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A new series of copper-linked polyoxoniobates

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Synthesis & characterization

Synthetic strategy

Use $[Nb_6O_{19}]^{8-}$ or $[Nb_6O_{19}H_2]^{6-}$ Lindqvist ions

Use $[ML_x]^{n+}$ type complexes as linkers

M = Cu, Co ; L = (en), NH_3, H_2O

Reactions carried out at high (10.5 – 12.0) pH range where the PON clusters are stable

Reflux for 30 min @ 60°C , pH ~ 12
Crystallization @ room temperature, 3-5 days

Characterization: Structures solved by single crystal methods
FTIR, Magentic measurements (SQUID),
Chemical analysis (Galbraith Labs, Inc.)

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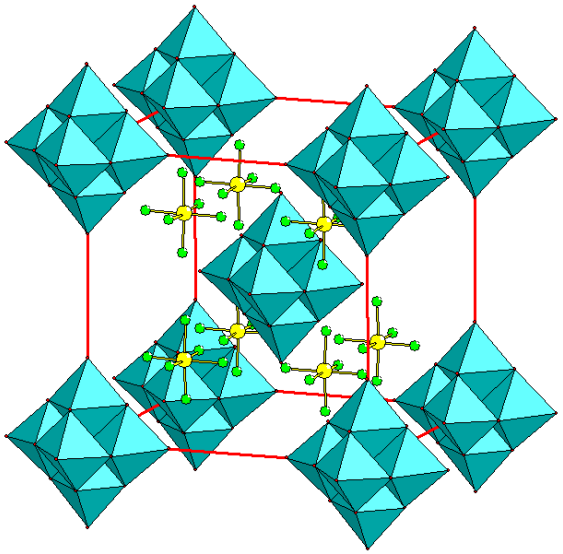
$[CoL_x] / [Nb_6O_{19}H_2]$ – type phases

L = NH_3

$[Co(NH_3)_6]_3[Nb_6O_{19}H_2]$

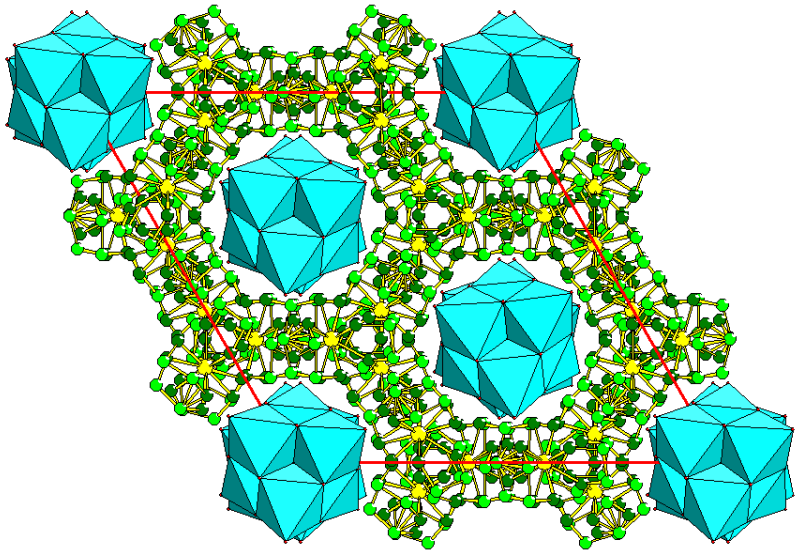
Cubic, SG I23; a = 14.302 Å



L = (en)

