Contribution from the Department of Chemistry,
Michigan State University, East Lansing, Michigan 48823

Synthesis and Crystal Structure of Triytterbium Chloroorthosilicate, $Yb_3(SiO_4)_2Cl$

CONRAD AYASSE and HARRY A. EICK*

Received November 15, 1972

Crystals of a new lanthanide orthosilicate, $Yb_3(SiO_4)_2Cl$, were prepared by vapor transport in a chlorine atmosphere. A complete single-crystal structural analysis showed that the crystal class is orthorhombic, $a = 6.731$ (2), $b = 17.556$ (8), $c = 6.129$ (2) Å. With 4 formula units in space group *Pnma* the calculated density is 6.77 g cm^{-3}. A full-matrix least-squares structure factor refinement effected with the 460 observed reflections collected by the ω-scan procedure and anisotropic thermal parameters for the Yb atoms gave $R = 3.0\%$ and $R_w = 2.2\%$. The ytterbium atoms are in two sites and are eight-coordinated as YbO_6Cl_2 square antiprisms and as YbO_7Cl dodecahedra that can also be described as $Yb(SiO_4)_5Cl$ octahedra. The presence of the chlorine atoms causes some long Yb–O bonds.

Introduction

The preparation of a series of lanthanide oxide chlorides which exhibit hexagonal symmetry and an unknown structure type has been reported.[1] During an attempt to repeat this preparation for YbOCl and grow a single crystal by heating the powder under an atmosphere of chlorine, a few transparent crystals which displayed orthorhombic symmetry were found. A detailed structural analysis of this orthorhombic phase was undertaken to elucidate this apparent discrepancy in symmetry.

Experimental Section

Thin transparent plate crystals, which were later determined to be $Yb_3(SiO_4)_2Cl$, were obtained when YbOCl was heated at 1150° for 5 days and subsequently cooled slowly. The noncrystalline YbOCl powder, prepared by dehydration of $YbCl_3 \cdot xH_2O$ at 600° in air,[2] was assumed to be stoichiometric and was sealed in a quartz ampoule under approximately 1 atm of Cl_2. In addition to $Yb_3(SiO_4)_2Cl$ a second phase, which consisted of thin white sheets and slivers found adjacent to and on the tube wall, contributed weak extra lines to the X-ray powder diffraction pattern but could not be identified. The X-ray powder diffraction pattern for $Yb_3(SiO_4)_2Cl$, obtained with a forward-focusing Guinier-Haegg camera, 80-mm radius, Pt internal standard ($a = 3.92370$ (1) Å, Cu Kα radiation),[3] has been submitted to the ASTM file.

A small quantity of the crystalline plates was dissolved in nitric acid and portions of this solution were treated with ammonia and silver nitrate. The precipitation which resulted in each case indicated the presence of Yb^{3+} and Cl^- ions. The presence of ytterbium was substantiated by X-ray fluorescence analysis. The chemical formula was determined ultimately from the structural analysis.

The crystal used for the structural analysis was a thin plate with dimensions 0.078 × 0.070 × 0.008 mm and was oriented such that the $00l$ reflections were ϕ independent. The density calculated for 4 molecules per cell was 6.774 g cm^{-3}; there were insufficient crystals for a dependable measurement. From the extinction conditions observed in precession photographs, $hk0$ where $h = 2n + 1$ and $0kl$ where $k + l = 2n + 1$, the space group was established as either *Pnma* (No. 62) or $Pn2_1a$ (No. 33).[4] The structure was assumed to be centric, and further refinement was based on the former group. Lattice parameters and intensities were measured on a Picker four-circle goniometer (Mo Kα radiation, $\lambda(\alpha_1)$ 0.07093 nm; graphite monochromator) interfaced with a PDP-8 computer, through use of orientation, least-squares, and data collection programs of Busing, *et al.*[5] The lattice constants $a = 6.731$ (2), $b = 17.556$ (8) and $c = 6.129$ (2) Å, at 23 (2)°, were obtained from the least-squares refinement of 12 high-angle reflections.

