It is interesting to note that even though the transition state associated with the postulated mechanism has the composition $\{Cr(CN)Hg^{4+}\}^{\ddagger}$, the rate was found to be independent of $[Hg^{2+}]$. This situation arises because the laboratory rate expression is based on variations for formal concentrations rather than concentrations of predominant species. In the present situation $C_{CrCN} \cong [Cr(CN)Hg^{4+}]$ so that the rate expression, eq 10, when written in terms of the predominant species, does correctly reflect the composition of the transition state.

This system can be contrasted to the Hg^{2+} "catalysis" of the aquation of $CrCl^{2+}$,[21] where the rate varied as the first power of $[Hg^{2+}]$. In that case no evidence was obtained for a cation association complex.

Structure of the Cation–Cation Complex.—The association of two cations as in eq 2 is a very unusual type of reaction, especially an association as stable as the one encountered here. Chromium(III) and neptunyl(VI) ions are known to associate in a rather weak but kinetically stable complex.[37] Mercury(II) is known to form rather stable complexes with $Co(NH_3)_5CN^{2+}$,[38] and the ion $CrNCSHg^{4+}$ is formed in the reaction of $(H_2O)_5CrNCS^{2+}$ with Hg^{2+}.[39] Other M–thiocyanate and M–azide association reactions with Hg^{2+} have been reported.[40,41]

The reaction of $CrNCS^{2+}$ and Hg^{2+} (eq 20) stands in contrast to that occurring between $CrSCN^{2+}$ and Hg^{2+} (eq 21). Since mercury(II), a soft acid, will coordinate to the softer base site of an ambidentate ligand, the high stability of the cyano dinuclear species is surprising. A species of the structure $(H_2O)_5Cr\text{–}CN\text{–}Hg_{aq}^{4+}$ would seem to stand little chance of being a stable one, as nitrogen donors generally do not provide especially stable complexes with mercury(II).

$$(H_2O)_5CrNCS^{2+} + Hg_{aq}^{2+} = (H_2O)_5Cr\text{–}NCS\text{–}Hg_{aq}^{4+} \quad (20)$$

$$(H_2O)_5CrSCN^{2+} + Hg_{aq}^{2+} = Cr(H_2O)_6^{3+} + Hg\text{–}SCN^{+} \quad (21)$$

We propose that a structural change accompanies formation of the dinuclear complex, as represented by

$$(H_2O)_5CrCN^{2+} + Hg_{aq}^{2+} = (H_2O)_5Cr\text{–}NC\text{–}Hg^{4+} \quad (2')$$

The proposed internal isomerization of cyanide finds support in the spectral shifts accompanying this reaction [$\lambda_{max}(CrCN^{2+})$ 5250 Å, $\lambda_{max}(Cr\text{–}NC\text{–}Hg^{4+})$ 5650 Å], considering that the nitrogen end of cyanide has a smaller ligand field strength than the carbon end.[42] The spectra of the "supercomplexes" (between $(NH_3)_5Co\text{–}CN^{2+}$ and Hg^{2+}) found by Siebert[38] suggest that a similar rearrangement to form $(NH_3)_5Co\text{–}NC\text{–}Hg^{4+}$ has taken place [$\lambda_{max}(Co(NH_3)_5CN^{2+})$ 4400 Å, λ_{max} (Hg^{2+} adduct) 4480 Å]. Support for the postulated internal isomerization comes from our observation[43] that the same species, $Cr\text{–}NC\text{–}Hg^{4+}$, arises from the reaction of mercury(II) with the isocyano complex, $(H_2O)_5CrNC^{2+}$, the latter prepared from the reaction of $(NH_3)_5CoCN^{2+}$ with chromium(II).[3]

A precedent for the proposed linkage isomerization accompanying dinuclear complex formation in eq 2′ can be cited. The main products of the reaction of $(H_2O)Cr\text{–}SCN^{2+}$ and Hg^{2+} were Cr^{3+} and $HgSCN^{4+}$ (eq 21), but an appreciable yield of $(H_2O)_5Cr\text{–}NCS\text{–}Hg^{4+}$ was also formed,[44] contrary to the original report.[39] Further work to verify the proposed structure of $Cr\text{–}NC\text{–}Hg^{4+}$ is in progress.