$[Co(en)_3]_3[Nb_6O_{19}H_2].10H_2O$

SG R-3c; a = 18.205 Å, c = 35.719 Å



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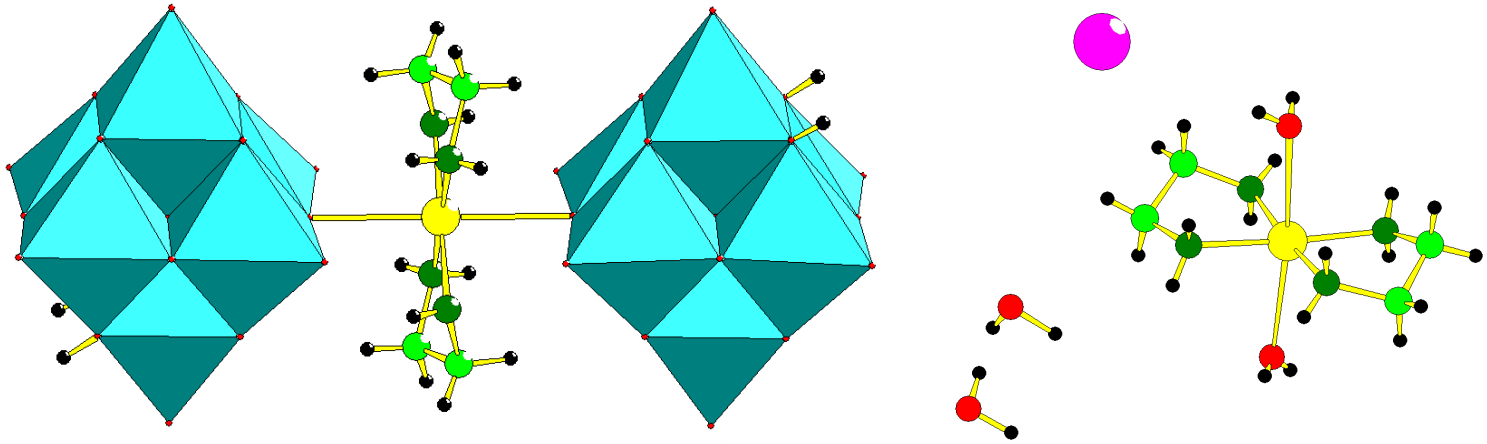
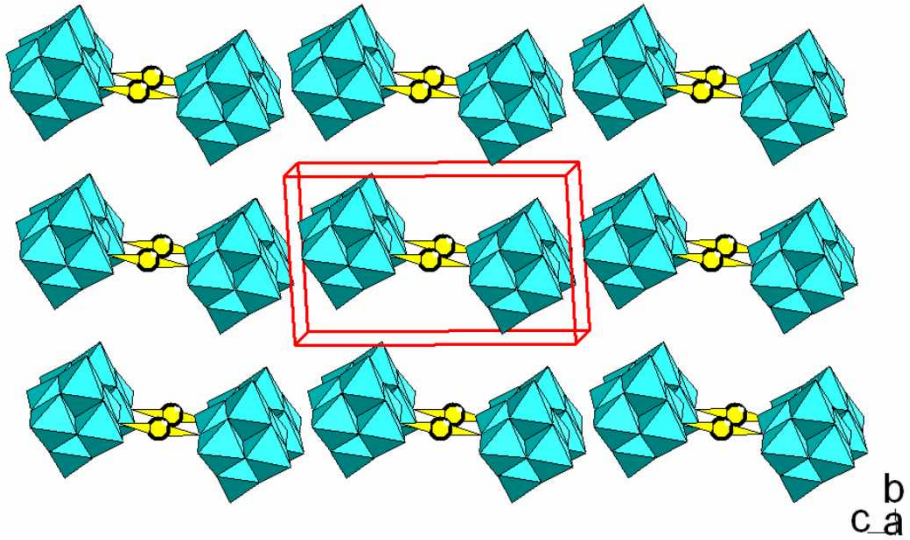
$Rb_4[Cu(en)_2(H_2O)_2]_3[(Nb_6O_{19}H_2)_2Cu(en)_2].24H_2O$





Triclinic, P-1 (#2)

a = 11.9708(13) Å	α = 88.917(1) deg.
b = 12.3451(13) Å	β = 89.445(1) deg.
c = 17.4481(19) Å	γ = 61.601(1) deg.
V = 2267.8(4) Å^3	Z = 2

R1 = 0.0273 ; wR2 = 0.0671 (I > 2σ(I))
R1 = 0.0305 ; wR2 = 0.0687 (all data)