Intensity data were collected by the ω-scan procedure. A scan rate of 0.25°/min was used over a 0.8° scan range; the α_1, α_2 dispersion factor was 0.692. The background was counted for 10 sec at each end point of the scan and was assumed to vary linearly through the scan range. Attenuators were not used. The full set of 793 reflections with $2.5 < 2\theta < 50°$ was measured in one octant. Reflections (200) and (040) were used as standards and were counted after every 50 reflections. The count rate of these standards remained constant within counting statistics.

Data reduction was accomplished on a CDC 6500 computer. A standard deviation, $\sigma(I)$, was assigned to each reflection according to the equation

$$\sigma(I) = [N_T + R^2(N_{bg1} + N_{bg2}) + (0.01N_{pk})^2]^{1/2}$$

in which N refers to the number of counts, pk the peak, T the total, and bg the background; R is the ratio of the counting times (t) for the peak and the background

$$R = t_{pk}/(t_{bg1} + t_{bg2})$$

Of the 656 space group permitted reflections, 461 were observed according to the criterion

$$\text{intensity} - \text{background} \geq 2\sigma(I)$$

An absorption correction was made by the analytical method with the program of Katz and Knox;[6] a calculated linear absorption coefficient of 410.7 cm^{-1} was used. Transmission coefficient extremes were 0.113 and 0.724, respectively, for the (011) and (101) reflections.

Solution and Refinement of the Structure

The usual Lorentz and polarization corrections were effected with the Program INCOR[7] modified to include a correction for the graphite monochromator. From a three-dimensional Patterson map eight Yb atoms were determined to occupy position 8(d). Two cycles of full-matrix least-squares structure factor refinement with isotropic temperature factors and unit weights gave $R = 30\%$. These R indices were computed as $R = \Sigma|\Delta F|/\Sigma|F_o|$ and $R_w = (\Sigma w(\Delta F)^2/\Sigma w F_o{}^2)^{1/2}$.[8] The function $\Sigma w(\Delta F)^2$ was minimized.

Difference Fourier syntheses were then used to locate the other atoms. Inclusion of the remaining ytterbium atoms in site 4(c) reduced R to 15% and inclusion of the chlorine atoms in site 4(c) reduced it to 9%. At this point silicon and oxygen atoms were identified in the difference map, and with their inclusion the discrepancy index, R, reduced to 4%. With isotropic thermal parameters for all the atoms, but with weights related to the counting statistics, R_w reduced to 2.4%.

Use of anisotropic thermal parameters for the Yb atoms and 460 of the 461 observed reflections gave the final discrepancy indices $R_w = 2.2\%$, $R = 3.0\%$. The ϕ-independent (004) reflection was deleted because the observed intensity was low by $\sim$25%, apparently

---

(1) N. A. Fischel, Ph.D. Thesis, Michigan State University, East Lansing, Mich., 1970.

(2) W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **9**, 136 (1959).

(3) J. D. H. Donnay, Ed., "Crystal Data Determinative Tables," 2nd ed, American Crystallographic Association, Washington, D. C., 1963, p 841.

(4) "International Tables for Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1963.

(5) W. R. Busing, R. D. Ellison, H. A. Levy, S. P. King, and R. T. Roseberry, Report ORNL-4143, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1968.

(6) K. Knox and I. Katz, *Rev. Sci. Instrum.*, **38**, 289 (1967).

(7) Crystallographic programs for data reduction, least-squares refinement, and distance and angles provided by A. Zalkin.

(8) W. H. Hamilton, "Statistics in Physical Science," Rowland Press, New York, N. Y., 1964, p 158.

