

Supporting information for the paper:

**Effect of chalcogen bond on the packing and coordination geometry in hybrid
organic-inorganic Cu(II) networks.**

Emmanuele Parisi,^a Antonio Carella,^a Fabio Borbone,^a Fabio Chiarella,^b Francesco Silvio Gentile^a and Roberto Centore^a

Corresponding authors: Emmanuele Parisi and Roberto Centore.

a. Department of Chemical Sciences, University of Naples "Federico II", 80126, Naples

b. CNR-Spin, Piazzale Tecchio 80, 80125, Napoli

e-mail: emmanuele.parisi@unina.it, roberto.centore@unina.it

Thermogravimetric analysis

In Figure S1 are reported the thermogravimetric analysis (TGA) of the four compounds. TGA was performed with a PerkinElmer TGA 4000 apparatus.

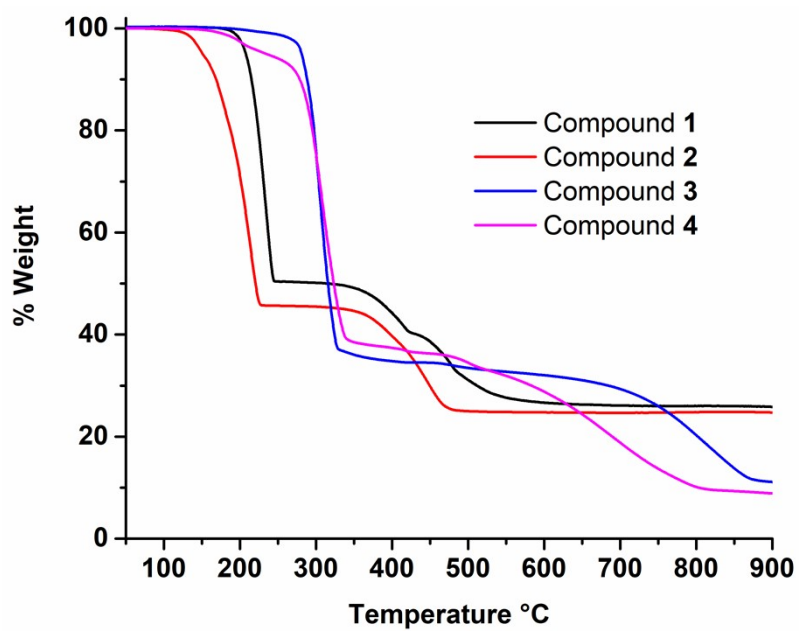


Fig. S1. TGA analysis of the four compounds in air. Heating rate 10 K/min.

Powder X-ray diffraction analysis

X-ray powder diffraction profiles were obtained with Ni filtered CuK α radiation using an Empyrean diffractometer by Malvern Panalytical operating in the reflection geometry with continuous scans of the 2 θ angle and scanning rate of 0.02 degree/s. Experimental PXRD spectra are compared with spectra calculated from the single crystal X-ray crystal structure (Figures S2- S5). The calculated spectra were produced by the Mercury program.¹

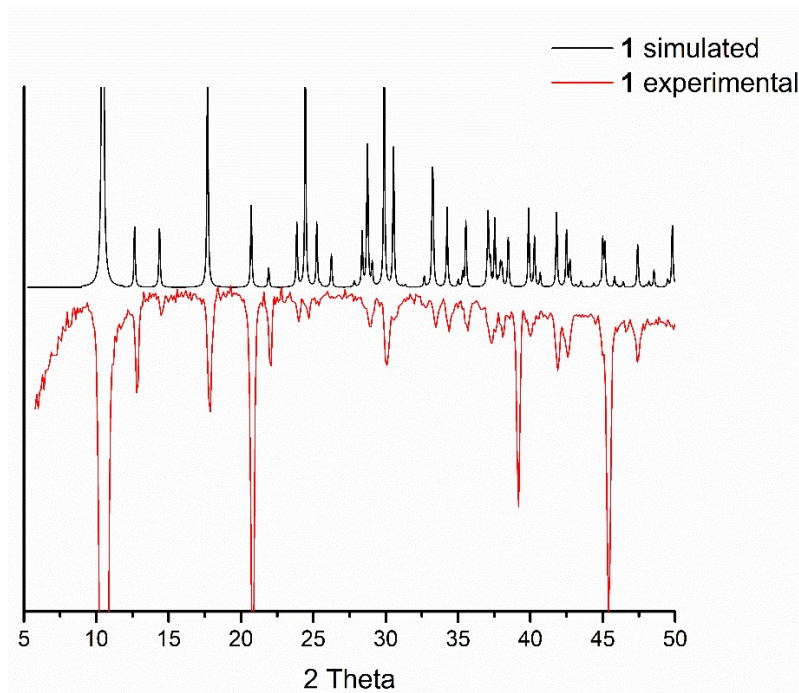


Fig. S2. Experimental and calculated PXRD pattern of **1**.

