

Synthesis, structure and thermodynamics of supermolecular compound $[\text{Ni}_3(\text{Hdatrz})_6(\text{sca})_2(\text{H}_2\text{O})_4]\text{sca}\cdot 11\text{H}_2\text{O}$ (Hdatrz = 3,5-diamino-1,2,4-triazole, H_2sca = succinic acid)

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Abstract A new supramolecular compound $[\text{Ni}_3(\text{Hdatrz})_6(\text{sca})_2(\text{H}_2\text{O})_4]\text{sca}\cdot 11\text{H}_2\text{O}$ (Hdatrz = 3,5-diamino-1,2,4-triazole, H_2sca = succinic acid) was synthesized and characterized by elemental analysis, single crystal X-ray diffraction and thermogravimetric analysis. X-ray structural analysis reveals that the crystal is triclinic, space group $P-1$ with lattice parameters $a = 10.192(2)$ Å, $b = 11.671(2)$ Å, $c = 13.600(3)$ Å, $\beta = 68.086(3)^\circ$, $Z = 1$, $D_c = 1.689$ g/cm⁻³, $F(000) = 728$. The enthalpy change of the reaction of formation in water was determined by an RD496–CK2000 microcalorimeter at 25 °C with the value of -23.71 ± 0.023 kJ mol⁻¹. In addition, the thermodynamics of the reaction of formation in water for the compound was investigated by changing the temperature of the reaction and the fundamental parameters k , E , n , ΔS_{\neq}^θ , ΔH_{\neq}^θ and ΔG_{\neq}^θ were obtained.

Keywords Crystal structure · 3,5-Diamino-1,2,4-triazole · Succinic acid · Enthalpy change · Thermodynamic and thermokinetic parameters

Introduction

The design and synthesis of metal–organic framework structures have been extensively studied owing to the potential discovery of novel functional materials to be applied in the areas of absorption, catalysis, optics sensors,

magnetism and molecular recognition [1–9]. The generation of supramolecular frameworks rests on the coordination geometry of metal ion, structural characteristics of organic ligand, solvent system and counter ion [10–12]. The most useful strategy to construct such supramolecular frameworks is to employ appropriate organic linker capable of binding metal centers through direct bond formation. 1,2,4-Triazole and its derivatives are very interesting polydentate building blocks because they combine the coordination geometry of both pyrazoles and imidazoles with regard to the arrangement of their three heteroatoms and exhibit an extensively documented ability to bridge metal ions to afford polynuclear clusters [13]. We are currently interested in the 1,2,4-triazole and its derivatives, and carboxylate ligand as mixed ligand for the syntheses of polymeric compounds with transition metals [14].

Herein, we choose 3,5-diamino-1,2,4-triazole and succinic acid for the synthesis of compound $[\text{Ni}_3(\text{Hdatrz})_6(\text{sca})_2(\text{H}_2\text{O})_4]\text{sca}\cdot 11\text{H}_2\text{O}$. The X-ray structure analysis reveals the bonding mode of two ligands with Ni^{2+} . TG-DTG of the investigated compound is discussed. The enthalpy change of the reaction of formation in water at 25 °C is determined. The thermodynamics of the reaction of formation in water at different temperatures are investigated, and fundamental parameters are obtained on the basis of reaction thermodynamic and thermokinetic equations.

Experimental

Materials and measurements

All reagents used for the synthesis were purchased from commercial sources and used without further purification.

