arguments that the nitrogen cleavage is the rate-determining step. If the nickel–acetate cleavage was the rate step then structure IV would be possible and an appreciable rate of reaction with copper would be expected. The complete absence of any detectable attack by copper confirms both the importance of the nitrogen–nickel cleavage and the need for nitrogen bonding to the attacking metal. The cyclohexane ring prevents the complete rotation of the two iminodiacetate segments so that the dinuclear reaction intermediates so important with EDTA reactions cannot form. As a result we find that even as labile a metal ion as zinc forms sluggish CyDTA complexes.

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Inorganic Coördination Polymers. V. The Use of Neutral Ligands[1]

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The attempt to make $Zn(IDP)C_6H_5PO_3$ led, instead, to $Zn_2(IDP)(C_6H_5PO_3)_2$, where IDP represents 2,2′-iminodipyridine. $Zn(py)C_6H_5PO_3$ was also prepared. It is suggested that these substances are polymers. Their thermal stabilities, however, are not high. This is related to the presence of neutral ligands and a strong bridging group.

In our search for coördination polymers with inorganic backbones we have attempted the synthesis of representatives of a number of different patterns. Our efforts to make the type $(-M(AB)X-)_x$, where AB represents a uninegative, bidentate ligand and X a uninegative catenating group, resulted in a dimer for the composition $Be(AcCHAc)(OP(C_6H_5)_2O)$,[2] and we have indications that a dimer also results from attempts to make the composition $Zn(AcCHAc)(OP(C_6H_5)_2O)$.[3] Another type of polymer that we have attempted to prepare is $(-M(AA)Y-)_x$, where AA represents a neutral bidentate ligand and Y a catenating group with two negative charges. The specific composition we sought is $Zn(IDP)(C_6H_5PO_3)$, where the bidentate ligand is 2,2′-iminodipyridine (represented by IDP) and the catenating group is the phenylphosphonate anion. It was our hope that the use of a doubly charged catenating group would lead to a single bridged, rather than double bridged (as found with diphenylphosphinate[4]), structure while at the same time yielding a strong backbone.

Experimental

The reaction of $Zn(IDP)(OAc)_2$ with $C_6H_5P(O)(OH)_2$ was carried out both in methanol and in pyridine. (1) In methanol. A solution of 3.55 g. (0.0225 mole) of $C_6H_5P(O)(OH)_2$ (Eastman Organic Chemical recrystallized from methanol) in 50 ml. of methanol was added dropwise to a solution of 7.97 g. (0.0225 mole) of $Zn(IDP)(OAc)_2$[5] in 150 ml. of methanol with rapid stirring. The thick milky suspension that formed was filtered through a medium porosity filter funnel to give 6.0 g. of a white solid after washing with methanol and drying at 95°. *Anal.* Calcd. for $Zn_2(NH(C_5H_4N)_2)(C_6H_5PO_3)_2$: N, 6.8; P, 10.1; Zn, 21.3; and for $Zn(NH(C_5H_4N)_2)C_6H_5PO_3$: N, 10.7; P, 7.9; Zn, 16.7. Found: N, 6.9; P, 9.7; Zn, 21.0. The mother liquor and washings were evaporated to dryness on a steam bath, yielding 1.9 g. of residue shown by infrared spectrum to consist mainly of 2,2′-iminodipyridine.

The compound $Zn_2(IDP)(C_6H_5PO_3)_2$ exhibits a crystalline X-ray diffraction pattern and gives the infrared absorption bands shown in Table I. It does not appear to melt in a capillary tube at temperatures up to 400°, and is not soluble in organic solvents such as ethanol, benzene, acetone, chloroform, diethyl ether, and 1,4-dioxane. When a 1.95-g. sample was extracted with pyridine in a Soxhlet extractor, the soluble fraction was found to contain 2,2′-iminodipyridine as identified by infrared. The insoluble fraction, weighing 1.85 g., was shown by infrared (absorption bands in Table I) not to contain 2,2′-iminodipyridine, but pyridine instead. *Anal.* Calcd. for $Zn(C_5H_5N)(C_6H_5PO_3)$: N, 4.7; Zn, 21.8. Found: N, 4.9; Zn, 21.8.

