Grinding-Induced Equimolar Complex Formation between Thiourea and Ethenzamide

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We prepared and characterized a grinding-induced equimolar complex of thiourea with ethenzamide. When thiourea and ethenzamide were co-ground at a molar ratio of 3 : 1, new powder X-ray diffraction (PXRD) peaks were observed in addition to PXRD peaks of thiourea crystals. The optimum stoichiometry of the new structure was confirmed as 1 : 1 mol/mol. Effect of grinding time on the thiourea–ethenzamide equimolar complex formation was investigated by using PXRD, differential scanning calorimetry and Fourier transform infrared spectroscopy. The equimolar crystal structure was confirmed by X-ray diffraction measurements of the single crystal which was recrystallized from ethanol. It was found that the intermolecular hydrogen bond formations between thiourea and ethenzamide molecules contributed to the equimolar complex formation. The complex formation was not observed in the cases where benzamide, salicylamide or 3-ethoxybenzamide was co-ground with thiourea. 2-Alcoxyl benzamide structures should be required for the grinding-induced equimolar complex formation with thiourea.

Key words thiourea; ethenzamide; grinding; complex; hydrogen bond; powder X-ray diffraction

Thiourea and urea have been known to form crystalline host–guest inclusion complexes as a tunnel structure.[1)] Difference of the internal diameter of thiourea (5.8—7.1 Å) and urea (5.5—5.8 Å) tunnels,[2,3)] the diameter of which periodically changed along the tunnel depth, influenced on the kind of drugs included and the stoichiometry. Among urea inclusion complexes with a hexagonal channel structure, *n*-alkanes, fatty acids[4,5)] and polymers[6)] have been known as the guest compounds. In the case of thiourea inclusion complexes, larger size of compounds, such as alkanes and alicyclic compounds were included in the hexagonal channel. The host–guest stoichiometry was usually higher than 3 : 1, depending on size, shape and degree of saturation of the guest molecules.[1)] Most of the thiourea inclusion complexes showed incommensurate structural properties.[7,8)] Temperature-dependent phase transition of a thiourea inclusion complex from conventional rhombohedral tunnel structure to the monoclinic form at low temperature was also reported.[9)] Complexation property of thiourea has been applied for extraction and stabilization of foods and medicinal drugs.[1)] Thiourea inclusion complex of layered structure with the host–guest stoichiometry of 2 : 1 has also been reported by using hexamethylenetetramine[10)] and 1,2-diazabicyclo-[2.2.2]octane.[11)] Basicity and symmetrical location of amines in guest molecules could be a determinant factor for the formation of corrugated or laminar structure.

Host–guest inclusion compounds were usually prepared by coprecipitation from a solution in which host and guest molecules were dissolved. However, some solvents were easily included in the place of guest[12,13)] or interacted with guest and host molecules to form a complex.[14)] Grinding was an alternative methodology to prepare the host–guest inclusion complexes more easily and rapidly without using solvent.[15,16)]

We tried to make thiourea inclusion complexes induced by grinding with medicinal drugs. Among them, ethenzamide was found to form a complex with thiourea. Purpose of the present study was to prepare and characterize the thiourea–ethenzamide complex induced by grinding. Factors affecting the complex formation were also investigated in terms of the chemical structure of drugs.

Experimental

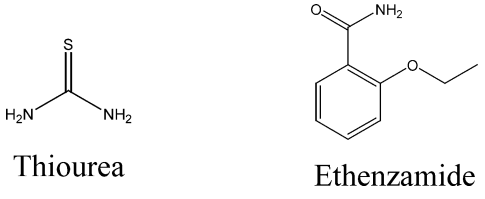
Materials Thiourea and ethenzamide was purchased from Nacalai Tesque, Inc. (Japan) and Iwaki Seiyaku (Japan), respectively and the chemical structures were shown in Fig. 1. d_4-Thiourea was obtained from Aldrich Chemical Co., Inc. (WI, U.S.A.). All other reagents were of analytical grade. Thiourea was pre-ground for 10 s to reduce the effect of crystal orientation for powder X-ray analysis.

