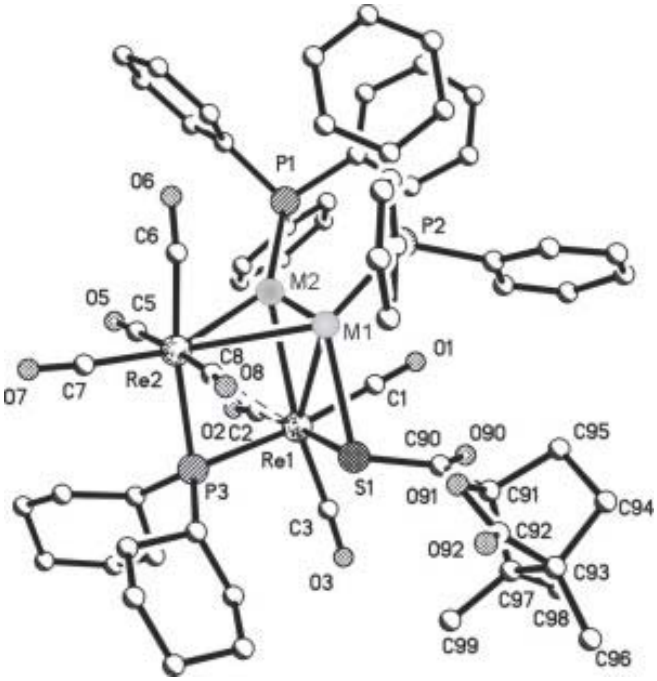
Synthesis, Structure and chiroptical Properties of diastereomeric Metallatetrahedra containing Metals of Group 7 and 11

Any synthesized metallatetrahedron can be derived from the generalised system $M^{I}M^{II}(M^{1}ER_3)(M^{2}ER_3)(\mu\text{-}PCy_2)(CO)_7(ax\text{-}L^*)$ of C_1-symmetry with M^{I} and M^{II} being a transition metal of group 7, M^1 and M^2 one of group 11, E a group 15 element, R an organic rest and L* a chiral organic ligand.

Because of the C_1 symmetric ligandsphere of the centrically tetrahedral metal framework diastereomers are synthesised using a chiral organic ligand L* (carboxylates and thiocarboxylates). By choice of (-)-thiocamphanate as such an auxiliar their diastereomeric pure separation was performed sucessfully for several derivatives. For $M^{I} = M^{II}$ = Re, M^2 = Au, M^1 = Au, Ag, Cu; M^2 =Ag, M^1 =Ag, the stereoisomerically pure preparation and the absolute configuration of the chiral tetrahedral metal core have been proved by single crystal X-ray analysis (see figure).



The chiroptical properties of all diastereomerically pure derivatives have been studied by CD-spectroscopy in order to analyse the influence of M^1, M^2, E, R and L* on the CD-effect. Most of these properties are dominated by the chromophores of the tetrahedral metal core and the type of chiral ligand L* (oxo / thio).

This effect on the CD-effect was confirmed by time dependent density functional calculations (TDDFT). CD spectra were calculated and the frontier orbitals were analysed.

The first stereoisomerically pure metallatetrahedra containing four different metals have been isolated for M^{I} = Re, M^{II} = Mn, M^2 = Au, M^1 = Ag, Cu and M^2 =Ag, M^1 = Cu. Their stereoisomerically pure structure was derived from comparing their spectroscopic data (^{1}H-, ^{31}P-NMR, IR, CD) with those of the Re_2-system containing mixed coinage metal fragments.