CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

Some Reactions of the Octahalodirhenate(III) Ions. VIII. The Structure of a Phosphine-Substitution Product of Octachlorodirhenate(III)[1]

BY F. A. COTTON AND BRUCE M. FOXMAN[2]

Received April 30, 1968

The crystal and molecular structure of hexachlorobis(triethylphosphine)dirhenium(III), $Re_2Cl_6[P(C_2H_5)_3]_2$, has been determined by single-crystal X-ray diffraction methods. The green crystals belong to the monoclinic system, space group $P2_1/n$, with $a = 7.644 \pm 0.003$ Å, $b = 10.985 \pm 0.005$ Å, $c = 14.206 \pm 0.006$ Å, $\beta = 96.5 \pm 0.1°$, density by flotation 2.29 ± 0.02 g cm^{-3}; calculated density (for $Z = 2$) 2.30 g cm^{-1}. Using 911 reflections above background collected on a manually operated counter diffractometer, the structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least squares to final unweighted and weighted residuals of 0.052 and 0.063, respectively. The molecular structure is similar to that of the $Re_2Cl_8^{2-}$ anion, with one of the chlorine atoms in each half of the centrosymmetric anion replaced by a triethylphosphine group. The Re–Re distance is 2.222 ± 0.003 Å, and the molecule possesses the eclipsed configuration, indicative of the fact that the δ component of the quadruple bond is preserved for nonredox substitution reactions of $Re_2Cl_8^{2-}$. A structural *trans* effect is observed, the Re–Cl bonds opposite the Re–P bonds being 2.352 (7) Å long while the *cis* Re–Cl bonds are 2.296 (5) Å long.

Introduction

Previous papers in this series have described a variety of ligand-substitution reactions[3–6] and redox reactions[7,8] of the $Re_2X_8^{2-}$ ions. One of the first substitution reactions to be discovered[3] was that in which triphenylphosphine molecules displaced one halide ion from each rhenium atom of $Re_2X_8^{2-}$ (X = Cl, Br) to give the neutral molecules, $Re_2X_6(P(C_6H_5)_3)_2$. Unfortunately the postulated structure for these species could be neither proved conclusively nor determined in detail, because the products formed instantly upon mixing solutions of the reactants and were deposited as noncrystalline powders, rather insoluble in all solvents tested. The binuclear, 1,2-disubstituted structures were postulated solely on the evidence of reflectance spectra.

Efforts were therefore made to obtain a more soluble and crystalline compound of the same type by using different phosphines. Success was attained with triethylphosphine; the compound $Re_2Cl_6(P(C_2H_5)_3)_2$ has been prepared and characterized by the determination of its structure by single-crystal X-ray methods.

Experimental Section

In order to obtain more soluble compounds of the type $(ReCl_3(phosphine))_n$, suitable for crystallographic study, products of the reaction of liquid phosphines with the octahalodirhenium(III) anions were studied. Triethyl- and phenyldiethylphosphine were prepared, employing slight modifications of the method of Adams and Raynor.[9] The rhenium derivatives were prepared in a manner similar to that outlined by Cotton, Curtis, and Robinson[3] for $(ReCl_3P(C_6H_5)_3)_n$. Preliminary X-ray investigations (Laué photographs) showed the crystals of the phenyldiethylphosphine derivative to be unsuitable; efforts were therefore concentrated on the triethylphosphine complex. Small, green, prismatic crystals suitable for X-ray diffraction studies were obtained by recrystallization of the crude reaction product from warm 1-chlorobutane. *Anal.* Calcd for $C_6H_{15}Cl_3PRe$: C, 17.55; H, 3.68; Cl, 25.90. Found: C, 17.9; H, 3.71; Cl, 25.8.

The monoclinic prisms were examined by Weissenberg (levels $0kl$–$2kl$) and precession photography (levels $h0l$, $h1l$, $hk0$, $hk1$). The observed systematic absences, $h0l$ for $h + l$ odd and $0k0$ for k odd, are consistent with the space group $P2_1/n$ (C_{2h}^5, no. 14; general positions: x, y, z; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; $\bar{x}, \bar{y}, \bar{z}$). In addition, a set of special absences or reduction in intensity of general reflections indexed hkl for $h + k + l$ odd implied that a considerable portion of the total scattering power (probably the rhenium atom) was located either near a coordinate of the type $(x, 0, z)$ or $(0, y, 0)$ or near the origin.

