of interest. The precision obtainable did not justify trying to fit two formation constants and two extinction coefficients to the data.[5] Application of the methods of Newton and Arcand[6] and McConnell and Davidson[7] gave values of β_1 ranging between 10 and 24, with indications that the higher values were being the least affected by the presence of other absorbing species. Values in the literature[8] range from 4.6 to 44, at various ionic strengths, the most reliable of which would appear to be about 9 for unit ionic strength.[2] The large value observed here is to be expected in view of the high activity coefficients of lead ion in sodium perchlorate solutions more concentrated than 2.0 M.[9] The ion $PbCl^+$ was found to exhibit maximum absorption at 226 mμ with a molar extinction coefficient of 6500.

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Inorganic Coördination Polymers. IV. The Attempted Replacement of Acetylacetonate Ligands with Picolinate Ligands[1]

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Recently the synthesis of poly-[di-μ-diphenylphosphinatoacetylacetonatochromium(III)] was reported as an example of a substitution–addition polymerization leading to the formation of a coördination polymer possessing a completely inorganic backbone.[2] In principle other polymers belonging to the same structural class, *i.e.*, based on chelated, double-bridged octahedral central elements, can be made by analogous substitution–addition reactions between a neutral tris-chelate of a trivalent metal and a suitable catenating agent. We report here a study of the reaction between tris-(picolinato)-chromium(III) and diphenylphosphinic acid in stoichiometry expected to yield $[Cr(C_5H_4NCOO)(OP(C_6H_5)_2O)_2]$.

Experimental

All chemicals and solvents employed were reagent grade and were not purified further.

$Cr(C_5H_4NCOO)_3 \cdot H_2O$.—The method described in the literature for the preparation of $Cr(C_5H_4NCOO)_3 \cdot H_2O$[3] also produces $Cr(C_5H_4NCOO)_2OH$. The formation of this side product effectively prevents high yields of the desired product. Consequently, the following procedure, which gives high yields, was employed. A solution of 11.5 g. (0.046 mole) of $Cr(OAc)_3 \cdot H_2O$ dissolved in 200 ml. of water was added to a filtered solution of 18.5 g. (0.15 mole) of picolinic acid in 200 ml. of water. The resulting mixture then was heated on a hot plate until it changed from green to wine red, transferred to a steam bath, and concentrated to a volume of about 100 ml. under a stream of nitrogen. The red precipitate was filtered off, washed with water and acetone, dried by aspiration, and taken to constant weight at 100°; yield 14.3 g. The residue obtained by evaporating the filtrate to dryness was treated with 200 ml. of water, filtered, and washed with acetone. This second crop weighed 3.8 g., so the combined yield was 85%. *Anal.* Calcd. for $Cr(C_5H_4NCOO)_3 \cdot H_2O$: Cr, 11.9; C, 49.5; H, 3.2; N, 9.6; H_2O, 4.1. Found: Cr, 12.0; C, 49.7; H, 3.2; N, 9.3; H_2O, 4.4.

Fusion of $Cr(C_5H_4NCOO)_3 \cdot H_2O$ with $(C_6H_5)_2P(O)OH$. (a) **In 1:2 Molar Ratio.**—Fusion of 2.10 g. (0.0048 mole) of $Cr(C_5H_4NCOO)_3 \cdot H_2O$ with 2.18 g. (0.0100 mole) of $(C_6H_5)_2P(O)OH$ under a current of nitrogen at an oil bath temperature of 170–220° for 1.25 hr. volatilized picolinic acid (m.p. 136.5–138.0°). Successive concentrations of the solution made by dissolving the ground residue in 200 ml. of ethanol gave precipitates totaling 0.72 g. Elemental analysis and infrared spectra suggested that these fractions were mixtures of $Cr(C_5H_4NCOO)_3 \cdot H_2O$, $(C_6H_5)_2P(O)OH$, and $[Cr(C_5H_4NCOO)_2OP(C_6H_5)_2O]_2$, the first fraction containing more of the third compound and later fractions more of the first. Evaporation of the filtrate to dryness followed by heating to constant weight under vacuum at 100° in an Abderhalden gave 2.46 g. of a gray-green product. Extraction with benzene for 19 hr. left 0.80 g. of product. *Anal.* Calcd. for $[Cr(C_5H_4NCOO)(OP(C_6H_5)_2O)_2]_n$: Cr, 8.6; C, 59.2; H, 4.0; N, 2.3; P, 10.2; mol. wt., 608.5n. Calcd. for $[Cr(C_5H_4NCOO)_2(OP(C_6H_5)_2O)]_n$: Cr, 10.1; C, 56.1; H, 3.5; N, 5.5; P, 6.0; mol. wt., 513.4n. Found: Cr, 8.2; C, 56.7; H, 4.1; N, 3.9; P, 7.4; H_2O, 1.70; mol. wt. by ebulliometry in $CHCl_3$, 1190. Several additional runs gave benzene-insoluble products with molecular weights ranging from 430 to 1400 and compositions lying between the two calculated. Work-up of the benzene-soluble fraction also failed to give materials of high molecular weight as measured ebulliometrically in C_6H_6.