(2) In pyridine. A solution of 1.6 g. (0.01 mole) of $C_6H_5P(O)(OH)_2$ in 50 ml. of pyridine was added to a solution of 3.5 g. (0.01 mole) of $Zn(IDP)(OAc)_2$ in 100 ml. of pyridine with stirring at room temperature. The resulting mixture, containing a white precipitate, was diluted to 250 ml. with pyridine, refluxed for 20 hr., and filtered. After the precipitate was washed with diethyl ether and dried, there was 2.8 g. of insolubles shown by infrared and X-ray spectra to be identical with the $Zn(py)(C_6H_5PO_3)$ prepared by extraction of $Zn_2(IDP)(C_6H_5PO_3)_2$ with pyridine. The filtrate upon evaporation yielded a 1.6-g. residue found by infrared and melting point of 90° (lit.[6] 95°) to be 2,2′-iminodipyridine. The weight of 2,2′-iminodipyridine in the $Zn(IDP)(OAc)_2$ taken is 1.7 g.

A dispersion of 2.20 g. (0.01 mole) of $Zn(OAc)_2 \cdot 2H_2O$ (Baker Analyzed Reagent) and 1.70 g. (0.01 mole) of 2,2′-iminodipyridine (Reilly Tar and Chemical Corp.) in 100 ml. of methanol was warmed on a steam bath and then filtered through a medium porosity filter funnel. To the filtrate was added dropwise a solution of 1.58 g. (0.01 mole) of $C_6H_5P(O)(OH)_2$ in 50 ml. of methanol with heating (steam bath) and stirring. The gelatinous mixture was filtered after 1 hr., and the precipitate was washed back into a beaker, dispersed in methanol, and refiltered. The dried product weighed 2.69 g. *Anal.* Calcd for $Zn_2(IDP)(C_6H_5PO_3)_2$ already given. Found: N, 6.8; P, 10.0;

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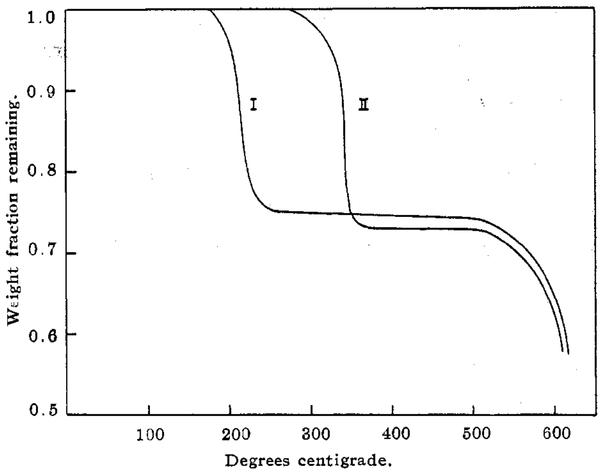

Fig. 1.—TGA of Zn(py)($C_6H_5PO_3$), curve I, and Zn_2(IDP)($C_6H_5PO_3)_2$, curve II.

TABLE I

INFRARED ABSORPTION BAND FREQUENCIES IN CM.$^{-1}$ (NUJOL MULLS)^{h}

Zn_2(IDP)($C_6H_5PO_3)_2$	Zn(py)($C_6H_5PO_3$)	$ZnC_6H_5PO_3$
3067 (w)^{a}	3058 (w)^{a}	3058 (w)^{a}
1658 (m)^{b}	1610 (m)^{g}	1439 (s)^{c}
1621 (w)^{b}	1575 (vw)^{g}	1178 (s)^{d}
1603 (m)^{b}	1493 (w)^{g}	1159 (sh)^{d}
1585 (m)^{b}	1453 (m)^{g}	1147 (s)^{d}
1536 (m)^{b}	1439 (m)^{c,g}	1096 (sh)
1481 (s)^{b}	1242 (vw)^{g}	1073 (sh)
1433 (s)^{b,c}	1222 (vw)	1064 (vs)^{e}
1339 (sh)	1142 (vs)^{d}	1025 (m)
1307 (w)	1130 (vs)^{d}	999 (m)^{c}
1279 (w)^{b}	1094 (vs)^{e}	962 (vs)
1241 (m)^{b}	1074 (s)^{e,g}	752 (m)^{f}
1232 (m)^{b}	1045 (s)^{g}	747 (m)^{f}
1196 (m)	1032 (m)	722 (m)
1168 (m)^{b}	1016 (sh)^{g}	692 (s)^{f}
1160 (m)^{b}	1011 (s)^{g}	
1134 (sh)	997 (s)^{c}	
1124 (vs)^{d}	764 (m)^{f}	
1111 (vs)^{d}	757 (m)^{f}	
1085 (vs)^{e}	753 (m)^{g}	
1073 (s)^{e}	717 (s)	
1065 (s)^{e}	698 (s)^{f}	
1028 (m)$^{b?}$		
1024 (m)$^{b?}$		
1005 (s)		
993 (s)^{c}		
910 (w)^{b}		
887 (w)		
847 (w)		
770 (m)^{b}		
753 (sh)		
748 (m)^{f}		
732 (w)		
717 (m)		
695 (m)^{f}		
672 (w)		
653 (w)^{b}		