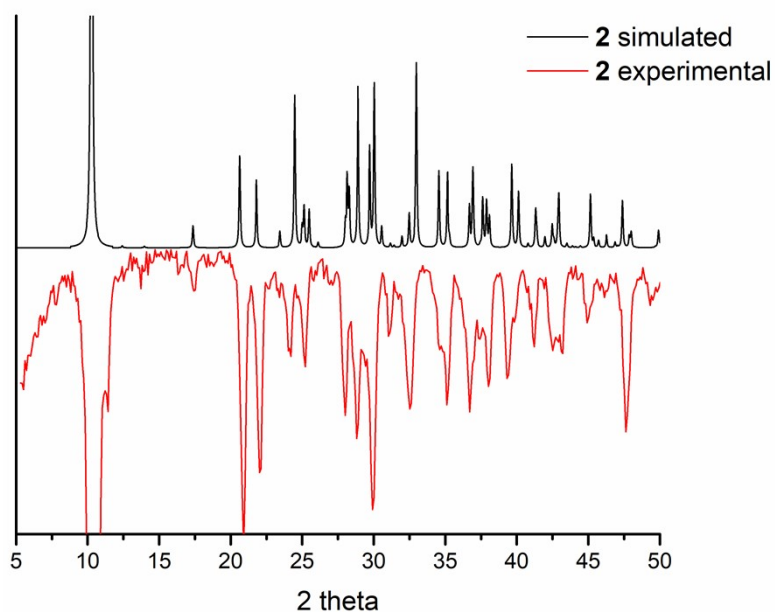


Fig. S3. Experimental and calculated PXRD pattern of **2**.

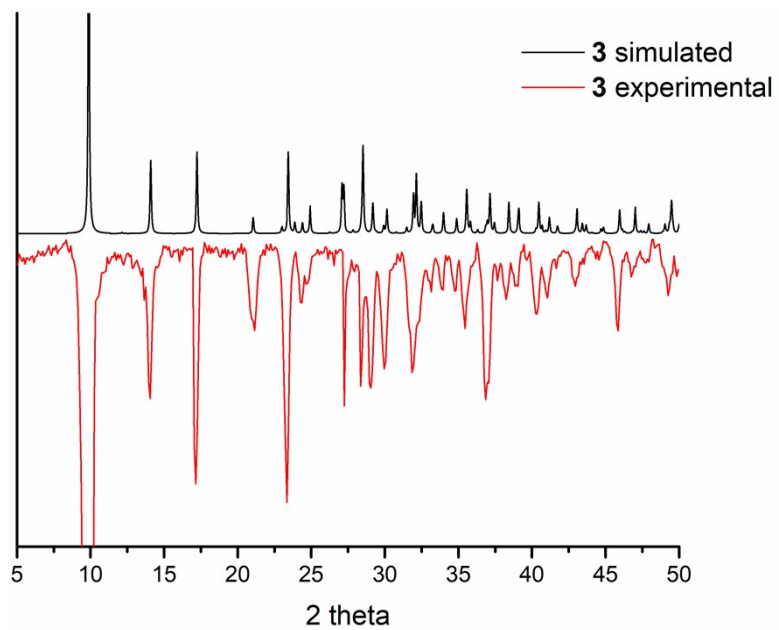


Fig. S4. Experimental and calculated PXR D pattern of **3**.

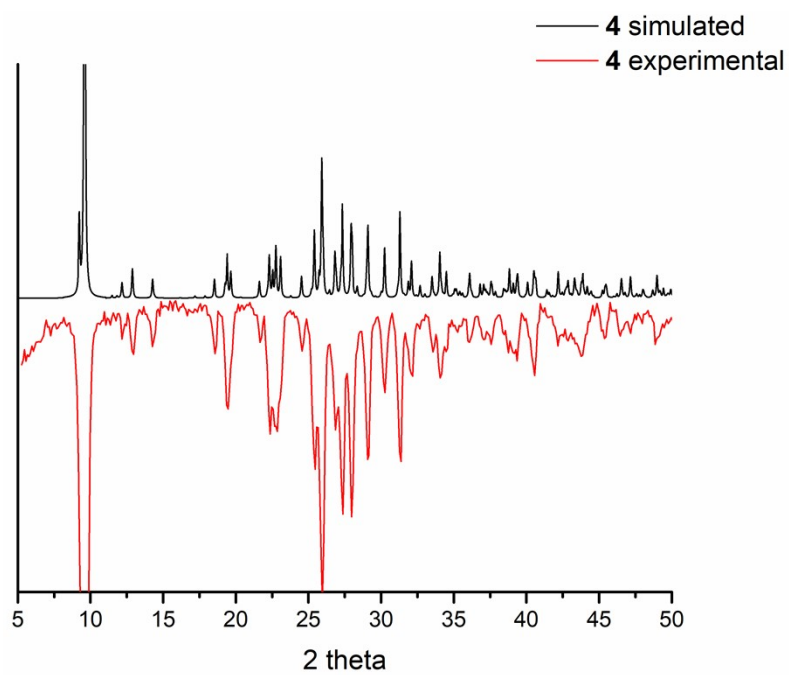


Fig. S5. Experimental and calculated PXR D pattern of **4**.

