

The Crystal and Molecular Structure of Dichloro-*N,N'*-ethylenebis(salicylideneiminato)titanium(IV)-Tetrahydrofuran

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$C_{16}H_{14}N_2O_2Cl_2Ti \cdot C_4H_8O$ crystallizes in space group $C2/c$ with $a = 12.357$, $b = 18.896$, $c = 9.210$ Å, $\beta = 107.15^\circ$; $Z = 4$. The structure has been determined by Patterson and Fourier methods and refined to an R value of 0.065, using three-dimensional diffractometer data. The structure consists of monomeric units of $C_{16}H_{14}N_2O_2Cl_2Ti$ and C_4H_8O , both with symmetry C_2 . The titanium atom is approximately octahedrally coordinated to two chlorine atoms in a *trans* configuration, two *cis* oxygen atoms and two *cis* nitrogen atoms. The bond distances Ti-Cl, Ti-O and Ti-N are respectively 2.346, 1.835 and 2.141 Å.

Introduction

The reaction between tris(tetrahydrofuran)Ti(III)-trichloride and salen [*N,N'*-ethylenebis(salicylideneimine)] has been investigated at UMIST by F. L. Bowden and D. Ferguson as part of a study of titanium(III) coordination chemistry. Addition of a tetrahydrofuran (THF) solution of salen to a solution of $(THF)_3Ti(III)Cl_3$ in the same solvent, at room temperature and in an atmosphere of dry nitrogen, produces a green precipitate, which, after some 12 hours and in absence of air, changes into red crystals. The possibility that the red product contained titanium(IV) was suggested by chemical analysis, and the present crystallographic analysis was undertaken to examine this possibility and to extend the range of information on titanium-Schiff's base complexes.

Experimental

By recrystallization from THF in an atmosphere of dry nitrogen, dark-red crystals of the compound were obtained as thin needles elongated along the c axis and usually twinned. An untwinned needle was selected with a cross section 0.25×0.15 mm, and was partially dissolved in THF to a length of 0.50 mm. Although the crystals were somewhat unstable in moist air, the selected crystal, protected by a collodion film, was stable throughout the period of data collection. The intensity data were collected on an automatic four-circle Hilger & Watts diffractometer using Mo $K\alpha$ radiation, Zr filter and $\omega/2\theta$ scan. Intensities were measured for each independent, non-systematically

absent, reflexion with $\sin \theta/\lambda < 0.6388$ Å⁻¹, integrating over 60 steps of 1 sec. 2240 reflexions were recorded (of which only 1392 were greater than 2σ in F) in four shells with increasing values of $\sin \theta/\lambda$. Lorentz and polarization corrections were applied as usual. An absorption correction was not considered necessary, because μR for the crystal was 0.20.

The scattering factors for the hydrogen atoms were taken from the data of Stewart, Davidson & Simpson (1965), and for all the other atoms from the data of Cromer & Waber (1965). Allowance was made for the $\Delta f'$ and $\Delta f''$ terms for the Ti and Cl atoms.

Crystal and molecular data

Dichloro-*N,N'*-ethylenebis(salicylideneiminato)-titanium(IV)-tetrahydrofuran,

$C_{16}H_{14}N_2O_2Cl_2Ti \cdot C_4H_8O$, F.W. 457.23

Monoclinic: $a = 12.357$ (2), $b = 18.896$ (1), $c = 9.210$ (2) Å, $\beta = 107.146$ (5)°; $U = 2055$ Å³, calculated density = 1.48 g.cm⁻³ for $Z = 4$, experimental density = 1.49 g.cm⁻³, $F(000) = 944$, absorption coefficient = 7.2 cm⁻¹ ($\lambda = 0.71069$ Å).

Systematic absences: hkl absent when $h+k \neq 2n$, $h0l$ absent when $h \neq 2n$ or when $l \neq 2n$; these absences are characteristic of space groups Cc or $C2/c$.