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High-Pressure Synthesis of Pyrite-Type Nickel Diphosphide and Nickel Diarsenide

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Received November 14, 1967

Synthesis of diphosphide and diarsenide phases of Fe, Co, Ni, Cu, and Pd has been investigated in a high-pressure tetrahedral anvil press at 65 kbars (1100–1400°). Pyrite-type NiP_2 and $NiAs_2$ compounds with low, nearly temperature-independent resistivity and weak Pauli paramagnetism were formed. The phosphides and arsenides of Fe, Co, Cu, and Pd occurred as the known low-pressure forms. The occurrence of the pyrite structure in the Ni dipnictides and its absence in the others may be explained in terms of stability derived from the electronic configuration of the cation and the high density of the structure.

Introduction

Pyrite-type compounds may be prepared by high-pressure techniques.[1,2] This discovery has led to a study of the diphosphides and diarsenides of the transition metals Fe, Co, Ni, Cu, and Pd at high pressure for the purpose of forming new pyrite-type compounds. Except for Co, all of these metals are known to form diphosphides, and their crystal struc-

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tures differ from that of pyrite. This also pertains for the diarsenides of Fe, Co, and Ni.

Iron diphosphide and diarsenide exhibit the orthorhombic marcasite-type structure[3,4] which is related to the pyrite type. Cobalt forms the phosphides CoP[5] and CoP_3,[6] the former having the orthorhombic MnP-type structure, and the latter the cubic skutterrudite-type structure. In contrast, a diarsenide of cobalt has the monoclinic arsenopyrite-type structure.[7] Nickel and palladium diphosphides have an isotypic monoclinic structure,[8] whereas $NiAs_2$ exhibits two crystalline forms,[9] a high-temperature marcasite modification (rammelsbergite) and a low-temperature orthorhombic modification (pararammelsbergite) whose crystal structure has not yet been completely investigated. The normal structure of $PdAs_2$ is the pyrite type.[10] Copper diphosphide has a unique monoclinic structure.[11]

Our studies resulted in the formation of pyrite-type NiP_2 and $NiAs_2$ only at high pressure. The occurrence of this structure in the Ni dipnictides and its absence in the others may be explained in terms of stability derived from the electronic configuration of the cation and the high density of the pyrite structure.

Experimental Section

Reactions were run in a tetrahedral anvil press of National Bureau of Standards design[12] using a boron nitride crucible surrounded by a graphite sleeve resistance heater inserted in a pyrophyllite tetrahedron. Temperature was measured with a Pt–Rh thermocouple, uncorrected for pressure effects, which was adjacent to the graphite heater. The operating procedure has been described elsewhere.[1] Elements from Electronics Space Products, Inc., of stated purity of "four nines plus" were used as reactants. They were ground together in their proper ratios and pelleted prior to reaction. Two series of reactions were used to prepare phosphides: (1) 65 kbars, heat at 1200° for 2 hr, cool for 2 hr to 1100°, quench; (2) 65 kbars, heat at 1400° for 1 hr, cool for 2 hr to 1200°, quench. The arsenides were prepared in the same manner as the first series but were cooled for 4 hr to 400° prior to quenching. Because of a temperature gradient from the ends of the crucible to the center during heating, excess of the lower melting phosphorus or arsenic was used in a number of runs in an effort to enhance single-crystal growth at the ends.

The products of all reactions were characterized by Debye–Scherrer X-ray powder diffraction measurements at 25°. Films were read on a David Mann film reader, Model No. 1222. Unit cell dimensions were refined by a least-squares method with the Nelson–Riley function as one parameter. Density measurements, to determine stoichiometry, were made on 10–100 mg of solid sample pieces by a liquid displacement technique. This involved four weighings on a microbalance of a platinum-gauze basket, empty and containing sample, in both air and in a liquid of accurately determined density (usually bromoform). Precision of these measurements is in the order of 1 part/1000. Electrical resistivities were measured on single crystals by a four-probe technique described previously.[13]

