Fig. 4. Coordination polyhedra of Sm(9) and Sm(10). Assumed sphere radii are proportional to atomic radii.

In spite of the complexity of the structure which presents 16 site sets for the Pd atoms, they are four, five or six coordinated with Sm atoms in only a few ways. Around Pd(7), Pd(8) and Pd(11), the Sm atoms form a slightly puckered square; Pd(1), Pd(2), Pd(3), Pd(4), Pd(5), Pd(6) and Pd(10) are at the centre of a more or less irregular trigonal bipyramid; the environment of Pd(12), Pd(13), Pd(15) and Pd(16) appears to approximately tetragonal pyramidal but with the axial Sm–Pd bond generally longer than the equatorial ones; Pd(9) is octahedrally surrounded; finally, Pd(14) is a hybrid, as it is coordinated with four Sm and one Pd(14), the latter giving the only Pd–Pd distance which shows a slight contraction (2·71 Å).

Finally, we compare the present structure with that of the previously mentioned cubic Laves phase, which is adopted by Eu and by the alkaline earths Ca, Sr and Ba (Pearson, 1967) in the corresponding MPd_2 compounds. Although these two structural types do have something in common (e.g. both are layered), they are quite different. In $Sm_{10}Pd_{21}$ short contacts occur only between atoms of a different kind. Moreover, whereas in the Laves phase Pd is surrounded by an icosahedron, i.e. a bicapped pentagonal antiprism, in $Sm_{10}Pd_{21}$, even if all the atoms up to the second gap are considered, the environments around Pd(12),

Pd(13), Pd(15) and Pd(16) can be described as bicapped pentagonal prisms, and the situation differs further for the remaining Pd atoms.

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Synthesis and Crystal Structure of Diamagnetic ReP₄, a Polyphosphide with Re—Re Pairs

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Abstract

Microcrystalline ReP_4 was prepared by heating the elemental components in the presence of iodine. Single crystals were obtained by reaction of the components in molten tin. They are orthorhombic, *Pbca*, $a = 6·227$ (2), $b = 9·231$ (2), $c = 10·854$ (3) Å, $Z = 8$. The structure is of a new type. It was determined and refined from single-crystal diffractometer data to $R = 0·042$ for 1195 structure factors. The Re atoms have

six P neighbors forming a distorted octahedron. The P atoms are approximately tetrahedrally coordinated by Re and P atoms. In common with other transition-metal polyphosphides with this composition, all near-neighbor interactions can be rationalized as two-electron bonds. Thus the Re atoms obtain formal oxidation numbers +2 (d^5 system). They are displaced from the centers of their P octahedra to permit Re–Re bonding (3·012 Å) via edges of the paired octahedra. In this way all spins are compensated and this is confirmed by the diamagnetism of the compound. The P atoms form puckered ten-membered rings which are condensed to a two-dimensionally infinite net, which is a variation of the net found in the CrP$_4$ structure.

Introduction

In the first systematic study of the rhenium–phosphorus system Haraldsen (1935) identified four phases with the approximate compositions Re$_2$P, ReP, ReP$_2$, and ReP$_3$. Later on, the structures of the two compounds with relatively high Re content were determined from powder data and their ideal compositions were established as Re$_2$P (Rundqvist, 1961) and Re$_3$P$_4$ (Rundqvist, 1966). The compounds with high phosphorus content remained poorly characterized, apparently because of the difficulty in growing crystals of sufficient size for structure determinations. In the course of our reinvestigations of the phosphorus-rich parts of transition-metal–phosphorus systems, employing previously little used preparative methods, we have already reported on FeP$_4$ (Jeitschko & Braun, 1978), and on RuP$_4$ and OsP$_4$ (Braun & Jeitschko, 1978a). We have now grown crystals of ReP$_4$ and determined their structure.