Table I. Least-Squares Parameters for $Yb_3Si_2O_8Cl^a$

Atom	Set	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Yb(1)	8(d)	130 (1)	903 (1)	1276 (2)	110 (15)	29 (2)	254 (19)	−5 (6)	0 (22)	3 (9)
Yb(2)	4(c)	2902 (1)	2500	8849 (2)	94 (24)	34 (3)	287 (31)	0	3 (33)	0
Si	8(d)	232 (7)	996 (3)	6213 (12)	0.38 (8)^b					
Cl	4(c)	367 (10)	2500	2357 (11)	0.83 (11)					
O(1)	8(d)	89 (17)	310 (6)	7935 (18)	0.58 (22)					
O(2)	8(d)	1915 (17)	966 (7)	4470 (19)	1.00 (25)					
O(3)	8(d)	3284 (17)	1187 (7)	282 (20)	0.55 (23)					
O(4)	8(d)	356 (18)	1750 (6)	7717 (20)	0.72 (23)					

^{a} The positional parameters are multiplied by 10^4. The anisotropic thermal parameters are multiplied by 10^5 and are of the form $\exp(-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl])$. ^{b} Isotropic thermal parameters.

Table II. Bond Distances and Angles^a

Distances, Å	
$Yb(1)_8$-$O(1)_5$	2.19
-$O(1)_8$	2.30
-$O(2)_8$	2.30
-$O(2)_1$	2.22
-$O(3)_8$	2.26
-$O(3)_1$	2.50
-$O(4)_8$	2.64
-Cl_8	2.885
$Yb(2)_1$-$O(3)_1$	2.48
-$O(3)_7$	2.48
-$O(4)_1$	2.27
-$O(4)_2$	2.32
-$O(4)_7$	2.27
-$O(4)_8$	2.32
-Cl_1	2.745
-Cl_8	2.856
Si_8-$O(1)_8$	1.60
-$O(2)_8$	1.56
-$O(3)_1$	1.64
-$O(4)_8$	1.62
Cl–Cl	3.37

Angles, deg		
X	Y	
X–$Yb(1)_8$–Y		
$O(1)_5$	$O(1)_8$	75.8
	$O(2)_8$	83.9
	$O(2)_1$	91.6
	$O(3)_8$	109.7
	$O(3)_1$	88.5
	$O(4)_8$	137.2
	Cl_8	153.9
$O(1)_8$	$O(2)_8$	141.9
	$O(2)_1$	80.0
	$O(3)_8$	82.6
	$O(3)_1$	146.8
	$O(4)_8$	61.3
	Cl_8	130.2
$O(2)_8$	$O(2)_1$	133.1
	$O(3)_8$	148.2
	$O(3)_1$	71.2
	$O(4)_8$	81.2
	Cl_8	74.3
$O(2)_1$	$O(3)_8$	148.2
	$O(3)_1$	71.2
	$O(4)_8$	81.8
	Cl_8	93.0
$O(3)_8$	$O(3)_1$	130.5
	$O(4)_8$	66.5
	Cl_8	78.2
$O(3)_1$	$O(4)_8$	127.8
	Cl_8	68.9
$O(4)_8$	Cl_8	68.9
X–$Yb(2)_1$–Y		
$O(4)_8$	$O(4)_1$	94.7
	$O(4)_7$	137.8
	$O(4)_2$	69.1
	$O(3)_1$	63.0
	$O(3)_7$	126.9
	Cl_1	140.1
	Cl_8	85.6
$O(4)_1$	$O(4)_7$	70.9
	$O(4)_2$	137.8
	$O(3)_1$	69.4
	$O(3)_7$	136.5
	Cl_1	76.7
	Cl_8	133.4
$O(4)_7$	$O(4)_2$	94.7
	$O(3)_1$	136.5
	$O(3)_7$	69.4
	Cl_1	76.7
	Cl_8	133.4
$O(4)_2$	$O(3)_1$	126.9
	$O(3)_7$	63.0
	Cl_1	140.1
	Cl_8	85.6
$O(3)_1$	$O(3)_7$	136.7
	Cl_1	77.7
	Cl_8	69.6
$O(3)_7$	Cl_1	77.7
	Cl_8	69.6
Cl_1	Cl_8	74.0
X–Si_8–Y		
$O(1)_8$	$O(2)_8$	118.0
	$O(3)_1$	118.3
	$O(4)_8$	104.1
$O(2)_8$	$O(3)_1$	161.9
	$O(4)_8$	112.7
$O(3)_1$	$O(4)_8$	101.1

