Structure and magnetic properties of polynuclear complexes containing Re(IV)

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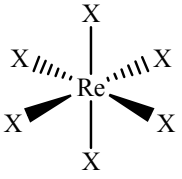
Re(IV): chemistry

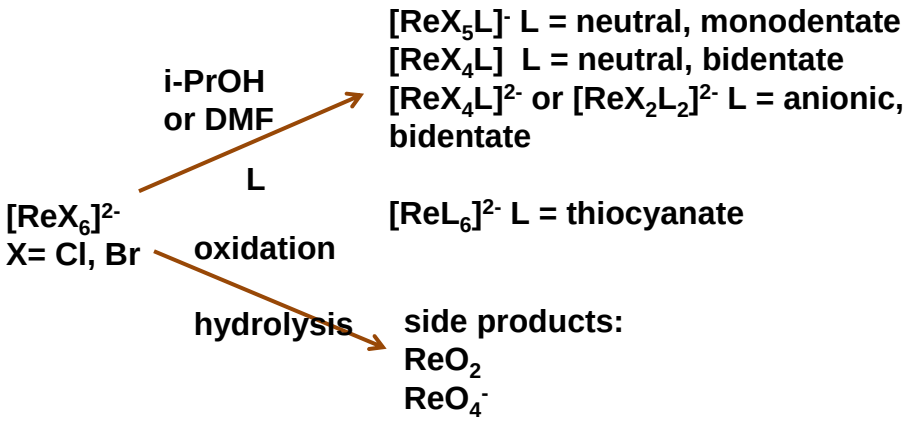
- Usually forms octahedral complexes
- Hydrolysis (forming ReO_2) is always a decomposition product
- Complexes are reasonably stable against redox processes
- Complexes are inert to ligand substitution



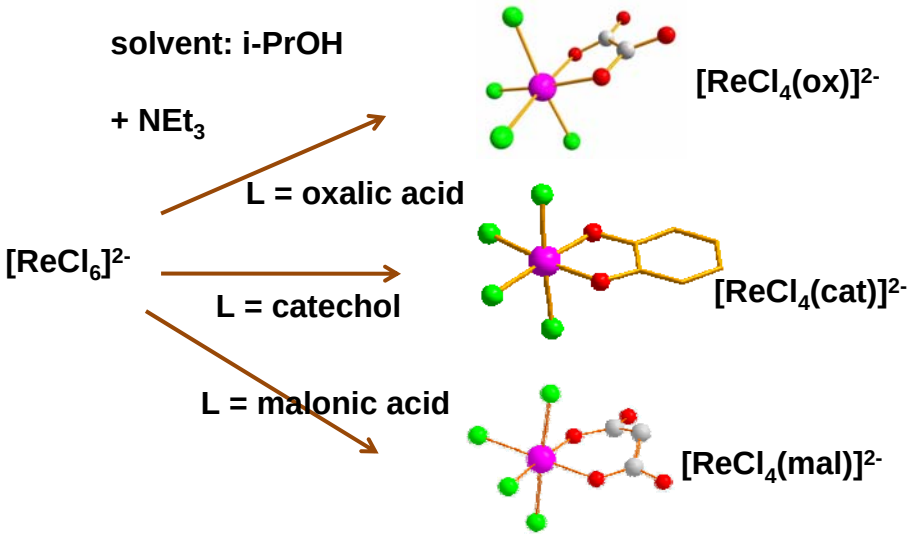
d_{Re-X} (Å)
1.953 (F)
2.353 (Cl)
2.502 (Br)
2.721 (I)

Substitution reactions

General route



Substitution by O,O-bidentate ligands

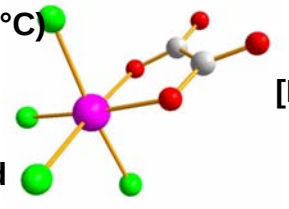


Substitution by O,O-bidentate ligands

solvent: DMF (100-130 °C)

