FULL PAPER

Dalton
www.rsc.org/dalton

Reversible and selective amine interactions of $[Cd(\mu_2\text{-}N,O\text{-}p\text{-}NH_2C_6H_4SO_3)_2(H_2O)_2]_n$†

Jin-Sen Zhou, Jiwen Cai,* Li Wang and Seik-Weng Ng
School of Chemistry & Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, P. R. China

Received 16th January 2004, Accepted 5th March 2004
First published as an Advance Article on the web 31st March 2004

$[Cd(\mu_2\text{-}N,O\text{-}p\text{-}NH_2C_6H_4SO_3)_2(H_2O)_2]_n$ (**1**) is a layered coordination compound. The solid–vapor reactions between crystalline **1** and a series of volatile amines were investigated and the corresponding amine adducts were characterized by EA, TGA, PXRD and IR. Among them, the $C_2H_5NH_2$ and $C_3H_7NH_2$ adducts, namely $[Cd(C_2H_5NH_2)_4(H_2O)_2](H_2NC_6H_4SO_3)_2$ (**3**) and $[Cd(C_3H_7NH_2)_4(O\text{-}p\text{-}H_2NC_6H_4SO_3)_2]\cdot C_3H_7NH_2$ (**4**), grew into single crystals *in situ* from the solid–vapor reaction processes and their crystal structures were characterized. In both cases, 4 mol equiv. of amine molecules coordinate to Cd(II) *via* replacing the $N,O\text{-}p\text{-}NH_2C_6H_4SO_3$ ligands or coordinated water molecules. The single-phase product suggests that the solid–vapor reaction between the metal sulfonate and volatile alkylamines could be used as a green process to synthesize monoamine-coordinated Cd(II) complexes without any solvent and routine separation. Finally, the substitution reaction is reversible at room conditions and selective for primary alkylamines.

Introduction

Reversible solid–gas or solid–vapor reactions of metal–organic compounds have attracted much attention recently due to their potential application as functional materials, such as chemical sensors for toxic gases or volatile organic compounds.[1–5] The guest up-taking capabilities of the metal–organic frameworks of interest are caused by vacant or expanded coordination sites of the metal centers,[2] also, by the accessible lattice space of the crystalline supramolecular frameworks.[4,5] Reversible solid–vapor substitution reaction occurring under mild conditions represents another unique category with only a few known examples.[1]

On the other hand, metal sulfonates are a class of compounds showing interesting functional properties[6] contributed by the flexible and soft interaction between the metal atom and the sulfonate groups. Côté and Shimizu have reviewed recent progress in this field.[7] Herein, as part of our systematic investigation into the solid state chemistry of metal sulfonates,[8,9] we report the reversible solid–vapor substitution reactions of a neutral polymeric compound $[Cd(\mu_2\text{-}N,O\text{-}p\text{-}NH_2C_6H_4SO_3)_2(H_2O)_2]_n$ (**1**) with volatile alkylamines with $C \leq 4$ at room conditions.

Results and discussion

Characterization of the amine adducts

The matrix compound **1** does not react with NH_3, $(C_2H_5)_2NH$, $PhNH_2$, pyridine, as well as CH_3OH, $CH_3COOC_2H_5$ and HCl, indicating that the reaction of **1** with primary amines is selective. The stoichiometry of the reaction product was established by elemental analyses and the amine adducts were further characterized by TGA, IR and PXRD. The matrix complex **1**, and $C_2H_5NH_2$ and $C_3H_7NH_2$ adducts **3** and **4** were also characterized by X-ray single crystal structural analyses. Since the $C_3H_7NH_2$ adduct releases amine molecules once it is removed from the reaction vessel, the chemical formula derived from EA and TGA, which is $Cd(H_2NC_6H_4SO_3)_2(C_3H_7NH_2)_{2.5}$ (**4′**), is different from what we obtained from X-ray single crystal structural analysis, which is $[Cd(C_3H_7NH_2)_4(H_2NC_6H_4SO_3)_2]\cdot C_3H_7NH_2$ (**4**). The EA results reveal that **1** can quantitatively uptake primary alkylamines. In particular, **1** took up to 4 equiv. of CH_3NH_2 and $C_2H_5NH_2$ and 5 equiv. of $C_3H_7NH_2$. It is noted that there is a sharp decrease in the molar amount of amines adducted to **1** from 5 mol equiv. for $C_3H_7NH_2$ (**4**) to 0.5 mol equiv. for iso-$C_3H_7NH_2$ (**5**), and 0.5–1.5 mol equiv. for the $C_4H_9NH_2$ isomers (**6**–**8**).

