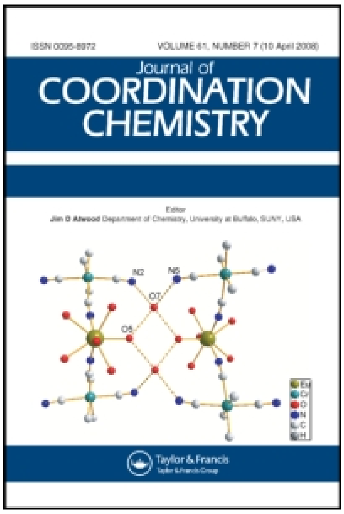

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STRUCTURAL ISOMERS OF SOME TRIVALENT TRANSITION METAL OXINATES

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The oxinates of Co(III), Rh(III) and Ir(III) were prepared in relatively high *cis/trans* isomer ratios. These isomers were separated by silica gel column chromatography and characterized by TLC, HPLC, elemental analyses and proton NMR. The existence of the expected *trans* and *cis* structural isomers for trivalent metal oxinates was conclusively demonstrated.

INTRODUCTION

The structure of trivalent metal chelates of oxine (8-quinolinol) has been given only limited attention and their *cis* and *trans* isomers are either seldom considered or when mentioned, contradictory information is given.[1-3]

The structures of most *tris*-metal oxinates are derived principally from the octahedral coordination geometry of the metal ion. Oxine is an unsymmetrical bidentate ligand, thus its chelates can exist as *cis* (1, 2, 3) and *tran* (1, 2, 6) isomers. In the *cis* isomer, all three chelate rings are geometrically identical. In contrast, the *trans* isomer has three non-identical ligands. The formation of the isomers will depend upon several factors. The statistical factor will acount for the eight possible ways to position three ligands regardless of the arrangement of the three locations. Of these eight ways, there are only two ways to form the *cis* isomer but six to form the *trans* isomer. Therefore, the statistical ratio *cis/trans* should be 1/3.

The *cis* isomer has all three of the hydrogen atoms in the 2 position on the ligand within van der Waals contact with the π-orbital system of neighboring heteroaromatic rings, while in the *trans* isomer, there is only one such hydrogen-ring interaction. The average molecular volume of the *trans* isomer also appears to be greater than that of the *cis* isomer, making the former a less compact, less sterically crowded molecule. As a result, the *cis* isomer should be relatively more sterically hindered than the *trans* isomer.

Although the molecule M(oxine)$_3$ is neutral, the oxygen atoms still bear a partial negative charge. In the *cis* isomer, the three oxygens are located at the corners of one face of the coordination octahedron, whereas two of the oxygens in the *trans* isomer are separated by the metal cation. Coulombic repulsion of the oxygens' negative charges in the *cis* isomer is therefore stronger than that in the *trans* isomer, and formation of the latter should be energetically favored. The heat of formation of the *cis* isomer should be greater than that of the *trans* isomer. Therefore, an increase in temperature is expected to favor the formation of the *cis* isomer to some extent.

Finally, and not so predictable as aforementioned factors, solvent effects (of reactants, intermediates, and products; solvent coordination, *etc.*) can play a considerable role in determining product-isomer ratios. From these considerations, the formation of the *trans* isomer is expected to be much more predominant in the preparation of *tris* metal oxinates.

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In the present report, the oxinates of Co(III), Rh(III), and Ir(III) are prepared by methods which yield relatively high *cis/trans* isomer ratios. These isomers are separated and characterized by TLC, HPLC, elementary analyses, and proton NMR.

EXPERIMENTAL

Synthesis of Oxinates.

All chemicals and solvents used in the syntheses were analytical reagent grade unless otherwise noted. Water was purified by a combination of reverse osmotic filtration, ion exchange, and glass distillation.

Preparation of Cobalt(III) Oxinate.

A solution of 9.684 g of $CoCl_2.6H_2O$ (0.042 mol) in 100 cm^3 acetone was first treated with 81.0 cm^3 of 30% hydrogen peroxide and then added to a stirred solution of 23.633 g of oxine (0.168 mol) in 100 cm^3 acetone. The mixture was then heated with stirring under reflux for three hours. The volume was reduced to a slurry and a 100 cm^3 of water was added. The brownish green precipitate which formed was collected on a sintered glass filter and washed thoroughly with 0.1 M HCl and then with water, and dried at 105° for two hours.