Results

A. Nickel Diphosphide.—Nickel diphosphide was prepared under the conditions stated above starting with Ni + 2.5P in the first case and Ni + 3P in the second. A third confirmatory reaction was run with Ni + 2.5P at 65 kbars heating at 1200° for 2 hr, cooling for 4 hr to 900°, and quenching. In all cases, black, lustrous, rod-shaped crystals grew at the ends of the boron nitride crucibles with the excess phosphorus remaining in the center. Debye–Scherrer diffraction patterns of the crystals showed the pyrite-type structure. The patterns of the above three nickel diphosphides were indexed and the unit cells refined by least squares to: (1) $a = 5.4706 \pm 0.0002$ Å (Table I), (2) $a = 5.4831 \pm 0.0002$ Å, and (3) $a = 5.4788 \pm 0.0002$ Å. The variation in cell dimension suggests a range of composition. Density measurements on the first and third samples gave the respective values (1) $d = 4.70$ g/cm^3 and (3) $d = 4.74$ g/cm^3. Theoretical densities calculated from the above cell dimensions, assuming stoichiometric NiP_2, are 3–4% greater than these values. Since excess phosphorus was present, it may be assumed that the crystals are nickel deficient. This allows the formulas $Ni_{0.92}P_2$ (*Anal.* Calcd: P, 53.43. Found: P, 53.38) and $Ni_{0.94}P_2$, respectively, to be calculated.

The pyrite-type structure was also obtained by the reaction of Ni + 2.2P at 15 kbars, 1100°, cooling to 900°, and quenching, but it failed to form at 3 kbars, 1000°, cooling to 700°, and quenching.

Single crystals of the sample with cell size $a = 5.4706$ Å were used in characterization studies. The structure was verified by a least-squares refinement of the X-ray intensities obtained from the powder diffraction pattern. The data were recorded using a Norelco diffractometer at a scanning rate of 0.25°/min with the chart scaled to 1 in./deg. Intensities were measured by weighing cutout tracings of the diffractometer pattern. Twenty-five pieces of data were collected and converted to F^2 observed by correcting for Lorentz and polarization effects. Space group Pa3, the positions of the pyrite-type structure, and atomic scattering factors were used in the calculation. The occupancy factors of Ni and P were held at 1 and 2, respectively. Unit weights were used and the quantity $R = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$ was reduced to 14.1% (Table II). The single-position parameter was refined to 0.3881 ± 0.0015 and isotropic temperature factors to 0.3 for Ni and 0.3 for P. Bond distances and angles were calculated (Table III).

The nickel atoms are in a trigonally distorted octahedron surrounded by P atoms. The P atoms are in the form of a dianion that has the formal valence P_2^{4-}. Each P is surrounded by three cations and the other half of the dianion at the corners of a trigonally

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TABLE I

DEBYE-SCHERRER X-RAY POWDER DIFFRACTION PATTERNS

	NiP_2, $a = 5.4706$ Å		$NiAs_2$, $a = 5.7634$ Å	
	Cu Kα (Ni), λ 1.54178 Å		Co Kα (Fe), λ 1.79021 Å	
	* Cu Kα_1 (Ni), λ_1 1.54051 Å		* Co Kα_1 (Fe), λ_1 1.78892 Å	
HKL	*d*	I/I_0	*d*	I/I_0
111	3.1583	80	...	...
200	2.7339	100	2.8790	65
210	2.4465	90	2.5760	100
211	2.2328	90	2.3519	95
220	1.9342	75	2.0362	40
311	1.6492	100	1.7371	85
222	1.5784	35	1.6625	10
320	1.5171	35	1.5979	45
321	1.4621	45	1.5395	60
400	...	...	1.4401	15
331	1.2556	15	...	...
420	1.2236	20	1.2891	10
421	1.1940	20	1.2572	35
332	1.1663*	10	1.2282	20
422	1.1163*	20	1.1769	10
511, 333	1.0525*	50	1.1084*	35
520, 432	1.0156*	20	1.0695*	35
521	0.9988*	15	1.0518*	15
440	0.9670*	25	1.0184*	30
600, 442	0.9117*	15	0.9603*	5
610	...	...	0.9473*	10
611, 532	0.8874*	15	0.9348*	20
620	0.8647*	5		
533	0.8342*	20		
622	0.8246*	10		
630, 542	0.8155*	15		
631	0.8067*	10		

TABLE II

REFINED F_o^2 AND F_c^2 FOR NiP_2

HKL	F_o^2	F_c^2	*HKL*	F_o^2	F_c^2
111	35	45	233	47	50
200	113	132	422	144	136
210	132	115	333, 511	493	440
211	139	124	250, 432	138	157
220	145	197	521	89	92
311	408	402	440	239	260
222	75	96	531	31	38
230	119	128	442, 600	88	128
321	183	180	610	70	29
400	5	1	532, 611	143	149
322, 410	7	13	260	81	56
411	6	7	533	79	121
240	137	116	622	52	59
421	113	100			

distorted tetrahedron. The P–P distance is smaller than the sum of the normal tetrahedral covalent radii (1.10 Å, Pauling) but compares with that calculated for PtP_2 (2.09 ± 0.08 Å).[14] The octahedral covalent radius of nickel is 1.23 Å (2.29–1.06 Å), which is the same as the normal metallic radius.