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Table 1 Crystal data and structure refinement parameters for the compound

Empirical formula	C ₂₄ H ₇₄ N ₃₀ Ni ₃ O ₂₇
Formula weight	1391.26
Crystal system	Triclinic
Space group	<i>P</i> – 1
<i>a</i> (Å)	10.192(2)
<i>b</i> (Å)	11.671(2)
<i>c</i> (Å)	13.600(3)
α (°)	69.154(5)
β (°)	68.086(3)
γ (°)	71.112(4)
<i>V</i> (Å ³)	1368.2(5)
<i>Z</i>	1
<i>F</i> (000)	728
<i>D</i> _{calc.} (g cm ⁻³)	1.689
μ (mm ⁻¹)	1.133
Reflections collected	6,901
<i>T</i> _{max} / <i>T</i> _{min}	0.8395/0.7275
Data/restraint/param	4763/17/406
Goodness-of-fit on <i>F</i> ²	1.008
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0497, <i>wR</i> 2 = 0.1329
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0808, <i>wR</i> 2 = 0.1619
Largest peak and hole (e Å ⁻³)	0.633 and -0.564

C, H and N analyses were carried out using an instrument of Vario EL III CHNOS of Germany. Infrared (IR) spectra drawn at regular intervals were recorded on a Bruker FTIR instrument as KBr pellets. The TG-DTG analysis was conducted on a P. E. 2100 company thermal analyzer in a static air atmosphere from room temperature to 600 °C. ICP-AES experiment was carried out on a T. E. IRIS advantage inductively coupled plasma atomic emission spectrophotometer. The calorimetric experiments were performed with an RD496-CK2000 microcalorimeter (Southwest Institute of Electron Engineering, China) [15]. The calorimetric constant at 25.15 °C was determined by the Joule effect before experiment, which was $63.901 \pm 0.030 \mu\text{V mW}^{-1}$. The enthalpy of dissolution of KCl (spectral purity) in deionized water was measured to be $17.246 \pm 0.004 \text{ kJ mol}^{-1}$, which was in good agreement with the value of $17.241 \pm 0.018 \text{ kJ mol}^{-1}$ from reference [16].

The single crystal X-ray experiment was performed on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) using ω and φ scan mode. The single-crystal structure of compound was solved by direct methods and refined with full-matrix least-squares refinements based on *F*² using SHELXS 97 and SHELXL 97 [17]. All non-H atoms were located using subsequent Fourier-difference methods. In all cases hydrogen

atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms. Other details of crystal data, data collection parameters and refinement statistics are given in Table 1.

Synthesis of compound

NiCl₂·6H₂O (0.1 mmol, 0.024 g), Hdatrz (0.2 mmol, 0.020 g) and H₂sca (0.1 mmol, 0.012 g) were dissolved in 8 mL distilled H₂O, respectively, and the water solution of NiCl₂·6H₂O was added slowly to the mixture solution of the two ligands with continuous stirring. The resultant mixture was filtered and the solution was kept undisturbed at room temperature for 3 days. Light green single crystals suitable for X-ray analysis were obtained. Yield: 41% (based on metal nickel). IR (KBr, cm⁻¹) 3425(s), 1622(s), 1588(s), 1448(s) and 1340(s). Analysis: calculated C₂₄H₇₄N₃₀Ni₃O₂₇ mass (%): C 20.72, H 5.36, N 30.21. Found: C 20.68, H 5.30, N 30.29.

Results and discussion

Crystal structure of compound

The X-ray structure analyses reveal that the crystals are triclinic and the compound consists of one linear trinuclear cation, one discrete sca²⁻ anion and eleven lattice water molecules (Fig. 1). In the trinuclear cation, three nickel ions are bridged by six neutral Hdatrz ligands. The central nickel ion is located at the inversion center, exhibits a distorted octahedron coordination geometry afforded by six nitrogen atoms from six Hdatrz ligands. The terminal nickel ions are bonded to three nitrogen atoms from three bridging Hdatrz ligands, two oxygen atoms from two coordination water molecules, and one oxygen atom from one sca ligand,

