Mini Review

Substitution on Re(IV) complexes: a tool for the synthesis of novel mono- and polynuclear compounds

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Abstract: Rhenium(IV) complexes are relatively scarce if compared with those of other oxidation states as Re(V) or Re(VII). It is a $5d^3$ ion, and usually forms octahedral complexes which are reasonably stable against redox processes and inert to ligand substitution. This is the basis for the preparation of mononuclear species that can act as ligands towards other transition metal ions. For example, complexes containing dicarboxylic ligands, $[ReX_4(ox)]^{2-}$ and $[ReX_4(mal)]^{2-}$ (X = Cl, Br; ox = oxalato; mal = malonato), or N-donor ligands, $[ReCl_5(pyz)]^-$ (pyz = pyrazine) have been used as building blocks to construct heteropolynuclear complexes. The different synthetic routes, as well as the designed structures, from discrete binuclear complexes to extended chain-like compounds, are reviewed in this contribution.

Keywords: *Rhenium(IV); coordination compounds; polynuclear complexes.*

1. Re(IV): AN OVERVIEW

Coordination compounds of rhenium with the metal ion in the oxidation states +1 up to +7 have been characterized and reported. Different reviews cover the relevant rhenium coordination chemistry [1-3].

Rhenium(IV) complexes are relatively scarce if compared with those of rhenium(III) or the most representative rhenium(V). One of the reasons is the tendency to hydrolyze when exposed to water. This fact has been recognized and studied many years ago in the simple hexahalorhenate(IV) complexes $[ReX_6]^{2-}$ (X = Cl, Br) which, in the presence of water, finally yield ReO_2 rather quickly [4]. The stepwise formation constants (K_6) of hexacloro- and hexabromorhenate(IV) at 15 °C, I = 3M $HClO_4$ are 2.20 x 10^6 and 1.8x10^5 respectively, indicating a better stability for the chloro analogue. In this line, the exchange rates for halide isotopic exchange at 60 °C are very low, 1.29 x 10^{-4} and 81.6 x 10^{-4} M^{-1} h^{-1} respectively. The relative stability (thermodynamic and kinetic) seems to be originated in the stronger Re-X bond interaction for X = Cl (stretching force constants 1.62 and 1.35 mdyne $Å^{-1}$ for Re-Cl and Re-Br, respectively) [5].

On the other hand, this is an intermediate oxidation state with the possibility to be either oxidized or reduced. The standard reduction potentials $E°$ ($ReO_4^-/ReO_2 \cdot 2H_2O$) and $E°$ ($ReO_2 \cdot 2H_2O$/Re) are 0.49 and 0.29 V respectively [6]. This accounts for the general tendency of Re(IV) complexes to be oxidized and/or reduced under mild conditions. ReO_4^- is a common undesirable byproduct in the synthesis of Re(IV) complexes if they are not performed under inert atmosphere [7]. The easy reduction to Re(III) complexes can be also verified, as reported in the compounds $[Re^{IV}X_4(bpym)]$ (X = Cl, Br; bpym = 2,2'-bipyrimidine). The reversible reduction of $[Re^{IV}X_4(bpym)]$ to $[Re^{III}X_4(bpym)]^-$ occurs at +0.19 V (vs. NHE) in acetonitrile. These Re(IV) complexes can also be oxidized to Re(V) compounds in a non reversible process [8].

The most numerous Re(IV) complexes are octahedral halo species of the type $[ReX_6]^{2-}$, $[ReX_5L]^-$, $[ReX_4L_2]$, and $[ReX_4(L')]$, where L and L' are monodentate and bidentate neutral ligands, respectively [1-3]. The heptacyano anion $[Re(CN)_7]^{3-}$ is a remarkable exception containing seven-coordinate metal ion [9, 10].

2. SYNTHESIS AND STRUCTURE OF HEXAHALORHENATES

Hexachlororhenate is the simplest Re(IV) complex. It can be conveniently prepared by the reduction of $[ReO_4]^-$ with H_3PO_2 in HCl [11, 12]. Different salts have been isolated and characterized. Those whose structure has been determined either by x-ray or neutron diffraction include:

a) salts with discrete small cations, $K_2[ReCl_6]$ [13,14], $Cs_2[ReCl_6]$ [15], $(NH_4)_2[ReCl_6]$ [16,17], $Se_4[ReCl_6]$ [18], $Ag_2[ReCl_6]$ [19],

b) salts with larger organic cations, $(NR_4)_2[ReCl_6]$ (R = Me, Et) [20, 21], $(PPh_4)_2[ReCl_6] \cdot 2CH_3CN$ [22], $(MePPh_3)_2[ReCl_6]$ [23], $(PPN)_2[ReCl_6]$ (PPN = (triphenylphosphine)iminium) [24], $(DTF)_2[ReCl_6]Cl_2 \cdot 3H_2O$ (DTF = dithiobisformamidium) [25], a -(BEDT-TTF)$_4[ReCl_6] \cdot C_6H_5CN$ (BEDT-TTF = bis (ethylenedithio)tetrathiafulvalene) [26], (p-rad)$_2[ReCl_6]$ and (m-rad)$_2[ReCl_6]$ (p/m-rad = 2-(4/3-*N*-methylpyridinium)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl-3-*N*-oxide) [27],

c) salts with protonated bases as cations, $(HB)_2[ReCl_6]$ (B = p-toluidine, pyridine, quinoline, 2,2'-bipyridine, 18-crown-6) [28-31], $(H_4cyclam)[ReCl_6]Cl_2 \cdot 4dmso$ (cyclam = tetraazacyclotet-