^{a} Standard errors: (a) bond lengths Yb–O and Si–O, 0.01 Å; Yb–Cl, 0.004 Å; (b) bond angles Yb–Cl–Yb, 0.1°; Yb–O–Si, 0.7°; all others, 0.4°.

as a result of primary extinction or multiple reflection. Both β_{12} and β_{23} were fixed at zero for the atoms in the 4(c) site.[9] The scattering factors reported by Cromer and Waber[10] were used for Yb^{3+} and Cl^-, those of Tokonami[11] for O^{2-}, and those listed in ref 12 for Si^{4+}. These curves were corrected for both the real and imaginary parts of the anomalous dispersion with Cromer's[13] values for $\Delta f'$ and $\Delta f''$. Correction for secondary extinction did not appear to be necessary, and none was carried out. In the final difference synthesis, the maximum electron density corresponded to 1.76 e/Å^3. In the last cycle of refinement the largest parameter shift was 0.25 of the standard deviation of the coordinate.

In Table I the final position and thermal parameters and their standard errors are listed. Selected bond distances and angles, computed with the program DISTAN,[7] are compiled in Table II. In this table the subscripts refer to the transformations for the general site of space group *Pnma* as they are listed in ref 4 and are intended to identify uniquely each atom in the unit cell.[14]

Discussion of the Structure

The structure is composed of three kinds of anion polyhedra which are shown in Figure 1. The Yb(1)-O_7Cl polyhedron is a dodecahedron represented by two interlocking tetrahedra [$O(4)_8$, $O(1)_8$, $O(3)_1$, $O(2)_8$ and $O(2)_1$, $O(3)_8$, $O(1)_5$, Cl_8]. The Yb(2)-O_6Cl_2 polyhedron is a distorted square antiprism, and the SiO_4 polyhedron, as usual, is an irregular tetrahedron. Figure 1A shows all the atoms which occur in the 8(d) general site. The Yb(1), Si, O(2), and O(3) atoms are almost coplanar at approximately $y = {}^1/_{12}$, ${}^5/_{12}$, ${}^7/_{12}$, and ${}^{11}/_{12}$ (*cf.* Figure 2B). The Yb(1) atom is coordinated to tetrahedra above and below (z direction) by edge sharing and to three other tetrahedra by corner sharing, so that each Yb(1) cation is surrounded by five SiO_4 tetrahedra and the centers of four of these occur approximately in a plane ($y = {}^1/_{12}$). The center of the fifth tetrahedron, which is joined *via* the $O(1)_5$ atom, is in the next unit cell and is not shown. A chlorine atom is located on the far side of the Yb(1)-$(SiO_4)_4$ plane, so that the coordination can also be considered a distorted octahedron consisting of five (SiO_4) units and one Cl atom. The two tetrahedra which have centers closest to the Yb(1) atom (above and below) have the maximum separation across the diagonal of the $(SiO_4)_4$ distorted square.

Tetrahedral faces which are closest to each other [for example, $O(3)_1$, $O(4)_8$, $O(1)_8$ and $O(2)_1$, $O(4)_1$, $O(1)_1$

---

(9) W. J. A. M. Peterse and J. H. Palm, *Acta Crystallogr.*, 20, 147 (1966).

(10) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965).

(11) M. Tokonami, *Acta Crystallogr.*, 19, 486 (1965).

(12) "International Tables for Crystallography," Vol. 2, Kynoch Press, Birmingham, England, 1963.

(13) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

(14) A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1140.

