metal-to-ligand charge-transfer excited state. The present work supports the idea that the coordination number of copper may tend to increase in the excited state.

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Registry No. $Cu(tmbp)_2ClO_4$, 15633-36-0; $Cu(tmbp)_2(ClO_4)_2$, 80800-41-5; $Cu(tmbp)_2(ClO_4)_2 \cdot 2H_2O$, 80844-90-2.

Supplementary Material Available: Interatomic bond distances and angles for the tmbp ligands (Tables VII and VIII), selected least-squares planes (Tables IX–XI), molecular dimensions for the perchlorate groups (Table XII), contact distances (Table XIII), hydrogen atom coordinates (Tables XIV and XV), thermal parameters (Tables XVI–XVIII), and observed and calculated structure amplitudes for $Cu(tmbp)_2ClO_4$, $Cu(tmbp)_2(ClO_4)_2$, and $Cu(tmbp)_2(ClO_4)_2 \cdot 2H_2O$ (59 pages). Ordering information is given on any current masthead page.

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Preparation and Crystal Structure of Dirhenium Pentaphosphide, Re_2P_5, a Diamagnetic Semiconducting Polyphosphide with Rhomboidal Re_4 Clusters

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The new compound Re_2P_5 was prepared by reaction of the elemental components in a tin flux. It crystallizes with triclinic symmetry, space group $P\bar{1}$, and the lattice constants $a = 8.229$ (2) Å, $b = 8.336$ (5), $c = 7.329$ (2) Å, $\alpha = 112.28$ (2)°, $\beta = 87.11$ (2)°, $\gamma = 110.18$ (2)°, and $Z = 4$. The crystal structure was determined from 4675 single-crystal diffractometer data and refined to a conventional R value of 0.038 and 129 variable parameters. It can be rationalized completely by classical two-electron Re–Re, Re–P, and P–P bonds in agreement with the diamagnetism and the semiconductivity of the compound. Formal oxidation numbers are +3 and +4 for the Re atoms and 0, −1, −2, and −3 for the P atoms. The Re atoms are situated in P octahedra which are distorted by Re–Re bonds (between 2.85 and 2.96 Å) across common edges thus forming rhomboidal Re_4 clusters. The P atoms are all tetrahedrally coordinated by P and Re atoms. In stressing ionicity they may be considered as forming homonuclear polyanions of P pairs and four-membered zigzag chains. One kind of P atoms is surrounded only by four Re atoms, while others form a branched infinite P chain. Chemical bonding in Re_2P_5 and closely related Re_6P_{13} is briefly discussed to rationalize their different physical properties.

Introduction

The first and systematic study of the rhenium–phosphorus system was carried out by Haraldsen,[1] who—using Biltz's[2] tensimetric technique of thermal decomposition under vacuum—found the four compositions $ReP_{0.56}$, $ReP_{1.18}$, $ReP_{2.06}$, and $ReP_{2.98}$ in equilibrium with vaporous phosphorus. In aiming for simple atomic ratios, he assigned to them the tentative formulas Re_2P, ReP, ReP_2, and ReP_3. The crystal structures of the two metal-rich compounds were determined by Rundqvist,[3,4] who established their ideal compositions as Re_2P and Re_3P_4. A compound "Re_3P_7" was mentioned by Hulliger[5] and found its way into review articles[6,7] but later was shown[4] to be identical with Re_3P_4. More recently we have prepared and characterized ReP_4[8] and Re_6P_{13}[9,10] which—as judged from similarities in X-ray powder patterns—seem to correspond to the two compounds with high P content prepared by Haraldsen. The latter compound was reported independently also by others.[11] The new compound Re_2P_5 described in the present paper has many similarities with Re_6P_{13} including the Re_4 clusters.

Preparation and Properties

The direct synthesis of transition-metal phosphides and especially polyphosphides is difficult. At relatively low temperatures (e.g. 800 K), the reaction is usually very slow because of the inertness of the components, and at higher temperatures polyphosphides tend to decompose into lower phosphides and phosphorus vapor. With the tin flux technique—which was already used by Jolibois[12] to grow crystals of NiP_2 and NiP_3—these difficulties can be overcome as long as the desired transition-metal polyphosphides are thermodynamically more stable than the mixture of the corresponding transition-metal stannides and tin phosphides. Tin is especially useful as a solvent because of its low melting point and because the tin-rich matrix can be dissolved with hydrochloric acid, which usually does not attack the crystals of the transition-metal phosphides. Recent examples for the use of a tin flux to grow transition-metal phosphides are the growth of CuP_2,[13] PtP_2,[14] RuP_2 and IrP_2,[15] and RhP_3.[16] In our laboratory this technique was used extensively to prepare new phosphides and polyphosphides such as $LaFe_4P_{12}$[17] and $ThFe_4P_{12}$,[18] $EuCo_2P_2$,[19] $EuNi_2P_2$,[20] $La_6Ni_6P_{17}$,[21] $Er_2Ni_{12}P_7$,[22] FeP_4,[23] RuP_4 and OsP_4,[24] three modifications of MnP_4,[24-26] as well as Re_6P_{13}[10] and ReP_4.[8]

