# SYNTHESIS AND CIRCULAR DICHROISM CHARACTERIZATION OF NEW OPTICALLY ACTIVE TRANSITION METAL COMPLEXES: M[(−)bdtp]$_3$, M = $Co^{3+}$, $Rh^{3+}$, $Ir^{3+}$*

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The chiral octahedral diastereoisomeric tris[(−)cyclic O,O′,1($R$),2($R$)(−)dimethylethylene dithiophosphato]metal(III) complexes, M[(−)bdtp]$_3$, M(III) = Co, Rh, Ir, have been obtained stereoselectively in the Λ or Δ absolute configuration at the metal centre. The formation reaction and the characterization of the obtained complexes have been followed by circular dichroism spectroscopy. The complexes prove optically labile in various solvents. A configuration inversion has been observed in all complexes giving diastereoisomeric equilibria $\Lambda(R,R)(R,R)(R,R) \rightleftarrows \Delta(R,R)(R,R)(R,R)$ with an excess of one form, occasionally stabilized by the solvent.

New chiral, $d^6$, low-spin, coordination compounds could be synthesized and characterized through their chiroptical properties to examine the effects of the metal ion on the stereochemical features of tris chelated octahedral complexes. There is a great deal of interest on the chiral and energy discriminations due to a chiral ligand in transition metal(III) complexes[1−3]. Aim of this work is the study of the diastereoselectivity of the formation reaction of Λ or Δ-M[(−)bdtp]$_3$ with M = $Co^{3+}$, $Rh^{3+}$, $Ir^{3+}$ and (−)bdtp$^-$ = (−)cyclic-O,O′-1($R$),2($R$) dithiophosphate, as done on similar $Cr^{3+}$ complexes[3,4].

Potassium (−)cyclic O,O′-1($R$),2($R$)dimethylethylene dithiophosphate, (−)bdtpK, and the corresponding achiral ligand, bdtpK, were prepared as previously reported[5].

Tris[(−)cyclic O,O′-1($R$),2($R$)dimethylethylene dithiophosphate] metal(III) complexes as $\Lambda(+)_{745cd}(-)_{589}$\{Co[(−)bdtp]$_3$\} (*I*); $\Delta(-)_{460cd}(-)_{589}$Rh[(−)bdtp]$_3$ (*II*); $\Delta(-)_{360cd}(+)_{589}$Ir[(−)bdtp]$_3$ (*III*) were synthesized dissolving 2 mmol of the metal salt ($CoCl_2.6\,H_2O$, $RhCl_3.xH_2O$ or $Na_3IrCl_6.H_2O$) in 150 cm$^3$ of ethanol (or ethanol–water), (2 mmol of hydrogen peroxide were added to the solution of Co(II) salt). Adding 6 mmol of (−)bdtpK and stirring for 12−24 h at room temperature, the solutions changed colour and separated a solid coloured complex mixed with white potassium chloride. The solvent of the reaction solution was evaporated under vacuum and the residual mixture was crystallized (dichloromethane) yielding a coloured complex which was characterized and analysed as (*I*), (*II*) or (*III*) (see Table I).