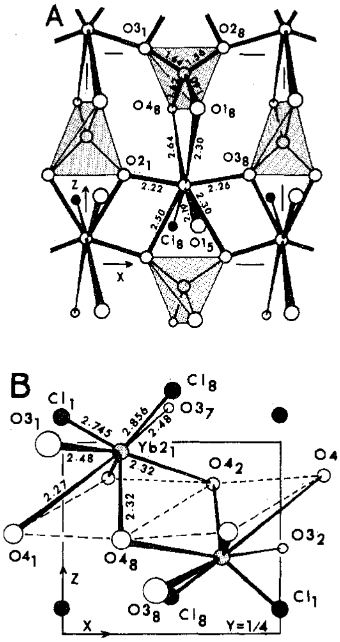

Figure 1. Perspective drawings of the coordination about Yb(1) and Si (A) and about Yb(2) (B) in $Yb_3(SiO_4)_2Cl$.

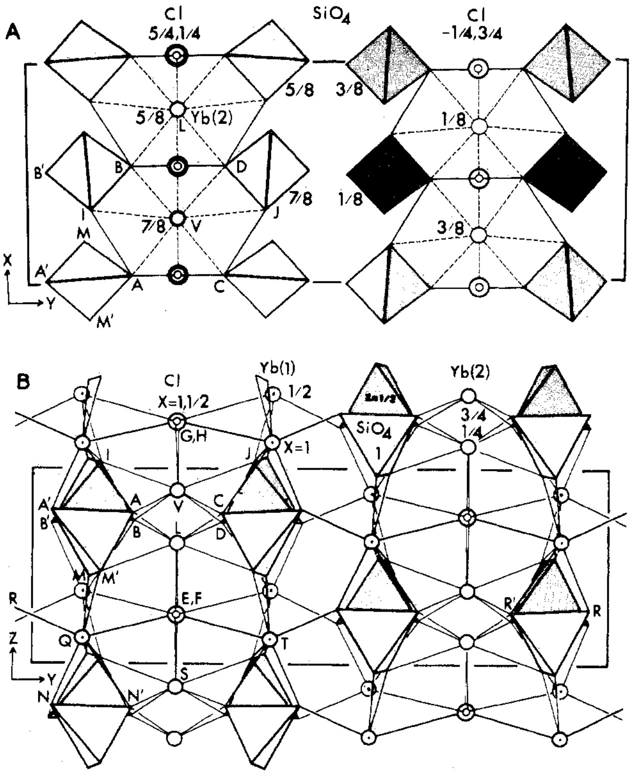

Figure 2. Projections in the z direction (A) and in the x direction (B) of $Yb_3(SiO_4)_2Cl$. The stated coordinates are approximate. Atom types are identified at the top of the figures.

centered at x, $z = 0$, $^5/_8$ and $^1/_2$, $^7/_8$] are twisted so that they are approximately parallel and thereby minimize the oxygen-oxygen interactions. The shortest oxygen-oxygen distance in the structure (2.47 Å), for the $O(3)_1$-$O(2)_8$ atoms, occurs within the tetrahedra. The SiO_4 units are discrete and use each kind of oxygen atom.

The Yb(2) square antiprisms, which are shown in Figure 1B, share edges at the O(4) anions and form chains in the x direction. The chlorine apices of these square antiprisms point alternately up and down in the z direction. Adjacent chains in the z direction are joined only at a single chlorine atom.

Figure 2A shows the entire structure viewed down the z axis. The solid lines across the SiO_4 tetrahedra join the oxygen atoms nearest the viewer. The Yb(1) atoms, which are almost directly above and below the tetrahedra, are not shown. Points A, B, C, D, I, J show the positions of the oxygen atoms for the Yb(2) cation located at point V, and the dashed lines designate bonds. Each square antiprism shares edges with two SiO_4 tetrahedra. In the absence of the Yb(1) atoms there is no bonding across the $y = 0$ and $y = ^1/_2$ planes. Although it cannot easily be seen in the figures, the Yb(2) and Yb(1) polyhedra share a face—for example, in Figure 1 they share the atoms $O(3)_8$, $O(4)_8$, and Cl_8. A view down the x axis (Figure 2B) shows the O_4 planes of the square antiprisms seen along the edges BD and AC. The Yb(1) atom at Q is bonded to the tetrahedron above at M and M′, to the tetrahedron below at N and N′, and to a third tetrahedron at R in the next cell; the other two tetrahedra are above and below NN′.