The unit cell parameters were determined at 22° as $a = 7.644 \pm 0.003$, $b = 10.985 \pm 0.005$, $c = 14.206 \pm 0.006$ Å; $\beta = 96.5 \pm 0.1°$ from measurements on a General Electric XRD-5 manual diffractometer using copper Kα radiation ($\lambda\alpha_1$ 1.5405 Å, $\lambda\alpha_2$ 1.5443 Å). The quoted values for a, b, c, and β were derived in the manner previously described.[10]

The observed density (by flotation) was 2.29 ± 0.02 g/cm^3, which agrees well with the value of 2.30 g/cm^3, calculated for $Z = 2$, $M = 821.44$, and $V = 1185.2$. For $Re_2Cl_6(P(C_2H_5)_3)_2$, with $Z = 2$ in space group $P2_1/n$, the molecule must possess a crystallographic center of symmetry.

The crystal used in data collection and measurement of cell constants (a monoclinic prism, elongated on a, with dimensions $0.03 \times 0.05 \times 0.11$ mm) was aligned on the diffractometer with its crystallographic a^* axis coincident with the ϕ axis of the goniometer. Nickel-filtered Cu Kα radiation was used in the data collection in preference to Mo Kα radiation because of the small crystal size; the generally lower background and increased intensity obtained with Cu Kα outweighs the difference between absorption coefficients ($\mu_{Cu} = 265$, $\mu_{Mo} = 116$ cm^{-1}). The intensities of 1485 independent reflections (index sets hkl and $h\bar{k}\bar{l}$) within the sphere limited by $(\sin\theta)/\lambda \leq 0.53$ were monitored using the moving-crystal, moving-counter (θ–2θ scan) method of

---

[1] (a) This work was supported in part by the U. S. Atomic Energy Commission. (b) Part VII: M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *Inorg. Chem.*, **7**, 1570 (1968). (c) A preliminary report on this work has been published: M. J. Bennett, F. A. Cotton, B. M. Foxman, and P. F. Stokely, *J. Am. Chem. Soc.*, **89**, 2759 (1967).

[2] NIH Predoctoral Fellow, 1965–1966.

[3] F. A. Cotton, N. F. Curtis, and W. R. Robinson, *Inorg. Chem.*, **4**, 1696 (1965).

[4] F. A. Cotton, C. Oldham, and W. R. Robinson, *ibid.*, **5**, 1798 (1966).

[5] F. A. Cotton, C. Oldham, and R. A. Walton, *ibid.*, **6**, 214 (1967).

[6] F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, *ibid.*, **6**, 929 (1967).

[7] F. A. Cotton, W. R. Robinson, and R. A. Walton, *ibid.*, **6**, 1257 (1967).

[8] F. Bonati and F. A. Cotton, *ibid.*, **6**, 1353 (1967).

[9] D. M. Adams and J. B. Raynor, "Advanced Practical Inorganic Chemistry," Interscience Division, John Wiley & Sons, Inc., New York, N. Y., 1965, p 116.

[10] M. J. Bennett, F. A. Cotton, and B. M. Foxman, *Inorg. Chem.*, **7**, 1563 (1968).

Furnas[11] modified so that background counts were taken at maximum and minimum values of 2θ for each scan. A 40-sec scan of 2.66° allowed adequately for the mosaic spread of the crystal. The intensities were measured with a scintillation counter with the pulse height discriminator set to receive 95% of the Cu Kα radiation with the window centered on the Cu Kα peak. The crystal was placed 5.73 in. from the source and 7.05 in. from the 2° circular screening aperture; a takeoff angle of 2° was used. Each integrated intensity was obtained by subtracting the sum of the two 20-sec background counts from the total number of counts measured during the scan. Three standard reflections (110, 260, 371) were checked frequently and showed a maximum variation of ±3%, which was random with time. No reflections exceeded the linear response range of the counter.[12]

The experimental data were corrected for Lorentz and polarization effects and converted to values of $|F_o|$ by the FORTRAN program PMMO by M. J. Bennett. During the processing of the data, 574 reflections were rejected, since they failed to meet the tests: (1) integrated intensity >0 and (2) $I \geq 3$(total scan counts and total background counts)$^{1/2}$. The remaining 911 reflections were used in the structure solution and refinement.

Solution and Refinement of the Structure

The three-dimensional Patterson function[13] readily revealed the position of the rhenium atom, three chlorine atoms, and the phosphorus atom. An unambiguous identification of the phosphorus atom could not be made at this stage; all four light atoms were therefore designated as chlorine atoms. The rhenium atom was found to be located at (0, 0, 0.07); thus, the reason for the special set of systematic "weakenings" $h + k + l \neq 2n$ for all hkl (which are the body-centering absences, when rigorous) is evident.

The asymmetric unit was thus seen to consist of a rhenium atom, three chlorine atoms, and a phosphorus atom with its associated ethyl groups (yet to be found). The $Re_2Cl_6(P(C_2H_5)_3)_2$ *molecule* is composed of two of these units, related by a center of symmetry. The most striking feature of the structure which could be immediately deduced was that the δ bond (as expected) must be preserved since the halves of an M_2X_8 molecule are rigorously (*i.e.*, crystallographically) required to be eclipsed.