+ NEt_3

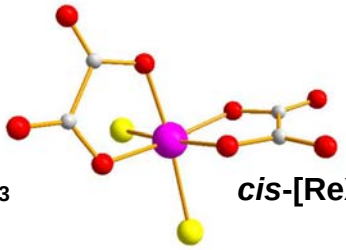
L = oxalic acid



$[ReX_4(ox)]^{2-}$

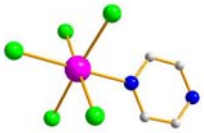
$[ReX_6]^{2-}$
X = Cl, Br

L = oxalic acid,
larger amount of NEt_3



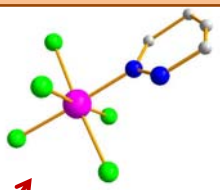
cis-$[ReX_2(ox)_2]^{2-}$

Substitution by neutral amines



$[ReCl_5(pyz)]^-$
pyz = pyrazine

$[ReCl_5(pym)]^-$
pym = pyrimidine

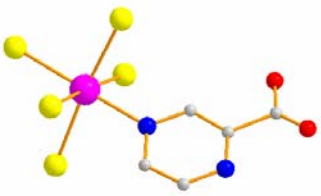


$[ReCl_5(pyd)]^-$
pyd = pyridazine

solvent: DMF
100-110 °C
2-5 hours

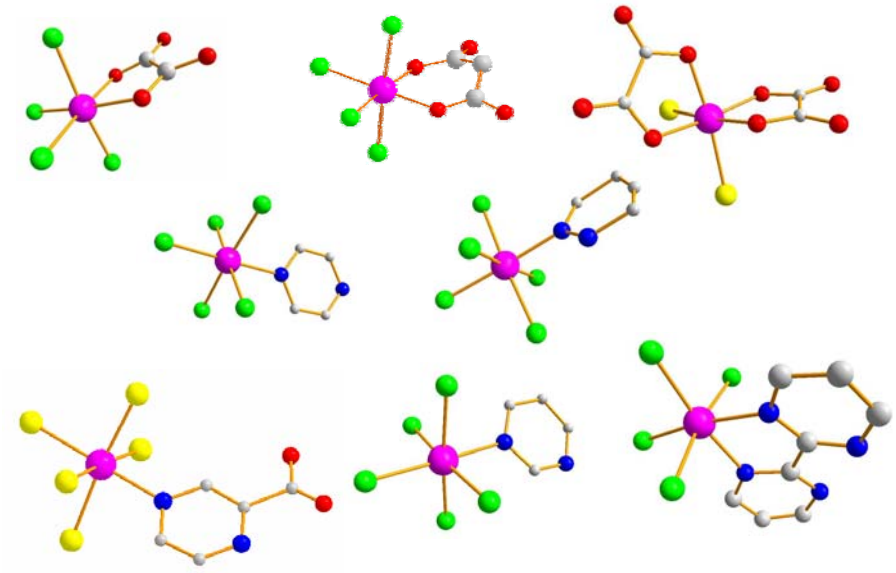
$[ReX_6]^{2-}$

solvent: i-PrOH:acetone 2:1
60-70 °C
3 hours



$[ReBr_5(pyzCOOH)]^-$

Re(IV) building blocks

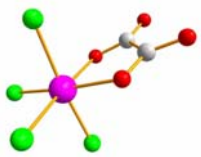


Re(IV): polynuclear complexes

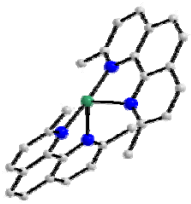
Strategy

Re(IV) monomer + M(II) + blocking ligand

Preformed complex



$[ReCl_4(ox)]^{2-}$



$[Ni(dmphen)_2]^{2+}$

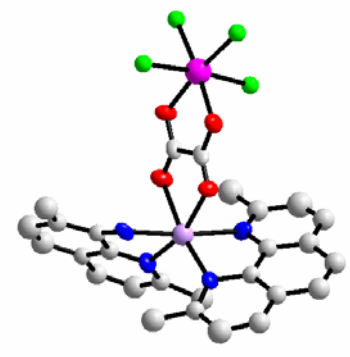
Re(IV): polynuclear complexes

The polynuclear complexes can be classified in three groups:

- **Dinuclear Re(IV)-M(II) complexes**
- **Clusters of discrete size**
- **Magnetic chains**

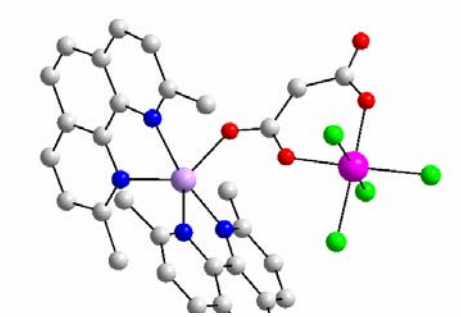
Dinuclear Re(IV)-M(II) complexes

$[ReCl_4(\mu\text{-ox})Cu(phen)_2]$
$[ReCl_4(\mu\text{-ox})M(dmphen)_2]$ (M = Ni, Co, Fe, Mn)
$[ReCl_4(\mu\text{-mal})Cu(bipy)_2]$
$[ReCl_4(\mu\text{-mal})Cu(phen)_2]$
$[ReCl_4(\mu\text{-mal})Cu(terpy)]$
$[ReCl_4(\mu\text{-mal})M(dmphen)_2]$ (M = Ni, Co, Fe)
$[ReCl_4(\mu\text{-mal})Ni(dmphen)(CH_3CN)_2(H_2O)]$
$[ReBr_4(\mu\text{-mal})Cu(bipy)_2]$
$[ReBr_4(\mu\text{-mal})Cu(phen)_2]$
$[ReBr_4(\mu\text{-mal})M(dmphen)_2]$ (M = Ni, Co, Mn)