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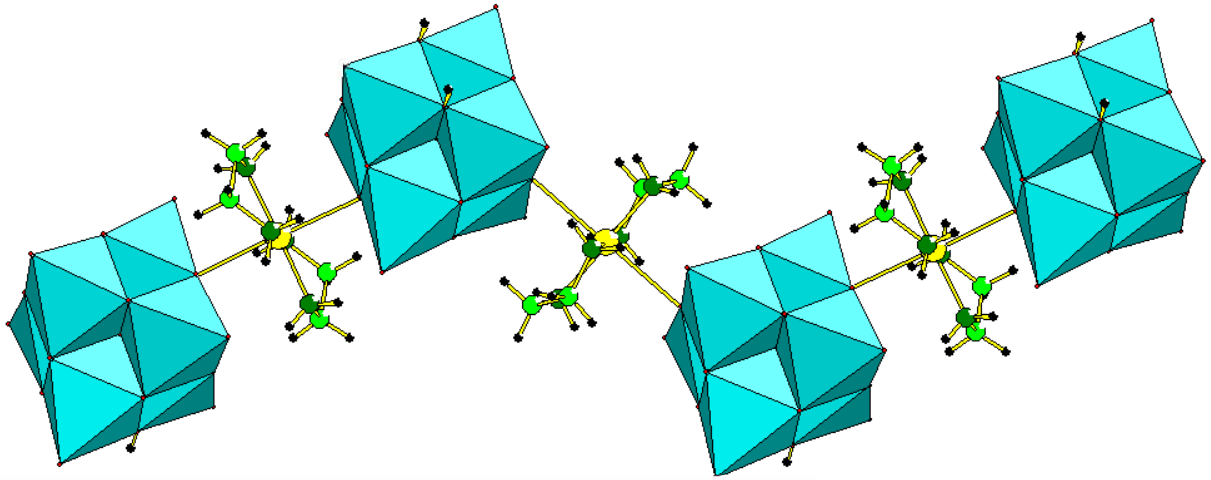
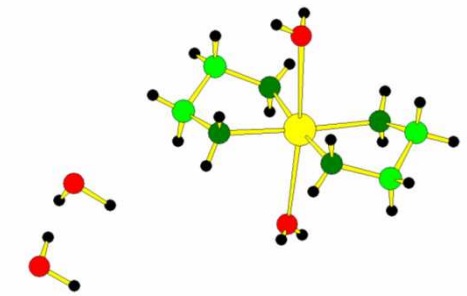
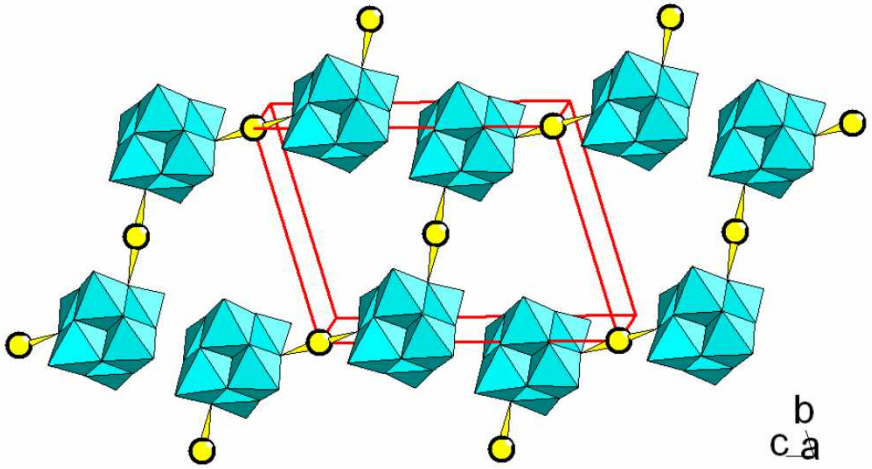
$[Cu(en)_2(H_2O)_2]_2[(Nb_6O_{19}H_2)Cu(en)_2].14H_2O$







Triclinic, P-1 (#2)

a = 12.6242(10)Å	α = 74.622(1) deg.
b = 12.6577(10) Å	β = 88.541(1) deg.
c = 16.4412(13) Å	γ = 81.502(1) deg.
V = 2505.1(3) Å^3	Z = 2

R1 = 0.0245 ; wR2 = 0.0657 (I > 2σ(I))
R1 = 0.0264 ; wR2 = 0.0743 (all data)