Determination of the structure

A sharpened three-dimensional Patterson synthesis indicated the space group $C2/c$ with the molecule of $TiCl_2(\text{salen})$ in a special position on the twofold axis. The positions of the Ti and Cl atoms were identified and used as the starting point for a three-dimensional Fourier synthesis, which showed all the atoms of the $TiCl_2(\text{salen})$ molecule except the atoms C(3), C(4) and

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C(5) of the benzene ring. The Fourier synthesis computed using the positions so obtained showed the last three atoms of the molecule; from this it also became evident that there was a molecule of THF of solvation in the crystal. The R value at this stage was 0.29.

Refinement

Three cycles of full-matrix least-squares refinement, varying one scale factor and the positional and isotropic thermal parameters for all the non-hydrogen atoms, reduced R to 0.13. One more cycle with anisotropic thermal parameters on the Ti and Cl atoms reduced R to 0.12. Only the 1392 observed reflexions were used.

Further anisotropic refinement was carried out using the *CRYLSQ* program written by F. A. Kundell. No attempt was made to locate the H atoms, but their positions were calculated after each cycle with significant positional shifts. In the calculation of structure factors their temperature factors were fixed as 10% greater than those of their bonding atoms. The unobserved reflexions were assigned the mean threshold values for their shells and they were allowed to contribute to the refinement only if $F_c > F$ (threshold).

A first refinement was attempted with all the reflexions collected; three full-matrix least-squares cycles with anisotropic temperature factors on all the non-hydrogen atoms reduced R to 0.093, but appreciable disagreement was observed for the great number of reflexions only just over the limit of 2σ . These reflexions were largely confined to the last shell and, because a redefinition of the threshold criterion would have left rather few scattered reflexions in this shell, it was considered best to eliminate the shell entirely. Accordingly the data were cut down at $\sin \theta/\lambda = 0.550 \text{ \AA}^{-1}$, reducing the total number of reflexions to 1432 ($1062 > 2\sigma$). After two more cycles the R value ($R_1 = \sum |d|/\sum |F_o|$) was 0.065, with an average improvement in the e.s.d.'s of the positional coordinates of 15%. Weights for the last cycle were calculated as $w =$

$1/(16 - 0.40|F_o| + 0.0030|F_o|^2)$. The constant weight of $1/10$ was used for the contributing unobserved reflexions (65 in the last cycle). In this cycle the largest shift/error was 0.4 and the average shift/error 0.1. A difference map calculated from the final parameters showed one

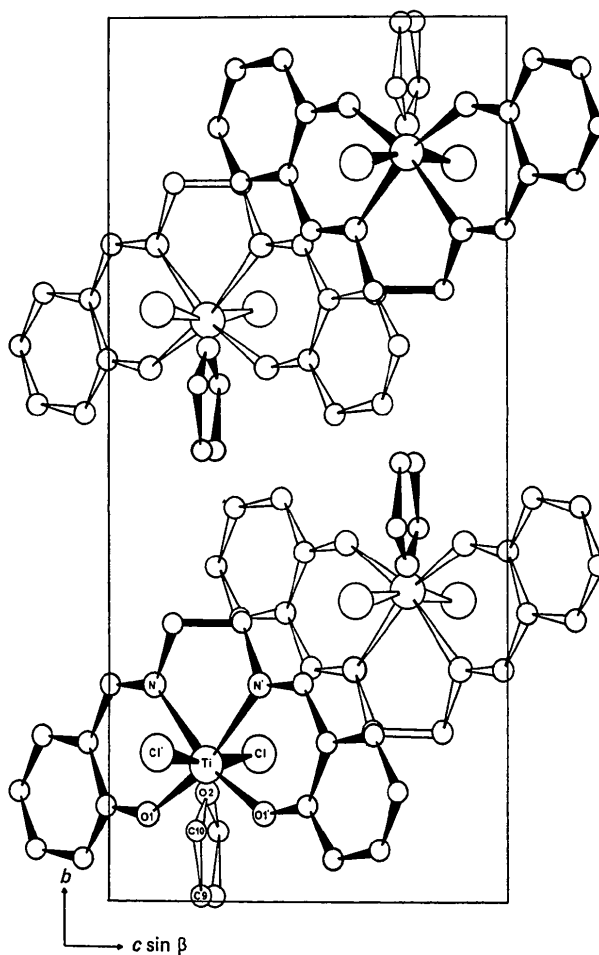


Fig. 1. Projection of the structure along a .

