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Registry No. **1**, 41879-37-2; **2**, 61012-64-4; **3**, 66417-55-8; **4**, 66417-56-9; **5**, 66417-57-0; **6**, 66417-58-1; **7**, 66417-59-2; **8**, 66417-60-5; **9**, 66417-61-6; **10**, 66417-62-7; **11**, 66417-63-8; **12**, 66417-64-9; **13**, 66417-65-0; **14**, 66417-66-1; **15**, 66417-67-2; **16**, 66417-68-3; **17**, 66417-69-4; **18**, 66417-70-7; **19**, 66417-71-8; **20**, 66417-72-9; **21**, 66417-32-1; **22**, 66417-33-2; **23**, 66417-34-3; **24**, 66417-35-4; **25**, 66417-36-5; **26**, 66417-37-6; **27**, 66417-38-7; **28**, 66417-39-8.

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Coordination Isomers of Antibiotic Thiohydroxamate–Metal Complexes. Geometrical Isomers of Tris(*N*-methylthioformohydroxamato)rhodium(III) and Bis(*N*-methylthioformohydroxamato)platinum(II)

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The low molecular weight bacterial products bis(*N*-methylthioformohydroxamato)copper(II) (fluopsin C) and tris(*N*-methylthioformohydroxamato)iron(III) (fluopsin F) display broad-spectrum antibiotic activity against both gram-positive and -negative bacteria and fungi. The kinetic lability of these complexes precludes the isolation of cis and trans geometrical coordination isomers in each case. Replacement of these metal ions with ions possessing large crystal field stabilization energies induces kinetic inertness and thereby allows the possibility of isomer separation. In the series of octahedral tris(*N*-methylthioformohydroxamate)–metal ion substituted complexes, $M(th)_3$ (M = Fe, Co, Cr, Rh), the latter two complexes were sufficiently substitution inert to permit the isolation and characterization of cis and trans geometrical isomers. Geometric isomerism occurs with a half-life of several hours for the chromium(III) complex and several days for the rhodium(III) complex. *cis*-$Rh(th)_3$ has NMR signals for the coordinated ligand at 3.70 ppm (CH_3N) and 7.17 ppm (HC(S)), whereas *trans*-$Rh(th)_3$ has corresponding signals at 3.51, 3.52, and 3.76 and 7.09, 7.46, and 7.53 ppm, respectively. The cis isomer has a visible absorption maximum at 437 nm (ϵ 490), whereas the trans isomer has the same band at 452 nm (ϵ 725). In the series of square-planar bis(*N*-methylthioformohydroxamate)–metal ion substituted complexes, $M(th)_2$ (M = Cu, Ni, Pd, Pt), cis and trans isomers were isolated and characterized in the last case. The infrared spectra of the two platinum(II) isomers are virtually superimposable except in the vicinity of 675 and 875 cm^{-1}. In these regions the trans isomer has absorption bands at 686 and 878 cm^{-1}, whereas the cis isomer has absorptions at 649 and 681 cm^{-1} and 874 and 893 cm^{-1}. The cis isomer has a visible absorption maximum at 429 nm (ϵ 126), whereas the trans isomer has the same absorption at 439 nm (ϵ 116). Geometric isomerism occurs with a half-life of several days.

Introduction

Certain low molecular weight bacterial products which contain cupric or ferric ion display broad-spectrum antibiotic activity against both gram-positive and -negative bacteria and fungi.[1] Bis(*N*-methylthioformohydroxamato)copper(II) (also known as fluopsin C, antibiotic YC 73, or antibiotic B_1) and tris(*N*-methylthioformohydroxamato)iron(III) (fluopsin F) have been isolated from the culture supernatant fluids of *Pseudomonas fluorescens* KY 4032[2] and MCRL 10107,[3] *Pseudomonas reptilivora* N-51968,[4-6] and *Streptomyces* ATCC 21775.[7] In *P. reptilivora* N-51968 the production of the cupric complex is dependent on the amount of cupric ion in the culture medium.[6] Unless the ferric to cupric ion ratio is significantly increased in the culture medium of *P. fluorescens* KY 4032, the cupric complex is the dominant product, suggesting that it has the higher formation constant.[1]

Ferric complexes of chemically synthesized N-substituted thioformohydroxamic acids, which are analogues of thioformin (*N*-methylthioformohydroxamic acid), and the native ferric and cupric complexes exhibit comparable antibiotic activity against *Bacillus subtilis* PCI 219, *Staphylococcus aureus* 209P, *Escherichia coli* NIHJ, and *Klebsiella pneumoniae*

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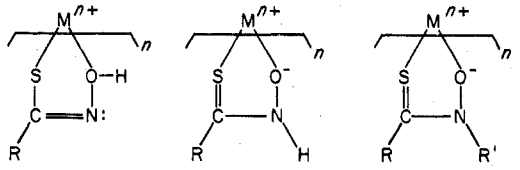
ATCC 10031 and the fungi *Candida albicans* Eiken, *Saccharomyces cereviciae* S-100, and *Trichophyton asteroides* 429 IMCF 07.[8-10] Ferric complexes of the corresponding N-substituted oxyhydroxamic acids presumably display no antibiotic activity since these ligands, which are known to have large formation constants for ferric ion, exhibited no antibiotic activity when tested in natural media rich in iron and other metals.[10] However, the ferric complex of the oxygen analogue of thioformin has yet to be tested for antibiotic action.