Synthesis, crystal growth and properties

In agreement with the aforementioned experiences, we have not obtained single crystals of rhenium polyphosphides by direct reaction of the elemental components. Apparently, these negative results are due to the inertness of red P at moderate (< 800 K) temperatures (Schäfer & Binnewies, 1978), whereas at higher temperatures the decomposition pressure of the polyphosphide may be exceeded. However, we have readily prepared microcrystalline Re polyphosphides by adding iodine to the mixture of the elemental components. Using tin as a reaction medium, we have obtained well-developed single crystals.

Starting materials were powders of Re (stated purity 99·99%), iodine (Merck, reinst), Sn (99·9%), and red P (Merck, rein), which was treated with an aqueous solution of NaOH (Brauer, 1975) to dissolve oxidation products and dried in a desiccator with P$_2$O$_5$. Samples with compositions varying between Re:P = 1:4 to 1:20 were heated in evacuated silica tubes with about 1 to 5 at.% iodine at temperatures of about 1200 K for 7 d. For the preparation with the tin flux the atomic ratios Re:P:Sn varied between 1:5:9 and 1:30:28 with annealing for 7 d at about 1050 K. The matrix of tin and tin phosphides was dissolved in moderately dilute (1:1) hydrochloric acid. In no case did the powder photographs of the resultant products show any indication of a Re phosphide with a phosphorus content higher than ReP$_4$. We have, however, obtained single crystals of a Re phosphide with a somewhat lower P content, which we are investigating.*

A sample of ReP$_4$ prepared in the tin flux was analyzed by X-ray fluorescence spectroscopy. No elements other than Re and P were found. The detectability limit for tin was about 1 wt%; however, as judged from previous experiences (Jeitschko & Braun, 1977), the solid solubility of such polyphosphides for tin should be much lower than that.

The single crystals of ReP$_4$ used for the structure determination were taken from a sample prepared in an evacuated alumina container with initial composition Re:P:Sn = 1:30:28, heated within a few hours to 1400 K, slowly cooled to 1100 K within 7 d, and cooled to room temperature in 5 min.

The ReP$_4$ crystals are shiny black with well-developed faces and no pronounced growth directions. They are stable in air and not attacked by non-oxidizing acids. Magnetic measurements with the Faraday technique indicate ReP$_4$ to be diamagnetic.

Cell dimensions and space group

Single crystals of ReP$_4$ were investigated in Weissenberg and Buerger precession cameras. They showed orthorhombic symmetry. Space-group extinctions (reflections $0kl$ were observed only with $k = 2n$, $h0l$ only with $l = 2n$, and $hk0$ only with $h = 2n$) led to the unique space group $Pbca$ (D_{2h}^{15}).

The lattice constants were refined from Guinier powder data with α-quartz ($a = 4·9130$, $c = 5·4046$ Å) as standard: $a = 6·227$ (2), $b = 9·231$ (2), $c = 10·854$ (3) Å, $V = 623·9$ (4) Å^3. Assuming $Z = 8$ formula units per cell, the calculated density is 6·60 Mg m^{-3}. Samples prepared by the different techniques and different heat treatments had lattice constants which were within the error limits given above in parentheses for the least significant digits. This suggests that the compound has only a narrow homogeneity range and that any inclusion of iodine or tin must be very limited.

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* Note added in proof: The structure determination of this compound resulted in the composition Re$_6$P$_{13}$. A detailed report will be published shortly.

Table 1. *Powder diagram of* ReP_4

The experimental powder pattern was obtained in a Guinier camera with Cu $K\alpha$ radiation. For the calculated pattern (Yvon, Jeitschko & Parthé, 1977), data of the refined structure were used. The Q values are defined by $Q = 10^4/d^2$ (Å^{-2}).