Starting materials for the preparation of Re_2P_5 were powders of rhenium (Ventron, 99.997), red phosphorus, and tin (both from Merck,

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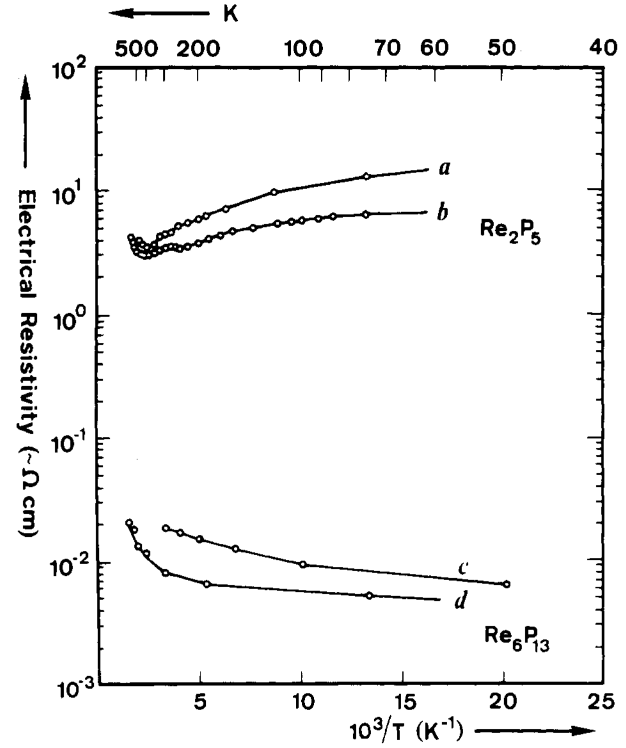

Figure 1. Temperature dependence of the electrical resistivity of Re_2P_5 and Re_6P_{13}. Curve *a* summarizes data obtained on raising and lowering the temperature for single crystals of Re_2P_5 prepared in a silica capsule by the Sn-flux technique. Curve *b* shows measurements for a cold-pressed sample of Re_2P_5 prepared similarly in an alumina container. The data of curve *c* for Re_6P_{13} were taken from ref 11. Curve *d* shows data for single crystals of Re_6P_{13} prepared by the Sn-flux technique in silica. Absolute specific resistivity values are estimated to be correct within a factor of 3.

"rein"). The phosphorus was purified by boiling in NaOH solution.[27] The mixed powders were annealed for 1 week in evacuated silica tubes. For annealing at 1120 K the atomic ratio Re:P:Sn was 10:33:57. At 1220 K single-phase Re_2P_5 was obtained with the ratio 8:42:50. After quenching, the tin-rich matrix of the samples was dissolved by boiling in hydrochloric acid. The products were identified through their Guinier powder patterns. With similar preparation conditions but slightly higher P content (ratios 9:36:55 at 1120 and 8:46:46 at 1220 K) Re_2P_5 was found to be in equilibrium with ReP_4. With somewhat lower P content (ratios 10:30:60 at 1120 and 9:39:52 at 1220 K), the Guinier patterns of the products showed besides Re_2P_5 the presence of another phase which is characterized by some diffuse diffraction lines. At still lower P contents we have also obtained Re_3P_4 and Re_6P_{13}. In samples annealed at lower temperatures (1000 K), we have not observed Re_2P_5 but still another phase with approximate composition ReP_3.

The crystals of Re_2P_5 were up to 0.5 mm large, shiny black, brittle, and had sharp edges, which indicates their resistance to boiling hydrochloric acid. An X-ray microanalysis in a scanning electron microscope showed no impurities. The detection limit for tin was estimated to be less than 0.2 atom %. We have also prepared Re_2P_5 in closed alumina containers, where a contamination with silicon can be excluded.

