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Synthesis and characterization of amantadinium iodoacetatobismuthate, a hybrid compound with mixed iodide–carboxylate anions

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Experimental Details

Synthesis. Used as starting materials were Bi (granules, 99.99%), I_2 (analytical grade), aminoadamantan (analytical grade), glacial acetic acid (analytical grade), acetone (pure grade). BiI_3 was synthesized from the elements, details of this procedure are described elsewhere.[S1] For the preparation of **1**, 40 ml of acetone was added to the starting reagents taken in a molar ratio of BiI_3: aminoadamantan = 1:2 with a total weight of 0.2 g, then 2 ml of glacial acetic acid was added to the solution. The flask with the resulting red solution was left for evaporation in open air for a day to yield orange-red well-shaped crystals. These crystals were separated by filtration and dried at room temperature.

Powder X-ray diffraction analysis (PXRD) was performed on the Imaging Plate Guinier Camera (Huber G670, Cu-$K_{\alpha 1}$ radiation, $\lambda = 1.540598$ Å) with the 2θ angles ranging from 3 to 100° with a 0.005° increment. The data were collected by scanning the image plate 4 times with an exposure time of 1200 s at room temperature. For the analysis, crystals of **1** were finely crushed in an agate mortar, and the resulting powder was fixed on a holder.

Raman spectroscopy. Raman spectrum of **1** was recorded on a Renishaw In Via spectrometer with the laser wavelength of $\lambda = 632.8$ nm (Ar, 20 mW) with capacity varied via ND (neutral density) filters in an interval of 0.00005–100%. Sample investigation was performed in the back scattering geometry using a confocal microscope Leica DMLM (100′ lens) at room temperature in air. Focus distance was 250 mm, and the size of laser beam was 20 μm. The CCD-camera (1024×368 pixels) was used as a detector. The scale calibration was done using monocrystalline silica (521.5 cm^{-1}) as a standard sample. WiRE 3.4 software was used for data processing.

Thermal analysis. Thermogravimetric analysis was performed using a NETZSCH 209 F1 Libra thermobalance. Calibration was performed with $CaC_2O_4 \cdot 2H_2O$ in order to make sure that the accuracy of mass detection was better than 0.1%. The sample was heated in an alumina crucible under dry nitrogen flow up to 450 ºC with the ramp rate of 10 K·min^{-1}. The NETZSCH Proteus Thermal Analysis program was used for the data processing.

Optical Spectroscopy. Optical diffuse reflectance spectra were recorded using a UV-viz spectrometer Perkin-Elmer Lambda 950 with an attached diffuse reflectance accessory. Measurements were performed at 298 K in the spectral range of 250–1200 nm, with the scanning rate of 2 nm/s using finely ground polycrystalline samples. The data were processed using the Kubelka-Munk theory approximation and linearized in the $[(k/s)\cdot h\nu]^{1/2} - (h\nu)$ coordinates with $h\nu$ along the x axis and $[(k/s)\cdot h\nu]^{1/2}$ along the y axis, where k is the absorption coefficient, s is the scattering coefficient, and h is the Planck constant.[S2] The k/s relation known as a remission function was calculated according to the literature as $k/s = (1-R)^2/2R$, where R is the absolute diffuse reflectance.[S3] Extrapolation to $k = 0$ gives an approximate value of optical E_g of the material.

