Homo and heteroclusters of Mn(II/III) and Co(II/III) containing aminoalcohols and carboxylate anions

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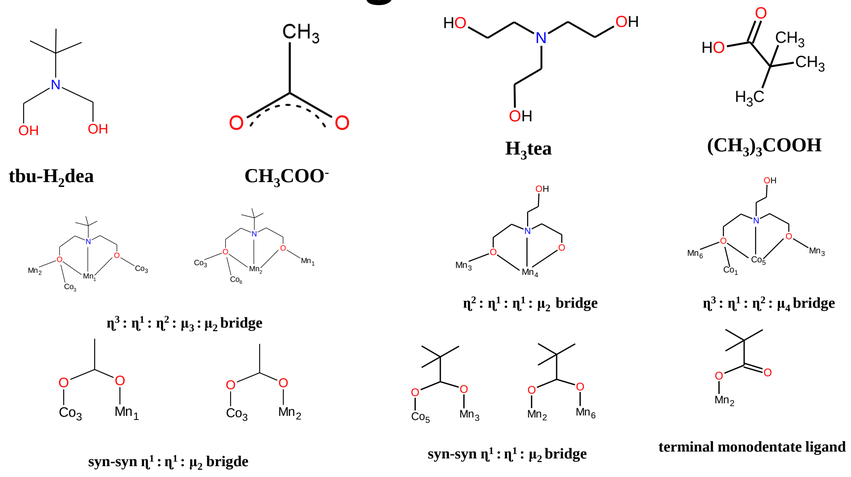
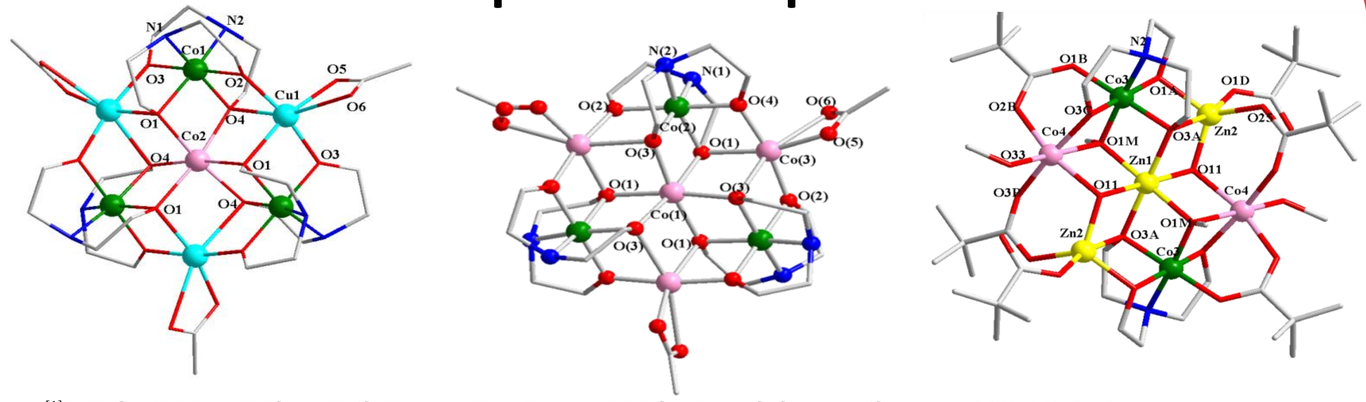
Magnetic clusters, meaning molecular assemblies consisting of a finite number of coupled paramagnetic centers, are currently receiving much attention in several active fields of research such as magnetism or biochemistry. [1] Of particular interest were Co/Mn heteroclusters due to the important and interesting applications that these metallic compounds present: catalysis, molecular magnetism, mimicking of active sites in biological systems.