All the amine adducts are crystalline materials, with moderate to strong reflection intensities, as shown in Fig. 1. TGA results, shown in Fig. 2, reveal that **2**–**4** release amine molecules below 150 °C, well before the decomposition of the framework around 350 °C. Complexes **5**–**8** release amine molecules in multiple steps, with the second batch of release followed by the decomposition of the framework. The TGA behaviour of the CH_3NH_2 adduct (**2**) is similar to those of both the $C_2H_5NH_2$ (**3**) and $C_3H_7NH_2$ (**4**) adducts, suggesting that the CH_3NH_2 adduct **2** could have a similar coordination structure as that of **3** and **4**, with 4 mol equiv. of CH_3NH_2 coordinated to Cd(II). Since the EA and TGA results match better with the formula of $[Cd(NH_2C_6H_4SO_3)(CH_3NH_2)_4]$, it is obvious that the coordinated water molecules have been replaced in the coordination sphere.

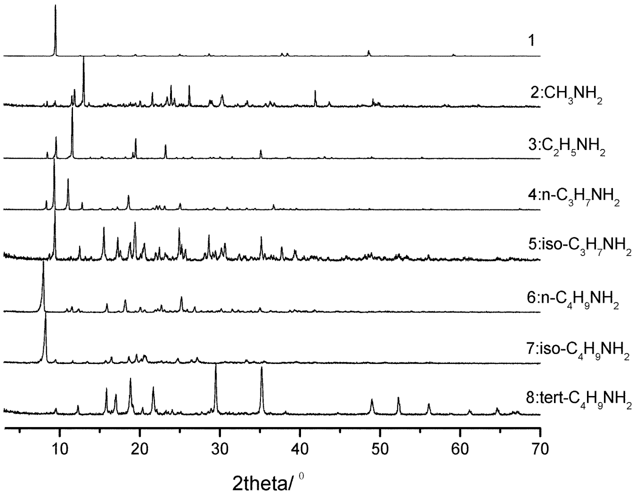


Fig. 1 PXRD of $[Cd(\mu_2\text{-}N,O\text{-}p\text{-}NH_2C_6H_4SO_3)_2(H_2O)_2]_n$ (**1**) and the amine adducts (**2**–**8**).

---

† Electronic supplementary information (ESI) available: Fig. S1: IR spectra of $[Cd(\mu_2\text{-}N,O\text{-}p\text{-}NH_2C_6H_4SO_3)_2(H_2O)_2]_n$ (**1**) and the amine adducts (**2**–**8**). Fig. S2: The reaction vessel containing the $C_3H_7NH_2$ adduct **4**, showing the wet crystals. Table S1: elemental analysis results. See http://www.rsc.org/suppdata/dt/b4/b400790p/

DOI: 10.1039/b400790p

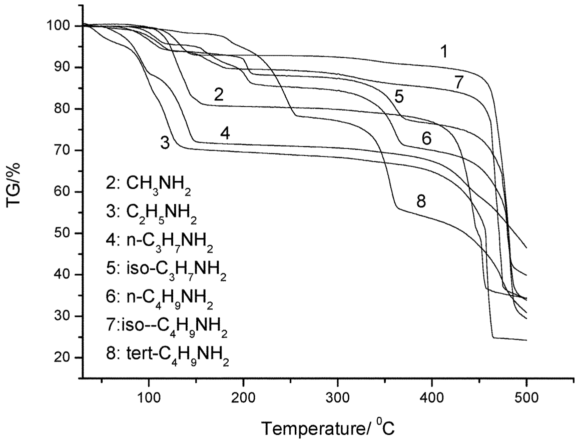


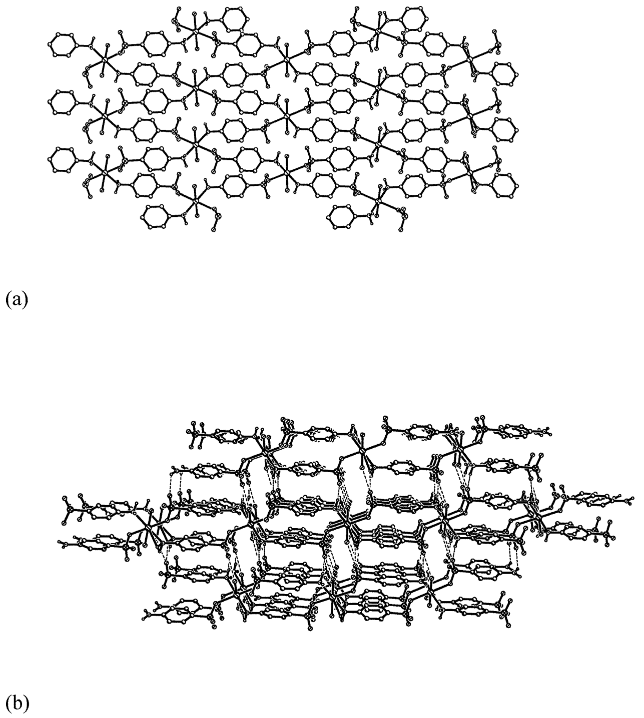
Fig. 2 TGA of $[Cd(\mu_2\text{-}N,O\text{-}p\text{-}NH_2C_6H_4SO_3)_2(H_2O)_2]_n$ (**1**) and the amine adducts (**2**–**8**).