(b) **In 1:1 Molar Ratio.**—An intimately ground mixture of 2.00 g. (0.0046 mole) of $Cr(C_5H_4NCOO)_3 \cdot H_2O$ with 1.00 g. (0.0056 mole) of $(C_6H_5)_2P(O)OH$ was placed in a three-neck flask. The system was evacuated to 2–3 mm. and heated in an oil bath for 1.33 hr. at 206°. The cooled residue, which weighed 2.1 g., was extracted first with 50 ml. of ethanol and then with 50 ml. of chloroform. Work-up of the ethanol yielded 0.8 g. of unreacted starting materials containing a small amount of $[Cr(C_5H_4NCOO)_2(OP(C_6H_5)_2O)]_2 \cdot H_2O$ (identified by infrared spectrum, *cf.* later characterization). The chloroform extract yielded 0.7 g. of residue after it was washed with benzene and dried at 110°. Infrared showed it, too, to be the dimer. Molecular weight calculated for the monohydrate of the dimer, 1045; found ebulliometrically in $CHCl_3$, 1060. The insoluble residue (0.5 g.) consisted essentially of $Cr\ (C_5H_4NCOO)_3 \cdot H_2O$.

(c) **Characterization of the Dimer.**—The most completely characterized sample of $[Cr(C_5H_4NCOO)_2(OP(C_6H_5)_2O)]_2 \cdot H_2O$ obtained in a fusion reaction resulted from a reaction carried out in 2:1 stoichiometry at 189–236° for 5 hr. After the residue had been extracted with ethanol and benzene, it was extracted with chloroform. Work-up of the chloroform extract yielded a violet solid melting at 344–346° dec. *Anal.* Calcd. for $[Cr(C_5H_4NCOO)_2(OP(C_6H_5)_2O)]_2 \cdot H_2O$: Cr, 10.0; C, 55.0; H, 3.66; N, 5.4; P, 6.0; mol. wt., 1045. Found: Cr, 9.6; C, 54.6; H, 3.72; N, 5.0; P, 5.7; mol. wt. by ebulliometry in $CHCl_3$, 1060. A substantial amount of insoluble residue was left which appeared

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to be impure $Cr(OP(C_6H_5)_2O)_3$. *Anal.* Calcd.: Cr, 7.4; C, 61.5; H, 4.3; P, 13.2. Found: Cr, 7.2; C, 60.4; H, 4.2; P, 12.4.

Infrared Spectra.—Infrared spectra were measured with a Perkin Elmer Model 21 or 221 spectrophotometer employing a sodium chloride prism in the 6–15 μ region. Spectra were obtained for solids in Nujol and hexachlorobutadiene mulls.

The infrared spectrum of the dimer corresponds to what is expected. Absorption bands clearly due to the diphenylphosphinate group are observed at the following frequencies (cm.$^{-1}$): 1440 (m), 1180 (vs), 1126 (vs), 1065 (sh), 997 (m), and 727 (s). Additional peaks overlapped with picolinate absorptions occur at approximately 1022 (m), 758 (s), and 690 (s). With the exception of the OPO stretching mode, these frequencies closely parallel those reported for $Co[OP(C_6H_5)_2O]_2$[4] in this region of the spectrum. Two sharp peaks attributed to the OPO antisymmetric stretching vibration are noted at 1180 and 1126 cm.$^{-1}$, and these correspond closely to the absorption pattern observed in the spectrum of $(AcCHAc)_2Cr[OP(C_6H_5)_2O]_2Cr(AcCHAc)_2$.[2]

