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Synthesis, structure and temperature-depended 2D IR correlation spectroscopy of an organo-bismuth benzoate with 1,10-phenanthroline

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ABSTRACT

An organo-bismuth benzoate with phen as auxiliary ligand, $[Bi(phen)(C_6H_5COO)(C_6H_4COO)]$ (**1**) (phen = 1,10-phenanthroline) has been hydrothermally synthesized from bismuth nitrate, 2-mercaptonbenzoic acid with phen as auxiliary ligand and characterized by single-crystal X-ray diffraction, elemental analyses, PXRD, IR spectra, TG analyses, temperature-depended 2D-IR COS (two-dimensional infrared correlation spectroscopy). Interestingly, benzoate anions in **1** came from the desulfuration reaction of 2-mercaptonbenzoic acid under hydrothermal condition. Compound **1** is a discrete organo-bismuth compound with benzoate and phen ligands. The offset face-to-face π-π stacking interactions and C–H···O hydrogen bonds link the isolate complex into a 3D supramolecular network. The temperature-depended 2D-IR COS indicates that the stretching vibrations of C=C/C=N of aromatic rings and C=O bonds are sensitive to the temperature change.

1. Introduction

The original two-dimensional (2D) correlation spectroscopy was first proposed by Noda in 1986 [1,2]. Then, Noda developed the generalized 2D correlation spectroscopy allowing one to produce synchronous or asynchronous 2D correlation maps from systematic variations of spectra induced by different types of external perturbations such as light, heat, electricity, magnetism, chemistry or mechanical force [3–10]. Recently, 2D correlation spectroscopy has been attracted enormous attention from the points of both basic science and a variety of applications and has been become a very versatile and broadly applicable technique [11–13]. This novel 2D technique can simplify complex spectra consisting of many overlapped peaks and enhance spectral resolution by spreading peaks along the second dimension, allowing one to exact useful information that cannot be obtained straightforwardly from one-dimensional spectra.

Many applications of the generalized 2D correlation spectroscopy have been reported, including IR [5,6,14], near-IR [15,16], Raman [6,17], UV–vis [18,19], and fluorescence spectroscopy [20,21]. 2D IR correlation spectroscopy is the most widely used. 2D infrared correlation spectroscopy could not only enhance spectral resolution and identify over-lapped peaks but also help elucidate the interaction relationship between functional groups. In this paper, we present a 2D IR correlation spectroscopy on the weak molecular interactions.

Disulfide bond formation has been usually observed in thioate systems under hydrothermal or solvothermal conditions [22], such as 2-mercaptonbenzoic acid or others. However, *in situ* desulfuration reaction of 2-mercaptonbenzoic acid to produce metal benzoate complexes is scarcely found under hydrothermal or solvothermal conditions [23,24]. Recently, our group have reported the *in situ* oxidation and desulfuration reactions of 2-mercaptonbenzoic acid to produce sulfonate-metal complexes or metal sulfate under hydrothermal or solvothermal conditions [25]. Herein, we report the synthesis, structure and temperature-dependant 2D IR correlation spectroscopy of a bismuth benzoate with phen as auxiliary ligand: $[Bi(phen)(C_6H_5COO)(C_6H_4COO)]$ (**1**), involving *in situ* desulfuration reaction of 2-mercaptonbenzoic acid. Complex **1** is a discrete organic-bismuth compound with benzoate and phen ligands. The offset face-to-face π-π stacking interactions and C–H···O hydrogen bonds link the isolate complex into a 3D

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Table 1
Crystal data and structure refinement for **1**.

Compound	**1**
Empirical formula	$C_{26}H_{17}O_4N_2Bi$
Formula weight	630.40
Crystal system,	Monoclinic
space group	$P2_1/c$
a (Å)	10.552(3)
b (Å)	26.026(6)
c (Å)	8.229(2)
α (°)	90
β (°)	108.106(4)
γ (°)	90
V (Å^3)	2148.0(9)
D_c (g/cm^3)	1.949
Z	4
F(000)	1208
μ (mm^{-1})	8.246
Reflns collected/unique	17757/4944
R_{int}	0.0495
GOOF on F^2	1.004
R_1[a], wR_2[b] (all data)	0.0419, 0.1079
R_1, wR_2 ($I > 2\sigma(I)$)	0.0371, 0.1025

[a] $R_1 = \sum||F_0|-|F_c||/\sum|F_0|$.
[b] $wR_2 = \{\sum[w(F_0^2-F_c^2)^2]/\sum[w(F_0^2)^2]\}^{1/2}$.

supramolecular network. In this study, a 2D IR correlation spectroscopy was used to investigate the molecular interactions between benzoate and phen ligands in **1**.

2. Experimental

2.1. Reagents and general techniques

All chemicals were of AR grade commercially available and used without further purification. The elemental analyses for C, H, N, O were performed with an Elementar Vario EL III elemental analyzer. Infrared spectra were recorded on a Perkin-Elemer Spectrum 2000 FT-IR Fourier transform spectrometer with pressed KBr pellets in the range of 400–4000 cm^{-1}. Powder X-ray diffraction (PXRD) patterns were acquired on D/MXA-2500 diffractometer measurements using Mo-Kα radiation in the ambient environment. Thermo-gravimetric analyses were recorded in Perkin–Elmer TGA 7 thermal analyzer at a heating rate of 10 °C/min. IR spectra were recorded in the range of 4000–400 cm^{-1} on a Perkin–Elmer FT-IR spectrum 2000 spectrometer using KBr pellets. In order to get the dynamic IR spectra, the temperature was varied from 50 to 120 °C at an interval of 10 °C by a Portable programmable temperature controller (Model 50-886, Love Control Corporation). 2D IR correlation spectra were obtained by treatment of the series of dynamic spectra with 2D IR correlation analysis software provided by Tsinghua University.