The nature of the amine interactions with **1** is more complicated in the cases of iso-$C_3H_7NH_2$ and the $C_4H_9NH_2$ isomers (**5**–**8**). Nevertheless, the amines released at a much higher temperature than that of their corresponding boiling points, indicating that coordinative interactions are involved.

In the IR spectra of all the amine adducts, there are alkyl C–H stretching bands observed around 2900–3000 cm^{-1} contributed by the alkylamines, confirming the existence of the adducted amine molecules.

Structure of the matrix compound $[Cd(\mu_2\text{-}N,O\text{-}p\text{-}NH_2C_6H_4\text{-}SO_3)_2(H_2O)_2]_n$ (1)

The crystal structure of **1** is shown in Fig. 3. Its Co^{2+} and Zn^{2+} analogues have been reported and all three of them have similar coordination and crystal structures.[10] Cd(II) is coordinated by two $-NH_2$ and two $-SO_3$ groups from four different $NH_2C_6H_4SO_3^-$ ligands, and two water molecules in the axial positions, resulting in an octahedral coordination sphere. The p-$NH_2C_6H_4SO_3^-$ anions behave as μ_2 bridging ligands to produce a two-dimensional layered structure, as shown in Fig. 3(a). Inter-layered hydrogen bonds formed between the coordinated water molecules and the $-NH_2$ groups with the free $-SO_3^-$ oxygen atoms generate an extended 3-D structure, as shown in Fig. 3(b), which is very similar to that of $[Cd(1,5nds)(H_2O)_2]_n$ (1,5nds = 1,5-naphthalenedisulfonate).[9] TGA analysis shows that **1** is stable until 100 °C when the water molecules are released. As shown in Fig. 4, the dehydrated compound **1′** is also a crystalline material, in which the inter-layered distance shrinks from 9.37 Å in **1** to 8.77 Å in **1′**. Interestingly, **1′** is a stable phase at room conditions, as shown by the unchanged PXRD pattern after air exposure for 12 h. However, when **1′** is exposed to water moisture, it can absorb water and rearrange to **1**. Therefore, the dehydration process of **1** is reversible.


(a)

(b)

Fig. 3 The 2-D layered structure of $[Cd(\mu_2\text{-}N,O\text{-}p\text{-}NH_2C_6H_4SO_3)_2\text{-}(H_2O)_2]_n$ (1) (a), and its 3-D extended structure showing the inter-layered hydrogen bonds formed between the $-SO_3$ oxygen and both the water and $-NH_2$ groups.

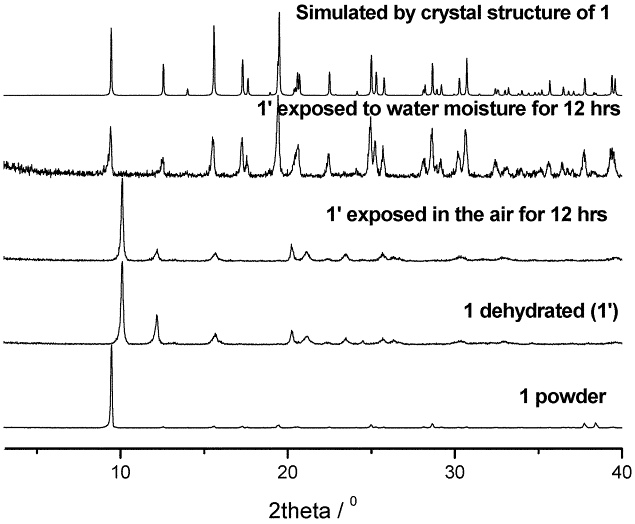


Fig. 4 PXRD showing the dehydration and hydration process of $[Cd(\mu_2\text{-}N,O\text{-}p\text{-}NH_2C_6H_4SO_3)_2(H_2O)_2]_n$ (1). Its dehydrated form is denoted as **1′**.

It is interesting to note that the title compound **1** has very similar layered structure as that observed in $[Cd(1,5nds)(H_2O)_2]_n$,[9] in which the Cd(II) is also coordinated octahedrally with two water molecules occupying the axial positions and the layers were connected by hydrogen bonds formed between the coordinated water molecules and the sulfonate oxygens. However, these two cadmium sulfonates show different reactivity toward NH_3 and secondary amines. **1** does not react with either NH_3 or the secondary amine $(C_2H_5)_2NH$. In contrast, $[Cd(1,5nds)(H_2O)_2]_n$ can uptake up to 3 mol equiv. of NH_3 and also react with secondary amines.[9]

Crystal structures of 3 and 4

In the case of $C_2H_5NH_2$ exposure, the powder matrix compound **1** became solidified, and then the volume expanded. Single crystals of $[Cd(C_2H_5NH_2)_4(H_2O)_2](H_2NC_6H_4SO_3)_2$ (**3**) suitable for X-ray analyses were found among the final powder crystalline product. Structural analysis shows that 4 equiv. of amine molecules substitute the p-$NH_2C_6H_4SO_3^-$ ligands from the Cd(II) coordination sphere, while the water molecules remained coordinated to the metal center, as shown in Fig. 5. The Cd–N distances are 2.334(2) and 2.3505(19) Å, while the bond length of Cd–OH_2 is 2.4629(17) Å.