Absorption maxima for the picolinate group are as follows (cm.$^{-1}$): 1665 (vs), 1610 (s), 1568 (m), 1477 (m), 1438 (s), 1340 (sh), 1330 (s), 1286 (s), 1257 (w), 1238 (w), 1155 (vs), 1093 (w), 1050 (s), 1022 (m), 860 (s), 758 (s), 714 (s), 680 (s), and 655 (s). Frequency values of these absorptions are practically similar to those observed in $Cr(C_5H_4NCOO)_3{\cdot}H_2O$, thus showing that the picolinate ring structure is preserved in the dimer. In particular the bands at 1286, 1155, 1050, and 1022 cm.$^{-1}$ are characteristic of the *ortho*-substituted pyridine group and corresponding vibrations[5] for compounds of similar structure are very close to the values observed for the dimer.

Discussion

The experimental results clearly show that the substitution of the picolinate ligand for the acetylacetonate ligand makes polymer formation difficult. Compositions lying between that of an infinite linear double-bridged polymer and that of a dimer give ebullioscopic molecular weights in benzene and $CHCl_3$ in the monomer-to-dimer range in value. It thus is apparent that either a polymer was not formed at all in the reaction or else that any polymer formed is quite unstable compared to $[Cr(AcCHAc)(OP(C_6H_5)_2O)_2]_x$.[2] An attempt to build a model of the double-bridged polymer containing picolinate instead of acetylacetonate ligands leads to the observation that there is considerable steric interaction between the chelating picolinate group and the phenyl groups of the catenating diphenylphosphinate anion. In fact models indicate that any chelating group larger than the acetylacetonate ion will interact sterically with the double-bridging diphenylphosphinate ions, severely limiting the possibilities for preparing analogs to $[Cr(AcCHAc)(OP(C_6H_5)_2O)_2]_x$. The picolinate group appears to be large enough to prevent the isolation and characterization of any units larger than the dimer. It is to be noted that theoretically the dimer can exist in six isomeric geometrical forms because the chelating group is not symmetrical. We have not investigated this possibility in any detail.

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Use of Ultrasonic Cavitation for Rapid Determination of Pressure–Composition Data

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The time required for determination of the pressure–composition phase diagrams of systems with relatively long equilibration times (several hours to several days) has been greatly reduced by applying ultrasonic cavitation to the samples.

The system $AgCl–NH_3$, studied by Biltz and Stollenwerk,[1] was examined by standard vacuum line techniques with the sample tube immersed in an ice bath through which ultrasonic waves of 38 kc./sec. were transmitted.[2] An essential feature of the ice bath, which is contained in the sonic generator tank, is that the liquid column surrounding the sample tube be relatively free of solid. This condition may readily be achieved by freezing part of the bath liquid on a suitably shaped cooling coil through which refrigerant is passed intermittently. The cooling coil, which encircles the sample tube, and the bath liquid frozen on the coil should be kept at least 5 cm. from the sample tube and free from the bottom of the tank. Automatic control of such a bath has been described elsewhere.[3] The use of crushed ice, instead of the single ice helix formed on the cooling coil, was found to greatly impede cavitation of the bath liquid, thus increasing the time required for equilibration to occur.

In Fig. 1 a plot of pressure *vs.* composition with and without ultrasonic cavitation reveals that the stoichiometries of the new phases formed ($AgCl{\cdot}NH_3$, $2AgCl{\cdot}3NH_3$, $AgCl{\cdot}3NH_3$) may be determined accurately using ultrasonic cavitation of the sample. The time required for the sample to reach equilibrium without ultrasonic cavitation was from 30 min. to 20 hr., in agreement with earlier work.[1] With cavitation the time was shortened to a minimum of 10 min. and a maximum of 2.5 hr.

When ultrasonic cavitation was applied, a definite increase in equilibrium pressure was observed at a given composition, but when the cavitation was discontinued, the pressure returned to its original value.

A procedure yielding accurate equilibrium pressures was developed in which ultrasonic cavitation was applied to the sample for 1 hr., after which the sample was allowed to equilibrate without cavitation for 0.5

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