Evaporation *in vacuo* gave a yellow resin, m.p. 104–115°, dec. 450–490°, which gave a positive flame test for boron and which was readily attacked by atmospheric moisture and/or oxygen.

Anal. Found: Al, 27.91; mol. wt. (cryoscopic in benzene), 1440.

Attempted Reactions of Triethylaluminum and Tris-(dialkylamino)b-oranes. (a).—Freshly distilled tris-(diethylamino)-borane (6.81 g., 0.030 mole) in 35 ml. of dodecane appeared to be unaffected by the addition of triethylaluminum (4.3 ml., 0.032 mole). No heat was evolved and the solution remained clear. Heating the solution under a short Vigreux column gave 3.53 g. of a liquid, b.p. up to 206°. An infrared spectrum showed no triethylborane was present and only a trace of tris-(diethylamino)-borane. In addition to dodecane, the distillate exhibited unknown absorption at 7.7, 8.35, 8.7, 9.4, 9.8, and 11.85 μ. An attempt to redistil the liquid was unsuccessful due to decomposition.

b.—To 4.10 g. (0.0286 mole) of tris-(dimethylamino)-borane at −80° was added 4.0 ml. (3.36 g., 0.0295 mole) of triethyl aluminum. The cold solids were brought to room temperature to give a clear colorless solution. Heating the liquid to a pot temperature of 140° produced no distillate. A clear liquid, 2.13 g., was obtained at a pot temperature of 164–189°. The infrared spectrum of this material was identical with that of tris-(dimethylamino)-borane.

Acknowledgment.—The research reported in this document was supported by the Directorate of Materials & Processes (Materials Central), Aeronautical Systems Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, under Contract AF 33(616)-7303.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
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Mixed Ligand Complex Formation in Lead-Chloride-Bromide Solutions

BY THOMAS G. SPIRO AND DAVID N. HUME

Received November 1, 1962

The clear separation of the well defined absorption peaks of lead(II) in 1 *M* or greater alkali chloride and alkali bromide solutions suggested the applicability of the spectrophotometric technique of Newman and Hume(1) to solutions of lead(II) in chloride–bromide mixtures for the investigation of possible mixed halide complex formation in these media. The binary complexes of lead with chloride and bromide are known, however, to be weak and even in 1 *M* halide medium there is no convincing evidence for the formation of species containing more than three chloride or bromide ions in aqueous solution.(2) In the present investigation, efforts to force the complexes to saturation were unsuccessful, even in 10 *M* aqueous hydrogen halide solutions, in alcoholic hydrogen halide solutions up to 6.4 *M*, in 3 *M* calcium chloride–95% ethanol medium, and in 3.4 *M* lithium chloride or bromide in 95% ethanol, as shown by persisting dependence of extinction coefficients and wave length of peak absorption on halide concentration. Nevertheless, the spectra of lead in chloride–bromide mixtures give clear-cut evidence of the presence of a mixed chloride–bromide complex or complexes. Figure 1 shows spectra of such mixtures in a 3.4 *M* mixture of lithium chloride and bromide in 95% ethanol. The curves 2, 3, and 4 cannot be generated by any combination of curves 1 and 5, and the conclusion that mixed species are formed is unavoidable. From the formation constants given for aqueous media(2) one would expect that the principal species present in the chloride and in the bromide media should be $PbCl_3^-$ and $PbBr_3^-$, respectively. In this event, the mixed ligand species would be $PbCl_2Br^-$ and $PbClBr_2^-$. The similarity of the curves to those in the corresponding bismuth system indicates that here, too, bromide replaces chloride more readily than chloride replaces bromide, and that both mixed species probably are formed.(1) This is in harmony also with previous results on the mercury mixed halide complexes(3,4) and supports the view that, in general, all the structurally feasible mixed ligand species are formed when metal ions are present in mixtures of ligands of comparable binding power with which they form labile complexes.

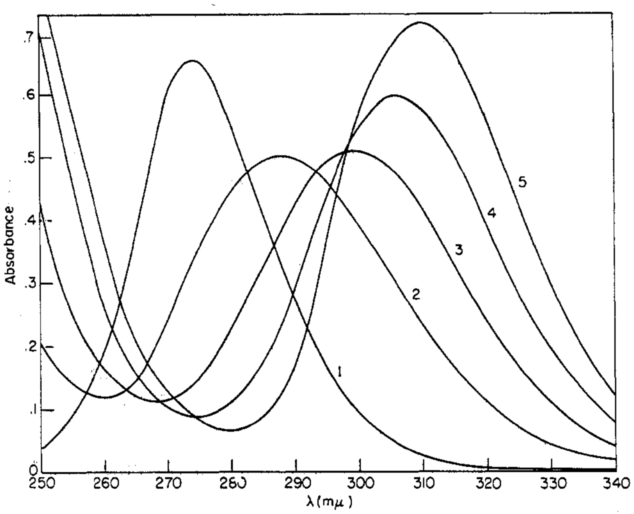

Fig. 1.—Spectra of 0.04 m*M* lead(II) perchlorate in 95% ethanol containing 3.4 *M* lithium halide with the following ratios of bromide to chloride: 1, 0.00; 2, 0.33; 3, 0.50; 4, 0.67; 5, ∞. Measurements were made on a Cary Model 11 spectrophotometer, at 25°.

Incidental to the mixed ligand investigation, a short study was made of the feasibility of determining spectrophotometrically the formation constants of the complexes of lead(II) with chloride ion. Absorption measurements with a Beckman DU spectrophotometer were made on 0.126 and 0.252 m*M* solutions of lead perchlorate over a range of 0.0 to 0.05 *M* chloride ion at a constant ionic strength of 4.00 *M*. Analysis of the data indicated three species (presumed to be Pb^{+2}, $PbCl^+$, and $PbCl_2$) to be present and contributing significantly to the absorption at the wave lengths

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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.

Acknowledgment.—This work was supported in part through funds provided by the U. S. Atomic Energy Commission under Contract AT(30-1)-905.

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

BY A. J. SARACENO AND B. P. BLOCK

Received December 3, 1962

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 $[Cr(C_6H_4NCOO)(OP(C_6H_5)_2O)_2]$.

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., 608.5*n*. 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., 513.4*n*. 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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