Preparation of Thiourea–Ethenzamide Physical Mixture (PM) and Ground Mixture (GM) Thiourea and ethenzamide PMs were prepared at a molar ratio of 3 : 1, 1 : 1 and 2 : 3 in a glass vial by using a vortex mixer. The PM was ground in a vibrational rod mill (CMT TI-200, CMT Co., Ltd., Japan) for 0.5, 1 and 30 min to obtain the GM (strongly-ground PM). The PM was also ground using a vibrational mill (CMTTI-500ET, CMT Co., Ltd., Japan) at −180 °C by cooling the sample chamber with liquid nitrogen.

Preparation of Thiourea–Ethenzamide Sealed-Heated Sample Thiourea and ethenzamide PMs (about 1 g) were sealed in a glass ampoule (25 ml) and heated in a gas chromatograph oven at various temperatures for 3 h. The temperature around the glass ampoule was monitored by using a thermocouple.

Preparation of Thiourea–Ethenzamide Single Crystals Thiourea (1.15 g) was dissolved in ethanol (100 ml) and heated to 70 °C. After the addition of ethenzamide (2.5 g) and the agitation for 10 min, the solution was stored at 25 °C for 24 h to obtain the colorless plate-like crystals. The precipitates were collected on a paper filter and dried in air.

Powder X-Ray Diffraction (PXRD) Powder X-ray diffraction patterns were obtained by using Rigaku Miniflex diffractometer with Cu$K\alpha$ radiation



Thiourea Ethenzamide

Fig. 1. Chemical Structures of Thiourea and Ethenzamide

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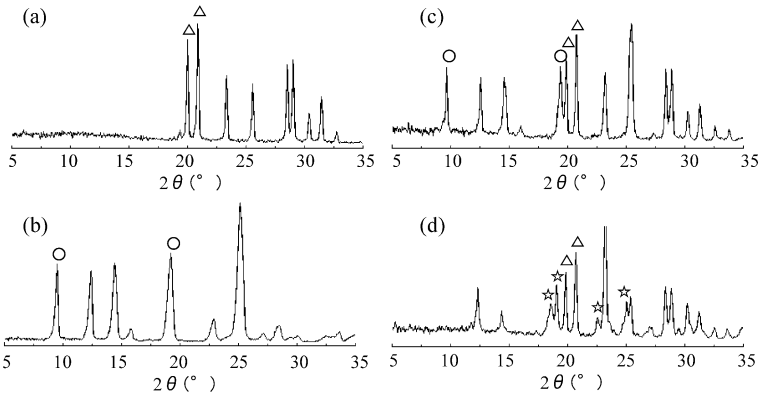

Fig. 2. Powder X-Ray Diffraction Patterns of Thiourea Co-ground with Ethenzamide

Molar ratio of thiourea : ethenzamide=3 : 1. New diffraction peaks were indicated by stars. (a) Thiourea; (b) ethenzamide; (c) physical mixture of thiourea and ethenzamide; (d) thiourea co-ground with ethenzamide for 30 min.

(Rigaku Corporation, Japan) at an ambient temperature. Followings were the measurement conditions: voltage 30 kV, current 15 mA, scanning speed 0.067° s^{-1} (4° min^{-1}), 2θ collection range 5—35°.

Differential Scanning Calorimetry (DSC) A DSC3100 differential scanning calorimeter (MAC Science Co., Japan) was used. About 5 mg of sample was loaded in a closed aluminum pan and measured at heating rate of 5 °C/min under nitrogen gas flow (50 ml/min).

Fourier Transform-Infrared Spectroscopy (FT-IR) Fourier transform-infrared spectroscopy measurements were carried out by KBr disc method. FT-IR spectra were recorded with JASCO 230 FT-IR spectrometer (JASCO Corporation, Japan). Spectral assignments of IR absorption bands were performed by comparison of the data between thiourea–ethenzamide and d_4-thiourea–ethenzamide PM and GMs.

Single X-Ray Structural Analysis Measurements were made on a Bruker Smart 1000 CCD plate area detector with graphite monochromated Mo$K\alpha$ radiation (Rigaku Corporation, Japan). The structure was solved by direct methods (SIR92)[17] and expanded using Fourier techniques (DIRDIF94).[18] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement on F was based on 1572 observed reflections ($I>3.00\sigma(I)$) and 146 variable parameters and converged (largest parameter shift was 0.98 times its esd) with unweighted and weighted agreement factors of: $R=0.038$, $R_w=0.043$.

