dine N-oxide and its derivatives has been assigned to the characteristic N–O stretching vibration.[4,14,15] Quagliano and co-workers[4] have found that the coordination of pyridine N-oxide to a metal ion results in a lowering of the N–O stretching energy. This was attributed to a decrease in the contribution of the resonance form which contains a nitrogen–oxygen double bond, *i.e.*, there is a decrease in the N–O bond order upon coordination. By and large the absorption energies of the N–O stretching vibration of the 1:1 complexes were lower than the values for the 1:2 complexes. This observation is in agreement with expectation; a larger electron donation from the NO group should be taken to form the Cu–O–Cu linkage of the 1:1 complexes than in forming the single coordinate bond of many of the 2:1 complexes.

Discussion

The structure of $[Cu(C_5H_5NO)Cl_2]_2$ has been established.[8] The binuclear molecule is formed by distorted tetrahedra which share an edge. On the basis of the similarity of the magnetic properties and the infrared spectral data, similar structures can be assigned to the other 1:1 complexes prepared in this study.

Assignment of structures to the 2:1 complexes is more complicated. The presence of two N–O bands in the spectrum of $Cu(C_5H_5NO)_2Cl_2$ suggests the presence of two kinds of pyridine N-oxide ligands in this molecule, and the magnetic data can only be explained on the basis of polynuclear units with Cu–O–Cu bridges. When $Cu(C_5H_5NO)_2Cl_2$ is heated to about 85–90° one pyridine N-oxide (per copper(II) ion) is lost and the high-energy band (at 1223 cm.$^{-1}$) in the infrared spectrum disappears. The simplest structure which encompasses these features retains the binuclear structure and contains a second pyridine N-oxide molecule in the coordination sphere of each copper ion in the dimeric unit. The facility of formation of complexes of the type $[Cu(C_5H_5NO)LX_2]_n$ where L is either dimethylformamide or dimethyl sulfoxide and X is chloride or bromide also supports a structure of this type.

However, not all 2:1 complexes have this structure; a case in point is $Cu(ClC_5H_4NO)_2Cl_2$. The magnetic data indicate the absence of Cu–O–Cu linkages in this compound. Other examples of CuL_2X_2 which are magnetically dilute have been characterized and will be reported in a subsequent publication.

Acknowledgments.—The authors wish to acknowledge the support of this research at Chapel Hill by the donors of the Petroleum Research Fund which is administered by the American Chemical Society, by the University Research Council of the University of North Carolina, and by the Advanced Research Projects Agency and at Tulane by the Office of Naval Research.

---

[14] H. Shindo, *Chem. Pharm. Bull.* (Tokyo), **4**, 460 (1956); **6**, 117 (1958); **7**, 191 (1959).

[15] G. Costa and P. Blasina, *Z. physik. Chem.* (Frankfurt), **4**, 24 (1955).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY

The Crystal Structure of Di-μ-diphenylphosphinatoacetylacetonatochromium(III)

BY C. E. WILKES AND R. A. JACOBSON[1]

Received August 24, 1964

The structure of di-μ-diphenylphosphinatoacetylacetonatochromium(III), with sixty atoms in the asymmetric unit, has been determined by Patterson superposition and Fourier techniques. Two molecules crystallize in a triclinic unit cell (space group $P\bar{1}$) with dimensions $a = 12.64$, $b = 15.57$, $c = 13.35$ Å., $\alpha = 112.4°$, $\beta = 112.50°$, $\gamma = 84.2°$. The ligands around the chromium atoms conform to octahedral symmetry and the bridge structure, $(CrOPO)_2$, is a puckered eight-membered ring. Block diagonal least-squares refinement with Cr, P, and O atoms anisotropic resulted in a final R value of 0.09 for 4400 observed reflections.

Introduction

The determination of the crystal and molecular structure of $(AcCHAc)_2Cr(OP(C_6H_5)_2O)_2Cr(AcCHAc)_2$, a dimer and the first member of a series of polymers[2] made up of $Cr(AcCHAc)(OP(C_6H_5)_2O)_2$ units, was carried out by single-crystal X-ray diffraction techniques. Much interest centers on the excellent thermal stability and fairly general insolubility of these inorganically-linked polymers and hence on their structures. It was postulated that the structures involve double diphenylphosphinate bridges between the chromium atoms,[2] similar to a structure given for $UO_2[OP(OC_4H_9)_2O]_2$.[3]

Experimental

Green, plate-like crystals of the dimer were prepared by the reaction of diphenylphosphinic acid with excess chromium(III) acetylacetonate at 240° and recrystallized from diglyme. Precession camera photographs were taken to obtain the space group and approximate lattice parameters. The crystal was triclinic and the space group was determined to be $P\bar{1}$ from an analysis of the Patterson map. Precision measurements of the lattice pa-

---

[1] Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa.