Electrical conductivities were measured for single crystals and cold-pressed pellets squeezed between two gold-coated copper blocks or between flat tungsten electrodes. Independent current and voltage probes were used and the potential differences were determined with a compensator. Because the contact areas of the crystals and the porosities of the pellets could not be determined accurately, the absolute resistivity values are estimated to be correct only within a factor of three. Relative values for one sample at different temperatures are judged to be much more reliable. Typical results are shown in Figure 1. The Re_2P_5 samples behave like doped semiconductors. At low temperatures the conductivities increase with temperature and reach a maximum at about room temperature. At higher temperatures the conductivities decrease again, because the electrons due to the impurity levels are essentially all promoted and lattice vibrations decrease the mobility of the conducting electrons. The intrinsic region was not reached in the temperature range studied. The sample of Re_6P_{13} which was also prepared by the tin-flux technique and measured in the same way shows metallic conductivity in agreement with literature values.[11]

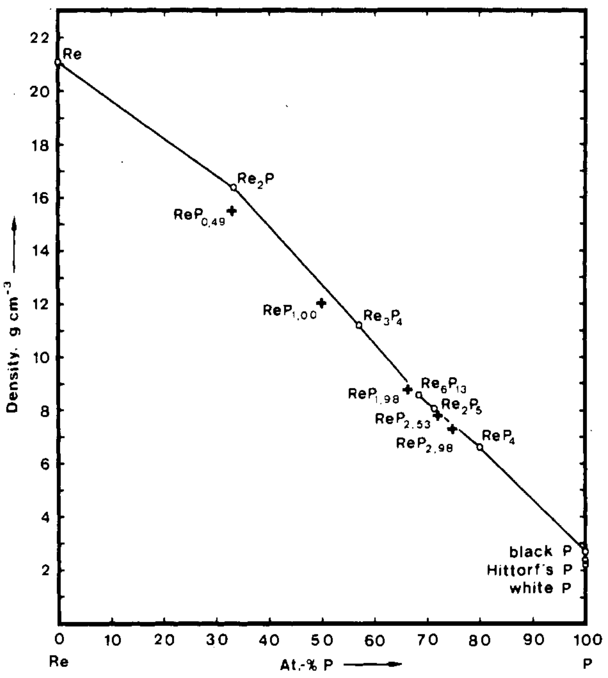

Figure 2. Experimental and X-ray densities in the Re–P system. The experimental densities marked with crosses were obtained by Haraldsen[1] from samples with the indicated overall compositions. The X-ray densities of the elements and compounds with known structures are shown as circles.

The magnetic susceptibility was determined with a Faraday balance at room temperature for selected single crystals. Because of the small size of the crystals the accuracy was low but the sample was clearly diamagnetic.

Structure Determination

Single crystals of Re_2P_5 have triclinic diffraction symmetry. Lattice constants were refined from Guinier powder data (see supplementary material) and α-quartz (a = 4.9130, c = 5.4046 Å) as standard: a = 8.229 (2) Å, b = 8.336 (5) Å, c = 7.329 (2) Å, α = 112.28 (2)°, β = 87.11 (2)°, γ = 110.18 (2)°, V = 434.8 (4) Å^3. The values in parentheses are the deviations in the least significant digits obtained from samples prepared under a variety of conditions and starting compositions. With $Z = 4$ formula units per cell, the calculated density is 8.06 g cm^{-3}. This agrees well with the densities determined by Haraldsen[1] for samples with similar overall compositions (Figure 2).

A crystal of 40 × 50 × 60 μm^3 was chosen for the X-ray data collection in a four-circle diffractometer with Mo Kα radiation, graphite monochromator, scintillation counter, and pulse-height discriminator. Scan rates of the ω–2θ scans varied. The longest measuring time was 2 min for the weakest reflections including background counts taken at both ends of each scan. Widths were 2.1° (2θ) plus the separation of the Kα doublet. A total of 6383 reflections were measured within half of the reciprocal sphere up to 2θ = 84°. A total of 4675 reflections remained after averaging of equivalent reflections and omitting those with intensities $<3\sigma$. An empirical absorption correction ($\mu_{\mathrm{Mo\,K\alpha}}$ = 549 cm^{-1}) was made from ψ-scan data. The ratio of the highest to lowest transmission was 1.81.

The structure was deduced from Patterson and difference Fourier maps. For the full-matrix least-squares refinements[28] scattering factors for neutral atoms[29] were used, corrected for anomalous dispersion.[30]

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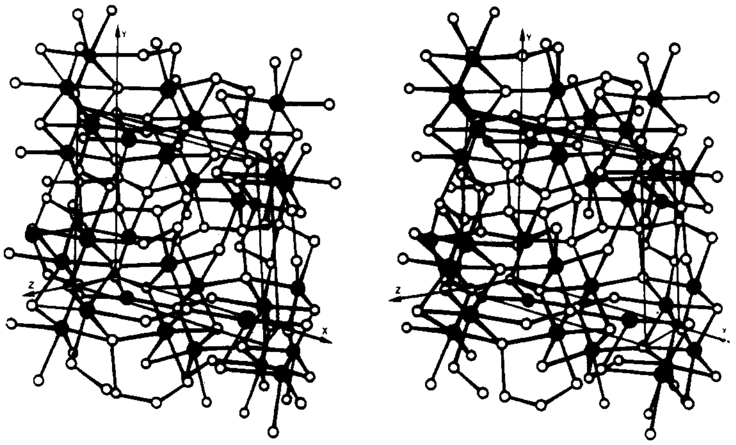

Figure 3. Stereoplot of the structure of Re_2P_5: Re atoms are black circles; P atoms are open circles.