Results and Discussion

Grinding-Induced Thiourea–Ethenzamide Equimolar Complex Formation Thiourea has been reported to form inclusion compounds as hexagonal channel structure and the molar ratio of thiourea : guest was usually higher than 3 : 1.[1] When thiourea was co-ground with ethenzamide at a molar ratio of 3 : 1, new PXRD peaks at $2\theta=18.5$, 19.0 and 22.5° were observed with PXRD peaks of intact thiourea crystals as shown in Fig. 2. Peak position of these new peaks was apparently different from those of conventional thiourea inclusion complexes. The PXRD peaks of thiourea-DL-camphor inclusion complex at the molar ratio of 3 : 1 were observed at $2\theta=18.7$, 21.6 and 23.6° (data not shown). Effect of molar ratio on the thiourea–ethenzamide complex formation was shown in Fig. 3. Thiourea–ethenzamide GMs at the molar ratio of 3 : 1 and 2 : 3 showed new PXRD peaks together with those of intact thiourea and ethenzamide, respectively. When the molar ratio of GM was 1 : 1, only the new PXRD peaks were observed. These results indicated that co-grinding formed thiourea–ethenzamide equimolar complex and the complex structure was different from that of thiourea inclusion complexes that have already been reported.

On the grinding process, mechanical stress induced by a vibrational rod mill would mainly contribute to the micronization of the sample. Moreover, the accompanied heat also plays an important role for the shape and size of the micronized particles when the grinding was performed at ambient temperature without temperature control. In the case of thiourea–ethenzamide complex, the accompanied heat may affect the complexation. To estimate the effect of mechanical stress on the complex formation, we prepared thiourea–ethenzamide GM by cooling the sample chamber with liquid nitrogen. By the low temperature grinding, sample temperature could be kept at −180 °C. The heat-induced complexation was also examined by sealed heating of the samples and these results were shown in Fig. 4. Thiourea–ethenzamide complex formation was observed by both methods. In the case of sealed heating, however, the temperature should be kept at least 100 °C for the complexation. Furthermore, that did not completely proceed by heating the sample at 110 °C

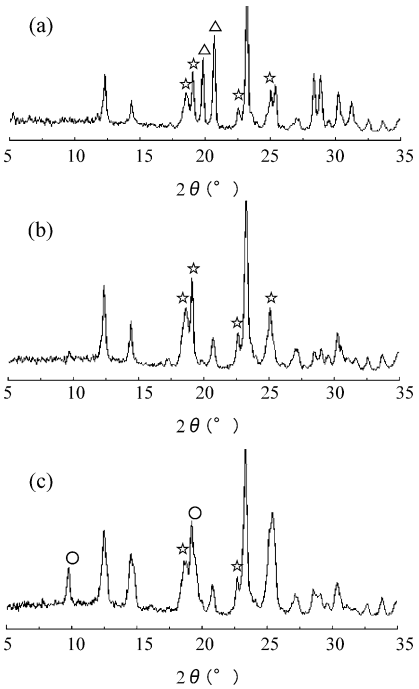

Fig. 3. Effect of Mixing Molar Ratio on the Thiourea–Ethenzamide Complex Formation Induced by Grinding

Molar ratio of thiourea : ethenzamide was (a) 3 : 1, (b) 1 : 1 and (c) 2 : 3. Samples were ground for 30 min.

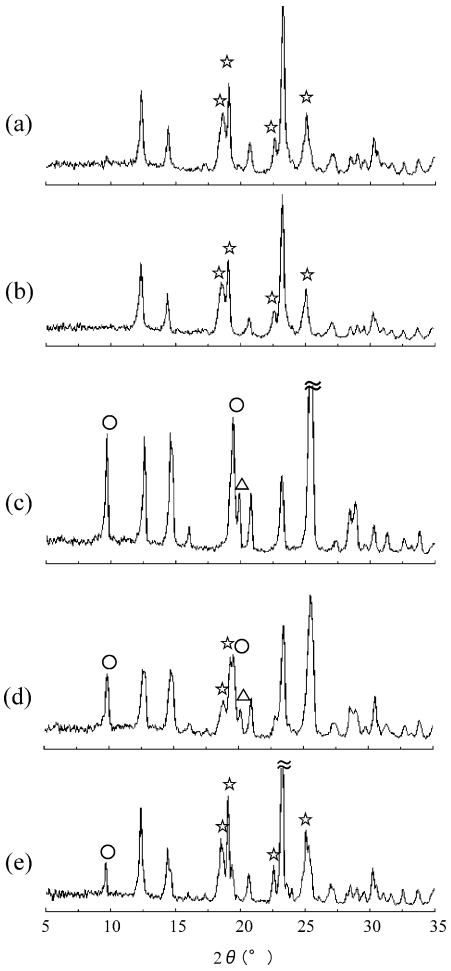

Fig. 4. PXRD Patterns of Thiourea/Ethenzamid Equimolar Complexes Prepared by Different Methods

