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Gas-adsorbing ability of tris-ethylenediamine metal complexes (M = Co(III), Cr(III), Rh(III), Ir(III)) as transformable ionic single crystal hosts†

Satoshi Takamizawa,*[ab] Masa-aki Kohbara,[a] Takamasa Akatsuka[a] and Ryosuke Miyake[a]

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We previously reported that a single crystal of $[Co(en)_3]Cl_3$ shows gas adsorbency for various gases and organic vapors accompanying channel expansion in its crystal structure. To investigate the possibility of a single crystal of tris-ethylenediamine metal complex as an ionic single-crystal host for vapor adsorption, a series of adsorbencies of single crystals of $[M^{III}(en)_3]Cl_3$ (M = Co **1**, Cr **2**, Rh **3**, Ir **4**) were studied. All complexes have channels in their crystal structures, which dynamically and reversibly change size with vapor adsorption and show similar vapor adsorbency similar to the adsorption behavior of $[Co(en)_3]Cl_3$.

Introduction

Polymorph conversion in a solid state is an important element for making functional devices based on dynamic motion.[1] In this field, dynamic porosity has been given much attention as being functionalized toward dynamic inclusion of guest molecules,[2–4] which can control guest reactivity and stability.[5] To construct such porosity, a host with a flexible skeleton is required. For this purpose, low-dimension porosities and/or with weak binding forces for the component skeleton were reported. The most actively investigated materials, however, generally consist of polymetric skeletons with the assistance of van der Waals interpolymer interactions. Compared with the van der Waals interaction, the Coulombic interaction is rather "loose" to structural changes in terms of binding interaction, which is generated in isotropic radial directions over a long distance proportional to r^{-1} (r = intermolecular distance), while that of the van der Waals interaction is proportional to r^{-6}. Thus, there is a great possibility for an ionic crystal to be a flexible host that can transform its crystal structure to sensitively adapt to various adsorbed guest properties even by weak physisorption.

We previously reported the gas-adsorbing property of a single crystal of racemic (±)-$[Co^{III}(en)_3]Cl_3$, which was observed for various gases with an increase of the cell volume of its crystal structure (Fig. 1).[6] In order to expand the use of ionic crystals as flexible hosts for dynamic adsorption of organic vapors, the adsorption behaviors of a series of tris-ethylendiamine metal complexes with different metal ions were studied. Here, we report and discuss the adsorbing properties of tris-ethylenediamine complexes of various metal ions with their crystal structures and thermal stabilities.

Results and discussion

Synthesis and crystal structures of $[M^{III}(en)_3]Cl_3$

Ir(III) complex **4** was synthesized by the reaction of the mixture of $IrCl_3$ and 8 eq. of ethylenediamine in an autoclave (170 °C, 10 days) followed by recrystallization from water.[10] All complexes except the Ir complex, $[M^{III}(en)_3]Cl_3$ (M = Co:[7] **1**, Cr:[8] **2**, Rh:[9] **3**), were synthesized according to the methods previously reported. For **1–3**, well-formed hydrated single racemic crystals were obtained as hexagonal rods by recrystallization from water. X-Ray analyses of these complexes at 90 K are summarized in Table 1. The crystal structures of Co complex **1**,[6] Cr complex **2**, and Rh complex **3** have the same crystal cell with the $P\bar{3}c1$ space group which has C_3 symmetry with one-third of the molecule being in the asymmetric unit. As shown in Fig. 2, all complexes **1–3** have similar crystal structures, that is, they have 1D channels that included 1D water chains. As estimated from the distance of neighboring metal ions in the ab plane (dashed line in Fig. 2), which are 11.4113(6) Å for **1**,[6] 11.4609(3) Å for **2**, and 11.4083(6) Å for **3**, the size of the

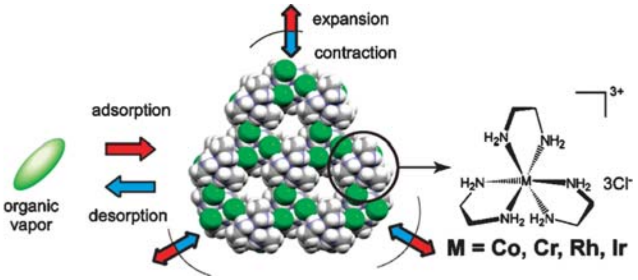

Fig. 1 Conceptual figure of gas-conforming transformability of racemic single crystals of tris-ethylendiamine metal complexes **1–4** (color of atoms: green, Cl; gray, C; white, H). N atoms and metal ions are hidden under the other molecules.