[2] B. P. Block, J. Simkin, and L. Ocone, *J. Am. Chem. Soc.*, **84**, 1749 (1962).

[3] C. Baes, Jr., R. Zingaro, and C. Coleman, *J. Phys. Chem.*, **62**, 129 (1958).

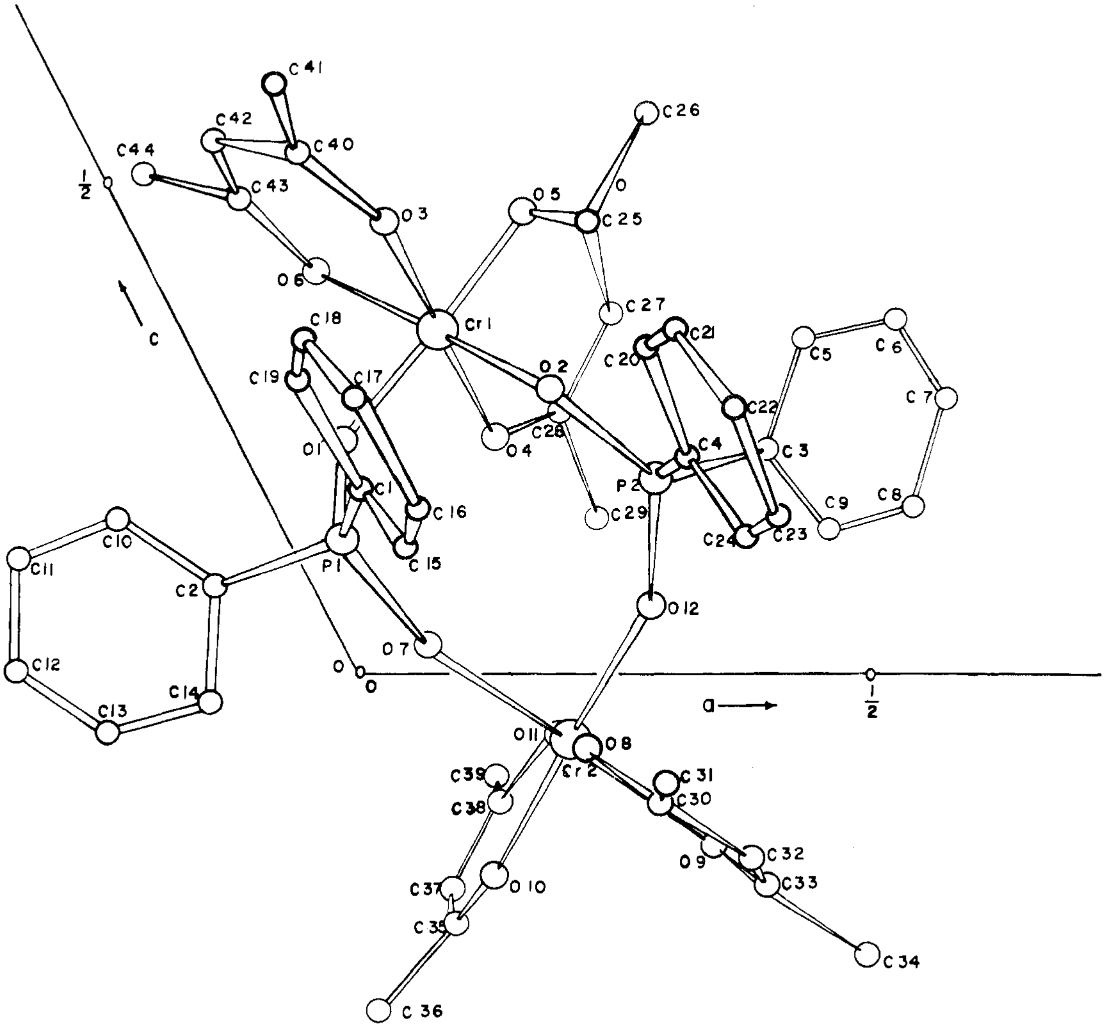

Figure 1.—Molecule viewed along the [010] axis.