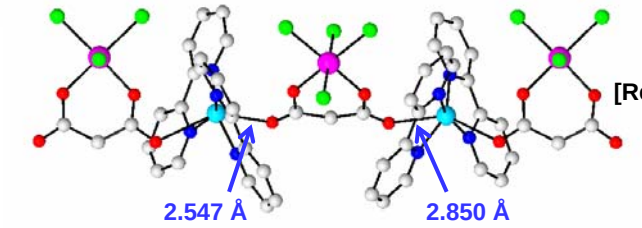


$[ReCl_4(\mu\text{-ox})Co(dmphen)_2]$

Dinuclear Re(IV)-M(II) complexes

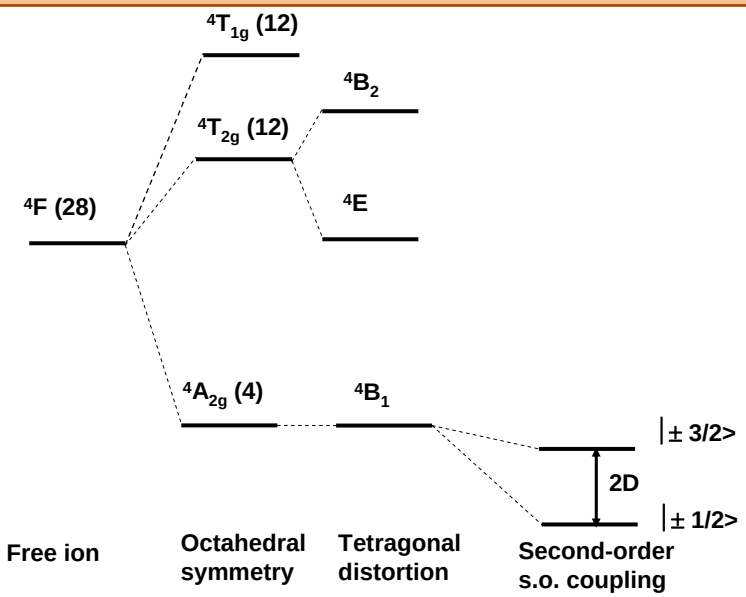


$[ReCl_4(\mu\text{-mal})Co(dmphen)_2]$



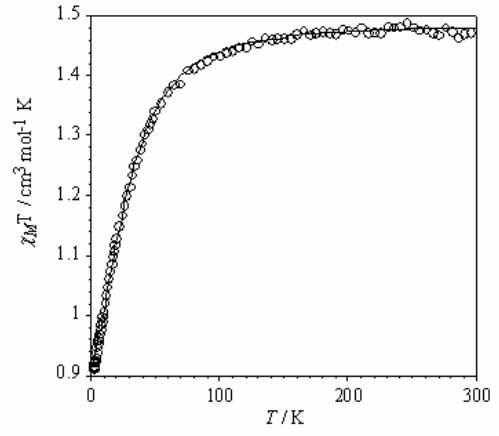
$[ReCl_4(\mu\text{-mal})Cu(bipy)_2]$

Re(IV)



Re(IV)

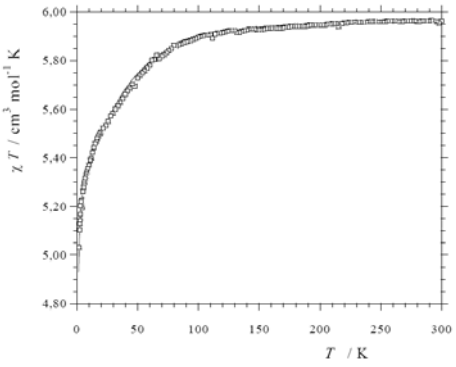
A typical susceptibility curve for a Re(IV) complex



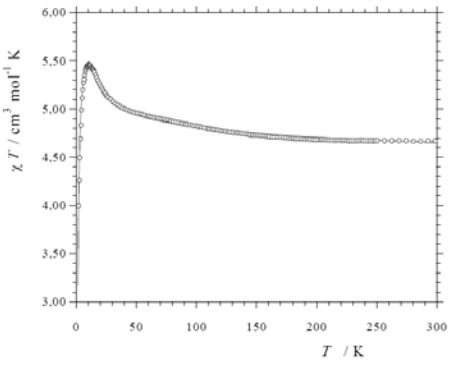
$(PPh_4)_2[ReCl_4(mal)]$

Dinuclear Re(IV)-M(II) complexes

Thermal variation of the $\chi_M T$ product



$[ReCl_4(\mu\text{-ox})Mn(dmphen)_2]$



$[ReCl_4(\mu\text{-ox})Co(dmphen)_2]$

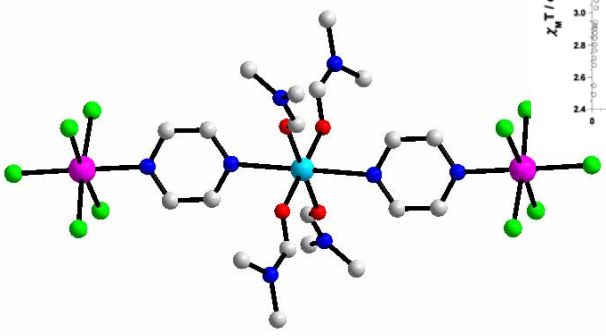
Dinuclear Re(IV)-M(II) complexes

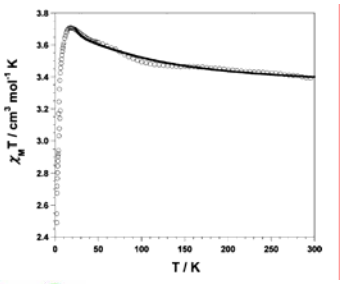
$$\mathbf{H} = -J\,\mathbf{S}_{\mathrm{Re}}\mathbf{S}_{\mathrm{M}} + D_{\mathrm{Re}}[\mathbf{S}^2_{z\,\mathrm{Re}} - 5/4] + D_{\mathrm{M}}[\mathbf{S}^2_{z\mathrm{M}} - n(n+2)/12] + (g_{\mathrm{Re}}\mathbf{S}_{\mathrm{Re}} + g_{\mathrm{M}}\mathbf{S}_{\mathrm{M}})\beta H$$