The chlorine atom (E, F) is four-coordinated to 2Yb(1) and 2Yb(2) at points Q, T, L, and S in a plane which forms a distorted square. The sum of the Yb-Cl-Yb angles in the plane is 361.1 (6)°. Like atoms are in the trans configuration and the Yb(2) atoms are collinear with Cl. The bond angles $Yb(1)_2$-Cl-$Yb(2)_8$ and $Yb(1)_8$-Cl-$Yb(2)_8$ are 81.6 (1)° and the other two are 98.9 (1)°. The chlorine atoms are in channels which run in the x direction. Points E,F in Figure 2B show that no other atoms are centered inside a cylinder of radius 6.5 Å.

Both O(1) and O(2) are three-coordinated in a plane to $Yb(1)_2Si$. The anion coordination of $O(2)_1$ can be seen in Figure 1A. In each case the sum of the M-O-M angles is 360 (2)°. The O(3) atoms are tetrahedrally coordinated to $Yb(1)_2Yb(2)Si$. Although O(4) is tetrahedrally coordinated to $Yb(1)Yb(2)_2Si$, the Yb(1)-O(4) bond distance is very long (2.64 Å) and the O(4) atom lies close to the plane of the other cations. The sum of the M-O-M angles in that plane is 344 (2)° compared with 360° for the case of exact planarity.

Conclusions

The Si-O bond lengths vary between 1.56 and 1.64 Å (Table III) comparable to values observed in the various modifications of quartz, 1.52-1.69 Å.[15]

Most of the Yb-O bond lengths are close to the value expected from the sum of the ionic radii, 2.26 Å.[16] The three long bond distances $Yb(1)_8$-$O(4)_8$, $Yb(1)_8$-O(3), and Yb(2)-O(3) can be explained by a consideration of the oxygen-chlorine distances. It can be seen in Figure 1 that a decrease in the Yb(2)-$O(3)_1$ bond length (2.48 Å) or in the Yb(1)-$O(3)_1$ bond length (2.50 Å) requires the $O(3)_1$ atom to move toward the Cl_8 atom. However the $O(3)_1$-Cl_8 distance is already the shortest oxygen-chlorine distance in the structure, 3.06 Å, and so anion-anion interaction can explain these long metal-oxygen bonds. Anion-anion interaction can also explain the very long Yb(1)-$O(4)_8$ bond distance (2.64 Å) since a decrease in this value would cause the $O(4)_8$-Cl_8 distance, already the second shortest O-Cl distance (3.13 Å), to decrease further. This can be seen in Figure 1A where the $O(4)_8$ and Cl_8 anions are both on the

---

(15) R. W. G. Wyckoff, "Crystal Structures," Vol. IV, Wiley, New York, N. Y., 1963.

(16) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 25, 925 (1969).

far side of the Yb(1)-$(SiO_4)_4$ plane. The shortest O(2)-Cl distance is 3.165 Å. Only the O(5) oxygen atoms are completely separated from the chlorines; one of these gives the shortest Yb-O bond: Yb(1)-$O(1)_5$, 2.19 Å.

Registry No. $Yb_3(SiO_4)_2Cl$, 37291-26-2.

Acknowledgment. Support of the U. S. Atomic Energy Commission [Contract AT(11-1)-716] is acknowledged gratefully.