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[a] *International Graduate School of Arts and Sciences, Yokohama City University, 22-2 Seto, Kanazawa-ku, Yokohama, Kanagawa 236-0027, Japan. E-mail: staka@yokohama-cu.ac.jp; Fax: +81-45-787-2187; Tel: +81-45-787-2187*
[b] *PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

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Table 1 X-Ray analysis of tris-ethylenediamine metal complex **1–3**.

Complex	**1**·4H_2O[6]	**1**[6]	**2**·3.72H_2O	**2**	**3**·3.37H_2O	**3**
Empirical formula	$C_6H_{32}Cl_3CoN_6O_4$	$C_6H_{24}Cl_3CoN_6$	$C_6H_{31.44}Cl_3CrN_6O_{3.72}$	$C_6H_{24}Cl_3CIrN_6$	$C_6H_{30.74}Cl_3RhN_6O_{3.37}$	$C_6H_{24}Cl_3RhN_6$
Crystal size/mm	0.33 × 0.28 × 0.20	0.44 × 0.22 × 0.22	0.30 × 0.28 × 0.18	0.38 × 0.32 × 0.28	0.22 × 0.16 × 0.10	0.22 × 0.16 × 0.10
M	417.64	345.59	405.67	338.66	450.27	389.57
Crystal system	Trigonal	Trigonal	Trigonal	Trigonal	Trigonal	Trigonal
Space group	$P\bar{3}c1$	$P\bar{3}c1$	$P\bar{3}c1$	$P\bar{3}c1$	$P\bar{3}c1$	$P\bar{3}c1$
T/K	90	90	90	90	90	90
a/Å	11.4113(6)	10.7476(5)	11.4609(3)	10.9745(16)	11.4083(6)	10.9593(5)
c/Å	15.4595(8)	15.4981(15)	15.4443(9)	15.421(3)	15.3968(16)	15.3981(14)
V/Å^3	1743.40(11)	1550.36(18)	1756.86(12)	1608.5(5)	1735.4(2)	1601.63(18)
Z	4	4	4	4	4	4
D_c/Mg m^{-3}	1.591	1.481	1.522	1.398	1.705	1.616
μ(Mo-Kα)/mm^{-1}	1.463	1.611	1.126	1.203	1.461	1.555
Reflections collected	11 952	10 091	12 196	10 853	11 878	10 901
Independent reflections	1453	1294	1467	1340	1456	1338
R_{int}	0.0246	0.0374	0.0296	0.0363	0.0737	0.0623
Goodness of fit	1.084	1.185	1.178	1.129	1.074	1.379
$R1$ ($I > 2\sigma(I)$) (all data)	0.0387 (0.0406)	0.0381 (0.0530)	0.0396 (0.0429)	0.0273 (0.0301)	0.0460 (0.0678)	0.0823 (0.0880)
$wR2$ ($I > 2\sigma(I)$) (all data)	0.1027 (0.1039)	0.0975 (0.1110)	0.1260 (0.1288)	0.0724 (0.0736)	0.1051 (0.1134)	0.1557 (0.1582)
Least diff. peak (hole)/e Å^{-3}	1.459 (−1.419)	1.043 (−0.537)	1.585 (−1.079)	0.523 (−0.323)	0.926 (−0.891)	1.368 (−2.418)
Accessible volume[a]/Å^3 (%)	385.7 (22.1)	213.3 (13.8)	359.0 (20.4)	227.0 (14.2)	349.0 (20.1)	232.0 (14.5)

[a] The accessible volume for H_2O included crystals was estimated from the host structure excluding any included guests.

channels are approximately the same. Those of the neighboring metal–metal distance along the c axis, which is related to channel length, were also the same (7.7298(8) Å for **1**,[6] 7.7221(8) Å for **2** and 7.6984(10) Å for **3**). In the case of Ir complex **4**, it was difficult to obtain a well-formed crystal suitable for X-ray analysis and we are unable to determine the crystal structure unequivocally at this time.