The mechanism of antibiotic action of these ferric or cupric complexes currently remains obscure except for the following report. Miyagishima quantitatively correlated the antibiotic activity of ferric complexes of N-substituted thioformohydroxamic acids with the hydrophobic character of the molecule for both gram-positive and -negative bacteria.[11] He proposed that the antibiotic activity of these agents is dependent upon their ability to penetrate the cell.[11,12] The more hydrophobic the N-substituent, the less effective that agent is against gram-negative bacteria. Miyagishima suggested that hydrophobic agents might be retained more strongly than hydrophilic ones by the relatively lipid-rich outer membrane of gram-negative bacteria; hence, this would account for their diminished antibiotic activity.[11]

The chemistry and coordination chemistry of thiohydroxamic acids including their properties, preparation, and reactions have recently been reviewed.[13,14] Thiohydroxamic acids have been used in the detection and quantitative determination of iron(III) and other metal ions.[15-23] Formation constants have been measured for several *N*-phenylthiobenzohydroxamate–metal complexes.[24] The ferric complexes of the above and other thiohydroxamates have been established as high spin from magnetic susceptibility measurements.[8,24,25] Thiohydroxamic acids can coordinate to metal ions via their sulfur and oxygen atoms.[26,27] The two possible modes of coordination of primary thiohydroxamic acids to metal ions are shown as I[28,29] and II.[30] Jensen et al. ruled out structure I since they



I II III

did not observe an OH stretch in the infrared spectrum of these complexes.[30] In addition, Abu-Dari and Raymond's reinterpretation[31] of existing data suggests that structure I is very unlikely. Of course, only structure III is possible for secondary thiohydroxamic acids such as *N*-methylthioformohydroxamic acid.

Scarce attention has been devoted to the coordination geometries of thiohydroxamate–metal complexes. Since thiohydroxamic acids are unsymmetrical bidentate ligands, cis (C_3 point symmetry) and trans (C_1) geometrical coordination isomers are possible for an octahedral tris complex, whereas cis (C_{2v}) and trans (C_{2h}) geometrical isomers are possible for a square-planar bis complex. In addition, each geometrical isomer in the octahedral case may consist of Δ and Λ optical coordination isomers.[32] Bis(thioacetohydroxamato)nickel(II)[26,27] crystallizes as entirely the cis or trans isomer depending on the crystallization conditions, indicating that these isomers are clearly in dynamic equilibrium in solution. Nagata and Mizukami isolated red and gray forms of bis(thiobenzohydroxamato)palladium(II) which they claim to be the trans and cis isomers, respectively, although their IR spectra are virtually superimposable.[33] Recently, Abu-Dari and Raymond prepared tris(thiobenzohydroxamate) complexes with iron(III), cobalt(III), and chromium(III).[31,34] Although both cis and trans isomers are possible for each complex from an examination of molecular models, only the cis isomer was isolated in each case.[31] In addition, Λ and Δ optical isomers were resolved not only in the chromium(III) and cobalt(III) complexes but also, surprisingly, in the high-spin iron(III) case, which should be kinetically labile since it has no crystal field stabilization energy.[35]

As a first step in probing the mechanism of antibiotic action of thioformin metal complexes, we began this investigation of their coordination chemistry. Since the square-planar bis(*N*-methylthioformohydroxamate)copper(II) complex and octahedral high-spin tris(*N*-methylthioformohydroxamate)-iron(III) complex possess little or no crystal field stabilization energy,[35] respectively, they should be kinetically labile and were found so in this study. The kinetic lability of these complexes precludes the isolation of their geometrical isomers. Replacement of cupric and ferric ions with metal ions possessing large crystal field stabilization energies should induce kinetic inertness and thereby allow the possibility of isomer separation. We report here the preparation of two series of bis- and tris(*N*-methylthioformohydroxamate)–metal ion substituted complexes, $M(th)_2$ (M = Cu, Ni, Pd, Pt) and $M(th)_3$ (M = Fe, Co, Cr, Rh), respectively. The octahedral chromium(III) and rhodium(III) and square-planar platinum(II) complexes were sufficiently substitution inert to facilitate the isolation and characterization of cis and trans geometrical isomers.

Experimental Section

Proton NMR spectra were obtained on a Varian HR-220 spectrometer; ultraviolet–visible spectra were measured with a Cary 17 spectrophotometer; infrared spectra were obtained as KBr pellets on a Beckman IR 18 A-X or Perkin-Elmer 180 spectrophotometer. Chemical analyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of California, Berkeley, Calif.

Materials. Reagent grade chemicals were used throughout. Thioformin (*N*-methylthioformohydroxamic acid) was prepared from potassium dithioformate[24] and *N*-methylhydroxylamine hydrochloride[36] by a literature procedure.[8,37] The ferric,[37] cupric,[8] and nickel(II)[2,8,37] complexes of thioformin were prepared by literature procedures. The nickel(II) complex has the following NMR data (CD_3COCD_3): δ 3.44 (3 H, s, NCH_3), 7.58 (1 H, s, HC(S)). In the preparation of the ferric complex,[37] the aqueous reaction mixture, which has been extracted with chloroform, was adjusted to pH 4.2, not pH 7,[37] with solid sodium bicarbonate.

Thin-Layer Chromatography. Camag Kieselgel D-O silica gel was used for thin-layer and column chromatography. Thin-layer chromatography on Kieselgel coated glass plates was performed on all metal complexes. Solvent systems were 50% CH_3OH–$CHCl_3$ for trivalent metal complexes and 100% methyl ethyl ketone for divalent ones. Spots were detected visually or stained with iodine vapor. The bis platinum(II) complex can also be visualized with $SnCl_2$–KI.[38]

Tris(*N*-methylthioformohydroxamato)cobalt(III). A solution of 80.6 mg (0.339 mmol) of $CoCl_2 \cdot 6H_2O$ in 5 mL of H_2O was added dropwise to a rapidly stirred solution of 92.8 mg (1.02 mmol) of thioformin in 5 mL of H_2O. Oxygen was bubbled through the green slurry for 1.5 h at 40–45 °C and for 12 h at room temperature. After the slurry was concentrated to dryness in vacuo, the residue was extracted with small portions of hot chloroform to afford a brown solution. This solution was concentrated to dryness in vacuo, and the residue was crystallized from acetonitrile to afford 13.9 mg (12%) of brown crystals. NMR ($CDCl_3$): δ 3.68 (3 H, s, NCH_3), 6.68 (1 H, s, HC(S)). Anal. Calcd for $Co(C_2H_4NOS)_3$: C, 21.89; H, 3.67; N, 12.76. Found: C, 22.08; H, 3.70; N, 12.26.