[a] Aromatic CH stretch. [b] Associated with IDP. [c] P–phenyl. [d] P → O. [e] P–O. [f] Aromatic CH out-of-plane deformation. [g] Associated with pyridine. [h] vs, very strong; s, strong; m, moderate; w, weak; vw, very weak; sh, shoulder.

Zn, 21.6. Its infrared and X-ray spectra matched those of the preceding sample of Zn_2(IDP)($C_6H_5PO_3)_2$.

$ZnC_6H_5PO_3$.[7]—A dispersion of 2.0 g. (0.01 mole) of $Zn(OAc)_2 \cdot 2H_2O$ in 200 ml. of 95% ethanol was filtered, and a solution of 1.58 g. (0.01 mole) of $C_6H_5P(O)(OH)_2$ in 300 ml. of 95% ethanol was added to the filtrate. After the resulting mixture was heated 30 min. on the steam bath, it was filtered through a medium porosity filter funnel. The insoluble fraction was washed several times with hot 95% ethanol, air dried, and then dried at 110°; yield 1.07 g. *Anal.* Calcd. for $ZnC_6H_5PO_3$: C, 32.5; H, 2.3; P, 14.0; Zn, 29.5. Found: C, 32.2; H, 2.5; P, 13.7; Zn, 30.4. Its infrared absorption bands are listed in Table I for comparative purposes.

Thermogravimetric Analysis.—The weight-temperature curves for Zn_2(IDP)($C_6H_5PO_3)_2$ and Zn(py)($C_6H_5PO_3$) are reproduced in Fig. 1. They were determined on a modified Chevenard thermobalance in a nitrogen atmosphere as described elsewhere.[8] In a separate run a sample of Zn_2(IDP)($C_6H_5PO_3)_2$ was taken to constant weight at 350°. *Anal.* Calcd. for $ZnC_6H_5PO_3$ already given. Found: C, 30.6; H, 2.8; P, 12.6; Zn, 27.4. The infrared and X-ray spectra of this residue corresponded to those for $ZnC_6H_5PO_3$.

Discussion

The reaction intended to yield Zn(IDP)($C_6H_5PO_3$) gave instead Zn_2(IDP)($C_6H_5PO_3)_2$ even though there was sufficient 2,2′-iminodipyridine present to give the desired product and the reaction conditions were mild. In the presence of pyridine the product was the presumably related Zn(py)($C_6H_5PO_3$). It seems quite unlikely that the three oxygen atoms from one phenylphosphonate anion will satisfy three of the four coördinate valences of one zinc, or even two in view of our results with the diphenylphosphinate anion.[4] Consequently, it is likely that these compositions are polymers. Our present information is not sufficient to permit us to assign detailed structures to these compounds, so we are not able to say whether the structures are one-, two-, or three-dimensional polymers, any one of which is possible. It is tempting to conclude that these substances are two- or three-dimensional polymers because they are not soluble without reaction in any solvent tried, but we do not believe that such a conclusion is justified on solubility evidence alone.