hkl	Q_c	Q_o	I_c	I_o	hkl	Q_c	Q_o	I_c	I_o	hkl	Q_c	Q_o	I_c	I_o
002	340	340	21	s	230	2097	2088	14	s	116	3432	–	1	–
111	460	462	71	vvs	231	2172	–	0	–	135	3436	–	2	–
020	469	471	2	vw	042	2217	2217	10	s	234	3446	3446	8	m
021	554	555	16	s	141	2220	–	1	–	331	3461	3463	5	w
102	597	599	24	vs	223	2265	–	0	–	144	3494	3494	17	vs
112	715	716	14	s	204	2309	–	0	–	026	3526}	3526	1}	w
022	809	–	1	–	232	2427	2428	26	vs	152	3531}		1}	
121	812	813	46	vs	142	2475	2475	17	s	323	3554	–	1	–
200	1031	–	0	–	115	2498	2497	7	m	225	3623	–	0	–
122	1067	–	0	–	214	2507	–	1	–	243	3673}	3674	8}	vs
113	1139	–	1	–	311	2523	2523	14	s	304	3679}		12}	
210	1149	1150	31	vs	025	2592	2591	10	m	332	3716	3716	5	w
211	1234}	1234	22}	vvs	043	2642	2641	4	w	126	3784	–	0	–
023	1234}		100}		302	2660	2660	14	s	314	3796	3796	12	s
004	1358	–	0	–	134	2672	2673	29	vs	153	3956	–	0	–
202	1371	–	0	–	312	2777	2777	9	m	250	3965	3964	2	vw
131	1399	1400	3	w	125	2850}	2851	9}	vs	045	4000	4000	1	vvw
212	1488	1488	7	w	233	2852}		16}		251	4050	4049	9	m
123	1491	–	1	–	224	2859	–	1	–	206	4088	–	0	–
220	1501	1502	13	s	321	2875	2875	23	vs	400	4125	4125	3	w
221	1586	–	0	–	143	2900	–	0	–	333	4141	–	0	–
104	1616	1616	7	m	240	2909	–	0	–	324	4148	4148	3	w
132	1654	1655	27	vs	241	2994	–	0	–	216	4205	4206	13	s
114	1734	1734	3	w	006	3056	3056	26	vvs	235	4210	–	1	–
024	1828	1827	1	vvw	322	3129	3131	2	vvw	060	4225	–	4	–
222	1840	–	0	–	313	3202	–	0	–	410	4242	–	1	–
040	1878	1878	6	m	044	3236	3235	3	w	145	4258	–	0	–
213	1913	1913	30	vs	242	3249	–	0	–	244	4267	–	0	–
041	1963	1963	1	vvw	215	3271}	3273	14}	vs	341	4283	4283	5	w
133	2078	–	0	–	151	3277}		23}		252	4305	–	0	–
124	2086	–	0	–	106	3314	3314	2	vvw					

The powder diagrams of ReP_4 (Table 1) have only a vague resemblance to the diagram drawn by Haraldsen (1935) for the Re phosphide with the highest P content found by him and to which he ascribed the tentative composition ReP_3.

Structure determination and refinement

A total of 1897 unique reflections were measured on a four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation, a scintillation counter and pulse-height discriminator. ω scans were taken with a speed of 0.05° s^{-1} and a scan angle of 1°. Background was counted for 22.5 s at both ends of the scan. All reflections within one octant up to $2\theta = 80^\circ$ were measured. The crystal had well-developed faces, but – for the purpose of the absorption correction – was approximated by a sphere of radius 0.037 mm. The linear absorption coefficient $\mu_{MoK\alpha}$ is 39.0 mm^{-1}.

The locations of the Re atoms were deduced from a Patterson map and the positions of the P atoms were

Table 2. *Atom parameters of* ReP_4

All atoms are in the general position of space group *Pbca*. Positional parameters are multiplied by 10^4. Numbers in parentheses are e.s.d.'s in the least significant digits. The last column contains B values (Å^2) as obtained in a least-squares refinement with isotropic thermal parameters.

