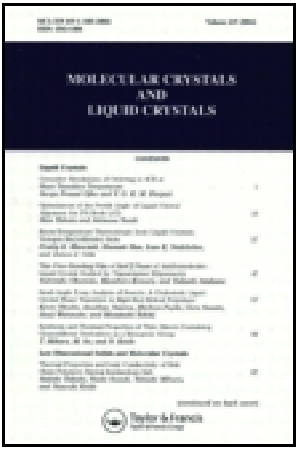

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Linear Metal Chains in a Chiral Environment: Diffuse Reflectance Spectra and an X-Ray Structure Analysis of Dicarbonyl Rhodium(I)- and Iridium(I)-β-Ketoenolates

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LINEAR METAL CHAINS IN A CHIRAL ENVIRONMENT: DIFFUSE REFLECTANCE SPECTRA AND AN X-RAY STRUCTURE ANALYSIS OF DICARBONYL RHODIUM(I)- AND IRIDIUM(I)-ß-KETOENOLATES

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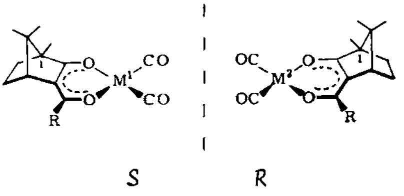
Abstract The introduction of chirality into the inner coordination sphere of d^8-metal ions proves to be an interesting parameter for the correlation of molecular structure, crystal packing and cooperative phenomena in the solid state [1].

RESULTS

Recently we reported on the construction of a chirality-controlled heteronuclear columnar structure in which the pairwise alternating Rh_2 and Ir_2 entities are arranged in a highly ordered one-dimensional chain *via* quasiracemate formation, 1c [2].
This alternating structural feature should express itself by electron spectroscopic data. Previous diffuse reflectance measurements revealed additional absorptions at 440 & 550 nm for racemic *R*,*S*-1a as compared to the optically pure form *R*-1a [3]. In analogy to spectroscopic properties of $(CO)_2M(Acac)$ (M = Rh, Ir) [4] we attribute these bands to M-M-interaction within the one-dimensional chain. We have now measured the diffuse reflectance spectra (22°C) of the four racemic or quasiracemic mixtures of $(CO)_2M$ (M = Rh, Ir) and *R*- & *S*- trifluoroacetyl camphorate ligands 1a - 1d (*cf* TABLE I) in the solid state.



R = CF_3
1a $M_1 = M_2 = Rh$
1b $M_1 = M_2 = Ir$
1c $M_1 = Rh$, $M_2 = Ir$
1d $M_1 = Rh$ & Ir, $M_2 = Rh$ & Ir

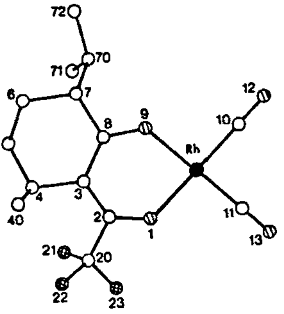
TABLE I. Absorption maxima of the solid state mixtures 1a - 1d measured as neat powders (Cary 14) [5]

Mixture	Absorption maxima (nm) 22°C			
1a		386	440(sh)	550
1b		399	480	695
1c	330	390	465	596
1d	310	375	450	610

1a and 1b constitute the pure homonuclear *R,S*-Rh and *R,S*-Ir racemates, resp., while 1c is the heteronuclear quasiracemate *R*-Ir/*S*-Rh and 1d represents the heteronuclear *racemate of quasiracemates, i.e.* *R*-Ir/*S*-Rh - *R*-Rh/*S*-Ir, obtained by *1:1* mixing of 1a and 1b. According to TABLE I significant differences in absorption are discerned in the 440 - 610 nm region which is attributed to M-M-interactions. In accordance with $(CO)_2M(Acac)$ [4] there is a bathochromic shift going from 1a (Rh) to 1b (Ir). The absorption of 1c does not represent an averaging effect. The difference of absorption between 1c and 1d may be tentatively explained by random distribution of Rh and Ir in the stack as expected for the latter. A better understanding of the spectroscopic properties might be obtained from single crystal polarized reflectance spectra and/or from symmetry related band structure computations [6].

An inherent instability of the one-dimensional metal chain has been observed in 1b ($R = n\text{-}C_3F_7$) as the dichroic material spontaneously changes into an orange-red modification in which pairs of homochiral Ir_2 entities are arranged in such a way as to avoid stacking [7].