Table 1. Final parameters

E.s.d.'s are shown in parentheses; the vibration parameters (\AA^2) have been multiplied by 100.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti	0.00	0.15250 (8)	0.25	4.40 (10)	3.90 (9)	4.00 (9)	0.00	1.70 (7)	0.00
Cl	0.19370 (13)	0.16475 (10)	0.37761 (18)	4.67 (10)	7.58 (13)	5.41 (11)	0.58 (9)	1.02 (8)	0.21 (10)
O(1)	0.0339 (3)	0.0991 (2)	0.1028 (5)	6.00 (28)	4.53 (25)	5.08 (25)	-0.72 (21)	2.75 (22)	-0.70 (21)
N	0.0223 (4)	0.2417 (3)	0.1183 (6)	4.38 (30)	4.64 (33)	5.20 (33)	-0.31 (26)	0.76 (27)	1.03 (27)
C(1)	0.0672 (5)	0.2401 (4)	0.0091 (8)	5.0 (4)	6.6 (5)	5.8 (5)	-0.8 (4)	0.7 (4)	1.9 (4)
C(2)	0.1054 (5)	0.1770 (4)	-0.0497 (7)	4.2 (4)	7.5 (5)	4.4 (4)	-1.1 (4)	1.3 (3)	0.4 (4)
C(3)	0.1606 (5)	0.1838 (4)	-0.1654 (8)	4.0 (4)	10.6 (6)	5.0 (4)	-0.8 (4)	0.9 (3)	2.1 (4)
C(4)	0.1942 (6)	0.1251 (6)	-0.2263 (8)	5.5 (5)	13.6 (9)	5.0 (5)	-0.1 (5)	2.6 (4)	-0.6 (5)
C(5)	0.1752 (6)	0.0580 (5)	-0.1784 (9)	5.5 (5)	11.3 (7)	5.9 (5)	-1.4 (5)	2.7 (4)	-2.7 (5)
C(6)	0.1217 (5)	0.0496 (4)	-0.0667 (8)	4.3 (4)	8.1 (5)	5.7 (4)	-1.4 (4)	2.0 (4)	-1.8 (4)
C(7)	0.0874 (5)	0.1087 (4)	-0.0021 (7)	3.9 (4)	7.3 (5)	3.6 (4)	-0.4 (4)	1.5 (3)	-1.0 (4)
C(8)	-0.0154 (6)	0.3099 (3)	0.1629 (8)	6.4 (5)	5.0 (4)	8.0 (5)	0.4 (4)	1.7 (4)	1.2 (4)
O(2)	0.50	0.1232 (4)	0.25	8.4 (7)	7.4 (6)	18.2 (9)	0.00	0.3 (6)	0.00
C(9)	0.4364 (8)	0.0083 (6)	0.2336 (17)	8.4 (7)	10.3 (8)	26.7 (16)	-1.1 (6)	7.5 (9)	-0.1 (9)
C(10)	0.4041 (8)	0.0809 (5)	0.2189 (14)	6.6 (6)	9.6 (7)	18.7 (12)	0.3 (6)	2.0 (7)	-0.8 (7)

peak of $0.39 \text{ e.}\text{\AA}^{-3}$ near the Ti atom; no other features greater than $0.33 \text{ e.}\text{\AA}^{-3}$ were found.