	x	y	z	B
Re	1218 (1)	1095 (1)	0755 (1)	0.53 (1)
P(1)	0613 (5)	2829 (3)	2364 (3)	0.70 (4)
P(2)	1889 (5)	9479 (3)	2386 (3)	0.60 (3)
P(3)	7538 (5)	0436 (3)	0817 (3)	0.64 (3)
P(4)	4986 (5)	2089 (3)	0693 (2)	0.62 (3)

obtained from difference Fourier syntheses. The structure was refined with a full-matrix least-squares program (Sheldrick, 1976) using scattering factors for neutral atoms (Cromer & Mann, 1968), corrected for anomalous dispersion (Cromer & Liberman, 1970). Weights were assigned according to counting statistics. An isotropic extinction parameter was refined and applied to the F_c values. Reflections which were over-corrected by this procedure, as well as reflections with $F_o < 6\,\sigma$ were assigned zero weight in the last least-squares cycles. For a refinement with isotropic thermal parameters a conventional R value of 0.043 was obtained for the 1195 reflections with non-zero weight. The introduction of anisotropic thermal parameters reduced R only to 0.042. Thus the anisotropic parameters deviate only slightly from the isotropic ones.*

* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34403 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Interatomic distances* (Å) *in* ReP_4

Standard deviations are all less than 0.005 Å. All distances shorter than 3.6 Å (for Re) and 3.1 Å (for P atoms) are listed.

Re: P(3)	2.347	
P(2)	2.352	
P(3)	2.372	
P(1)	2.399	
P(4)	2.423	
P(4)	2.521	
Re	3.012	

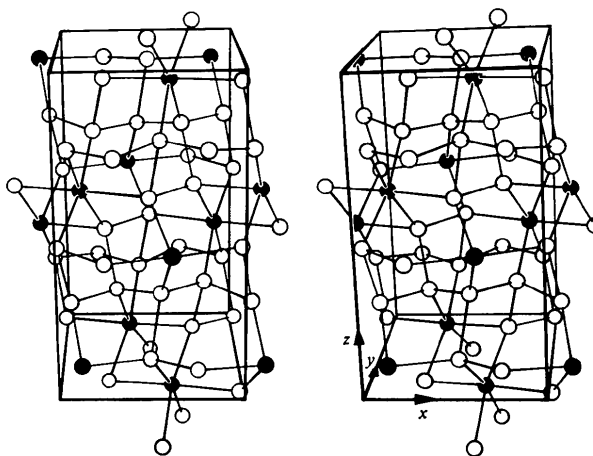|				
P(1): Re	2.399		P(2): Re	2.352
P(2)	2.177		P(1)	2.177
P(2)	2.196		P(3)	2.179
P(4)	2.251		P(1)	2.196
P(3): Re	2.347		P(4): Re	2.423
Re	2.372		Re	2.521
P(2)	2.179		P(3)	2.207
P(4)	2.207		P(1)	2.251

Fig. 1. Stereoplot of the ReP_4 structure drawn with Johnson's (1965) program. Filled circles: Re, open circles: P.
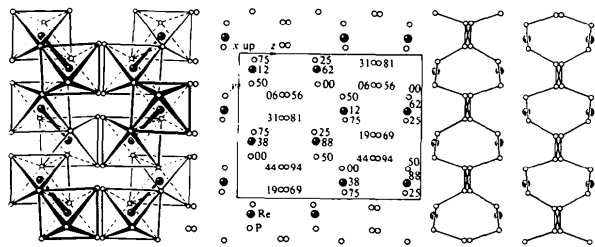
Fig. 2. Projection of the ReP$_4$ structure along the x axis. The left hand side shows the sheets of edge- and corner-shared ReP$_6$ octahedra extending parallel to the xy plane. The two-dimensional P poly-'anions' extending parallel to the same plane are emphasized in the right hand part of the drawing. Coordinates in the x direction are given in hundredths.
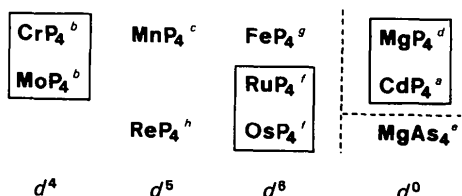
For the total of 1897 unique reflections, R equals 0·086. A difference synthesis revealed no features lower than −3·6 e Å^{-3} or higher than +3·1 e Å^{-3}. Atomic parameters and interatomic distances are given in Tables 2 and 3. The structure is shown in Figs. 1 and 2.

