



STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 78 (2022)

Supporting information for article:

The bond valence model as a prospective approach: examination of the crystal structures of copper chalcogenides with Cu bond valence excess

Yves Moëlo, Aurelian Florin Popa and Vincent Dubost

Figure list.

S1. Bond lengths in the crystal structure of HNO₃.

S2. Crystal structure of CuSe₂.

S3. Crystal structure of NaCu₄S₄.

S4. Crystal structure of TiCu₂Se₂.

S5. Crystal structure of NaCu₄Se₃.

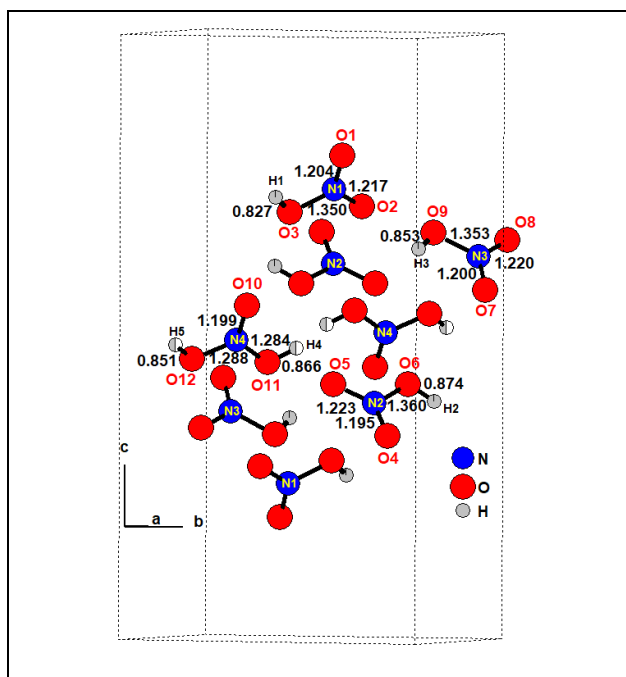
S6. Crystal structure of KCu₄Se₃.

S7. Crystal structure of YBi₂O₄Cu₂Se₂.

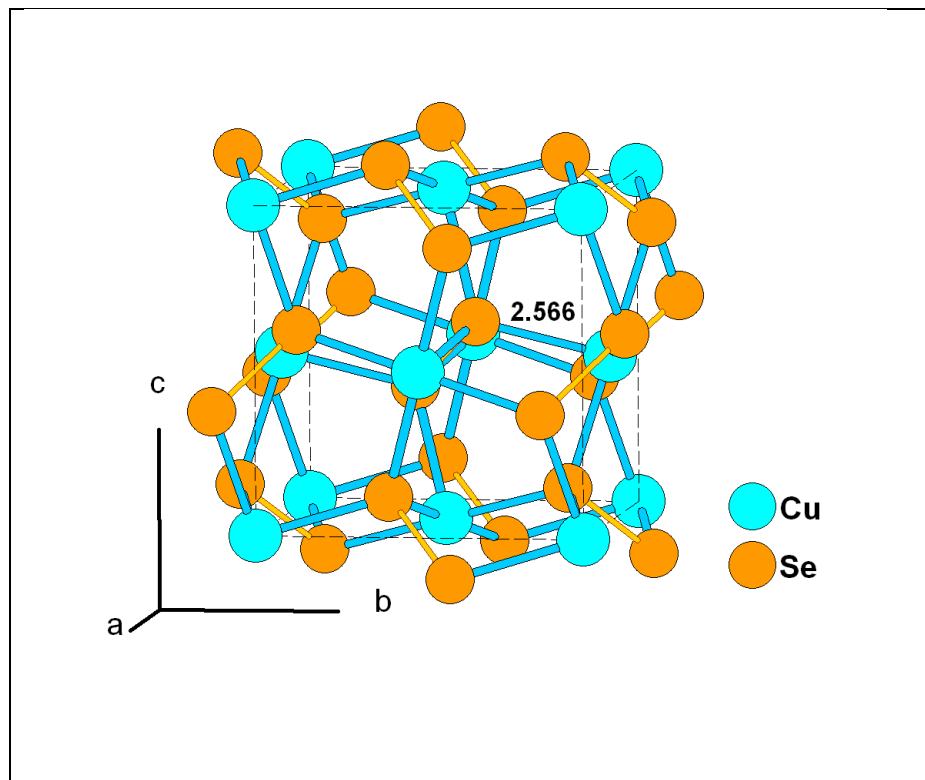
S8. Crystal structure of BiCuOSe.

