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INORGANIC COORDINATION POLYMERS. XXII. CHROMIUM (III) BIS(PHOSP--ETC(U)
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INORGANIC COORDINATION POLYMERS. XXII. CHROMIUM(III) BIS(PHOSPHINATE) POLYMERS CONTAINING SOME ORGANIC ANIONS

by

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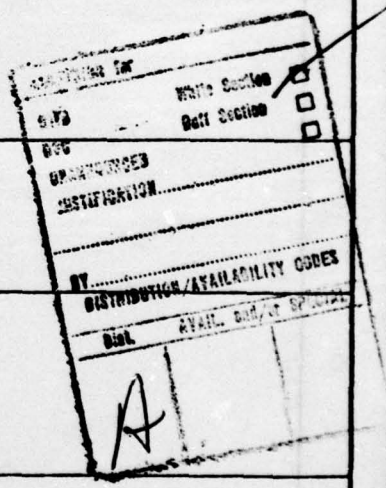

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Synthesis

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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 $R=CH_3$, $R'=C_6H_5$; $L=OCH_3$, $(OCH_2CH_2O)_{0.5}$, $OCH_2CH_2NH_2$,

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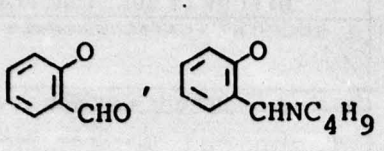
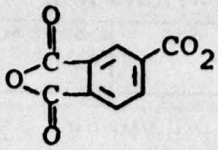
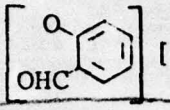
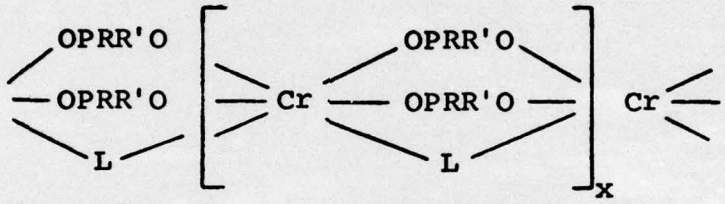




] is reported. These alkoxides, aryloxides and carboxylate derivatives were prepared by the reaction of mu-chloro-bis(mu-phosphinato)-chromium(III) with the appropriate alcohol or carboxylic acid in the presence of excess triethyl amine in THF. The imines were prepared by treating  with the appropriate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



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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 α 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

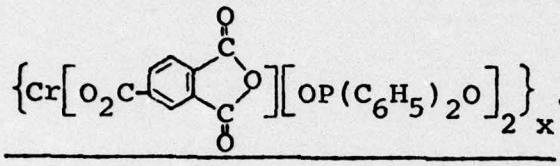
The phosphinic acids, which were supplied by Hynes Chemical Research (Durham, North Carolina 27704), were purified by recrystallization from ethanol. The chromium(III) polymers $\{Cr(OH)[OP(C_6H_5)_2O]_2\}_x$ and $\{Cr(OH)[OP(CH_3)(C_6H_5)O]_2\}_x$ were prepared as previously described.[2] Other chemicals 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.

$\{Cr(OCH_3)[OP(CH_3)(C_6H_5)O]_2\}_x$. A solution-suspension of anhydrous $CrCl_3$ (4.025 g, 0.0254 mole) 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 mole) and $N(C_2H_5)_3$ (6.5 g, 0.064 mole) and then refluxed for 1 hr. The suspension was allowed to cool to room temperature, treated with CH_3OH (1.60 g, 0.05 mole) and $N(C_2H_5)_3$ (3.0 g, 0.03 mole), 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° under vacuum after which the product weighed 9.4 g (94% yield).

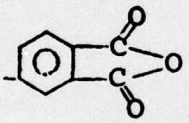
$\{Cr_2[OCH_2CH_2O][OP(C_6H_5)_2O]_4\}_x$. The same procedure was used to treat 2.177 g of $CrCl_3$ (0.01375 mole) in 150 ml of THF, first with 6.000 g of $(C_6H_5)_2P(O)OH$ (0.02750 mole) and

3.18 g of $N(C_2H_5)_3$ (0.0314 mole) and then with 2.0 g of $HOCH_2CH_2OH$ (0.032 mole) and 2.0 g of $N(C_2H_5)_3$ (0.020 mole). Yield 94%.