Table I. Atom Parameters of Re_2P_5[a]

	x	y	z	B, Å^2
Re(1)	0.85847	0.70981	0.69581	0.347
Re(2)	0.51939	0.74941	0.17865	0.355
Re(3)	0.08855	0.90258	0.05623	0.346
Re(4)	0.42223	0.85720	0.57410	0.346
P(1)	0.0404	0.6329	0.1371	0.50
P(2)	0.8352	0.5358	0.3196	0.57
P(3)	0.0836	0.0462	0.3986	0.52
P(4)	0.4161	0.5206	0.8387	0.47
P(5)	0.5485	0.6370	0.6243	0.52
P(6)	0.4137	0.9518	0.1067	0.43
P(7)	0.7481	0.4050	0.7194	0.50
P(8)	0.3063	0.0552	0.5344	0.49
P(9)	0.1573	0.7403	0.7282	0.47
P(10)	0.7816	0.8312	0.0239	0.41

[a] All atoms are in the general position of the centrosymmetric space group $P\bar{1}$. Standard deviations are all 0.000 04 for the Re atoms and 0.0003 for the P atoms. The B values were obtained in a least-squares refinement with isotropic thermal parameters. Their standard deviations are 0.003 Å for the Re and 0.03 Å for the P atoms.

Table II. Interatomic Distances (Å) in Re_2P_5[a]

Re(1)-P(3)	2.282
-P(10)	2.377
-P(9)	2.398
-P(5)	2.444
-P(7)	2.457
-P(2)	2.563
-Re(3)	2.886
-Re(3)	2.931
Re(2)-P(8)	2.286
-P(6)	2.370
-P(7)	2.381
-P(10)	2.394
-P(4)	2.442
-P(4)	2.462
-Re(4)	2.852
-Re(4)	2.960
Re(3)-P(3)	2.340
-P(10)	2.388
-P(10)	2.389
-P(9)	2.420
-P(1)	2.436
-P(6)	2.587
-Re(3)	2.865
-Re(1)	2.886
-Re(1)	2.931
Re(4)-P(8)	2.280
-P(8)	2.300
-P(6)	2.417
-P(7)	2.449
-P(9)	2.470
-P(5)	2.540
-Re(2)	2.852
-Re(4)	2.864
-Re(2)	2.960
P(1)-P(2)	2.224
-P(7)	2.248
-P(1)	2.265
-Re(3)	2.436
P(2)-P(9)	2.215
-P(1)	2.224
-P(4)	2.236
-Re(1)	2.563
P(3)-P(8)	2.095
-P(3)	2.151
-Re(1)	2.282
-Re(3)	2.340
P(4)-P(5)	2.203
-P(2)	2.236
-Re(2)	2.442
-Re(2)	2.462
P(5)-P(4)	2.203
-P(5)	2.215
-Re(1)	2.444
-Re(4)	2.540
P(6)-P(6)	2.247
-Re(2)	2.370
-Re(4)	2.417
-Re(3)	2.587
P(7)-P(1)	2.248
-Re(2)	2.381
-Re(4)	2.449
-Re(1)	2.457
P(8)-P(3)	2.095
-Re(4)	2.280
-Re(2)	2.286
-Re(4)	2.300
P(9)-P(2)	2.215
-Re(1)	2.398
-Re(3)	2.420
-Re(4)	2.470
P(10)-Re(1)	2.377
-Re(3)	2.388
-Re(3)	2.389
-Re(2)	2.394

[a] All distances shorter than 3.57 Å (for Re atoms) and 2.98 Å (for P atoms) are listed. Standard deviations for Re-Re, Re-P, and P-P distances are 0.002, 0.003, and 0.004 Å, respectively.

Weights accounted for counting statistics. An isotropic secondary extinction parameter was refined and applied to the F_c values. Because of the unusually short P(3)-P(8) distance of 2.095 Å, we examined the possibility of a refinement to a wrong minimum by resetting parameters to the values obtained in distance least-squares refinements[31] without getting different results.

The final conventional R value is 0.038 for 129 variables and 4675 reflections in the refinement with anisotropic thermal parameters. The weighted R value is 0.036. A final difference Fourier synthesis showed as extreme values +4.7 and −4.0 e Å^{-3}. Positional and isotropic thermal parameters are listed in Table I. Structure factors and ellipsoidal thermal parameters are available as supplementary material. Table II lists interatomic distances.

