

## Inorganic Coordination Polymers.

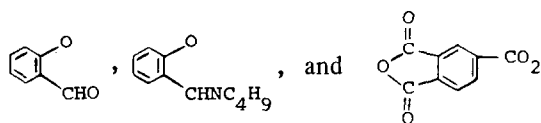
### XXI. Chromium(III) Bis(phosphinate) Polymers Containing Some Organic Anions\*

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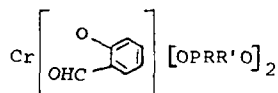
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Received November 17, 1976

The preparation and characterization of a variety of chromium(III) bis(phosphinate) polymers  $\{Cr(L)[OPRR'O]_2\}_x$  [with  $R = R' = C_6H_5$  and  $R = CH_3$ ,  $R' = C_6H_5$ ;  $L = OCH_3$ ,  $(OCH_2CH_2O)_{0.5}$ ,  $OCH_2CH_2NH_2$ ,



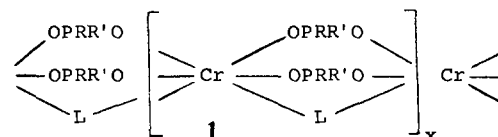
is reported. These alkoxides, aryloxides and carboxylate derivatives were prepared by the reaction of  $\mu$ -chloro-bis( $\mu$ -phosphinato)-chromium(III) with the appropriate alcohol or carboxylic acid in the presence of excess triethyl amine in THF. The imines were prepared by treating



with the appropriate amine in benzene. These materials are generally soluble in organic solvents in which their molecular weights range from 1,600 to 10,600. In both the solid state and in solution these polymers are hydrolytically stable. Their properties suggest octahedral chromium(III) centers bridged by double phosphinate bridges as well as bridging (L) groups.

#### Introduction

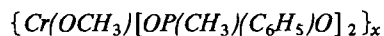
In our search for tractable inorganic polymers suitable for high temperature applications we have investigated a variety of chromium(III) bis(phosphinate) polymers  $\{Cr(L)[OPRR'O]_2\}_x$  including those with  $L =$  hydroxide [2], halide [3], acetylacetonate [4], and perfluorocarboxylate [5]. These polymers, which have inorganic backbones, contain octahedral chromium(III) centers linked by phosphinate bridges, and in some cases the ligands (L) also function as bridges.



The hydroxides, halides, and acetylacetonates have been prepared pure; however, the perfluorocarboxylates always contained less carboxylate than required for a 1:1 carboxylate to chromium ratio. In addition, attempts to prepare the  $\alpha$ -picolinate [6] polymers  $\{Cr[OP(C_6H_5)_2O]_2(C_5H_4NCOO)\}_x$  were unsuccessful probably because of steric effects. Thus it was of interest to extend these studies further and to prepare chromium(III) bis(phosphinate) polymers with other organic anionic ligands.



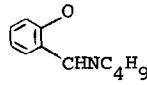
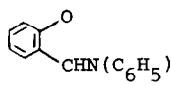
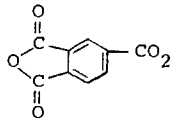
#### Experimental Materials

The phosphinic acids, which were supplied by Hynes Chemical Research (Durham, North Carolina 27704), were purified by recrystallization from ethanol. The chromium(III) polymers  $\{Cr(OH)[OP(C_6H_5)_2O]_2\}_x$  and  $\{Cr(OH)[OP(CH_3)(C_6H_5)O]_2\}_x$  were prepared as previously described [2]. Other chemicals and solvents were reagent grade and were used without further purification. The analytical results for the new polymers prepared in this study are given in Table I.

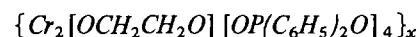


A solution-suspension of anhydrous  $CrCl_3$  (4.025 g, 0.0254 mol) in 125 ml of deaerated THF was prepared by shaking the components in the presence of a trace of  $CrCl_2$  under nitrogen. This suspension was treated with  $(CH_3)(C_6H_5)P(O)OH$  (7.931 g, 0.0508 mol) and  $N(C_2H_5)_3$  (6.5 g, 0.064 mol) and then refluxed for 1 hr. The suspension was allowed to cool to room temperature, treated with  $CH_3OH$  (1.60 g, 0.05 mol) and  $N(C_2H_5)_3$  (3.0 g, 0.03 mol), and then refluxed for an additional hour. The reaction mixture was filtered, and then the filtrate was evaporated under nitrogen to dryness. The green residue was dried for 3 hr at 200 °C under vacuum after which the product weighed 9.4 g (94% yield).

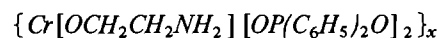
TABLE I. Analytical Results for  $\{\text{CrL}[\text{OPRR}'\text{O}]_2\}_x$ .