$\{Cr[OCH_2CH_2NH_2][OP(C_6H_5)_2O]_2\}_x$. An analogous procedure was followed starting with 3.191 g of anhydrous $CrCl_3$ (0.02015 mole) in 100 ml of THF, 8.793 g of $(C_6H_5)_2P(O)OH$ (0.0403 mole) and 5.0 g of $N(C_2H_5)_3$ (0.049 mole), followed by 1.23 g of $HOCH_2CH_2NH_2$ (0.020 mole) and 3.0 g of $N(C_2H_5)_3$ (0.030 mole). Yield 96%.



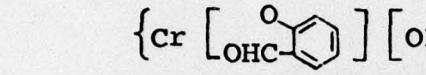
. A similar procedure was used for the preparation of this polymer except that a solution of $N(CH_3)_3$ in THF was used instead of $N(C_2H_5)_3$. Thus 2.131 g of $CrCl_3$ (0.01346 mole) in 150 ml of THF was treated with 5.874 g of $(C_6H_5)_2P(O)OH$ (0.02692 mole) and 1.78 g of $N(CH_3)_3$ (0.030 mole) in 45 ml of THF. After the solution was refluxed 0.5 hr,

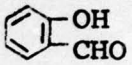
2.586 g of 

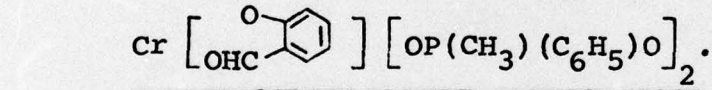
(0.01346 mole) and 1.0 g of $N(CH_3)_3$ (0.017 mole) were added and the solution was refluxed another 0.5 hr. The workup was analogous to the previous experiments; however, the residue was heated to 140° for several days to sublime out $(CH_3)_3NHCl$ impurity. Yield 98%.

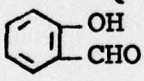
$\{Cr(OCH_3)[OP(C_6H_5)_2O]_2\}_x$. After 2.758 g of $CrCl_3$ (1.742 mole) was dissolved in 100 ml of deaerated CH_3OH (with the aid of a trace of $CrCl_2$ under nitrogen), a solution of 8.362 g of $Na[OP(C_6H_5)_2O]$ (0.0348 mole) in 80 ml of CH_3OH

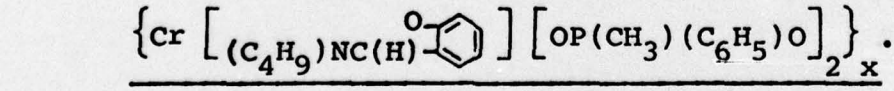
was added slowly under nitrogen, and the mixture was refluxed 3 hr. During this time a white precipitate formed. The solution was treated with 8.0 g of $N(C_2H_5)_3$ (0.078 mole), the solvent was evaporated to 100 ml, and 400 ml of benzene was added. The solvent was again evaporated to 100 ml, the suspension 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°.

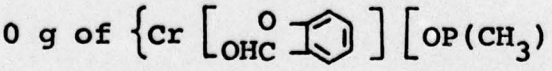


A solution containing 10.0 g of $\{Cr(OH)[OP(C_6H_5)_2O]_2\}_x$ (0.020 mole) and 6.0 g of  (0.049 mole) in 500 ml of toluene was stirred at room temperature until the reagents had dissolved. The solvent was then slowly distilled off and the residue dried at 150° overnight. Yield. 92%.



A similar procedure using 5.0 g of $\{Cr(OH)[OP(CH_3)(C_6H_5)O]_2\}_x$ (0.0132 mole) and 2.0 g of  (0.0164 mole) 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%.

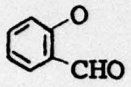
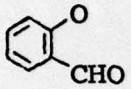
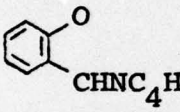
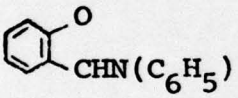
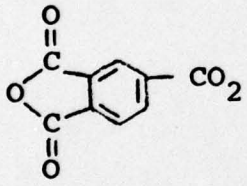


A solution containing 3.0 g of  (0.0062 mole) and 1.0 g of $C_4H_9NH_2$ (0.014 mole) in 250 ml of benzene was refluxed for 2 hr. and then the solvent was distilled off. The residue was dried at 120° overnight.