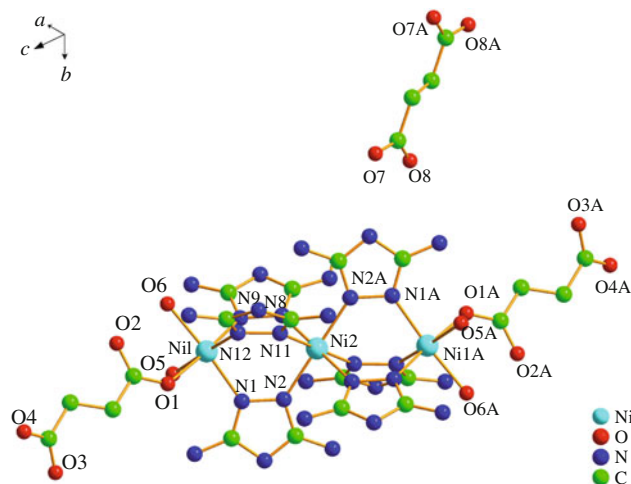


Fig. 1 Molecular structure for the compound, uncoordinated water molecules and H atoms are omitted for clarity

Table 2 Selected bond lengths (Å) and bond angles (°) for the compound

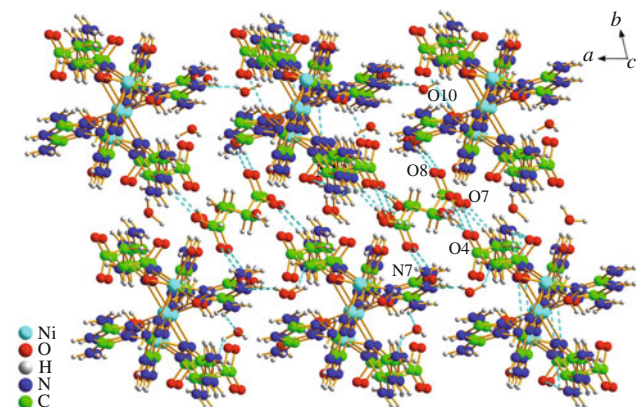
Ni(1)–N(12)	2.066(5)
Ni(1)–N(9)	2.076(4)
Ni(1)–O(5)	2.105(4)
Ni(2)–N(2)	2.082(4)
Ni(2)–N(11)	2.134(4)
N(12)–Ni(1)–N(1)	91.14(2)
N(1)–Ni(1)–N(9)	94.64(2)
N(1)–Ni(1)–O(5)	175.67(2)
O(6)–Ni(1)–O(5)	88.13(2)
N(2)–Ni(2)–N(8)	91.74(2)
N(8)–Ni(2)–N(11)	91.65(2)
Ni(1)–N(1)	2.070(4)
Ni(1)–O(6)	2.081(4)
Ni(1)–O(1)	2.117(4)
Ni(2)–N(8)	2.092(4)
N(12)–Ni(1)–N(9)	94.09(2)
N(12)–Ni(1)–O(6)	93.19(2)
N(9)–Ni(1)–O(5)	90.10(2)
O(6)–Ni(1)–O(1)	89.03(2)
O(5)–Ni(1)–O(1)	86.03(2)
N(2)–Ni(2)–N(11)	91.23(2)

respectively, also form distorted octahedron geometry. Related bond distances and bond angles are given in Table 2.

As shown in Fig. 2, the compound is further extended into 3D supermolecular networks through large amounts of hydrogen bonding interactions (Table 3) between the crystal waters, coordinated waters, nitrogen atoms of the Hdartz ligands and oxygen atoms of discrete sca^{2-} anions.

Thermogravimetric analysis

Thermogravimetric analysis (TG-DTG) for the compound is performed from room temperature to 600 °C at a heating

**Fig. 2** 3D supermolecular networks for the title compound along *c* axis**Table 3** Hydrogen bonding interactions in the compound