Molar ratio of thiourea/ethenzamide was 1 : 1. (a) GM (30 min, at room temperature); (b) GM (30 min, at −180 °C); (c) sealed heated PM (90 °C for 3 h); (d) sealed heated PM (100 °C for 3 h); (e) sealed heated PM (110 °C for 3 h).

for 3 h. Though the sample temperature will increases in the case of ambient temperature grinding, contribution of the grinding-accompanied heat for the thiourea–ethenzamide complex formation would be small. From the results, we speculated that grinding facilitated the complexation mainly by the mechanical stress, not by the heat.

Effect of grinding time on the thiourea–ethenzamide equimolar complex formation under the experimental conditions was investigated by using PXRD, DSC and FT-IR spectroscopy. Figure 5 shows changes of PXRD patterns of thiourea–ethenzamide equimolar mixture depending on the grinding time. X-Ray diffraction peak intensities of intact thiourea and ethenzamide crystals in the PM decreased with increasing grinding time. Structural changes to the equimolar complex completed after grinding at least for 20 min where PXRD peaks of both intact thiourea and ethenzamide completely disappeared and only new PXRD peaks were observed.

Changes in the thermal behavior of thiourea–ethenzamide equimolar GMs were shown in Fig. 6. Intact ethenzamide and thiourea crystals showed endothermic peaks due to the fusion at 129 and 178 °C, respectively. The PM showed an endothermic peak due to the fusion of ethenzamide, a small exothermic peak and an endothermic peak around 165—170 °C, while the peak due to the fusion of thiourea was not observed. As expected by the results of sealed-heated samples shown in Fig. 4, heat-induced equimolar complex formation was also probable for the heating of PM. Since the new endothermic peak at about 168 °C was also observed in thiourea–ethenzamide GMs, the exothermic and endothermic peaks in PM were estimated to be due to the crystallization and the fusion of the equimolar complex, respectively. Lowering of the fusion temperature and the subsequent decrease of endothermic peak area of ethenzamide depending on the grinding time would be attributed to the increase of thiourea–ethenzamide complex as impurity for ethenzamide molecules. The DSC peak area of the ethenzamide melting finally disappeared after grinding for 3 min, indicating the grinding-induced progress of thiourea–ethenzamide complex forma-

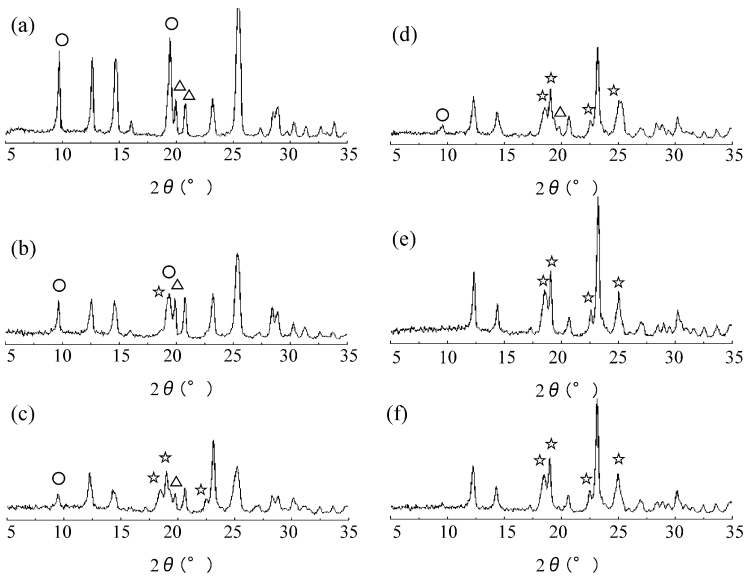

Fig. 5. Effect of Grinding Time on the Thiourea–Ethenzamide Complex Formation

(a) An equimolar physical mixture was ground for (b) 1, (c) 5, (d) 15, (e) 20 and (f) 30 min.