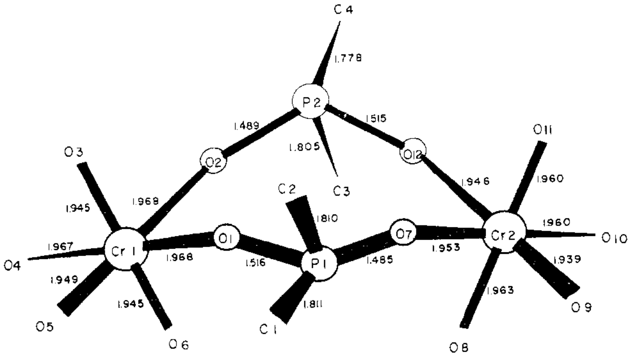

Figure 2.—Perspective drawing of central portion of the molecule showing bond distances.

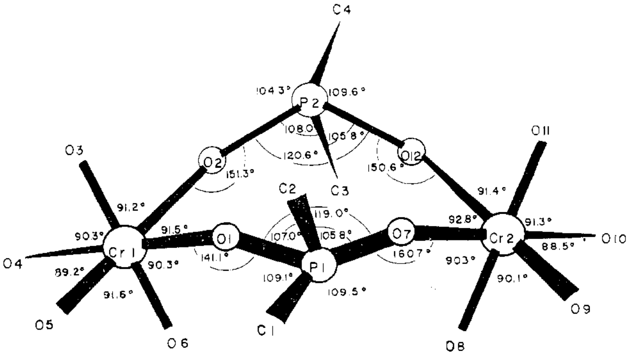

Figure 3.—Perspective drawing of central portion of the molecule showing bond angles.

rameters yielded the following values: $a = 12.64 \pm 0.05$, $b = 15.57 \pm 0.05$, $c = 13.35 \pm 0.01$ Å., $\alpha = 112.4 \pm 0.2°$, $\beta = 112.5 \pm 0.2°$, and $\gamma = 84.2 \pm 0.1°$. The calculated density of 1.383 g./cc., based on two molecules per unit cell, compares favorably with the observed value of 1.4 g./cc.

Using Mo Kα radiation, 5100 intensities of a total of 10,300 within a 2θ sphere of 56° were collected on a General Electric goniostat equipped with a scintillation counter. Although over 10,000 reflections were investigated, only those with a reasonable peak to background intensity ratio were recorded. The method of balanced-filter peak heights[4,5] corrected by an experimental peak–integrated intensity curve was used. This technique provided monochromatic radiation, excellent counting statistics, and considerable speed. Intensities were corrected for Lorentz and polarization factors. Because of the small size of the crystal, no absorption corrections were made.

Structure Determination

Although the chromium atoms are what are usually referred to as "heavy atoms," which would suggest using the heavy atom approach to the investigation of the structure, these atoms (actually trivalent, positive ions) were not dominant enough to determine the phases

---

(4) R. Young, *Z. Krist.*, **118**, 223 (1963).

(5) L. Alexander and G. Smith, *Acta Cryst.*, **15**, 983 (1962).

TABLE I

(a) Final Atomic Parameters

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
Cr$_1$	0.2458	0.2449	0.3490	0.0036	0.0020	0.0043	−0.0005	0.0015	0.0020
Cr$_2$	0.1722	0.2008	−0.0658	0.0034	0.0017	0.0040	−0.0009	0.0002	0.0021
O$_1$	0.0999	0.2654	0.2372	0.0036	0.0034	0.0052	−0.0014	0.0028	0.0012
O$_2$	0.3341	0.2919	0.2852	0.0050	0.0044	0.0087	−0.0011	0.0042	0.0065
O$_3$	0.2493	0.3708	0.4591	0.0062	0.0035	0.0049	−0.0001	0.0016	0.0028
O$_4$	0.2485	0.1165	0.2432	0.0052	0.0043	0.0066	0.0006	0.0031	0.0020
O$_5$	0.3871	0.2290	0.4672	0.0070	0.0030	0.0063	−0.0002	0.0020	0.0015
O$_6$	0.1591	0.1972	0.4116	0.0058	0.0044	0.0068	−0.0006	0.0040	0.0056
O$_7$	0.0824	0.2526	0.0326	0.0066	0.0031	0.0063	0.0008	0.0015	0.0065
O$_8$	0.1832	0.3223	−0.0747	0.0070	0.0037	0.0085	−0.0009	0.0045	0.0070
O$_9$	0.2570	0.1475	−0.1675	0.0079	0.0060	0.0098	0.0040	0.0073	0.0112
O$_{10}$	0.0316	0.1765	−0.2052	0.0058	0.0035	0.0056	−0.0032	0.0021	0.0004
O$_{11}$	0.1577	0.0766	−0.0659	0.0050	0.0023	0.0061	−0.0004	0.0025	0.0016
O$_{12}$	0.3165	0.2284	0.0680	0.0043	0.0036	0.0059	−0.0018	0.0002	−0.0006
P$_1$	0.0533	0.3005	0.1378	0.0032	0.0017	0.0055	0.0004	0.0025	0.0036
P$_2$	0.3850	0.2785	0.1968	0.0030	0.0025	0.0052	−0.0018	0.0010	0.0018