Discussion

Transition-metal phosphides can be divided into high-coordination and low-coordination compounds depending on the number of electrons available for bonding interactions.[32] All known phosphides of the Ti and V group metals have high coordination numbers for all atoms as is typical for (electron-deficient) intermetallic phases. On the other hand the polyphosphides, especially those of the late transition metals, have low coordination numbers for all atoms: the metal atoms are in octahedral, square-planar, or tetrahedral P coordination, and the P atoms are tetrahedrally coordinated by metal and P atoms. Magnetic and electrical properties of the low-coordination compounds are more easily understood than those of the high-coordination compounds because bonding in the low-coordination compounds can be rationalized by classical two-electron bonds.[33-35] Of the five now well-characterized

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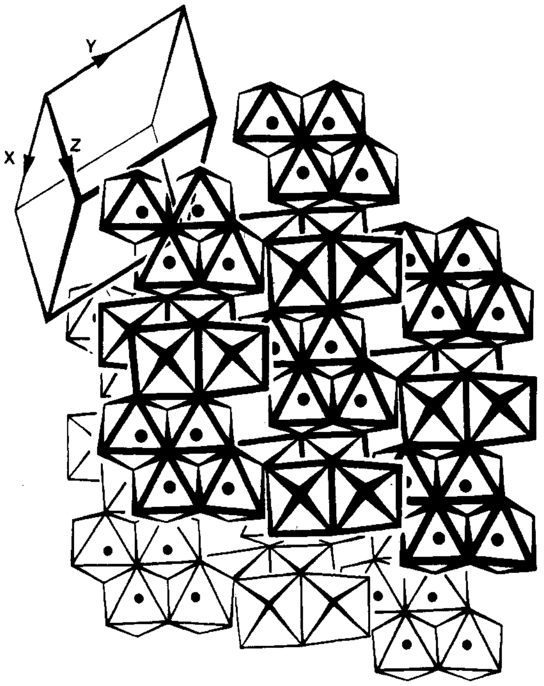

Figure 4. Crystal structure of Re_2P_5 projected along a direction approximately perpendicular to the plane $(10\bar{1})$. P atoms are represented by the corners of the octahedra. Only the Re atoms (black dots) inside those clusters which are parallel to the projection plane are shown.

rhenium phosphides, Re_2P is a high-coordination comound, while Re_3P_4, Re_6P_{13}, Re_2P_5, and ReP_4 can be considered as compounds with low near-neighbor coordinations.

In Re_2P_5 the metal atoms are all in approximately octahedral P coordination (Figures 3 and 4). The octahedra are distorted to allow for Re–Re bonds across common edges, thus forming planar nearly equilateral rhomboidal Re_4 clusters (Figure 5). The P atoms are all tetrahedrally coordinated by P and/or Re atoms.

So that formal oxidation numbers could be established, the electrons of the Re–P bonds are counted as belonging to the P atoms and the P–P bonds are split homolytically. In this way the P(1) and P(2) atoms with one Re and three P neighbors attain the oxidation number zero. The P(3), P(4), P(5) and P(6), P(7), P(8), P(9) atoms have oxidation numbers –1 and –2, respectively, while P(10), which is surrounded solely by four Re atoms, is ascribed the oxidation number –3. Thus—with the language of organic chemistry—the P atoms may be considered as forming anions and polyanions corresponding to methane, ethane, butane, and branched infinite chains of poly(1,2,7,8-tetramethyloctamethylene) (Figure 6). Many more similar P polyanions have been found in recent years especially in alkali, earth, and rare-earth polyphosphides.[36] The great variety of formal oxidation numbers of the P atoms in Re_2P_5 suggests that the Re–P and P–P bonds are approximately of equal strength. In a more ionic, thermodynamically stable compound such a variety of oxidation numbers for one element would not be possible.

As a consequence of the thus established oxidation numbers for the P atoms, the average Re atom obtains an oxidation number of +3.5 (i.e., on average a $d^{3.5}$ system). With consideration of the Re–Re bonds within the Re_4 clusters, d^3 systems are suggested for the Re(3) and Re(4) atoms and d^4 systems for Re(1) and Re(2). The Re–Re bonds are then formed by the three $\sim t_{2g}$ orbitals of the Re(3) and Re(4) atoms and by two of the $\sim t_{2g}$ orbitals of Re(1) and Re(2). The third t_{2g} orbital of the latter atoms will be occupied by a pair of nonbonding electrons, while the $\sim e_g$ orbitals of all Re atoms participate in the bonds to the distorted octahedral P ligands ("d^2sp^3 hybrid"). In this way all valence electrons are accounted for, in agreement with the diamagnetism and semiconductivity of the compound.