Statistical analysis of chalcogen bonding interactions

The CSD search was performed by using the CSD version 5.43 (November 2021). Structures were searched containing intermolecular contacts between chalcogen atoms (S/Se) and donor atoms (N, halogenide ions). The query used for the search of the contacts $\text{Se}\cdots\text{N}$ is shown in Fig. S6 as example.

Database(s):	CSD version 5.43 (November 2021)
Restriction Info:	No refcode restrictions applied
Filters:	None
Percentage Completed:	100%
Number of Hits:	26

Single query used. Search found structures that:

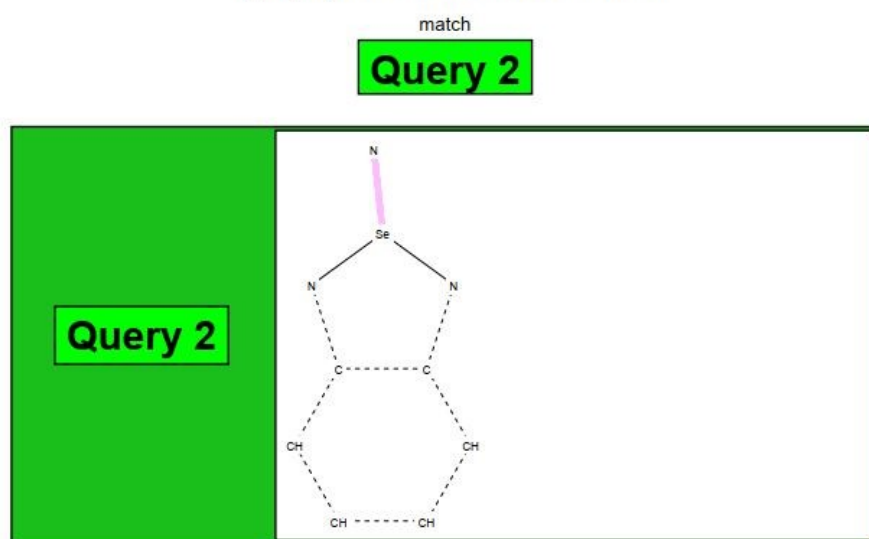


Fig. S6. Parameters used for the search of $\text{Se}\cdots\text{N}$ intermolecular contacts in the CSD.

The histogram of the intermolecular distances between sulphur and chloride is shown in Fig. S7. The histogram is based on the structures deposited in the CSD and having the following refcodes: AZUJUC, CUWSEU, CUSOE, KAFMOV, QORBEE.

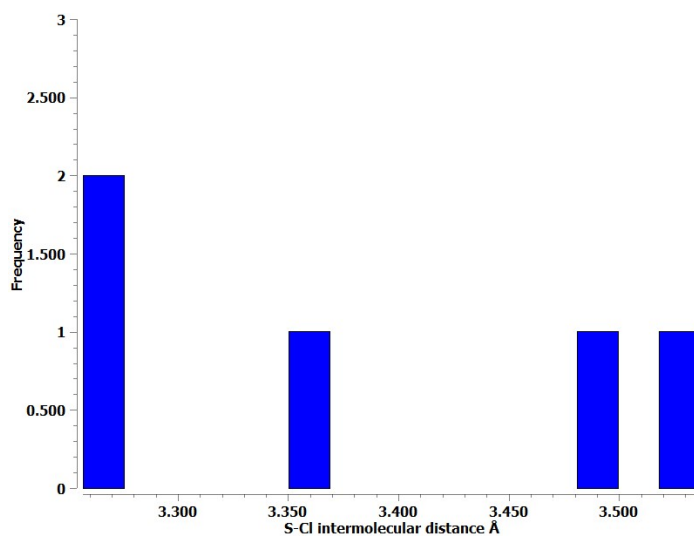


Fig. S7. Histogram of intermolecular contacts $\text{S}\cdots\text{Cl}$ retrieved in the CSD.

The $\text{S}\cdots\text{Cl}$ distances found in **1** are 3.269(3) Å e 3.356(2) Å.

