

LUMINESCENT TETRAHEDRAL AND OCTAHEDRAL MANGANESE(II) COMPLEXES WITH [O=P]-DONOR LIGANDS

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Luminescent Mn(II) complexes are of potential interest for lighting applications, for instance as replacement of expensive rare earths-based phosphors in fluorescent lamps [1]. The emission is related to the ${}^4T_1(G) \rightarrow {}^6A_1(6S)$ transition and is strongly dependent upon the coordination geometry: tetrahedral complexes are normally green emitters, while octahedral species emit in the red range. However, the luminescent properties can be enhanced by the presence of rigid structures and light harvesting fragments, able to reduce the non-radiative decay and improve the absorption in the UV region [2].

On the basis of recent outcomes on dihalide derivatives with phosphine oxides, our research group exploited phosphoramides, arylphosphonic diamides, amidophosphates and phosphonates as ligands for the preparation of tetrahedral Mn(II) complexes having general formula $[MnX_2L_2]$ (X = Cl, Br, I). The complexes were isolated from the reaction between the proper anhydrous MnX_2 salt and L under mild conditions. The structure of the derivatives was ascertained by single-crystal X-ray diffraction. The species revealed to be appreciably luminescent in the green region upon excitation with UV-light, with emission maxima centered between 510 and 535 nm. The luminescence lifetimes are in the hundreds of μs range, strongly influenced by the choice of the coordinated halide. In general, the lifetime decreases passing from the chloro- to the bromo- and the iodo- derivative as a consequence of the increased spin-orbit coupling effect [3-5]. Instead, when 2-naphthyl or carbazolyl fragments were introduced in the skeleton of the [O=P]-donor ligands the corresponding tetrahedral Mn(II) complexes were characterized by dual emissions, with a band in the green region attributable to the metal center and another one, centered in the red region, ascribed to triplet states of the aromatic substituents [6-7]. Similar results were achieved with [O=P]-ligands based on P(III) such as dibenzo[*d,f*][1,3,2]dioxaphosphepine 6-oxide (BPPO) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) [8]. On the other hand, the coordination of Mn(II) to phosphonates containing the (*R/S*)-BINOL fragment determined an almost pure 3LC emission with complete disappearance of the green band. Bidentate ligands prepared from DOPO allowed the isolation of the corresponding octahedral Mn(II) complexes characterized by intense emissions centered at 611 nm. Differently from tetrahedral derivatives the luminescent lifetimes are in tens of ms range for octahedral derivatives as the ${}^4T_1(G) \rightarrow {}^6A_1(6S)$ transition is both parity and spin forbidden.

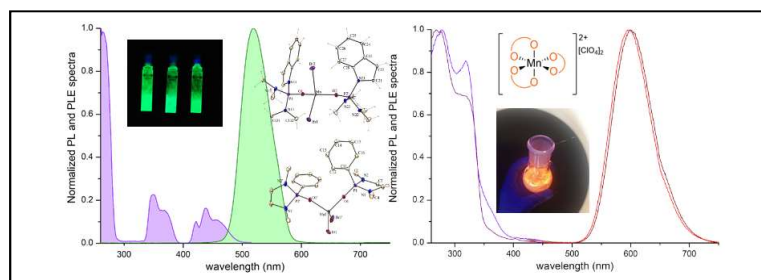


Figure 1. Green- and red-emitting Mn(II) complexes.

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