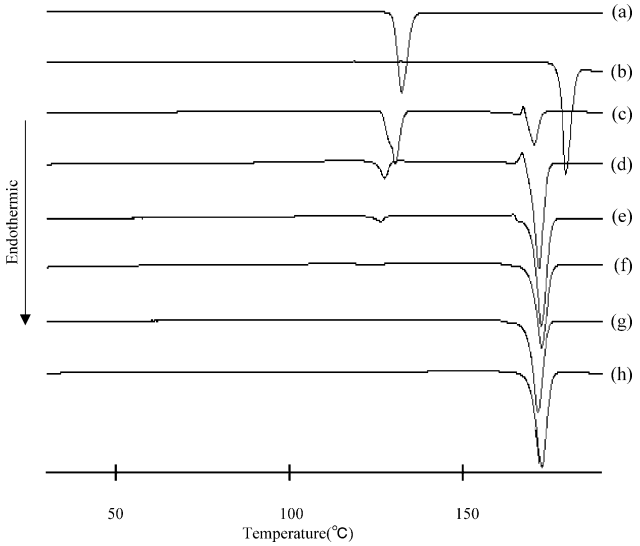

Fig. 6. Differential Scanning Calorimetry (DSC) Curves of Thiourea, Ethenzamide and the Equimolar Ground Mixtures

Heating rate: 5 °C/min, sealed pan. (a) Ethenzamide; (b) thiourea; (c) equimolar physical mixture; (d)—(h) equimolar ground mixtures ground for 30 s, 1, 2, 3 and 30 min, respectively.

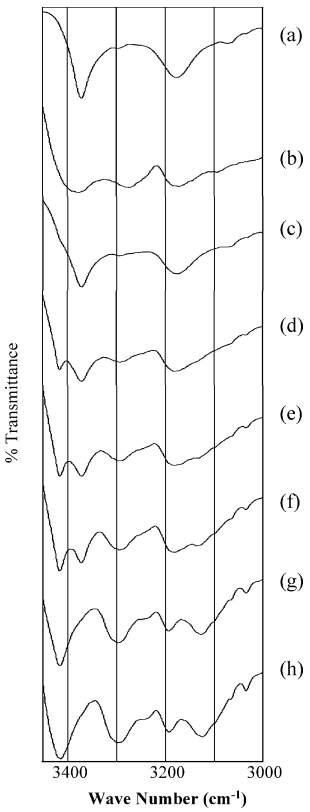

Fig. 7. Changes in IR Spectra of Thiourea–Ethenzamide Equimolar Mixture Induced by Grinding

KBr disc method. (a) Thiourea; (b) ethenzamide; (c) equimolar physical mixture; (d)—(h) equimolar ground mixtures ground for 30 s, 1, 2, 3 and 30 min, respectively.

tion.

Molecular interaction between thiourea and ethenzamide in the GMs was investigated by FT-IR spectroscopy and the spectral changes with the grinding times were shown in Fig. 7. N–H asymmetric and symmetric vibration bands of ethenzamide at 3371 and 3177 cm^{-1} observed in intact crystals were shifted to higher and lower wave number, 3413 and 3124 cm^{-1}, respectively, by grinding. It was suggested that the amide group in ethenzamide interacted with thiourea molecules by the complex formation. Further spectral changes were not observed after 3 min grinding as same as in the case of DSC measurements.