References of crystal structures according to ICSD data base.

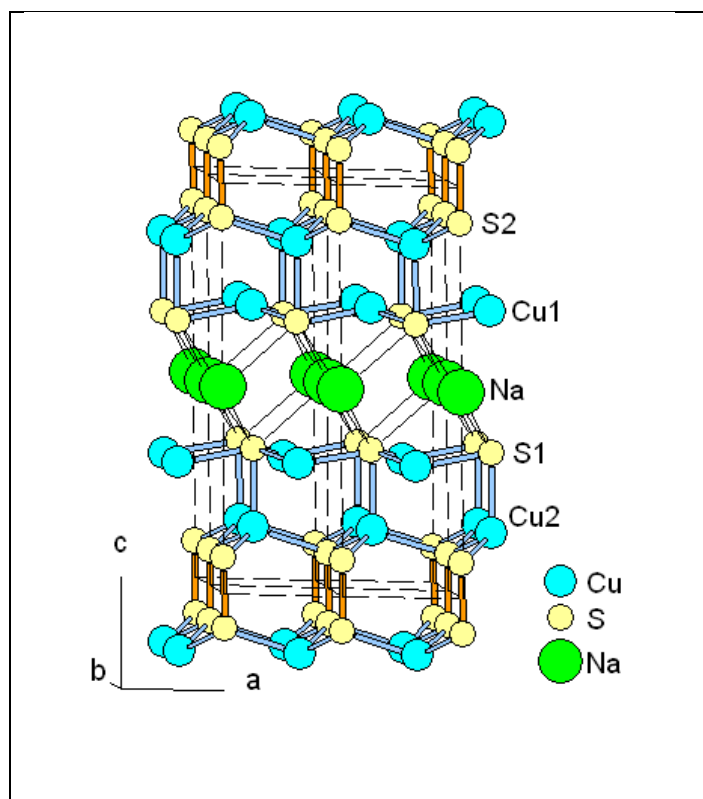
In Figs. S2 to S8, thick blue bonds connect Cu and chalcogen atoms implicated in the distribution of the ligand electron in excess.

Figure S1. Bond lengths in the crystal structure of HNO₃. H4 and H5: s.o.f. 0.5.

ICSD 166940 – Allan, D.R., Marshall, W.G., Francis, D.J., Oswald, I.D.H., Pulham, C.R. & Spanswick, C. (2010). The crystal structures of the low-temperature and high-pressure polymorphs of nitric acid. *Dalton Transactions*, **39**, 3736-3743.

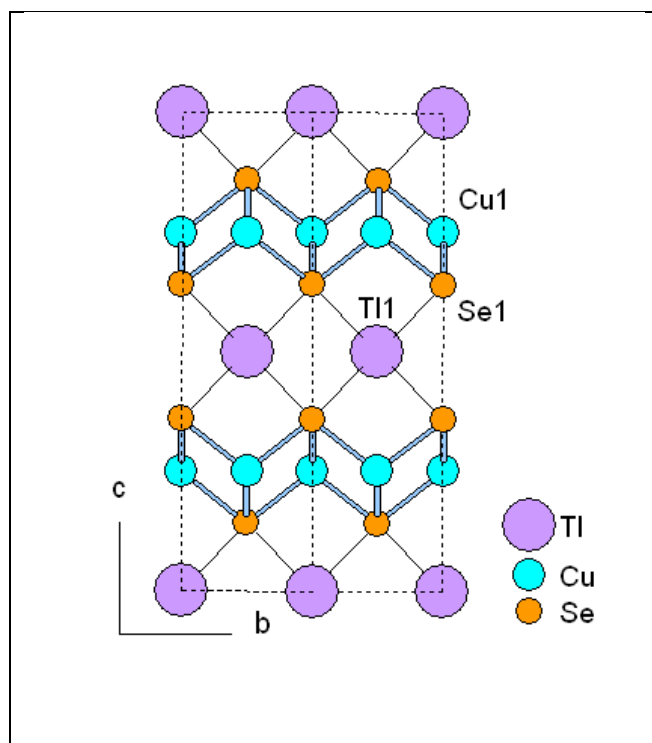
Figure S2. Crystal structure of CuSe_2 .