After vacuum drying at 60 °C, single-crystal X-ray diffraction analyses can be performed to determine the vacant-host structures of **2–4** as for **1**.[6] The dried crystals contain no water molecules, and the cell volumes of each complex are 8–9% (11% for **1**) less than are those of the hydrated crystal while essentially the same structures are maintained. After removal of the water molecules from the crystals, a large decrease of the neighboring metal–metal distance in the ab plane (0.66 Å for **1**,[6] 0.49 Å for **2**, and 0.45 Å for **3**) was observed in all crystals while the metal–metal distance along the c axis was negligible (0.02 Å for **1**,[6] 0.01 Å for **2**, and 0.00 Å for **3**). These results indicate that the anisotropy narrowing occurred in these crystals by removal of the guest water molecules in all complexes **1–3**.

The interatomic distances of the water molecules and metal complexes within the sum of the corresponding van der Waals radii for water included in the complexes of **1–3** (short distance) are summarized in Table 2. In addition to the short contact distances observed in the 1D water chain (guest–guest contact in Table 2), short contacts were also observed in all complexes between the carbon atoms of the methylene group of ethylenediamine and the oxygen atoms of the water molecules (guest–host contact in Table 2). These values indicate that there are van der Waals interactions between the metal complexes and the water molecules in the channel. All complexes **1–3** show essentially the same distance (O(1S)–H(2A): 2.53–2.55 Å, O(1S)–H(1A): 2.63–2.74 Å, and O(1S)–Cl(1): 3.16–3.18 Å). These results suggest that all complexes provide similar channel spaces.

TG-DTA study of [M^{III}(en)$_3$]Cl$_3$

Thermogravimetric measurements (TG-DTA) were performed to investigate the thermal stability of hydrated crystals (Fig. 3). DTA measurements show a sharp signal near 40 °C for all complexes. In the TGA measurements, the water molecules were removed at this temperature. The amount of water molecules removed per single metal complex was 2.9, 3.2, 3.2 and 3.4 molecules for **1**, **2**, **3** and **4**, respectively, which were estimated from the decreases in the weight of the crystals. Although the amount was slightly less than that estimated from X-ray analysis at 90 K (4, 3.72 and 3.37 molecules for **1**, **2** and **3**, respectively), considering partial evaporation by air drying before the measurement, the amounts of included crystal water agree with the water composition observed by X-ray analysis. For Co complex **1** it was known that the amount of included water in its crystal is approximately three molecules.[7] The removal temperature for each complex was nearly the same: 46, 40, 46 and 48 °C for **1**, **2**, **3** and **4**, respectively. In contrast, the temperature of the other signal, which was assigned as the decomposition temperature, is different for each complex (249 °C for **1**, 279 °C for **2**, 332 °C for **3** and 371 °C for **4**). These results suggest that the step of removing the water molecules in this system is not related to the stability of the metal complexes but is related to the unique channel structure of [M^{III}(en)$_3$]Cl$_3$.