radecane; dmso = dimethylsulfoxide) [32], $(H_4biim)[ReCl_6]\cdot 4H_2O$ (H_2biim = 2,2'-biimidazole) [33], and

d) salts with complex cations, $[Os^{III}Cl(NH_3)_5][ReCl_6]$ [34], $[M^{III}Cl(NH_3)_5]_2[ReCl_6]Cl_2$ (M = Ru, Ir) [35-37], $[RuCl_2(en)_2]_2[ReCl_6]\cdot 2CH_3CN$ [37], $[Fe(C_5R_5)_2]_2[ReCl_6]$ (R = H, Me) [38], $[Re^{III}Cl_2(CH_3CN)_4]_2[ReCl_6]\cdot 2CH_3CN$ [17], and [*cis*-$Re(CH_3CN)_4(CO)_2]_2[ReCl_6]$ [39]. $[ReBr_6]^{2-}$ can also be prepared from $[ReO_4]^-$ by reduction with H_3PO_2 [11]. The reported structures with this anion is limited to $M_2[ReBr_6]$ (M = K, Rb, Cs, NH_4, PPh_4) [15, 40-43], $[Fe(C_5H_5)_2]_2[ReBr_6]$ [38], $[Rh^{III}Cl(NH_3)_5][ReBr_6]$ [44], and $(C_{15}H_{13}N_4)_4[Re^VBr_4O(H_2O)]_2[ReBr_6]Br_4\cdot 2H_2O$ [45].

Different salts of hexaiodorhenate have been prepared by direct reduction of perrhenate or perrhenic acid with concentrated HI [46-48]. Only two compounds with this anion are fully characterized, $K_2[ReI_6]$ and $(NH_4)_2[ReI_6]$ [48].

The hexafluororhenate analogue has been very scarcely studied. $M_2[ReF_6]$ salts (M = Na, K, NH_4, Rb, Cs) have been prepared by a solid-state reaction in a mixture $M_2[ReI_6]$:MHF_2 [49]. K_2ReF_6 is the only crystal structure reported for this anion [50].

From a structural point of view, the $[ReX_6]^{2-}$ compounds present the rhenium(IV) center surrounded by six halide anions in a regular or slightly distorted octahedral environment. The average Re-X distances follow the expected trend, Re-F 1.953 Å , Re-Cl 2.353 Å, Re-Br 2.502 Å, and Re-I 2.721 Å.

3. SYNTHESIS OF THE OTHER MONONUCLEAR Re(IV) COMPLEXES.

Mononuclear Re(IV) complexes can be prepared by different synthetic routes. Many of them include a redox process. Examples are the reduction of Re(VII) or Re(V) compounds, and the oxidation of lower state rhenium complexes [1-3]. Indeed, Re (IV) complexes are often isolated as unexpected byproducts in many reactions of Re(V) or Re(III) compounds. The reaction of $[Re^VOCl_2(C_2H_5O)(PPh_3)_2]$ (Ph = phenyl) with acetylacetone gives $[Re^{IV}Cl_2(acac)_2]$ (acac = acetylacetonate) [51].

Treatment of the dinuclear $[Re^{II}_2Cl_4(PEt_3)_4]$ (Et = ethyl) with H_2 in dichloromethane produces a mixture of complexes containing *trans*-$[Re^{IV}Cl_4(PEt_3)_2]$ and $[PEt_4][Re^{IV}Cl_5(PEt_3)]$ [52]. $[Re^{IV}Cl_4(bipy)]$ (bipy = 2,2´-bipyridine) is directly obtained from $ReCl_5$ [53] (it can also be obtained by a substitution route as will be discussed later). *cis*-$[Re^{IV}(NCS)_4(Ph_3P)(Ph_3PO)]$ is formed during the reaction of $[Re^VOCl_3(Ph_3P)_2]$ and Me_3SiNCS (Me = methyl) [54], while $[Re^{IV}Cl_4(dppom\text{-}P,O)]$ (dppom-*P*,*O* = $Ph_2PCH_2P(=O)Ph_2$) and $[Re^{IV}Cl_4(OPPh_3)_2]$ are also obtained from the same Re(V) precursor [55, 56]. The reaction of $[Re^VNCl_2(PPh_3)_2]$ with Me_3SiNCS produces *trans*-$[Re^{IV}(OH)(NCS)_3(Ph_3P)_2]\cdot$MeOH [57]. Other starting compounds have been *mer*-$[Re^VOBr_3(bipy)]$ [58] and $KReO_4$ [59].

These syntheses are quite difficult to control. The final product can be a mixture of rhenium complexes in different oxidation states from which the Re(IV) compound should be isolated. With this in mind, preparative methods based on halide substitution on $[ReX_6]^{2-}$ (X = Cl, Br) complexes have been used, in spite of their known inertness to substitution. Table 1 lists the fully characterized complexes obtained by substitution on $[ReX_6]^{2-}$ anions. The reactions are performed mostly in non aqueous solvents with excess of the incoming ligand. Dimethylformamide has been the solvent used with better results. The mechanism of the substitution is not known, however, the solubility of the reactants and the temperature allowed by this sol-

Table 1. Table 1. Re(IV) mononuclear complexes prepared by ligand substitution on hexahalorhenates and characterized by x-ray diffraction. pyz = pyrazine; pym = pyrimidine; pyd = pyridazine; DMF = *N*, *N*-dimethylformamide; pyzCOOH = 2-pyrazinecarboxylic acid; ox = oxalato; mal = malonato; H_2cat = catechol; pyim = 2-(2'-pyridyl) biimidazole ; HMepy = 2-methylpyridinium; 4,4'-bipy = 4,4'-bipyridine; phen = 1,10-phenanthroline; dmbpy = 4,4'-dimethyl-2,2'-bipyridine; Pr = propyl.