ICSD 243 – Heyding, R.D. & Murray, R.M. (1976). Crystal structures of $\text{Cu}_{1.8}\text{Se}$, Cu_3Se_2 , α - and γ - CuSe , CuSe_2 , and CuSe_2II . *Can. J. Chem.* **54**, 841-848.

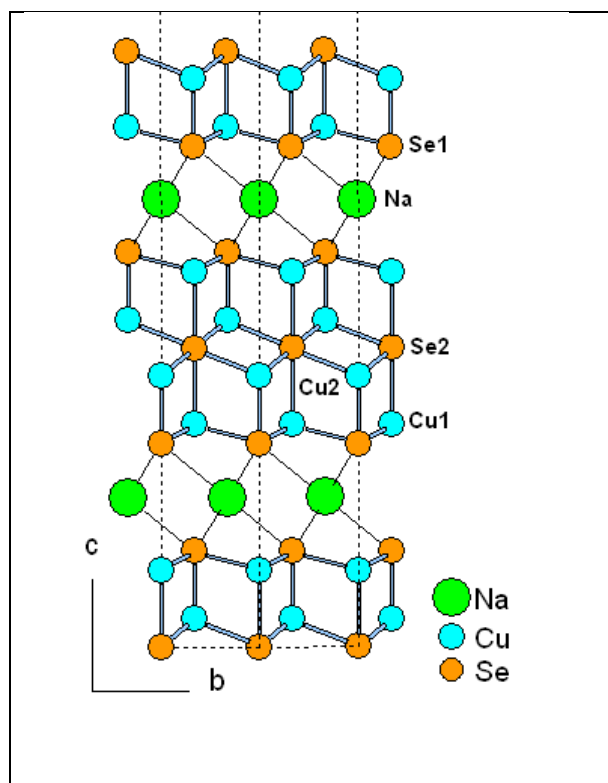
Figure S3. Crystal structure of NaCu_4S_4 .

ICSD 81 306 – Zhang, X., Kanatzidis, M.G., Hogan, T. and Kannewurf, C.R. (1996).

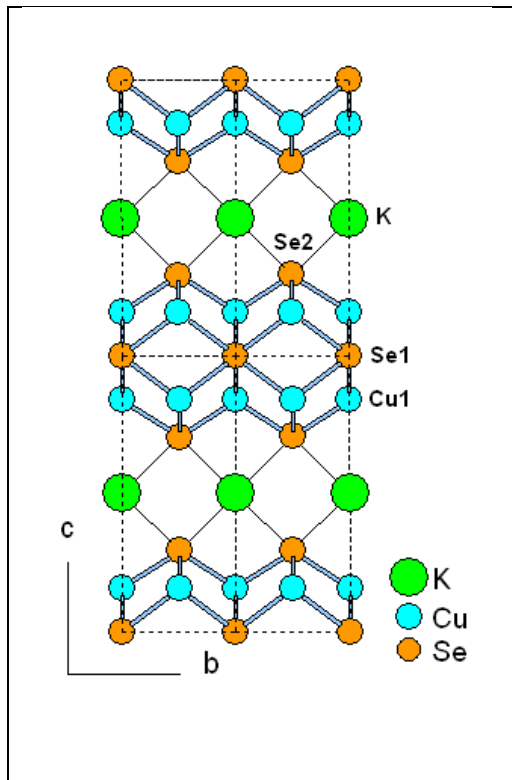
NaCu_4S_4 , a simple new low-dimensional, metallic copper polychalcogenide, structurally related to CuS . *J. Amer. Chem. Soc.* **118**, 693-694.

Figure S4. Crystal structure of TlCu_2Se_2 .

