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Chiral Chromium(III) and Ruthenium(III) Complexes of Salicylaldimine Ligands

K. S. FINNEY and G. W. EVERETT, JR.
Department of Chemistry, The University of Kansas, Lawrence, Kansas, 66045, U.S.A.
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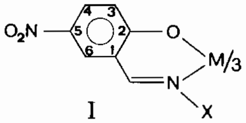
Tris(N-(R- or S-)α-phenylethyl-5-nitrosalicylaldiminato)chromium(III) and tris(N-S-α-benzylethyl-5-nitrosalicylaldiminato)ruthenium(III) have been prepared, and two diastereomers for each complex have been isolated. Relative configurations of the Cr(III) diastereomers and their Co(III) analogs, which were reported previously, are assigned from a comparison of CD spectra and chromatographic behavior. Assignments of configuration of the Ru(III) diastereomers relative to the analogous Co(III) and Cr(III) diastereomers are based on the similarity of chromatographic behavior for these species. Empirical relationships among low-energy CD bands for Co(III), Cr(III), and Ru(III) salicylaldimine complexes believed to have the same configuration are discussed and predictions of absolute configuration of diastereomers in this series are made from stereoselectivity observations.

Introduction

Previous publications from this laboratory have been directed toward establishing relationships between the signs of Cotton effects and absolute configuration of certain chiral, tris-bidentate complexes of Co(III), Cr(III), Rh(III), and Ru(III).[1–5] These relationships are now established for β-diketonate complexes of the above ions by a combination of physical methods[1–3] including a single crystal x-ray study in one case.[6]

Although complexes of structure I have six-membered, conjugated chelate rings like the β-diketonates, at present it is not known whether the same Cotton effect configuration relationships apply since definitive x-ray structural data is lacking. In an earlier publication[5] we provided chromatographic and CD arguments for assigning *relative* configurations of the diastereomers found for I, M = Co(III), X = *S*- and *R*-α-benzylethyl and *R*-α-phenylethyl; M = Cr(III), X = *S*- and *R*-α-benzylethyl. More recently a consistent relationship between thin-layer chromatographic behavior and absolute configuration was found to exist for chiral β-diketonate complexes of several metal ions.[1–3] Thus the arguments used previously for complexes I are supported, and herein is reported on extension of the work on this series of complexes to include diastereomers of I, M = Cr(III), X = *S*- and *R*-α-phenylethyl and M = Ru(III), X = *S*-α-benzylethyl.



I

Results and Discussion

Although four stereoisomers (Δ-*trans*, Λ-*trans*, Δ-*cis*, and Λ-*cis*) are possible for tris salicylaldiminate complexes, only the *trans* or *meridional* isomers have been found in every case.[7,8] This may be rationalized on steric grounds since three amine substituents would have to occupy the same octahedral face in the *cis* isomers. The existence of *cis* isomers in very small quantities cannot be ruled out from our studies, however. The 5-nitro ligand substituent in complexes I was included initially to stabilize the cobalt(III) complexes[4] and was retained for the chromium(III) and ruthenium(III) complexes in order that molecules in the series differ only in the metal ion.

Complexes of structure I, where M = Cr(III), X = *R*- or *S*-α-phenylethyl (*R*- or *S*-PhEt) and M = Ru(III), X = *S*-α-benzylethyl (*S*-BzEt) were synthesized by methods described in the Experimental Section. Thin-layer chromatography of the reaction products revealed two predominant bands in each case. Several considerably weaker bands are attributed to free ligand and to mixed ligand complexes resulting from optical impurities in the ligand as discussed previously.[4] Elemental analyses (Table I) show that products isolated from the predominant chromatographic bands are the desired tris complexes, and it is presumed that they are the *trans* diastereomers, differing only in the helical arrangement of ligands (Δ and Λ) about the pseudo three-fold axis in each case.

TABLE I. Characterization of the Individual Diastereomers.

Complex	% Calcd			% Found			$[M]_{589}$[a]
	C	H	N	C	H	N	
Cr((*R*)-PhEt-5-NO_2sal$)_3$–C	62.9	4.6	9.8	63.0	4.6	9.0	[b]
Cr((*R*)-PhEt-5-NO_2sal$)_3$–D				63.0	4.7	9.3	[b]
Cr((*S*)-PhEt-5-NO_2sal$)_3$–C′				62.7	5.3	9.6	−2690
Cr((*S*)-PhEt-5-NO_2sal$)_3$–D′				63.3	4.8	9.1	−6080
Ru((*S*)-BzEt-5-NO_2sal$)_3$–A	60.6	4.8	8.8	60.8	4.8	8.6	+16,200
Ru((*S*)-BzEt-5-NO_2sal$)_3$–B				60.7	4.7	8.6	−14,300

[a] Molecular rotation (degrees molarity^{-1}cm^{-1}) in dichloromethane solution.
[b] Not measured. C and D are enantiomers of C′ and D′, respectively.

Tris(N-R-α-phenylethyl-5-nitrosalicylaldiminato) chromium(III)

Compounds isolated from the two dominant brown chromatographic bands are labeled C and D, where D is the more rapidly eluted diastereomer. These labels are the same as those used earlier for the analogous Co(III) diastereomers.[4] Circular dichroism spectra (Figure 1) show that C and D have opposite helicities as expected for the two *trans* diastereomers.