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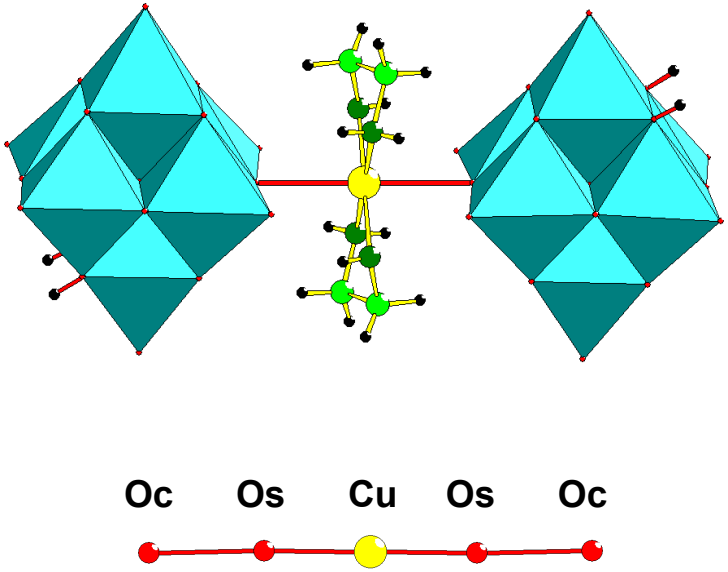
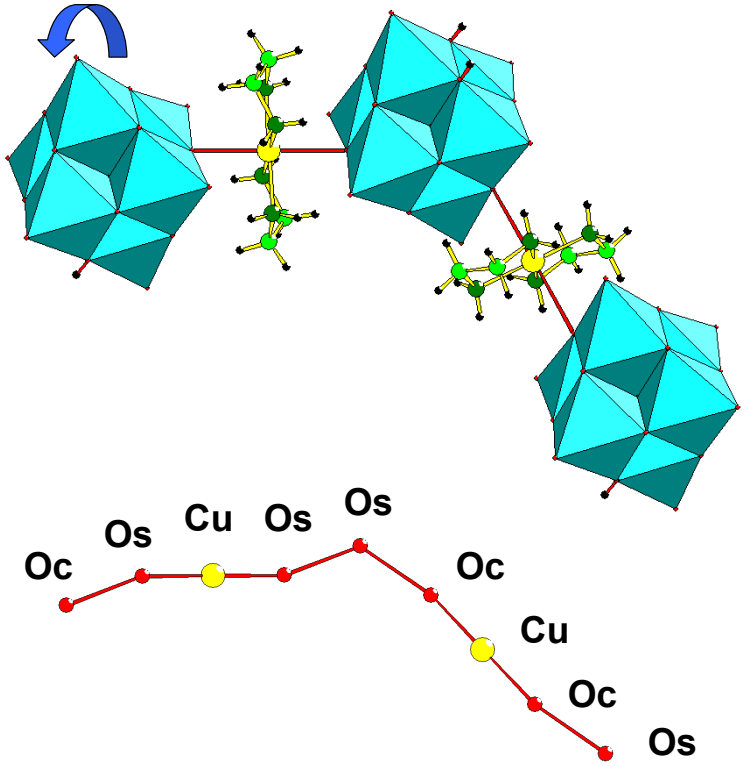
Structural comparison





Oc-Os-Cu = 177.9 deg.

Cu-Os = 2.53 Å

Cu-N = 2.00 – 2.02 Å

Oc-Os-Cu = 159.5 / 162.1deg.

Cu-Os = 2.45 / 2.67 Å

Cu-N = 2.00 – 2.03 Å

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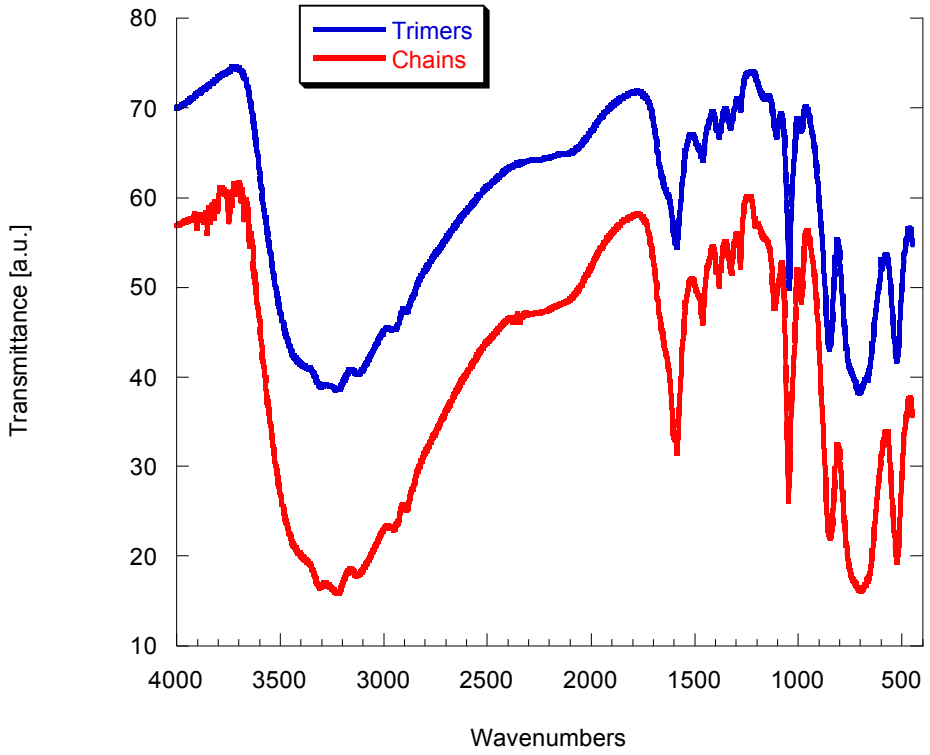
FTIR & chemical analysis