Discussion

The structure of ReP$_4$ is of a new type and is best discussed together with the other polypnictides of that stoichiometry which are summarized in Table 4. In these ten compounds − which crystallize in seven different structure types − the metal atoms are always approximately octahedrally coordinated by pnicogen atoms (P, As) and the pnicogen atoms are all tetrahedrally coordinated, one half of them by two pnicogen and two metal atoms and the other half by one metal and three pnicogen atoms. If classical two-electron bonds are assumed for each of these near-neighbor interactions and if the electrons in the metal−pnicogen bonds are counted as belonging to the pnicogen atoms, the metal atoms all obtain formal oxidation numbers

Table 4. *Pnictides with composition M*P$_4$ *and M*As$_4$

Isostructural compounds are enframed. The numbers of d electrons not used for M−P bonding are indicated. References are (a) Krebs, Müller & Zürn (1956); (b) Jeitschko & Donohue (1972); (c) Jeitschko & Donohue (1975); (d) Gibiński, Cisowska, Zdanowicz, Henkie & Wojakowski (1974); El Maslout, Zanne, Jeannot & Gleitzer (1975); von Schnering & Menge (1976); (e) Gèrardin, Aubry, Courtois & Protas (1977); (f) Braun & Jeitschko (1978a); (g) Jeitschko & Braun (1978); (h) this work.

CrP$_4$ [b]	MnP$_4$ [c]	FeP$_4$ [g]	MgP$_4$ [d]
MoP$_4$ [b]		RuP$_4$ [f]	CdP$_4$ [a]
	ReP$_4$ [h]	OsP$_4$ [f]	MgAs$_4$ [e]
d^4	d^5	d^6	d^0

+2. Thus, for instance, Cr in CrP$_4$ obtains a d^4 system and Re in ReP$_4$ a d^5 system.

Considering their tetrahedral environment, sp^3 hybridization can be assumed for the pnicogen atoms. In the essentially ionic Mg and Cd compounds, the electrons of the metal−pnicogen interactions will certainly belong predominantly to the pnicogen atoms and thus may also be considered as lone-pair electrons of the pnicogen anions which are directed towards the metal cations. In the transition-metal pnictides, these electrons will essentially be covalent and interacting with the d^2sp^3 hybrid of the metal atoms. Since the e_g ($d_{x^2-y^2}$ and d_{z^2}) orbitals are used for this interaction, the remaining valence electrons of the metal atoms have to be accommodated in the t_{2g} (d_{xy}, d_{xz} and d_{yz}) orbitals of the metal atoms which therefore all obtain low-spin systems. Thus, in FeP$_4$ the Fe atoms obtain a low-spin d^6 system and the compound is diamagnetic. In analogy, low-spin d^6 systems were assumed for the metal atoms in RuP$_4$ and OsP$_4$ and recent magnetic measurements (Braun & Jeitschko 1978b) confirm these compounds to be diamagnetic.

Like Mn in MnP$_4$, Re in ReP$_4$ has a d^5 system which permits metal−metal bonding by interaction of one of the half-occupied t_{2g} orbitals of each metal atom. As can be seen in Fig. 3, the ReP$_6$ octahedra are paired by sharing one edge. The distortions of the octahedra clearly indicate the bonding Re−Re interaction: the tetrahedral bonding angles of ideally 109° are compressed to 79° and the octahedral angle of ideally 90° is stretched to 101° to permit a close approach of the two Re atoms. The diamagnetism of ReP$_4$ proves that the spins are compensated in a covalent bond. The Re−Re distance of 3·012 Å is within the range 2·96–3·04 Å found for unbridged single Re−Re bonds in organometallic compounds (Ciani, Sironi & Albano, 1977).