The final values of the positional and vibrational parameters are listed in Table 1, together with their e.s.d.'s derived from the inverse least-squares matrix. The variations in the vibrational parameters for the different atoms show that the positions need some correction for librational motion. In view of the complexity of the structure this correction has not been attempted. The observed structure factors and those calculated with the parameters of Table 1 are obtainable as Supplementary Publication No. SUP 30003 (8 pp.).*

Because of the high vibration parameters found in the THF molecule, it was decided to check the occupancy of this molecular site. Refinement gave an occupation factor of 0.94 ± 0.03 with a slight increase in the *R* value. There is no significant evidence from this refinement or from the difference map that the site is not fully occupied.

Discussion

A projection of the structure is shown in Fig. 1. There is only one intermolecular contact of less than 3.4 \AA ; this is $3.367 (8) \text{ \AA}$ between O(1) and C(6) of two molecules related by the centre of symmetry at (0, 0, 0).

The molecule of $\text{TiCl}_2(\text{salen})$ is shown in Fig. 2 and the bond lengths and angles, with standard deviations, are reported in Table 2(a) and (b). The coordination around the Ti atom is approximately octahedral but considerably distorted, with angles varying from 76.1 to 113.3° . The O(1) and O(1') atoms are respectively above and below the plane defined by the Ti, N and N' atoms, the distances from it being 0.0974 \AA . The Cl atoms are not on the normal to this plane, but are

symmetrically bent towards the N atoms in a plane normal to the first plane. The angle Cl—Ti—Cl' is $168.7 (1)^\circ$. The intramolecular contacts with the Cl atom are reported in Table 2(c).

Table 2. Bond lengths, angles and intramolecular contacts with the Cl atom

(a) Bond lengths (\AA), with e.s.d.'s in parentheses

Ti—Cl	2.346 (2)	C(4)—C(5)	1.384 (14)
Ti—O(1)	1.835 (5)	C(5)—C(6)	1.386 (12)
Ti—N	2.141 (5)	C(6)—C(7)	1.388 (10)
O(1)—C(7)	1.334 (9)	C(7)—C(2)	1.401 (10)
N—C(1)	1.285 (10)	C(8)—C(8')	1.536 (10)
N—C(8)	1.469 (9)	O(2)—C(10)	1.387 (11)
C(1)—C(2)	1.446 (11)	C(10)—C(9)	1.424 (15)
C(2)—C(3)	1.431 (11)	C(9)—C(9')	1.511 (13)
C(3)—C(4)	1.363 (13)		

(b) Bond angles ($^\circ$), with e.s.d.'s in parentheses.

Cl—Ti—O(1)	90.2 (1)	C(1)—C(2)—C(7)	123.0 (7)
Cl—Ti—N	85.6 (1)	C(3)—C(2)—C(7)	118.1 (7)
Cl—Ti—Cl'	168.7 (1)	C(2)—C(3)—C(4)	120.2 (8)
Cl—Ti—O(1')	96.1 (1)	C(3)—C(4)—C(5)	120.9 (8)
Cl—Ti—N'	85.5 (1)	C(4)—C(5)—C(6)	120.2 (8)
O(1)—Ti—N	85.4 (2)	C(5)—C(6)—C(7)	120.0 (7)
O(1)—Ti—O(1')	113.3 (2)	O(1)—C(7)—C(2)	120.6 (6)
N—Ti—N'	76.1 (2)	O(1)—C(7)—C(6)	118.7 (6)
Ti—O(1)—C(7)	136.9 (4)	C(2)—C(7)—C(6)	120.6 (7)
Ti—N—C(1)	125.6 (5)	N—C(8)—C(8')	106.9 (5)
Ti—N—C(8)	115.3 (4)	C(10)—O(2)—C(10')	109.7 (8)
C(1)—N—C(8)	119.0 (6)	O(2)—C(10)—C(9)	109.7 (8)
N—C(1)—C(2)	125.2 (7)	C(10)—C(9)—C(9')	105.4 (9)
C(1)—C(2)—C(3)	118.9 (7)		

(c) Intramolecular contacts with the Cl atom (\AA).