Characteristic bands

Nb_6O_{19}: 500 – 850 cm^{-1}

(en): 900 – 1450, 2800 – 3300 cm^{-1}

H_2O: 1600, 3300 cm^{-1}

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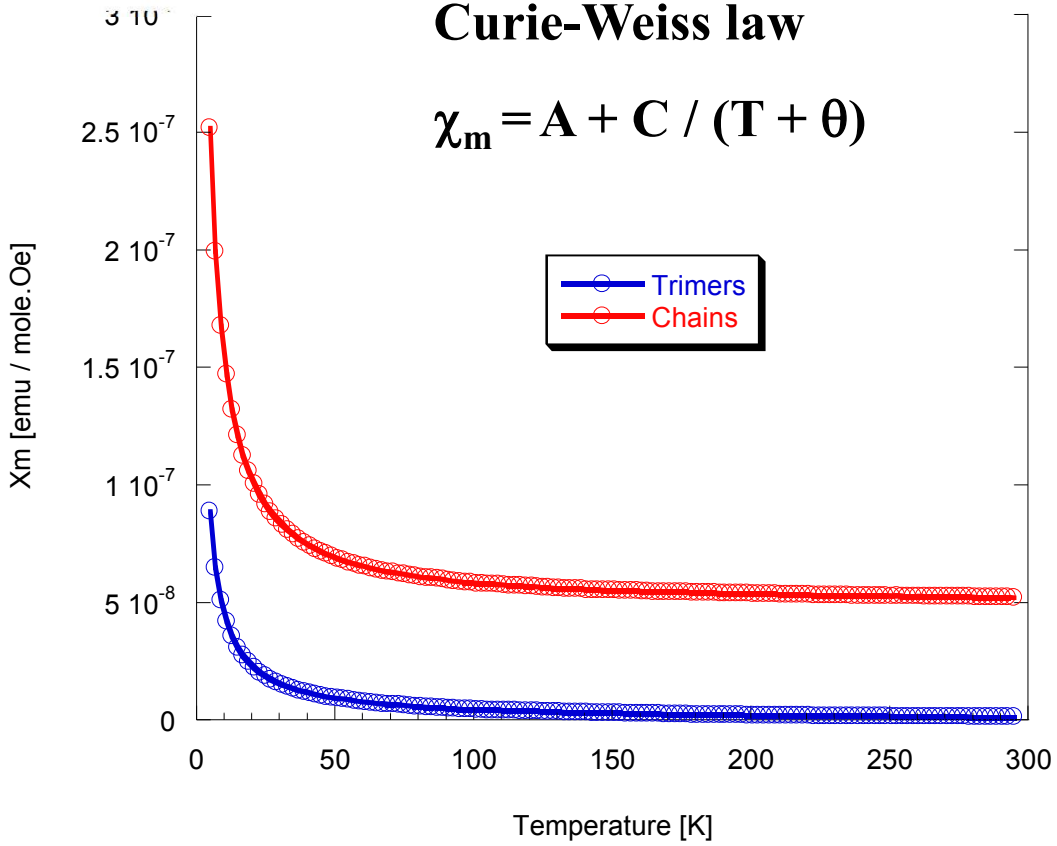
Magnetic properties



3-parameter fit (A , C and θ)