The histogram of intermolecular contacts Se...N is reported in Fig. S8, and it is based on a far larger number of structures: ACIYOD, ANQSDZ, ASIQU, BESEAZ, BESEAZ01, BEVPID, BEVPOJ, BEVPUP, BEVQAW, BEVQEA, COFMUF10, DEXTEI, DOLROO, EJIYED, GAJQIU, GAJQUG, GAJLAN, GAJRER, GAJRIV, GAJROB, GAJRUH, GAJSAO, GAJSAO01, GAJSIW, GAJSOC, GASDUC, GASFAK, GASFEO, HARCOU, IFOGAM, IJOBOZ, JUQTEW, NABSAN, NABSER, NABSIV, NABSOB, NABSUH, NUDCAR, POFGIB, PUBBAS, PUBBAS01, QARSEI01, QIBREB, QIBROL, SAYKIN, SAYKOT, TUFJUA, TUSZAL, TUSZEP, TUTCAP, VEHVUC, VOPBIO, VOPMAR, XADWAD, XOQBUA, YEVWII, YIWLOG, ZIJRIV, ZIJROB.

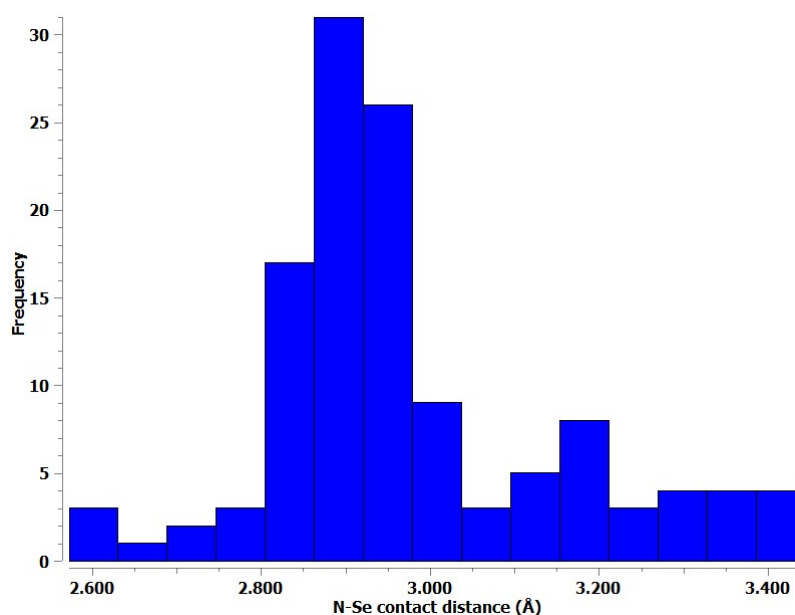


Fig. S8. Histogram of intermolecular contacts Se...N retrieved in the CSD.

The histogram has a gaussian-like shape, centred approximately at 2.90-2.95 Å. The two Se...N distances found in **4** are 2.944(9) Å e 2.722(1) Å. The first is in the most populated central region of the histogram, while the second in the low values tail.

The histogram of the Se...Cl intermolecular distances is based on the CSD structures with refcodes REFCODE: QIBREB, TUFKAH, VINPOZ, VINPUF, VOPLOE, VOPLUK. It is shown in Fig. S9.

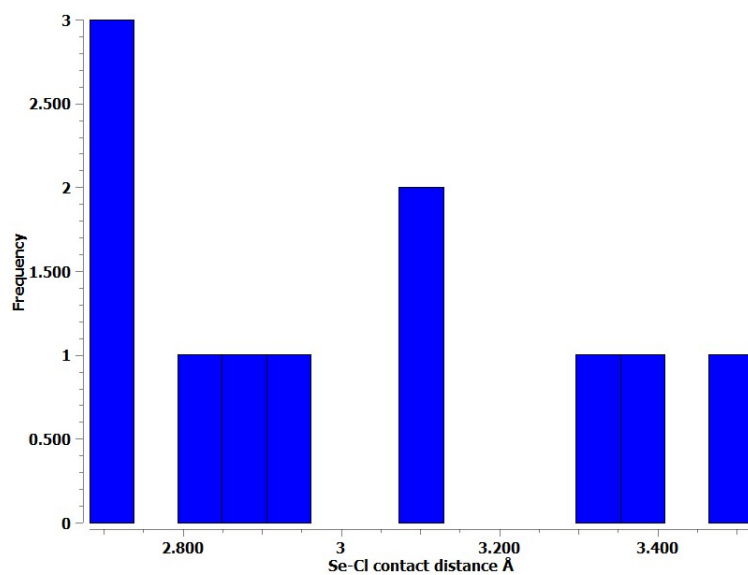


Fig. S9. Histogram of intermolecular contacts Se...Cl retrieved in the CSD.

The experimental distances found in **3** are 3.378(3) Å and 3.148(4) Å.

Concerning the Se...Br intermolecular contacts, we have found in the CSD only one hit, refcode QIBRAX, with a Se...Br distance of 3.2759(2) Å to be compared with the value of 3.547(2) Å found in **4**.