Chromatographic conditions used to separate these diastereomers are very similar to those used earlier for the analogous Co(III) diastereomers where a 1:3 (v/v) toluene: CH_2Cl_2 eluting solvent and silica gel tlc plates were used. Polarities of Co(III) and Cr(III) complexes having identical ligands are expected to be very similar if the complexes have the same absolute configuration. Under identical chromatographic conditions, relative rates of elution of the Cr(III) diastereomers should parallel those of Co(III) diastereomers having the same absolute configurations. This argument was used previously in relating configurations of Co(III) and Cr(III) complexes I, where X = *R*-, and *S*-BzEt.[5] More recently it was demonstrated that in an entire series of tris complexes of Co(III), Cr(III), Rh(III), and Ru(III) with the chiral β-diketonate ligand, (+)-3-acetylcamphor, diastereomers having the same absolute configuration have the same relative rates of elution on silica gel tlc plates.[1–3] This relationship is maintained even when the eluting solvent is different for each complex. Thus Cr(III) and Co(III) diastereomers C are believed to have identical absolute configurations; the same is believed true of Cr(III) and Co(III) diastereomers D.

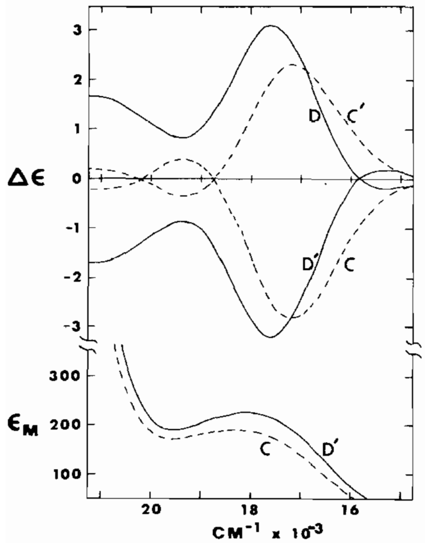


Figure 1. Circular dichroism and absorption spectra of tris (N-α-phenylethyl-5-nitrosalicylaldiminato)chromium(III) diastereomers in dichloromethane solution. Letters in the figure correspond to those in Table I.

These assignments are supported by a comparison of the CD spectra of Cr(III) and Co(III) diastereomers C and D. Since the components of the low energy ligand field transition for trigonal Cr(III) and low spin Co(III) belong to the same symmetry species, Cr(III) and Co(III) complexes of identical ligands and having identical absolute configurations should show similar Cotton effects for this transition.[1] The low energy transition for the Cr(III) complex occurs ~1500 cm^{-1} toward higher energy than for the Co(III) complex, however the sign of the predominant CD band is positive in each case for diastereomer D and negative in each case for diastereomer C.

Tris (N-S-α-phenylethyl-5-nitrosalicylaldiminato) chromium(III)

The two diastereomers obtained from the predominant chromatographic bands are labeled C′ and D′, where D′ is the more rapidly eluted isomer. CD spectra of C′ and D′ (Figure 1) show that their helicities are opposite those of C and D respectively. Since C′ and D′ differ from C and D also in ligand chirality, it is clear that C and C′ and D and D′ are enantiomeric pairs. Consistent with this are the facts that the enantiomers show identical chromatographic behavior on silica gel, have identical absorption spectra, and have CD spectra which bear a mirror image relationship.

Attempts were made to isomerize C′ and D′ by refluxing $CHCl_3$ solutions of the separate diastereomers for 24 hours both in the presence and absence of activated charcoal. However in each case only a small amount of the other isomer was formed (as detected by tlc). It is apparent that thermodynamic equilibrium, which was obtained for the Co(III) complexes in the presence of charcoal,[4] is not obtained for these Cr(III) complexes under similar conditions.

Tris(N-S-α-benzylethyl-5-nitrosalicylaldiminato) ruthenium(III)

Relatively little effort has been directed toward establishing absolute configurations of chiral Ru(III) complexes. CD spectra and configurational assignments have been reported for tris Ru(III) complexes of en[9] and (+)-3-acetylcamphorate ligands,[2] and for the latter it was possible to distinguish *cis* and *trans* diastereomers by nmr.

Thin-layer chromatography of products from the ligand exchange reaction described in the Experimental Section yielded two predominant bands. The red-brown product from the more rapidly eluted band is hereafter designated as isomer B, consistent with symbolism used for Co(III) and Cr(III) diastereomers of the same ligand. The dark material isolated from the other intense chromatographic band is labeled A. Both isomers were characterized by elemental analyses (Table I), CD, and absorption spectra (Figure 2). CD spectra of A and B clearly show they have opposite helicities. Proton nmr signals proved too broad to provide unequivocal proof of the *trans* geometry, however it is reasonable to assume they are the two *trans* diastereomers. The chromatographic behavior of Ru–A and Ru–B suggests they have the same absolute configurations as Co, Cr–A and Co, Cr–B, respectively.

