structure. Chem Commun. 1998;9:959–60.
11. Rabu P, Janvier P, Bujoli B. Magnetic properties of a new 3D-cobalt phosphonate: $CO_3(O_3PC_2H_4CO_2)_2$. J Mater Chem. 1999;9:1323–6.
12. Serpaggi F, Ferey G. Hybrid organic-inorganic frameworks (MIL-n). Hydrothermal synthesis of a series of pillared lanthanide carboxyethylphosphonates and X-ray powder ab initio structure determination of MIL-19, $Pr[O_3P(CH_2)_2CO_2]$. Inorg Chem. 1999;38:4741–4.
13. Zhu J, Bu X, Feng P, Stucky GD. An open-framework material with dangling organic functional groups in 24-ring channels. J Am Chem Soc. 2000;122:11563–4.
14. Stock N, Frey SA, Stucky GD, Cheetham AK. Synthesis and characterization of two manganese phosphonocarboxylates: $Mn_3(O_3PCH_2COO)_2$ and $Mn_3(O_3PCH_2CH_2COO)_2$. J Chem Soc Dalton Trans. 2000;23:4292–6.
15. Sanselme M, Riou-Cavellec M, Greneche JM, Ferey G. Hydrothermal synthesis, structure, and magnetic properties of a layered Fe(III) carboxymethylphosphonate: $[Fe(H_2O)(O_3P\text{–}CH_2\text{–}CO_2)]$ or MIL-49. J Solid State Chem. 2002;164:354–60.
16. Hix GB, Turner A, Kariuki BM, Termayne M, MacLean EJ. Strategies for the synthesis of porous metal phosphonate materials. J Mater Chem. 2002;12:3220–7.
17. Zhang X-M, Fang RQ, Wu HS. Extended water tapes of cyclic hexamers encapsulated in the channels of a metal phosphonocarboxylate network. Cryst Growth Des. 2005;5:1335–7.
18. Hou J-J. Zhang X–M. Structures and magnetic properties of a series of metal phosphonoacetates synthesized from in situ hydrolysis of triethyl phosphonoacetate. Cryst Growth Des. 2006;6:1445–52.
19. Zhang Y-Y, Zeng MH, Qi Y, Sang SY, Liu ZM. Honeycomb-like layered cobalt(II) phosphonate with $[O_2CCH(OH)PO_3]^{3-}$ as ligand: hydrothermal synthesis, crystal structure, and magnetic properties. Inorg Chem Commun. 2007;10:33–6.
20. Sun Z-M, Mao JG, Sun YQ, Zeng HY, Clearfield A. Synthesis, characterization, and crystal structures of three new divalent metal carboxylate-sulfonates with a layered and one-dimensional structure. Inorg Chem. 2004;43:336–41.
21. Okude K, Ichida H, Miyamoto TK, Sasaki Y. Absolute structure of di-μ-sulfoacetato-bis{[(1R,2R)-1,2-diaminocyclohexane]platinum(II)} trihydrate. Acta Cryst. 1989;C45:949–51.
22. Miyamoto TK, Ichida H. Syntheses, crystal structures, and antitumor activities of dinuclear platinum(II) complexes, di-μ-sulfoacetato-bis[(diamine)platinum(II)] trihydrate. Bull Chem Soc Jpn. 1991;64:1835–9.
23. Premkumar T, Govindarajan S, Pan W-P. Preparation, spectral and thermal studies of pyrazinecarboxylic acids and their hydrazinium salts. Proc Indian Acad Sci (Chem Sci). 2003;115:103–11.
24. Yasodhai S, Govindarajan S. Preparation and thermal behaviour of some hydrazinium dicarboxylates. Thermochim Acta. 1999;338:113–23.
25. Kuppusamy K, Sivasankar BN, Govindarajan S. Preparation, characterisation and thermal properties of some new hydrazinium carboxylates. Thermochim Acta. 1995;259:251–62.
26. Vairam S, Govindarajan S. New hydrazinium salts of benzene tricarboxylic and tetracarboxylic acids—preparation and their thermal studies. Thermochim Acta. 2004;414:263–70.
27. Premkumar T, Govindarajan S. Thermoanalytical and spectral properties of new rare-earth metal 2-pyrazinecarboxylate hydrates. J Therm Anal Calorim. 2005;79:685–9.
28. Premkumar T, Govindarajan S, Xie R, Pan W-P. Preparation and thermal behaviour of transition metal complexes of 4, 5-imidazoledicarboxylic acid. J Therm Anal Calorim. 2003;74:325–33.
29. Premkumar T, Govindarajan S. Divalent transition metal complexes of 3, 5-pyrazoledicarboxylate. J Therm Anal Calorim. 2006;84:395–9.

30. Premkumar T, Govindarajan S. Transition metal complexes of pyrazinecarboxylic acids with neutral hydrazine as a ligand. J Therm Anal Calorim. 2005;79:115–21.

31. Premkumar T, Govindarajan S. The chemistry of hydrazine derivatives—thermal behavior and characterisation of hydrazinium salts and metal hydrazine complexes of 4, 5-imidazoledicarboxylic acid. Thermochim Acta. 2002;386:35–42.

32. Premkumar T, Govindarajan S. Synthesis and spectroscopic, thermal, and XRD studies on trivalent lighter rare-earth complexes of 2,3-pyrazinedicarboxylate with hydrazinium cation. Inorg Chem Commun. 2003;6:1385–9.

33. Premkumar T, Govindarajan S, Coles AE, Wight CA. Thermal decomposition kinetics of hydrazinium cerium 2,3-pyrazinedicarboxylate hydrate: a new precursor for CeO_2. J Phys Chem B. 2005;109:6126–9.

34. Premkumar T, Govindarajan S, Rath NP, Manivannan V. New nine and ten coordinated complexes of lanthanides with bidentate 2-pyrazinecarboxylate containing hydrazinium cation. Inorg Chim Acta. 2009;362:2941–6.

35. Vairam S, Premkumar T, Govindarajan S. Preparation and thermal behaviour of divalent transition metal complexes of pyromellitic acid with hydrazine. J Therm Anal Calorim. 2010;101:979–85.

36. Premkumar T, Govindarajan S. Thermoanalytical and spectroscopic studies on hydrazinium lighter lanthanide complexes of 2-pyrazinecarboxylic acid. J Therm Anal Calorim. 2010;100:725–32.

37. Socrates G. Infrared characteristic group frequency. Bristol: John Wiley; 1980.

38. Mehran Rezaei M, Khajenoori M, Nematollahi B. Synthesis of high surface area nanocrystalline MgO by pluronic P123 triblock copolymer surfactant. Powder Tech. 2011;205:112–6.

39. Mohandes F, Davar F, Salavati-Niasari M. Magnesium oxide nanocrystals via thermal decomposition of magnesium oxalate. J Phys Chem Solids. 2010;71:1623–8.

40. Peia L-Z, Yin W-Y, Wang J-F, Chen J, Fan C-G, Zhang Q-F. Low temperature synthesis of magnesium oxide and spinel powders by a sol-gel process. Mater Res. 2010;13:339–43.