A structure factor calculation at this point had a discrepancy index $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.355$ (where F_c's are the calculated and F_o's the observed structure factors); the weighted residual $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$ using equal (unit) weights was 0.355. Three cycles of full-matrix least-squares refinement[14] of scale factor, positional parameters, and isotropic thermal parameters for each atom led to $R_1 = 0.154$ and $R_2 = 0.176$. An electron density difference map at this stage revealed the positions of the six ethyl carbon atoms; three more cycles of full-matrix refinement resulted in convergence of the isotropic refinement, with $R_1 = 0.072$ and $R_2 = 0.078$. At this point the atomic scattering factors[15] were corrected for the real and imaginary parts of anomalous scattering.[16] A further cycle of refinement reduced R_1 to 0.066 and R_2 to 0.072. The data were then reprocessed and standard deviations similar to those of Corfield, Doedens, and Ibers[17] were computed for each reflection. Three more cycles of full-matrix least-squares refinement, in which the scale factor, the positional parameters, and an anisotropic temperature factor of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ for each atom were refined, resulted in convergence, with $R_1 = 0.052$ and $R_2 = 0.063$.

During the course of the refinement, the temperature factors of several of the ethyl carbon atoms became somewhat high (~10–12 Å^2), and some of the associated P–C and C–C bond lengths were different from those expected by as much as 0.1 Å. It was assumed that carbon atoms C(3) through C(6) were subject (in varying degrees) to an orientational disorder. Attempts were made to elucidate the nature of this disorder more fully, essentially utilizing the methods outlined by Corfield, Doedens, and Ibers for treatment of the disordered ethyl groups in $ReNCl_2(P(C_2H_5)_2C_6H_5)_3$.[17] Since the results of our disorder study were inconclusive, we have chosen to describe the disordered ethyl groups in terms of an ordered model. However, it should be pointed out that the apparent "disorder" may actually be a reflection of the poor quality of data uncorrected for absorption (*vide infra*). One thus cannot have much faith either in the temperature parameters of these atoms or in the P–C or C–C distances directly involved with the "disordered" atoms. The uncertainty concerning disorder should have no effect on the parameters of other atoms, which are virtually uncorrelated with those of the disordered ethyl carbon atoms. It is the positions of these other atoms which are of principal interest.

A final electron density difference map[18] revealed a peak of 1.0 e$^-$/Å^3 near C(4), a peak of 0.8 e$^-$/Å^3 near the rhenium atom, peaks of 0.6–0.7 e$^-$/Å^3 near the disordered carbon atoms, and seemingly random features ($\leq$0.5 e$^-$/Å^3) elsewhere. On the final cycle of least-squares refinement, no parameter shift was greater than 0.2 esd.

Absorption corrections were not made. It has been demonstrated[19] in particular cases that failure to make absorption corrections causes no significant changes in atomic positional parameters, although the temperature factors may be affected severely. An experimental absorption curve for the $h00$ reflections, obtained by rotation about the ϕ axis at $\chi = 90°$, revealed a variation of ±12% in the intensities of these reflections.

---

(11) T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," X-Ray Department, General Electric Co., Schenectady, N. Y., 1967.

(12) D. P. Shoemaker's "MIXG-2, MIT X-Ray Goniometer Package," 1962, was used to compute the diffractometer settings for data collection.

(13) Computed using the program of W. G. Sly, D. P. Shoemaker, and J. H. van den Hende, "A Two- and Three-Dimensional Fourier Program for the IBM 709/7090, ERFR-2," 1962.

(14) C. T. Prewitt, "A FORTRAN-IV Full-Matrix Least-Squares Program, SFLS5," 1966. In this program the function minimized is $\Sigma w(|F_o| - |F_c|)^2$.

(15) (a) Re atom: D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965); (b) lighter atoms: J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

(16) (a) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965); (b) C. T. Prewitt, Ph.D. Thesis, MIT, 1962, p 163.

(17) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967). Our weighting scheme differs only in that p, the "uncertainty factor," was assigned a value of 0.04.

(18) Calculated using our local modification of the FORDAP program by A. Zalkin.

(19) R. C. Srivastava and E. C. Lingafelter, *Acta Cryst.*, **20**, 918 (1966); P. Werner, *Acta Chem. Scand.*, **18**, 1851 (1964).