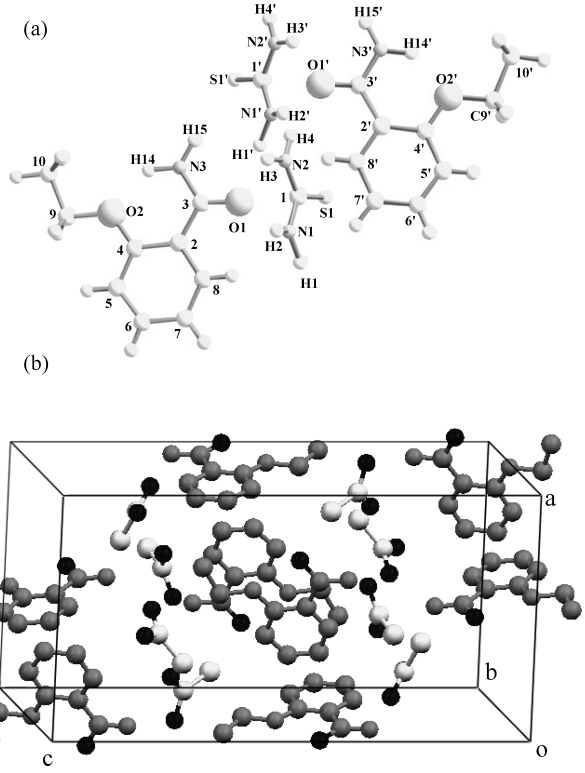

Fig. 8. Structure and Packing of Thiourea–Ethenzamide Complex in the Crystal Lattice

(a) Structure of thiourea–ethenzamide equimolar complex with atomic numbering. (b) Packing of thiourea–ethenzamide complex in the crystal lattice. Hydrogen atoms were not shown on the figure.

Crystal Structure of Thiourea–Ethenzamide Equimolar Complex To determine the crystal structure of the thiourea–ethenzamide equimolar complex induced by grinding, single crystals of the complex were prepared and collected from ethanolic solution. PXRD angles of the hand-ground single crystals were identical to that of the ground sample. As shown in Fig. 8, the determined structure confirmed an equimolar complex of thiourea and ethenzamide and the crystal structure was entirely different from that of tunnel-type thiourea inclusion complexes previously reported. Selected structural parameters, bond distances, angles and non-bonded contacts were listed on Tables 1 and 2. Because the positions of H atoms in the crystal were not refined, bond lengths connected to H atoms were not listed on Table 2. Taking van der Waals radii of atoms related to the hydrogen bond formation into consideration, the maximum Donor···Acceptor distances enough to form the hydrogen bonding were estimated to be less than 3.0 Å in N–H···O and 3.45 Å in N–H···S hydrogen bond formations. In thiourea–ethenzamide equimolar complex, a ethenzamide molecule formed N3–H14···O2 intramolecular hydrogen bonding (2.642 Å) and interacted with thiourea molecules through N1–H2···O1 (2.984 Å) and N3–H15···S1′ (3.361 Å) inter-

molecular hydrogen bondings. Thiourea–thiourea intermolecular hydrogen bond networks formed in thiourea crystals were not observed in the equimolar complex. That is, the shortest N–H···S distance between thiourea molecules in the equimolar complex was 3.549 Å, which was much longer than the distance observed in thiourea crystals (3.39 Å).[18)]

As shown before, grinding-induced thiourea–ethenzamide equimolar complex formation was occurred through solid–solid interaction mainly by the mechanical stress-induced interaction between them, not by the heat-induced liquefied or vaporized ethenzamide. The stoichiometry was close to 1 : 1 within the detection limit of PXRD and DSC measurements. One of the reasons facilitating the mechanical stress-induced equimolar complexation on the solid state would be the stabilization of the complexes by the strong hydrogen-bond network formation between thiourea and ethenzamide molecules.

Effect of Chemical Structure of Drugs on the Complex Formation with Thiourea Factors affecting the grinding-induced complex formation were investigated in terms of the chemical structure of drug molecules as shown in Fig. 9. When 2-methoxybenzamide was co-ground with thiourea, the equimolar complex formation was confirmed from the PXRD measurements. However, complex formation was not observed in the cases where benzamide, salicylamide or 3-ethoxybenzamide was co-ground with thiourea. While salicylamide molecules formed O–H···O intramolecular hydrogen bonding, the contributing functional groups to the hydrogen bonding was different from that of 2-methoxybenzamide,