The thermogravimetric study indicates quite straightforward decompositions. The observed weight losses to the first plateaus of 25 and 29% for Zn(py)$C_6H_5PO_3$ and Zn_2(IDP)($C_6H_5PO_3)_2$, respectively, are in good agreement with the calculated losses of 26 and 28% for conversion to $ZnC_6H_5PO_3$ in each case. The residue from a sample of Zn_2(IDP)($C_6H_5PO_3)_2$ heated at 350° was found to be $ZnC_6H_5PO_3$ containing some water (apparently adsorbed during storage). Although all the absolute percentages except H are low, the Zn:P:C ratio found in the residue is 1:1.0:6.1, compared to an expected ratio of 1:1:6. The infrared and X-ray spectra indicate the presence of $ZnC_6H_5PO_3$ when compared with the spectra of the independently prepared sample.

It is interesting to attempt to fit Zn_2(IDP)($C_6H_5PO_3)_2$ into the relative stability series we recently reported for other 2,2′-iminodipyridine coördination compounds of zinc.[9] The isolated compound is, of course,

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not strictly analogous to the $Zn(IDP)X_2$ type of compound we studied earlier. The failure to form $Zn(IDP)(C_6H_5PO_3)$ at room temperature would seem to indicate that phenylphosphonate is a stronger bridging group than cyanide, whereas the decomposition temperature of $Zn_2(IDP)(C_6H_5PO_3)_2$ would indicate that both cyanide and acetate are stronger bridging groups than phenylphosphonate. The apparent discrepancy in the strength of the bridging by phenylphosphonate groups can be resolved by the consideration that there are two kinds of bridges involved which have different strengths, one in which each oxygen is bonded to only one zinc atom and a second in which some oxygen atoms are shared by two zinc atoms. In the compounds reported in our earlier paper this is not the case, there being only one kind of bridge formed.

Even though both $Zn_2(IDP)(C_6H_5PO_3)_2$ and $Zn(py)(C_6H_5PO_3)$ are probably coördination polymers with inorganic backbones, their decomposition temperatures (275 and 185°, respectively) are not high enough to make them of practical interest. It appears that neutral coördinating groups are not bonded strongly enough to zinc for polymers containing such ligands to have substantial thermal stability.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
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Covalency of Metal–Ligand Bonds in Potassium Hexachloroiridate(IV) and Hexachloroösmate(IV) Studied by the Pure Quadrupole Resonance of Chlorine

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The pure quadrupole resonance of chlorine in paramagnetic complexes, K_2IrCl_6 and K_2OsCl_6, was observed at liquid nitrogen, Dry Ice, and room temperatures. Each of these complexes shows a single resonance line at all temperatures studied, indicating that all chlorine atoms in each complex are crystallographically equivalent, in agreement with the results of X-ray crystal analysis. With the greater π-bond character of metal–ligand bonds due to vacancies in the dϵ orbitals of iridium and osmium ions, the σ-bond character decreases in the order of hexachloroplatinate(IV), hexachloroiridate(IV), and hexachloroösmate(IV), whereas the ionic character remains almost constant.

Introduction

We already have observed the pure quadrupole resonance of halogens in the hexahalo complexes of platinum, palladium, tellurium, selenium, and tin as well as the tetrabromo complexes of platinum and palladium and discussed the nature of metal–halogen bonds in these complexes.[2–6] Unlike these diamagnetic complexes having the dϵ orbitals of the central atom completely filled with electrons, the hexahalo complexes of iridium and osmium are paramagnetic[7–9] owing to the presence of one and two holes, respectively, in the dϵ orbitals. Accordingly, it is conceivable that partial π-bonds are formed between the dπ orbitals of the central atom and the pπ orbitals of ligand atoms. In fact, Griffiths, Owen, and others[10–13] have observed the electron spin resonance of some hexachloroiridates and concluded from the measurements of hyperfine structure and g-values that the π-bond character is involved in the metal–ligand bonds.

The present investigation of potassium hexachloroiridate(IV) and hexachloroösmate(IV) has been undertaken in order to examine the nature of metal–ligand bonds having a partial π-bond character.

Experimental

Apparatus.—The signals of pure quadrupole resonance were displayed on an oscilloscope of a super-regenerative spectrometer already described.[2]

Materials.—A commercial preparation of potassium hexachloroiridate(IV) was recrystallized from a hot aqueous solution to which a few drops of nitric acid were added in advance.[14] About 9 g. of the resulting black crystals was used. Commercial potassium hexachloroösmate(IV) was recrystallized from hot dilute hydrochloric acid solution to obtain dark red crystal grains (about 10 g.).

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