Complex	$\lvert D_{Re}\rvert$/cm^{-1}	$\lvert D_{M}\rvert$/cm^{-1}	g_{Re}	g_{M}	J/cm^{-1}
[$ReCl_4$(μ-ox)Cu(phen)$_2$]	24(1)	-	1.88(1)	2.02(1)	–0.90(2)
[$ReCl_4$(μ-ox)Ni(dmphen)$_2$]	44	6.1	1.82	2.08	+5.9
[$ReCl_4$(μ-ox)Co(dmphen)$_2$]	49	6.2	1.85	2.49	+5.2
[$ReCl_4$(μ-ox)Fe(dmphen)$_2$]	48	14	1.83	2.20	+2.8
[$ReCl_4$(μ-ox)Mn(dmphen)$_2$]	45	0	1.85	2.0	–0.1
[$ReCl_4$(μ-mal)Cu(bipy)$_2$]	60	-	1.79	2.13	–0.09
[$ReCl_4$(μ-mal)Cu(phen)$_2$]	44	-	1.78	2.12	–0.39
[$ReCl_4$(μ-mal)Cu(terpy)]	57	-	1.7	2.08	+1.51
[$ReCl_4$(μ-mal)Ni(dmphen)$_2$]	52(2)	16.1(2)	1.81(1)	2.20(2)	–0.65(2)
[$ReCl_4$(μ-mal)Ni(dmphen)(CH_3CN)$_2$(H_2O)]	52(1)	8.2(2)	1.80(1)	2.15(1)	–6.8(1)
[$ReCl_4$(μ-mal)Co(dmphen)$_2$]	57(2)	27.1(3)	1.80(1)	2.48(2)	–0.50(2)
[$ReCl_4$(μ-mal)Fe(dmphen)$_2$]	58(2)	9.1(2)	1.81(1)	2.09(1)	–0.44(2)
[$ReBr_4$(μ-mal)Cu(bipy)$_2$]	17(1)	-	1.80(1)	2.15(1)	–0.26(1)
[$ReBr_4$(μ-mal)Cu(phen)$_2$]	29(1)	-	1.80(1)	2.16(2)	–1.83(2)
[$ReBr_4$(μ-mal)Ni(dmphen)$_2$]	30(2)	15(2)	1.80(1)	2.17(2)	–1.37(2)
[$ReBr_4$(μ-mal)Co(dmphen)$_2$]	59(2)	18(1)	1.80(1)	2.30(1)	–0.90(3)

Re(IV) clusters of discrete size

Trinuclear complexes





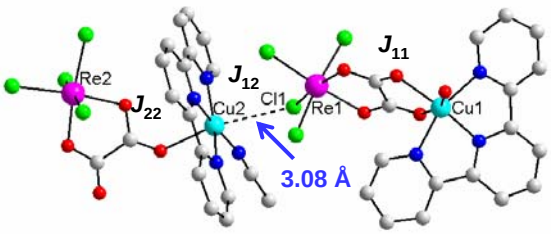
$|D_{Re}| = 34.3$ cm^{-1}

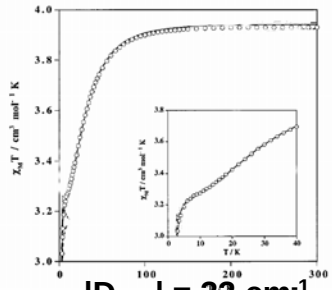
$J = +11.8$ cm^{-1}

[{$ReCl_5$(μ-pyz)}$_2$Cu(dmf)$_4$]