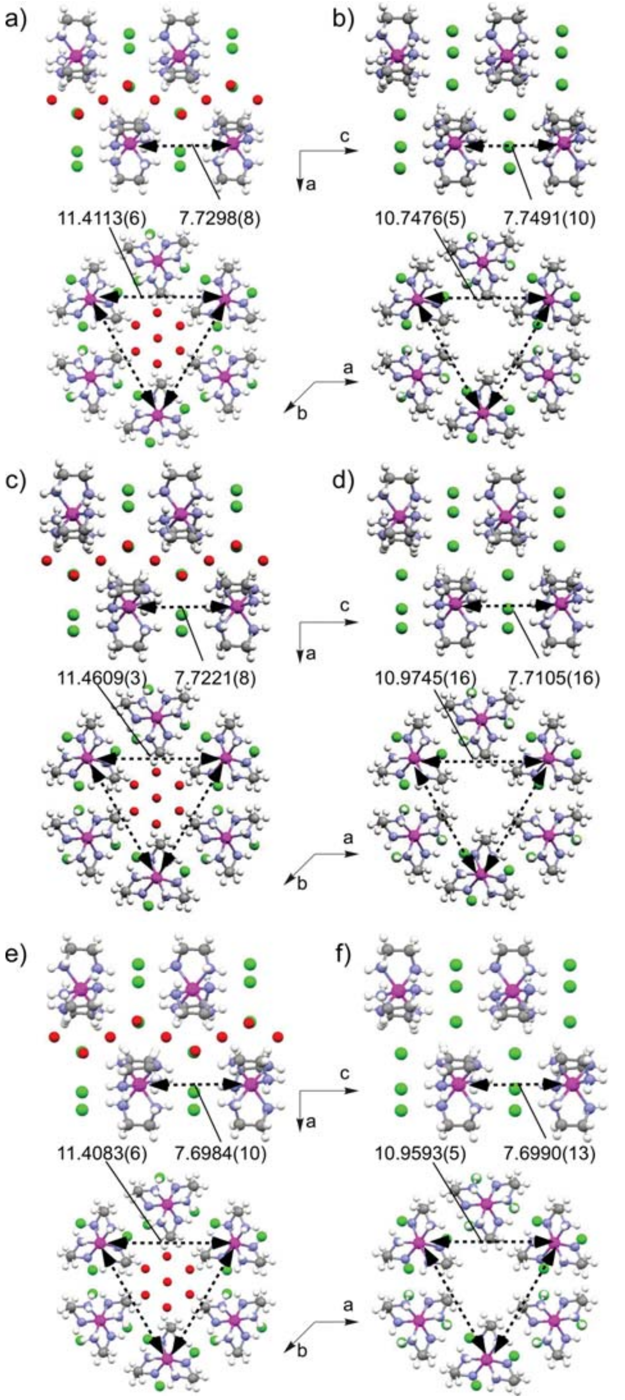

Fig. 2 Channel view (ball and stick model) of tris-ethylenediamine metal complexes with water molecules (a, c, e) and without water molecule (b, d, f) determined by single-crystal X-ray diffraction analysis at 90 K. (a, b) Co complex **1**; (c, d) Cr complex **2**; (e, f) Rh complex **3**; in each case, side view (upper structure) and top view (lower structure). Metal ion–metal ion separations within the lattice are shown in Å (green, Cl; gray, C; light blue, N; white, H; pink, Co; Cr; Rh). Some H_2O and Cl^- molecules are omitted for clarity.

Table 2 Short contacts shown in the channels of the complexes **1–3**

	1$\cdot 4H_2O$	**2**$\cdot 3.72H_2O$	**3**$\cdot 3.37H_2O$
Guest–host contact			
O(1S)···H(2A)	2.55	2.53	2.53
O(1S)···H(1A)$^{\#1}$	2.74	2.67	2.63
O(1S)···Cl(1)$^{\#2}$	3.164(5)	3.184(5)	3.161(11)
Guest–guest contact			
O(1S)···O(2S)^a	2.976(4)	2.890(3)	2.877(9)
O(1S)···O(3S)	2.851(4)	2.882(3)	2.783(9)

^{a} Symmetry codes: #1: $-y$, $x - y$, z, #2: y, x, $0.5 - z$.

Vapor adsorption behavior

Pressure–selective adsorption behaviors were clearly observed in water vapor adsorption isotherm measurements (Fig. 4). The adsorption curves show a sharp increase at around 0.1 relative pressure at which the sharp increases in adsorption shift significantly higher as the temperature increases, which indicates that the adsorption enthalpy is larger than that of water condensation. An estimation based on the Clausius–Clapeyron equation gives adsorption enthalpies of 52[6], 51, 51 and 54 kJ mol^{-1} in **1**, **2**, **3** and **4**, respectively[11] (inset in Fig. 4), which are slightly larger than that of bulk water condensation (44 kJ mol^{-1}). This indicates that the moderate hydrating and dehydrating ability of $[M^{III}(en)_3]Cl_3$ occurs not only by the Coulombic potential for the stabilization of adsorbed polar water molecules but also by reduction of the ionic character of $[M^{III}(en)_3]^{3+}$ through encapsulation of organic ligands. The abrupt increase in the adsorption of water vapor by all complexes **1–4** indicates a “mass-induced phase transition,”[12] which suggests their reversible shrinkage and expansion through gas adsorption triggered by the formation of specific water aggregation as well as by the increased amount of adsorbed water.