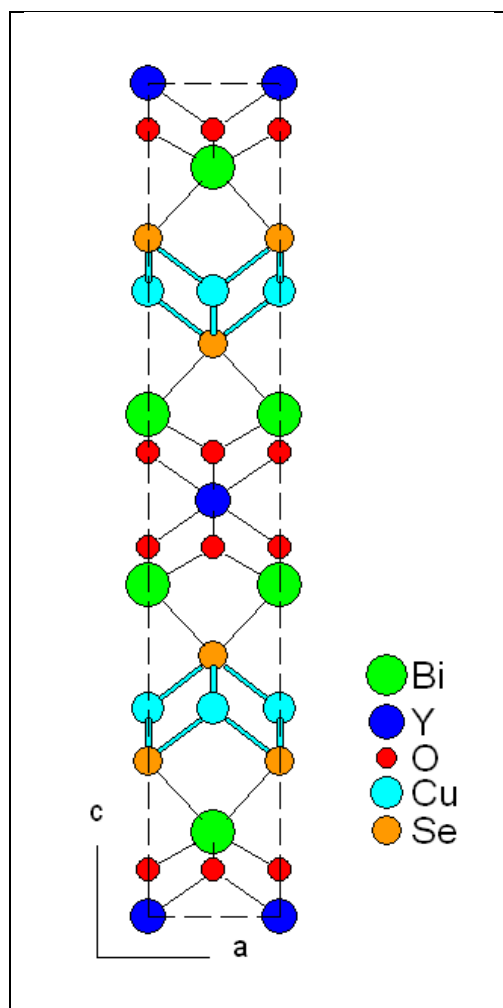
ICSD 629 136 – Brun, G., Gardes, B., Tedenac, J.C., Raymond, A. and Maurin, M. (1979).
Structure et propriétés physiques des phases Cu_2TlX_2 , $\text{Cu}_3\text{YTi}_2\text{X}_4$ (avec X = Se, Te et Y = Fe,
Ga, Al). *Mat. Res. Bull.* **14**, 743-749.

Figure S5. Crystal structure of NaCu₄Se₃.

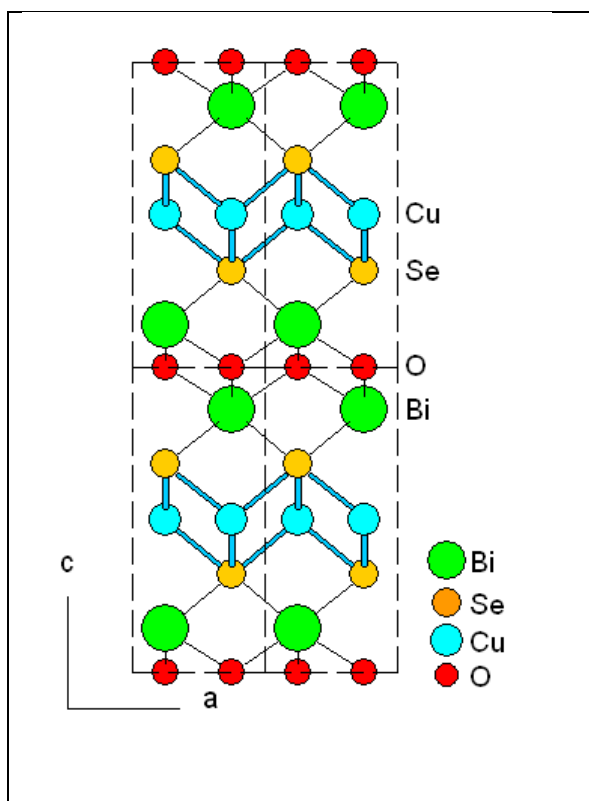
ICSD 32 016 – Sturza, M., Bugaris, D.E., Malliaks, C.D., Han, F., Chung, D.Y. and Kanatzidis, M.G. (2016). Mixed-valent NaCu₄Se₃: A two-dimensional metal. *Inorg. Chem.* **55**, 4484-4490.

Figure S6. Crystal structure of KCu_4Se_3 .

ICSD 628 205 – Klepp, K., Boller, H. & Vollenkle, H. (1980). Neue Verbindungen mit KCu_4S_3 Struktur. *Monatsh. Chem.* **111**, 727-733.

Figure S7. Crystal structure of $\text{YBi}_2\text{O}_4\text{Cu}_2\text{Se}_2$.

ICSD 95 369 – Evans, J.S.O., Brogden, E.R., Thompson, A.L. & Cordiner, R.L. (2002).
Synthesis and characterisation of the new oxyselenide $\text{Bi}_2\text{YO}_4\text{Cu}_2\text{Se}_2$. *Chem. Com.* **2002**, 912-913.

Figure S8. Crystal structure of BiCuOSe.

ICSD 75 128 – Kusainova, A.M., Berdonosov, P.S., Akselrud, L.G., Kholodkovskaya, L.N., Dolgikh, V.A. & Popovkin, B.A. (1994). New layered compounds with the general composition $(MO)(CuSe)$, where $M=Bi,Nd,Gd,Dy$ and $BiOCuS$: syntheses and crystal structure. *J. Solid State Chem.* **112**, 189-191.