Atom	x/a	y/b	z/c	β	Atom	x/a	y/b	z/c	β
C$_1$	0.0907	0.4236	0.1945	2.59	C$_{23}$	0.4874	0.5027	0.1622	4.68
C$_2$	−0.1014	0.2908	0.0864	2.56	C$_{24}$	0.4523	0.4101	0.1370	3.90
C$_3$	0.5130	0.2151	0.2305	2.85	C$_{25}$	0.4478	0.1584	0.4598	3.67
C$_4$	0.4269	0.3929	0.2224	2.82	C$_{26}$	0.5566	0.1713	0.5668	5.05
C$_5$	0.5252	0.1345	0.1452	3.91	C$_{27}$	0.4244	0.0763	0.3654	4.28
C$_6$	0.6263	0.0835	0.1729	5.77	C$_{28}$	0.3266	0.0631	0.2652	4.06
C$_7$	0.7091	0.1144	0.2808	6.04	C$_{29}$	0.3113	−0.0315	0.1625	7.69
C$_8$	0.6968	0.1941	0.3641	5.79	C$_{30}$	0.2313	0.3474	−0.1289	3.92
C$_9$	0.5999	0.2470	0.3406	4.35	C$_{31}$	0.2231	0.4438	−0.1238	6.27
C$_{10}$	−0.1642	0.2804	−0.0280	3.49	C$_{32}$	0.2884	0.2864	−0.1949	4.99
C$_{11}$	−0.2848	0.2811	−0.0680	4.29	C$_{33}$	0.2961	0.1892	−0.2141	4.31
C$_{12}$	−0.3410	0.2854	0.0045	5.90	C$_{34}$	0.3561	0.1282	−0.2935	8.36
C$_{13}$	−0.2758	0.2939	0.1211	4.92	C$_{35}$	−0.0351	0.1043	−0.2549	3.43
C$_{14}$	−0.1560	0.2984	0.1610	3.41	C$_{36}$	−0.1373	0.1081	−0.3571	5.57
C$_{15}$	0.0867	0.4812	0.3005	4.86	C$_{37}$	−0.0214	0.0279	−0.2229	4.45
C$_{16}$	0.1124	0.5772	0.3415	6.04	C$_{38}$	0.0737	0.0175	−0.1329	3.44
C$_{17}$	0.1342	0.6178	0.2752	5.58	C$_{39}$	0.0800	−0.0712	−0.1078	6.23
C$_{18}$	0.1372	0.5602	0.1692	5.70	C$_{40}$	0.2005	0.4011	0.5302	4.22
C$_{19}$	0.1115	0.4642	0.1282	6.11	C$_{41}$	0.2146	0.5067	0.6018	6.01
C$_{20}$	0.4397	0.4652	0.3294	4.54	C$_{42}$	0.1265	0.3451	0.5388	6.69
C$_{21}$	0.4789	0.5538	0.3517	5.13	C$_{43}$	0.1173	0.2474	0.4868	4.68
C$_{22}$	0.5013	0.5723	0.2669	5.57	C$_{44}$	0.0427	0.1946	0.5134	6.96

(b) Standard Deviations in Final Atomic Parameters

	x/a	y/b	z/c	β	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
Cr	0.00008	0.00008	0.0008		0.00000	0.00000	0.00000	0.00008	0.00008	0.00008
P	0.00017	0.00012	0.00016		0.00012	0.00000	0.00012	0.00017	0.00014	0.00019
O	0.00052	0.00040	0.00053		0.00042	0.00027	0.00043	0.00060	0.00055	0.00069
C	0.00099	0.00076	0.00097	0.21						