The vapor-adsorbing abilities of **1–4** were also observed for various organic vapors (MeOH, EtOH, benzene, CCl_4, *n*-hexane) (Fig. 5). The results show that all the complexes **2–4** also act as ionic single-crystal hosts for various guests. **1–4** show similar alcohol (MeOH and EtOH) adsorbing ability, indicating that the mechanism of adsorption of these complexes is the same. The adsorptions of all other organic vapors also show a similar behavior. Since organic vapors are located in the channels in the crystal of Co complex **1**,[6] it was suggested that these complexes also expanded their channels through the adsorption of organic vapors. Thus, the adsorption mechanism and selectivity of single crystals of these complexes was mainly related to the channel structure and its expansion process. In addition, there were small differences in the adsorption of organic vapors. For example, the CCl_4 adsorption curves of **2** were different from those of the others. The adsorption behaviors of benzene were different in terms of the amounts of adsorption and the pressures for the abrupt increase for each complex. Since X-ray analyses showed that the properties and structures of the crystal surfaces were the same for **1–4**, these small differences are probably caused by the nature of the metal ion.

Conclusion

All tris-ethylenediamine metal complexes **1–3** have a similar crystal structure. These complexes have 1D channels in the crystals, which are suitable for the adsorption of various organic vapors depending on their reversible changes in crystal

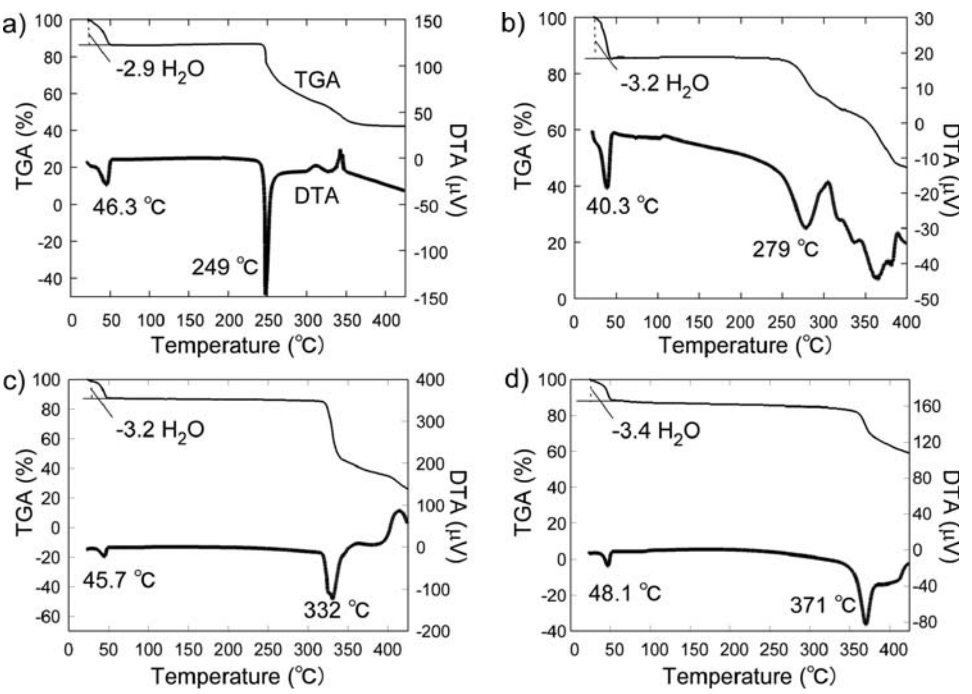

Fig. 3 TG-DTA curves of tris-ethylenediamine metal complexes. Fine and bold curves are TGA and DTA curves, respectively: (a) Co complex **1**; (b) Cr complex **2**; (c) Rh complex **3**; (d) Ir complex **4**.