New Co/Mn heteroclusters were synthesized using cobalt perchlorate ($(Co(ClO_4)_2\cdot 6H_2O$), manganese perchlorate ($(Mn(ClO_4)_2\cdot 6H_2O$), triethanolamine (H_3tea), pivalic acid (Hpiv) and triethylamine (Et_3N), resulting $[Co^{II}_2Mn^{II}_2Mn^{III}_2$ $(Htea)_4(piv)_6(Hpiv)_2]\cdot 8H_2O$ and using the same salts, but changing the aminoalcohol with N-tertbutyldiethanolamine and using sodium acetate for $[Co^{II}_3Mn^{II}_2Mn^{III}_2(N\text{-}tbdea)_4(AcO)_4(OH)_2(H_2O)_2].2ClO_4\cdot H_2O$.

Ligands



Reported compounds



[1] V. Tudor, G. Marin, F. Lloret, V. Ch. Kravtsov, Y. A. Simonov, M. Julve, M. Andruh, *Inorg. Chim. Acta* , **2008**, *361*, 3446.

[2] E. Martin, V. Tudor, A. M. Madalan, C. Maxim, F. Tuna, F. Lloret, M. Julve, M. Andruh, *Inorg. Chim. Acta*, **2018**, *475*, 98–104.

Synthesis

$Co(ClO_4)_2\cdot 6H_2O + Mn(ClO_4)_2\cdot 6H_2O + tbH_2dea + CH_3COONa \xrightarrow{iPrOH}$ **brown crystals**

(tbH_2dea = N-tert-butyldiethanolamine)
(CH_3COONa = sodium acetate)

$Co(ClO_4)_2\cdot 6H_2O + H_3tea + Mn(ClO_4)_2\cdot 6H_2O + Hpiv \xrightarrow{EtOH/ACN/Et_3N}$ **brown single crystals**

IR and UV-Vis characterizations

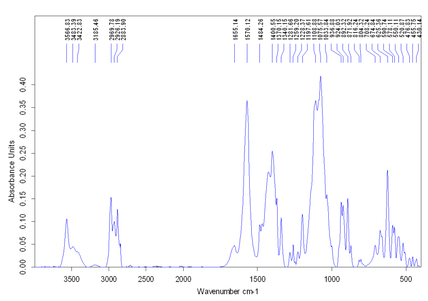


Figure 1. IR spectrum of the brown single crystals $[Co^{II}_3Mn^{II}_2Mn^{III}_2(tbdea)_4(AcO)_4(OH)_2(H_2O)_2].2ClO_4\cdot H_2O$

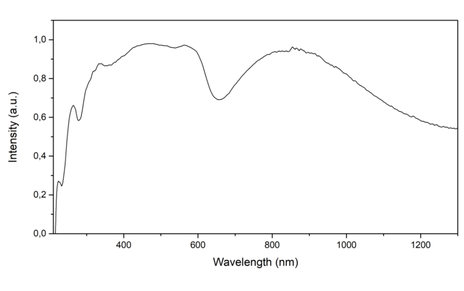


Figure 2. UV-VIS spectrum of $[Co^{II}_3Mn^{II}_2Mn^{III}_2(tbdea)_4(AcO)_4(OH)_2(H_2O)_2].2ClO_4\cdot H_2O$

Transitions;

- **Mn^{II} – forbidden transitions, very weak bands;**
- **Mn^{III} – octahedral:**

  ^5E_g $^5T_{2g}$. (16000-21000 cm^{-1}/476 - 625 nm)
- **Co^{II} – octahedral:**

  $^4T_{1g} \longrightarrow {}^4T_{2g}$ (8000-10000 cm^{-1}/1000 - 1250 nm)

  $^4T_{1g} \longrightarrow {}^4T_{1g}(P)$ (~20000 cm^{-1}/500 nm)

  $^4T_{1g} \longrightarrow {}^4A_{2g}$ (~12000 cm^{-1}/830 nm)

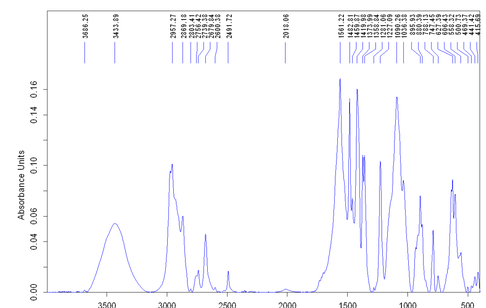


Figure 3. IR spectrum of the brown single crystals

H_3tea: 3433 cm^{-1} (ν OH), 2957 cm^{-1} (ν_{as} CH_2), 2869cm^{-1} (ν_s CH_2), 1482cm^{-1} (δ CH_2), 1281 cm^{-1} (ν C–N);

