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Anhydrous Cobalt and Nickel Hypophosphites

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Anhydrous $Co(H_2PO_2)_2$ and $Ni(H_2PO_2)_2$ as well as $[Ni(py)_2(H_2PO_2)_2]$ were prepared. Infrared and electronic spectra and magnetic susceptibility measurements indicate that all are high-spin octahedral complexes. Anion coordination is proposed as bridging and chelating bidentate ligands.

Introduction

Hypophosphorous acid, H_3PO_2, is a strong monobasic acid which reacts readily with most metal oxides, hydroxides, and carbonates to form hypophosphite salts. In cases where the metal ion can be readily reduced, for example copper(II), a redox reaction occurs instead of salt formation [1].

Lovejoy and Wagner [2] have obtained the infrared spectrum of hypophosphorous acid at liquid air temperature. The spectrum was assigned on the basis of C_1 symmetry, and a structure was postulated in which the individual acid molecules are held together in a crystalline aggregate by strong hydrogen bonds.

The structure of the hypophosphite anion has been shown by X-ray diffraction of the ammonium salt to be a distorted tetrahedron with oxygen atoms at two of the corners, hydrogen atoms at the other two corners, and the phosphorus atom at the tetrahedral center [3]. Raman and infrared studies [2, 4, 5] of hypophosphite salts have indicated C_{2v} symmetry for the anion, except for the calcium salt where the H_2PO_2 group displays C_1 symmetry.

Mayants and Matrosov [6] studied the infrared spectra of many metal hypophosphites in order to determine the influence of the metal on polymeric properties of the anion. It was concluded that salts of the alkali and alkaline earth metals are ionic and the hypophosphite ion may be represented by a model with equalized PO bond lengths. For salts of nonionic structure (*e.g.*, bivalent cobalt, lead, zinc, and manganese hypophosphites), a chain model with equalized PO bond distances was proposed. In this model the metal ion is bonded to one oxygen atom of each anion; a coordination number of four was assumed.

Brun and Dumail [1] have reported the preparation of anhydrous iron(II), nickel(II), cobalt(II), and zinc(II) hypophosphites. The cobalt(II) and zinc(II) salts were crystallized from a warm (30 °C) aqueous solution; the hexahydrates crystallized around 20 °C. $Fe(H_2PO_2)_2$ and $Ni(H_2PO_2)_2$ were precipitated from acetone and the nickel(II) salt was dried over P_4O_{10}. Upon stirring the anhydrous hypophosphites in pyridine [1], the iron(II) and nickel(II) compounds underwent self-oxidation–reduction. The cobalt(II) and zinc(II) hypophosphites, however, combined with pyridine (py) to give $Co(H_2PO_2)_2py_2$ and $Zn(H_2PO_2)_2py_2$. These compounds slowly lose pyridine at room temperature. Brun and Dumail concluded from infrared data that the hypophosphite anion was coordinated to the metal in the pyridine compounds and in the anhydrous salts, but not in the hexahydrates. They were unable to determine whether the hypophosphite ion was monodentate or bidentate.

A literature search has revealed a number of infrared and Raman spectral studies of metal hypophosphites; [1–10]; however, other methods of characterization have received little attention. Therefore, it seemed desirable to prepare and study several anhydrous hypophosphite compounds. This paper describes the synthesis and characterization of cobalt(II) and nickel(II) hypophosphites along with their bispyridine complexes.

Experimental

Reagents

Fisher Scientific Company was the source of 50 per cent aqueous solution of hypophosphorous acid. Because the commercial grade acid usually contains a small amount of phosphorous acid [11], iodometric titrations [12] were carried out on the acid as received. The phosphite ion concentration was found to be no greater than five mole per cent and could be ignored for this work.

Anhydrous hypophosphorous acid was prepared by refluxing the aqueous acid solution with an excess of benzene for 30 minutes. The benzene–water azeotrope was removed by distillation. The temperature of the liquid in the pot could not be allowed to

TABLE I. Analytical Data and Decomposition Temperatures.