Trimers: $A = -9.41 \times 10^{-4}$ emu/M.Oe

$C = 1.55$ emu.K/M.Oe

$\theta = 0.4$ K

$R = 0.9999$

$\mu_{eff}(Cu^{2+}) = 1.81\ \mu_B$

Chains: $A = 3.85 \times 10^{-2}$ emu/M.Oe

$C = 0.91$ emu.K/M.Oe

$\theta = 0.4$ K

$R = 0.9998$

$\mu_{eff}(Cu^{2+}) = 1.55\ \mu_B$

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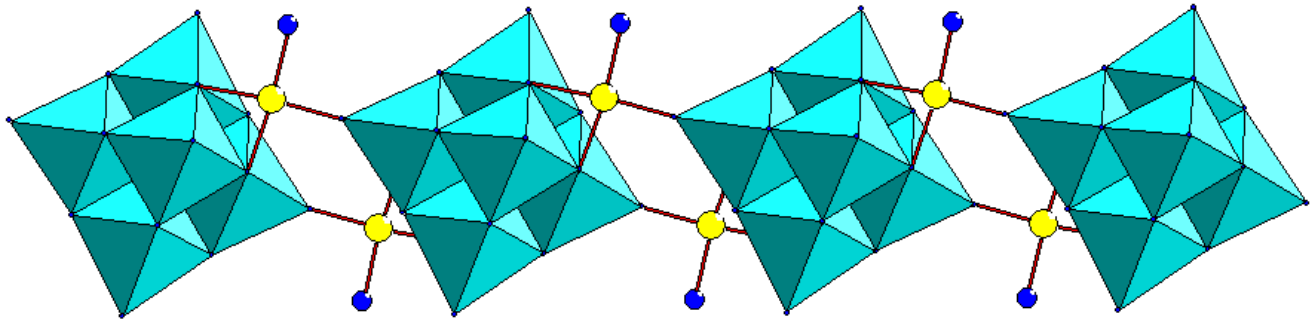
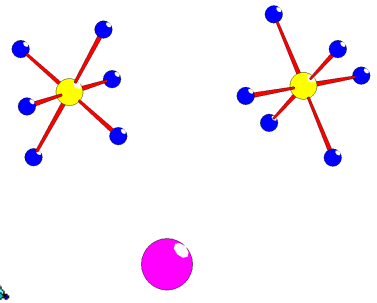
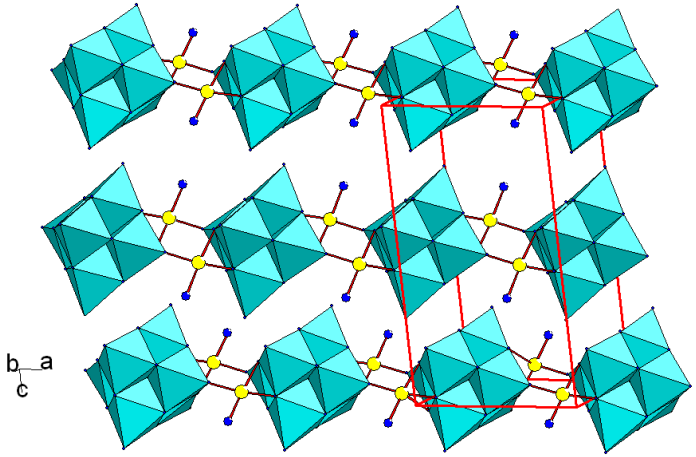
$Rb_2[CuL_6]_3[(Nb_6O_{19})(CuL)_2]_2.6H_2O$ L = NH_3, H_2O

$\{Nb_6Cu_2L_2\}.6H_2O$







Cu-O = 1.92 – 2.00 Å
Cu-L = 1.97 Å

Triclinic, P-1 (#2)
a = 8.7520(7) Å **α = 86.619(1) deg.**
b = 13.0771(10) Å **β = 83.649(1) deg.**
c = 15.9280(10) Å **γ = 88.044(1) deg.**
V = 1807.9(3) Å^3 **Z = 2**
R1 = 0.0293; wR2 = 0.0667 (I > 2σ(I))
R1 = 0.0337; wR2 = 0.0752 (all data)