L	Analysis <sup>a</sup>						Molecular Weight <sup>c</sup>
	R	R'	C, %	H, %	P, %	Cr, %	
I. OCH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	45.3 (45.8)	4.85 4.87	15.8 15.8	12.4 13.2)	<sup>b</sup>
II. OCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	57.3 (58.0)	4.67 4.48	12.0 12.0	9.6 10.1)	5,200
III. (OCH <sub>2</sub> CH <sub>2</sub> O) <sub>0.5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	58.3 (58.2)	4.61 4.29	12.0 12.0	9.4 10.1)	10,600
IV. OCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	57.0 (57.2)	5.10 4.80	11.7 11.3	9.2 9.5)	7,600
V. 	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	51.9 (52.2)	4.51 4.38	13.1 12.8	10.6 10.8)	1,700
VI. 	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	60.9 (61.3)	4.52 4.15	10.4 10.2	8.4 8.6)	<sup>b</sup>
VII. 	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	55.6 (55.8)	5.79 5.62	11.4 11.5	9.4 9.7)	1,600
VIII. 	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	58.3 (58.1)	4.77 4.69	11.3 11.1	9.0 9.3)	2,700
IX. 	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	58.2 (58.5)	4.11 3.42	9.20 9.14	7.34 7.67)	<sup>b</sup>

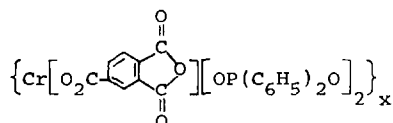
<sup>a</sup>Calculated values in parentheses. <sup>b</sup>Only partially soluble in CHCl<sub>3</sub>. <sup>c</sup>Determined in chloroform.



The same procedure was used to treat 2.177 g of CrCl<sub>3</sub> (0.01375 mol) in 150 ml of THF, first with 6.000 g of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(O)OH (0.02750 mol) and 3.18 g of N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (0.0314 mol) and then with 2.0 g of HOCH<sub>2</sub>CH<sub>2</sub>OH (0.032 mol) and 2.0 g of N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (0.020 mol). Yield 94%.

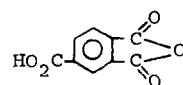


An analogous procedure was followed starting with 3.191 g of anhydrous CrCl<sub>3</sub> (0.02015 mol) in 100 ml of THF, 8.793 g of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(O)OH (0.0403 mol) and 5.0 g of N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (0.049 mol), followed by 1.23 g of HOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (0.020 mol) and 3.0 g of N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (0.030 mol). Yield 96%.

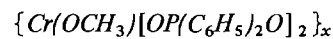


A similar procedure was used for the preparation of this polymer except that a solution of N(CH<sub>3</sub>)<sub>3</sub> in THF was used instead of N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>. Thus 2.131 g of

CrCl<sub>3</sub> (0.01346 mol) in 150 ml of THF was treated with 5.874 g of (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(O)OH (0.02692 mol) and 1.78 g of N(CH<sub>3</sub>)<sub>3</sub> (0.030 mol) in 45 ml of THF. After refluxing the solution for 0.5 hr 2.586 g of

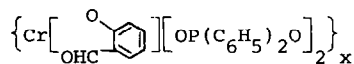


(0.01346 mol) and 1.0 g of N(CH<sub>3</sub>)<sub>3</sub> (0.017 mol) were added and the solution was refluxed another 0.5 hr. The workup was analogous to the previous experiments; however, the residue was heated to 140 °C for several days to sublime out (CH<sub>3</sub>)<sub>3</sub>NHCl impurity. Yield 98%.

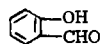


After 2.758 g of CrCl<sub>3</sub> (1.742 mol) was dissolved in 100 ml of deaerated CH<sub>3</sub>OH (with the aid of a trace of CrCl<sub>2</sub> under nitrogen), a solution of 8.362 g of Na[OP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>O] (0.0348 mol) in 80 ml of CH<sub>3</sub>OH was added slowly under nitrogen, and the mixture was refluxed 3 hr. During this time a white precipitate formed. The solution was treated with 8.0 g of N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (0.078 mol), the solvent was

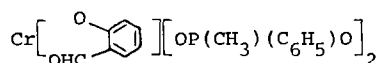
evaporated to 100 ml, and 400 ml of benzene was added. The solvent was again evaporated to 100 ml, the suspension was allowed to cool to room temperature, and the precipitate was then removed by filtration. The filtrate was evaporated under nitrogen and the residue was dried for several hours under vacuum at 200 °C.



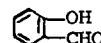
A solution containing 10.0 g of  $\{\text{Cr}(\text{OH})[\text{OP}(\text{C}_6\text{H}_5)_2\text{O}]_2\}_x$  (0.020 mol) and 6.0 g of



(0.049 mol) in 500 ml of toluene was stirred at room temperature until the reagents had dissolved. The solvent was then slowly distilled off and the residue dried at 150 °C overnight. Yield 92%.



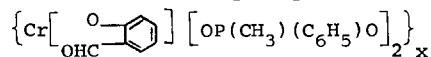
A similar procedure using 5.0 g of  $\{\text{Cr}(\text{OH})[\text{OP}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{O}]_2\}_x$  (0.0132 mol) and 2.0 g of



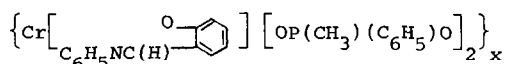
(0.0164 mol) in 500 ml of toluene and 10 ml of methanol was followed. This reaction mixture also contained 15 ml of 2,2-dimethoxy propane to insure dryness. Yield 97%.