Contribution No. 1977 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Group VI Metal Carbonyl Phosphine Complexes. Hydrogen-Deuterium Exchange and the Crystal Structure of *cis*-Tetracarbonyldiphosphinechromium(0)

L. J. GUGGENBERGER, U. KLABUNDE,* and R. A. SCHUNN

Received September 27, 1972

Convenient, large-scale syntheses of the phosphine complexes $Cr(CO)_5PH_3$, *cis*-$M(CO)_4(PH_3)_2$, and *fac*-$M(CO)_3(PH_3)_3$ (M = Cr, Mo, W) are described and results of hydrogen-exchange experiments of some of these complexes are presented. The crystal and molecular structures of *cis*-$Cr(CO)_4(PH_3)_2$ were determined from counter data. Crystals are orthorhombic, space group $Pna2_1$, with cell dimensions of a = 12.677 (9), b = 11.415 (9), and c = 6.759 (6) Å. The structure was refined to a conventional R of 0.050 for 621 observed reflections. The molecular structure has an octahedrally coordinated (within 1.5°) chromium atom with two cis equatorial PH_3 ligands (Cr–P = 2.349 (2) Å), two equatorial CO ligands (Cr–C = 1.847 (4) Å, C–O = 1.162 (6) Å), and two axial CO ligands (Cr–C = 1.914 (7) Å, C–O = 1.11 (3) Å). The structural parameters are consistent with related structures and current σ–π bonding schemes.

Introduction

Phosphine complexes of chromium, molybdenum, and tungsten were among the first examples of transition metal phosphine complexes characterized.[1,2] Examples of group VI phosphine complexes include $Cr(CO)_{6-x}(PH_3)_x$ (x = 1,[1,3] 2,[2,4] 3,[5] 4[6]), $Mo(CO)_{6-x}(PH_3)_x$ (x = 1,[1,3] 2,[2,4,6] 3[7]), and $W(CO)_{6-x}(PH_3)_x$ (x = 1,[1,3] 2[2,4]).

We report here the synthesis and characterization of the new complex *fac*-$W(CO)_3(PH_3)_3$, convenient, large-scale syntheses of $Cr(CO)_5PH_3$, *cis*-$M(CO)_4(PH_3)_2$, and *fac*-$M(CO)_3(PH_3)_3$ (M = Cr, Mo), and hydrogen-exchange experiments with some of these complexes. We report also the crystal and molecular structure of *cis*-$Cr(CO)_4(PH_3)_2$; structural parameters are compared with other chromium-carbonyl complexes with phosphorus-containing ligands.[8-14]

Experimental Section

Phosphine, PH_3, is a highly toxic, spontaneously flammable gas. At low pressure, its reaction with oxygen is violent. The off-gases from a reaction mixture should be burned.

Commercially available phosphine (Matheson) contains traces of hydrogen and *biphosphine, P_2H_4, a highly toxic and spontaneously flammable liquid.* The biphosphine was removed by passing the gas through a trap at −78°.

All procedures were carried out under nitrogen in either a nitrogen drybox or equipment modified with nitrogen inlet tubes. Prior to use solvents were either distilled from CaH_2 or passed over Linde 4A molecular sieves under nitrogen.

$Cr(CO)_5PH_3$. Phosphine was bubbled slowly through a solution of 56.0 g (0.16 mol) of $[(C_2H_5)_4N][CrCl(CO)_5]$[15] in 300 ml of methanol at 0° for 2 hr. Part of the methanol was removed under reduced pressure and the solution was cooled. The pale yellow crystals of $Cr(CO)_5PH_3$ which formed were collected on a filter. The crystals, which contained 5–10% $Cr(CO)_4(PH_3)_2$ as an impurity, were dissolved in 150 ml of tetrahydrofuran and to this solution 19 g of 2,4-pentanedione and 0.5 g of NaOH in 40 ml of water were added. The solution was stirred for 1 hr at 25° and was filtered to remove a yellow solid,[16] and 100 ml of water was added to the filtrate. After part of the solvent was removed under reduced pressure, pale yellow crystals of pure $Cr(CO)_5PH_3$ were collected and sublimed at 1 μ (65°). The yield of $Cr(CO)_5PH_3$ was 26.7 g (74%). *Anal.* Calcd for $C_5H_3CrO_5P$: C, 26.4; H, 1.3; Cr, 22.9; O, 35.2; P, 14.1. Found: C, 26.9; H, 1.9; Cr, 22.4; O, 36.0; P, 13.4.