When crystalline material **1** was exposed to $C_3H_7NH_2$ vapor, it became solidified, damp, and then crystalline material appeared which further grew into single crystals suitable for X-ray structural analyses. The crystal structure of $[Cd(C_3H_7\text{-}NH_2)_4(O\text{-}p\text{-}H_2NC_6H_4SO_3)_2]\cdot C_3H_7NH_2$ (**4**) is shown in Fig. 6(a). 4 equiv. of amine molecules replaced the two coordinated water molecules and $-NH_2$ groups of the two p-$NH_2C_6H_4SO_3^-$ ligands. The sulfonate group remained coordinated to Cd(II),

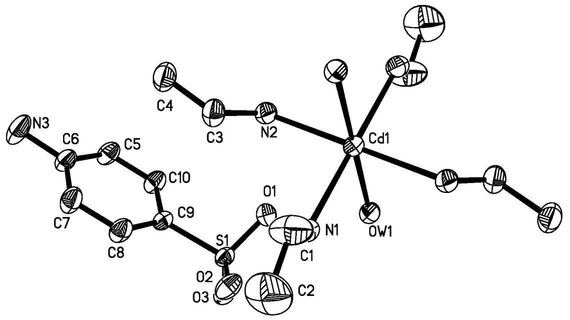


Fig. 5 Coordination structure of $[Cd(C_2H_5NH_2)_4(H_2O)_2](H_2NC_6H_4SO_3)_2$ (**3**).

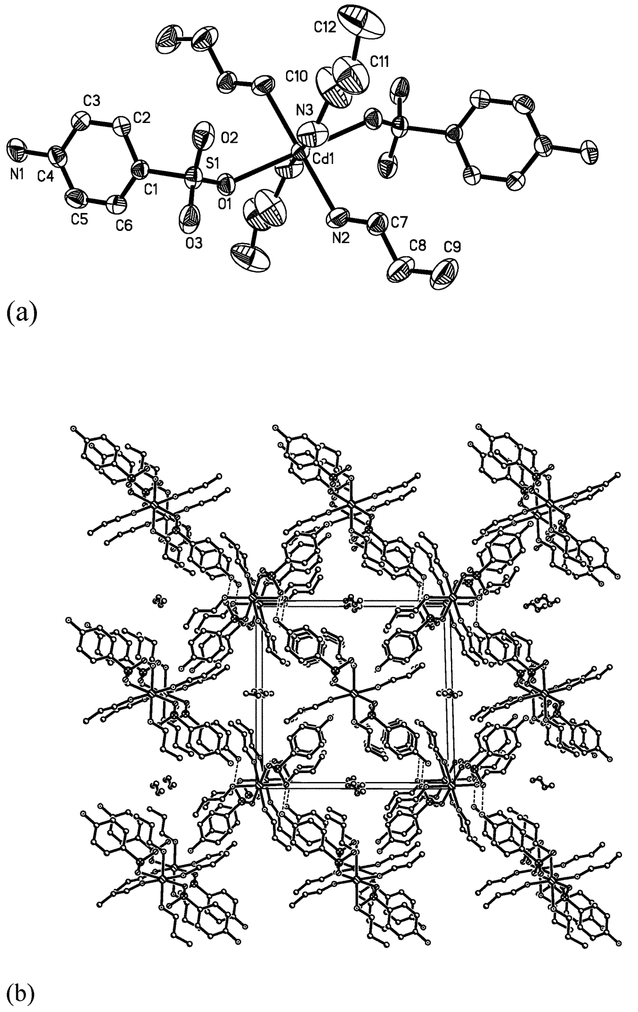


Fig. 6 Coordination structure of $[Cd(C_3H_7NH_2)_4(O\text{-}p\text{-}H_2NC_6H_4SO_3)_2]\cdot C_3H_7NH_2$ (**4**) (a) and its packing structure showing the included amine molecules in channels running along the *a* axis (b).

with the Cd–O distance expanded significantly from 2.294(2) Å in **1** to 2.474(4) and 2.453(4) Å in **4**. Interestingly, molecules packed along the crystallographic *a* axis form void spaces of 200 Å^3 per unit cell, which accommodates one free amine molecule, as shown in Fig. 6(b). In other words, **1** can take up to 5 equiv. of $C_3H_7NH_2$ and form crystalline **4**. Both the substitution and inclusion reactions occur during the reaction process. The calculated crystal density of compound **4** is 1.314 g cm^{-3}, which is significantly lower than that of the matrix compound **1** with a density of 2.033 g cm^{-3}. When an unprotected crystal of **4** was exposed to the air, it lost its diffraction intensity quickly.