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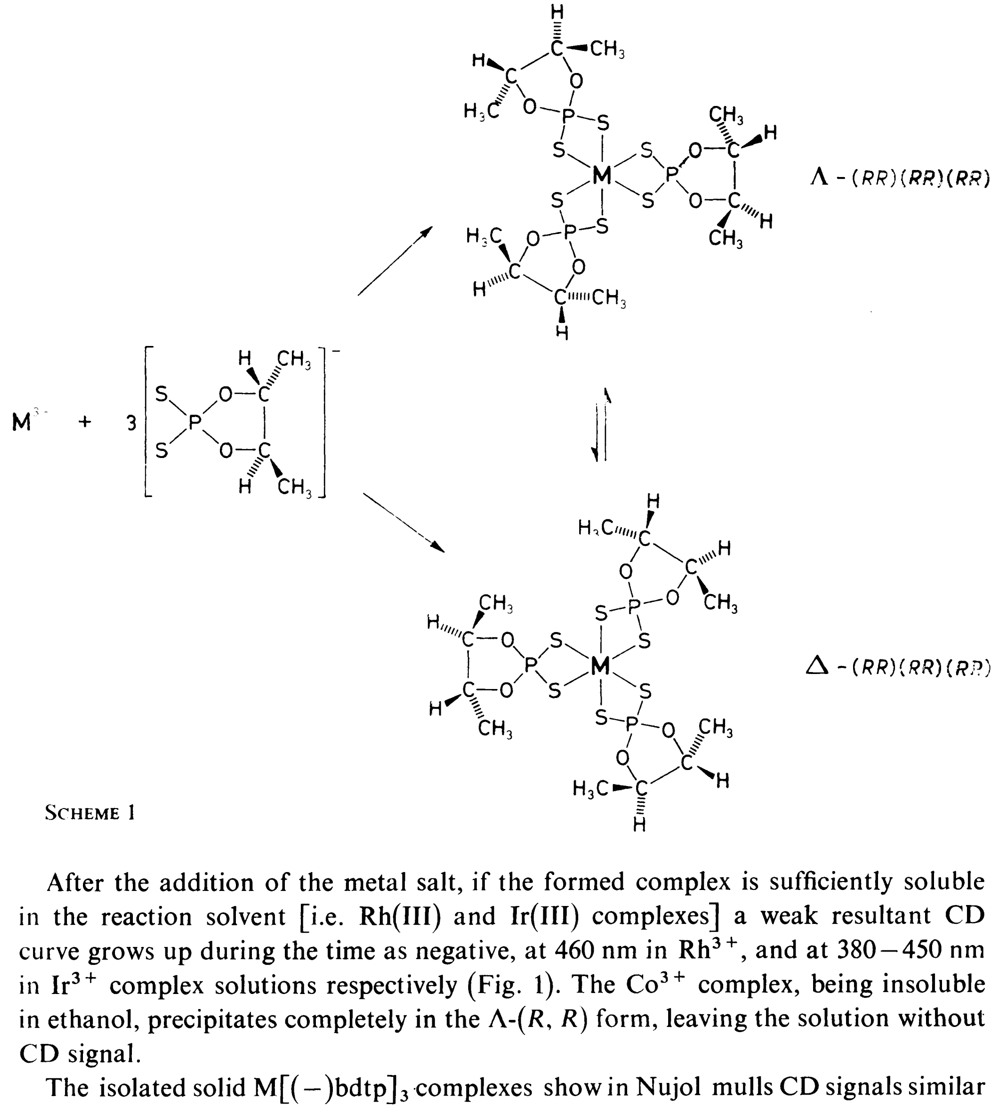
The CD spectra of the reaction solutions show at the same time positive or negative Cotton effects growing in the range of the *d–d*, $^1A_1 \rightarrow {}^1T_1$ and $^1A_1 \rightarrow {}^1T_2$, transitions showing the formation of the Λ - (*R*, *R*) or Λ - (*R*, *R*) diastereoisomer in excess with respect to the opposite propeller form.

Scheme 1 shows the reactions of the chiral ion (−)bdtp$^-$ in ethanol or ethanol–water with $M^{3+}$ ions to give the complexes (*I*), (*II*) or (*III*).



SCHEME 1

After the addition of the metal salt, if the formed complex is sufficiently soluble in the reaction solvent [i.e. Rh(III) and Ir(III) complexes] a weak resultant CD curve grows up during the time as negative, at 460 nm in $Rh^{3+}$, and at 380–450 nm in $Ir^{3+}$ complex solutions respectively (Fig. 1). The $Co^{3+}$ complex, being insoluble in ethanol, precipitates completely in the Λ-(*R*, *R*) form, leaving the solution without CD signal.

The isolated solid M[(−)bdtp]$_3$ complexes show in Nujol mulls CD signals similar to those recorded in the solution immediately after the beginning of the synthesis (Figs 2 and 3).

The reactions were monitored accurately by CD spectroscopy for long time. An inversion process Δ → Λ takes place together with the formation reaction.