***cis*-$Cr(CO)_4(PH_3)_2$.** An 800-ml stainless steel pressure autoclave was charged with 49.3 g (0.134 mol) of $Cr(CO)_4DTO$[17] (DTO = 2,2,7,7-tetramethyl-3,6-dithiaoctane), 450 ml of tetrahydrofuran, and 25 g (0.74 mol) of phosphine.

The autoclave was heated to 65° and kept at this temperature for 8 hr. After cooling to 25°, the autoclave was vented and twice purged with nitrogen to ensure complete removal of the phosphine. The solution was transferred in air to a 1000-ml round-bottom flask and the solvent was removed under reduced pressure. The yellow crystals were collected, washed with petroleum ether, and dissolved in 500 ml of hot diethyl ether. The solution was filtered through Celite. After removal of about 400 ml of the ether under reduced pressure, 27.0 g (89% yield) of $Cr(CO)_4(PH_3)_2$ was collected on a filter and dried at 25° (0.1 mm, 16 hr). *Anal.* Calcd for $C_4H_6CrO_4P_2$: C, 20.7; H, 2.6; Cr, 22.4; O, 27.6; P, 26.7. Found: C, 20.7; H, 2.8; Cr, 22.0; O, 27.1; P, 27.2.

***cis*-$Mo(CO)_4(PH_3)_2$.** The above procedure was used with 67.0 g

---

(1) E. O. Fischer, E. Louis, and R. J. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, 7, 136 (1968).

(2) (a) F. Klanberg and E. L. Muetterties, *J. Amer. Chem. Soc.*, 90, 3296 (1968); (b) F. Klanberg, U. S. Patent 3,695,853 (1972).

(3) E. O. Fischer, E. Louis, W. Bathelt, and J. Muller, *Chem. Ber.*, 102, 2547 (1969).

(4) E. O. Fischer, E. Louis, and W. Bathelt, *J. Organometal. Chem.*, 20, 147 (1969).

(5) E. O. Fischer, E. Louis, and C. G. Kreiter, *Angew. Chem., Int. Ed. Engl.*, 8, 377 (1969).

(6) E. O. Fischer and E. Louis, *J. Organometal. Chem.*, 18, P26 (1969).

(7) C. G. Barlow and G. C. Holywell, *J. Organometal. Chem.*, 16, 439 (1969).

(8) M. J. Bennett, F. A. Cotton, and M. D. LaPrade, *Acta Crystallogr., Sect. B*, 27, 1899 (1971).

(9) G. Huttner and S. Schelle, *J. Organometal. Chem.*, 19, P9 (1969).

(10) G. Huttner and S. Schelle, *J. Cryst. Mol. Struct.*, 1, 69 (1971).

(11) O. S. Mills and A. D. Redhouse, *J. Chem. Soc. A*, 1274 (1969).

(12) H. S. Preston, J. M. Stewart, H. J. Plastas, and S. O. Grim, *Inorg. Chem.*, 11, 161 (1972).

(13) H. J. Plastas, J. M. Stewart, and S. O. Grim, *J. Amer. Chem. Soc.*, 91, 4326 (1969).

(14) F. A. Cotton and M. D. LaPrade, *J. Amer. Chem. Soc.*, 91, 7000 (1969).

(15) E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 2068 (1963).

(16) This solid is the complex $Cr(CO)_4[PH_2C(CH_3)(OH)]_2CH_3]$; U. Klabunde, U. S. Patent 3,702,336 (1972).

(17) G. R. Dobson, *Inorg. Chem.*, 8, 90 (1969).