Evaluation of the energy of chalcogen bonding intermolecular interactions

In the framework of the optimization of the crystal structure with the program CRYSTAL17,² we have tried to estimate the energy of the chalcogen bonding intermolecular interaction Se...N in compound **4**. This was accomplished in the following way. From the optimized crystal structure of **4** we have extracted a monomer (Figure S10 (I)), in which no chalcogen bond is present, and then a dimer (Figure S10(II)), in which the [Se...N]₂ is present. We have then calculated the difference between the energy of the dimer and two times the energy of the monomer (all at DFT B3LYP level with 6-31G** basis set, as explained in the typescript). The result is $\Delta E = -13.00$ kcal/mol. The energy difference is negative because the energy of the chalcogen bonded dimer is less than the sum of the energies of two isolated molecules. The difference was divided by two, because, as shown in Fig. S10, the [Se...N]₂ chalcogen bond synthon involves two Se...N bonds, and this result, -6.50 kcal/mol, can be considered as a measure of the energy of the chalcogen bond Se...N in the [Se...N]₂ synthon in the system investigated.

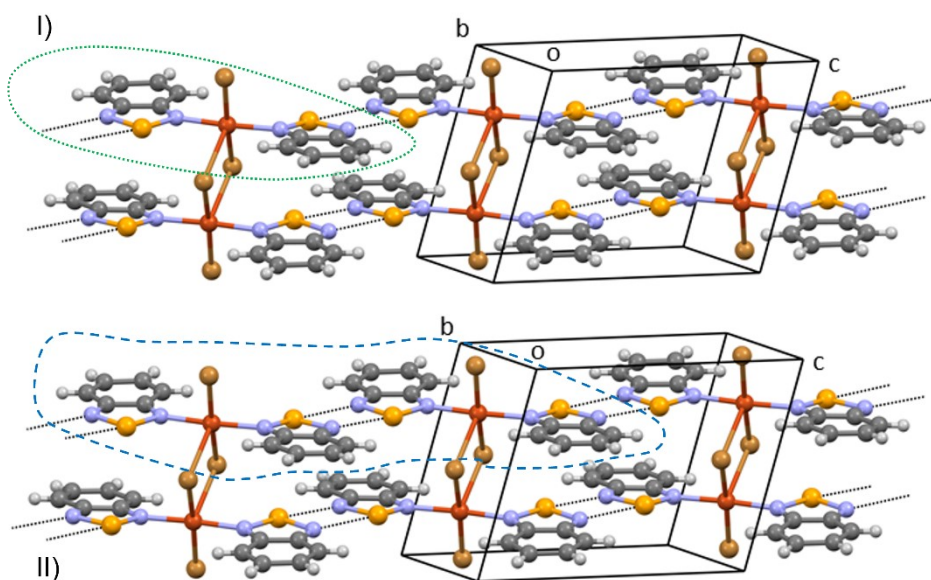


Fig. S10. I) Monomer of **4** in green dot line. II) Dimer of **4** in blue dashed line.

In another approach, we have used the facilities of the program *CrystalExplorer17* to estimate the energy of intermolecular interactions.³ In this program, the first step is to build a portion of the crystal structure, i. e. a cluster of molecules surrounding a given one and whose barycentres are within 3.8 Å from the central molecule. Then the molecular wavefunction is calculated (in our case at level HF/3-21G because it is the only one supporting Se) and from that the interaction energies between the central molecule and the other molecules of the cluster. Concerning the chalcogen bonding interactions, the results indicate that the energy of the [Se...N]₂ synthon is -28.5 kJ/mol, that is -6.81 kcal/mol. This value is not far from both the literature value (-5.29 kcal/mol in ref. 4) and the DFT calculations performed.

ORTEP drawings

Here are reported the ORTEP drawings of all four compounds (S11-S14). Thermal ellipsoids are drawn at the 30% probability level.

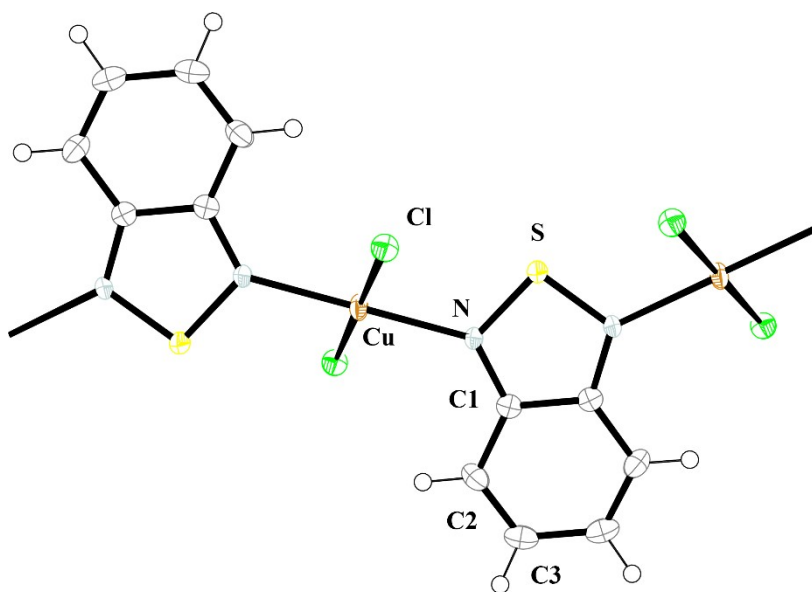


Fig. S11. ORTEP diagram of compound 1.