Table 1. Crystal and Experimental Data of Thiourea–Ethenzamide Equimolar Complex

Empirical formula:	$C_{10}H_{15}N_3O_2S$
Formula weight:	241.31
Crystal color:	clear
Crystal dimensions:	0.50×0.40×0.30 mm
Crystal system:	orthorhombic
a =	10.658(3) Å
b =	10.997(3) Å
c =	20.680(5) Å
V =	2423.8(9) Å^3
Space group:	Pbca (#61) Z=8
D_{calc}:	1.322 g/cm^3
μ(Mo$K\alpha$):	2.57 cm^{-1}
Radiation:	Mo$K\alpha$ (λ=0.71069 Å)
Monochromator:	graphite
Temperature:	23.0 °C
No. of observations:	1572 (I>3.00σ(I))
No. of variables:	146
Residuals:	R=0.038 R_w=0.043
Goodness of fit indicator:	1.19
Maximum peak in final diff. map:	0.25 e Å^{-3}
Minimum peak in final diff. map:	−0.21 e Å^{-3}
Measurement:	Bruker Smart 1000
Program system:	teXsan
Structure solution:	Direct methods (SIR92)

Table 2. Bonds and Angles of Thiourea–Ethenzamide Equimolar Complex

Bond lengths (Å)			
S1–C1	1.693 (3)	C2–C3	1.498 (3)
O2–C4	1.367 (3)	C2–C8	1.393 (3)
O2–C9	1.441 (3)	C2–C4	1.407 (3)
O1–C3	1.244 (3)	C8–C7	1.382 (3)
N1–C1	1.334 (3)	C4–C5	1.393 (3)
N2–C1	1.333 (3)	C5–C6	1.379 (3)
N3–C3	1.338 (3)	C9–C10	1.521 (4)
		C7–C6	1.381 (4)
Angles (°)			
C4–O2–C9	119.5 (2)	N3–C3–C2	119.2 (2)
S1–C1–N1	121.5 (2)	C2–C8–C7	122.2 (2)
S1–C1–N2	120.4 (2)	O2–C4–C2	117.7 (2)
N1–C1–N2	118.1 (2)	O2–C4–C5	122.1 (2)
C3–C2–C8	116.6 (2)	C2–C4–C5	120.1 (2)
C3–C2–C4	125.5 (2)	C4–C5–C6	120.0 (2)
C8–C2–C4	117.8 (2)	O2–C9–C10	106.8 (2)
O1–C3–N3	120.1 (2)	C8–C7–C6	118.8 (2)
O1–C3–C2	120.7 (2)	C5–C6–C7	121.1 (2)
Hydrogen bond interactions (Å)		D···A	
N3–H14···O2		2.642	
N1–H2···O1		2.984 (3)	
N3–H15···S1′		3.361 (2)	

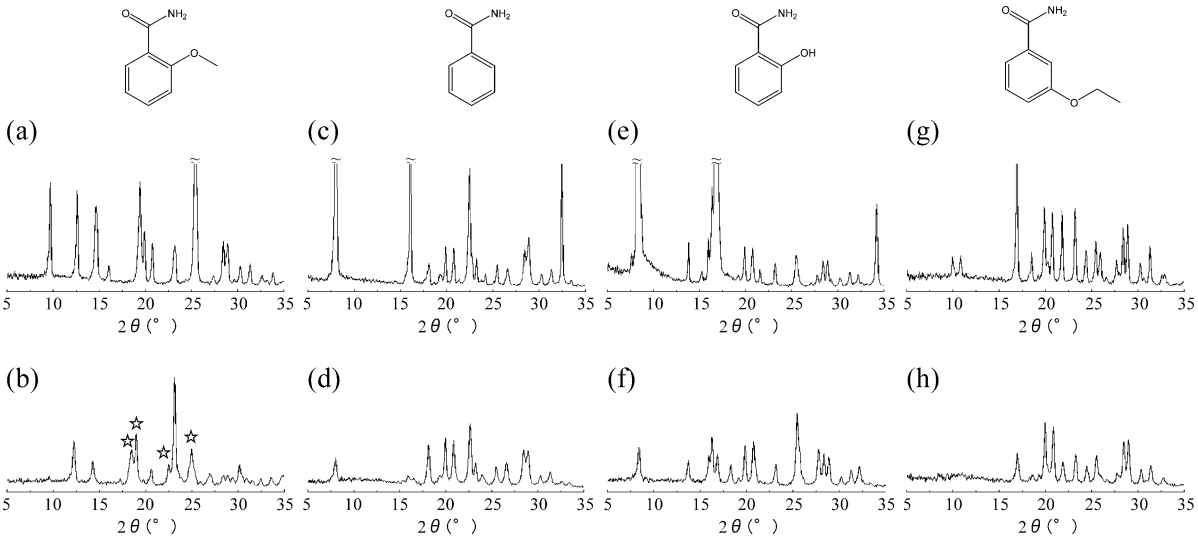

Fig. 9. Effect of Chemical Structure of Drugs on the Grinding-Induced Equimolar Complex Formation with Thiourea