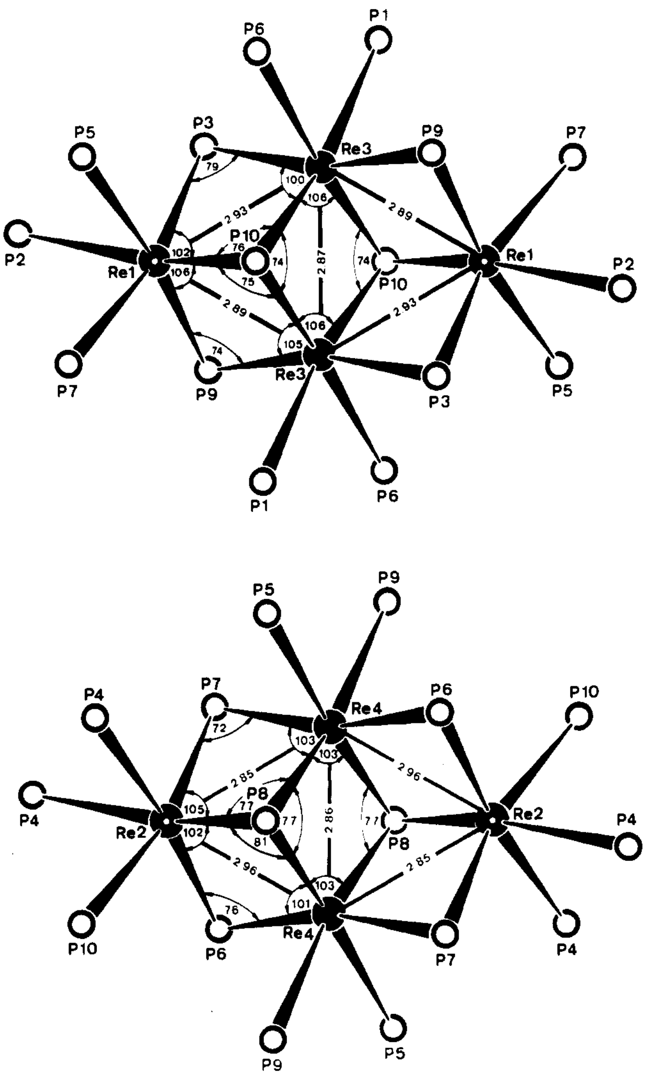

Figure 5. Near-neighbor environments of the Re atoms in Re_2P_5. Distances are in Å units. The clusters are centrosymmetric.

Rhomboidal Re_4 clusters with five nearly equally long Re–Re bonds occur also in the structure of Re_6P_{13}.[10,11] The other near-neighbor environments in the two compounds are also quite similar. In contrast to diamagnetic semiconducting Re_2P_5, however, Re_6P_{13} is paramagnetic and a metallic conductor. Its structure shows this electron deficiency of 109 electrons per formula unit would be needed to saturate all short near-neighbor Re–Re, Re–P, and P–P bonds and to fill the (inferred) nonbonding 5d orbitals of the three Re(1) atoms.[10] There are, however, only 6 × 7 + 13 × 5 = 107 electrons per formula unit of Re_6P_{13}. Because of their similarity in near-neighbor coordinations, the two compounds should have similar band structures, and one might be tempted to guess which bands (bonds) are the highest occupied ones and thus unsaturated in Re_6P_{13}. Most likely this will be those resulting from bonding Re–P and/or P–P interactions because they extend throughout the structure (which is required by the metallic conductivity of Re_6P_{13}) and because they could be filled in Re_2P_5 (which is needed to account for the diamagnetism and semiconductivity of this compound). The nonbonding 5d levels and the bonding and antibonding levels