Cl—N	3.053 (5)	Cl—O(1)	2.983 (4)
Cl—N'	3.050 (6)	Cl—O(1')	3.128 (5)

The two *N*-alkylsalicylaldimine (sal) groups of the salen group are approximately planar as shown in Table 3. The sal groups are bent in a stepped configuration and slightly twisted, as shown in Fig. 3; moreover the two planes of the ligand do not contain the Ti atom, which is equidistant from them. This distortion can be correlated, through the stress imposed by the

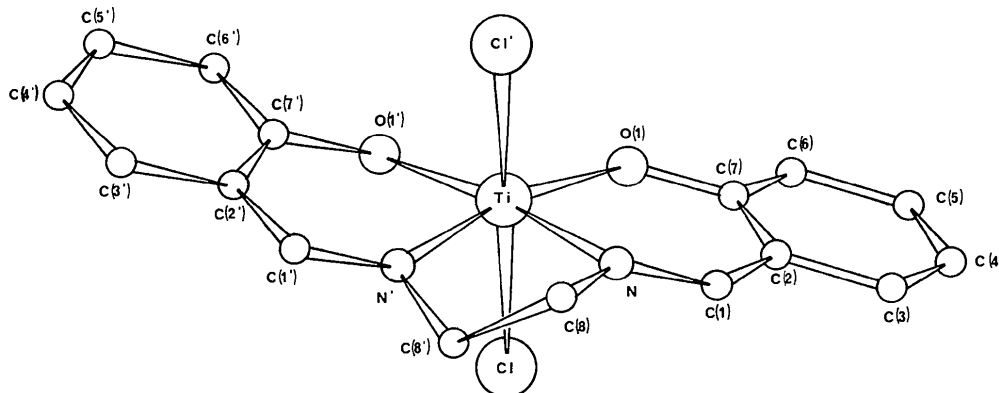


Fig. 2. The molecule of $\text{TiCl}_2(\text{salen})$.

* This table has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30003. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

ethylenediamine bridge, with the large difference in length of the bonds Ti–N and Ti–O. Among the monomeric complexes of salen studied, the salen group is nearly planar in $Co(salen) \cdot CHCl_3$ (Schaefer & Marsh, 1969) and in $[Cu(salen)]_2 \cdot NaClO_4$ (Milburn, Truter & Vickery, 1968), where $M-N \approx M-O$ and distorted in $FeCl(salen)$ (Gerloch & Mabbs, 1967), where $M-N > M-O$.

Table 3. Planarity of the *N*-alkylsalicylaldimine group

Displacements from least-square plane in Å.			
	Displacement	Other atoms	Displacement
C(8)	–0.035	Ti	0.360
N	0.055	C(8')	0.980
O(1)	–0.013	N'	0.793
C(1)	–0.022	O(1')	0.655
C(2)	0.016		
C(3)	0.007		
C(4)	–0.003		
C(5)	–0.011		
C(6)	–0.006		
C(7)	0.013		

$\chi^2 = 111.9$ (9 degrees of freedom).

The Ti–Cl bond length is 2.346 (2) Å and is comparable with the length in other hexacoordinate Ti compounds, namely 2.30 or 2.32 Å in $[TiCl(C_5H_7O_2)_2]_2O \cdot CHCl_3$ (Watenpaugh & Caughlan, 1967) and 2.283 Å in $TiCl_2(C_9H_6NO)_2$ (Studd & Swallow, 1968). There is a trend with the coordination number, as the length is 2.209 (or 2.219) Å in penta-coordinate $TiCl_2(C_6H_5O)_2$ (Watenpaugh & Caughlan, 1966), and 2.185 Å in tetra-coordinate $TiCl_4$ (Kimura, Kimura, Aoki & Shibata, 1956).

The Ti–O and Ti–N bond lengths of 1.835 (5) and 2.141 (5) Å are comparable with the lengths of 1.888 and 2.200 Å in $TiCl_2(C_9H_6NO)_2$. The Ti–N bond is considerably longer than the Ti–O bond. A comparison of these bond distances for different salen complexes is reported in Table 4. A similar examination of the 8-quinolinato complexes of several different metals was carried out by Schlemper (1967) and Studd & Swallow (1968). As suggested by Schlemper and Swallow (1968). As suggested by Schlemper, the difference between the bond lengths M–N and M–O can be rationalized in terms of Pearson's hard and soft acid–base concept (Pearson, 1963, 1966). Since the nitrogen is a softer base than oxygen, comparatively stronger bonds are formed with the nitrogen by rather

soft Lewis acids, Cu(II) and Co(II), than by hard acids, Ti(IV) and Fe(III).