D–H...A	H...A/ Å	D...A/ Å	D–H...A/ Å	D–H...A/ ^o
O(5)–H(5WB)...O(14)	0.85	1.94	2.715(7)	153.9
O(9)–H(9C)...N(3)	0.85	2.66	3.341(8)	137.8
O(10)–H(10A)...O(1)	0.85	2.05	2.834(7)	153.4
N(7)–H(7A)...O(14)	0.86	2.41	3.121(9)	140.7
N(15)–H(15A)...O(2)	0.86	2.25	3.102(7)	173.9
N(5)–H(5B)...O(8)	0.86	2.33	3.010(7)	136.0
N(10)–H(10)...O(3)#3	0.86	1.90	2.741(6)	164.2
N(13)–H(13)...O(7)#4	0.86	1.94	2.791(6)	172.0
O(11)–H(11D)...O(4)#5	0.92	2.51	3.039(11)	117.0
O(12)–H(12A)...O(7)#6	0.85	2.11	2.873(8)	151.1
O(14)– H(14D)...O(10)#7	0.85	2.40	2.937(8)	121.8
O(10)–H(10B)...N(6)#1	0.85	2.70	3.108(7)	110.9
O(10)– H(10B)...O(14)#8	0.85	2.18	2.937(8)	149.0
O(13)– H(13B)...O(12)#9	0.85	2.01	2.747(8)	145.1
O(13)– H(13A)...O(4)#10	0.85	2.15	2.948(11)	157.4
N(7)– H(7B)...N(14)#7	0.86	2.23	3.081(7)	170.9
N(6)–H(6A)...N(2)#2	0.86	2.57	3.086(7)	119.6
N(15)– H(15B)...O(2)#10	0.86	2.11	2.874(6)	147.4

Symmetry transformations: #1 $-x + 1, -y + 1, -z + 1$; #2 $-x + 2, -y, -z$; #3 $x - 1, y, z + 1$; #4 $x, y + 1, z$; #5 $-x + 1, -y + 1, -z$; #6 $-x + 1, -y, -z + 1$; #7 $x - 1, y, z$; #8 $x + 1, y, z$; #9 $-x, -y + 1, -z + 1$; #10 $-x + 1, -y + 2, -z$

rate of 10 °C min⁻¹ under a static air atmosphere, as shown in Fig. 3.

The decomposition process of the compound can be divided into four steps. The first step in the range of

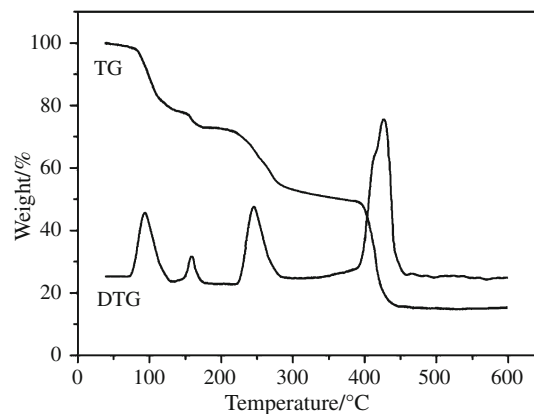
**Fig. 3** TG-DTG curves of the compound at 10 °C min⁻¹

