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Synthesis, Characterization and Catalytic and Biological Activity of New Manganese(II) Carboxylate Complexes

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The aim of this work was to prepare a series of novel carboxylate and dicarboxylate complexes of manganese(II), to study their spectroscopic and physicochemical properties and where possible to fully structurally characterize them by X-ray crystallography. The catalytic and biological properties of the new compounds were also examined.

Four new manganese(II) aliphatic dicarboxylate complexes of general formula $[Mn(O_2C-R-CO_2)] \cdot xH_2O$ { $R=CH_2$, $(CH_2)_8$, $CH_2-C(CH_3)_2-CH_2$ and $CH_2-CH_2-C(CH_3)_2$, $x=0-2$ } were synthesized by ligand exchange reactions between manganese (II) acetate and the appropriate dicarboxylic acids. These complexes and other previously reported manganese (II) aliphatic dicarboxylate complexes were subsequently reacted with the bidentate donor ligands 1,10-phenanthroline and 2, 2'-bipyridine to give five new manganese (II) dicarboxylate 1,10-phenanthroline complexes and eight new manganese(II) dicarboxylate 2, 2'-bipyridine complexes. The X-ray crystal structure of $[Mn(3dmepda)(phen)_2] \cdot 7.5H_2O$ was determined.

New manganese(II) complexes of phthalic acid (1,2-benzenedicarboxylic acid), isophthalic acid (1,3-benzenedicarboxylic acid), terephthalic acid (1,4-benzenedicarboxylic acid) and diphenic acid {[1,1'-biphenyl]-2,2'-dicarboxylic acid} were prepared. These complexes were reacted with 1,10-phenanthroline and 2, 2'-bipyridine to give new manganese (II) dicarboxylate 1,10-phenanthroline and 2, 2'-bipyridine derivatives. The X-ray crystal structures of $[Mn(ph)(phen)_2(H_2O)] \cdot 4H_2O$, $\{[Mn(isoph)(bipy)_4] \cdot 2.75bipy\}_n$ and $[Mn(phen)_2(H_2O)_2]_2(isoph)_2(phen) \cdot 12H_2O$ were determined.

A new manganese(II) complex of benzene-1,2-dioxyacetic acid and 2,2'-bipyridine was synthesized and fully characterized.

Two new manganese(II) complexes of fumaric acid [(E)-2-butenedioic acid] and maleic acid [(Z)-2-butenedioic acid] were prepared. These complexes were reacted with 1, 10-phenanthroline and 2, 2'-bipyridine to give five new manganese(II) fumarate/maleate 1,10-phenanthroline and 2,2'-bipyridine complexes. The X-ray crystal structures of $\{[Mn(fum)(bipy) \cdot H_2O]\}_n$ and $[Mn(phen)_2(H_2O)_2](fum) \cdot 4H_2O$ were determined.

A new manganese(II) complex of L-tartaric acid [(2R,3R)-2,3-dihydroxybutanedioic acid] was prepared. This complex was reacted with 1,10-phenanthroline and 2,2'-bipyridine to give two new manganese(II) tartrate 1,10-phenanthroline and 2,2'-bipyridine complexes.

One new manganese(II) complex of dipicolinic acid (2,6-pyridinedicarboxylic acid) was prepared. This complex was reacted with 1,10-phenanthroline and 2,2'-bipyridine to give three new manganese(II) dipicolinate 1,10-phenanthroline and 2,2'-bipyridine complexes. The structure of $[Mn(dipic)(bipy)_2] \cdot 4.5H_2O$ was determined by X-ray crystallography.

One new manganese(II) complex of chelidamic acid (1,2-dihydro-4-oxo-2,6-pyridinedicarboxylic acid) was prepared. This complex was reacted with 1,10-

phenanthroline and 2,2'-bipyridine to give two new manganese(II) chelidamate 1,10-phenanthroline and 2,2'-bipyridine complexes.

Four new manganese(II) complexes of monocarboxylic acids, [mandelic acid [α -hydroxybenzeneacetic acid], quinic acid [(-)-a. 3a.4a. 5b-tetrahydroxy-1-cyclohexanecarboxylic acid], 2-pyrazine carboxylic acid {pyrHx} and 3-amino-1,2,4-triazole-5-carboxylic acid] were prepared and fully characterized. The structure of [Mn(pyr)₂] was determined by X-ray crystallography.

Whereas all of the manganese(II) carboxylate complexes catalytically disproportionate hydrogen peroxide in the presence of added imidazole, only the manganese(II) dicarboxylate complexes containing 1,10-phenanthroline or 2,2'-bipyridine ligands are catalytically active in the absence of added imidazole.

All the manganese(II) complexes were tested for antifungal activity against *Candida Albicans* but only the manganese(II) complexes containing 1,10-phenanthroline ligands exhibited fungitoxic activity.