It is noted that complex **1** shows a distinct reactivity towards $C_2H_5NH_2$ and $C_3H_7NH_2$. Four equiv. of $C_2H_5NH_2$ exclude the $p\text{-}NH_2C_6H_4SO_3^-$ ligands from the Cd(II) coordination sphere. However, this does not occur in the case of the $C_3H_7NH_2$ reaction, where the sulfonate groups of the $p\text{-}NH_2C_6H_4SO_3^-$ ligands still remain coordinated to Cd(II). Further experiments are required in order to decipher this behaviour, which could be caused by steric and electronic factors. On the other hand, based upon what we have documented about the readily modified coordination mode of sulfonate due to its weak coordination nature,[8] what is observed here is not unexpected.

When single crystals of **1** were used directly for amine uptake, the crystals fractured and became a white powder immediately. In the case of $C_2H_5NH_2$, as shown in Fig. 7, the PXRD simulated by the single crystal structure is very similar to the PXRD pattern of the sample obtained by grinding the polycrystalline material and single crystals of **3** together. The EA results also match the formula of the single crystal, indicating that the reaction is complete with **3** as the only phase. However, in the case of $C_3H_7NH_2$, since **4** released amine molecules rapidly when it was removed from the reaction vessel, characterization of the batch product **4** could not be conducted. Nevertheless, according to the consistency of the crystalline appearance, it can be tentatively assumed that the resulting complex consists of a uniform phase. Two single crystals selected from the same batch were submitted for X-ray analyses and showed very similar cell parameters.

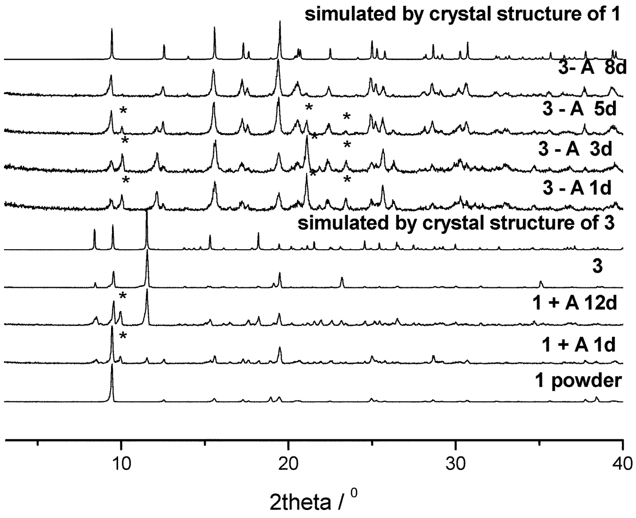


Fig. 7 PXRD tracking the reversible transformations between $[Cd(\mu_2\text{-}N,O\text{-}p\text{-}NH_2C_6H_4SO_3)_2(H_2O)_2]_n$ (**1**) and the $C_2H_5NH_2$ adduct $[Cd(C_2H_5NH_2)_4(H_2O)_2](H_2NC_6H_4SO_3)_2$ (**3**). A = $C_2H_5NH_2$ vapor. Reflections contributed by the third phase are marked by *.

It is remarkable that both **3** and **4** grew into single crystals *in situ* in the solid–vapor reactions. However, with the replaced water molecules and the amine deposited from the vapor as the potential solvent, it is not clear whether the transformation between the matrix compound **1** and its final amine adduct is a solid-to-solid transformation or localized dissolution of one phase with subsequent growth of another is involved.

As a closely related family, water-coordinated metal phosphonates also display interesting amine up-taking properties after dehydration and have attracted extensive investigations.[11,12] The amine intercalation process could be topotactic or imparted by a guest-directed phase transformation. However, in most cases, the solid-state structures of the resulting adducts formed *via* solid–vapor or solid–liquid reaction cannot be explored directly. The up-taking of guest molecules causes considerable stress and intermolecular reorganization in the metal–organic framework. With the loss of crystallinity, the characterization of the solid-state structures becomes quite challenging. One of the common approaches to overcome this problem is to grow single crystals of the targeted compound and compare the simulated PXRD pattern with that of the reaction product.[4] This method is only achievable when the targeted compound can be crystallized and the phases obtained

$$[Cd(\mu_2\text{-}N,O\text{-}p\text{-}NH_2C_6H_4SO_3)_2(H_2O)_2]_n \xrightleftharpoons[-C_2H_5NH_2]{C_2H_5NH_2} n[Cd(C_2H_5NH_2)_4(H_2O)_2](NH_2C_6H_4SO_3)_2$$

from the solid state reaction and from solution are the same. Therefore, our results reported herein, with the growth of single crystals *in situ* of a solid–vapor reaction process is rather unique, which made direct structural characterization possible.

