Electronic Supporting Information (ESI)

Synthesis, crystallographic characterization and structural relations of Cu[SeCN]

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Contents

1. Experimental section

1.1. General remarks

General synthetic methods. All reactions and manipulations were performed under in air.

Copper sulphate pentahydrate (Honeywell, puriss.) and sodium sulphite (Grüssing, 98%, anhydrous for analysis) were used from the university storage, the purity was verified by PXRD. Potassium selenocyanate was prepared by literature procedure.[1]

Elemental analyses were performed by the in-house service personnel. CHN(S) analyses were performed on a *CHNS(S)-Analysator vario MICRO CUBE* (Elementar).

TGA/DSC measurements were performed by the in-house service personnel under nominally dry nitrogen atmosphere (glovebox) using a *DSC-TGA 3* (Mettler Toledo) device. A sample amount of 9.4311 mg was used. The heating rate was 5,00 K/min with a N_2-flow rate of 30 ml/min. A 70 µL aluminium crucible with a bore hole in the lid was used as sample container.

Raman spectroscopy was performed on a microscope laser Raman spectrometer (Jobin Yvon, 4 mW, equipped with a HeNe laser with an excitation line at $\lambda = 532$ nm, $10 \cdot 5$ s accumulation time). The sample was provided in a flame-sealed glass capillary with 0.3 mm inner diameter (Hilgenberg, Malsberg, Germany).

1.2. Synthesis of Cu[SeCN]

Cu[SO_4] · 5 H_2O (500 mg, 2.0 mml, 1.2 eq.) was dissolved in 30 mL warm (70 °C) deionized water and combined with 0.5 mL of concentrated hydrochloric acid. Na_2[SO_3] (160 mg, 1.7 mmol, 1.0 eq.) was dissolved in 20 mL warm deionized water (70 °C), combined with 1 mL of diluted (8:1) hydrochloric acid, and added to the solution of $CuSO_4$ · 5 H_2O. The resulting blue solution was then precipitated with the solution of K[SeCN] (303 mg, 2.1 mmol, 1.2 eq.) in 20 mL deionized water. The resulting brownish suspension was filtered through paper filter, washed with 50 ml portions of H_2O, ethanol and diethyl ether, and dried in desiccator under reduced pressure and over silica gel. The product was obtained in form of a brown microcrystalline powder (254 mg, 1.5 mmol, 75%) suitable for powder X-ray diffraction.

Elemental analysis for Cu[SeCN] found % (calc. %): C 7.37 (7.13), N 8.23 (8.31).

2. Crystallographic data for Cu[SeCN]

Powder X-ray diffractometry: Powder X-ray diffraction patterns were recorded on a STADI MP (STOE, Darmstadt) powder diffraction system equipped with mirror monochromatized Cu-$K_{\alpha 1}$ radiation (λ = 1.54175 Å) and a silicon-strip MYTHEN 1K detector. Data were collected at room temperature in transmission mode (Debye-Scherrer geometry). The powder samples were ground in agate mortars. In case of air-sensitive compounds the samples were flame-sealed in glass capillaries (inner diameter: 0.3 mm, Hilgenberg, Malsberg, Germany). For additional details see Table S1.

High-temperature powder X-ray diffraction: Powder X-ray diffraction patterns were recorded on a STADI MP (STOE, Darmstadt) powder diffraction system equipped with mirror monochromatized Cu-$K_{\alpha 1}$ radiation (λ = 1.54175 Å), a Silicon-strip MYTHEN 1K detector and a STOE capillary furnace. Data were collected at in transmission mode (Debye-Scherrer geometry). The powder samples were ground in agate mortars and flame sealed in a quartz capillary (inner diameter: 0.3 mm, Hilgenberg, Malsberg, Germany). This capillary was then placed inside an open quartz capillary (inner diameter: 0.7 mm, Hilgenberg, Malsberg, Germany) to facilitate rotation of the sample.

Rietveld refinements[2] were performed with the TOPAS 7.0 program package.[3] The structural models derived from single-crystal X-ray data of Cu[SCN] (CCDC 1590744[4]kab) were used as starting points for the refinements. Background functions were modelled using shifted Chebyshev polynomials, profile functions were described with the modified Thompson-Cox-Hastings pseudo-Voigt "TCHZ" function as implemented in TOPAS. For additional details see Table S1.

Table S1. Selected powder X-ray data collection and refinement parameters for Cu[SeCN] measured at 298 K.