Compound	Substitution solvent	Ref.
$(NBu_4)[ReCl_5(pyz)]$	DMF	[60]
$(NH_2Me_2)[ReCl_5(pyz)]$	DMF	[60]
$(NH_4)[ReCl_5(pyz)]\cdot 0.75H_2O$	DMF	[60]
$(NBu_4)[ReCl_5(pym)]$	DMF	[61]
$(NBu_4)[ReCl_5(pyd)]$	DMF	[61]
$(NBu_4)[ReCl_5(dmf)]$	DMF	[62]
$(NH_2Me_2)[ReCl_5(dmf)]$	DMF	[63]
$(HMepy)[ReCl_5(py)]\cdot$4,4'-bipy	py	[64]
$(AsPh_4)_2[ReCl_4(ox)]$	2-PrOH	[65]
$(NBu_4)_2[ReCl_4(ox)]$	H_2O	[66]
$(AsPh_4)(HNEt_3)[ReCl_4(mal)]$	2-PrOH	[67]
$(AsPh_4)_{1.5}(HNEt_3)_{0.5}[ReCl_4(mal)]$	2-PrOH	[67]
$(NBu_4)(HNEt_3)[ReCl_4(cat)]\cdot H_2$cat	2-PrOH	[68]
trans-$[ReCl_4(py)_2]$	py	[69]
$[ReCl_4(H_2biim)]\cdot 2$dmf	DMF	[70]
$[ReCl_4(pyim)]\cdot$dmf	DMF	[70]
$[ReCl_4(bipy)]$	DMF	[70]
$[ReCl_4(bpym)]$	DMF	[8]
$[ReCl_4(phen)]$	DMF	[71]
$[ReCl_4(dmbpy)]$	DMF	[71]
$(AsPh_4)_2$ *cis*-$[ReCl_2(ox)_2]$	DMF:H_2O (95:5, v:v)	[7]
$(NBu_4)[ReBr_5(dmf)]$	DMF	[62]
$(NH_2Me_2)[ReBr_5(dmf)]$	DMF	[63]
$(NBu_4)[ReBr_5(pyzCOOH)]\cdot C_3H_8O$	2-PrOH: acetone (2.2:1 v:v)	[72]
$(PPh_4)_2[ReBr_4(ox)]$	DMF	[7]
$(NBu_4)[ReBr_4(OCN)(dmf)]$	DMF	[73]
$[ReBr_4(bpym)]$	DMF	[8]
$(PPh_4)_2$ *cis*-$[ReBr_2(ox)_2]$	DMF	[7]
$(NBu_4)_2[ReBr(OCN)_2(NCO)_3]$	DMF	[73]
$(NBu_4)_2[Re(NCS)_6]$	DMF	[74]
$[Zn(NO_3)(Me_2phen)_2]_2[Re(NCS)_5(SCN)]$	DMF	[74]

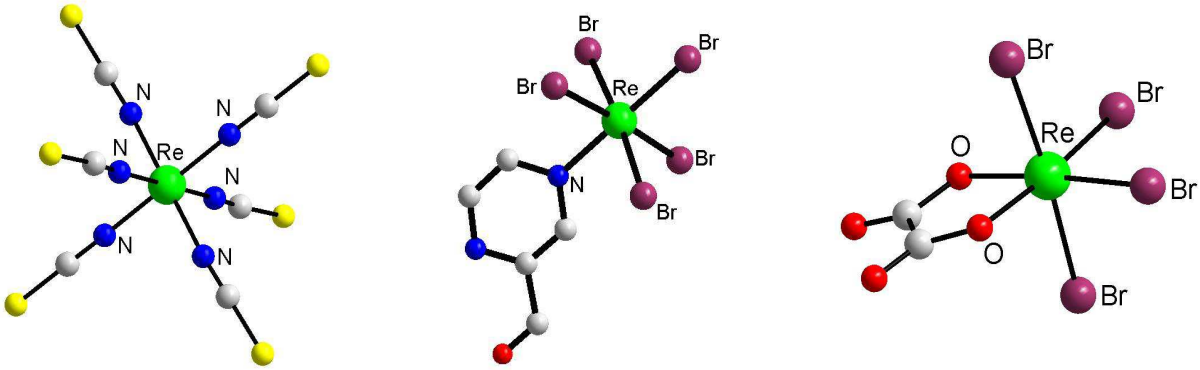

Figure 1. Perspective drawing of selected Re(IV) anionic complexes. From left to right, $[Re(NCS)_6]^{2-}$, $[ReBr_5(pyzCOOH)]^-$, and $[ReBr_4(ox)]^{2-}$.

vent seems to be the reasons for the selection of DMF as reaction solvent [7]. An interesting point is that accidental water amounts during substitution seem to play a crucial role in the success of the syntheses [7].

The complete halogen substitution is kinetically hindered, hence mixed-ligand complexes are normally obtained. The exceptions are $(NBu_4)_2[Re(NCS)_6]$ and $[Zn(NO_3)(Me_2phen)_2]_2[Re(NCS)_5(SCN)]$. Both linkage isomers are obtained together from the reaction of $[ReBr_6]^{2-}$ with a large excess of SCN^- and separated by solubility differences [74].

Alternatively, direct ligand substitution reactions of other Re(IV) parent complexes are accomplished as well. *cis*-$[ReCl_4(NH{=}CMeNHPh)_2]$ was prepared from *cis*-$[ReCl_4(CH_3CN)_2]$ in acetone [75], $(NBu_4)_2$*trans*-$[ReCl_4(CN)_2]\cdot 2dma$ (dma = N,N-dimethylacetamide) from cis-$[ReCl_4(thf)_2]$ in acetone [76], *mer*-$[ReCl_3(psal)(PMe_2Ph)]$ (psal = N-phenylsalicylidenaminate) from $[ReCl_4(PMe_2Ph)_2]$ in CCl_4 [77], and $[Re(sah)_2]$ (sah = salicylaldehyde-2-hydroxy(mercapto)anil) from$[ReCl_4(PPh_3)_2]$ in ethanol [78].

