

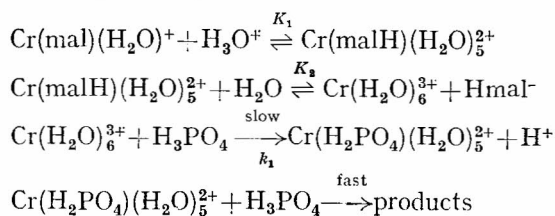
strength increases the rate constant indicating that the reaction is between ions of the same charge type.

The reaction is followed at two temperatures, viz. 30° and 46.5°. The energy of activation for the substitution process is found to be 27.0 kcal/mole.

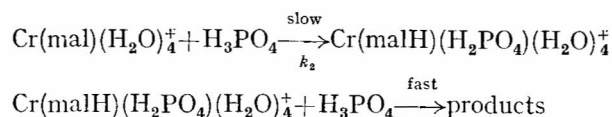
The absorption spectrum of the product in these studies is identical with that obtained in the substitution studies of tris(malonato) chromate(III) complex by H₃PO₄, with two peaks at 440 (ε = 19.0) and 630 nm (ε = 19.0). Ion exchange studies on the product species failed to show the presence of either cationic or anionic phosphate complexes. Hence the product species may be neutral possibly of the type Cr(HPO₄)(H₂PO₄).

The following mechanism is suggested to explain the experimental observations.

Acid dependent path:



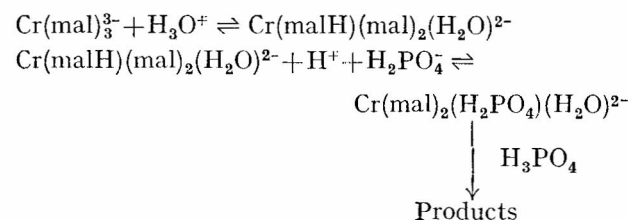
Acid independent path:



This leads to the rate law

$$\begin{aligned} \text{Rate} &= \frac{k_1 K_1 K_2 [\text{complex}][\text{H}_3\text{PO}_4][\text{H}_3\text{O}^+]}{[\text{Hmal}^-]} + k_2 [\text{complex}][\text{H}_3\text{PO}_4] \\ &= \left\{ \frac{[k_1 K_1 K_2 [\text{H}_3\text{O}^+]}{[\text{Hmal}^-]} + k_2 \right\} [\text{complex}][\text{H}_3\text{PO}_4] \end{aligned}$$

In the substitution of tris(malonato)chromate(III) by H₃PO₄, the first step is observed to be the attack of H₃O⁺ on Cr(mal)₃³⁻ to give a monodentate malonato complex, Cr(malH)(mal)₂(H₂O)²⁻. This monodentate complex enters into reaction with H₃PO₄ to give the products.



In the present case the monodentate malonato complex in the equilibrium step yields hexaaquochromium(III) which is attacked by H₃PO₄. This may be the cause for the relative slowness of substitution of the monocomplex.

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2-Methylbenzothiazole Complexes of Hg(II) Halides & Pseudohalides

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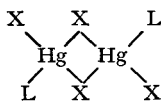
Hg(II) chloride, bromide, cyanide and thiocyanate form 1:1 complexes with 2-methylbenzothiazole. The complexes have been characterized by molar conductance, IR and far-IR spectral data. The Hg(II) chloride, bromide and thiocyanate complexes are tentatively suggested to have halogen/pseudohalogen-bridged dimeric tetrahedral structures in the solid state. The Hg(II) cyanide complex possesses a cyano-bridged polymeric structure.

THE ligand, 2-methylbenzothiazole having two bonding sites — sulphur and nitrogen in the thiazole ring — possesses strong anti-bacterial, anti-tubercular and anti-viral activities. Metal complexes of biologically important ligands are sometimes more effective than the free ligands. Although complexes of 2-methylbenzothiazole with some metal(II) salts are known¹ its complexes with Hg(II) salts which are likely to have significant biological effects have not been reported. In this note we report the preparation and characterization of the solid complexes of 2-methylbenzothiazole (L) with Hg(II) halides and pseudohalides.

Hg(II) chloride, bromide and cyanide complexes with 2-methylbenzothiazole were obtained by adding an excess of the ligand to a hot solution of the respective Hg(II) salt in ethanol. Hg(II) thiocyanate complex was prepared by boiling a suspension of the metal thiocyanate with an excess of the ligand, in ethanol. The solution was filtered hot and the complex which crystallized out on cooling was suction-filtered, washed with ethanol and dried. Stoichiometry of the complexes isolated was established by standard analytical methods. Hg(L)Cl₂, m.p. 220° (Found: Hg, 48.0; Cl, 17.0. Calc.: Hg, 47.6; Cl, 16.9%); Hg(L)Br₂, m.p. 202° (Found: Hg, 39.1; Br, 31.5. Calc.: Hg, 39.3; Br, 31.4%); Hg(L)(CN)₂, m.p. 145° (Found: Hg, 50.0. Calc.: Hg, 49.9%); and Hg(L)(SCN)₂, m.p. 113° (Found: Hg, 43.1; SCN, 25.1. Calc.: Hg, 43.0; SCN, 24.9%).