$\{Cr\left[C_6H_5NC(H)\text{-}C_6H_3O\right]\left[OP(CH_3)(C_6H_5)O\right]_2\}_x$. The same procedure was used with 3.0 g of $\{Cr\left[OHC\text{-}C_6H_3O\right]\left[OP(CH_3)(C_6H_5)O\right]_2\}_x$ and 1.0 g of $C_6H_5NH_2$ (0.011 mole). The product was dried at 150° overnight.

Elemental analyses were performed by standard methods in the Pennwalt Analytical Department. Infrared spectra in the 4000-400 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 $CHCl_3$ and THF solutions with a Perkin-Elmer 450 spectrophotometer. Intrinsic viscosities were determined at 30.0 ± 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.

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

	L	R	R'	Analysis[a] C, %	H, %	P, %	Cr, %	Molecular Weight[c]
I.	OCH_3	CH_3	C_6H_5	45.3 (45.8	4.85 4.87	15.8 15.8	12.4 13.2)	b
II.	OCH_3	C_6H_5	C_6H_5	57.3 (58.0	4.67 4.48	12.0 12.0	9.6 10.1)	5,200
III.	$(OCH_2CH_2O)_{0.5}$	C_6H_5	C_6H_5	58.3 (58.2	4.61 4.29	12.0 12.0	9.4 10.1)	10,600
IV.	$OCH_2CH_2NH_2$	C_6H_5	C_6H_5	57.0 (57.2	5.10 4.80	11.7 11.3	9.2 9.5)	7,600
V.		CH_3	C_6H_5	51.9 (52.2	4.51 4.38	13.1 12.8	10.6 10.8)	1,700
VI.		C_6H_5	C_6H_5	60.9 (61.3	4.52 4.15	10.4 10.2	8.4 8.6)	b
VII.		CH_3	C_6H_5	55.6 (55.8	5.79 5.62	11.4 11.5	9.4 9.7)	1,600
VIII.		CH_3	C_6H_5	58.3 (58.1	4.77 4.69	11.3 11.1	9.0 9.3)	2,700
IX.		C_6H_5	C_6H_5	58.2 (58.5	4.11 3.42	9.20 9.14	7.34 7.67)	b

a. Calculated values in parentheses.

b. Only partially soluble in $CHCl_3$.

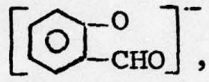
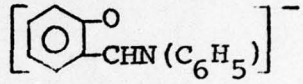
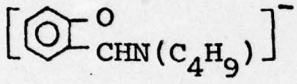
c. Determined in chloroform.

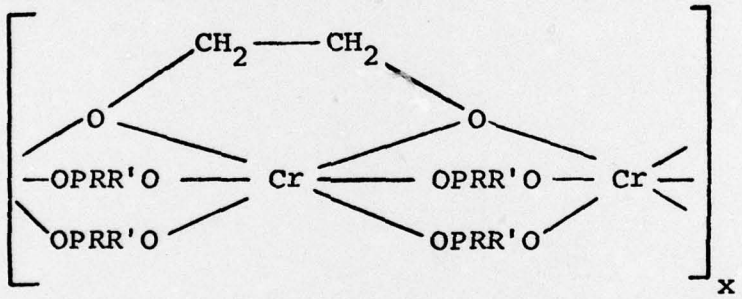
Results and Discussion

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 $\{Cr[L](OPRR'O)_2\}_x$ 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 alkoxyl 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 mμ) that overlaps the other visible band. The positions of the visible bands (645-580 and 458-450 mμ) in these polymers are similar to those found in other $\{Cr[L][OPRR'O]_2\}_x$ systems.[2-6]

In contrast to the chromium(III) bis(phosphinate) halides[3] these polymers are stable in THF and $CHCl_3$ 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 octhedral 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.



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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 crosslinked 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.

Acknowledgement

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References

1. Part XX. P. Nannelli, H. D. Gillman, H. G. Monsimer, and S. B. Advani, Makromol. Chem., 177, 2607 (1976).
2. P. Nannelli, H. D. Gillman, and B. P. Block, J. Polym. Sci. Part A-1, 9, 3027 (1971).
3. H. D. Gillman, P. Nannelli, and B. P. Block, J. Inorg. Nucl. Chem., 35, 4053 (1973).
4. B. P. Block, J. Simkin, and L. R. Ocone, J. Am. Chem. Soc., 84, 1749 (1962).
5. P. Nannelli and H. D. Gillman, J. Polym. Sci., Polym. Chem. Ed., 12, 221 (1974).
6. A. J. Saraceno and B. P. Block, Inorg. Chem., 2, 864 (1963).
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