of a sufficient number of structure factors. They did, however, produce vectors in the Patterson map which were easily discernible from other interatomic vectors and which could be used as Patterson superposition vectors. Two superpositions, using two chromium–chromium double vectors in the same subset, were sufficient to decompose the Patterson into one image of the structure. The chromium, phosphorus, and oxygen positions stood out extremely well, but some of the carbon atoms evolved poorly. It was thus decided to compute an electron-density map with signs determined by the position of the two chromium, two phosphorus, and twelve oxygen atoms; 37 of the 44 carbon atoms emerged unambiguously in this map. These 53 atoms were then used to calculate a new set of phases and a second electron-density map revealed the missing carbon atoms. The agreement factor, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, was 0.33 at the first stage (16 heavy atoms determined) and 0.28 at the second stage (53 atoms determined—no refinement). The R value then dropped below 0.20 with block diagonal least-squares refinement, and, after the chromium, phosphorus, and oxygen atoms were made anisotropic, it decreased to 0.06 for 2600 reflections. The residual $r = \Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2$ was 0.008. For 4400 reflections (using all F_o greater than 4.0) the final values were $R = 0.09$, $r = 0.02$. Computations were done on the Control Data Corporation 1604 computer.[6]

Analysis of the final difference electron-density map and subsequent calculation of bond distances and angles revealed approximately three-fourths of the 48 hydrogens present in the molecule. While the average background in the map was 0.1 to 0.2 e/Å.^{3}, the hy-

---

(6) R. Jacobson, B. Gorres, A. Mighell, and F. Muller, Crystallographic Programs for the Control Data Corporation 1604 Computer, Technical Reports 1–6, DA-ARO(D)-31-124-G265.

TABLE II

(a) Bond Distances (Å.) and Angles

Cr_1-O_1	1.968	$O_1-Cr_1-O_2$	91.5°
Cr_1-O_2	1.968	$O_1-Cr_1-O_3$	90.3°
Cr_1-O_3	1.967	$O_1-Cr_1-O_4$	92.3°
Cr_1-O_4	1.949	$O_1-Cr_1-O_5$	176.6°
Cr_1-O_5	1.945	$O_1-Cr_1-O_6$	88.8°
Cr_1-O_6	1.945	$O_2-Cr_1-O_3$	88.9°
Cr_2-O_7	1.953	$O_2-Cr_1-O_4$	91.2°
Cr_2-O_8	1.960	$O_2-Cr_1-O_5$	90.5°
Cr_2-O_9	1.960	$O_2-Cr_1-O_6$	179.3°
Cr_2-O_{10}	1.939	$O_3-Cr_1-O_4$	177.4°
Cr_2-O_{11}	1.963	$O_3-Cr_1-O_5$	87.0°
Cr_2-O_{12}	1.946	$O_3-Cr_1-O_6$	91.6°
Average	1.955 ± 0.009[a]	$O_4-Cr_1-O_5$	90.3°
		$O_4-Cr_1-O_6$	88.2°
		$O_3-Cr_1-O_6$	89.2°
Cr–Cr	5.030 ± 0.005[b]	$O_7-Cr_2-O_8$	90.3°
		$O_7-Cr_2-O_9$	178.2°
P_1-O_1	1.516	$O_7-Cr_2-O_{10}$	89.8°
P_1-O_7	1.485	$O_7-Cr_2-O_{11}$	91.3°
P_1-O_2	1.489	$O_7-Cr_2-O_{12}$	92.8°
P_2-O_{12}	1.515	$O_8-Cr_2-O_9$	90.1°
Average	1.501 ± 0.013	$O_8-Cr_2-O_{10}$	86.2°
		$O_8-Cr_2-O_{11}$	177.1°
		$O_8-Cr_2-O_{12}$	91.0°
P_1-C_1	1.811	$O_9-Cr_2-O_{10}$	88.5°
P_1-C_2	1.810	$O_9-Cr_2-O_{11}$	88.2°
P_2-C_3	1.805	$O_9-Cr_2-O_{12}$	88.9°
P_2-C_4	1.778	$O_{10}-Cr_2-O_{11}$	91.3°
Average	1.801 ± 0.011	$O_{10}-Cr_2-O_{12}$	176.2°
		$O_{11}-Cr_2-O_{12}$	91.4°
		Average (adj.)	90.3 ± 1.3°
$O_1-P_1-C_1$	109.1°	Average (opp.)	177.6 ± 1.1°
$O_1-P_1-C_2$	107.0°		
$O_7-P_1-C_1$	109.5°		
$O_7-P_1-C_2$	105.8°	$O_1-P_1-O_7$	119.0°
$O_2-P_2-C_3$	108.0°	$O_2-P_2-O_{12}$	120.6°
$O_2-P_2-C_4$	104.3°		
$O_{12}-P_2-C_3$	109.6°	$C_1-P_1-C_2$	105.7°
$O_{12}-P_2-C_4$	105.8°	$C_3-P_2-C_4$	109.0°
Average	107.4 ± 1.7°		
		$Cr_1-O_1-P_1$	141.1°
		$Cr_2-O_7-P_1$	160.7°
		$Cr_1-O_2-P_2$	151.3°
		$Cr_2-O_{12}-P_2$	150.6°