Re(IV) clusters of discrete size

Tetranuclear complexes





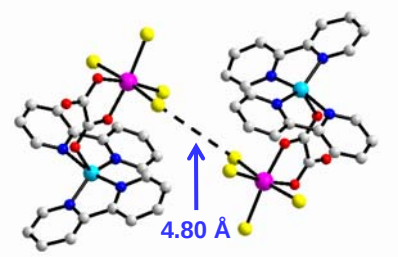
$|D_{Re1}| = 32\ cm^{-1}$
$|D_{Re2}| = 34\ cm^{-1}$

$J_{11} = -0.83\ cm^{-1}$
$J_{12} = +0.70\ cm^{-1}$
$J_{22} = +5.6\ cm^{-1}$

$[ReCl_4(\mu\text{-ox})Cu(terpy)(H_2O)][ReCl_4(\mu\text{-ox})Cu(terpy)(CH_3CN)]$

Re(IV) clusters of discrete size

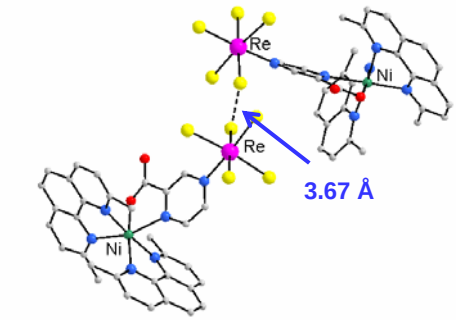
Tetranuclear complexes



$|D_{Re}| = 83\ cm^{-1}$

$J_{ReCu} = -0.65\ cm^{-1}$
$J_{ReRe} = -1.51\ cm^{-1}$

$[ReBr_4(\mu\text{-ox})Cu(bipy)_2]$



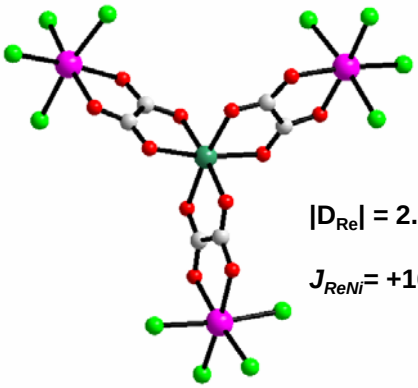
$|D_{Re}| = 8.8\ cm^{-1}$

$J_{ReNi} = +0.66\ cm^{-1}$
$J_{ReRe} = -0.12\ cm^{-1}$

$[ReBr_5(\mu\text{-pyzCOOH})M(dmphen)_2]$
(M = Ni, Co)

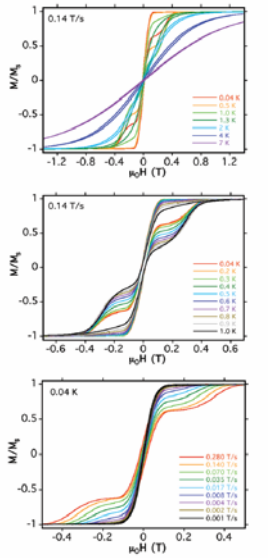
Re(IV) clusters of discrete size

Tetranuclear complexes



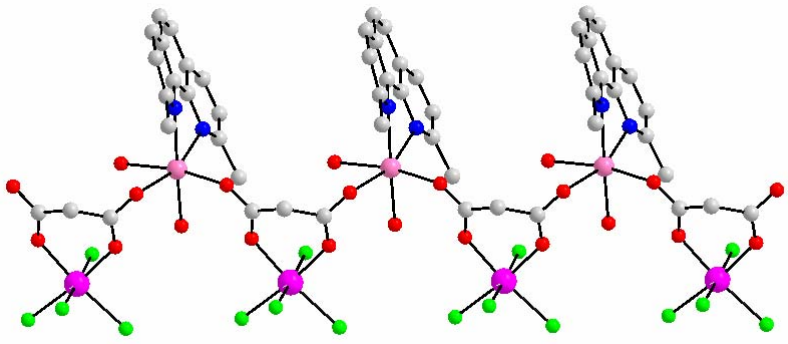
$|D_{Re}| = 2.8\ cm^{-1}$

$J_{ReNi} = +16.5\ cm^{-1}$



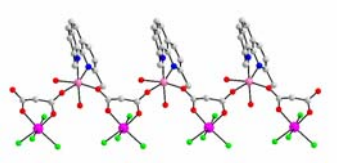
$(NBu_4)_4[\{ReCl_4(\mu\text{-ox})\}_3M]$ (M = Ni, Co, Fe)