4. STRUCTURE OF MONONUCLEAR Re(IV) COMPLEXES

Coordination number six for the rhenium atom is the most common situation in Re(IV) complexes. Octahedral complexes have been reported, with only slight distortion from the expected disposition of the ligands. In particular, some distortion can be observed due to the steric requirements of bidentate ligands like oxalato, malonato, catecholate or bipyrimidine. Figure 1 shows the variation in the structures for three selected complexes.

A regular octahedral geometry is observed in $[Re(NCS)_6]^{2-}$ with only slight deviations from theoretical values in N-Re-N angles and N-Re distances [74]. The inclusion of a bulky ligand in $[ReBr_5(pyzCOOH)]^-$ do not originate a great distortion around the metal centre. The minimum Br-Re-N angle is 86.3(4)°, not far from the ideal value [72].

The structure of $[ReBr_4(ox)]^{2-}$, presents a distorted octahedral geometry. The main distortion from the ideal octahedral geometry is due to the short byte angle of the bidentate oxalate ligand (O-Re-O angle is 78.8°) [7].

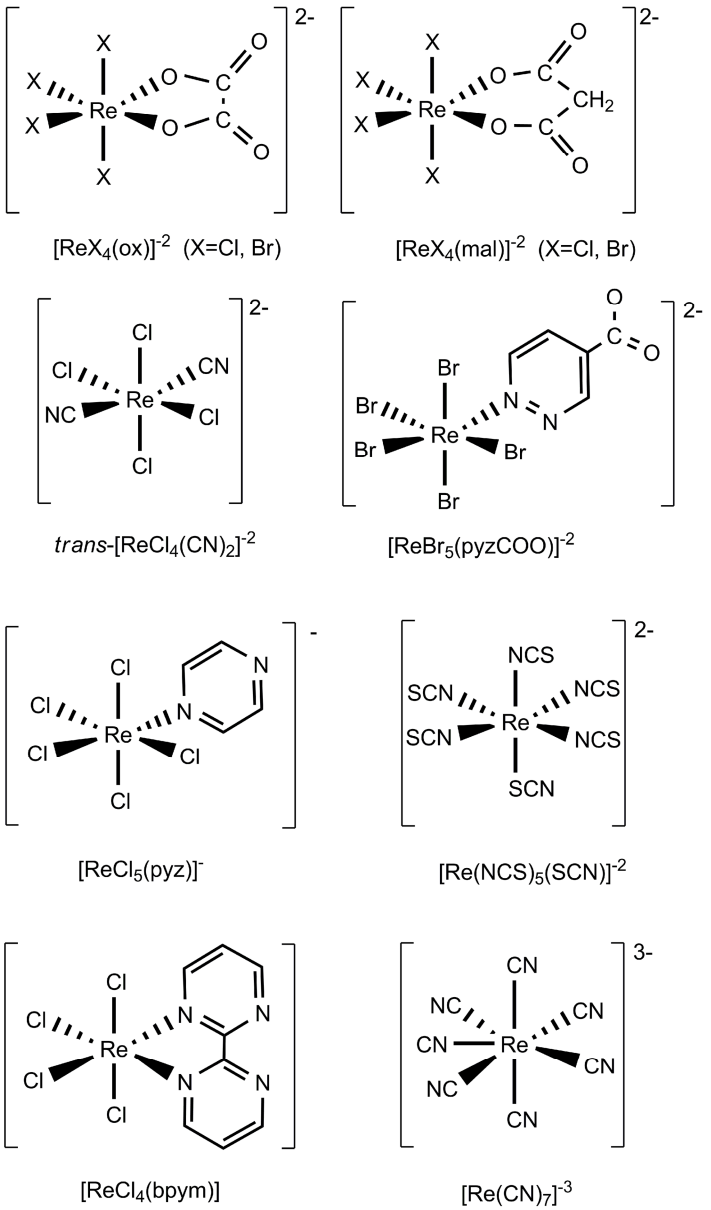

Figure 2. Mononuclear Re(IV) complexes used as building blocks in heteropolynuclear complexes.

5. SYNTHESIS AND STRUCTURE OF POLYNUCLEAR Re(IV) COMPLEXES

Re(IV) complexes are reasonably stable against redox processes and are reluctant to ligand substitution. These conditions together with the adequate choice of a bridging ligand in the coordination sphere opened the gate to the design of heteropolynuclear complexes. The formation of such polynuclear complexes is a self-assembling process based on complementary and specific interactions between building blocks which generate the final product. Most of them were specifically designed to study the magnetic interaction between a 5d metal ion (Re(IV)) and different paramagnetic 3d ions [60, 72].

The anions $[ReX_4(ox)]^{2-}$, $[ReX_4(mal)]^{2-}$ (X = Cl, Br), $[ReBr_5(pyzCOOH)]^-$, $[ReCl_5(pyz)]^-$, *trans*-$[ReCl_4(CN)_2]^{2-}$, $[ReCl_4(bpym)]$, $[Re(NCS)_5(SCN)]^{2-}$ and $[Re(CN)_7]^{3-}$ (Figure 2) contain ligands which can act as donor toward a second metal ion. The second ion can be fully solvated or as the central atom of a preformed complex with the coordination sphere partially blocked. This is the "complex as ligand" strategy that has been used to prepare different Re(IV) heteropolynuclear complexes. The slow evaporation of solutions containing the Re(IV) monomer, the metal ion and the blocking ligand (if used) has been the most used synthetic pathway. The choice of solvent is based on the different solubilities of the starting materials, being acetonitrile the most successful to get crystalline products. Their structures include well defined dinuclear complexes, tri-, tetra- and pentanuclear compounds, and chains. They are compiled in Table 2.