Tris(*N*-methylthioformohydroxamato)chromium(III). A solution of 54.4 mg (0.204 mmol) of $CrCl_3 \cdot 6H_2O$ in 2 mL of pH 5 acetate buffer (0.1 N) was added dropwise to a rapidly stirred solution of 61.3 mg (0.673 mmol) of thioformin in 25 mL of the same buffer. The reaction mixture was stirred 12 h at room temperature and then concentrated to dryness in vacuo. Acetone was added to the residue, and the resulting slurry was concentrated to dryness in vacuo. This procedure was repeated three more times. After the green solid was washed with several portions of ethyl ether, it was extracted with small portions of hot chloroform. This solution was then concentrated to dryness in vacuo, and the green solid was stored away from light. Anal.

Calcd for $Cr(C_2H_4NOS)_3$: C, 22.36; H, 3.75; N, 13.04. Found: C, 22.09; H, 3.64; N, 12.88.

Separation of Geometrical Isomers of Tris(*N*-methylthioformohydroxamato)chromium(III). The cis and trans isomers were separated by column chromatography as follows. Kieselgel (29 g) in chloroform was packed under nitrogen pressure in a glass column with an o.d. of 25 mm. The column was flushed with 50% CH_3OH–$CHCl_3$ under nitrogen pressure before topping the column with washed Monterey sand. The column was then flushed for 2 h with chloroform before a solution of the chromic complex in ca. 30 mL was applied to the column. After the chromic solution had seeped into the sand, the column was eluted with 50% CH_3OH–$CHCl_3$ under nitrogen pressure. Two blue-green fractions were collected within 90 min at 0 °C and stored in solution at −70 °C away from light until spectra were obtained. Cis and trans isomers were ascertained to be greater than 90% pure by TLC of the individual isomers.

Tris(*N*-methylthioformohydroxamato)rhodium(III). A solution of 62.1 mg (0.236 mmol) of $RhCl_3 \cdot 3H_2O$ (Alfa Products, Danvers, Mass.) in 10 mL of H_2O containing 0.25 g of sodium acetate was added dropwise to a rapidly stirred solution of 75.3 mg (0.826 mmol) of thioformin in 20 mL of methanol. The reaction mixture was stirred 12 h at room temperature, refluxed for 3 h, and then concentrated to dryness in vacuo. Acetone was added to the residue, and it was further treated as described in the chromic preparation. Anal. Calcd for $Rh(C_2H_4NOS)_3$: C, 19.31; H, 3.24; N, 11.31. Found: C, 19.62; H, 3.29; N 11.22.

Separation of Geometrical Isomers of Tris(*N*-methylthioformohydroxamato)rhodium(III). The cis and trans isomers were separated as described for the chromic complex. NMR ($CDCl_3$): cis δ 3.70 (3 H, s, NCH_3), 7.17 (1 H, s, HC(S)); trans δ 3.51 (3 H, s, NCH_3), 3.52 (3 H, s, NCH_3), 3.76 (3 H, s, NCH_3), 7.09 (1 H, s, HC(S)), 7.46 (1 H, s, HC(S)), 7.53 (1 H, s, HC(S)).

Bis(*N*-methylthioformohydroxamato)palladium(II). This compound was prepared by the following two methods.

(i) A solution of 66.2 mg (0.373 mmol) of $PdCl_2$ (Alfa Products) in 500 mL of pH 6.0 phosphate buffer (0.1 M) was added slowly to a rapidly stirred solution of 74.9 mg (0.822 mmol) of thioformin in 30 mL of the same buffer. The brown solution was stirred 2 days at room temperature and then concentrated to dryness in vacuo. Acetone was added to the residue, and the resulting slurry was concentrated to dryness in vacuo. This procedure was repeated three more times. After the red solid was washed with several portions of ethyl ether, it was extracted with small portions of hot methyl ethyl ketone, and the resulting solution was then concentrated to dryness in vacuo. The red product was recrystallized from acetone. NMR (CD_3COCD_3): δ 3.63 (3 H, s, NCH_3), 3.54 (0.3 H, s, NCH_3), 7.78 (1 H, s, HC(S)), 7.96 (0.1 H, s, HC(S)). Anal. Calcd for $Pd(C_2H_4NOS)_2$: C, 16.76; H, 2.81; N, 9.77. Found: C, 17.02; H, 2.86; N, 10.03.

(ii) A solution of 98.2 mg (1.08 mmol) of thioformin in a few milliliters of 50% ethanol–water was added dropwise to a rapidly stirred solution of 88.4 mg (0.499 mmol) of $PdCl_2$ (Alfa Products) in 10 mL of 1 N HCl. The resulting deep red solution was stirred 4 h at room temperature and then adjusted to pH 7 with solid $NaHCO_3$. The resulting red precipitate was filtered and then recrystallized from hot methanol to afford 29 mg (20%) of red crystals.

Bis(*N*-methylthioformohydroxamato)platinum(II). A solution of 305.1 mg (0.735 mmol) of K_2PtCl_4 (Alfa Products) in 10 mL of H_2O was added dropwise to a rapidly stirred solution of 145.5 mg (1.597 mmol) of thioformin in 5 mL of acetone. The reaction mixture was heated for 15 min at 55 °C, stirred 12 h at room temperature, and then heated again for 3 h at 55 °C. After the mixture was cooled, the yellow slurry was concentrated to dryness in vacuo. Acetone was added to the residue, and the slurry was further treated as described in the palladium(II) preparation. Anal. Calcd for $Pt(C_2H_4NOS)_2$: C, 12.80; H, 2.15; N, 7.46. Found: C, 13.02; H, 2.17; N, 7.61.