Re(IV): magnetic chains



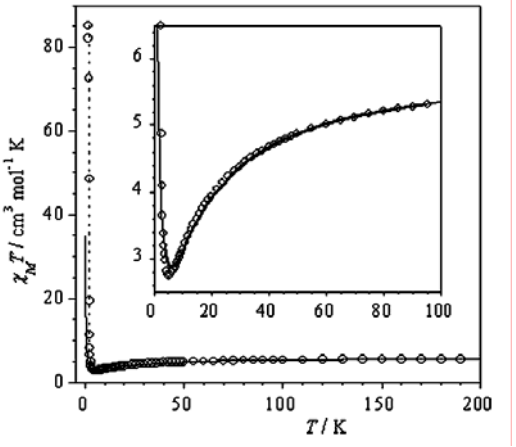
$[ReX_4(\mu\text{-mal})Mn(dmphen)(H_2O)_2]$ (X = Cl, Br)

Re(IV): magnetic chains



$|D_{Re}| = 49\ cm^{-1}$

$J = -3.0\ cm^{-1}$



$[ReX_4(\mu\text{-mal})Mn(dmphen)(H_2O)_2]$ (X = Cl, Br)

Conclusions (chemistry)

- Different Re(IV) building blocks can be obtained by substitution on $[ReX_6]^{2-}$ compounds.
- 2-propanol and DMF are the most adequate solvents for the synthesis. They provide good yields and reasonable reaction times.
- A full substitution is difficult to achieve, due to the inertness of the Re(IV) ion.
- Rhenium(IV)-containing heterobimetallic species have been synthesized by using the rational ‘‘complex as ligand’’ approach.
- Their structures include well-defined dinuclear complexes, tri- tetra- and pentanuclear compounds and chains.

Conclusions (magnetism)

- **Very interesting magnetic behaviours can be found in new materials based on Re(IV) complexes.**
- **Large values of the zero field splitting are observed in the substituted Re(IV) complexes, in particular in those containing a bidentate ligand.**
- **Both, ferro- and antiferromagnetic interactions have been observed in different structural units.**
- **The magneto-structural studies of all of these mono- and polynuclear compounds have provided a reasonable understanding of the magnetic behavior of the Re(IV) mononuclear complexes as well as those of the heterometallic Re(IV)–M(II) species.**

Participants

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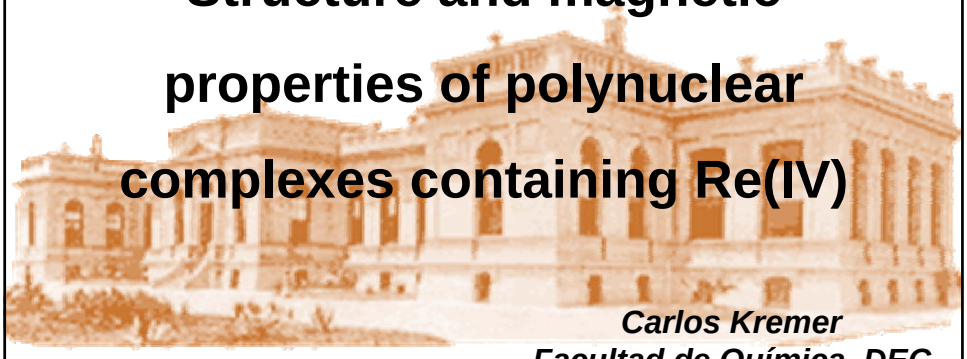

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