Compound	Preparation Method	Decomposition Temperature °C	Elemental Analysis	
			%H Calcd	%H Found
$Co(H_2PO_2)_2$	Dehydration	220	2.13	2.37
$Co(H_2PO_2)_2$	Benzoate-acid	220	2.13	2.27
$Ni(H_2PO_2)_2$	Dehydration	225	2.14	2.52
$Ni(H_2PO_2)_2$	Benzoate-acid	205	2.14	2.83
$Ni(H_2PO_2)_2H_2O$ (Calculated)	–	–	2.93	–

exceed 100 °C or hypophosphorous acid would undergo decompositionto phosphine and phosphorous acid.

Metal benzoates were prepared by adding hydrated metal chloride (Baker) to an aqueous solution of sodium benzoate (Merck). The precipitate was filtered, washed with distilled water, and dried at 78 °C for three days.

Cobalt(II) and nickel(II) carbonates were used as received from J. T. Baker Chemical Company. Methanol, anhydrous ethyl ether, benzene and pyridine were supplied by Fisher Scientific Company. Practical grade 2,2-dimethoxypropane was obtained from Eastman Organic Chemicals.

Synthesis

Anhydrous cobalt(II) and nickel(II) hypophosphites

Two synthetic routes were employed to prepare nearly anhydrous cobalt(II) and nickel(II) hypophosphites. The first procedure involved formation of the hydrated salt and its subsequent dehydration by stirring with 2,2-dimethoxypropane.

A dilute solution of hypophosphorous acid (9 X 10^{-2} mol, 10 ml of the 50 per cent acid solution diluted to 100 ml volume) was added slowly and with stirring to an aqueous slurry of the metal carbonate (6 X 10^{-2} mol, approximately 7 grams). To prevent reduction of cobalt(II) to the metal, it was necessary that carbonate be in excess and that the system be cooled in an ice as the reaction proceeded. These precautions were not required for nickel(II).

Stirring was continued for two hours to ensure complete reaction. Excess carbonate was removed by filtration and the solution was partially evaporated at room temperature to induce crystallization. The hydrated salt was oven dried at 78 °C for several days. Some water of hydration appeared to be lost during the drying as evidenced by color changes: pink $Co(H_2PO_2)_2 \cdot 6H_2O$ became purple when heated, whereas green $Ni(H_2PO_2)_2 \cdot 6H_2O$ turned chartreuse on heating.

The partially dehydrated metal(II) hypophosphites were insoluble in methanol, ethanol, isopropyl alcohol, acetonitrile, nitromethane, dichloromethane, and tetrahydrofuran; they dissolved readily in water.

Complete dehydration [13] was attempted by stirring the metal hypophosphite in methanol containing a small amount of 2,2-dimethoxypropane for four hours. The slurry was filtered and the recovered solid stirred with fresh methanol and dimethoxypro-plane for another hour, after which it was filtered and washed with anhydrous ether in a nitrogen atmosphere in the dry box. The solid was dried at 100 °C under reduced pressure in an Abderhalden drying pistol for approximately 12 hours. $Co(H_2PO_2)_2$ remained purple as it underwent nearly complete dehydration; $Ni(H_2PO_2)_2$ became a brilliant yellow as it lost water of hydration.

The second method for preparing nearly anhydrous cobalt(II) and nickel(II) hypophosphites was based on that used by Alleyne *et al.* for the synthesis of bisfluorosulfates [14]. To a saturated solution of metal benzoate (3 X 10^{-2} mol, approximately 9 grams) in methanol and dimethoxypropane, a large excess of anhydrous acid was added. Purple cobalt(II) hypophosphite precipitated immediately; addition of almost one pint of ether was required to force yellow $Ni(H_2PO_2)_2$ out of solution. The product was filtered and washed with ether in the dry box and then dried for four hours at 100 °C at reduced pressure.

Table I presents analytical data and decomposition temperatures for the hypophosphites.

The authors were unable to repeat the results of Brun and Dumail [1] to obtain anhydrous cobalt(II) and nickel(II) hypophosphites. Considerable absorption due to OH stretching and bending was indicated in the infrared spectra of the compounds prepared by their procedures.