Investigation into the intercalation process and its reversibility

PXRD recorded every 24 h showed that after $C_2H_5NH_2$ exposure for one day, reflections contributed by **3** appeared, together with reflections contributed by **1** and a third phase. After 2 weeks, both reflections contributed by **1** and the third phase disappeared, and **3** was the only phase obtained. As shown in Fig. 7, when **3** was exposed in the air for one day, reflections contributed by **3** almost disappeared, while those corresponding to **1** appeared, together with reflections contributed by the third phase observed during the **1** to **3** transformation process, as represented by reflections around 10.0, 21.0 and 23.4°. After 8 days, reflections contributed by the third phase also disappeared and the diffraction pattern became identical to that of **1** simulated by the single crystal structure. This observation indicates that the substitution reaction, including the breakdown and formation of four coordinative bonds, is completely reversible at room conditions. Moreover, the phase transformations between **1** and **3** involve a third phase associated with either **1** or **3**.

Similar amine-releasing processes at room temperature were observed in all the other complexes. In the case of both **2** and **4**, the phases obtained after losing all the amine molecules have to be exposed to moisture in order to form the phase identical to that of **1**. This observation is consistent with the fact that the two water molecules were substituted by the amine molecules and are not in the coordination sphere anymore, which is different from that observed in **3**. In order to accelerate the amine-releasing process, amine adducts **2**–**4** were heated to 150–200 °C to remove the amine molecules. As shown in Fig. 8, the phases generated after amine releasing of **3** and **4** are identical to that of **1′**. By contrast, the phase **1″** generated by **2** is different. However, after moisture exposure, **1″** rearranged back to **1**.

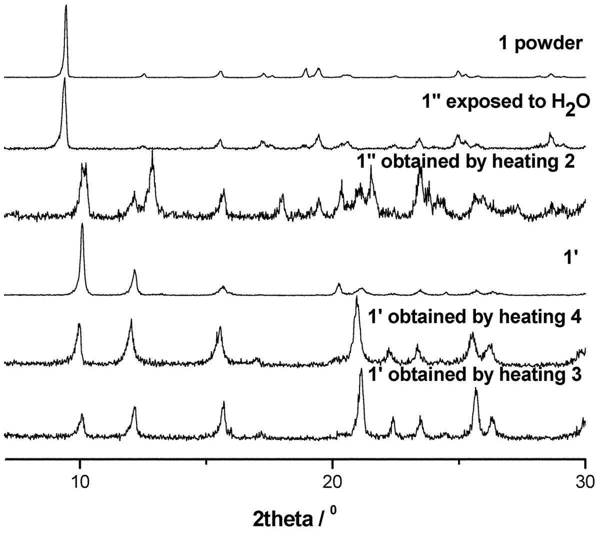


Fig. 8 PXRD showing that the phases obtained *via* heating the amine adducts at 150–200 °C are identical to that of dehydrated $[Cd(\mu_2\text{-}N,O\text{-}p\text{-}NH_2C_6H_4SO_3)_2(H_2O)_2]_n$ (**1′**) in the cases of $[Cd(C_2H_5NH_2)_4(H_2O)_2](H_2NC_6H_4SO_3)_2$ (**3**) and $[Cd(C_3H_7NH_2)_4(O\text{-}p\text{-}H_2NC_6H_4SO_3)_2]\cdot C_3H_7NH_2$ (**4**), or different from that of **1′** but can be converted back to **1** after moisture exposure.

Summary

We have presented the systematic investigation into the solid–vapor substitution reactions between the title compound **1** and a series of volatile primary amine molecules with C ≤ 4. The corresponding amine adducts were characterized. The results show that single phase monoamine coordinated Cd(II) complexes could be obtained *via* solid–vapor reaction between the metal sulfonate and amine vapor, without using any solvent and routine separation. Moreover, the substitution reaction process is reversible under mild conditions and selective for primary alkylamines, which could be regarded as an advantage to further explore the potential application of the stable crystalline material **1** as a chemical sensor or switch for volatile primary alkylamines. As far as we are aware, the fact that **3** and **4** were obtained as single crystals *in situ* from a solid–vapor substitution reaction has never been reported for a coordination compound.

The readily achieved transformations between **1** and its amine adducts could be contributed by the compatible coordination strength of the $-NH_2$ and $-SO_3^-$ groups of the $NH_2C_6H_4SO_3^-$ ligand, the $-NH_2$ group of the alkylamine and the water molecule. By nature, the reaction process of metal sulfonates with amine vapor could be understood as a solid-state substitution reaction driven by Lewis acid–base interactions. Primary experiments show that cadmium salts other than the sulfonates, such as $CdCl_2$ and $CdCO_3$, do not react with amine vapor under the same reaction condition investigated for **1** and $[Cd(1,5nds)(H_2O)_2]_n$,[9] indicating that the sulfonate group is critical to drive the amine intercalating process.

Experimental

Materials and methods

All materials were commercially available and used without further purification. Elemental analyses (C, H, N) were conducted by the Vario EL elemental analyzer. PXRD (Powder X-ray diffraction) was performed on a Rigaku D/Max-IIIA diffractometer operated using a 0.02° step scan from 3 to 70° in 2θ and 0.2 s preset time. Infrared spectra were obtained as KBr pellets on a Bruker EQUINOX 55 FTIR spectrometer. TG-IR (thermogravimetry-infrared) was carried out with a Netzsch TG-209 analyzer under flowing nitrogen.