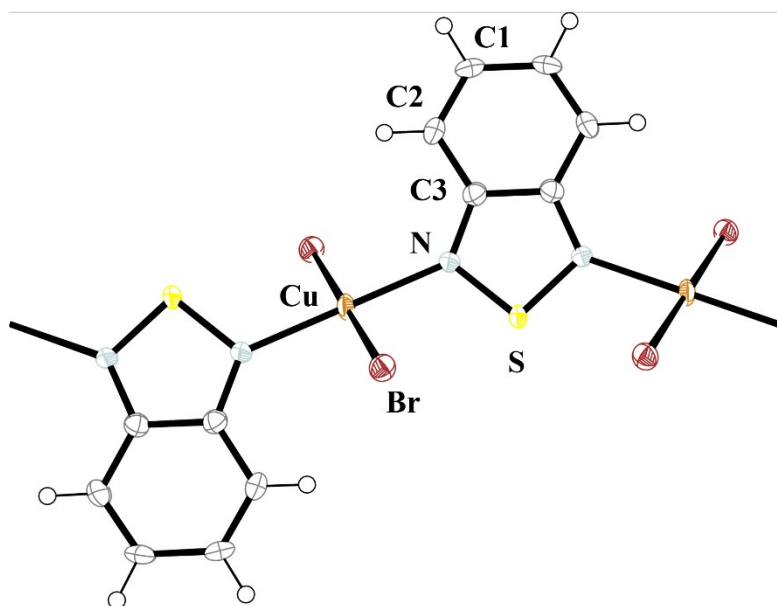


Fig. S12. ORTEP diagram of compound 2.

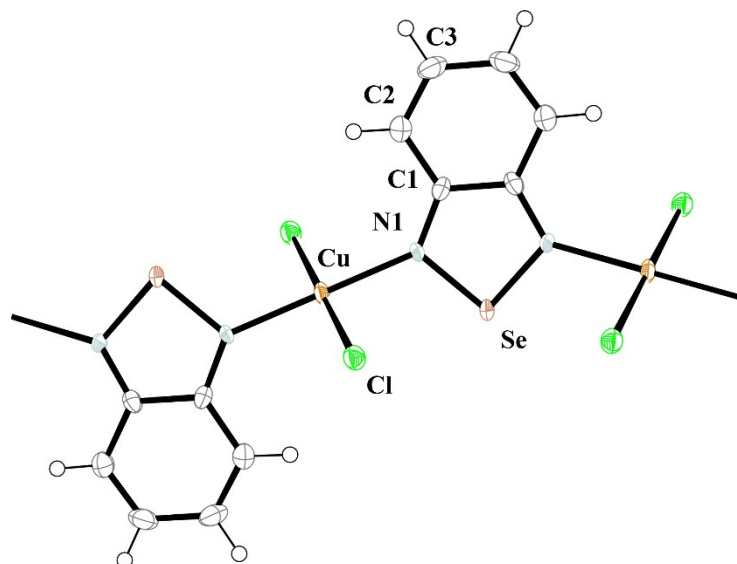


Fig. S13. ORTEP diagram of compound 3.

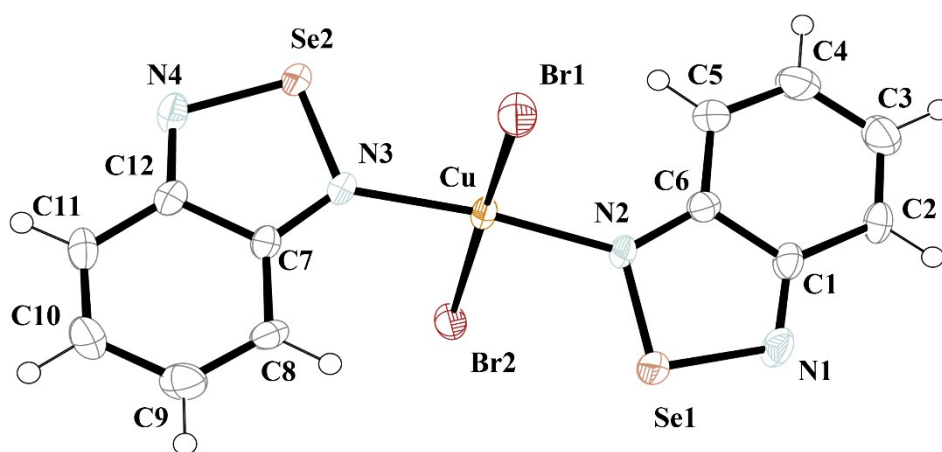


Fig. S14. ORTEP diagram of compound 4.