Table 4 Thermokinetic data of the reaction of formation in water

25 °C			30 °C			35 °C			40 °C		
<i>t/s</i>	H_t/H_0	$10^3 dH_t / (dt)^{-1} / J s^{-1}$	<i>t/s</i>	H_t/H_0	$10^3 dH_t / (dt)^{-1} / J s^{-1}$	<i>t/s</i>	H_t/H_0	$10^3 dH_t / (dt)^{-1} / J s^{-1}$	<i>t/s</i>	H_t/H_0	$10^3 dH_t / (dt)^{-1} / J s^{-1}$
225	0.3630	17.034	225	0.4188	16.063	180	0.2757	22.369	240	0.4225	20.1140
240	0.3895	16.371	240	0.4469	15.378	195	0.3025	21.562	255	0.4501	19.167
255	0.4154	15.676	255	0.4739	14.626	210	0.3286	20.713	270	0.4766	18.240
270	0.4406	15.002	270	0.4997	13.908	225	0.3538	19.936	285	0.5021	17.348
285	0.4648	14.509	285	0.5245	13.219	240	0.3783	19.185	300	0.5265	16.496
300	0.4882	13.722	300	0.5481	12.561	255	0.4019	18.459	315	0.5498	15.681
315	0.5107	13.121	315	0.5707	11.933	270	0.4247	17.759	330	0.5722	14.900
330	0.5323	12.543	330	0.5922	11.336	285	0.4466	17.083	345	0.5935	14.157
345	0.5530	11.988	345	0.6127	10.781	300	0.4678	16.444	360	0.6138	13.480
360	0.5728	11.426	360	0.6322	10.223	315	0.4882	15.803	375	0.6331	12.772
375	0.5917	10.950	375	0.6507	9.7075	330	0.5079	15.199	390	0.6515	12.130
390	0.6097	10.466	390	0.6683	9.2178	345	0.5267	14.619	405	0.6690	11.518
405	0.6270	10.003	405	0.6851	8.7520	360	0.5449	14.061	420	0.6856	10.939
420	0.6435	9.7196	420	0.7009	8.3116	375	0.5623	13.524	435	0.7014	10.379
435	0.6591	9.1415	435	0.7160	7.7965	390	0.5790	13.009	450	0.7163	9.8699
450	0.6741	8.7398	450	0.7303	7.4960	405	0.5951	12.516	465	0.7304	9.3769
465	0.6884	8.3570	465	0.7438	7.1192	420	0.6105	12.007	480	0.7438	8.9100
480	0.7020	7.9931	480	0.7566	6.7599	435	0.6253	11.584	495	0.7565	8.4675
495	0.7150	7.6434	495	0.7687	6.3943	450	0.6395	11.114	510	0.7685	8.0478
510	0.7274	7.3110	510	0.7802	6.1065	465	0.6532	10.726	525	0.7799	7.7957
525	0.7393	6.9943	525	0.7911	5.8045	480	0.6663	10.355	540	0.7907	7.2718
540	0.7505	6.7234	540	0.8014	5.4865	495	0.6789	10.014	555	0.8010	6.9156
555	0.7612	6.4052	555	0.8111	5.2480	510	0.6910	9.4662	570	0.8106	6.5788
570	0.7714	6.1311	570	0.8203	5.0556	525	0.7026	9.1386	585	0.8198	6.2616
585	0.7811	5.8396	585	0.8290	4.7663	540	0.7138	8.7934	600	0.8284	6.0094

Notes: $H_0 = 9.2114$ J (25 °C), 7.3147 J (30 °C), 7.1963 J (35 °C), 6.8806 J (40 °C). H_t is the total reaction enthalpy; H_t , the reaction heat in a certain time; $dH_t/(dt)^{-1}$, the exothermic rate at time t

70–140 °C is confirmed as the loss of uncoordinated water and discrete sca^{2-} anion with 22.55% (calculated value 22.62%). The second step from 150 to 180 °C is considered as the loss of coordinated water with 6.62% (calculated value 6.70%). The third and fourth steps from 220 to 450 °C are considered as the break of the sca and $Hdatz$ ligands, respectively, and then the compound is completely converted to NiO with the residual mass of 16.20%, which

is in good agreement with the calculated value 16.11%. The remainder NiO is evidenced by X-ray powder diffraction analysis.

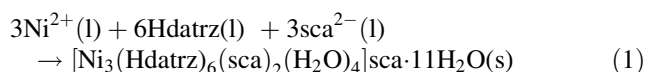
Enthalpy change of the reaction of formation in water

The reaction of formation in water of hexahydrate nickelous chloride with $Hdatz$ and H_2sca was shown as follows:

Table 5 Thermokinetic and thermodynamic parameters of the reaction of formation in water

