Organic-inorganic hybrid chains and layers constructed from copper-amine cations and early transition metal (Nb, Mo) oxyfluoride anions.

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Supplementary Material

1. Composition space diagrams for the 4 pairs of synthetic systems. Behaviour is essentially the same for the Mo / Nb systems within each diagram.

(a) Products 1 and 2 are formed in the left-hand bottom region
(b) Products 3 and 4 are formed in the right-hand bottom region

(c) Products 5 and 6 are formed in the bottom region
(d) Products 7 and 8 are formed in the left-hand region.
2. **Rietveld plots for each pure bulk phase, based on the single crystal models.**

Data were collected overnight to assure the best quality to confirm phase purity for subsequent studies. Rietveld refinements were performed with the GSAS program suite using the atomic co-ordinates determined from the single crystal study. These structural models were kept fixed; only instrumental parameters (background, zero-point, peak profile coefficients) and unit cell were refined. In each case a good fit to the observed data was achieved, with no evidence for secondary phases.

![Rietveld plot](image)

(1) [Cu(C₂H₄N₄)₂][MoO₂F₄]. H₂O, Rwp=8.07%
(2) \([\text{Cu(C}_2\text{H}_4\text{N}_4)_2][\text{NbOF}_3]\).\text{H}_2\text{O}, \text{Rwp}=14.6\% \\

(3) \([\text{Cu(C}_3\text{H}_4\text{N}_2)_4][\text{MoO}_2\text{F}_4]\), \text{Rwp}=7.90\%
(4) $[\text{Cu(C}_3\text{H}_4\text{N}_2\text{)}_4][\text{NbOF}_5]$, $\text{Rwp}=9.90\%$

(5) $[\text{Cu}_2\text{F}_2(\text{C}_{10}\text{H}_9\text{N}_3)_2][\text{MoO}_2\text{F}_4]$, $\text{Rwp}=11.22\%$
(6) [Cu$_2$F$_2$(C$_{10}$H$_9$N$_3$)$_2$][NbOF$_5$], Rwp=13.28%

(7) [Cu(C$_{10}$H$_8$N$_2$)$_2$(H$_2$O)$_2$][MoO$_2$F$_4$], Rwp=16.63%
3. Experimental details of fluoride analysis

The fluorine content in the sample was determined by using a fluoride ion-selective electrode calibrated with different concentration of standard NaF solutions. The sample was ground into fine powder and dissolve in water with continuous shaking. A TISAB solution with pH 5.5 was used to adjust the ionic strength and keep the fluoride activity coefficient constant. Compounds 1 – 4 and 7,8 were dissolved in an HCl aqueous solution and the pH was then adjusted by adding NH₄OH. 5 and 6 were completely dissolved in water only. Analysis was carried out for each sample and for ten standard solutions with different fluoride concentrations and the same added amount of TISAB solution. Three independent measurements were taken and averaged for each solution.
Calibration curve for fluoride ion-selective electrode.

4. Magnetic susceptibility data ($1/\chi_p$ versus $T$) for 3, 4 and 8.