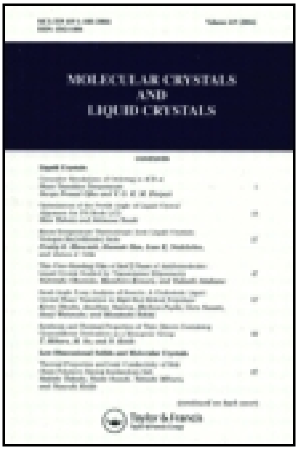

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'Chirodichroism' in a Planar d^8-Metal Coordination Compound

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'CHIRODICHROISM' IN A PLANAR d^8-METAL COORDINATION COMPOUND

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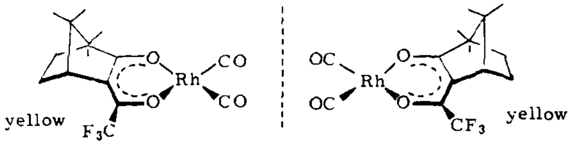
Abstract The introduction of chirality into the inner coordination sphere of a d(8)-metal ion provides an interesting parameter for the study of steric influences of ligands with like or unlike configurations on cooperative phenomena in the solid state.

RESULTS

The introduction of chirality into the inner coordination sphere of d^8-metal ions proves to be an interesting parameter for the correlation of molecular structure, crystal packing and cooperative phenomena in the solid state. Thus, a remarkable difference in the optical properties of the pure enantiomers (*R* or *S*) and the 1:1 racemate (*R*,*S*) has been detected in the solid state for the chiral planar d^8-metal complex dicarbonyl-rhodium(I)-(3-trifluoroacetylcamphorate) (1) - an observation that has been tentatively referred to as 'chirodichroism' [1].



1*S*-(*1*)   1*R*-(*1*)

red ⊥ green

The pure enantiomers of (1) (*R* or *S*) form yellow crystals while the racemate (*R,S*) crystallizes as red-green *dichroic* solid exhibiting additional bands at 550 and 450 (sh) nm in the diffuse reflection spectrum. The formation of the stable red racemate can be monitored visually as solid state reaction on mixing the yellow antipodal enantiomers of (1) derived from *1R*- and *1S*-trifluoroacetylcamphor. The remarkable influence of the handedness of the ligands (*homochiral vs. heterochiral*) on the observed optical properties of (1) is the result of the different crystal packing between the racemate and the pure enantiomers. The oppositely configurated molecules in the racemate are ideally stacked in a columnar structure exhibiting one-dimensional cooperative phenomena with homochiral pairs of molecules packed in anti geometry and heterochiral pairs of molecules residing in staggered conformation (cf. FIGURE 1). For the pure enantiomers the formation of a stable columnar structure is prevented by the like configuration of the molecules giving rise to a zig-zag chain of metal atoms (cf. FIGURE 2). It should be noted, however, that the enantiomers occur also in a metastable red modification. The alternating packing mode of the antipodal chiral handles in the racemate is suited to the crystal-engineering of highly ordered *alternating columnar structures* consisting of structurally related molecules. Thus, when the yellow quasi-enantiomer $(CO)_2Rh$(3-TFA-*1S*-camphorate) and the yellow quasi-antipode $(CO)_2Ir$(3-TFA-*1R*-camphorate) are mixed a black quasi-racemate (or *active* racemate [2]) is formed containing a one-dimensional metal chain of alternating pairs of *Rh,Rh* and *Ir,Ir* atoms [3]. Thus, the preparation of quasi-racemates may be suggested as a general method for obtaining highly ordered structures exhibiting alternating properties in the solid state.

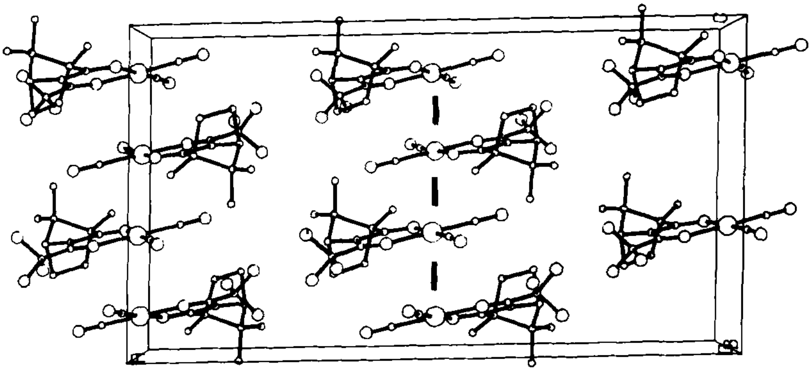


FIGURE 1. X-ray single crystal structure of (*1S,1R*)-(1)[4]
RACEMATE
(a=24.726, b=9.365, c=13.447 Å, ß=91.56°,Z=8,
space group C2/c, Rh-Rh: 3.38 Å)

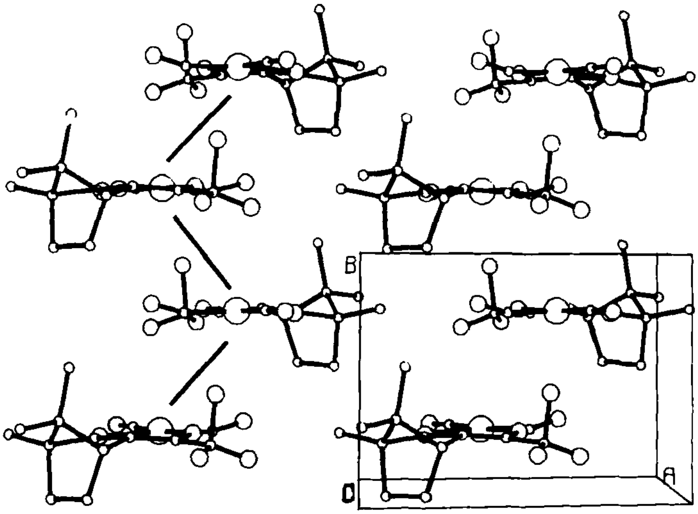


FIGURE 2. X-ray single crystal structure of (*1R*)-(1)[4]
PURE ENANTIOMER
(a=10.007, b=7.254, c=11.134 Å, ß=102.05°, Z=4,
space group $P2_1$, Rh-Rh: 4.32 Å)

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