Synthesis

$[Cd(\mu_2\text{-}p\text{-}N,O\text{-}NH_2C_6H_4SO_3)_2(H_2O)_2]_n$ (**1**): sulfanilic acid (17.319 g, 0.1 mol) was dissolved in distilled water (400 mL) at 343 K and cadmium acetate dihydrate (13.317 g, 0.05 mol) was added to the above solution. After stirring for 1 h and concentration, the white precipitate was collected as $[Cd(\mu_2\text{-}N,O\text{-}p\text{-}NH_2C_6H_4SO_3)_2(H_2O)_2]$, yield 59%. Single crystals suitable for diffraction data collection were obtained *via* slow evaporation of the saturated aqueous solution.

Solid–vapor reaction

Crystalline **1** and the amine liquid were placed in two different but connected vessels. The reaction process was monitored *via* the net weight gain. It took a few days to 2 weeks for the reaction process to be complete. The adducts were placed in an N_2 flow to remove the deposited amine and moisture on the crystalline surface before submission for characterization. All solid–vapor reactions were performed at room temperature. Single crystals of the $C_2H_5NH_2$ adduct **3** were found among the polycrystalline product. In the case of $C_3H_7NH_2$, all the adduct **4** grow into large and shiny crystals. For the reversibility study, the amine adduct was either exposed in the air and its PXRD was recorded every day, or heated at 150–200 °C for 2 h and its PXRD was recorded.

Table 1 Crystallographic data

Compound	1	3	4
Empirical formula	$C_{12}H_{16}CdN_2O_8S_2$	$C_{20}H_{44}CdN_6O_8S_2$	$C_{27}H_{57}CdN_7O_6S_2$
M_r	492.79	673.13	752.32
T/K	293(2)	293(2)	293(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	7.210(4)	10.680(3)	7.9686(9)
b/Å	5.962(3)	7.863(2)	15.4694(19)
c/Å	18.975(10)	18.906(6)	15.7489(19)
α/°	90	90	88.932(2)
β/°	99.336(9)	100.152(6)	88.548(2)
γ/°	90	90	78.565(2)
V/Å^3	804.9(8)	1562.8(8)	1902.0(4)
Z, D_c/g cm^{-3}	2, 2.033	2, 1.430	2, 1.314
μ/mm^{-1}	1.663	0.880	0.728
F(000)	492	700	792
Crystal size/mm	0.50 × 0.37 × 0.28	0.47 × 0.26 × 0.20	0.43 × 0.29 × 0.12
θ Range/°	3.57–27.03	2.81–29.87	2.59–25.00
Limiting indices, hkl	−8/9, −7/6, −22/24	−6/14, −10/9, −26/25	−9/9, −18/17, −18/18
Reflections collected	4696	10887	14060
Unique (R_{int})	1732 (0.0391)	4171 (0.0170)	6686 (0.0246)
Completeness (%)	98.2	92.7	99.5
Data/restraints/parameters	1732/0/118	4171/0/177	6686/12/371
Goodness-of-fit	1.195	1.032	1.020
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0278$	$R1 = 0.0301$	$R1 = 0.0458$
	$wR2 = 0.0735$	$wR2 = 0.0791$	$wR2 = 0.1178$

Complex **1** was also exposed to NH_3, vapors of $(C_2H_5)_2NH$, $PhNH_2$, pyridine, as well as CH_3OH, $CH_3COOC_2H_5$ and HCl. No weight gain was however observed and the PXRD of the matrix compound remained unchanged.

X-Ray crystallography

Single crystal X-ray data were collected on a Bruker SMART 1000 CCD diffractometer at room temperature. Absorption corrections were applied. The space groups were determined from systematic absences and confirmed by the results of refinement. The structures were solved using direct methods and all non-H atoms were refined with anisotropic displacement parameters.[13] All H atoms of the organic ligands were placed at idealized positions and refined as riding atoms. The crystallographic data were listed in Table 1. The single crystal of **4** was covered by wax and therefore protected from decomposition before it was submitted for data collection.

CCDC reference numbers 222142-222144.

See http://www.rsc.org/suppdata/dt/b4/b400790p/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We are thankful for the financial support from the National Natural Science Foundation of China (Grant Nos. 20271053 and 20131020).

References

1 L. H. Poppel, S. G. Bott and A. R. Barron, *J. Am. Chem. Soc.*, 2003, **125**, 11006; L. H. Poppel, S. G. Bott and A. R. Barron, *J. Chem. Soc., Dalton Trans.*, 2002, 3327.