Separation of Geometrical Isomers of Bis(*N*-methylthioformohydroxamato)platinum(II). The cis and trans isomers were separated by column chromatography as follows. Kieselgel (28 g) in chloroform was packed under nitrogen pressure in a glass column with an o.d. of 25 mm. The column was flushed with methyl ethyl ketone under nitrogen pressure before topping the column with washed Monterey sand. A solution of the platinum(II) complex in 2–3 mL of methyl ethyl ketone was applied to the column, and the column was eluted with methyl ethyl ketone under nitrogen pressure. Two yellow fractions were collected within 90 min at 0 °C and stored in solution at −70 °C until spectra were obtained. Cis and trans isomers were ascertained to be greater than 95% pure by TLC of the individual isomers. NMR (CD_3COCD_3): cis δ 3.74 (3 H, s, NCH_3), 7.91 (1 H, t, J_{Pt-H} = 46 Hz, HC(S)); trans δ 3.61 (3 H, s, NCH_3), 8.13 (1 H, t, J_{Pt-H} = 53 Hz, HC(S)). IR (KBr) (relative intensity): cis 3045 (w), 2945 (w), 1585 (s), 1459 (w), 1447 (w), 1419 (w), 1402 (w), 1138 (s), 1096 (w), 893 (m), 874 (s), 808 (m), 681 (m), 649 (s), 517 (w), 502 (w), 397 (w) cm^{-1}; trans 3040 (w), 2930 (w), 2860 (w), 1581 (s), 1438 (w), 1420 (w), 1403 (m), 1127 (s), 1091 (m), 878 (s), 821 (m), 686 (s), 647 (w), 515 (w), 500 (w), 396 (w) cm^{-1}.

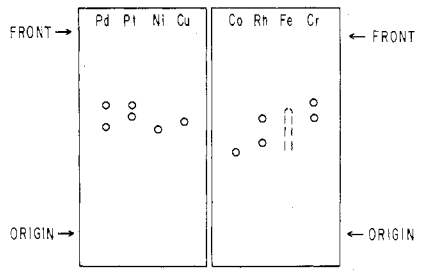


Figure 1. Silica gel thin-layer chromatography of $M(th)_2$ (M = Cu, Ni, Pd, Pt) in methyl ethyl ketone solution and of $M(th)_3$ (M = Fe, Co, Cr, Rh) in 50% CH_3OH–$CHCl_3$ solution. The R_f of $Fe(th)_3$ is dependent upon the amount of complex applied at the origin.

Physical Measurements. Visible spectra of all trivalent metal complexes were determined in chloroform solution at room temperature except for the geometrical isomers of the chromic complex, which were determined in 50% CH_3OH–$CHCl_3$ solution at room temperature. Visible spectra of the geometrical isomers of the platinum(II) complex were determined in methyl ethyl ketone solution at room temperature. The concentrations of chromium(III) solutions were determined spectrophotometrically as $[CrO_4]^{2-}$ (ϵ_{max}(372) 4815 L mol^{-1} cm^{-1} [39]) after oxidation of an aliquot of the chromium-containing solution with alkaline hydrogen peroxide. Excess hydrogen peroxide was removed by boiling the solution for 0.5 h. The concentrations of platinum(II) and rhodium(III) solutions were determined spectrophotometrically by the stannous chloride–hydrochloric acid method[40] (ϵ_{max}(403) 8140 L mol^{-1} cm^{-1} [41,42] and ϵ_{max}(470) 3900 L mol^{-1} cm^{-1},[43] respectively) after oxidation of an aliquot of the metal-containing solution first with aqua regia[40] and then with hydrogen peroxide. All geometrical isomers were at least 90% pure after spectra had been obtained as determined by TLC of the solutions.

Results and Discussion

Tris(*N*-methylthioformohydroxamate)–Metal Complexes. In the series of octahedral trivalent metal complexes of *N*-methylthioformohydroxamic acid (thioformin), $M(th)_3$ (M = Fe, Co, Cr, Rh), the latter two were sufficiently substitution inert to permit the isolation of cis and trans geometrical coordination isomers. (The properties of the above trivalent metal complexes are summarized in Table I.)

Silica gel TLC (Figure 1) of the rhodium(III) complex results in two orange bands, corresponding to the cis and trans isomers. Since the proton NMR spectrum (Figure 2) of the band with the greater R_f value shows three sets each of HC(S) and of CH_3N resonances for the coordinated ligand, this band is assigned the trans isomer which consists of three magnetically nonequivalent ligands. The band with the smaller R_f exhibits only one set of HC(S) and of CH_3N resonances in the NMR spectrum for the coordinated ligand. Therefore, this band is assigned the cis isomer which consists of three magnetically equivalent ligands. Analogous NMR data have been observed for cis and trans isomers of other tris(bidentate)rhodium(III) complexes.[44-49] This assignment of geometrical isomers is also consistent with their polarity; i.e., the more polar cis isomer elutes slower on TLC since it is more strongly bound by the adsorbent.[50] The low-spin, d^6, octahedral cis and trans isomers have absorption bands in the visible spectrum (Figure 3). The trans isomer has a spin-allowed d–d transition $^1A_1 \rightarrow {}^1T_1$ at 452 nm (ϵ 725), whereas the cis isomer has this transition at 437 nm (ϵ 490). In each case,

Table I. Characterization of Bis- and Tris(*N*-methylthioformohydroxamate)–Metal Complexes