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10), IN ELECTRONS, FOR $Re_2Cl_6(P(C_2H_5)_3)_2$

TABLE II

FINAL ATOMIC POSITIONAL PARAMETERS FOR $Re_2Cl_6(P(C_2H_5)_3)_2$[a]

	x	y	z
Re	−0.00708 (12)	0.00973 (9)	0.07734 (6)
Cl(1)	0.07057 (94)	0.20114 (52)	0.14351 (45)
Cl(2)	−0.29316 (74)	0.06619 (57)	0.08784 (41)
Cl(3)	0.26415 (73)	−0.05829 (64)	0.14285 (42)
P	−0.11338 (85)	−0.19577 (57)	0.10620 (43)
C(1)	−0.3292 (30)	−0.2348 (25)	0.0379 (18)
C(2)	−0.4298 (37)	−0.3397 (28)	0.0798 (23)
C(3)	−0.1822 (44)	−0.1862 (35)	0.2358 (21)
C(4)	−0.0425 (54)	−0.1444 (32)	0.3028 (21)
C(5)	0.0470 (32)	−0.3187 (27)	0.0872 (26)
C(6)	0.0296 (61)	−0.4413 (36)	0.1290 (27)

Anisotropic Temperature Factors (×10⁵)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Equivalent isotropic B
Re	162.0 (18)	80.1 (9)	36.5 (5)	−14.3 (17)	18.2 (6)	−3.9 (9)	3.48
Cl(1)	352 (18)	121 (7)	62 (4)	−70 (10)	60 (7)	−28 (4)	6.17
Cl(2)	193 (12)	114 (6)	60 (4)	23 (7)	32 (5)	−1 (4)	4.85
Cl(3)	164 (12)	177 (8)	56 (4)	−2 (8)	−12 (5)	4 (4)	5.68
P	240 (16)	87 (6)	48 (4)	−20 (8)	18 (6)	4 (4)	4.50
C(1)	150 (53)	172 (36)	70 (18)	−14 (34)	24 (24)	−6 (21)	5.77
C(2)	300 (71)	190 (43)	109 (25)	−106 (45)	47 (34)	41 (26)	8.17
C(3)	430 (100)	281 (56)	57 (19)	−123 (62)	14 (34)	57 (27)	9.37
C(4)	729 (137)	218 (51)	61 (21)	−197 (70)	−49 (43)	61 (26)	11.00
C(5)	169 (61)	120 (34)	200 (38)	15 (36)	0 (38)	32 (29)	8.60
C(6)	854 (165)	175 (47)	117 (31)	85 (73)	−90 (57)	−13 (32)	12.91

[a] Estimated standard deviations (in parentheses) in this and following tables occur in the last significant digit in each case.

Calculation of the structure factors for the rejected reflections gave no $|F_c|$ greater than twice the minimum observable. The final standard deviation of an observation of unit weight (*i.e.*, $\Sigma w[|F_o| - |F_c|]^2/(m - n)$ where m is the number of observations and n is the number of parameters varied) is 1.23, in accord with the observed disorder and lack of absorption corrections. Table I lists the observed and calculated structure amplitudes, $10|F_o|$ and $10|F_c|$, respectively, each in electrons. Final atomic fractional coordinates and anisotropic thermal parameters are shown in Table II, in which the quoted estimated standard deviations were obtained from the inverse matrix of the final least-squares refinement cycle.

Results

The molecular structure and numbering scheme are shown in Figure 1. Table III reports pertinent intramolecular distances and angles, while intermolecular contacts less than 4.0 Å are presented in Table IV. Vibrational amplitudes, computed from the anisotropic thermal vibration tensors, are given in Table V. Fig-

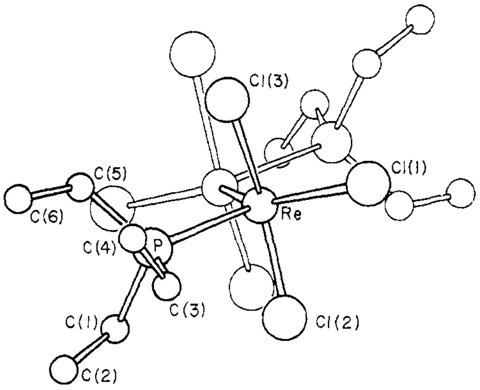


Figure 1.—A perspective view of the molecular structure of $Re_2Cl_6[P(C_2H_5)_3]_2$. The numbering scheme is also shown.