In order to test the influence of steric bulk of the chiral ligands on cooperative phenomena in the solid state the bicyclic 3-TFA-camphorate (TFA = trifluoroacetyl) in 1a has been replaced by the monocyclic 2-TFA-menthonate. Herein we describe the molecular and crystal structure of racemic (*1R,4S/1S,4R*)-dicarbonyl rhodium(I) TFA-menthonate 2. It crystallizes monoclinic (space group C2/c, a = 25.173, b = 10.648, c = 13.222 Å, ß = 116.11°, Z = 8) [8]. As compared to 1a [1] the c-axis (*i.e.* the direction of the M-M-chain) of 2 is by 0.225 Å shorter due to the different spatial requirement of the keto-



Molecular structure of 2

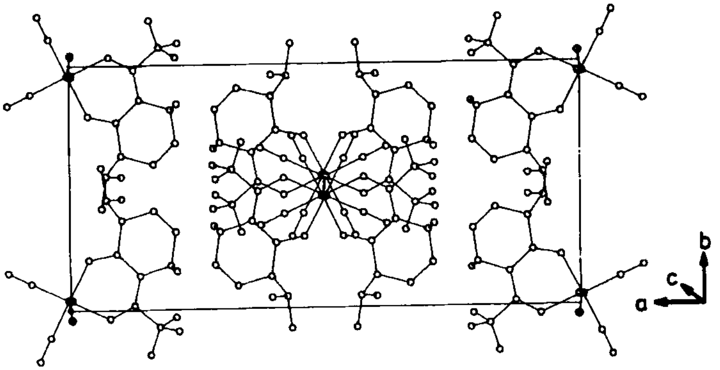


FIG. 1: Crystal structure of racemic 2 viewed along the c-axis [8] (showing distinct metal positions for homochiral pairs)

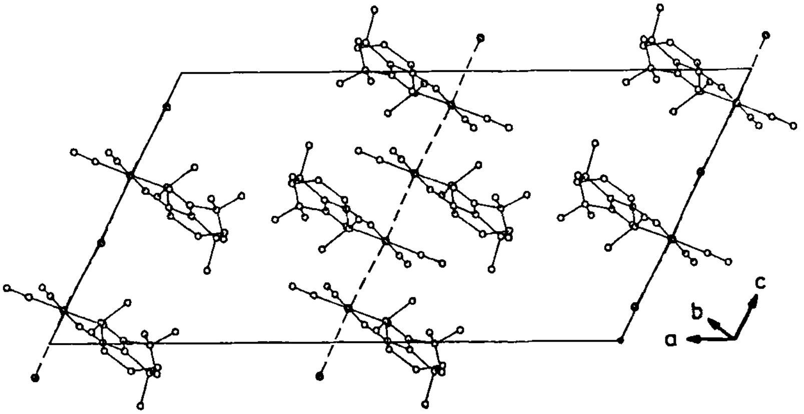
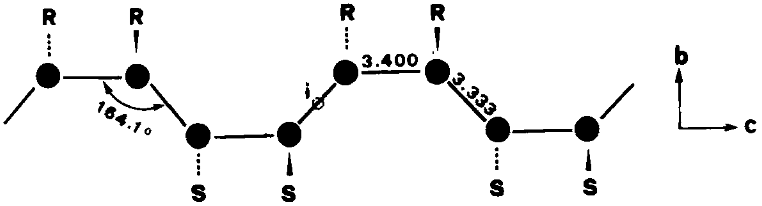


FIG. 2: Crystal structure of racemic 2 viewed on the (010) plane [8] (showing deformation of the linear metal chain)

enolate ligands. In the crystal structure of 2 (*cf* FIG 1 & 2) anti-orientated racemic pairs (*R,S*) of molecules are stacked in such a way that an overall alternating arrangement of ligands $(R,R,S,S)_\infty$ along the c-axis arises. This provides another example of a highly ordered columnar structure controlled by chiral ligands. It is therefore anticipated that on *1:1* mixing of *Rh* & *Ir* quasienantiomers a highly ordered quasiracemic structure with a $(Rh,Rh,Ir,Ir)_\infty$ metal chain will be formed as in 1c [2]. In 1c and 2 the one-dimensional metal chain is not strictly linear since the alternatingly arranged homochiral pairs of molecules (*R,R* & *S,S*) each lie in chains parallel to the c-axis and separated by 0.91 Å. Unexpectedly, the Rh-Rh distance within neighboring homochiral molecules parallel to the direction of the stack is greater (*i.e.* 3.400 Å) than that of the neighboring anti-orientated heterochiral molecules which form an angle of 15.9° with the c-axis (*i.e.* 3.333 Å).



Whether the deviation from ideal linear stacking in 2 (which in the case of 1b ($R = n\text{-}C_3F_7$) eventually leads to a collapse of the columnar structure) is due to spatial effects of the chiral ligands or represents a manifestation of Jahn-Teller [6] or Peierls distortion, resp., remains to be elucidated.

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REFERENCES

1 V.Schurig, Mol.Cryst.Liq.Cryst. 96, 271 (1983)
2 V.Schurig, W.Pille, W.Winter, Angew.Chem.Int.Engl. 22, 327 (1983)
3 V.Schurig, Angew.Chem.Int.Ed.Engl. 20, 807 (1981)
4 T.A.Dessent, R.A.Palmer, S.M.Horner, A.C.S.Symp.Ser.5, 301 (1974)
5 We thank Prof. D. Oelkrug, Tübingen, for advice
6 I.Bozović, J.Delhalle, Physical Review, 29, 4733 (1984)
7 F.Frolow, L.Leiserowitz, Weizmann Institute, Rehovoth, unpublished
8 *cf*. Fachinformationszentrum, D 7414 Eggenstein-L.,