2 M. Albrecht, M. Lutz, A. L. Spek and G. von Koten, *Nature*, 2000, **406**, 970; M. Albrecht, M. Lutz, A. M. M. Schreurs, E. T. H. Lutz, A. L. Spek and G. von Koten, *J. Chem. Soc., Dalton Trans.*, 2000, 3797; M. Albrecht and G. van Koten, *Angew. Chem., Int. Ed.*, 2001, **40**, 3750.

3 D. Braga, G. Cojazzi, D. Emilliani, L. Maini and F. Grepioni, *Chem. Commun.*, 2001, 2272; D. Braga, G. Cojazzi, D. Emilliani, L. Maini and F. Grepioni, *Organometallics*, 2002, **21**, 1315.

4 C. E. Buss, C. E. Anderson, M. K. Pomijie, C. M. Lutz, D. Britton and K. R. Mann, *J. Am. Chem. Soc.*, 1998, **120**, 7783; C. E. Buss and K. R. Mann, *J. Am. Chem. Soc.*, 2002, **124**, 1031; S. M. Drew, D. E. Janzen, C. E. Buss, D. I. MacEwan, K. M. Dublin and K. R. Mann, *J. Am. Chem. Soc.*, 2001, **123**, 8414.

5 M. Kato, A. Omura, A. Toshikawa, S. Kishi and Y. Sugimoto, *Angew. Chem., Int. Ed.*, 2002, **41**, 3183; E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, J. Pérez, A. Laguna, A. A. Mohamed and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, 2003, **125**, 2022.

6 S. K. Mäkinen, N. J. Melcer, M. Parvez and G. K. H. Shimizu, *Chem. Eur. J.*, 2001, **4**, 5176; A. P. Côté, M. J. Ferguson, K. A. Khan, G. D. Enright, A. D. Kulynych, S. A. Dalrymple and G. K. H. Shimizu, *Inorg. Chem.*, 2002, **41**, 287; A. P. Côté and G. K. H. Shimizu, *Chem. Commun.*, 2001, 251; G. K. H. Shimizu, G. D. Enright, C. I. Ratcliffe, G. S. Rego, J. L. Reid and J. A. Ripmeester, *Chem. Mater.*, 1998, **10**, 3282; S. A. Dalrymple and G. K. H. Shimizu, *Chem. Eur. J.*, 2002, **8**, 3010; J. O. Yu, A. P. Côté, G. D. Enright and G. K. H. Shimizu, *Inorg. Chem.*, 2001, **40**, 582; B. D. Chandler, A. P. Côté, D. T. Cramb, J. M. Hill and G. K. H. Shimizu, *Chem. Commun.*, 2002, 1900.

7 A. P. Côté and G. K. H. Shimizu, *Coord. Chem. Rev.*, 2003, **245**, 49.

8 C.-H. Chen, J. Cai, C.-Z. Liao, X.-L. Feng, X.-M. Chen and S.-W. Ng, *Inorg. Chem.*, 2002, **41**, 4967; J. Cai, C.-H. Chen, X.-L. Feng, C.-Z. Liao and X.-M. Chen, *J. Chem. Soc., Dalton Trans.*, 2001, 2370; J. Cai, C.-H. Chen, C.-Z. Liao, J.-H. Yao, X.-P. Hu and X.-M. Chen, *J. Chem. Soc., Dalton Trans.*, 2001, 1137; C. H. Chen, J. W. Cai, X. L. Feng and X. M. Chen, *J. Chem. Crystallogr.*, 2001, **31**, 271; J. W. Cai, C. H. Chen and J. S. Zhou, *Chin. J. Inorg. Chem.*, 2003, **19**, 81; J. W. Cai, C. H. Chen, C. Z. Liao, X. L. Feng and C. M. Chen, *Acta Crystallogr., Sect B*, 2001, **57**, 520.

9 J. Cai, J.-S. Zhou and M.-L. Lin, *J. Mater. Chem.*, 2003, **13**, 1806.

10 V. Shakeri and S. Haussuhl, *Z. Kristallogr.*, 1992, **198**, 165.

11 D. M. Poojary and A. Clearfield, *J. Am. Chem. Soc.*, 1995, **117**, 11278.

12 Y. Zhang and A. Clearfield, *Inorg. Chem.*, 1992, **31**, 2821; G. Cao, V. M. Lynch and L. N. Yacullo, *Chem. Mater.*, 1993, **5**, 1000; Y. Zhang, K. J. Scott and A. Clearfield, *Chem. Mater.*, 1993, **5**, 495; G. Cao and T. E. Mallouk, *Inorg. Chem.*, 1991, **30**, 1434; K. J. Frink, R.-C. Wang, J. L. Colon and A. Clearfield, *Inorg. Chem.*, 1991, **30**, 1438; F. Fredoueil, D. Massiot, P. Janvier, F. Gingl, M. Bujoli-Doeuff, M. Evain, A. Clearfield and B. Bujoli, *Inorg. Chem.*, 1999, **38**, 1831.

13 G. M. Sheldrick, SHELX97, Program for R-ray Crystal Structure Solution and Refinement, Göttingen University, Göttingen, Germany, 1997.