Table III

Principal Intramolecular Distances and Angles[a,b]

Bond Distances, Å

Re–Re	2.222 (3)	P–C(3)	1.97 (3)
Re–Cl(1)	2.352 (7)	P–C(5)	1.86 (3)
Re–Cl(2)	2.294 (6)	C(1)–C(2)	1.54 (4)
Re–Cl(3)	2.299 (6)	C(3)–C(4)	1.42 (5)
Re–P	2.449 (6)	C(5)–C(6)	1.48 (5)
P–C(1)	1.87 (2)		

Interbond Angles, Deg

Re′–Re–Cl(1)	116.3 (2)	Re–P–C(1)	115 (1)
Re′–Re–Cl(2)	104.1 (2)	Re–P–C(3)	104 (1)
Re′–Re–Cl(3)	103.1 (2)	Re–P–C(5)	114 (1)
Re′–Re–P	97.5 (2)	P–C(1)–C(2)	115 (2)
Cl(1)–Re–Cl(2)	86.1 (2)	P–C(3)–C(4)	112 (3)
Cl(1)–Re–Cl(3)	87.3 (2)	P–C(5)–C(6)	121 (3)
Cl(1)–Re–P	146.2 (1)	C(1)–P–C(3)	101 (1)
Cl(2)–Re–Cl(3)	152.1 (1)	C(1)–P–C(5)	108 (1)
Cl(2)–Re–P	84.4 (2)	C(3)–P–C(5)	115 (1)
Cl(3)–Re–P	86.2 (2)		

Nonbonded Contacts, Å

Re–Cl(1)′	3.89	Cl(2)–Cl(3)′	3.31
Re–Cl(2)′	3.56	Cl(1)–C(1)′	3.44
Re–Cl(3)′	3.54	Cl(1)–C(5)′	3.54
Re–P′	3.52	Cl(2)–C(1)	3.39
Cl(1)–Cl(2)	3.17	Cl(2)–C(3)	3.52
Cl(1)–Cl(3)	3.21	Cl(3)–C(4)	3.57
Cl(2)–P	3.19	Cl(3)–C(5)	3.36
Cl(3)–P	3.25	Cl(3)–C(6)	3.67
Cl(1)–P′	3.60		

[a] Molecular dimensions were calculated using the data of Table II and the programs MGEOM by J. S. Wood and DISTAN by D. P. Shoemaker. [b] Certain distances and angles involving carbon atoms have a true uncertainty which is greater than that implied by the standard deviations, as explained in the text.

ures 2 and 3 show the crystal structure in projection down (010) and (100), respectively. The numbering system shown in Figure 1 is used throughout, with centrosymmetrically related atoms (lighter lined in Figure 1) indicated by a *prime* symbol.

Table IV

Intermolecular Contacts Less Than 4.0 Å

Atom I	Atom J	Distance, Å	Vector from molecule containing I to molecule containing *J*
C(6)	Cl(3)	3.67	$(^1/_2 - x, y - {}^1/_2, {}^1/_2 - z)$
C(1)	Cl(2)	3.71	(1, 0, 0)
C(3)	Cl(2)	3.72	$(-{}^1/_2 - x, y - {}^1/_2, {}^1/_2 - z)$
C(4)	C(2)	3.76	$(-{}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z)$
C(4)	C(1)	3.79	$(^1/_2 + x, -{}^1/_2 - y, {}^1/_2 + z)$
C(3)	Cl(1)	3.80	$(-{}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z)$
Cl(3)	Cl(2)	3.81	(1, 0, 0)
C(4)	Cl(2)	3.81	$(-{}^1/_2 - x, y - {}^1/_2, {}^1/_2 - z)$
C(6)	C(6)	3.86	(0, 1, 0)
C(4)	C(2)	3.94	$(^1/_2 + x, -{}^1/_2 - y, {}^1/_2 + z)$
C(6)	Cl(1)	3.94	(0, 1, 0)
C(4)	Cl(1)	3.98	$(^1/_2 - x, y - {}^1/_2, {}^1/_2 - z)$

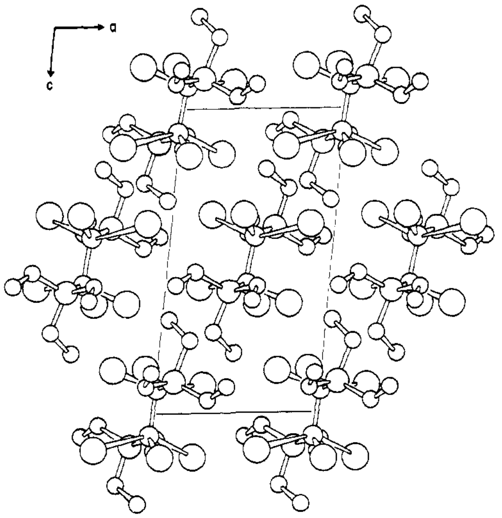


Figure 2.—The molecular packing as seen in projection down the crystallographic *b* axis.