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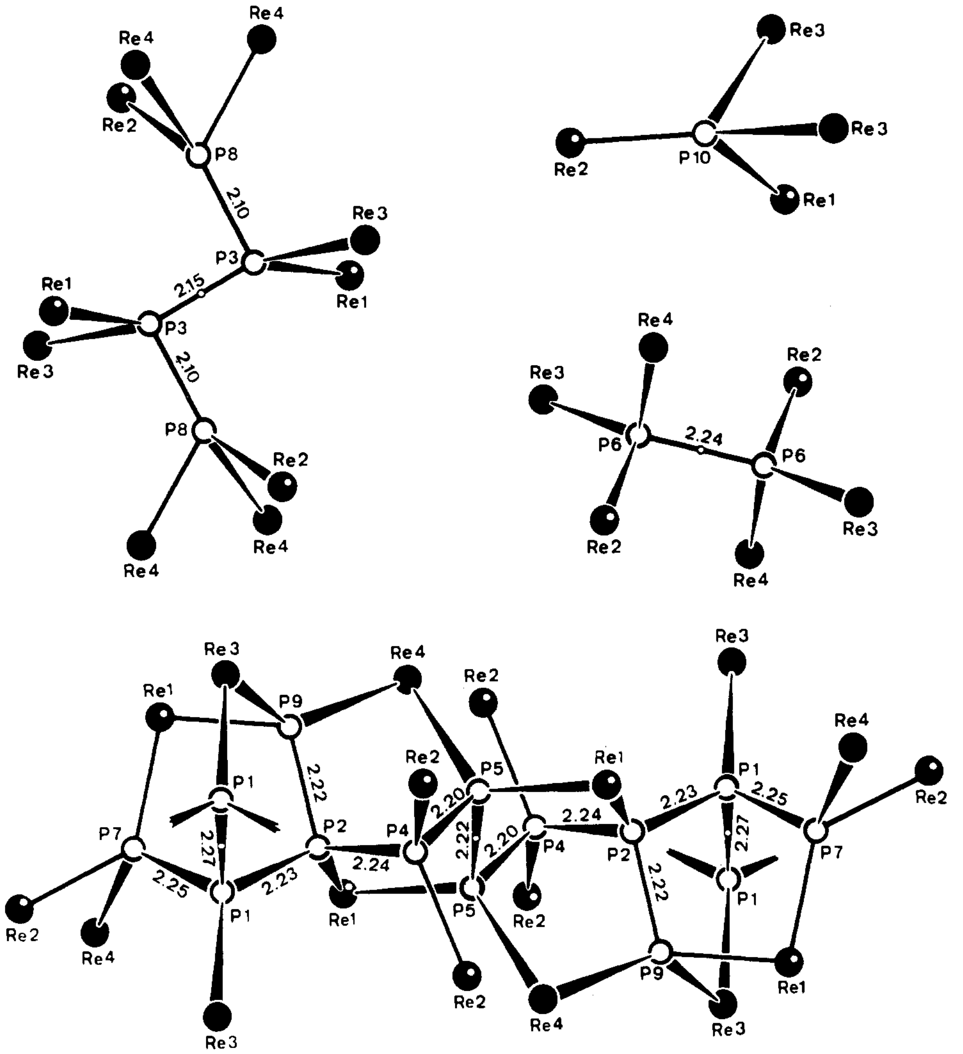

Figure 6. Near-neighbor environments of the P atoms and polyanions. Distances are given in Å units. Symmetry centers are indicated by small open circles. In the lower part of the figure, a portion of the polymeric P chain is shown. A repeat unit consists of the sequence P(1)-P(2)-P(4)-P(5)-P(5)-P(4)-P(2)-P(1).

resulting from Re–Re interactions probably can be excluded because they are most likely localized at the Re_4 clusters and thus cannot account for metallic conductivity. Finally, the antibonding Re–P and P–P bands need to be above the Fermi level because their partial overlap in energy with filled levels should result in metallic conductivity for both compounds. Although such a simple band model seems to rationalize the physical properties of the compounds, it is somewhat at variance with the expectancy: one could suppose that—because of the higher electronegativity of phosphorus—the bonding Re–P and P–P levels should be lower in energy than the nonbonding 5d and bonding Re–Re interactions.

The variance of interatomic distances in the two compounds is similar. Average distances (in Å units) are as follows in Re_2P_5 (with the values for Re_6P_{13} in parentheses): for Re–Re, 2.899 (2.853); for Re–P, 2.411 (2.421); for P–P, 2.208 (2.211). These small differences in the average distances may be due to strains in the structures and do not necessarily indicate filling or nonfilling of bonding or antibonding levels.

Strains within the edge-sharing octahedra are probably also the main reason for the long Re–Re bonding distances. They vary between 2.85 and 2.96 Å in Re_2P_5 and between 2.76 and 2.94 Å in Re_6P_{13} as compard to the expected single-bond Re–Re distance of 2.57 Å,[37] or twice the metallic radius (for coordination number 12) of 2.75 Å,[38] or—most appropriate for this case—twice the single-bond radius for covalence 9 of 2.78 Å.[39] The deviations from the ideal bond angles within the Re_4P_{16} groups indicate the bonding Re–Re interactions: the octahedral P–Re–P angles of ideally 90° are stretched to between 100 and 106°, and the tetrahedral Re–P–Re angles of ideally 109° are compressed to between 74 and 81° to allow for short Re–Re bonds. A further shortening of the Re–Re distances would cause further deviations from ideal bond angles and thus a compromise is reached. These "matrix effects" for metal–metal bonds were discussed recently for a large number of clusters.[40]

The Re–P distances in Re_2P_5 (Re_6P_{13}) cover a wide range from 2.28 (2.29) to 2.59 (2.70) Å. It is noteworthy that the distances from the Re atoms to those P atoms which bridge within one cluster are shorter (average Re–P distances of 2.363 Å in Re_2P_5 and 2.365 Å in Re_6P_{13}) than the distances to "terminal" P atoms (average Re–P distances of 2.480 and 2.500 Å, respectively) which connect Re atoms of one cluster with Re atoms of a neighboring cluster. Similar differences between bridging (inner) and terminal (outer) ligands were also found in ReP_4[8] and in several transition-metal halide cluster compounds, e.g., in $[(Nb_6Cl_{12})Cl_6]^{3-}$,[41] β-Nb_3Br_8,[42]