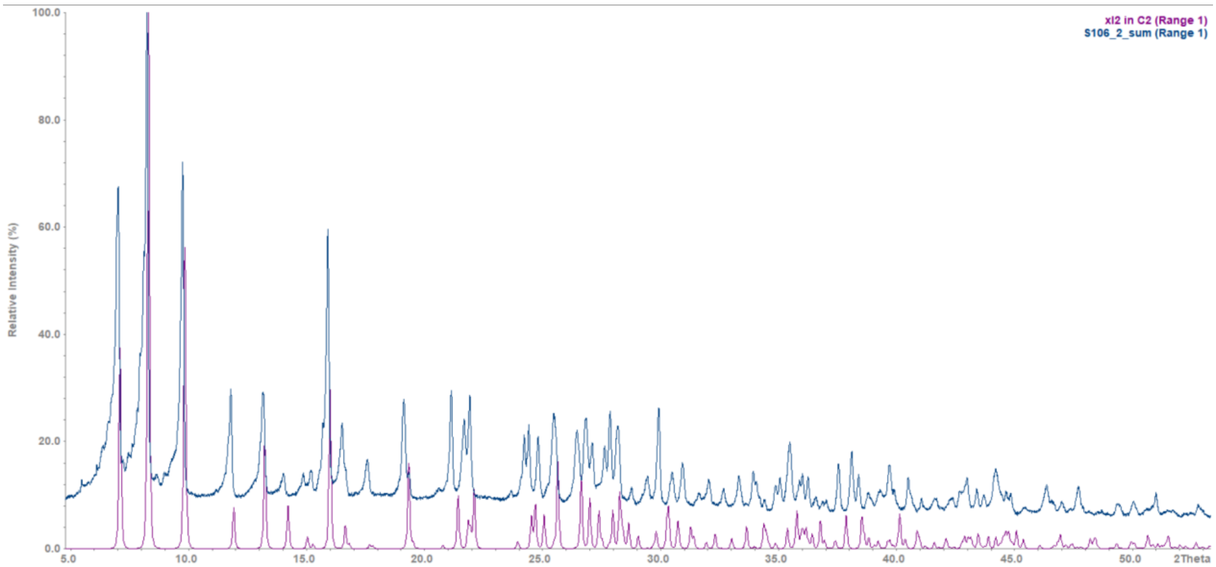

Figure S1. X-ray powder diffraction pattern for **1** Experimental profile (measured at room temperature), blue; calculated from the crystal data (measured at 100K), magenta.

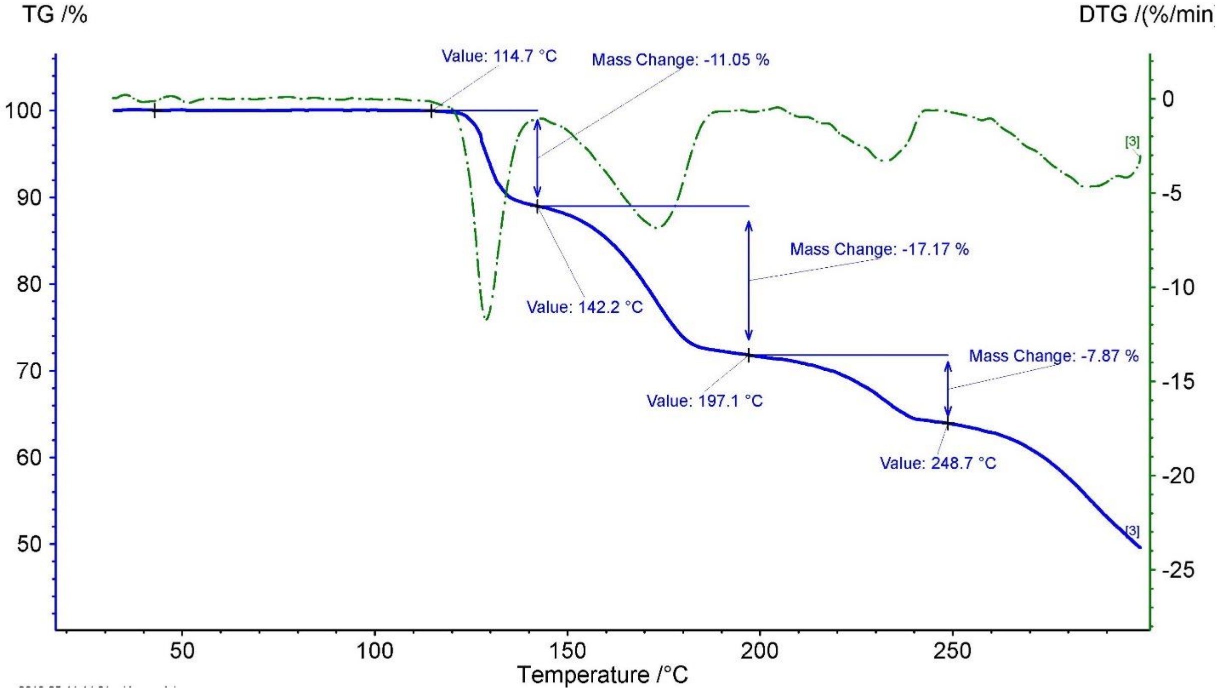

Figure S2. Thermal analysis data for **1**.