Compd	Abundance, % of total[a]	Absorp max, nm (ϵ)[b]	Chem shift,[c] ppm HC(S)	Chem shift,[c] ppm CH_3N
$Fe(th)_3$		367 (2456), 507 (2075), 611 (1841)		
$Co(th)_3$		477 (748), 645 (393)	6.68	3.68
cis-$Cr(th)_3$	50	640 (185)		
trans-$Cr(th)_3$	50	675 (195)		
cis-$Rh(th)_3$	60	437 (490)	7.17	3.70
trans-$Rh(th)_3$	40	452 (725)	7.09, 7.46, 7.53	3.51, 3.52, 3.76
$Cu(th)_2$[d]		230 (10 720), 252 (10 470), 266 (12 300), 318 (6457)		
$Ni(th)_2$			7.58	3.44
cis-$Pd(th)_2$	95		7.78	3.63
trans-$Pd(th)_2$	5		7.96	3.54
cis-$Pt(th)_2$	40	429 (126)	7.91 (J_{Pt-H} = 46 Hz)	3.74
trans-$Pt(th)_2$	60	439 (116)	8.13 (J_{Pt-H} = 53 Hz)	3.61

[a] The abundance of cis and trans isomers was determined as follows. An acetone solution of a bis complex or a chloroform solution of a tris complex was equilibrated at reflux temperature until TLC did not indicate any further changes in the isomer distribution. Abundances were estimated visually from iodine-stained chromatograms. [b] Units are L mol^{-1} cm^{-1}. [c] Internal reference is tetramethylsilane at δ 0.00 ppm. [d] K. Shirahata, T. Deguchi, T. Hayashi, I. Matsubara, and T. Suzuki, *J. Antibiot.*, **23**, 546 (1970).

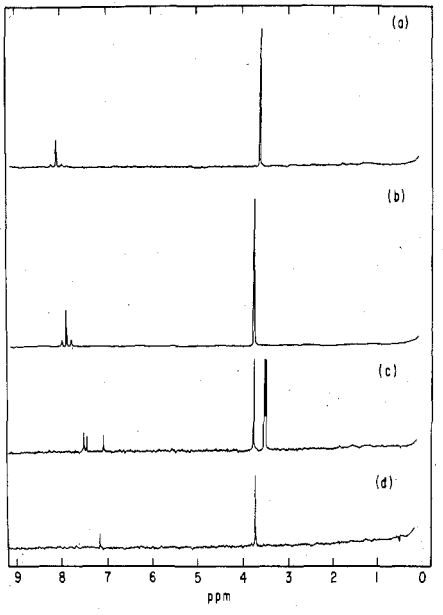


Figure 2. Proton NMR spectra of (a) *trans*-$Pt(th)_2$ and (b) *cis*-$Pt(th)_2$ in CD_3COCD_3 and (c) *trans*-$Rh(th)_3$ and (d) *cis*-$Rh(th)_3$ in $CDCl_3$.

the higher energy spin-allowed $^1A_1 \rightarrow {}^1T_2$ transition is obscured by charge-transfer and/or ligand absorptions. Both rhodium(III) isomers exhibit very limited kinetic lability. Geometric isomerism occurs with a half-life of several days in solution at room temperature.[51a]

In the absence of any thermodynamic difference in energy, the trans isomer is expected to be more abundant, since the probability of forming the trans isomer is three times that of forming the cis. Having ensured that the rhodium(III) isomers were equilibrated by treatment in refluxing chloroform until the isomer distribution remained constant as determined from TLC, the observed trans to cis ratio was 0.67 (Table I). This value differs significantly from the statistical value of 3.0. This difference suggests that the cis isomer is thermodynamically more stable than the trans isomer. In bis and tris complexes of unsymmetrical bidentate ligands in which one donor atom is a sulfur, Busch accounted for the increased stability of the cis isomer in terms of the π-bonding tendencies of the sulfur atoms and the symmetry of the appropriate metal d orbitals.[49,52,53]

Tris(*N*-methylthioformohydroxamato)chromium(III) elutes as two blue-green bands on TLC (Figure 1). Since the geometrical isomers of the chromium(III) complex should be

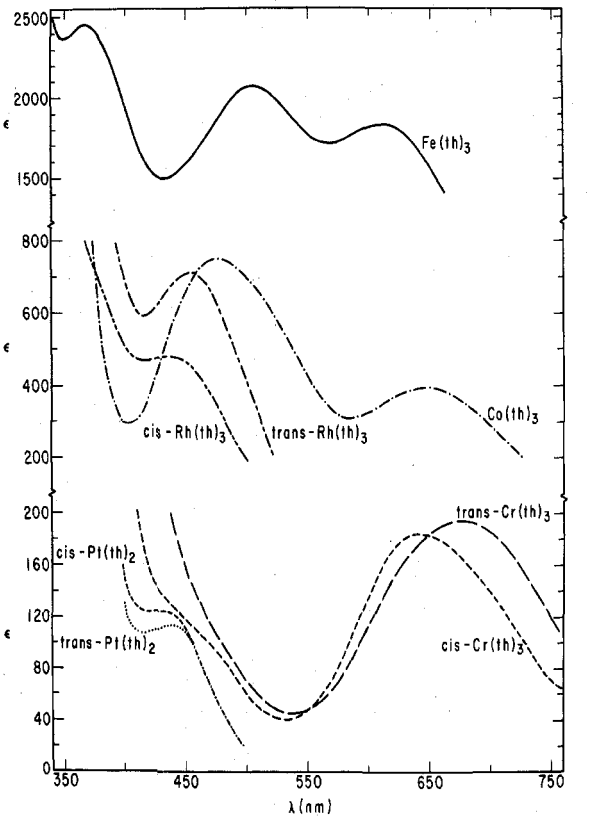


Figure 3. Visible absorption spectra of $M(th)_3$ (M = Fe, Co, Rh) in chloroform solution, $Cr(th)_3$ in 50% CH_3OH–$CHCl_3$ solution, and $Pt(th)_2$ in methyl ethyl ketone solution.