Dihypophosphitobispyridinenickel(II), $[Ni(py)_2(H_2PO_2)_2]$

Hydrated nickel hypophosphite (7 X 10^{-2} mol, approximately 2 grams) was stirred in 10 ml methanol plus 10 ml dimethoxypropane for several hours. Pyridine (py) was added dropwise until all the hydrated $Ni(H_2PO_2)_2$ dissolved producing a blue solution. Upon addition of ether, an oil formed;

TABLE II. Hypophosphite Vibrations in Anhydrous Compounds (cm^{-1})^a.

$Co(H_2PO_2)_2$	$Ni(H_2PO_2)_2$	$[Ni(py)_2(H_2PO_2)_2]$	Assignment
2430s	2420sh	–	PH_2 symmetric stretch
2370s	2390–2340s	2380–2275^{b}m	PH_2 assymmetric stretch
1160s	1190–1140s	1175–1165s	PO_2 assymmetric stretch
1145sh			
1120s		1130sh	PH_2 scissor
1085s	1080s	1090m	PH_2 wag
1070m	1060sh	1062m	PO_2 symmetric stretch
1055s	1045–1015s	1030–1015m	
1005w			
825s	820^{b}s	808^{b}s	PH_2 rock
805s			
510s	500s	513s	PO_2 scissor

^{a}s, strong; m, medium; w, weak; sh, shoulder. ^{b}Band broader than a single absorption but could not be resolved.

trituration of the oil with ether produced a green solid. This product was dried at 65 °C under reduced pressure for 12 hours. It decomposes at 130 °C. *Anal.* Calcd for $C_{10}H_{14}N_2O_4P_2Ni$: C, 34.62; H, 4.07; N, 8.08. Found: C, 34.43; H, 4.13; N, 7.96%.

Attempted Preparation of $[Co(py)_2(H_2PO_2)_2]$

The same procedure as for the analogous Ni(II) compounds was followed for this synthesis. Elemental analysis indicated that a badly defined mixture of pyridine complexes formed. *Anal.* Calcd for $C_{10}H_{14}N_2O_4P_2Co$: C, 34.60; H, 4.07; N, 8.07. Found: C, 32.82, H, 4.12, N. 7.69%.

Physical Measurements

Analyses of the compounds were made under anhydrous conditions by Galbraith Laboratories, Knoxville, Tennessee.

Infrared spectra were obtained for the solid samples as Nujol mulls spread between sodium chloride plates. Perkin–Elmer model 257 and Beckman IR-5A recording spectrophotometers were used to scan the 4000–625 cm^{-1} region. The spectra were calibrated using polystyrene film. Far-infrared spectra (700–150 cm^{-1} region) were obtained as Nujol mulls sandwiched between polyethylene plates using a Digilab FTS-IR20 spectrometer.

Spectra of the complexes in the visible and near-infrared region were obtained using a Cary 171 recording spectrophotometer manufactured by the Applied Physics Corporation. The spectra of solid samples were obtained as Nujol mulls spread on a piece of Kimwipe. The mulls were prepared in a dry nitrogen atmosphere. Kimwipe saturated with Nujol was placed in the reference beam to equalize light scattering.

Magnetic susceptibilities of the compounds were measured using a Gouy balance, consisting of an electromagnet, power supply, and current regulator (Alpha Scientific Laboratories) and a semi-micro balance (Mettler). $HgCo(SCN)_4$ was used as a calibrant. All measurements were made at 23 ± 2 °C.

Results and Discussion

Due to the hygroscopic character of these compounds, it was necessary that they be stored in a dry atmosphere.

The results of magnetic susceptibility measurements are typical of cobalt(II) and nickel(II) compounds in high-spin octahedral stereochemistries. Values of 5.03, 3.36, and 3.07 BM were obtained for $Co(H_2PO_2)_2$, $Ni(H_2PO_2)_2$, and $[Ni(py)_2(H_2PO_2)_2]$, respectively.

The infrared spectral features associated with the hypophosphite group for the compounds prepared in this study are listed in Table II.