The 1:1 complexes are quite stable and soluble in methanol and dimethylformamide. Molar conductance of ~10⁻³M solutions in purified dimethylformamide (Philips conductivity bridge) indicate

them to be essentially non-electrolytic ($\Lambda_M \sim 30$ ohm⁻¹ cm² mole⁻¹). IR spectra (band positions in cm⁻¹) of these complexes are similar to those of 2-methylbenzothiazole complexes with other metal salts¹, confirming coordination through the nitrogen atom only¹. In addition to the absorption bands due to coordinated 2-methylbenzothiazole the far IR spectra (Beckman IR-12) of the 1:1 Hg(II) chloride and bromide complexes with this ligand show bands at 267 in the chloro and at 207 in the bromo derivative. The frequencies of these bands are halogen-dependent and are identified as ν Hg-Cl and Hg-Br modes, respectively, consistent with terminal Hg-X stretching modes in HgLX₂ complexes³, where L=Ph₃P, pyridine, pyridine-N-oxide or their ring substituted methyl or dimethyl derivatives, which are considered to have halogen-bridged dimeric tetrahedral structures in the solid state. Moreover, the Hg(II) chloride complex shows an additional band at 202 (but not the bromo complex) due to ν Hg-Cl involving bridging halogens³. The bridging Hg-Br stretching mode expected at ~ 150 could not be recorded with the present range of the spectrophotometer. The observed frequencies of the terminal and bridging Hg-halogen stretching modes in the 1:1 Hg(II) chloride and bromide complexes with 2-methylbenzothiazole lend support to the halogen-bridged dimeric tetrahedral structure (I) for the complexes in the solid state.



I
X=Cl, Br or SCN

IR spectrum of the 1:1 Hg(II) cyanide-2-methylbenzothiazole complex shows additional absorption bands at 2200, 455 and 360 which are identified as ν CN, ν Hg-C and δ Hg-C-N modes, respectively, due to coordinated cyano groups. Hg(II) cyanide has a linear cyanide-bridged polymeric chain structure⁴ in the solid state and absorbs⁵ at 2193, 442 and 341 due to ν CN, ν Hg-C and δ Hg C-N modes, respectively. The frequency of ν CN suffers a significant negative shift when the cyano bridges break down and Hg(II) cyanide complexes with terminal cyano groups absorb at lower energies⁶ than pure mercury cyanide while bridging cyano groups absorb at higher energies⁷. Complexes having both terminal and bridging cyano groups display split bands in each of the ν CN, ν Hg-C and δ Hg CN regions⁷; the one appearing at higher wave number being assigned to the bridging cyano groups while the other at lower wave number to the terminal cyano groups. The observed frequencies of ν CN (2200), ν Hg-C (455) and δ Hg CN (360) are consistent with the presence of only bridging cyano groups. The 1:1 Hg(II) cyanide-2-methylbenzothiazole complex may thus be assigned a cyanobridged polymeric structure in the solid state.

In addition to the ligand bands IR spectrum of the 1:1 Hg(II) thiocyanate-2-methylbenzothiazole complex shows absorption bands at 2133, 2125

and 2090 due to ν CN and two bands (770, 690) in the ν CS region supporting the presence of both bridging and terminal thiocyanato groups⁸ in the complex. On the basis of the stoichiometry and the IR spectral data the 1:1 Hg(II) thiocyanate complex with 2-methylbenzothiazole is tentatively assigned a thiocyanato-bridged dimeric structure in the solid state with two —SCN— bridges and a terminal SCN group bonded through sulphur to each mercury atom.

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Complexes of Organotin(IV) Halides with Neutral Schiff Bases of Salicylaldehyde & 2-Hydroxy-1-naphthaldehyde with 2-Aminopyridine

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Schiff base complexes of the type $R_nSnX_{4-n}(SB)_2$ (where X = Cl, Br, I, SB = Schiff bases derived from 2-aminopyridine and salicylaldehyde or 2-hydroxy-1-naphthaldehyde) have been synthesized and characterized by elemental analysis, infrared and electronic spectroscopy and conductivity measurements. The ligands behave as monodentate coordinating through azomethine nitrogen atom. An octahedral structure is suggested for the complexes in solid state.

RECENTLY transition metal complexes of N-2-(2'-pyridyl)-ethylsalicylidimines (Ia) have been reported¹, in which the bases behave as monofunc-