Computational details

Frequencies at the Γ point have been obtained within the harmonic approximation by diagonalising the mass-weighted Hessian matrix, W , whose elements are defined as⁵⁻⁹:

$$W_{\alpha i, \beta j}^{\Gamma} = \frac{H_{\alpha i, \beta j}^0}{\sqrt{M_{\alpha} M_{\beta}}} \text{ with } H_{\alpha i, \beta j}^0 = \left(\frac{\partial^2 E}{\partial u_{\alpha i}^0 \partial u_{\beta j}^0} \right) \quad (1)$$

where M_{α} and M_{β} are the masses of atoms associated with the i and j atomic coordinates. Once the Hessian matrix, $H_{\alpha i, \beta j}$, has been calculated, frequency shifts due to isotopic substitutions can be calculated readily, at no additional computational cost, by simply changing the mass values in eqn (1).

Energy first derivatives with respect to the atomic positions, $v_{\alpha, i} = \partial E / \partial u_{\alpha, i}$, were calculated analytically for all the $u_{\alpha, i}$ coordinates (E is the total energy, $u_{\alpha, i}$ is the displacement coordinate with respect to the equilibrium, α labels each atom), whereas second derivatives at $\vec{u} = 0$ are calculated numerically using a single displacement along each coordinate ($N = 2$, the central point and a point on the right side of the parabola):

$$\left[\frac{\partial v_{\alpha j}}{\partial u_{\beta i}} \right] \approx \frac{v_{\alpha j}(0, \dots, u_{\beta i}, \dots)}{u_{\beta i}} \quad (2)$$

or averaging two displacements ($N = 3$):

$$\left[\frac{\partial v_{\alpha j}}{\partial u_{\beta i}} \right] \approx \frac{v_{\alpha j}(0, \dots, u_{\beta i}, \dots) - v_{\alpha j}(0, \dots, -u_{\beta i}, \dots)}{2u_{\beta i}} \quad (3)$$

Previous calculations⁵⁻¹⁰ have shown that in bulk systems the influence of both u and N is very small (less than 1 cm^{-1}) when H atoms are not present; much larger effects have been found for katoite,¹¹ brucite¹² and diaspore,¹³ related to the anharmonicity of the OH stretching. More generally, anharmonicity is large in all cases in which H atoms are involved (*vide infra*). In this work, we are particularly interested in characterizing the spectrum in the range $100\text{--}1800 \text{ cm}^{-1}$, so that we do not consider the strong anharmonic contribution of the aromatic hydrogen. Integrated intensities for IR absorption I_p are computed for each mode p by means of the mass-weighted effective-mode Born-charge vector \vec{Z}_p ,¹⁴⁻¹⁵ evaluated through a CPHF/KS approach:¹⁶⁻¹⁷

$$I_p \propto |\vec{Z}_p|^2 \quad (4)$$

Raman activities for each i^{th} normal mode ($\partial \alpha_{xy} / \partial Q_i$) are computed analytically by exploiting a scheme illustrated in ref. 17 and 18. Both schemes are based on the solutions of first- and second order Coupled-Perturbed-Hartree-Fock/Kohn-Sham (CPHF/KS) equations.^{19,20} According to the general theory of Raman scattering,²¹ calculated Raman activities are converted into relative Raman intensities (I_i) making use of the relationship:

$$I_{xy}^i \propto C \left(\frac{\partial \alpha_{xy}}{\partial Q_i} \right)^2 \quad (5)$$

where the C coefficient accounts for the experimental conditions and is given by:

$$C = (\omega_L - \omega_i)^4 \frac{1 + n(\omega_i)}{30\omega_i} \quad (6)$$

In eqn (6) ω_L and ω_i are, respectively, the laser and the Raman frequencies and $n(\omega_i)$ is the Bose occupancy factor, given by:

$$1 + n(\omega_i) = \left[1 - \exp\left(-\frac{\hbar\omega_i}{K_B T}\right) \right]^{-1} \quad (7)$$