The hypophosphite ion belongs to the C_{2v} point group. According to group theoretical methods, $H_2PO_2^-$ should have nine fundamental vibrations, eight of which would be infrared active [5]. The four totally symmetric (A_1) vibrations could be described as a PH_2 symmetric stretch, a PH_2 scissor, a PO_2 symmetric stretch, and a PO_2 scissor. The asymmetric vibrations include PH_2 and PO_2 asymmetric stretches, a PH_2 wag, and a PH_2 rock. The PH_2 twisting motion is infrared inactive. Upon coordination through an oxygen atom the symmetry is lowered to C_1. No degeneracy exists for this point group and all twelve fundamental modes of vibration are infrared and Raman active. The same PH_2 vibra-

TABLE III. Visible and Near-Infrared Spectral Data. Absorption Maxima (cm^{-1}) and Assignments[a,b].

Compound	$^3A_{2g} \to {}^3T_{2g}$	$\to {}^3T_{1g}\,(^3F)$	$\to {}^1E_g\,(^1D)$	$\to {}^1T_{2g}\,(^1D)_1\ {}^1A_{1g}\,(^1G)$	$\to {}^3T_{1g}\,(^3P)$
$Ni(H_2PO)_{2\,2}$	7690m	12,800s (12,900)	14,600sh		24,100vs
$[Ni(py)_2(H_2PO_2)_2]$	8620s	13,500s (14,100)	14,700m	19,800w	24,700vs

Compound	$^4T_{1g} \to {}^4T_{2g}$			$\to {}^4T_{1g}\,(^4P)$	
$Co(H_2PO_2)_2$	7870m	17,200s	19500sh	20,200vs	21,100sh

[a]Calculated values in parentheses. [b]vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

tions (plus the PH_2 twist) are expected on monocoordination as for the anion. The PH_2 twist should give rise to a band near 900 cm^{-1} for the acid [1] but was not detected; frequencies of the PH_2 scissor and PH_2 wag vibrations were lowered nearly forty wavenumbers. The phosphorus-oxygen modes are somewhat different from those of the salts and consist of a P=O stretch, a P–O* stretch, and a POO* scissor deformation.

If bidentate coordination of the hypophosphite group occurred as either a chelating or bridging ligand, it would possess local C_{2v} symmetry. Eight infrared active vibrations would be expected and the P–O bond order would approximate a value of one. Similar to the F_2PO_2 group [15], the PH stretching modes should be found at higher frequency for bidentate hypophosphite coordination than for monodentate groups. The asymmetric PO stretching mode would be lowered considerably whereas the symmetric mode would shift little. The net result would be a lowering of the average PO stretch. This lowering is caused to some extent by charge withdrawal from the phosphorus–oxygen into the metal–oxygen bond region. Back donation from the oxygen lone pairs to phosphorus can partially compensate for the charge withdrawal and can account for the observed increase in the PH stretching frequencies [15].

All hydrated hypophosphite salts absorb in the 3300 and 1640 cm^{-1} regions [8], which presumably correspond to O–H stretching and bending, respectively. Frequencies higher than 3450 cm^{-1} are absent in most salts indicating that no completely free O–H stretching occurs and that hydrogen bonding is probable. Several sharp peaks between 3450 and 2860 cm^{-1} are usually observed due to more than one type of hydrogen bonding.

Spectral comparison of anhydrous and hydrated hypophosphite salts [8] reveals several differencies below 1500 cm^{-1}. When hydrated, a general shift of peaks to lower frequencies occurs; the PO stretching region is especially sensitive to hydration. The frequency of the PH_2 rock has been observed to split into a doublet or triplet in the anhydrous salt [8].

Neither $Co(H_2PO_2)_2$ nor $Ni(H_2PO_2)_2$ absorbs above 2550 cm^{-1}. Nickel hypophosphite absorbs weakly at 1650 cm^{-1} possible due to O–H bending; there is no corresponding absorption for the cobalt compound. The PH_2 symmetric and asymmetric stretching vibrations are shifted to higher frequencies than for the anion as would be expected on coordination. The large number of bands in the 1200 to 1000 cm^{-1} region suggests that more than one type of H_2PO_2 group is present. Since the anion vibrations are nondegenerate, the bands cannot be the result of symmetry reduction by covalent bond formation.