The dinuclear entities are the most numerous ones. Different spatial arrangements can be found in this group depending on the bridging ligand. Those containing oxalato as bridging ligand, exhibit a bis(bidentate) disposition of the dicarboxylate (Figure 3a). The bridge can be very symmetric toward the second metal ion as in $[ReCl_4(\mu\text{-ox})Co(dmphen)_2]\cdot CH_3CN$ (Co-O distances 2.208(11) and 2.211(9) Å) [80] or slightly asymmetric with different M-O(oxalate) distances. This last disposition is

Table 2. Re(IV) heteropolynuclear complexes characterized by x-ray diffraction and solvents used for the synthesis. dmphen = 2,9-dimethyl-1,10-phenanthroline; L^1 = 6,6'-(pyridin-2-ylmethylazanediyl)bis-(methylene)bis(*N*-tert-butylpicolinamide. [a] Solvent ratios are quoted as volume:volume. ACN: Acetonitrile, DMF: Dimethylformamide , EtOAc :Ethylacetate, $MeNO_2$: Nitromethane.

Compound	solvent[a]	Ref.
Dinuclear complexes		
$[ReCl_4(\mu\text{-ox})Cu(phen)_2]\cdot CH_3CN$	ACN: DMF 5:1	[79]
$[ReCl_4(\mu\text{-ox})Cu(phen)_2]$	ACN : DMF 5:1	[79]
$[ReCl_4(\mu\text{-ox})Co(dmphen)_2]\cdot CH_3CN$	ACN	[80]
$[ReCl_4(\mu\text{-ox})Mn(dmphen)_2]\cdot CH_3CN$	ACN:DMF 5:1	[80]
$(PPh_4)_2[ReCl_4(\mu\text{-ox})MoO_2Cl_2]$	ACN:EtOAc 1:1	[81]
$[ReBr_4(\mu\text{-ox})Co(4,7\text{-}Cl_2phen)_2]\cdot CH_3CN\cdot CH_3NO_2$	ACN:$MeNO_2$ 4.5:1	[82]
$[ReCl_4(\mu\text{-mal})Ni(dmphen)(CH_3CN)_2(H_2O)]\cdot (CH_3CN)_{0.5}\cdot (H_2O)_{0.5}$	ACN:DMF 20:0.3	[83]
$[ReCl_4(\mu\text{-mal})Co(dmphen)_2]\cdot CH_3CN$	ACN	[83]
$[ReCl_4(\mu\text{-mal})Fe(dmphen)_2]\cdot CH_3CN$	ACN	[83]
$[ReBr_4(\mu\text{-mal})Cu(phen)_2]\cdot 0.25H_2O$	ACN	[84]
$[ReBr_4(\mu\text{-mal})Co(dmphen)_2]\cdot CH_3CN$	ACN	[84]
$[ReBr_4(\mu\text{-pyzCOO})Co(dmphen)_2\cdot 2CH_3CN$	ACN	[72]
$[ReBr_4(\mu\text{-pyzCOO})Ni(dmphen)_2\cdot 2CH_3CN$	ACN	[72]
$[ReCl_4(\mu\text{-bpym})NiBr_2(H_2O)_2]$	ACN : $MeNO_2$ 1:1	[85]
$[Re(NCS)_5(\mu\text{-NCS})Ni(dmphen)_2]\cdot CH_3CN$	ACN	[86]
$[Re(NCS)_5(\mu\text{-NCS})Co(dmphen)_2]\cdot CH_3CN$	ACN	[86]
$[Re(NCS)_5(\mu\text{-NCS})Fe(dmphen)_2]\cdot CH_3CN$	ACN	[86]
$[Re(NCS)_5(\mu\text{-NCS})Mn(dmphen)_2]\cdot CH_3CN$	ACN	[86]
$[ReCl_4(CN)(\mu\text{-CN})FeL^1]$	ACN	[87]