isostructural with the corresponding rhodium(III) isomers, the chromium(III) band with the greater R_f is tentatively assigned the trans isomer as in the rhodium(III) case, whereas the band with the smaller R_f is tentatively assigned the cis isomer. The visible absorption spectra of the d^3 chromic isomers are shown in Figure 3. The trans isomer has a spin-allowed d–d transition $^4A_2 \rightarrow {}^4T_2$ at 675 nm (ϵ 195), whereas the cis isomer has the same transition at 640 nm (ϵ 185). Once again the higher energy spin-allowed $^4A_2 \rightarrow {}^4T_1$ transition is obscured by charge-transfer and/or ligand absorption bands. Geometric isomerism occurs with a half-life of several hours in solution at room temperature.[51a] The observed trans to cis ratio of 1.0 (Table I), which differs from the expected statistical value of 3.0, suggests that the cis isomer is thermodynamically more

stable than the trans isomer as in the rhodium(III) case.

Thin-layer chromatography of tris(*N*-methylthioformohydroxamato)cobalt(III) results in one brown band with an R_f value that is very similar to that of the rhodium(III) cis isomer (Figure 1). Its proton NMR spectrum consists of a single set of HC(S) and of CH_3N resonances for the coordinated ligand (Table I). The low-spin, d^6, cobalt(III) complex has spin-allowed d–d transitions $^1A_1 \rightarrow {}^1T_1$ at 645 nm (ϵ 393) and $^1A_1 \rightarrow {}^1T_2$ at 477 nm (ϵ 748). If methanolic solutions of the cobalt(III) complex and cupric sulfate are mixed together, TLC indicates a new band with an R_f value identical with that of authentic bis(*N*-methylthioformohydroxamato)copper(II) (see below) in addition to the original band for the cobalt(III) complex. This suggests that the cobalt(III) complex is fairly labile. The above data are consistent with either rapid equilibration of the cis and trans isomers (faster than the NMR time scale) or the cobalt(III) complex being comprised of exclusively the cis isomer. Since geometrical isomers were isolated in the rhodium(III) and chromium(III) cases, this question was not pursued further.

Finally, tris(*N*-methylthioformohydroxamato)iron(III) elutes on TLC as one extremely broad purple band whose R_f value is dependent on the amount applied to the origin, and this band is bracketed approximately by the R_f values of the chromium(III) and rhodium(III) isomers (Figure 1). Since the high-spin, d^5, ferric complex has no spin-allowed d–d transitions in octahedral symmetry, only charge-transfer or ligand absorption bands are observed at 367 (ϵ 2456), 507 (ϵ 2075), and 611 nm (ϵ 1841). The ferric complex must be extremely labile since its purple solution decolorizes almost instantaneously with either sodium citrate or sodium nitrilotriacetate in pH 7 phosphate buffer. The extreme kinetic lability of the ferric complex is expected from its lack of crystal field stabilization energy. The TLC data is consistent with rapid equilibration of the isomers of the ferric complex, which elutes at a rate which is a weighted average of the individual isomer elution rates. In summary, the observed order of lability of the trivalent complexes, Fe > Cr > Rh, is in accord with the expected magnitude of the crystal field stabilization energies for each of the complexes.[51b]

Abu-Dari and Raymond measured the kinetics of racemization of the Δ and Λ optical isomers of *cis*-tris(thiobenzohyroxamate) complexes of iron(III), cobalt(III), and chromium(III).[31] The half-life for racemization for the cobalt(III) and chromium(III) complexes is greater than 50 h in chloroform at room temperature and greater than 18–22 h for the ferric complex in acetone at room temperature.[31] Thus, their cobalt(III) and chromium(III) complexes appear to be more substitution inert than the corresponding *N*-methylthioformohydroxamate complexes. Subtle differences in structure between the primary thiobenzohydroxamate–metal complexes and the secondary *N*-methylthioformohydroxamate complexes are expected as are electronic differences as manifested in the visible spectra of these complexes. In general, the absorption maxima and extinction coefficients of the former complexes differ appreciably from the latter complexes for the same metal ion. With thiobenzohydroxamic acid, absorption maxima are observed at 480 (ϵ 270) and 640 nm (ϵ 230) for the chromium(III) complex, 430 (ϵ 900) and 635 nm (ϵ 350) for the cobalt(III) complex, and 490 (ϵ 2740) and 580 nm (ϵ 2410) for the ferric complex.[31] These values can be compared with those for the *N*-methylthioformohydroxamate complexes (Table I).

Bis(*N*-methylthioformohydroxamate)–Metal Complexes. In the series of square-planar divalent metal complexes of *N*-methylthioformohydroxamic acid, $M(th)_2$ (M = Cu, Ni, Pd, Pt), only the platinum(II) cis and trans geometrical coordination isomers were separable. (The properties of the above divalent metal complexes are summarized in Table I.)

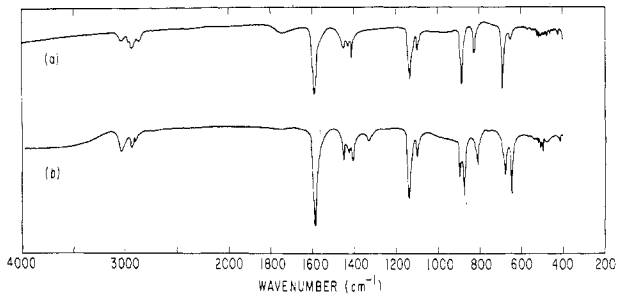


Figure 4. Infrared absorption spectra of (a) *trans*-$Pt(th)_2$ and (b) *cis*-$Pt(th)_2$ as KBr pellets.