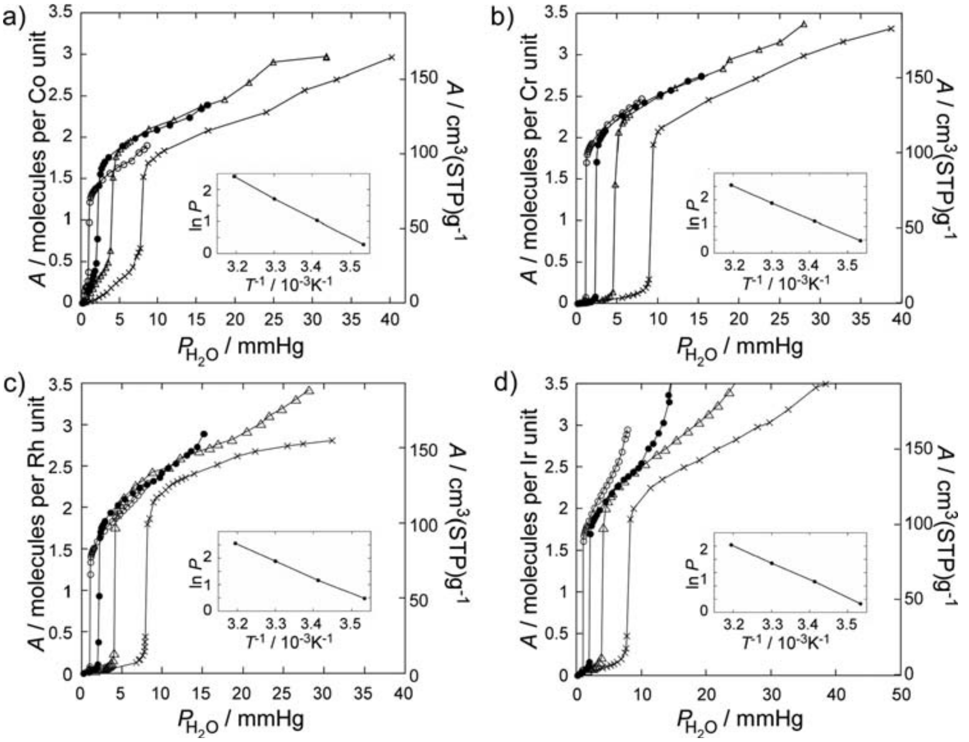

Fig. 4 Water-vapor adsorption isotherm curves of tris-ethylenediamine metal complexes: (a) Co complex **1**; (b) Cr complex **2**; (c) Rh complex **3**; (d) Ir complex **4** at 10 °C (○), 20 °C (●), 30 °C (△), and 40 °C (×). Inset: Clausius–Clapeyron plot using the starting pressure of the sharp increase in adsorption at measurement temperatures[11] (*A*: amount of adsorbed water vapor).

structure. X-Ray structural study and thermal study of the adsorption behavior suggest that the adsorbing behaviors were essentially the same for all complexes and were mainly related to the channel structures and their expanded process, that is, these complexes dynamically capture and release gaseous guests while expanding and contracting during the adsorption