The general pattern of bond distances in the salicylaldehyde group is in reasonable agreement with the values reported by Lingafelter & Braun (1966) for several salicylaldehyde complexes. The tetrahydrofuran molecule has a slightly twisted configuration, which is in agreement with the spectroscopic evidence (Scott, 1970). The displacements from the best plane are ± 0.018 Å for the atoms C(10) and C(10') and ± 0.026 Å for the atoms C(9) and C(9'). The high values of the thermal parameters and especially the strong anisotropy, with the principal motion nearly perpendicular to the plane of the molecule, suggest some kind of disorder across the plane of the molecule, but this disorder is not confirmed by the difference map. The static disorder as well as the anisotropic vibration can at least partially explain the very short bond C(9)–C(10).

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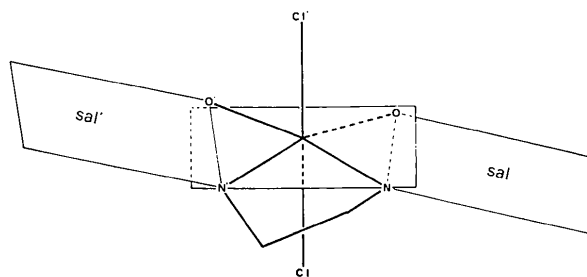


Fig. 3. Geometry of the molecule of $TiCl_2(salen)$.

References

- BAKER, E. N., HALL, D., MCKINNON, A. J. & WATERS, T. N. (1967). *Chem. Commun.* p. 134.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
 GERLOCH, M. & MABBS, F. E. (1967). *J. Chem. Soc. (A)*, p. 1598.
 KIMURA, M., KIMURA, K., AOKI, M. & SHIBATA, S. (1956). *Bull. Chem. Soc. Japan*, **29**, 95.
 LINGAFELTER, E. C. & BRAUN, R. L. (1966). *J. Amer. Chem. Soc.* **88**, 2951.

Table 4. Comparison of metal–nitrogen metal–oxygen bond lengths (Å) in different salen complexes

Compound	M–N	M–O	Difference	Reference
$Ti(IV)Cl_2(salen) \cdot THF$	2.14	1.84	0.25	This work.
$Fe(III)Cl(salen)$	2.08*	1.88*	0.20	Gerloch & Mabbs (1967).
$Cu(II)(salen) \cdot CHCl_3$	1.94*	1.91*	0.03	Baker, Hall, McKinnon & Waters (1967).
$Co(II)(salen) \cdot CHCl_3$	1.85*	1.85*	0.00	Schaefer & Marsh (1969).

*mean values

- MILBURN, G. H. W., TRUTER, M. R. & VICKERY, B. L. (1968). *Chem. Commun.* p. 1188.
 PEARSON, R. G. (1963). *J. Amer. Chem. Soc.* **85**, 3533.
 PEARSON, R. G. (1966). *Science*, **151**, 172.
 SCHLEMPER, O. (1967). *Inorg. Chem.* **6**, 2012.
 SCOTT, D. W. (1970). *J. Chem. Thermodyn.* **2**, 833.
 SCHAEFER, W. P. & MARSH, R. E. (1969). *Acta Cryst.* **B25**, 1675.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
 STUDD, B. F. & SWALLOW, A. G. (1968). *J. Chem. Soc. (A)*, p. 1961.
 WATENPAUGH, K. & CAUGHLAN, C. N. (1966). *Inorg. Chem.* **5**, 1782.
 WATENPAUGH, K. & CAUGHLAN, C. N. (1967). *Inorg. Chem.* **6**, 963.