$T/°C$	$k/10^3/s^{-1}$	n	r^n	$E/kJ mol^{-1}$	$\ln A/s^{-1}$	r^n	$\Delta G_{\neq}^0/kJ mol^{-1}$	$\Delta H_{\neq}^0/kJ mol^{-1}$	$\Delta S_{\neq}^0/J mol^{-1} S^{-1}$	r^n
25	1.106	0.9991	0.9998	17.15	0.1161	0.9990	89.847	14.62	-252.45	0.9989
30	1.240	0.9980	0.9999				91.108			
35	1.380	0.9979	0.9999				92.379			
40	1.543	1.0002	0.9999				93.631			

Notes: k the apparent reaction rate constant; A the pre-exponential constant; n the reaction order; r^n linear correlation coefficient; E apparent activation energy; ΔG_{\neq}^0 activation Gibbs free energy; ΔH_{\neq}^0 activation enthalpy; ΔS_{\neq}^0 activation entropy



The crude products of the reaction from the calorimetric experiments were collected and separated by the centrifugal effect. The solid crude products were purified and identified as being the same product as that obtained in the direct synthesis. The concentration of Ni^{2+} retained in the centrifugal liquid were determined to be $6 \times 10^{-3} \mu\text{g mL}^{-1}$ by the ICP-AES experiment, indicating that the starting reactants have been transformed fully to the title product. Within the range of the experimental temperature, the complexation reaction was exothermic. The concentrations of the Ni^{2+} , Hdatrz and H_2sca were respectively, 0.2000, 0.0600 and 0.0300 mol L^{-1} . The consumption volumes were 0.30, 2.00 and 2.00 mL, respectively. For reaction 1, Q was measured for six times at 25 °C and the values are -1425.8 , -1420.9 , -1421.0 , -1427.2 , -1421.9 and -1418.4 mJ, respectively. The enthalpy change of reaction, $\Delta_r H_m^0$, was calculated as $-23.71 \pm 0.023 \text{ kJ mol}^{-1}$. The value of $\Delta_r H_m^0$ is negative, indicating that it is favorable to the formation of product.

Thermodynamics of the reaction of formation in water

The solutions collected from each experiment were filtered and the precipitant dried. The analytical results identified that the compound had the composition $[\text{Ni}_3(\text{Hdatrz})_6(\text{sca})_2(\text{H}_2\text{O})_4]\text{sca} \cdot 11\text{H}_2\text{O}(\text{s})$, indicating that the reaction of formation in water is irreversible. The energy change of the reaction system depended on the reaction progression. The experimental data are presented in Table 4. Based on the thermodynamic equations [18], the thermodynamic and thermokinetic parameters of the reaction were obtained and are listed in Table 5.

In general, when the apparent activation energy of a reaction is less than 63 kJ mol^{-1} the reaction proceeds feasibly. Therefore, the reaction 1 is easy to proceed.

Conclusions

In summary, we have prepared successfully the title compound $[\text{Ni}_3(\text{Hdatrz})_6(\text{sca})_2(\text{H}_2\text{O})_4]\text{sca} \cdot 11\text{H}_2\text{O}$. X-ray diffraction analyses indicated that each Ni(II) was six-coordinated in distorted octahedron geometry and the compound was extended into 3D supermolecular networks constructed by large amounts of hydrogen bonding interactions. The compound was thermodecomposed in four steps and finally converted to NiO. The enthalpy change of the reaction of formation in water at 25 °C was obtained with the value of $-23.71 \pm 0.023 \text{ kJ mol}^{-1}$. Based on

thermokinetic data of the reaction of formation in water at different temperatures, the thermodynamic and thermokinetic parameters of the reaction were obtained.