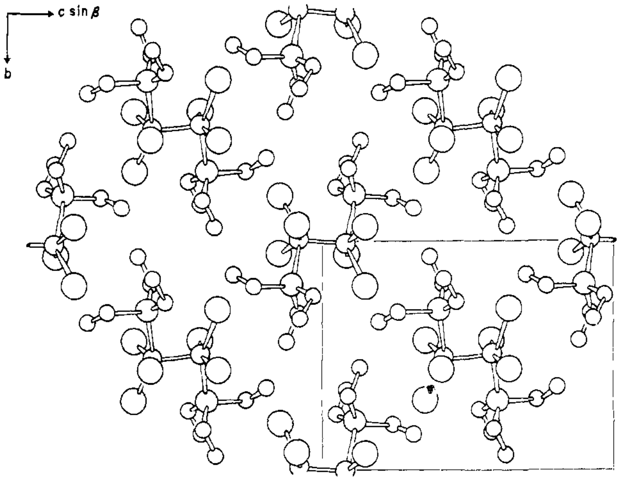


Figure 3.—The molecular packing as seen in projection down the crystallographic *a* axis.

Discussion

The molecular structure, shown in Figure 1, consists of an asymmetric unit (*i.e.*, $ReCl_3PC_6$) and its inverse (shown in lighter lines). The imposition of a crystallographic center of symmetry upon the molecule demands that $Re_2Cl_6(P(C_2H_5)_3)_2$ have an *eclipsed* configuration. We believe that the eclipsed configuration is a consequence of the δ component of the quadruple bond[20] and demonstrates in this case that nonredox substitution reactions may be carried out on $Re_2X_8^{2-}$ species without destruction of the various features of

---

(20) F. A. Cotton, *Inorg. Chem.*, **4**, 334 (1965).

TABLE V

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION AND THEIR DIRECTION COSINES[a]

Atom	Minor axis	Medium axis	Major axis
Re	0.185 (−0.420, 0.025, 0.907)	0.206 (0.651, 0.705, 0.282)	0.235 (−0.632, 0.709, −0.312)
Cl(1)	0.212 (−0.158, 0.498, 0.853)	0.239 (0.656, 0.698, −0.286)	0.363 (0.738, −0.514, 0.437)
Cl(2)	0.208 (0.802, −0.316, −0.508)	0.255 (0.304, −0.516, 0.801)	0.275 (0.514, 0.797, 0.317)
Cl(3)	0.200 (0.778, −0.015, 0.628)	0.258 (−0.627, −0.077, 0.775)	0.329 (−0.037, 0.997, 0.069)
P	0.210 (−0.330, −0.579, 0.746)	0.231 (0.221, 0.721, 0.657)	0.271 (0.918, −0.381, 0.110)
C(1)	0.203 (0.985, 0.072, −0.158)	0.266 (0.145, 0.156, 0.977)	0.326 (−0.095, 0.985, −0.143)
C(2)	0.191 (0.709, 0.591, −0.386)	0.338 (0.545, −0.111, 0.831)	0.399 (−0.448, 0.799, 0.400)
C(3)	0.191 (−0.268, −0.404, 0.874)	0.316 (0.817, 0.385, 0.429)	0.468 (−0.510, 0.831, 0.226)
C(4)	0.192 (−0.087, −0.506, 0.858)	0.300 (0.574, 0.678, 0.459)	0.539 (0.814, −0.532, −0.231)
C(5)	0.216 (0.934, −0.302, 0.188)	0.267 (0.328, 0.937, −0.123)	0.458 (−0.139, 0.176, 0.975)
C(6)	0.305 (0.390, −0.473, 0.790)	0.318 (0.001, 0.858, 0.514)	0.544 (0.921, 0.199, −0.335)

[a] Direction cosines are referred to the orthogonal coordinate system *a*, *b*, *c**.

the Re–Re quadruple bond. The salient features of the structure are discussed below in detail.

The Re–Re distance, 2.222 Å, is very close to those found in $Re_2(O_2CC_6H_5)_4Cl_2$[1b] and in $K_2Re_2Cl_8 \cdot 2H_2O$,[21] *viz.*, 2.235 (2) and 2.241 (7) Å, respectively.

The two independent, chemically equivalent Re–Cl bonds, 2.294 and 2.299 Å, are within the range found for Re(III)–Cl bonds in a number of structures, for example, $K_2Re_2Cl_8 \cdot 2H_2O$ (2.26–2.31 Å), $Re_2Cl_5(DTH)_2$ (2.33–2.34 Å),[22] and $Re_3Cl_9(PC_6H_5(C_2H_5)_2)_3$ (2.31–2.32 A).[23] The significantly longer Re–Cl bond, 2.352 Å, occurs for the chlorine atom *trans* to the phosphine, and the difference, 0.05 Å, is of the magnitude and in the direction one would expect if the phosphine is here exercising a structural *trans* effect similar to that which has been observed in square complexes of Pt(II), where Pt–Cl bonds *trans* to Pt–P bonds have been found to be ~0.08 Å longer than those which are *trans* to another Pt–Cl bond.[24,25]