Thin-layer chromatography (Figure 1) of the platinum(II) complex results in two yellow bands, corresponding to the cis and trans isomers. The infrared spectra (Figure 4) of these two TLC bands are virtually superimposable in the 4000–400 cm^{-1} range except for absorption bands in the vicinity of 675 and 875 cm^{-1}. The band with the greater R_f has single absorptions in each of the above regions at 686 and 878 cm^{-1}, whereas the band with the smaller R_f has two absorptions in each of the same regions at 649 and 681 cm^{-1} and 874 and 893 cm^{-1}. Since the cis isomer (C_{2v}) is expected to have more absorption bands than the trans isomer (C_{2h}) from a group-theoretical treatment involving Cartesian displacement coordinates for all atoms, the faster eluting TLC band is assigned the trans isomer, whereas the slower eluting band is assigned the cis isomer. For the sake of comparison, in these two regions, the free ligand has bands at 875 and 906 cm^{-1}, and bis(*N*-methylthioformohydroxamato)copper(II) (see below) has absorptions at 638, 875, 888, and 908 cm^{-1}.[2] Few definitive assignments of molecular vibrations to infrared absorption bands of thiohydroxamate–metal complexes[28,33] have been made, especially in the above regions, since several vibrational modes are often coupled together. However, Suzuki completed an elegant normal-coordinate analysis of *N*-methylthioformamide,[54] which is a close structural analogue of *N*-methylthioformohydroxamic acid. Suzuki observed a band at 868 cm^{-1} (neat) which he assigned to a combination of stretching vibrations, ν(CS) and ν(C′N), where C′ is the *N*-methyl carbon atom. Thus, the IR band(s) observed in the 875-cm^{-1} region could be assigned analogously for the platinum(II) isomers. Alternatively, absorptions in this region could be assigned as the NO stretching vibration, ν(NO), since this vibration has been assigned to absorption bands at approximately 900 cm^{-1} for thiohydroxamate–metal complexes,[28,29] 900–1100 cm^{-1} for oximes,[28,29,55,56] and 850–950 cm^{-1} for methyl-substituted hydroxylamines.[57,58] Treating either the CS or NO stretching vibrations as displacement vectors in a group-theoretical treatment, one absorption band is expected, and is observed, for the trans isomer, whereas two absorption bands are expected and observed for the cis isomer. We assign the bands in the 675-cm^{-1} region in direct analogy to Suzuki's assignment of a 600-cm^{-1} band in *N*-methylthioformamide as a combination of NCS and CNC′ deformations, δ(NCS) and δ(CNC′), respectively.[54] The prominent band around 1600 cm^{-1} which appears in both of the platinum(II) isomers is probably due to a combination of vibrational modes, with the CN stretching vibration, ν(CN), being dominant, in direct analogy with thiohydroxamate–metal complexes[59] and *N*-methylthioformamide.[54]

The assignment of geometrical isomers to the platinum(II) complex is also consistent with observed differences in their visible absorption spectra. Since the cis isomer does not have an inversion center, its d–d transition is expected to be more allowed and hence exhibit a larger extinction coefficient than that of the trans isomer, which does have an inversion center

(Figure 3 and Table I). As expected the more polar cis isomer has the smaller R_f on TLC (Figure 1). Analogous spectral intensities[49] and TLC behavior[49,60] have been observed for other bis(bidentate)platinum(II) complexes. Although an assignment of isomers is not explicit from their proton NMR spectra (Figure 2), small differences in their chemical shifts and platinum–hydrogen coupling constants, J_{Pt-H}, are nonetheless observed. Geometric isomerism occurs with a half-life of several days in solution.[51a]

Bis(*N*-methylthioformohydroxamato)palladium(II) elutes as two red bands on TLC with the band with the smaller R_f constituting approximately 95% of the mixture. Since the geometrical isomers of the palladium(II) complex should be isostructural with the corresponding platinum(II) isomers, the palladium(II) band with the greater R_f is tentatively assigned the trans isomer as in the platinum(II) case, whereas the band with the smaller R_f is tentatively assigned the cis isomer. The proton NMR spectrum (Table I) of the unresolved palladium(II) complex consists of two sets of coordinated ligand resonances, corresponding to the cis and trans isomers. On the basis of the abundance of the isomers as determined by TLC, the cis isomer consists of the more intense set of ligand resonances at 3.63 and 7.78 ppm, whereas the trans isomer has the less intense set of resonances at 3.54 and 7.96 ppm. In both the palladium(II) and platinum(II) complexes, the CH_3N proton NMR signals are further upfield and the HC(S) resonances are further downfield for the trans isomer than for the cis isomer. If methanolic solutions of the palladium(II) complex and ferric perchlorate are mixed together, TLC indicates a new band with an R_f value identical with that of authentic tris(*N*-methylthioformohydroxamato)iron(III) in addition to the original band for the palladium(II) complex. This suggests that the palladium(II) complex has finite lability. Since geometrical isomers were isolated in the platinum(II) case, no attempt was made to separate the small (5%) amount of trans isomer from the cis isomer in the palladium(II) case.

Thin-layer chromatography of bis(*N*-methylthioformohydroxamate)nickel(II) and -copper(II) complexes reveals only one band in each case with nearly identical R_f values (Figure 1). Since the structurally similar bis(thioacetohydroxamato)nickel(II)[26,27] crystallizes as entirely the cis or trans isomer depending on the crystallization conditions, these isomers appear to be in dynamic equilibrium in solution. This suggests that the TLC data are consistent with rapid equilibration of the isomers of the present nickel(II) complex, which elutes at a rate which is a weighted average of the individual isomer elution rates. Furthermore, the isomerization rate is probably faster than the NMR time scale since only a single set of coordinated ligand resonances are observed (Table I). The TLC data of the cupric complex are also consistent with rapid equilibration of its geometrical isomers (Figure 1).