Hpiv: 2957 cm^{-1} (ν_{as} CH_3), 2869 cm^{-1} (ν_s CH_3), 1482 cm^{-1} (δ_{as} CH_3), 1561 cm^{-1} (ν_{as} (COO)), 1419 cm^{-1} (ν_s (COO)), 1036 cm^{-1};

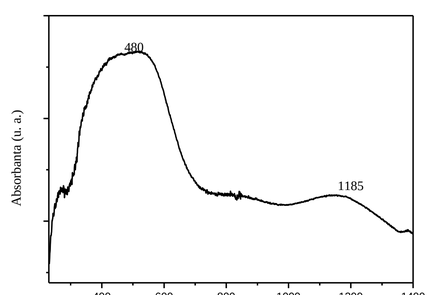


Figure 4. UV-VIS spectrum of $[Co^{II}_2Mn^{II}_2Mn^{III}_2$ $(Htea)_4(piv)_6(Hpiv)_2]\cdot 8H_2O$

Transitions:

- **Mn^{II} – forbidden transitions, very weak bands;**
- **Mn^{III} – octahedral:**

  ^5E_g $^5T_{2g}$ (16000-21000 cm^{-1} / 476 - 625 nm)
- **Co^{II} – octahedral:**

  $^4T_{1g} \longrightarrow {}^4T_{2g}$ (8000-10000 cm^{-1} / 1000 - 1250 nm)

  $^4T_{1g} \longrightarrow {}^4T_{1g}(P)$ (~20000 cm^{-1} / 500 nm)

  $^4T_{1g} \longrightarrow {}^4A_{2g}$ (~12000 cm^{-1} / 830 nm)

Crystal structure

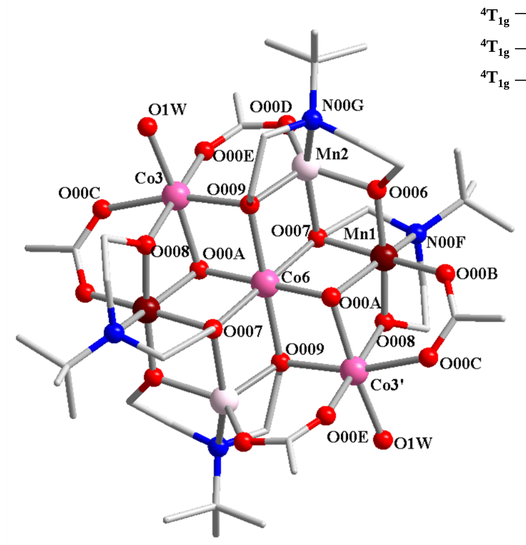


Figure 5. Metal ions and donor atoms in $[Co^{II}_3Mn^{II}_2Mn^{III}_2(N\text{-}tbdea)_4(AcO)_4(OH)_2(H_2O)_2].2ClO_4\cdot H_2O$

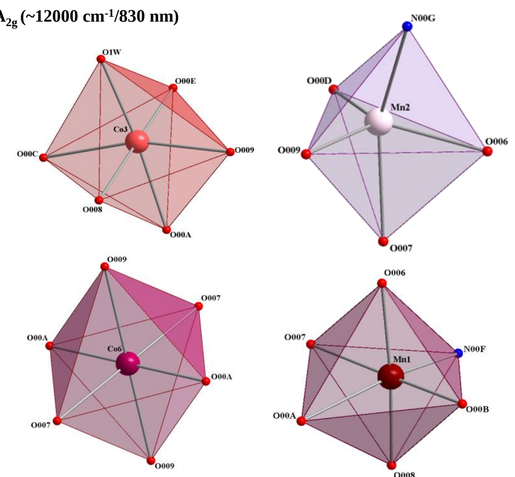


Figure 6. Coordination geometries of metal ions in $[Co^{II}_3Mn^{II}_2Mn^{III}_2(tbdea)_4(AcO)_4(OH)_2(H_2O)_2].2ClO_4\cdot H_2O$