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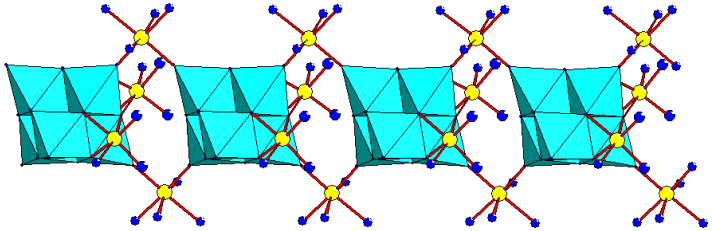
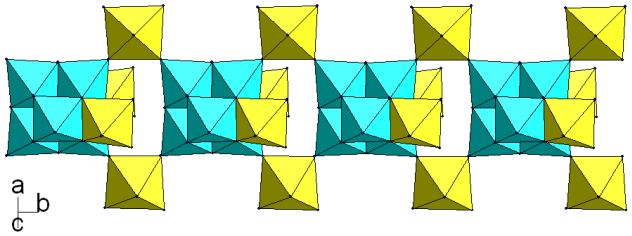
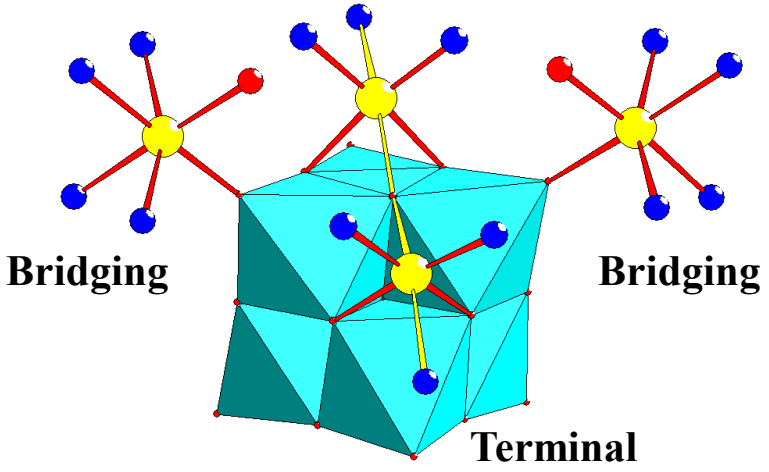
$[(Nb_6O_{19})(CuL_3)_2(CuL_4)_2].3H_2O$ L = NH_3, H_2O

$\{Nb_6Cu_4L_{14}\}.3H_2O$







Terminal: Cu-O, Cu-L = 1.99 – 2.07 Å
Cu-O, Cu-L = 2.35 , 2.54 Å

Bridging: Cu-O, Cu-L = 2.13 , 2.16 Å
Cu-O, Cu-L = 2.29 – 2.37 Å

a = 13.639(3) Å α = 90.00 deg.
b = 8.870(2) Å β = 96..84(3) deg.
c = 13.639(3) Å γ = 90.00 deg.
V = 1663.2(6) Å^3 Z = 2
R1 = 0.0904; wR2 = 0.1777 (I > 2σ(I))
R1 = 0.1033; wR2 = 0.1902 (all data)

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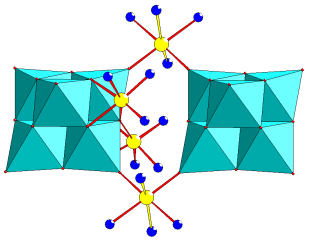
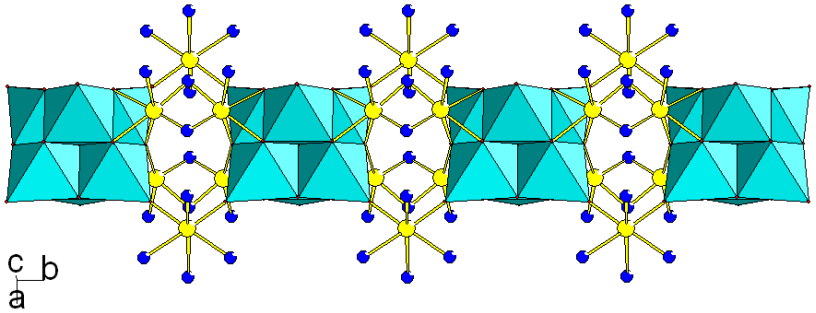
$(Nb_6O_{19})(CuL_3)_2(CuL_4)_2]$ L = NH_3, H_2O

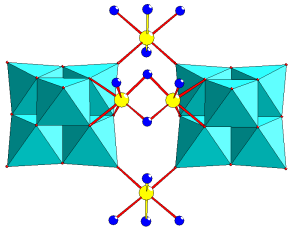
$\{Nb_6Cu_4L_{14}\}$



Cu-Cu = 4.60 Å

Dehydrated, disordered form

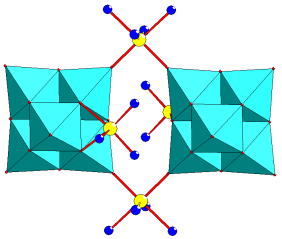




Cu-Cu = 2.72 Å

Positional disorder of the terminal

CuO_3L_3 , 50% occupancy



Cu-Cu = 5.34 Å

Monoclinic, C2/m (#12)

a = 18.266(5) Å α = 90.00 deg.

b = 8.913(5) Å β = 130.840(5) deg.

c = 13.591(5) Å γ = 90.00 deg.