TABLE III

BOND DISTANCES AND ANGLES FOR PYRITE-TYPE NiP_2

Atoms	Distance, Å	Angle,[a] deg
P–P	2.12 ± 0.03	
Ni–P	2.290 ± 0.01	
P–Ni–P		94.8[b]
P–Ni–P		85.9[b]
Ni–P–P		103.1[c]
Ni–P–Ni		115.0[c]

[a] Estimated error in angles ±1°. [b] Angles of trigonally distorted octahedron. [c] Angles of trigonally distorted tetrahedron.

The formation of the pyrite-type structure is favored by pressure since the density of pyrite-type NiP_2 is greater than that of the low-pressure form (4.7 g/cm^3 *vs.* 4.58 g/cm^3) and the coordination of nickel increases from four to six. In the low-pressure form the nickel is surrounded in a square-planar arrangement of P anions which are linked in infinite chains.

Nickel diphosphide is isoelectronic with the pyrite-type compounds FeS_2 and CoPS which are diamagnetic semiconductors with their cations in a low-spin d^6 state.[15,16] This electronic configuration leads to the smallest unit cells observed in the MS_2 and MPS pyrite series (FeS_2, $a = 5.418$ Å; CoPS, $a = 5.422$ Å). The fact that NiP_2 also has a small unit cell and is isoelectronic with these compounds suggests that the nickel is in the same low-spin d^6 state.

Nickel diphosphide is also isoelectronic with the known platinum group dipnictide pyrite-type compounds PtP_2, $PtAs_2$, $PtSb_2$, $PtBi_2$, $PdAs_2$, and $PdSb_2$. These compounds have been shown to be diamagnetic with the electronic configuration of the cation in the octahedral low-spin d^6 state.[17] Except for $PtBi_2$ which is a metallic conductor, the platinum compounds are semiconductors. In contrast, the palladium compounds are metallic. This has been ascribed to overlap of bonding with antibonding bands in the palladium compounds.[18] The type of conductivity of NiP_2 is, therefore, of interest.

Resistivity was found to be 1.6×10^{-3} ohm cm and was independent of temperature from 4.2 to 298°K. A measurement of magnetic susceptibility showed weak Pauli paramagnetism (1.0×10^{-6}–0.3×10^{-6} emu/g, 10–298°K). These results are consistent with metallic-type behavior but are inconclusive since a highly doped semiconductor may show the same effect. If NiP_2 were a semiconductor, the observed degree of nonstoichiometry might also account for this behavior.

B. Nickel Diarsenide.—Nickel diarsenide with the pyrite-type structure was formed at 65 kbars pressure as readily as was NiP_2. In the presence of excess arsenic, black, metallic crystals of unit cell dimension $a = 5.788$ Å were grown. In a second experiment, reaction of stoichiometric amounts of Ni and As gave nickel diarsenide of unit cell size $a = 5.7634 \pm 0.0003$ Å (Table I), $d_{measd} = 7.20$ g/cm^3. Deviations in stoichiometry are again suggested from these results, with the latter composition having the formula $Ni_{0.98}As_2$. *Anal.* Calcd: Ni, 27.75. Found: Ni, 27.32. From experiments at ambient pressure in the pyrite-type ternary system $Ni_xPd_{1-x}As_2$ ($0 \leq x \leq 0.567$), Bennett and Heyding[18] extrapolated their data to a cell dimension of $a = 5.796$ Å for the then hypothetical, stoichiometric, pyrite-type $NiAs_2$. This value is consistent with those of our high-pressure phases.

The transformation of $NiAs_2$ from the marcasite to pyrite-type structure at high pressure can be related to the fact that $NiAs_2$ belongs to the group of d^6 marcasite compounds having a large *c/a* ratio[15] and relatively low density (7.05 g/cm^3).