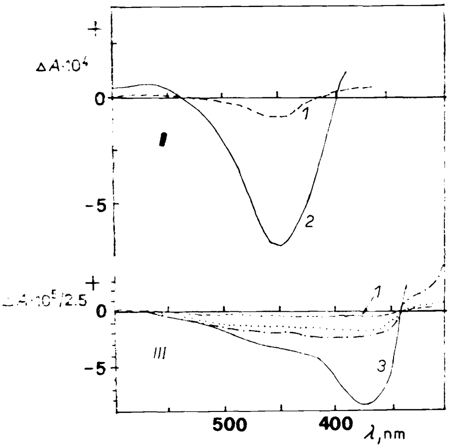


FIG. 1

CD spectra of the reaction solution at different times since the start, showing at 460 and 360 nm the formation of Δ(−)Rh[(−).bdtp]$_3$ *II* and Δ(+)Ir[(−)bdtp]$_3$ *III*, respectively. *1* Zero time, *2* 1 h, *3* 30 h

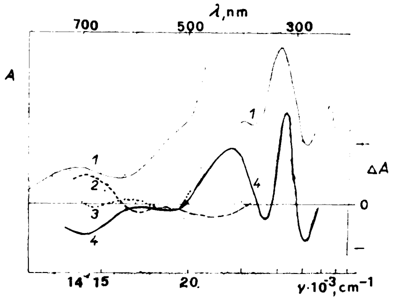


FIG. 2

UV-VIS (*1*) and CD spectra of Co[(−)bdtp]$_3$ in Nujol mulls (*2*); in solution of $CH_3CN$ (*3*) and $CHCl_3$ (*4*) at equilibrium

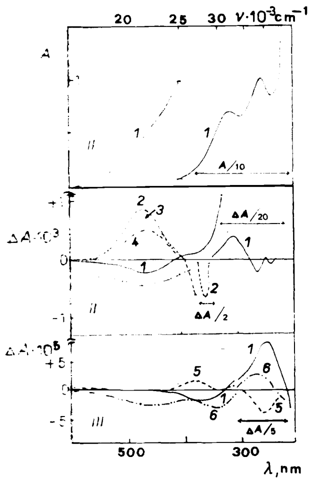


FIG. 3

UV-VIS and CD spectra of Δ(−)Rh[(−).bdtp]$_3$ *II* and Δ(+)Ir[(−)bdtp]$_3$ *III* immediately after the solubilization in ethanol (*1*); at equilibrium, in $C_6H_6$ (*2*); in $CHCl_3$ (*3*); in $CH_3CN$ (*4*); in $CH_2Cl_2$ (*5*); and solid, in Nujol mulls (*6*)

The obtained complexes are highly soluble in various solvents such as acetone, acetonitrile, benzene, ethanol, methylene chloride and chloroform. They show spectra similar to those observed in nujol mulls: a positive Cotton effect at 745 nm for the $Co^{3+}$ complex, negative Cotton effects at 465 nm for the $Rh^{3+}$ and at 450 and 360 nm for the $Ir^{3+}$ complexes, respectively. The intensity and frequency of these bands change with time, eventually reaching equilibrium. Figure 2 and 3 show the UV-VIS and CD spectra of the solid complexes after the solubilization and at equilibrium.

The bands are assigned to the $^1A_1 \rightarrow {}^1T_1$ and $^1A_1 \rightarrow {}^1T_2$ transitions on the basis of an octahedral symmetry $O_h$ in the complexes. The splitting of the excited state is observed and is due to the lowering of the symmetry to $D_3$ by the influence of the ligand field, in the tris-chelate complexes of $Co^{3+}$, $Rh^{3+}$ and $Ir^{3+}$. It is possible to observe the $^1A_1 \rightarrow {}^1E$ and the $^1A_1 \rightarrow {}^1A_2$ components at lower and the $^1A_1 \rightarrow {}^1E_b$ at higher energies respectively.

The absolute configuration of the isolated complex Λ-(−)Co[(−)bdtp]$_3$ (*I*), has been tentatively attributed on the basis of the positive Cotton effect recorded in nujol and ethanol at ~710−745 nm, in the region of the magnetic dipole allowed $d_{xy} - - d_{x^2-y^2}$ $(^1A_1 \rightarrow {}^1T_1)$ transitions. In the spectra of Λ-Cr[(−)bdtp]$_3$ a similar $d_{xy} \rightarrow \rightarrow d_{x^2-y^2}$ transition was observed as positive Cotton effect at ~690 nm in Nujol and in other solvents[3]. The Δ-Cr[(−)bdtp]$_3$ shows a negative Cotton effect corresponding to the same transition at 665 nm in THF and $CHCl_3$ (ref.[4]).