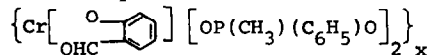
A solution containing 3.0 g of



(0.0062 mol) and 1.0 g of  $\text{C}_4\text{H}_9\text{NH}_2$  (0.014 mol) in 250 ml of benzene was refluxed for 2 hr and then the solvent was distilled off. The residue was dried at 120 °C overnight.



The same procedure was used with 3.0 g of



and 1.0 g of  $\text{C}_6\text{H}_5\text{NH}_2$  (0.011 mol). The product was dried at 150 °C overnight.

Elemental analyses were performed by standard methods in the Pennwalt Analytical Department. Infrared spectra in the 4000–400  $\text{cm}^{-1}$  region were recorded with a Perkin-Elmer 337 grating spectrophotometer on either Nujol or hexachlorobutadiene mulls between KBr disks. Visible spectra were recorded as  $\text{CHCl}_3$  and THF solutions with a Perkin-Elmer 450 spectrophotometer. Intrinsic viscosities were determined at  $30.0 \pm 0.1$  °C with a Cannon-Ubbelohde dilution viscometer. Molecular weight data were obtained at various concentrations with a

thermoelectric vapor pressure molecular weight apparatus.

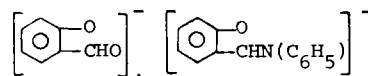
## Results and Discussion

It is apparent from the synthetic success of this study that it is possible to incorporate a variety of organic anions into chromium(III) bis(phosphinate) backbones. Therefore, the difficulty encountered previously with incorporating perfluorocarboxylate and picolinate groups into chromium(III) bis(phosphinate) chains may be characteristic of these species although not necessarily limited to them.

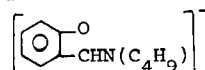
The  $\{\text{Cr}(\text{L})[\text{OPRR}'\text{O}]_2\}_x$  polymers prepared for this study are generally soluble in organic solvents, and their number average molecular weights in chloroform correspond to  $x$  values from 3 to over 20. The visible spectra of the alkoxy and carboxylate derivatives contain the two bands characteristic of octahedral chromium(III). Only one band is observable in the spectra of the aryloxy derivatives due to the presence of a UV charge transfer band (415–388  $m\mu$ ) that overlaps the other visible band. The positions of the visible bands (645–580 and 458–450  $m\mu$ ) in these polymers are similar to those found in other  $\{\text{Cr}(\text{L})[\text{OPRR}'\text{O}]_2\}_x$  systems [2–6].

In contrast to the chromium(III) bis(phosphinate) halides [3] these polymers are stable in THF and  $\text{CHCl}_3$  solutions, and no hydrolysis of the Cr–L bonds occurs even on boiling their solutions in a moist atmosphere. The salicylaldehydes (V and VI) are still reactive at the carbonyl centers as is shown by the preparation of the imine derivatives (VII and VIII), and the anhydride portion of the trimellitic anhydride polymer IX was found to form amide bonds on reaction with amines.

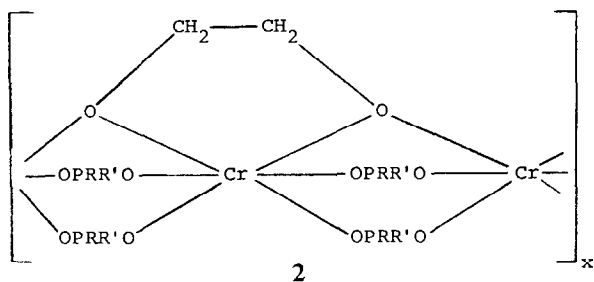
These chromium(III) bis(phosphinates) are similar to those studied previously such that they all are polymeric and contain octahedral chromium(III) atoms [2, 3]. Thus the structure of the chromium(III) phosphinates prepared in this study probably also consists for the most part of linear, triple bridged chains with two phosphinate bridges and one (L) bridge between metal centers (1). The L bridges act as one atom bridge in the case of the alkoxide and aryloxides and one or three atom bridges for the carboxylate bridges. It is unlikely that the aryloxides are chelating or crosslinking because only a very slight frequency difference was observed for the C=O and C=N infrared bands between the coordinated and uncoordinated



and



groups. Perhaps the most interesting structure occurs for the glycol derivative III, the stoichiometry of which suggests structure 2.



Space filling models show this unusual structure to be plausible because the bridging phosphinate groups bring the chromium atoms together in such a way that the glycol methylene groups do not interfere with the metal atoms they encircle. Another structural possibility involves glycol groups bridging between chains but this is less likely because a cross-linked polymer would result and it would be insoluble. Ladder polymers are also possible, but the

chances of forming a ladder structure in this system without crosslinks is very small.

### Acknowledgment

This work was supported in part by the Office of Naval Research and the Advanced Research Projects Agency.

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