Table 3
Parameters of aromatic–aromatic Interactions for compound **1**.

Two rings	Dihedral angle	Cent-to-cent distance	Symmetry code
Cg(6) > Cg(8)	4.432°	3.679 Å	2-x,-y,2-z
Cg(8) > Cg(6)	4.432°	3.679 Å	2-x,-y,2-z

Cg(6): C(2) > C(3) > C(4) > C(5) > C(6) > C(7).
Cg(8): C(18) > C(19) > C(20) > C(21) > C(25) > C(26).

Table 4
Selected hydrogen bonds for **1**.

D–a···a	d(D–H) (Å)	d(H···A) (Å)	d(D···A)(Å)	<DHA(°)
C17–H17···O1#1	0.93	2.60	3.520(9)	171
C19–H19···O3#1	0.93	2.50	3.417(9)	168
C20–H20···O4#2	0.93	2.53	3.339(11)	166

Symmetry codes: #1,1 + x, y, z; #2, 1 + x,1/2- y,1/2 + z.

2.2. Synthesis of [Bi(phen)(C_6H_5COO)(C_6H_4COO)] (**1**)

A mixture of 2-mercaptobenzoic acid (0.1233 g, 0.8 mmol), 1,10-phenanthroline (0.1585 g, 0.8 mmol), $Bi(NO_3)_3.5H_2O$ (0.0970 g, 0.2 mmol), Nd_2O_3 (0.0672 g, 0.2 mmol) and 12 ml H_2O was stirred for 30 min and the pH was adjusted to 3.0 with HNO_3, then sealed in a 23 ml Teflon-lined autoclave. The mixture was heated to 160 °C for 3 days. Accordingly brown columnar crystals were isolated by filtering, washed with distilled water and dried in air. Yield: 62% (based on $Bi(NO_3)_3.5H_2O$). Calc for $C_{26}H_{17}N_2O_4Bi$ (**1**): C, 49.68; H, 2.76; N, 4.34; O, 10.35 wt%; Found: C, 49.49; H, 2.70; N, 4.44; O, 10.15 wt%. IR (KBr, cm^{-1}): 3050(m), 1643(s), 1516(s), 1413(s), 1292(s), 1136(w), 858(s), 746(m), 719(s), 686(m), 428(m).

2.3. X-ray crystallographic determination

Suitable single crystals were selected and mounted on a glass fiber. All data were collected at room temperature on a Rigaku Satum 724 CCD diffractometer with graphite-monochromated MoKα ($\lambda = 0.71073$ Å) radiation in the ω scanning mode at room temperature. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL-97 program package [26]. Crystallographic data and structure refinements for **1** are summarized in Table 1 and selected bond distances and angles, parameters of aromatic–aromatic Interactions and selected hydrogen bonds are listed in Tables 2–4, respectively.

3. Results and discussion

3.1. In situ reaction analysis

Fortunately, the *in situ* desulfuration reaction of 2-

Table 2
Selected bond distances (Å) and angles (deg) for **1**.

Bond	Dist.(Å)	Bond	Dist.(Å)	Bond	Dist.(Å)
Bi(1)-C(10)	2.200(5)	Bi(1)-O(1)	2.477(5)	Bi(1)-N(1)	2.566(5)
Bi(1)-O(3)	2.282(4)	Bi(1)-O(2)	2.457(5)	Bi(1)-N(2)	2.571(5)
Angle	(°)	Angle	(°)	Angle	(°)
C(10)-Bi(1)-O(3)	75.80(17)	O(3)-Bi(1)-N(1)	141.52(17)	O(3)-Bi(1)-C(1)	107.61(17)
C(10)-Bi(1)-O(2)	85.84(19)	O(2)-Bi(1)-N(1)	76.93(16)	O(2)-Bi(1)-C(1)	26.68(15)
O(3)-Bi(1)-O(2)	132.84(16)	O(1)-Bi(1)-N(1)	129.42(17)	O(1)-Bi(1)-C(1)	26.31(16)
C(10)-Bi(1)-O(1)	85.19(19)	C(10)-Bi(1)-N(2)	84.77(19)	N(1)-Bi(1)-C(1)	103.45(18)
O(3)-Bi(1)-O(1)	82.09(16)	O(3)-Bi(1)-N(2)	80.53(18)	N(2)-Bi(1)-C(1)	165.37(17)
O(2)-Bi(1)-O(1)	52.98(15)	O(2)-Bi(1)-N(2)	141.17(16)	N(1)-Bi(1)-N(2)	64.74(18)
C(10)-Bi(1)-N(1)	84.66(19)	O(1)-Bi(1)-N(2)	161.61(17)	C(10)-Bi(1)-C(1)	85.54(19)