The Re–P bond length, 2.449 Å, agrees well with those found, for example, in $ReNCl_2(P(C_2H_5)_2C_6H_5)_3$,[17] 2.442 (4), 2.490 (5), and 2.469 (5) Å, and in $ReNCl_2(P(C_6H_5)_3)_2$,[26] 2.448 (2) Å; the distance of 2.442 Å in the former represents an Re–P bond *trans* to an Re–Cl bond. The distances and angles in the triethylphosphine moiety, excluding those where the possibly disordered atoms are involved, are all normal.

TABLE VI

BEST WEIGHTED LEAST-SQUARES PLANES[a]

Plane no.	Atoms	Equation
1	PCl(1)Cl(2)Cl(3)	$-0.201x - 0.053y + 0.978z = 1.720$
2	ReCl(1)P	$0.278x + 0.945y + 0.172z = 0.240$
3	ReCl(2)Cl(3)	$0.924x - 0.312y + 0.220z = 0.042$

Distances of atoms from mean plane 1, (Å)

Re	−0.622	Cl(3)	−0.073
Cl(1)	0.081	P	0.069
Cl(2)	−0.068		

[a] Direction cosines of the planes refer to the orthogonal axis system *a*, *b*, *c**. The planes were calculated using the method outlined in "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1962, p 93.

The Re′–Re–Cl(2) and Re′–Re–Cl(3) angles, 104.1 and 103.1°, as well as the set of Cl–Re–Cl angles, parallel those observed for similar environments in $K_2Re_2Cl_8$; further, the two Cl–Re–P angles do not deviate greatly from the Cl–Re–Cl angles. However, marked angular distortions occur for the angles Re′–Re–Cl(1) (116.3°) and Re′–Re–P (97.5°). The "opening up" of the Re′–Re–Cl(1) angle probably arises from contacts such as Cl(1)–C(1)′ and Cl(1)–C(5)′, which would be very short in the absence of an angular distortion. The fact that no concomitant effect occurs for the phosphine may be due to some restriction of the phosphine to a certain hybridization. In $ReNCl_2(P(C_6H_5)_3)_2$, where the geometry about the rhenium atom is not unlike that in the present case, the N–Re–Cl angle is 109.7° and the N–Re–P angle is 98.4°. It seems unlikely that packing forces would cause such a large effect. The intermolecular contacts, listed in Table IV, the crystal packing shown in Figures 2 and 3, and the possibility of orientational disorder of some of the ethyl carbon atoms appear to indicate that this is a normally if not loosely packed crystal structure. There are no intermolecular contacts to Re at distances ≤4.5 Å. Thus, a clear interpretation of the distortion of the Re′–Re–P angle awaits the determination of other related structures,

---

(21) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **4**, 330 (1965).

(22) M. J. Bennett, F. A. Cotton, and R. A. Walton, *J. Am. Chem. Soc.*, **88**, 3866 (1966); *Proc. Roy. Soc.* (London), **A303**, 175 (1968).

(23) F. A. Cotton and J. T. Mague, *Inorg. Chem.*, **3**, 1094 (1964).

(24) G. G. Messmer and E. L. Amma, *ibid.*, **5**, 1775 (1966).

(25) G. G. Messmer, E. L. Amma, and J. A. Ibers, *ibid.*, **6**, 725 (1967).

(26) R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

including that of $Re_2Br_6(PC_6H_5(C_2H_5)_2)_2$, currently under investigation in this laboratory.

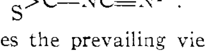
Table VI shows that the atoms Cl(1)–Cl(2)–Cl(3)–P form a plane with no deviations >0.1 Å and that the rhenium atom lies 0.62 Å out of this plane toward the other rhenium atom in the molecule. Also, the data of Table V show that the dihedral angle between planes 2 and 3 is 90.0°. Thus the symmetry of the $Cl_3PRe–ReCl_3P$ skeleton of the molecule is C_{2h} to a very good approximation.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASSACHUSETTS 02139, AND THE INORGANIC MATERIALS RESEARCH DIVISION OF
LAWRENCE RADIATION LABORATORY AND THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA 94720

The Structure of Tetraphenylarsonium Bis(N-cyanodithiocarbimato)nickelate(II)[1]