Δ-(−)Rh[(−)bdtp]$_3$ (*II*) and Δ-(+)Ir[(−)bdtp]$_3$ (*III*), show negative Cotton effects observed at 465 nm and 450, 360 nm respectively for similar $^1A_1 \rightarrow {}^1T_{1g}$ transition (Table II).

TABLE I

Analytical data for the complexes *I*—*III*

| No. | Compound | Colour | M.p. °C | Found/Calculated | |
|---|---|---|---|---|---|
| | | | | % C | % H |
| *I* | Λ(−)Co[(−)bdtp]$_3$ | brown | 220−240 | 22·6<br>23·7 | 3·8<br>3·95 |
| *II* | Δ(−)Rh[(−)bdtp]$_3$ | orange | >300 | 20·45<br>22·1 | 3·55<br>3·7 |
| *III* | Δ(+)Ir[(−)bdtp]$_3$ | yellow | >340 | 18·55<br>19·4 | 3·1<br>3·25 |

The reactions give the kinetic prevailing formation of the Λ-(*R*, *R*)(*R*, *R*) (*R*, *R*) in the case of $Co^{3+}$ complex (*I*) and of the Δ-(*R*, *R*) (*R*, *R*) (*R*, *R*) diastereoisomer in the $Rh^{3+}$ (*II*), or $Ir^{3+}$ (*III*), complexes formation.

The formation of the Δ-(*R*, *R*) (*R*, *R*) (*R*, *R*) diastereoisomer is favoured, as observed for the Δ-(−)Cr[(−)bdtp]$_3$ (ref.[4]) on account of the lower hindrance between the alkyl groups of the three ligands coordinating on the metal, and of the stronger molecule–solvent interactions on this type of absolute configuration. Thus the higher dimensions of the metal cation favour the formation of a right-handed propeller Δ-(*R*, *R*) (*R*, *R*) (*R*, *R*) and the chiral ligand (−)bdtp$^-$ can interact in this form better with the $Ir^{3+}$ and $Rh^{3+}$, than with $Co^{3+}$ metal ions.

In the latter case the crystal packing energy prevails on the higher steric factors and alkyl group interactions or molecule–solvent interactions promoting the stereoselective precipitation of the Λ-(*R*, *R*) form.

The obtained kinetic Λ-(*R*, *R*) (*I*) and Δ-(*R*, *R*) (*II*) and (*III*), diastereoisomers are produced in pure optical form using ethanol as solvent. Subsequent to their formation, the complexes precipitate, reducing the possibility of the configurational inversion to the opposite diastereoisomer. In fact the isolated complexes are optically labile and, after the dissolution in a solvent, invert to the opposite form. Thus fractionated crystallizations by $CH_2Cl_2$–petroleum ether or dissolution in various solvents, separate or generate a mixture of the two diastereoisomers.

It is known that $Co^{3+}$ complexes are optically labile, but the tri(thiocarbamato)-rhodium(III) complex, studied by temperature dependent p.m.r. spectra, resulted always stereochemically rigid[6]. It is clear from these results that Rh(III) and Ir(III)

TABLE II
Assignments to the CD transitions of the chiral M[(−)bdtp]$_3$ complexes

| | Compound | Symmetry | Assignments | | |
|---|---|---|---|---|---|
| | | $O_h$ | $^1A_1 \rightarrow {}^1T_1$ | | $^1A_1 \rightarrow {}^1T_{2g}$ |
| | | $D_3$ | $^1A_1 \rightarrow {}^1A_2$ | $^1A_1 \rightarrow {}^1E_a$ | $^1A_1 \rightarrow {}^1E_b$ |
| *I* | Λ(−)Co[(−)bdtp]$_3$ | | 745 | | −530 |
| | ΔCo[(−)bdtp]$_3$ | | −695 | | −535 |
| *II* | Δ(−)Rh[(−)bdtp]$_3$ | | −460 | | 410 |
| | ΛRh[(−)bdtp]$_3$ | | 450 | | |
| *III* | Δ(+)Ir[(−)bdtp]$_3$ | | −450 | −360 | 280 |
| | ΛIr[(−)bdtp]$_3$ | | 480 | 380 | −260 |

complexes with the $MS_6$ chromophore are optically labile. To our knowledge these are the first cases of inversion of configuration in Rh(III) and Ir(III) complexes.

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