Preparation of Rhodium(III) Oxinate.

A solution of 0.854 g of $RhCl_3.3H_2O$ (0.0007 mol) in 40 cm^3 of 100% ethanol was slowly added to a solution of 0.914 g of oxine (0.0063 mol) in 20 cm^3 of 100% ethanol, and was allowed to reflux for 20 hours. The volume was then reduced to about 10 cm^3 and 50 cm^3 of water was added. The bright yellow precipitate was collected on a sintered glass filter and washed with 0.1 M HCl, then with water, and finally dried at 105° for two hours.

Preparation of Iridium(III) Oxinate.

A solution of 0.2468 g of $IrCl_3.3H_2O$ (0.0007 mol) was added to 300 cm^3 of glacial acetic acid containing 5 g of potassium acetate and was refluxed for two hours (the iridium salt did not dissolve completely). A solution of 1.219 g of oxine (0.0084 mol) in 50 cm^3 of glacial acetic acid was added and the mixture was refluxed for 15 hours. The volume was then reduced, whereupon a brownish-yellow slurry appeared, and the temperature was elevated to about 140°. The slurry was refluxed for two hours at that temperature. After cooling, 100 cm^3 of water was added. The precipitate was then filtered, washed and dried as above.

Chromatographic Analysis.

Thin layer chromatography (TLC) was performed on Eastman 13181 silica gel sheets, using a mixture of chloroform and acetone in a ratio of 3:1 by volume, and detected by visual inspection under 254 nm irradiation. High performance liquid chromatograms (HPLC) were obtained using a Waters Associates Liquid Chromatograph ALC CPC(201) equipped with a column of Bondapak AX-CORASIL (2 mm I.D. x 610 mm), a Varian Varichrom variable wavelength detector and an E & K strip chart recorder (model 255), using chloroform (UV grade) as the solvent for the samples and acetonitrile (UV grade) the eluant. The detection wavelength was 260 nm.

Separation of the Cis and Trans Isomers.

To a glass column (35 mm I.D.) fitted with a Teflon stopcock and a solvent reservoir, a glass fibre plug was inserted above the stopcock as the bed support. Chromatographic grade silica gel (J.T. Baker, 60-200 mesh) was dried for two hours at 150°, and then a slurry was prepared by stirring the dried silica gel with chloroform in a 1:3 ratio by voluem. It was quickly poured into the column under flowpacking conditions. The final height of packed column bed was approximately 15 cm and it was free of trapped air bubbles.

TABLE I
R_f values of crude metal oxinates on TLC (Average of 10 determination for each isomer).

R_f	cobalt	rhodium	iridium
trans-M(oxine)$_3$	0.39	0.41	0.46
cis-M(oxine)$_3$	0.11	0.16	0.26
impurity	0.0	0.0	0.0

The chromatographic samples were prepared by stirring 0.5 g of crude product in 300 cm^3 of chloroform for three hours. After filtering, the solution was carefully transferred to the silica gel bed at a flow rate of 2 cm^3/min. The elution was carried out at room temperature at a flow rate of 1.0 to 1.5 cm^3/min., using a mixture of chloroform and acetone in a ratio of 2:1 by volume. Fractions were collected separately in Erlenmeyer flasks and monitored frequently by TLC. The solutions containing a single isomer were immediately filtered and evaporated to dryness. Since *cis* isomers were less soluble in acetone or chloroform than their *trans* counterparts, the isolated *cis* isomers were further purified by a washing technique to remove traces of the *trans* isomer and any unidentified impurity. The *cis* compound (0.2 g) was mixed with 5 cm^3 of chloroform and 50 cm^3 of acetone, then stirred for 30 min. at room temperature. The mixture was then filtered on a sintered glass filter and the solid was washed with four 10 cm^3 portions of acetone. The isolated *trans* isomers were used without further purification. Because of its unusual sensitivity to the light, the iridium product was purified in a darkroom. All the purified products were dried for two hours at 120° before further study.

Elemental Analyses.

All elemental analyses for carbon, hydrogen, and nitrogen were carried out by Galbraith Laboratories Inc., Knoxville Tennessee.

Proton NMR Analyses.