(b) Bond Distances (Å.) and Angles, Acetylacetonate Groups

$C-CH_3$		CH_3-C-O	
$C_{25}-C_{26}$	1.520	$C_{26}-C_{25}-O_5$	114.3°
$C_{28}-C_{29}$	1.551	$C_{29}-C_{28}-O_4$	113.5°
$C_{30}-C_{31}$	1.472	$C_{31}-C_{30}-O_8$	119.2°
$C_{33}-C_{34}$	1.518	$C_{34}-C_{33}-O_9$	115.4°
$C_{35}-C_{36}$	1.494	$C_{36}-C_{35}-O_{10}$	112.8°
$C_{38}-C_{39}$	1.527	$C_{39}-C_{38}-O_{11}$	115.6°
$C_{40}-C_{41}$	1.544	$C_{41}-C_{40}-O_3$	117.1°
$C_{43}-C_{44}$	1.526	$C_{44}-C_{43}-O_6$	115.1°
Average	1.519 ± 0.018	Average	115.4 ± 1.4°

(b) (*Continued*)

$C-CH$		CH_3-C-CH	
$C_{25}-C_{27}$	1.369	$C_{26}-C_{25}-C_{27}$	119.7°
$C_{28}-C_{27}$	1.392	$C_{29}-C_{28}-C_{27}$	116.4°
$C_{30}-C_{32}$	1.382	$C_{31}-C_{30}-C_{32}$	118.4°
$C_{33}-C_{32}$	1.436	$C_{34}-C_{33}-C_{32}$	119.4°
$C_{35}-C_{37}$	1.383	$C_{36}-C_{35}-C_{37}$	120.4°
$C_{38}-C_{37}$	1.387	$C_{39}-C_{38}-C_{37}$	118.6°
$C_{40}-C_{42}$	1.404	$C_{41}-C_{40}-C_{42}$	120.0°
$C_{43}-C_{42}$	1.406	$C_{44}-C_{43}-C_{42}$	118.5°
Average	1.395 ± 0.015	Average	118.9 ± 1.0°
$C-O$		$CH-C-O$	
$C_{25}-O_5$	1.269	$C_{27}-C_{25}-O_5$	125.9°
$C_{28}-O_4$	1.246	$C_{27}-C_{28}-O_4$	130.1°
$C_{30}-O_8$	1.282	$C_{32}-C_{30}-O_8$	122.4°
$C_{33}-O_9$	1.287	$C_{32}-C_{33}-O_9$	125.3°
$C_{35}-O_{10}$	1.270	$C_{37}-C_{35}-O_{10}$	126.8°
$C_{38}-O_{11}$	1.273	$C_{37}-C_{38}-O_{11}$	125.8°
$C_{40}-O_3$	1.246	$C_{42}-C_{40}-O_3$	122.7°
$C_{43}-O_6$	1.274	$C_{42}-C_{43}-O_6$	126.3°
Average	1.268 ± 0.012	Average	125.8 ± 1.6°
$Cr-O-C$		$C-CH-C$	
$Cr_1-O_3-C_{40}$	129.2°	$C_{25}-C_{27}-C_{28}$	121.0°
$Cr_1-O_4-C_{28}$	124.4°	$C_{30}-C_{32}-C_{33}$	124.3°
$Cr_1-O_5-C_{25}$	128.1°	$C_{35}-C_{37}-C_{38}$	123.7°
$Cr_1-O_6-C_{43}$	124.8°	$C_{40}-C_{42}-C_{43}$	123.9°
$Cr_2-O_8-C_{30}$	130.5°	Average	123.2 ± 1.1°
$Cr_2-O_9-C_{33}$	127.4°		
$Cr_2-O_{10}-C_{35}$	125.7°		
$Cr_2-O_{11}-C_{38}$	126.4°		
Average	127.1 ± 1.7°		