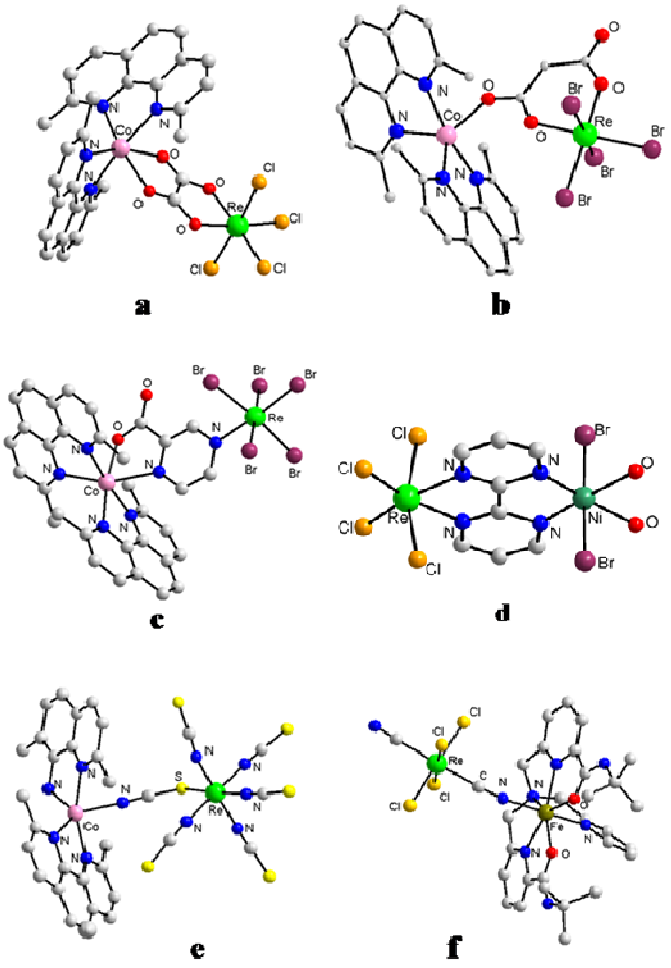

Figure 3. Perspective drawing of Re(IV) dinuclear complexes. a: $[ReCl_4(\mu\text{-ox})Co(dmphen)_2]$; b: $[ReBr_4(\mu\text{-mal})Co(dmphen)_2]$; c: $[ReBr_5(\mu\text{-pyzCOO})Co(dmphen)_2]$; d: $[ReCl_4(\mu\text{-bpym})NiBr_2(H_2O)_2]$; e: $[Re(NCS)_5(\mu\text{-NCS})Co(dmphen)_2]$; f: $[ReCl_4(CN)(\mu\text{-CN})FeL^1]$.

found, for example, in $(PPh_4)_2[ReCl_4(\mu\text{-ox})MoO_2Cl_2]$ (Mo-O distances 1.778(8) and 1.812(13) Å) [81]. Largest deviation are found in $[ReCl_4(\mu\text{-ox})Cu(phen)_2]$, with Cu-O distances of 2.355 (6) and 2.465(8) Å [79].

The change of oxalato by malonato as bridge provokes different arrangements in the dinuclear compounds. The bis(bidentate) behavior is forbidden for malonato. In the dinuclear units the metal ions are linked through a malonato ligand in the *anti–syn* conformation. The malonato adopts simultaneously the bidentate (at Re(IV)) and monodentate (at M(II)) coordination modes (Figure 3b for $[ReBr_4(\mu\text{-mal})Co(dmphen)_2]\cdot CH_3CN$).

The opposite situation is found in the two complexes $[ReBr_5(\mu\text{-pyzCOO})M(dmphen)_2]\cdot 2CH_3CN$ (M = Co, Ni) [72]. The pyzCOO bridge is monodentate toward Re(IV) (through one of the nitrogen atoms) and bidentate toward M(II), using the other nitrogen atom and one oxygen atom of the carboxylate group. This is shown in Figure 3c.

The crystal structure of $[ReCl_4(\mu\text{-bpym})NiBr_2(H_2O)_2]$ (Figure 3d) also shows a dinuclear unit with 2,2'-bipyrimidine as bridging ligand. The metal ions are interconnected by a bis(bidentate) bpym in a symmetric disposition, with Re-N distances of 2,23 (1) Å, and Ni-N distances of 1.98(2) Å [85].

The family of complexes $[Re(NCS)_5(\mu\text{-NCS})M(dmphen)_2]\cdot CH_3CN$ (M = Co, Ni, Fe, Mn) are isostructural (Figure 3e) [86]. The dinuclear units are formed by a quasi linear thiocyanate ligand with N-C-S angles between 169(4) and 179.5(9)°. In spite of this, the arrangement Re-N-C-S-M is not linear due to a large bending at the S atom (Re-S-C angles between 102.8 (3) and 106.9(13)°). A similar situation is found in $[ReCl_4(CN)(\mu\text{-CN})FeL^1]$ (L^1 = 6,6'-(pyridin-2-ylmethylazanediyl)bis-(methylene)bis(*N*-tert-butylpicolinamide) [87], with a Fe-N-C angle significantly bent (156.918(9)°) (Figure 3f).

Trinuclear compounds of the type Re(1)···M···Re(2)are presented in Table 3. The set of eight compounds of general formula $(NBu_4)_2[\{ReX_4(\mu\text{-ox})\}_2M(Him)_2]$ (X = Cl, Br; M = Cu, Ni, Co, Mn) has been prepared by direct reaction of $(NBu_4)_2[ReX_4(ox)]$, a salt of M(II) and imidazole as blocking ligand [88, 89].

The structure (Figure 4a) shows a six-coordinated M ion surrounded by four oxalate oxygen atoms from two $[ReBr_4(ox)]^{2-}$ units and two imidazole nitrogen atoms from two terminal imidazole ligands is cis positions. In the case of $[\{ReCl_5(\mu\text{-pyz})\}_2Cu(dmf)_4]$ [60], trinuclear neutral units are formed. Pyrazine is the bridging ligand which connects two independent Re(IV) ions with a Cu(II). The coordination sphere of the central Cu(II) is filled by dmf solvent molecules (Figure 4b), being Cu(II) in a distorted octahedral geometry (average Cu-O distance 1.964 Å and average Cu-N distance 2.477 Å).

Heterotetranuclear species are represented by $(NBu_4)_4[\{ReCl_4(\mu\text{-ox})\}_3M]$ (M = Cu, Ni, Co, Fe) (Figure 5a). The M atoms are six coordinated, with six oxalate O atoms from three $[ReCl_4(ox)]^{2-}$ units [90].