In conclusion, we have prepared square-planar divalent and octahedral trivalent metal ion substituted complexes, a number of which are sufficiently substitution inert to permit the isolation and characterization of cis and trans geometrical isomers. The platinum(II) and rhodium(III) complexes are also sufficiently kinetically inert to permit their use as probes into the mechanism of action of thioformin complexes. For example, the labile[61] divalent (Cu, Ni, Pd) and trivalent (Fe, Co, Cr) complexes display antibiotic activity against *E. coli* NIHJ, whereas the substitution-inert, unresolved complex of platinum(II) or of rhodium(III), as well as their respective individual isomers, does not exhibit any antibiotic activity.[62] Labilization of the ligand in labile metal complexes appears to be a requirement for antibiotic activity. Details of this study will be published shortly.[62]

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Registry No. $Fe(th)_3$, 31323-26-9; $Co(th)_3$, 33271-64-6; *cis*-$Cr(th)_3$, 66511-16-8; *trans*-$Cr(th)_3$, 66511-17-9; *cis*-$Rh(th)_3$, 66512-68-3; *trans*-$Rh(th)_3$, 66511-18-0; $Ni(th)_2$, 31541-90-9; *cis*-$Pd(th)_2$, 66511-19-1; *trans*-$Pd(th)_2$, 66511-20-4; *cis*-$Pt(th)_2$, 66358-74-5; *trans*-$Pt(th)_2$, 66511-21-5.

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Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. 12. Deuterium Solvent Isotope Effect on the Rate of Acid-Catalyzed Decarboxylation of the Carbonatobis(ethylenediamine)cobalt(III) Complex Ion. A Mechanistic Reappraisal

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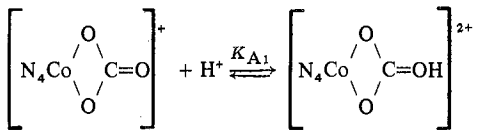
A recent study of the acid-catalyzed decarboxylation of the carbonatotetrakis(pyridine)cobalt(III) complex ion showed there to be rate acceleration in D_2O solvent, consistent with a proton-preequilibration mechanism. This observation directly contradicts the results of a similar study made some years ago of the analogous ion, carbonatobis(ethylenediamine)cobalt(III), for which there appeared to be deceleration in D_2O solvent. A reinvestigation of the latter reaction over a much wider acidity range has now shown the earlier work to be in error. The previously proposed generalized mechanism for aquation of chelated carbonato complex ions of the form $CoN_4CO_3^+$ ($N_4 \equiv$ various tetramine ligand groupings of uni-, bi-, or quadridentate type) has thus been revised to include a proton equilibration step. An unexpected complication arises in the interpretation of the data for the bis(ethylenediamine) complex ion in the acidity range $0.1 < [H^+] < 1.0$. Within these limits, the pseudo-first-order rate constant for carbonato chelate ring opening, which includes a $[H^+]$ term, overtakes and exceeds the true first-order rate constant for CO_2 release. The interesting implications of this unusual first-order successive reaction system are fully explored in the context of the present study.

Introduction

In a preceding paper in this series,[2] it was shown that the acid-catalyzed decarboxylation of the $Co(py)_4CO_3^+$ ion (py $\equiv$ pyridine) was best described by means of a proton pre-equilibration mechanism. Part of the evidence for this mechanism was the observed acceleration of the reaction in D_2O solvent. This observation contrasts with our earlier finding,[3] where an apparent *deceleration* of the corresponding reaction of the $Co(en)_2CO_3^+$ ion (en $\equiv$ ethylenediamine) in D_2O solvent was taken as evidence for proton transfer in the rate-determining step of the process. Specifically, the question involved is whether the first-order hydrogen ion concentration dependence of the catalyzed process arises from a carbonyl[4] preprotonation step (mechanism A) or a concerted proton-promoted carbonate dechelation (mechanism B) ($N_4 \equiv (py)_4$ or $(en)_2$).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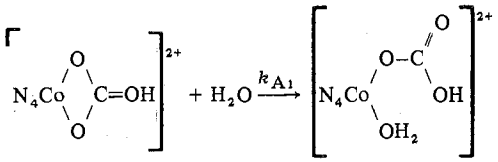
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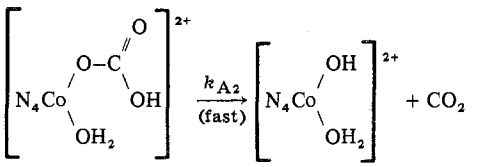
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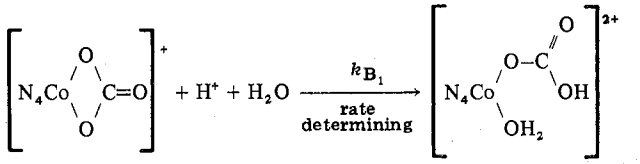
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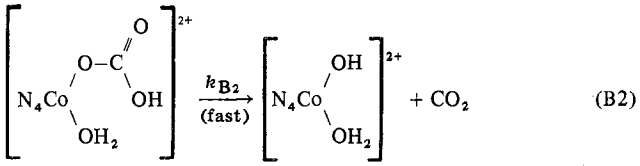
(B2)

Since K_{A1} is expected to be very small,[4] both mechanisms lead to pseudo-first-order observed rate constants at a fixed acidity (provided the final CO_2 release step is fast), viz.

$$k_A = k_{A1}K_{A1}[H^+] \quad (1)$$

$$k_B = k_{B1}[H^+] \quad (2)$$

However, the D_2O solvent isotope effects should be completely different for such mechanisms,[5] with acceleration in heavy water according to A and deceleration according to B. There seems to be no strong reason why the two types of complex should differ so widely in their mechanisms of acid-catalyzed decarboxylation, though there are large differences in their rates. We have therefore repeated the study of the kinetics of $Co(en)_2CO_3^+$ aquation in acidified heavy water and have indeed shown that our earlier data for this system[3] are in error and that mechanism A is to be preferred. In our new study, it has been possible to examine the kinetics of the reaction to much higher acid concentrations than previously since we now

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