The PH_2 rock (at 808 cm^{-1} in the anion) splits into two components in the $Co(H_2PO_2)_2$ spectrum. Since this vibration is not degenerate, the splitting presumably indicates that more than one type of H_2PO_2 group is present. A band considerably wider than a normal single absorption is observed in this region for the nickel(II) compound; it is expected that two absorptions are present but were not resolved.

The PO_2 scissor motion in the anion occurs at 476 cm^{-1}. Because this vibration has been shifted approximately 30 cm^{-1} to higher frequency in $Co(H_2PO_2)_2$ and in $Ni(H_2PO_2)_2$, coordination to the metal atom is indicated.

The observed frequencies in the 1200 to 1000 cm^{-1} region suggest that more than one type of hypophosphite group is present in $Co(H_2PO_2)$ and in $Ni(H_2PO_2)_2$. Infrared and far-infrared spectra have established coordination to the metal atom. If monodentate groups are present, certain spectral features should be found: (i) a P=O stretch at higher frequency than the asymmetric PO_2 stretch in the anion, (ii) a P–O* (O* representing oxygen covalently bound to the metal) stretch at lower frequency than the PO_2 symmetric stretch of the ion because of reduced PO bond order, and (iii) a significantly greater difference between the PO stretching vibrations than for the anion. Those features were not observed in the

TABLE IV. Electronic Spectral Parameters.

Compound	Dq	B^1	B
$Co(H_2PO_2)_2$	902	893	0.92
$Ni(H_2PO_2)_2$	769	930	0.88
$[Ni(py)_2(H_2PO_2)_2]$	862[a]	825	0.78

[a] Rule of average environment.

spectra of $Co(H_2PO_2)_2$ and $Ni(H_2PO_2)_2$. In conjunction with electronic spectral data and magnetic susceptibility values which indicate hexacoordination about the metal, it seems reasonable to postulate the presence of both chelating and bridging bidentate hypophosphite ligands. A clear distinction between bidentate bridging and chelating ligands cannot be made with vibrational spectra; therefore, definite assignments for PO stretching vibrations in $Co(H_2PO_2)_2$ and in $Ni(H_2PO_2)_2$ are not possible.

The hypophosphite vibrations for $[Ni(py)_2(H_2PO_2)_2]$ are listed in Table II. It is difficult to ascertain the extent of coordination of the hypophosphite group to the metal atom in this compound. A single broad absorption centered at 2300 cm^{-1} is detected in the PH stretching region. In conjunction with hexacoordination about the metal atom, the position and number of vibrations between 1200 to 1000 cm^{-1} suggest the presence of two types of bidentate hypophosphite groups. The PH_2 rock was not split; however, the band is too broad for a single absorption. The PO_2 scissoring motion is found at considerably higher frequency than in the anion, presumably due to coordination to the metal atom.

It is unlikely that intermolecular hydrogen bonding is an explanation for the broad bands in $Ni(H_2PO_2)_2$ and in $[Ni(py)_2(H_2PO_2)_2]$. David and Hallam [16] studied the hydrogen bonding ability of the PH group in a series of phosphonate esters. The PH group was found to be barely capable of forming hydrogen bonds even with the most powerful proton-accepting solvents. Intermolecular association was absent in the pure compounds.

The metal–oxygen vibration for the anhydrous hypophosphites is found around 300 cm^{-1}. This vibration in $[Ni(py)_2(H_2PO_2)_2]$ was assigned as that band at 265 cm^{-1}.

The pyridine absorption bands for $[Ni(py)_2(H_2PO_2)_2]$ are typical of coordination compounds containing this nitrogen base [17–19].

The visible and near-infrared spectral data for these compounds are listed in Tables III and IV. Absorption maxima and spectral parameters indicate that octahedral symmetry is closely approximated in the anhydrous compounds. The values of the ligand field parameters places the hypophosphite anion near the center of the spectrochemical series between H_2O and Cl^-. The spectrum of $[Ni(py)_2(H_2PO_2)_2]$ closely resembles a typical octahedral arrangement of ligands about the Nickel(II) ion.

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