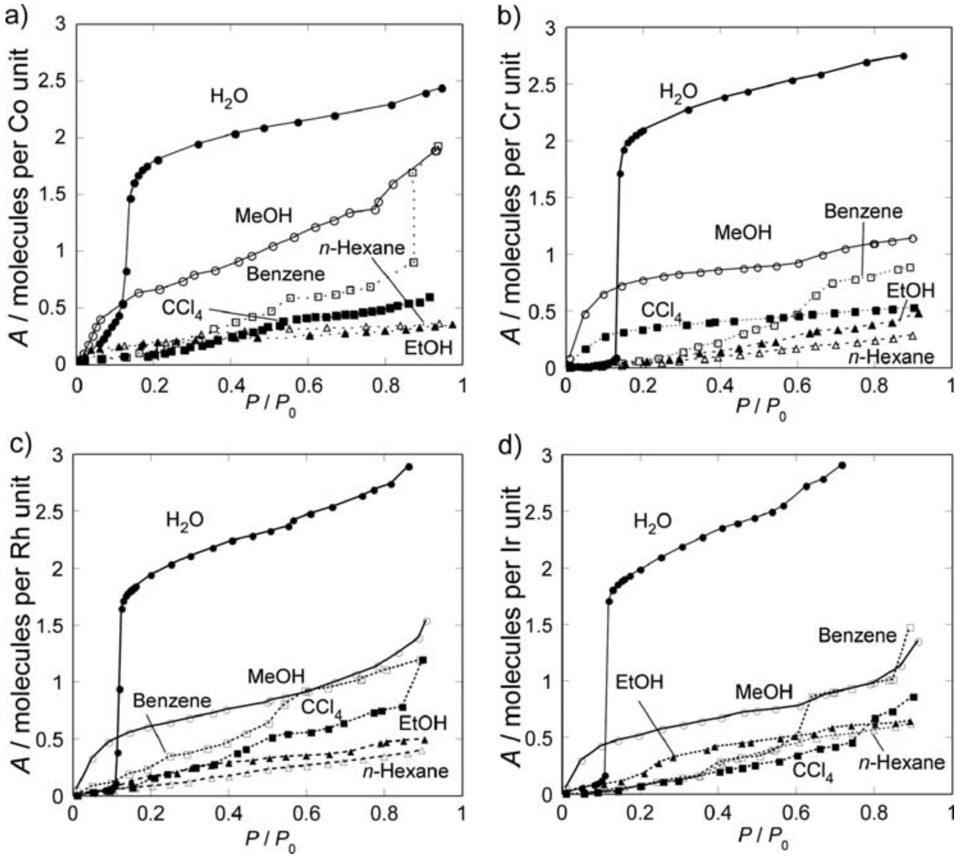

Fig. 5 Vapor-adsorption isotherm curves of tris-ethylenediamine metal complexes: Adsorption of various vapors at 20 °C: (a) Co complex **1**; (b) Cr complex **2**; (c) Rh complex **3**; (d) Ir complex **4**; H_2O (●), MeOH (○), EtOH (▲), benzene (□), CCl_4 (■), *n*-hexane (△) (*A*: amount of adsorbed vapor of water or organic solvent).

and desorption actions. Since there is sufficient room for replacing and combining ionic components with various shapes, charges, and charge distributions, systematic study will proceed through the expanding of tris-ethylenediamine metal complexes **1–4** as prototype crystals.

Experimental

General

Compounds **1–3** were synthesized according to a previously reported procedure. Ethylenediamine was purchased from Tokyo Chemical Industry. $IrCl_3$ and organic solvents were purchased from Wako Pure Chemicals Industries. All reagents and solvents were used without further purification. Well-shaped single crystals that were formed after recrystallization from hot water were used for all measurements.

Synthesis of $[Ir(en)_3]Cl_3$ 4

$IrCl_3$ 0.30 g (1.0 mmol) was added to an ethylendiamine 0.80 ml (8.3 mmol) water solution (1.5 mL) in an autoclave. The mixture was stirred at 170 °C for 10 days. The mixture was then diluted with water (approximately 10 mL) and filtered. The filtrate was concentrated until small yellow crystals were precipitated. The mixture was cooled with an ice-bath. The pale yellow precipitate was filtered off and recrystallized from water to obtain **4** (46 mg, 8%) as colorless hexagonal crystals. Calc. for $C_6H_{24}Cl_3IrN_6{\cdot}1.9H_2O$: C, 14.13; H, 5.43; N, 16.48. Found: C, 13.74; H, 5.36; N, 16.82%.

Adsorption isotherm measurement of various organic vapor

Adsorption isotherm measurements were performed by a volumetric method (Autosorb 1, Quantachrome). Before measurement, all complexes were carefully dried *in vacuo* at 60 °C for 1 h and all organic solvents used were of guaranteed grade and degassed by reduced pressure and ultrasonic vibration.

Thermogravimetry–differential thermal (TG-DTA) analysis measurement

Thermogravimetry–differential thermal (TG-DTA) analysis measurements were performed by using a Shimadzu DTG-60 in a nitrogen gas atmosphere. All crystals used for this measurement were stored at 25 °C and all measurements were started from this temperature.

Single-crystal X-ray analyses

All single-crystal X-ray analyses were performed on a Bruker Smart APEX CCD area diffractometer with a nitrogen-flow temperature controller (Japan Thermal Eng. TC-10KCP) using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). All procedures for the dried crystals were conducted with the crystal sealed in a glass capillary with pressurized gas or saturated vapor. Empirical adsorption corrections were applied using SADABS software.[13] The structures were solved by the direct method (SHELXS-97[14]) and refined by full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed at calculated positions and refined using a riding model.

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