Supporting Information

Structural Identification for the Reaction of Chlorosulfonic Acid with tertiary N-donor Ligand – Ionic Liquid or Zwitterionic Compound?

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EXPERIMENTAL DETAILS

Chemicals: Chlorosulfonic acid ($ClSO_3H$; 99% purity) was purchased from Sigma-Aldrich. Dichloromethane (DCM; 99.9% purity, extra dry) and 1-methylimidazole (C_1im, 99% purity) were purchased from ACROS Organics.

Characterization techniques

The NMR (^1H, ^{13}C) spectra were obtained utilizing a Bruker AVIII 500 with cryoprobe NMR spectrometer. Each sample was dissolved in dimethyl sulfoxide-d_6 (DMSO-d_6) solvent and loaded neat in a NMR tube. Elemental analyses were performed by Midwest Microlab, Inc. (Indianapolis, IN).

Single-crystal x-ray diffraction (SCXRD): Single crystals of [C_1im-SO_3] were subjected to low temperature X-ray structural analysis. Sets of unique diffraction data [2222 [C_1im-SO_3] reflections using 1.0°-wide ω- or ϕ-scan frames with scan times of 4-8 seconds] were collected[1] for single-domain crystals of compound using monochromated CuKα radiation (λ= 1.54178 Å) on a Bruker Proteum Single Crystal Diffraction System with dual CCD detectors and associated Helios high-brilliance multilayer optics and a shared Bruker MicroSTAR microfocus Cu rotating anode x-ray source operating at 45kV and 60mA. SCXRD was collected with a Platinum 135 CCD detector at a crystal-to-detector distance of 80 mm. The integrated data[2] were corrected empirically for variable absorption effects using equivalent reflections. The Bruker software package SHELXTL was used to solve both structures using "direct method" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL XL v2014 software package.[3] Final crystallographic details are summarized in **Table S1**.

The final structural model incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. All hydrogen atoms for both compounds were located using a difference Fourier analysis and incorporated into the structural model as independent isotropic atoms whose parameters were allowed to vary in least-squares refinement cycles.

Powder x-ray diffraction (PXRD): Room-temperature PXRD patterns of solid material for the compound were obtained with the Apex II detector on the Bruker Proteum Single Crystal Diffraction System. The powders were mixed with a small amount of Paratone N oil to form a paste that was placed in a small (< 0.5 mm.) nylon cryoloop and mounted on a goniometer head. The specimen was then positioned at the goniometer center-of-motion by translating it on the goniometer head. Three overlapping 1-minute 360º φ-scans were collected using the Bruker Apex2 v2014.11-0 software package[1] with the detector at 2θ = 30º, 60º and 90º using a sample-to-detector distance of 50.0 mm. These overlapping scans were merged and converted to a .RAW file using the Pilot/XRD2 evaluation option that is part of the APEX2 v2014.11-0 software package. This RAW file was then processed using the Bruker EVA powder diffraction software package.[4] Fractional atomic coordinates from single crystal structure determinations were used with the public-domain Mercury software package[5] to calculate PXRD for the [C_1im-SO_3] ZI salt.

Thermogravimetric analysis-Differential scanning calorimetry (TGA-DSC): Thermal properties for ZI were analyzed using TGA and DSC. Thermal decomposition temperature and melting point were determined using TA Instruments SDT Q600 under N_2 atmosphere. The analyses were conducted following a heating rate of 5 °Cmin^{-1} up to 600 °C under nitrogen flow.

Table S1. Crystal data and structure refinement for [C_1im-SO_3] ZI salt.

	[C_1im-SO_3]
Empirical formula	$C_4H_6N_2O_3S$
Formula weight	162.17
Temperature	200(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
a	7.0495(2) Å
b	8.9099(3) Å
c	10.4603(3) Å
a	90°
β	91.744(2)°
γ	90°
Volume	656.71(3) $Å^3$
Z	4
Density (calculated)	1.640 g/cm^3
Absorption coefficient	4.015 mm^{-1}
F(000)	336
Crystal size	0.09 x 0.05 x 0.02 mm3
Theta range for data collection	6.53 to 67.98°
Index ranges	$-8\leq h\leq 7$, $-10\leq k\leq 10$, $-9\leq l\leq 12$
Reflections collected	3439
Independent reflections	1154 [R_{int} = 0.030]
Completeness to θ=66.0°	98.0 %
Absorption correction	Multi-scan
Max. and min. transmission	1.000 and 0.840
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1154 / 0 / 115
Goodness-of-fit on F^2	1.044
Final R indices [I>2σ(I)]	R_1 = 0.033, wR_2 = 0.087
R indices (all data)	R_1 = 0.037, wR_2 = 0.090
Largest diff. peak and hole	0.24 and -0.25 $e^-/Å^3$

REFERENCES

[1] Data Collection: SMART Software in APEX2 v2014.11-0 Suite. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.

[2] Data Reduction: SAINT Software in APEX2 v2014.11-0 Suite. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.

[3] Refinement: SHELXTL Software in APEX2 v2014.11-0 Suite. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.

[4] PXRD Processing: EVA Software in Bruker DIFFRAC Suite. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.

[5] Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; Van de Streek, J.; Wood, P. A. Mercury CSD 2.0 - new features for the visualization and investigation of crystal structures. *J. Appl. Cryst*. **2008**, *41*, 466-470.