The NMR spectra were recorded with a Nicolet Instruments NTCFT-180 360 MHz NMR spectrometer at a probe temperature of 23°. Dimethylsulfoxide-d_6 (Baker grade, J.T. Baker) was used as the solvent for all spectra. The sample solutions were prepared by dissolving a 4 mg of the compound in 0.5 cm^3 of DMSO and were then filtered.

RESULTS AND DISCUSSION

All of the crude products were tested by TLC. Three spots were discovered for each product. The R_f values of the top spot and middle spot were slightly different for

TABLE II
The isomer ratio (*cis/trans*) of the original mixture (by HPLC).

crude product	cobalt oxinate	rhodium oxinate	iridium oxinate
isomer ratio	25/75	3/97	13/87

products of different metal ions, whereas those of bottom spots were the same (virtually the bottom spots did not move). These values are listed in Table I. The top spot was tentatively identified as the *trans* isomer, the middle spot as the *cis* isomer, and the bottom spot as an unidentified impurity. The *cis/trans* ratios for all three crude products were determined quantitatively by HPLC. The results are shown in Table II. The purified compounds were also identified by HPLC. The results are listed in Table III.

All the elemental analytical results and calculated data of corresponding empirical formulas of the purified *cis* and *trans* complexes are summarized in Table IV. Elemental analyses were not made for *cis*-Rh(oxine)$_3$ because the amount of the collected isomer was not sufficient.

The chemical shifts and assignments, obtained by first order analysis, for the proton NMR spectra of the *cis* and *trans* cobalt and iridium complexes as well as free oxine are summarized in Table V. The coupling constants for these compounds are shown in Table VI.

The elemental analytical results for all *trans* isomers as well as the *cis*-Ir(oxine)$_3$ are in good agreement with the calculated data and support the assignment of the empirical formula M(oxine)$_3$. The elemental analytical result for the *cis*-Co complex is slightly different from that of the *trans* isomer but is in good agreement with the formula Co(oxine)$_3$.H$_2$O. The degree of hydration found in some divalent oxinates[2] is probably related to the polarity of the complex as well as the usual crystal packing forces. In the case of *cis*-M(oxine)$_3$ complexes, like cobalt, the three basic facial oxygens form a good site for hydrogen bonding. The *cis* iridium oxinate is apparently not hydrated, but this is probably due to its much lower polarity, which is indicated by its R$_f$ value in Table I. From the TLC results, the polarity of the *trans* isomers decreases in the order Co > Rh > Ir, and the *cis* isomers follow the same order. This order is obviously due to the increase in the effective radius of the metal ions and a concomitant decrease in charge density.

The NMR spectra of oxine and *trans*-Co(oxine)$_3$ are virtually identical to the corresponding spectra reported by Baker and Sawyer.[3] The spectra of both *cis*-Co(oxine)$_3$ and *cis*-Ir(oxine)$_3$ appear to be as simple as the spectrum of the free oxine itself. Each spectrum has only 6 proton resonance signals, or one set of ligand resonances, which

TABLE III
Cis/trans ratios of separated isomers and further purified *cis* isomers.

isomer complex	*trans* ratio (*cis/trans*)	*cis* ratio (*cis/trans*)
Co(oxine)$_3$	0/100	5.6/94.4 0.7/99.3[a]
Rh(oxine)$_3$	0/100	–
Ir(oxine)$_3$	0/100	5.0/95.0

[a] further purified by washing technique.

TABLE IV
Elemental analysis of *trans* and *cis*-M(oxine)$_3$.

complex		C%	H%	N%
trans-Co(oxine)$_3$	Anal.	66.18	3.76	8.56
	Calc.	66.00	3.69	8.55
cis-Co(oxine)$_3$ $\cdot$H$_2$O	Anal.	63.80	3.73	8.08
	Calc.	63.66	3.96	8.25
trans-Rh(oxine)$_3$	Anal.	60.45	3.70	7.51
	Calc.	60.57	3.39	7.85
trans-Ir(oxine)$_3$	Anal.	51.73	2.75	6.54
	Calc.	51.90	2.90	6.72
cis-Ir(oxine)$_3$	Anal.	51.91	2.94	6.54
	Calc.	51.90	2.90	6.72

indicates that three ligands are situated around the metal ion such that each is chemically and magnetically equivalent. In contrast, the spectra of *trans*-Co(oxine)$_3$ and *trans*-Ir(oxine)$_3$ show a complicated set of 18 proton resonance signals consisting of three sets of ligand resonances for each complex, which indicates that the three oxine ligands are chemically and magnetically distinct. The NMR spectra conclusively show that trivalent metal oxinates can exist in both *trans* and *cis* configurations.