V = 1674.0(8) $Å^3$ Z = 2

R1 = 0.0912; wR2 = 0.1845 (I > 2σ(I))

R1 = 0.0985; wR2 = 0.1942 (all data)

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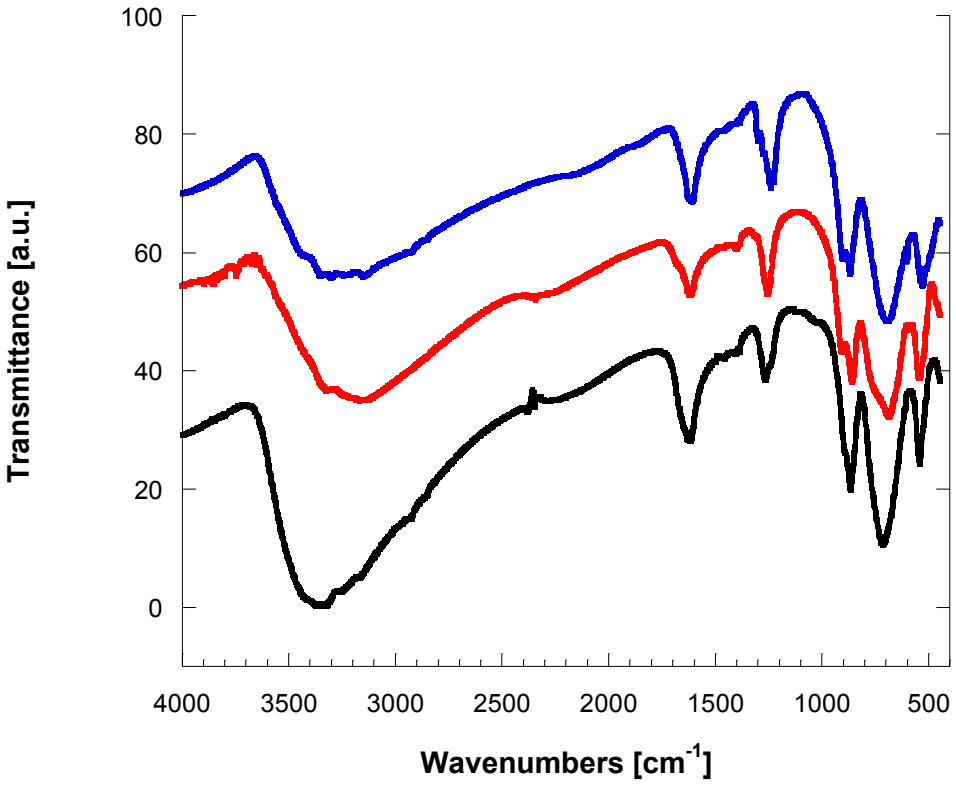
FTIR & chemical analysis

$\{Nb_6Cu_4L_{14}\}$

$\{Nb_6Cu_4L_{14}\}$ $.3H_2O$

$\{Nb_6Cu_2L_2\}.6H_2O$



Characteristic bands

Nb_6O_{19}: 500 – 850 cm^{-1}

NH_3 : 800, 1320, 1600, 3250 cm^{-1}

H_2O: 1600, 3300 cm^{-1}

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Summary & Conclusions

Compatibility of different Nb_xO_y structural motifs as secondary building units (SBUs) capable of forming complex cluster polyoxoniobates (PONs), proven on the example of $\{Nb_{24}\}$.

Confirmed ability to use PON clusters and metal complexes as SBUs in order to form extended -$\{Nb_n\}$-ML_x- type structures.

Low temperature self-assembly – a sound method for the synthesis of diverse PON cluster anions and extended structures.

Acknowledgments: Dr. M. Iliev (TCSAM, Houston) for the Raman spectra

Dr. E. Venturini (SNL) for the magnetic measurements

SNL for the technical and financial support

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