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Nb_6I_{11},[43] Ta_6Cl_{15},[44] and Mo_6Cl_{12}.[45] Such differences, however, are not common to all cluster compounds. For example, in W_6Br_{16}[46] there are no differences between the average W–Br bond lengths for inner and outer Br ligands, and in $[Zr_2I_9]^{3-}$,[47] where the ZrI_6 octahedra share faces, the differences are actually reversed. The overall average Re–P distances of 2.411 Å in Re_2P_5 and 2.421 Å in Re_6P_{13} are close to the average Re–P distance of 2.402 Å in ReP_4[8] and within the range of Re–P distances found in many molecular inorganic compounds.[8,48]

The P–P distances cover the range from 2.095 to 2.265 Å in Re_2P_5 (2.142 to 2.291 in Re_6P_{13}). To our knowledge the P(3)–P(8) distance of 2.095 Å is the shortest P–P distance found in any transition-metal polyphosphide. Even shorter P–P distances are observed sometimes in molecular compounds where they can be rationalized with some double-bond character.[49]

Planar, nearly equilateral rhomboidal clusters of metal atoms were found before in $CsNb_4Cl_{11}$,[50] in $[Re_4(CO)_{16}]^{2-}$,[51,52] and in several heteronuclear molecular related compounds with clusters of the composition T_2M_2 (T = Mn, Re; M = Ga, In, Ge, Sn).[53,54] More examples are known for nonplanar "butterfly" clusters of four metal atoms. The reviews by King,[55] Vahrenkamp,[56] Lewis and Johnson,[57] and Tachikawa and Muetterties[58] give references to some ten clusters with such tetranuclear cores in molecular inorganic compounds. Simon[59] has pointed out that condensed butterfly clusters can be regarded as building elements in many solid-state compounds such as Hf_3P_2, Nb_8P_5, or Mo_4P_3. We wish to conclude that we too believe that the division in "solid-state" and "molecular" inorganic chemistry—caused by some differences in preparation and characterization methods and deepened by tradition—should be overcome at least as regards structural chemistry.[60]

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Registry No. Re_2P_5, 80878-10-0.

Supplementary Material Available: Listings of structure factor amplitudes, anisotropic thermal parameters, and a Guinier powder pattern of Re_2P_5 (28 pages). Ordering information is given on any current masthead page.

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Magnetic Properties and Molecular Structure of Copper(II) Complexes of Pyrazinecarboxylic Acid

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Several copper complexes of pyrazinecarboxylic acid (HL = $C_4H_3N_2COOH$) have been prepared. The crystal structures of CuL_2 and $CuL_2(H_2O)_2$ were determined from single-crystal X-ray diffraction using counter methods, and the magnetic properties of these complexes plus the complex $[Cu(HL)Cl_2]_2$ were studied over the temperature range 6–300 K with an alternating force magnetometer. $CuL_2(H_2O)_2$ consists of six coordinated (distorted octahedral) copper(II) ions with L^- acting as a bidentate ligand and axially coordinated water molecules. CuL_2 is also a six-coordinate structure similiar to that of $CuL_2(H_2O)_2$ but with the axial positions now occupied by the carboxylate oxygens of a neighboring molecule to form a structural linear chain. The magnetic properties for CuL_2 and $CuL_2(H_2O)_2$ indicate weak ferromagnetic interactions are present. The magnetic data for $[Cu(HL)Cl_2]_2$ show that the chlorine bridged dimer is antiferromagnetically coupled ($g = 2.23$, $J/k = -8.79$ K). Crystal data for $CuL_2(H_2O)_2$: space group $P2_1/c$, $Z = 2$, $a = 5.438$ (1) Å, $b = 10.880$ (2) Å, $c = 10.385$ (2) Å, $\beta = 98.24$ (1)°, $V = 608.1$ Å^3, 1023 reflections. Crystal data for CuL_2: space group $P2_1/c$, $Z = 2$, $a = 5.0340$ (4) Å, $b = 15.3316$ (12) Å, $c = 7.0707$ (9) Å, $\beta = 106.627$ (9)°, $V = 523.3$ Å^3, 869 reflections.

Introduction

Pyrazine is an excellent bridging ligand when coordinated to transition metals and has been extensively studied as an active ligand in the course of electron-transfer and magnetochemistry research.[2-12] Binuclear and polynuclear systems which have a bridging pathway composed of a conjugated bonding network are of interest to experimental magneto-

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