References

- 1 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, and P. A. Wood, *Mercury CSD 2.0 – new features for the visualization and investigation of crystal structures*, *J. Appl. Cryst.* 2008, **41**, 466-470.
- 2 R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco, M. Llunel, M. Causà, Y. Noel, L. Maschio, A. Erba, M. Rerat, and S. Casassa, *CRYSTAL17 User's Manual*, 2017, University of Torino, Torino.
- 3 M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, P. R. Spackman, D. Jayatilaka, and M. A. Spackman, *CrystalExplorer17* 2017. University of Western Australia. See also <http://hirshfeldsurface.net>.
- 4 M. R. Ams, N. Trapp, A. Schwab, J. V. Milić, and F. Diederich, *Chem. Eur. J.*, 2019, **25**, 323-333.
- 5 F. Pascale, C. M. Zicovich-Wilson, F. Lopez Gejo, B. Civalleri, R. Orlando and R. Dovesi, The calculation of the vibrational frequencies of crystalline compounds and its implementation in the CRYSTAL code, *J. Comput. Chem.*, 2004, **25**, 888 —897.
- 6 C. Zicovich-Wilson, F. Pascale, C. Roetti, V. Saunders, R. Orlando and R. Dovesi, Calculation of the vibration frequencies of α -quartz: The effect of Hamiltonian and basis set, *J. Comput. Chem.*, 2004, **25**, 1873 —1881.
- 7 A. Erba, M. Ferrabone, R. Orlando and R. Dovesi, Accurate dynamical structure factors from *ab initio* lattice dynamics: The case of crystalline silicon, *J. Comput. Chem.*, 2013, **34**, 346 —354.
- 8 C. Carteret, M. De La Pierre, M. Dossot, F. Pascale, A. Erba and R. Dovesi, The vibrational spectrum of CaCO₃ aragonite: a combined experimental and quantum-mechanical investigation, *J. Chem. Phys.*, 2013, **138**, 014201.
- 9 J. Baima, M. Ferrabone, R. Orlando, A. Erba and R. Dovesi, Thermodynamics and phonon dispersion of pyrope and grossular silicate garnets from *ab initio* simulations, *Phys. Chem. Miner.*, 2016, **43**, 137 —149.
- 10 F. Pascale, C. M. Zicovich-Wilson, R. Orlando, C. Roetti, P. Ugliengo and R. Dovesi, Vibration frequencies of Mg₃Al₂Si₃O₁₂ pyrope. An *ab initio* study with the CRYSTAL code, *J. Phys. Chem. B*, 2005, **109**, 6146 —6152.
- 11 R. Orlando, F. Torres, F. Pascale, P. Ugliengo, C. Zicovich-Wilson and R. Dovesi, Vibrational spectrum of katoite Ca₃Al₂[(OH)₄]₃: A periodic *ab initio* study, *J. Phys. Chem. B*, 2006, **110**, 692 —701.
- 12 F. Pascale, S. Tosoni, C. Zicovich-Wilson, P. Ugliengo, R. Orlando and R. Dovesi, Vibrational spectrum of brucite, Mg(OH)₂: a periodic *ab initio* quantum mechanical calculation including OH anharmonicity, *Chem. Phys. Lett.*, 2004, **396**, 308 —315.
- 13 R. Demichelis, Y. Noel, B. Civalleri, C. Roetti, M. Ferrero and R. Dovesi, The vibrational spectrum of α -AlOOH diasopore: An *ab initio* study with the CRYSTAL code, *J. Phys. Chem. B*, 2007, **111**, 9337 —9346
- 14 G. M. Barrow, *Introduction to Molecular Spectroscopy*, McGraw-Hill, New York, 1962.
- 15 B. A. Hess Jr, L. J. Schaad, P. Carsky and R. Zahradnik, *Ab initio* calculations of vibrational spectra and their use in the identification of unusual molecules, *Chem. Rev.*, 1986, **86**, 709 —730.

- 16 L. Maschio, B. Kirtman, R. Orlando and M. R  rat, *Ab initio* analytical infrared intensities for periodic systems through a coupled perturbed Hartree-Fock/Kohn-Sham method, *J. Chem. Phys.*, 2012, **137**, 204113.
- 17 L. Maschio, B. Kirtman, M. R  rat, R. Orlando and R. Dovesi, Comment on “*Ab initio* analytical infrared intensities for periodic systems through a coupled perturbed Hartree-Fock/Kohn-Sham method” [*J. Chem. Phys.* 137, 204113 (2012)], *J. Chem. Phys.*, 2013, **139**, 167101.
- 18 L. Maschio, B. Kirtman, M. R  rat, R. Orlando and R. Dovesi, *Ab initio* analytical Raman intensities for periodic systems through a coupled perturbed Hartree-Fock/Kohn-Sham method in an atomic orbital basis. I. Theory, *J. Chem. Phys.*, 2013, **139**, 164101.
- 19 L. Maschio, B. Kirtman, M. R  rat, R. Orlando and R. Dovesi, *Ab initio* analytical Raman intensities for periodic systems through a coupled perturbed Hartree-Fock/Kohn-Sham method in an atomic orbital basis. II. Validation and comparison with experiments, *J. Chem. Phys.*, 2013, **139**, 164102.
- 20 M. Ferrero, M. R  rat, R. Orlando and R. Dovesi, The calculation of static polarizabilities of 1D, 2D and 3D periodic compounds. The implementation in the CRYSTAL code, *J. Comput. Chem.*, 2008, **29**, 1450 —1459
- 21 D. A. McQuarrie and J. D. Simon, *Physical Chemistry. A Molecular Approach*, University Science Books, Sausalito, CA, 1977