The average Re−P distance of 2·402 Å compares favorably with the average Ru−P distance of 2·367 Å in RuP$_4$ since atomic, covalent and ionic radii of Ru are all about 0·03 Å shorter than the corresponding radii of Re. It is also within the range of Re−P distances
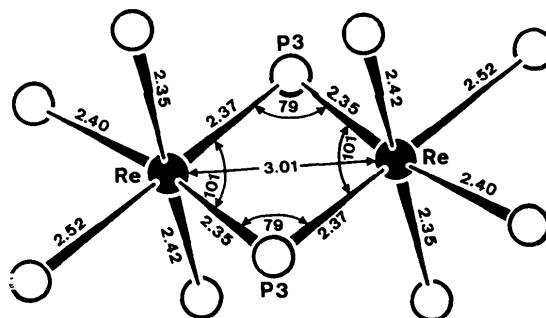

Fig. 3. Near-neighbor environments of the Re pairs in ReP$_4$. Distances are given in Å, angles in degrees of arc. Standard deviations are all less than 0·005 Å and 0·15°.

observed in molecular Re phosphine compounds with octahedral coordination of the Re atoms. Thus, for instance, for the two mutually *trans* Re—P interactions in $ReH_2(NO)(PPh_3)_3$, the Re—P distance is 2·39 Å (Ciani, Giusto, Manassero & Albinati, 1976). In $(PPh_3)_2(CO)_2Re(O_2CCH_3)$ the average Re—P distance is 2·415 Å (La Monica, Cenini, Forni, Manassero & Albano, 1976); in $(Ph_3P)_2(CO)_2Re(S_2CH)$ it is 2·418 Å (Albano, Bellon & Ciani, 1971); in $ReCl(N_2)(PMe_2Ph)_4$ it equals 2·422 Å (Davis & Ibers, 1971). In $[(Me_3P)_2(CO)_3Re]_2Se$, the Re—P distances vary between 2·46 and 2·47 Å (Röttinger, Küllmer & Vahrenkamp, 1978) and in $(PhMe_2P)_4ClReN_2MoCl_4$-(OMe) they range from 2·471 to 2·486 Å (Mercer, 1974). With a range of individual Re—P bond lengths from 2·347 to 2·521 Å, the variation in ReP_4 is even greater than in the aforementioned molecular compounds.

The short Re—P distances in ReP_4 occur in general on that side of the ReP_6 octahedron which is adjacent to the neighboring edge-shared ReP_6 octahedron. This is in an analogous way also true for MnP_4 and can be rationalized by the Re—Re (Mn—Mn) bonding interaction. If one assumes some rigidity of the P_6 octahedron due to P—P repulsion, the displacements of the Re atoms in the two edge-shared ReP_6 octahedra

toward each other will shorten the distances of the Re atoms to the bridging P atoms, and lengthen the distances to the P atoms at the opposite side.

The Re—P—P bond angles vary from 104·3 to 131·6° with an average of 116·3°. The P—P—P bond angles cover the range from 88·4 to 109·4° with the average value of 97·5°. Thus the average Re—P—P angle is greater than the average P—P—P angle. This can be rationalized with size considerations, since the Re atoms are larger than the P atoms. The Re—P(4)—Re angle is 124·3°. Those P—Re—P angles which are 90° in a regular octahedron vary between 83·7 and 96·1° with the exception of the one angle of 101° already discussed above.

The P atoms in ReP_4 form ten-membered rings which are found with the same conformation in many other MP_4 compounds. These rings are condensed to two-dimensionally infinite nets which are related to the nets found in CrP_4 (Fig. 4). In ReP_4, adjacent rows of rings extending along the x direction are antiparallel to each other while every other such row is parallel (zig-zag arrangement). In CrP_4 all rows are parallel (zig-zig arrangement). The different linking of these ten-membered rings is also reflected in the linking of the MP_6 octahedra which form edge-shared pairs or infinite chains respectively. More complicated variations of these building principles seem possible. Thus, for instance, a zig-zig-zag sequence of the rows would correspond to chains of four edge-shared octahedra followed by pairs of edge-shared octahedra. In the structures of FeP_4, RuP_4, and CdP_4, the ten-membered rings of P atoms are also condensed to infinite two-dimensional nets; however, the linking is different (Jeitschko & Braun, 1978).