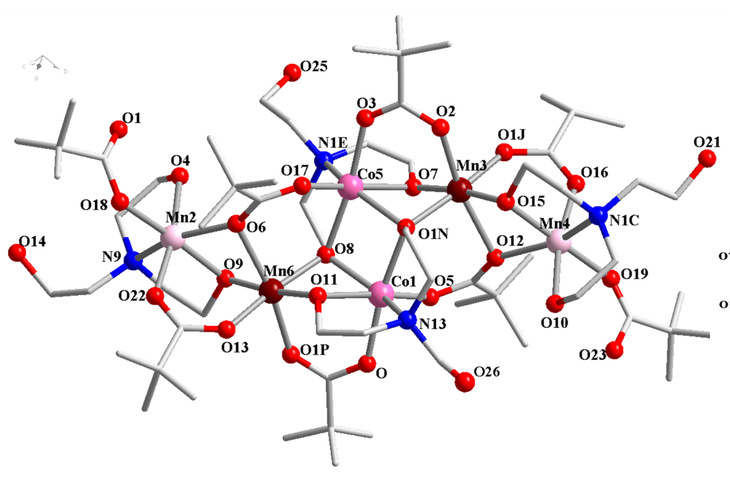


Figure 7. Structural unit in the compound $[Co^{II}_2Mn^{II}_2Mn^{III}_2$ $(Htea)_4(piv)_6(Hpiv)_2]\cdot 8H_2O$

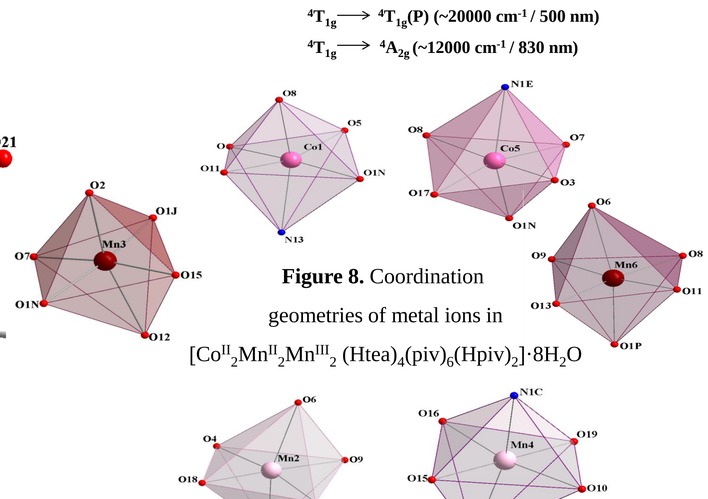


Figure 8. Coordination geometries of metal ions in $[Co^{II}_2Mn^{II}_2Mn^{III}_2$ $(Htea)_4(piv)_6(Hpiv)_2]\cdot 8H_2O$

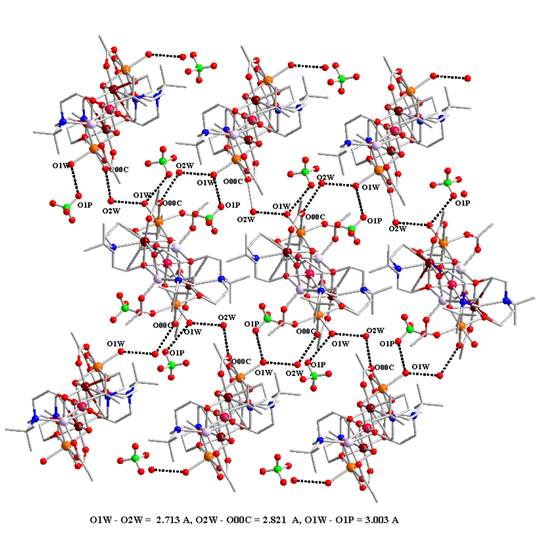


Figure 9. Hydrogen bonds between heterometallic units $[Co^{II}_3Mn^{II}_2Mn^{III}_2(N\text{-}tbdea)_4(AcO)_4(OH)_2(H_2O)_2].2ClO_4\cdot H_2O$