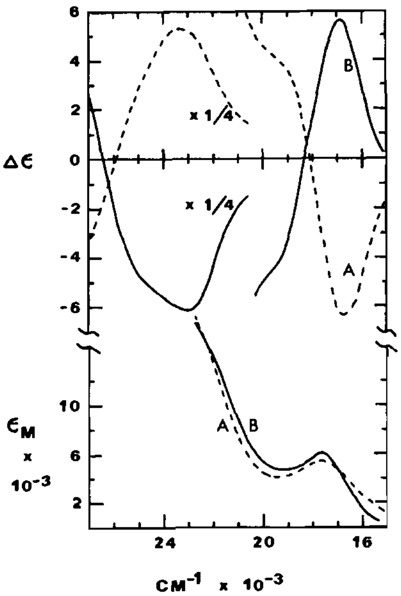


Figure 2. Circular dichroism and absorption spectra of tris(N-*S*-α-benzylethyl-5-nitrosalicylaldiminato)ruthenium(III) diastereomers in dichloromethane solution. Letters in the figure correspond to those in Table I.

Electronic transitions in these Ru(III) complexes are not as readily assigned as is the case for Co(III) and Cr(III) analogs, and no effort to do so will be made here. Also CD spectra of the Ru(III) complexes in the ligand field region will not necessarily bear any relation to those of Cr(III) and Co(III) complexes of the same configuration, since the symmetry species to which the transitions belong are different. It is nevertheless interesting to note that the sign of the dominant low-energy CD band for the Ru(III) diastereomers is opposite that of the Cr(III) and Co(III) diastereomers believed to have the same absolute configuration. A similar relationship is found among CD spectra of Co(III), Cr(III), and Ru(III) complexes of (+)-3-acetylcamphor.[1,2]

Although at present no firm assignments of absolute configuration can be made to diastereomers of complexes I, previously observed[4] differences in thermodynamic stabilities of the diastereomers for Co(III) allow a prediction of their configurations from simple steric considerations. Space-filling models indicate that for X = *R*-PhEt there is less steric strain in the *Λ-trans* isomer than in *Δ-trans*. In the presence of activated charcoal, Co(III) diastereomer D is the thermodynamically more stable *trans* isomer, suggesting that D has the *Λ-trans* configuration. This implies that in general for Co(III) and Cr(III) complexes I, X = BzEt or PhEt, those diastereomers with a positive dominant CD band in the low energy region have the *Λ* configuration, whereas the *Δ* configuration gives rise to a negative dominant CD band in this region. If these predictions prove to be correct, the relationship between the sign of the predominant low energy CD band and helical configuration is the same for Co(III) and Cr(III) complexes I as it is for Co(III) and Cr(III) complexes of β-diketones,[1,6,10] Co(III) complexes of α-aminoacids,[11,12] Co(III) and Cr(III) complexes of 1,2-diamines,[13,14] and Co(III) and Cr(III) oxalate complexes.[14,15]

Experimental Section

5-Nitrosalicylaldehyde was prepared according to the procedure given by Miller.[16] Tris(N-(*S*- or *R*-) α-phenylethyl-5-nitrosalicylaldiminato)chromium(III) complexes were prepared using Yamada's general procedure,[17] except that the chromium(III) salt was added last to the reaction mixture. The crude reaction products were chromatographed on 20 × 20 cm preparative layer plates of silica gel (2 mm thick layer) using techniques described previously.[4,5] The plates were developed 5–7 times with a 1:3 (v/v) mixture of toluene:chloroform. The center portions of the two brown predominant bands for each complex were removed from the plates and extracted as before.[4,5] Products were recrystallized at least three times using chloroform and heptane.

Tris(N-*S*-α-benzylethyl-5-nitrosalicylaldiminato)ruthenium(III) was prepared using a procedure similar to that used for preparing ruthenium(III) β-diketonate complexes.[18] The initial steps of the reaction were carried out under an inert atmosphere, and pre-formed ligand was employed. To 8.5 g (30 mmol) of N-*S*-α-benzylethyl-5-nitrosalicylaldimine in 60 ml of ethyl benzoate was added 2.0 g (5 mmol) of tris(2,4-pentanedionato)ruthenium(III). The mixture was heated to 160°C with stirring for 20 hr. During this time a slow stream of nitrogen was passed through the reaction vessel to remove volatile 2,4-pentanedione. The temperature was lowered to 85°C, and most of the solvent was removed under vacuum. The red–brown residue was dissolved in 30 ml acetone. This solution was filtered, then the solvent was removed under vacuum. The crude product was chromatographed on silica gel plates as described above using a 1:4 (v/v) toluene:chloroform mixture. Nine developments proved necessary to obtain good product separation. The central portions of the two predominant bands were removed from the plates and recrystallized as described above for the chromium complexes.

CD, ORD, and absorption spectra were recorded for the individual diastereomers in CH_2Cl_2 solutions using a Cary Model 60 spectropolarimeter and a Cary Model 14 spectrophotometer. Elemental analyses were obtained from an F and M Model 185 C, H, and N analyzer. Analyses for N were low as is the case for all other complexes in this series.[4,5]

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