Fig. 4. Projections of partial structures of ReP_4 and CrP_4 along axes perpendicular to the two-dimensional networks of the phosphorus atoms. The linking of the phosphorus atoms is shown on the left hand sides. At the right hand sides, the metal atoms above and beneath the phosphorus poly-'anion' are shown as large filled and open circles, respectively. The linkage of the MP_6 octahedra is shown in each drawing only for one metal atom layer. The phosphorus octahedra are somewhat idealized to simplify the projections.

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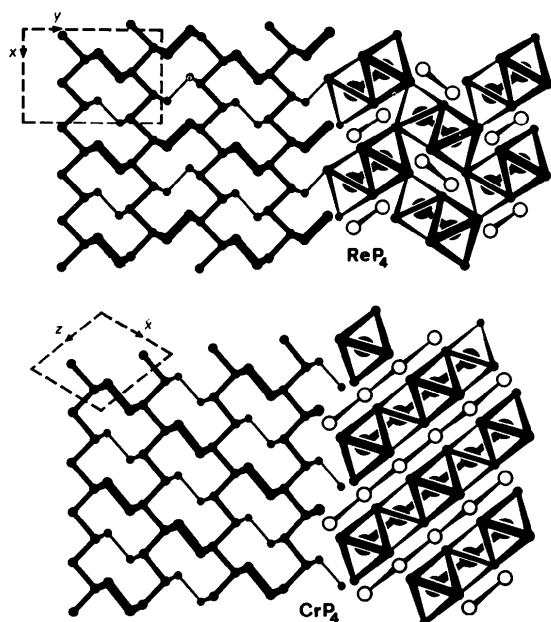CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

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The Crystal Structure of Tetraaqua-*cis*-dichloroiron(III) Tetrachloroferrate(III) Monohydrate (Ferric Chloride 2½-Hydrate)*

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Abstract

The crystal structure of ferric chloride 2½-hydrate, $FeCl_3.2\frac{1}{2}H_2O$, $[FeCl_2(H_2O)_4]^+.[FeCl_4]^-.H_2O$, has been determined from single-crystal X-ray diffractometer data using an average of three equivalent data sets, and refined to $R = 0.035$ for the 1617 unique reflections collected using Mo $K\alpha$ radiation. The structure is orthorhombic, space group $Pbc2_1$, with $a = 6.272$ (3), $b = 12.945$ (3) and $c = 16.654$ (4) Å, $Z = 4$, and consists of a somewhat distorted tetrahedral $FeCl_4^-$ anion, a distorted octahedral tetraaqua-*cis*-dichloroiron(III) cation and a single solvate water molecule. The tetrahedral Fe—Cl bonds range from 2.169 (4) to 2.220 (4) Å. The octahedral Fe—Cl bonds are 2.236 (4) and 2.251 (4) Å, and the Fe—water distances range from 2.004 (8) to 2.116 (7) Å. An extensive network of hydrogen bonds links the ions and the solvate water molecule.

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Introduction

The ferric chloride–water phase diagram (Roozeboom, 1892) reveals four hydrates: $FeCl_3.2H_2O$, $FeCl_3.2\frac{1}{2}H_2O$, $FeCl_3.3\frac{1}{2}H_2O$ and $FeCl_3.6H_2O$. The last of these has been examined crystallographically by Lind (1967), and shown to consist of tetraaqua-*trans*-dichloroiron(III) ions, with a Cl⁻ ion and two solvate water molecules. The crystal structure of ferric chloride 2½-hydrate was determined to provide a known structural background for the interpretation and use of parameters determined from infrared, Mössbauer and ultraviolet–visible absorption spectra of both the solid compound and the acidic ferric chloride solutions used to leach sulfide ores. Concentration and structural information about the complexes in these solutions is a necessary first step in the study of reaction mechanisms of these leaching reactions. This paper reports the results of the first of three crystal structure determinations of the three lower ferric chloride hydrates.