Molar ratio of thiourea : drug was 1 : 1. GMs were ground for 30 min. (a) Thiourea–2-methoxybenzamide PM; (b) thiourea–2-methoxybenzamide GM; (c) thiourea–benzamide PM; (d) thiourea–benzamide GM; (e) thiourea–salicylamide PM; (f) thiourea–salicylamide GM; (g) thiourea–3-ethoxybenzamide PM; (h) thiourea–3-ethoxybenzamide GM.

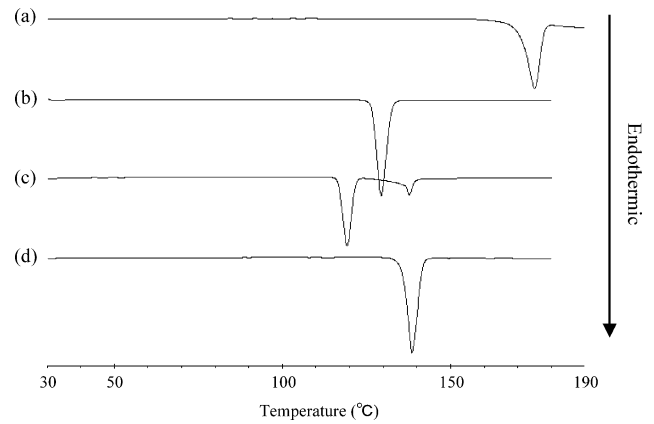

Fig. 10. DSC Curves of Thiourea/2-Methoxybenzamide Systems

Molar ratio of thiourea/2-methoxybenzhamide was 1 : 1. Heating rate: 5 °C/min, sealed pan.

(a) Thiourea; (b) 2-methoxybenzamide; (c) PM; (d) GM (40 min).

N–H···O. Not only intermolecular hydrogen bondings between thiourea and ethenzamide but also an intramolecular N–H···O hydrogen bonding in ethenzamide would play an important role for the equimolar complex formation. From the comparison of chemical structures of co-ground compounds, oxygen at 2-position seemed necessary for the complex formation, even salicylamide was exceptional, suggesting that 2-alcoxybenzamide structures should be required for guest molecules to form equimolar complex with thiourea.

Changes in the thermal behavior of thiourea–2-methoxybenzamide equimolar GMs were also shown in Fig. 10. Thermal behavior of PMs and GMs of thiourea with other drugs shown in Fig. 9 did not show any apparent peak changes (data not shown). Intact 2-methoxybenzamide showed endothermic peaks due to the fusion at 127 °C and the PM showed an endothermic peak around 138 °C, which was also observed in thiourea–2-methoxybenzamide GMs. Including the change of 2-methoxybenzamide endothermic peak depending on the grinding time, thermal behavior of thiourea–2-methoxybenzamide system was consistent with that of thiourea–ethenzamide system as shown in Fig. 6, indicating the equimolar complex formation.

In the case of urea, equimolar complex formation has been reported with α,ω-dinitriles,[19] maleic acid and phthalic acid.[20] In maleic acid and phthalic acid equimolar complexes, urea and drug molecules were arranged alternately. In the case of α,ω-dinitriles, the alternately-arranged molecules formed layered structure through N–H_{anti}···O hydrogen bondings between urea molecules. However, three dimensional crystal structures of urea–guest equimolar complex was completely different form those of thiourea–ethenzamide equimolar complex. These findings would give new insights into the design of three-dimensional crystal structure of urea and thiourea compounds.

Conclusion

Grinding-induced equimolar complex formation between thiourea and ethenzamide was demonstrated. The complex mode was completely different from that of tunnel-type thiourea inclusion complexes that have been reported. Chemical structure of the drug molecules was found to be a most important factor for the equimolar complex formation with thiourea. The cleavage of N–H···S intermolecular hydrogen bondings between thiourea molecules and formation of new intermolecular hydrogen bondings between thiourea and ethenzamide molecules contributed to the equimolar complex formation. Concerning about the preparation procedure, grinding was regarded as an advantageous methodology to prepare equimolar complexes of thiourea.

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