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The High Pressure Synthesis, Crystal Structure, and Properties of CrP₄ and MoP₄

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The new compounds CrP₄ and MoP₄ have been prepared by reaction of the elements at pressures of 15 to 65 kbar in a tetrahedral anvil high-pressure device. They have isotypic monoclinic crystal structures, space group *C2/c*, and four formula units per unit cell. The cell dimensions are, for CrP₄: $a = 5.1914$ (5), $b = 10.7600$ (8), $c = 5.7712$ (6) Å, $\beta = 110.648$ (6)°, and for MoP₄: $a = 5.313$ (2), $b = 11.139$ (7), $c = 5.820$ (2) Å, $\beta = 110.64$ (4)°. The structure of CrP₄ was determined from three-dimensional single-crystal counter data, and refined by a full-matrix least-squares method with isotropic thermal parameters, yielding a conventional *R* value of 0.034 for 1017 observed reflections. Two nonequivalent P atoms are tetrahedrally coordinated, one by three P atoms and one Cr atom, the other by two P atoms and two Cr atoms. All P–P distances are within 2.21 ± 0.02 Å. The Cr atom is coordinated by six P atoms, forming a distorted octahedron. Cr–P distances vary between 2.32 and 2.39 Å. The [CrP₆] octahedra share edges, forming zigzag chains along the *c* direction. Temperature-dependent resistivity measurements of CrP₄ and MoP₄ samples indicate metallic conductivity. CrP₄ is Pauli paramagnetic. The structure and bonding of CrP₄ are discussed and compared with those of other phosphorus-rich compounds.

Introduction

The binary systems chromium–phosphorus and molybdenum–phosphorus have been investigated repeatedly in the past (Årstad & Nowotny, 1937; Nowotny & Henglein, 1938; Vogel & Kasten, 1939; Faller, Biltz, Meisel & Zumbusch, 1941; Schönberg, 1954; Bachmayer, Nowotny & Kohl, 1955; Lundström, 1962; Rundqvist, 1962*a,b*; Rundqvist & Lundström, 1963; Rundqvist, 1965; Sellberg & Rundqvist, 1965; Baurecht, Boller & Nowotny, 1971). Reviews have been given by Rundqvist (1962*c*) and Lundström (1969). There was agreement that the compounds CrP₂ and MoP₂ were the compounds richest in phosphorus found so far in the respective systems. The present study was undertaken to explore the influence of high pressure on the formation of phosphorus-rich compounds in these systems. The compounds CrP₄ and MoP₄ were prepared for the first time, and their crystal structure and physical properties are reported.

Sample preparation

The samples were prepared in a tetrahedral anvil press of National Bureau of Standards design (Lloyd, Hut-

ton & Johnson, 1959), using a cylindrical boron nitride crucible of 0.6 cm length and 0.13 cm⁻³ volume, surrounded by a graphite sleeve resistance heater inserted in a pyrophyllite tetrahedron. The temperature was measured with a Pt, Pt–Rh thermocouple uncorrected for pressure effects and placed at the center of the cylinder surface. Detailed operating procedures have been described by Bither, Gillson & Young (1966).

High-purity Mo, Cr, and red P powders were ground together in the metal:phosphorus ratio 1:4, and pressed into a pellet, which was placed in the boron nitride crucible. Pressure was applied and then the temperature was raised. Optimum conditions are from 15–65 kbar and 900–1200°C. These conditions were generally held for two hours; the samples were cooled over a period of about two hours to 700–1000°C and then quenched.

To investigate the stability of CrP₄ at lower pressures, CrP₄ was also prepared by reaction of a 1:4 mixture of Cr and P sealed in a Pyrex tube (10 mm outside diameter, 6 mm inside diameter) held in a Pt jacket and heated to 700°C under 200 atm; the temperature and pressure were then raised to 1000°C and 3 kbar. Under these conditions, the Pyrex tube is soft, so that the external pressure equals the internal pressure. The reaction product was identified, through its X-ray

* Contribution No. 1847.