On the other hand, $[ReCl_4(\mu\text{-ox})Cu(terpy)(H_2O)][ReCl_4(\mu\text{-ox})Cu(terpy)(CH_3CN)]$ [79] is a tetranuclear entity of the type Cu(1)···Re(1)···Cu(2)···Re(2). In this case, dinuclear units $[ReCl_4(\mu\text{-ox})Cu(terpy)X]$ (X = H_2O, CH_3CN) are present. The oxalato is bidentate toward Re and monodentate toward Cu(II). Two of

Table 3. Re(IV) heteropolynuclear complexes characterized by x-ray diffraction and solvents used for the synthesis. Him = imidazole; $PY5Me_2$ = 2,6-bis(1,1-bis(2-pyrydil)ethyl)pyridine; L^2 = *N-dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene). [a] Solvent ratios are quoted as volume:volume. [b] Slow diffusion in acetonitrile/2-propanol mixtures. [c] Ether diffusion in acetonitrile. ACN: Acetonitrile, DMF: Dimethylformamide, PrOH: Propanol.

Compound	Solvent[a]	Ref.
Trinuclear complexes		
$(NBu_4)_2[\{ReCl_4(\mu\text{-ox})\}_2Cu(Him)_2]$	ACN:2-PrOH 10:1	[88]
$(NBu_4)_2[\{ReCl_4(\mu\text{-ox})\}_2Ni(Him)_2]$	ACN:2-PrOH 10:1	[88]
$(NBu_4)_2[\{ReCl_4(\mu\text{-ox})\}_2Co(Him)_2]$	ACN:2-PrOH 10:1	[88]
$(NBu_4)_2[\{ReCl_4(\mu\text{-ox})\}_2Mn(Him)_2]$	ACN:2-PrOH 10:1	[88]
$(NBu_4)_2[\{ReBr_4(\mu\text{-ox})\}_2Mn(Him)_2]$	[b]	[89]
$(NBu_4)_2[\{ReBr_4(\mu\text{-ox})\}_2Co(Him)_2]$	[b]	[89]
$(NBu_4)_2[\{ReBr_4(\mu\text{-ox})\}_2Ni(Him)_2]$	[b]	[89]
$(NBu_4)_2[\{ReBr_4(\mu\text{-ox})\}_2Cu(Him)_2]$	[b]	[89]
$[\{ReCl_5(\mu\text{-pyz})\}_2Cu(dmf)_4]$	DMF:2-PrOH 2:1	[60]
Tetranuclear complexes		
$[ReCl_4(\mu\text{-ox})Cu(terpy)(H_2O)][ReCl_4(\mu\text{-ox})Cu(terpy)(CH_3CN)]$	ACN	[79]
$(NBu_4)_4[\{ReCl_4(\mu\text{-ox})\}_3Cu]$	ACN:2-PrOH 20:1	[90]
$(NBu_4)_4[\{ReCl_4(\mu\text{-ox})\}_3Ni]$	ACN:2-PrOH 20:1	[90]
$(NBu_4)_4[\{ReCl_4(\mu\text{-ox})\}_3Co]$	ACN:2-PrOH 20:1	[90]
$(NBu_4)_4[\{ReCl_4(\mu\text{-ox})\}_3Fe]$	ACN:2-PrOH 20:1	[90]
Pentanuclear complexes		
$(NBu_4)_5[Gd\{ReBr_4((\mu\text{-ox})\}_4(H_2O)]\cdot H_2O$	2-PrOH:ACN 6:1	[91]
$[(PY5Me_2)_4Mn_4Re(CN)_7](PF_6)_5\cdot 6H_2O$	[c]	[92]
1D Chains		
$[ReCl_4(\mu\text{-ox})Cu(bipy)_2]$	ACN	[65]
$[ReCl_4(\mu\text{-ox})Cu(pyim)_2]$	$MeNO_2$:ACN 4:1	[93]
$[ReCl_4(\mu_3\text{-ox})CuL^2]\cdot dmf$	DMF:$MeNO_2$ 8:1	[94]
$[ReCl_4(\mu\text{-mal})Cu(phen)_2]\cdot CH_3CN$	ACN	[67]
$[ReCl_4(\mu_3\text{-mal})Cu(bipy)_2]$	ACN	[67]
$[ReCl_4(\mu_3\text{-mal})Mn(dmphen)(H_2O)_2]\cdot dmphen\cdot(CH_3CN)\cdot(H_2O)$	ACN	[83]
$[ReCl_4(\mu\text{-CN})_2Mn(dmf)_4]$	DMF	[76]
$[ReCl_4(\mu\text{-CN})_2Fe(dmf)_4]$	DMF	[76]
$[ReCl_4(\mu\text{-CN})_2Co(dmf)_4]$	DMF	[76]

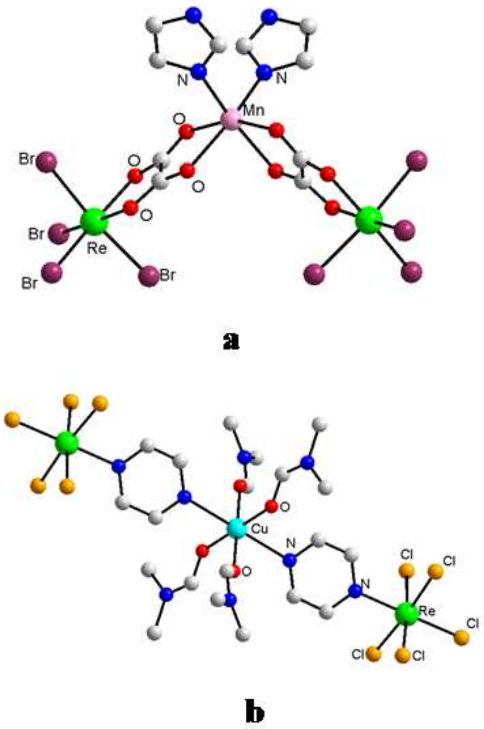

Figure 4. Perspective drawing of Re(IV) trinuclear complexes. a: $[\{ReBr_4(\mu\text{-ox})\}_2Mn(Him)_2]^{2-}$; b: $[\{ReCl_5(\mu\text{-pyz})\}_2Cu(dmf)_4]$.

these units are linked by an additional chloride bridge Re···Cl···Cu, giving a tetranuclear complex.