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References

- Biradha K, Su CY, Vittal JJ. Recent developments in crystal engineering. *Cryst Growth Des.* 2011;11:875–86.
- Czylkowska A, Czakis-Sulikowska D, Kaczmarek A, Markiewicz M. Thermal behavior and other properties of Pr(III), Sm(III), Eu(III), Gd(III), Tb(III) complexes with 4,4'-bipyridine and trichloroacetates. *J Therm Anal Calorim.* 2011;105:331–9.
- Zhang QC, Liu Y, Bu XH, Wu T, Feng PY. A rare (3, 4)-connected chalcogenide superlattice and its photoelectric effect. *Angew Chem Int Ed.* 2008;47:113–7.
- Wang WG, Zhou AJ, Zhang WX, Tong ML, Chen XM, Nakano M, Beedle CC, Hendrickson DN. Giant heterometallic $\text{Cu}_{17}\text{Mn}_{28}$ cluster with Td symmetry and high-spin ground state. *J Am Chem Soc.* 2007;129:1014–5.
- Li XY, Wu YQ, Gu DH, Gan FX. Synthesis, spectral and thermal properties of some transition metal(II) complexes with a novel ligand derived from thiobarbituric acid. *J Therm Anal Calorim.* 2009;98:387–94.
- Xue BD, Yang Q, Chen SP, Gao SL. Synthesis, crystal structure, and thermodynamics of a high-nitrogen copper complex with *N,N*-bis-(1(2)H-tetrazol-5-yl) amine. *J Therm Anal Calorim.* 2010;101:997–1002.
- Bhattacharjee A, Roy D, Roy M. Thermal degradation of a molecular magnetic material: $\{\text{N}(\text{n-C}_4\text{H}_9)_4[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\} \infty$. *J Therm Anal Calorim.* 2011. doi:10.1007/s10973-011-1829-6.
- Mereacre V, Lan YH, Clerac R, Ako AM, Hewitt IJ, Werndorfer W, Buth G, Anson CE, Powell AK. Family of $\text{Mn}^{\text{III}}\text{Ln}_2(\mu_4\text{-O})$ compounds: syntheses, structures, and magnetic properties. *Inorg Chem.* 2010;49:5293–402.
- Wei WX, Cui BB, Jiang XH, Lu LD. The catalytic effect of NiO on thermal decomposition of nitrocellulose. *J Therm Anal Calorim.* 2010;102:863–6.
- Robson R, Abrahams BF, Batten SR, Gable RW, Hoskins BF, Liu J. In supramolecular architecture. Washington DC: ACS Publications; 1992. p. 256–262.
- Tong ML, Hu S, Wang J, Kitagawa S. Supramolecular isomerism in cadmium hydroxide phases. Temperature-dependent synthesis and structure of photoluminescent coordination polymers of α - and β - $\text{Cd}_2(\text{OH})_2(2, 4\text{-pyda})$. *Cryst Growth Des.* 2005;3:837–9.
- Kasai K, Aoyagi M, Fujita M. Remarkable ability for induced-fit enclathration of organic molecules. *J Chem Am Soc.* 2000; 122:2140–1.
- Haasnoot JG. Mononuclear, oligonuclear and polynuclear metal derivatives as ligands. *Coord Chem Rev.* 2000;200–202:131–85.
- Yang Q, Chen SP, Gao SL. An unexpected 3D (6, 8)-connected metal–organic framework $\{[\text{Cu}_5(\text{trz})(\text{mal})_2(\text{fma})(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}\}$: synthesis, structure and catalytic thermodecomposition for ammonium perchlorate. *Inorg Chem Commun.* 2009;12:1224–6.
- Guan W, Xue WF, Chen SP, Fang DW, Huang Y, Gao SL. Enthalpy of dilution of aqueous $[\text{C}_4\text{mim}][\text{Gly}]$ at 298.15 K. *J Chem Eng Data.* 2009;54:2871–3.

16. Kilday MV. The enthalpy of solution of SRM 1665 (KCl). *J Res Natl Inst Stand.* 1980;85:467–81.
17. Sheldrick GM. SHELXS-97, program for X-ray crystal structure determination. Göttingen: Göttingen University; 1997.
18. Gao SL, Ji M, Chen SP, Hu RZ, Shi QZ. The thermokinetics of the formation reaction of cobalt histidine complex. *J Therm Anal Calorim.* 2001;66:423–9.