The electrical resistivity, measured on a single-

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crystal specimen ($a = 5.7634$ Å), was similar to that of NiP_2, being nearly independent of temperature from 4.2 to 298°K with a value of 3×10^{-4} ohm cm at room temperature. This behavior indicates that $NiAs_2$ is a metallic conductor analogous to $PdAs_2$.

C. FeP_2, $FeAs_2$, CoP_3, $CoAs_2$, CuP_2, and PdP_2.—The diphosphides of iron and palladium (quenched from 1100°), as well as the diarsenides of iron and cobalt (quenched from 400°), occurred in their respective low-pressure forms. In the case of cobalt, CoP_3 with the skutterudite-type structure and a small amount of an unidentified phase were formed.

The failure of these compounds to form the pyrite-type structure may be related to the density and electronic configurations of their low-pressure forms. Both FeP_2 and $FeAs_2$ belong to that class of marcasite-type compounds having the diamagnetic, low-spin d^4 electronic configuration and a small c/a ratio.[15] The density is already high ($FeAs_2$, 7.7 g/cm^3) and the structure is stabilized by metal–metal bonding. In the arsenopyrite-type structure of cobalt diarsenide, cobalt is formally tetravalent and occurs in pairs of edge-sharing octahedra. It is also diamagnetic[19] and stabilized by metal–metal bonding. In cobalt phosphide, the skutterudite-type structure was observed. This compound should also be diamagnetic, as is isotypic $CoAs_3$[20] with cobalt formally trivalent in an octahedral low-spin d^6 configuration.

Copper diphosphide retained the low-pressure form in which the divalent cation is found in pairs[11] and is also diamagnetic. Reaction of Cu + 2As gave a product admixed with As. The X-ray pattern matched that reported[21] for the mineral-phase Cu_2As, koutekite.

If pyrite-type dipnictides of Fe, Co, and Cu were formed, the electronic configuration of these cations would have unpaired electrons. It appears that the low-spin, diamagnetic state has the greater stability in the higher phosphides and arsenides of these elements, and consequently no transformation is observed.

Transformation of the PdP_2 structure to the pyrite-type structure would involve a change in formal oxidation state from divalent to tetravalent for the Pd and a change of configuration of the P from infinite chains to tetravalent dianions. Since pyrite-type phases of $PdAs_2$ and $PdSb_2$, as well as of PtP_2, $PtAs_2$, and $PtSb_2$, form readily, formation of a PdP_2 pyrite phase under appropriately high pressure seems likely.

Acknowledgments.—The authors wish to thank C. L. Hoover for supervision of the high-pressure experiments, J. L. Gillson for the electrical measurements, R. B. Flippen for the magnetic susceptibility data, and L. J. Guggenberger for helpful discussions.

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Studies on the Chemistry of Halogens and of Polyhalides. XXVIII. Complexes of Iodine with Substituted Pyridines in Carbon Tetrachloride Solutions

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Received August 8, 1967

Formation constants of the complexes formed by pyridine and 14 substituted pyridines with iodine have been determined spectrophotometrically in carbon tetrachloride solutions at 25°. A plot of Hammett σ constants *vs.* K_f yields a straight line given by the equation: $\log K_f = -2.25\sigma + 2.11$. Likewise a plot of $\log K_f$ *vs.* pK_a of the respective pyridines follows a linear relationship with the exception of cases where steric hindrance becomes an important factor. If the substituent groups are electron donors themselves (phenyl or nitrile), a simple spectrophotometric technique fails to give the formation constant of the complex, presumably owing to the stepwise formation of two complexes.

Introduction

Since the publication of the classical paper by Benesi and Hildebrand[1] in 1949 numerous papers have appeared in the chemical literature on the spectrophotometric studies of charge-transfer complexes. The seeming simplicity of the experimental techniques contributed heavily to the widespread use of this type of investigation. It is unfortunate, however, that all too frequently the limitations of this technique have been largely ignored and it is only relatively recently that a detailed analysis of possible experimental errors allows one to evaluate the significance of the experimental results. A recent paper by Person[2] clearly shows the limited validity of experimental results when the Benesi–Hildebrand technique is used to study very weak complexes. Likewise it has been shown that the linearity of the Benesi–Hildebrand plot by itself is not a sufficient criterion for assuming a simple 1:1

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