Bond lengths (Å)		Angles (°)		Bond lengths (Å)	
Co3 O008	2.096(4)	O1W Co3 O00E	88.8(2)	Co6 O007	2.173(4)
Co3 O009	2.160(4)	O00A Co3 O009	80.93(14)	Co6 O009	2.223(4)
Co3 O00A	2.129(4)	O00C Co3 O008	84.88(16)	Co6 O00A	1.983(3)
Co3 O00C	2.176(4)	O009 Co6 O007	99.27(13)	Mn1 O006	1.915(4)
Co3 O00E	2.074(5)	O00A Co6 O009	97.33(14)	Mn1 O007	1.966(4)
Co3 O1W	2.115(5)	O00A Co6 O007	98.44(14)	Mn1 O008	1.879(4)
Mn2 O006	1.963(4))	N00G Mn2 O006	84.12(17)	Mn1 O00B	1.933(4)
Mn2 O007	2.192(4)	O009 Mn2 O007	86.20(14)	Mn1 O00A	2.183(4)
Mn2 O009	1.968(4)	O00D Mn2 O009	117.35(17)	Mn1 N00F	2.452(5)
Mn2 O00D	1.961(4)	O00B Mn1 O008	93.21(18)		
Mn2 N00G	2.185(5)	O00A Mn1 O007	81.69(14)		

Bond lengths (Å)		Angles (°)		Bond lengths (Å)	
Mn2 - O18	2.041(12)	O18 - Mn2 - O22	86.5(5)	Mn4 - O16	2.045(11)
Mn2 - O22	2.065(11)	O15 - Mn3 - O2	89.0(5)	Mn4 - O15	2.043(10)
Mn3 - O15	1.874(10)	O7 - Mn3 - O2	97.9(5)	Mn6 - O11	1.895(11)
Mn3 - O7	1.879(12)	O16 - Mn4 - O15	89.3(4)	Mn6 - O9	1.906(12)
Mn3 - O2	2.083(12)	O9 - Mn6 - O8	96.2(5)	Mn6 - O1P	2.134(15)
Mn3 - O12	2.269(12)	O13 - Mn6 - O8	169.4(5)	Mn6 - O6	2.246(11)
Co1 - O5	2.059(11)	O5 - Co1 - O11	163.5(5)	Co5 - O17	2.027(11)
Co1 - O11	2.089(11)	O5 - Co1 - O	80.8(5)	Co5 - O3	2.071(11)
Co1 - O	2.093(12)	O11 - Co1 - O	90.0(5)	Co5 - O7	2.074(10)
Co1 - O1N	2.129(11)	O17 - Co5 - O3	83.0(5)	Co5 - O8	2.163(11)
Co1 - O8	2.212(11)	O17 - Co5 - O7	163.8(5)	Co5 - O1N	2.229(10)

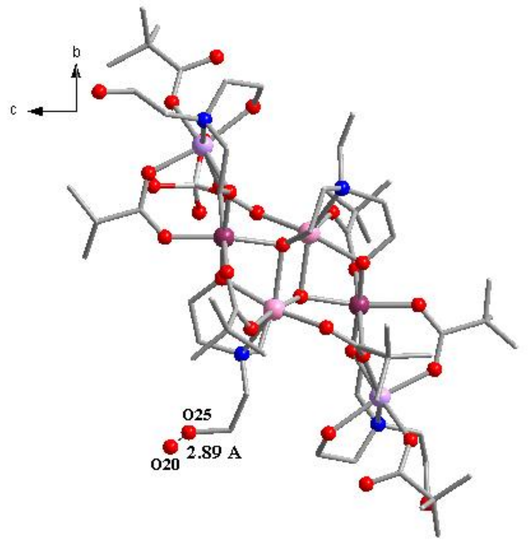


Figure 10. Hydrogen bonds between crystallization water molecules and alkoxo groups

Conclusions: The crystal structure of the new compounds confirm the presence of the Cobalt(II,III) and Manganese(II,III) metal ions, based on interatomic distances and stereochemical preference of these cations.

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