The final examples of discrete-size heterometallic clusters are two pentanuclear complexes. The pentanuclear cluster $[(PY5Me_2)_4Mn_4Re(CN)_7](PF_6)_5\cdot 6H_2O$ consists of a central $[Re(CN)_7]^{3-}$ complex connected through cyanide bridges to four surrounding $[(PY5Me_2)Mn]^{2+}$ units. The arrangements of the four Mn(II) centers can be described as a slightly distorted square, with two of the metals binding axial cyanide ligands and the other two binding non-neighboring equatorial cyanide ligands [92]. Very recently, a second pentanuclear complex was reported, $(NBu_4)_5[Gd\{ReBr_4((\mu\text{-ox})\}_4(H_2O)]\cdot H_2O$ [91]. Four Re(IV) ions (from $[ReBr_4(ox)]^{2-}$ units) and one Gd(III) ion are connected through four bis-bidentate oxalato ligands. The coordination sphere of the lanthanide ion is completed by a water molecule.

Nine chain-like polynuclear complexes have been reported up to now (Table 3). The chains are originated in different kind of bridges. In the case of $[ReCl_4(\mu_3\text{-mal})Mn(dmphen)(H_2O)_2]\cdot dmphen\cdot(CH_3CN)\cdot(H_2O)$, the malonato group adopts simultaneously the bidentate (towards the rhenium atom) and bis-monodentate (toward two manganese atoms) coordination modes [83]. The chain shows regular alternating Re(IV) and Mn(II) cations (Figure 5b). A similar spatial disposition is found in $[ReCl_4(\mu\text{-}CN)_2M(dmf)_4]$ (M = Mn, Fe, Co) [76]. The trans disposition of cyanide ligands in $[ReCl_4(CN)_2]^{2-}$ units provokes the formation of the chains ···Re···CN···M···.

The solid-state structure of $[ReCl_4(\mu_3\text{-ox})CuL^2]\cdot dmf$ [94], $[ReCl_4(\mu\text{-mal})Cu(phen)_2]\cdot CH_3CN$ and $[ReCl_4(\mu_3\text{-mal})Cu(bipy)_2]$ [67] show the carboxylato ligand as the only bridge. The skeleton of the chain is formed by Re-carboxylato-Cu alternating units (analogous to that shown in Figure 5b). On the other hand, $[ReCl_4(\mu\text{-ox})Cu(bipy)_2]$ [65] and $[ReCl_4(\mu\text{-ox})Cu(pyim)_2]$ [93] contain $[ReCl_4(ox)]^{2-}$ anions coordinated to the $[Cu(L)_2]^{2+}$ cations through one oxalate-oxygen, giving neutral heterometallic dinuclear units. These units arrange in such a way that a chlorine atom of one of them points toward the copper atom of the neighboring one, resulting in the formation of helical chains ···Re-O-Cu-Cl-Re···.

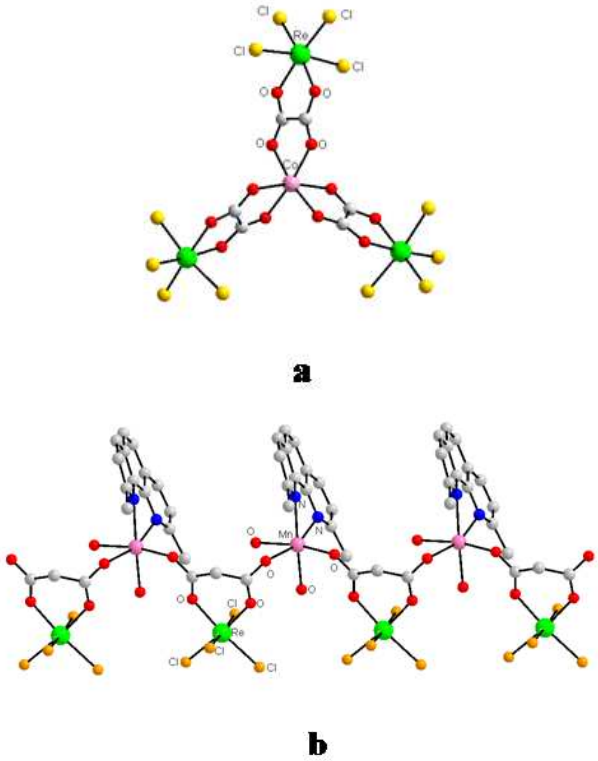

Figure 5. Perspective drawing of Re(IV) polynuclear complexes. a: tetranuclear $[\{ReCl_4(\mu\text{-ox})\}_3Co]^{2-}$; b: 1-D chain in $[ReCl_4(\mu_3\text{-mal})Mn(dmphen)(H_2O)_2]$.

6. CONCLUDING REMARKS

Great efforts have been done during the last years to prepare and characterize stable Re(IV) mononuclear complexes. The substitution route on hexahalocomplexes has demonstrated to be an efficient synthetic way to prepare new compounds. They have provided of several novel building blocks which have been used to design polynuclear compounds with different structural motifs. The rational ''complex as ligand'' approach, where a fully solvated transition metal ion or a preformed complex whose coordination sphere is unsaturated is allowed to react with an inert Re(IV) complex has been the strategy of choice. Hence, di-, tri- tetra-, pentanuclear discrete clusters and 1D chains have been reported and fully characterized.

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