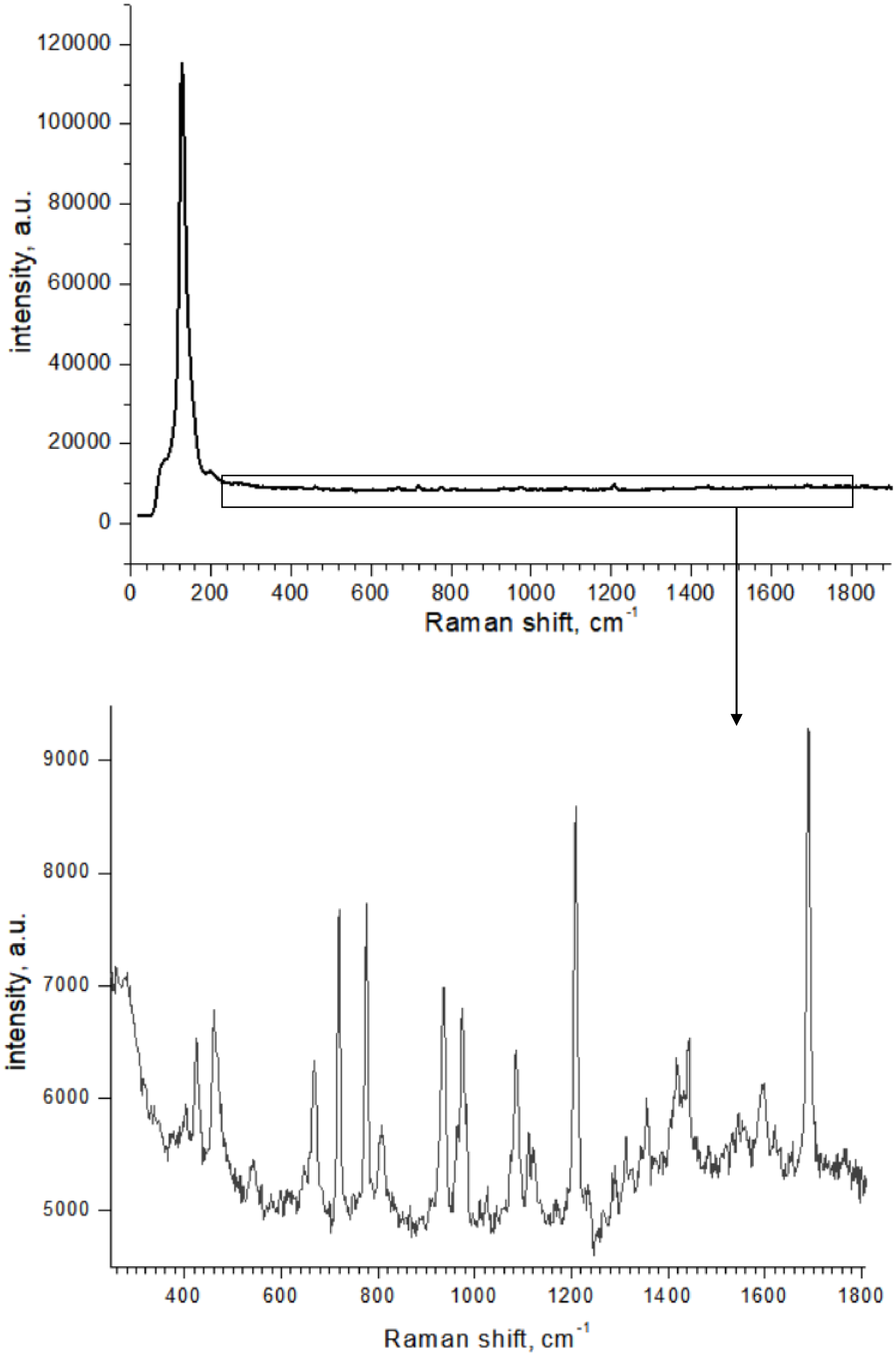

Figure S3. Full experimental Raman spectrum data for **1** (top), and a blow-up of its selected part (bottom)

Table S1. Assignment of Raman shifts in the 400-1700 cm^{-1} spectral window

Amantadinium in solid[S4]		Acetate[S5]		Acetone[S6]		Compound **1**
400w	Skeletal motions					398
421w	Skeletal motions					424
461m	Skeletal motions					464
552w	δ(CCN)	550	ν(Bi-O)			542
646w	Skeletal motions					667
721s	$\rho(CH_2)$, ν(CC)					716
781w	ν(CC), $\rho(CH_2)$, $\omega(CH_2)$					776
		800	$\delta(COO^-)$			807
933w	ν(CC), $\omega(NH_2)$, $\rho(CH_2)$, δ(CH)					935
986s	ν(CC), $\rho(NH_2)$, $\rho(CH_2)$					974/982
						1026
1092m	$\omega(CH_2)$, $t(CH_2)$, δ(CH)					1089
1103m	$t(CH_2)$, ν(CN)					1115
1218vs	$\omega(CH_2)$, δ(CH), ν(CC)					1206
1259w	ν(CN), $t(CH_2)$, δ(CH) ν(CC)					1240
						1265
1291w	$t(CH_2)$					1290
1317w	ν(CN), $\delta(NH_2)$, $\delta_s(CH_2)$, δ(CH)	1400-1300	ν_s (COO^-)			1314
1327w	$\delta_s(CH_2)$					1327
						1339
1350vw	ν(CN), $t(NH_2)$, δ(CH)			1360-1355	δ (CH_3-(C=O)-CH_3)	1356
1432-1473	$d(CH_2)$			1442m	$d(CH_2)$	1416-1442
		1650-1550	$\nu_{asymm}(COO^-)$			1596 1556
				1720-1740 cm^{-1}	C=O	1690

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