	Cu[SeCN]
Formula	C N Cu Se
CCDC	2405901
Fw / g mol^{-1}	168.52
Crystal system	orthorhombic
Space group	*Pbca* (no. 61)
a / Å	7.6625(1)
b / Å	6.9628(1)
c / Å	11.2821(2)
α / °	90
β / °	90
γ / °	90
V / Å^3	601.93(1)
Z	8
Radiation, λ / Å	1.54175
T / K	298(2)
ρ_{calc} / g cm^{-3}	3.720
R_{wp} / %	9.71
R_{p} / %	6.52
R_{Bragg} / %	5.18
GoF	1.53
Starting angle measured / ° 2θ	5
Final angle measured / ° 2θ	90
Starting angle refined/° 2θ	5
Final angle refined/ ° 2θ	90
Step width/ ° 2θ	0.015
Refined Parameters	38
Background Parameters	12
Profile Parameters	9

3. Details on quantum mechanical calculations

Periodic quantum-chemical calculations were carried out for Cu[SeCN] with the PBE0 hybrid density functional theory method (DFT-PBE0).[5,6] All calculations were performed out with the CRYSTAL17 program package.[7] Triple-zeta-valence + polarization (TZVP) level basis sets were applied for C, N, Se and Cu. The basis sets for C, N and Se have been previously derived from the Karlsruhe def2 basis sets[8–10], and the basis sets for Cu from Peintinger *et al*.[11] Reciprocal space was sampled by a Monkhorst-Pack-type *k*-mesh (4 × 3 × 6).[12] For the evaluation of the Coulomb and exchange integrals (TOLINTEG), tolerance factors of 8, 8, 8, 8, 16 were used for all calculations. Atomic positions and lattice parameters were fully optimized under consideration of the space-group symmetry. Default DFT integration grids and optimization convergence thresholds were applied in all calculations. The harmonic vibrational frequencies, Raman intensities were obtained as implemented in CRYSTAL.[13–16] Raman and intensities were calculated for a polycrystalline powder sample (total isotropic intensity in arbitrary units). The Raman spectra were obtained by using a pseudo-Voigt band profile (50:50 Lorentzian:Gaussian) and an FWHM of 8 cm^{-1} and were simulated taking into account the experimental setup ($T = 298.15$ K, $\lambda = 532$ nm). Bands were assigned by visual inspection of the normal modes with the Jmol program package on the website http://crysplot.crystalsolutions.eu/ .[17,18]

Table S2: Optimized atom positions for Cu[SeCN].

Atom	*x*	*y*	*z*
Cu	−0.1535	0.1754	0.3098
Se	−0.3806	0.1439	−0.2902
N	−0.2361	0.1134	0.4636
C	−0.2914	0.1234	−0.4402

Table S3: Band assignment for the calculated Raman spectra (>50 cm^{-1}) of Cu[SeCN]. The irreducible representations are given for the groups of the respective space group types of the crystal structures.

ν (calculated) [cm^{-1}]	ν (observed) [cm^{-1}]	irrep.	assignment
13.83	not collected	A_g	δ = lattice vibration
44.56		A_g	δ = lattice vibration
51.03	low resolution	B_{1g}	δ = lattice vibration
54.84		B_{1g}	δ = lattice vibration
56.23		B_{2g}	δ = lattice vibration
59.35		A_g	δ = lattice vibration
68.39		B_{3g}	δ = lattice vibration
82.38		B_{3g}	δ = lattice vibration
89.01		B_{2g}	δ = lattice vibration
99.84		A_g	δ = lattice vibration
103.22		B_{2g}	δ = lattice vibration
115.88		B_{3g}	δ = lattice vibration
121.33		B_{1g}	δ = lattice vibration
122.72		B_{3g}	
130.46		B_{2g}	δ = lattice vibration
134.62		A_g	δ = lattice vibration
135.41		B_{1g}	
142.09		B_{2g}	δ = lattice vibration
152.82		A_g	δ = lattice vibration
166.17		B_{1g}	
175.66		B_{3g}	δ = lattice vibration
177.55		B_{2g}	
185.68		B_{1g}	δ = lattice vibration
189.80		B_{3g}	δ = lattice vibration
198.90		B_{1g}	δ = lattice vibration
204.47		B_{2g}	δ = lattice vibration
207.00		A_g	δ = lattice vibration
225.92		B_{3g}	δ = lattice vibration
239.65		B_{3g}	δ = lattice vibration
245.27		A_g	
251.02		B_{2g}	
254.46		B_{1g}	
390.33	407	A_g	ν = wagging vibration of $[\mathrm{SeCN}]^-$
392.98		B_{2g}	
399.24	low resolution	B_{1g}	
403.69		B_{3g}	
415.34		A_g	ν = wagging vibration of $[\mathrm{SeCN}]^-$
429.76		B_{2g}	
438.79		B_{1g}	
443.08		B_{3g}	
630.95	603	B_{3g}	ν_s = symmetric stretching vibration of $[\mathrm{SeCN}]^-$
633.00		B_{2g}	
633.03		B_{1g}	
636.08		A_g	
2262.34	line broadening / shoulder	B_{1g}	ν_{as} = antisymmetric stretching vibration of $[\mathrm{SeCN}]^-$
2262.71		B_{3g}	
2281.98	2165	B_{2g}	
2282.71		A_g	

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