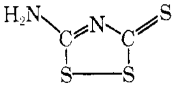
BY F. A. COTTON AND C. B. HARRIS

Received May 17, 1968

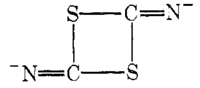
The crystal and molecular structures of tetraphenylarsonium bis(N-cyanodithiocarbimato)nickelate(II), $[(C_6H_5)_4As]_2[Ni(S_2CNCN)_2]$, have been determined by a single-crystal X-ray diffraction investigation. The substance crystallizes in the triclinic space group $A\bar{1}$ and has dimensions $a = 10.50 \pm 0.03$ Å, $b = 15.90 \pm 0.03$ Å, $c = 13.63 \pm 0.04$ Å, $\alpha = 90.02 \pm 0.05°$, $\beta = 101.74 \pm 0.07°$, and $\gamma = 89.51 \pm 0.07°$. The calculated and measured densities are: $\rho_{calcd} = 1.48$ g cm^{-3}; $\rho_{measd} = 1.51 \pm 0.04$ g cm^{-3} for $Z = 2$. The structure was refined by full-matrix least-square procedures to an R factor of 9.3% using 1671 statistically significant reflections collected by a θ–2θ scan technique on an automated diffractometer. The nickel atom is surrounded by a planar set of four sulfur atoms at an average distance of 2.188 Å. The transition metal complex has virtually C_{2h} point symmetry and its over-all structure confirms the conclusions previously put forward by Fackler and Coucouvanis and by Cotton and McCleverty as to the nature of the $C_2S_2N_2^{2-}$ ion and its metal complexes. It is, as proposed, the N-cyanodithiocarbimate ion,  $\overset{S}{\underset{S}{>}}C{=}NC{\equiv}N^{2-}$. Comparison of the present structure with that of bis(diethyldithiocarbamato)nickel(II) corroborates the prevailing view that there is appreciable double-bond character in the C—N bond in this and other complexes of dithiocarbamates.

Introduction

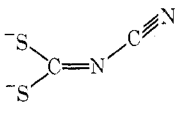
Transition metal complexes of the N-cyanocarbimate ion, $[S_2C_2N_2]^{2-}$, have been prepared in several laboratories.[2,3] Fackler and Coucouvanis[3] have prepared and characterized transition metal complexes with the general class of 1,1-dithioanionic ligands, $S_2C{=}X^{2-}$. In particular, they prepared the N-cyanocarbimate ligand *via* the reaction of CS_2 with NCN^{2-}. In our laboratory[2] the N-cyanocarbimic acid and anion were prepared utilizing the reaction of xanthane hydride (I)[4,5] with base.[6] Originally[4] a cyclic structure (II) was proposed for the N-cyanocarbimate anion. Later, however, Hantzsch and Wolvekamp[7] proposed a noncyclic structure (III), mainly because such a structure appears more consistent with the formation of Cu(II), Pb(II), and Ag(I) complexes.[6] The observation[2,3b] of sharp strong bands in the infrared spectra of various complexes at ~2180 cm^{-1} supports structure III.



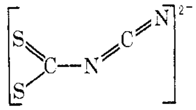
I



II



III



IV

Although the evidence just summarized is all indicative that a structure of type III is correct and that the S_2CNCN^{2-} ligand chelates through its two sulfur atoms, there has been no unequivocal proof of this. Furthermore, even if we assume that this type of structure is correct, it is of interest to know whether it is best represented by III, by IV, or by something intermediate.

A single-crystal X-ray diffraction study of a representative complex, $Ni(S_2CNCN)_2^{2-}$, in the form of its tetraphenylarsonium salt[3b] was therefore carried out. The results are reported here.

Procedure

Data Collection.—Crystals of tetraphenylarsonium bis(N-cyanodithiocarbimato)nickelate(II), $[(C_6H_5)_4As]_2[Ni(S_2CNCN)_2]$, were obtained by slow evaporation of a methanol solution. A well-formed crystal approximately 0.2 × 0.2 × 0.3 mm was mounted along the a^* axis. Systematic absences hkl for $k + l = 2n +$

---

[1] This work was supported by the National Science Foundation (Grant No. G. P. 7034X) and by Lawrence Radiation Laboratory, Inorganic Materials Research Division, under the auspices of the Atomic Energy Commission.

[2] F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **6**, 229 (1967).

[3] (a) J. P. Fackler, Jr., and D. Coucouvanis, *Chem. Commun.*, 556 (1965); (b) J. P. Fackler, Jr., and D. Coucouvanis, *J. Am. Chem. Soc.*, **88**, 3913 (1966).

[4] W. v. Schneider and E. Erlenmeyer, *Ber.*, **3**, 339 (1870).

[5] A. Hordvik, *Acta Chem. Scand.*, **17**, 2575 (1963).

[6] A. Fleischer, *Ann.*, **179**, 204 (1875).

[7] A. Hantzsch and M. Wolvekamp, *ibid.*, **331**, 265 (1904).