(c) Bond Distances (Å.) and Angles, Phenyl Groups

C_3-C_5	1.380	$C_3-C_5-C_6$	119.7°
C_5-C_6	1.435	$C_5-C_6-C_7$	119.7°
C_6-C_7	1.351	$C_6-C_7-C_8$	120.5°
C_7-C_8	1.359	$C_7-C_8-C_9$	120.0°
C_8-C_9	1.406	$C_8-C_9-C_3$	121.5°
C_9-C_3	1.391	$C_9-C_3-C_5$	119.1°
C_4-C_{20}	1.404	$C_4-C_{20}-C_{21}$	120.1°
$C_{20}-C_{21}$	1.397	$C_{20}-C_{21}-C_{22}$	119.7°
$C_{21}-C_{22}$	1.398	$C_{21}-C_{22}-C_{23}$	120.2°
$C_{22}-C_{23}$	1.373	$C_{22}-C_{23}-C_{24}$	120.0°
$C_{23}-C_{24}$	1.420	$C_{23}-C_{24}-C_4$	121.7°
$C_{24}-C_4$	1.414	$C_{24}-C_4-C_{20}$	117.9°
C_1-C_{15}	1.374	$C_1-C_{15}-C_{16}$	117.7°
$C_{15}-C_{16}$	1.407	$C_{15}-C_{16}-C_{17}$	122.3°
$C_{16}-C_{17}$	1.370	$C_{16}-C_{17}-C_{18}$	120.2°
$C_{17}-C_{18}$	1.380	$C_{17}-C_{18}-C_{19}$	117.5°
$C_{18}-C_{19}$	1.407	$C_{18}-C_{19}-C_1$	122.2°
$C_{19}-C_1$	1.374	$C_{19}-C_1-C_{15}$	119.9°
C_2-C_{10}	1.378	$C_2-C_{10}-C_{11}$	120.4°
$C_{10}-C_{11}$	1.400	$C_{10}-C_{11}-C_{12}$	120.5°
$C_{11}-C_{12}$	1.416	$C_{11}-C_{12}-C_{13}$	119.6°
$C_{12}-C_{13}$	1.384	$C_{12}-C_{13}-C_{14}$	119.2°
$C_{13}-C_{14}$	1.410	$C_{13}-C_{14}-C_2$	120.3°
$C_{14}-C_2$	1.379	$C_{14}-C_2-C_{10}$	120.0°
Average	1.392 + 0.018	Average	120.0 ± 0.8°

[a] Uncertainties are standard errors of the mean of molecularly equivalent distances or angles. These compare favorably with the standard deviations determined from the least-squares calculations. [b] The Cr–Cr standard deviation is from least squares.

drogens appeared at heights ranging from 0.4 to 1.0 e/Å.^{3}. No attempt was made to determine the positions of the remaining hydrogens, particularly since most of these were in methyl groups.

Table I lists the final atomic parameters and their calculated standard deviations. The important bond distances and angles are given in Table II. The observed and calculated structure factors are available.[7]

---

[7] A Table of observed and calculated structure factors has been deposited as Document No. 8119 with the ADI Auxiliary Publications Project, Photoduplication service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and by remitting $1.25 for photoprints, or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

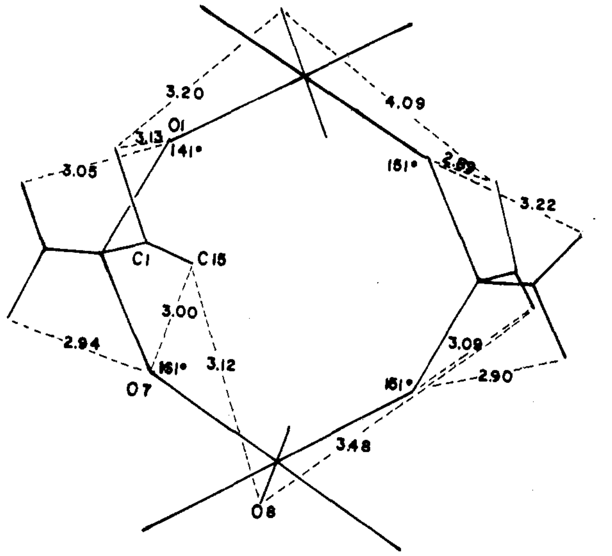

Figure 4.—Phenyl–oxygen contact distances.

Discussion

The chromium–oxygen distances, averaging 1.955 ± 0.009 Å., the phosphorus–carbon distances, 1.801 ± 0.011 Å., and the phosphorus–oxygen distances, 1.501 ± 0.013 Å., are normal for these types of bonding. The bridge group is stabilized by resonance, in part evidenced by the short phosphorus–oxygen bonds. The chromium–oxygen distances in the bridge are identical with those in the chromium acetylacetonate groups to within the standard deviations in the experiment.