Just as predicted, the formation of the *trans* isomer predominates over that of *cis* isomer to a high degree. For instance, the standard synthetic method for Co(oxine)$_3$ reported in literature[4] gives 4/96 as the approximate *cis*/*trans* isomer ratio. The preparative method of Rh(oxine)$_3$ in the present work gives result of the same order of magnitude. However, the reaction medium has been found to exert a considerable influence on the isomer ratio. The present method of synthesis of Co(oxine)$_3$ provides a much higher isomer ratio (25/75) than for the previous method. The mechanism of the solvent effect on the isomer ratio is not well understood. On the basis of trials, it appears that a less polar and more aprotic solvent favours the formation of the *cis* isomer.

The H2 proton on each ligand for the *cis* isomer exhibited a large upfield shift in comparison to that for oxine, which, as predicted before, results from being quite close to the heterocyclic ring of a neighboring ligand. Baker and Sawyer predicted that the relationship between H2 on ligand C and the heterocyclic ring of ligand A in the *trans* isomer should be identical to that for all three protons in the *cis* isomer. It follows that the H2 proton in the *cis* isomer should have the same chemical shift as proton H2C in the *trans* isomer. The prediction appears to be true for Co(oxine)$_3$ but not for Ir(oxine)$_3$, inasmuch as the chemical shift of proton H2C is significantly different from that of the H2 proton in the *cis* isomer. This might be attributable to the distortion of the coordination octahedron in *trans*-Ir(oxine)$_3$ which causes proton H2C to be slightly closer to the neighboring heteroaromatic ring. Such distortion is not unusual for iridium(III) complexes of rigid bidentate ligands, and has been alluded to elsewhere.[5-7]

Furthermore, the chemical shifts of all protons in the *cis* isomers are remarkably close to those corresponding protons on ligand C in the *trans* isomers, with proton H2 of the iridium oxinate being the sole exception. Thus it may be concluded that the chemical magnetic environments of ligand C in the *trans* isomer are similar to those of the ligands in the *cis* isomer.

TABLE V
Chemical shifts for oxine and the metal oxinates.

Compound	ppm vs TMS (± 0.005 ppm)					
	H2	H3	H4	H5	H6	H7
Oxine	9.184	7.880	8.657	7.720	7.770	7.400
cis-Co(oxine)$_3$	7.518	7.708	8.711	7.302	7.679	7.177
cis-Ir(oxine)$_3$	7.890	7.622	8.573	7.280	7.697	7.057
trans- cobalt oxinate A	8.664	7.909	8.731	7.352	7.679	7.269
B	8.578	7.866	8.696	7.344	7.679	7.264
C	7.474	7.705	8.696	7.344	7.679	7.211
trans- iridium oxinate A	8.585	7.766	8.580	7.294	7.707	7.190
B	8.498	7.724	8.567	7.291	7.707	7.176
C	7.679	7.627	8.567	7.278	7.707	7.087

TABLE VI
Coupling constants for oxine and metal oxinates.

Compound	Coupling constants, Hz (± 0.2 Hz)					
	$J_{2,4}$	$J_{2,3}$	$J_{3,4}$	$J_{5,6}$	$J_{6,7}$	$J_{5,7}$
Oxine	1.6	4.1	8.3	8.0	7.8	1.1
Trans & Cis Co(oxine)$_3$ Ir(oxine)$_3$	1.5	4.7	8.3	8.2	8.0	1.1

Some decomposition of the oxinates, in particular of the more strongly adsorbed *cis* isomers, was observed during the separation steps. Based on material balance, it was estimated that about 80% of *cis*-Co(oxine)$_3$ decomposed on silica gel. Furthermore, decomposition of the oxinate solution under ordinary fluorescent light was observed, increases in the order Co < Rh < Ir. The decomposition presented serious problems for the study. The decomposition of metal oxinates has been reported by some investigators[8-10] but its nature is beyond the scope of the present report.

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