Figure 1 is a view of the molecule along the [010] axis. Figures 2 and 3 give some of the important bond distances and angles. Inspection of Figure 3 shows divergence in the Cr–O–P angles. The angles at O_2 and O_{12}, on one side of the bridge, are identical, but the angles at O_1 and O_7 appear to be distorted. Calculations of contact distances between the phenyl groups and oxygens, both in the bridges and in the acetylacetonate groups, were made and are given in Figure 4. Notice, from Figure 1, that the C_2 and C_3 phenyl groups are situated well away from other atoms in the molecule. The C_4 phenyl group lies above and away from the bridge vicinity and the C_1 group lies above and closely approaching the acetylacetonate oxygens. The contact distance C_{15}–O_8, which is 3.12 Å., becomes approximately 2.70 Å. if the angle at O_7 is made equal to 151° (the apparent "average"). We conclude that, in order to eliminate steric crowding of the C_1 phenyl group with the acetylacetonate oxygens, the bridge group distorts at the O_7 and O_1 oxygens. This, of course, destroys the expected symmetry of an undistorted bridge group. There are no short (*i.e.*, less than 3.3 Å.) intermolecular distances which might contribute to the distortion.

An interesting extension of the study of the dimer, the first member in this series of polymers, would be to investigate the structure of the trimer. Since the acetylacetonate must occupy two *cis* coordination positions on the chromium, the two diphosphinate bridge groups attached to the middle chromium would have to be adjacent to each other. The steric hindrance of the phenyl groups on the phosphorus atoms should give rise to still more distortion of the bridge groups.

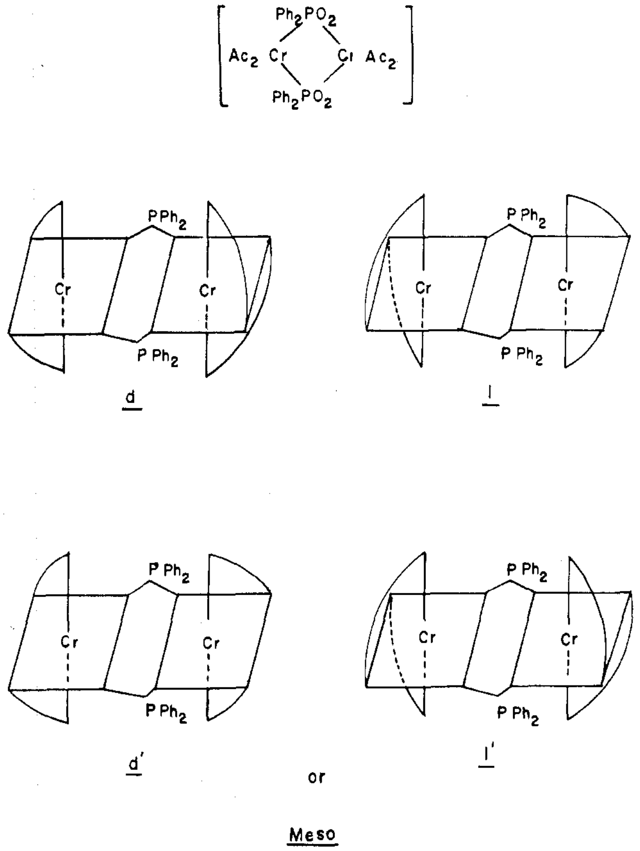

Figure 5.—Optical isomers of chromium phosphinate dimer.

Four optical isomers of the dimer can be drawn (Figure 5). If one makes analogy to the tetrakis(ethylenediamine)-μ-amido-μ-nitrodicobalt(II) nitrate molecule,[8] one may propose *d*, *l*, and *meso* forms. However, as pointed out in a recent paper on the structure determination of this molecule,[9] the "*meso*" form might be expected to show optical activity at wave lengths nearer the ultraviolet than the conventional sodium D-line. Since the bridge structure of this chromium dimer is asymmetrical, one might expect four optically active isomers, rather than two active and one inactive *meso* form. The asymmetric unit of the crystal, comprising one molecule of the chromium phosphinate dimer, is an optically active form. Since the other molecule in the unit cell is related to it by a center of symmetry, the crystal itself is racemic.

Acknowledgments.—We gratefully acknowledge the financial support of the Army Research Office (Durham), the National Institutes of Health for a fellowship for C. W., the National Science Foundation (grant No. GP579) for support of computer facilities, and J. Simkin of Pennsalt Chemicals Corporation for samples of the compound.

---

[8] A. Werner, *Ber.*, **46**, 3674 (1913).

[9] C. Wilkes, P. Goldstein, and R. Jacobson, to be published.