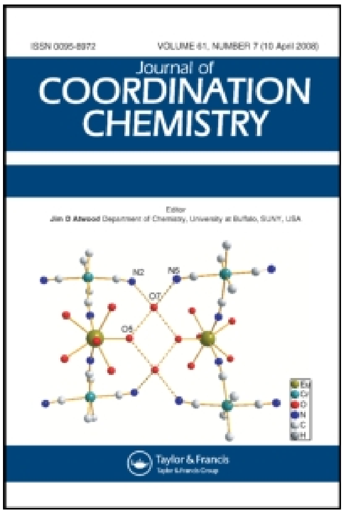

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THE CRYSTAL AND MOLECULAR STRUCTURE OF THE VIOLET ISOMER OF $(\phi_3P)_2[(CF_3)_2C_2S_2]$ RuCO

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The crystal structure and the details of the molecular configuration of the violet isomer of $(\phi_3P)_2[(CF_3)_2C_2S_2]$-RuCO were established from three dimensional, single crystal, X-ray diffraction data. This isomer crystallizes in the orthorhombic system, space group D_{2h}^{15}–Pbca, in a cell whose dimensions are: $a = 22.394(8)$, $b = 19.107(6)$ and $c = 17.480(5)$ Å. The measured and calculated densities are 1.56(2) and 1.56 gm-cm^{-3} and $z = 8$ molecules/unit cell. The shape of the polyhedron of ligands around the central Ru atom is a square pyramid distorted principally by the fact that the Ru–C bond length is shorter than the four bonds to the nearly equidistant phosphorus and sulfur ligands. The dithiolene sulfur atoms occupy adjacent positions in the basal plane; the two triphenylphosphine ligands occupy a basal plane site and the unique axial position while the carbonyl carbon occupies the fourth basal plane site.

The two Ru–S bond lengths are 2.298(3) and 2.287(3) Å, while the two Ru–P distances are 2.353(3) and 2.274(3) Å in length, the latter being the basal plane Ru–P bond. The Ru–C and C–O bond lengths are 1.849(11) and 1.133(11) Å, respectively. The bonds within the triphenylphosphines are normal and the phenyl rings are planar, nearly equilateral hexagons. The dithiolene ligand has C–S and (ethylene C)–(ethylene C) distances of 1.719(10) and 1.358(12) Å, respectively, which conform more closely to values expected from an unsaturated cis-dithiol than a dithioketone. The closest inter *or* intramolecular contact between the Ru atom and the phenyl hydrogens is 3.08 Å, which is about 0.5 Å longer than the sum of van der Waals' radii. When refinement was complete, the unweighted and weighted R(F) factors, for 2386 observed reflections, were 0.060 and 0.055, with an error of fit of 1.16.

INTRODUCTION

In the course of their synthetic studies of ruthenium-sulfur compounds, Balch and Miller[4] discovered an unusual substance with composition $(\phi_3P)_2$-$[(CF_3)_2C_2S_2]$ RuCO which crystallizes as orange prisms from most solvents. However, when it is recrystallized from a dichloromethane: hexane solution, two crystalline forms are obtained – one orange and the other one violet. Elemental analyses of both forms indicate that they have the same composition and that neither has solvent molecules of crystallization. Balch and Miller showed[4] that interconversion of the two forms can readily be achieved by selective use of solvents. For instance, the violet form can be converted to the orange one by recrystallization from acetonitrile.

Crystals of both forms, suitable for x-ray studies, can be obtained from the dichloromethane:hexane solution. The orange and violet crystals are not intergrown and can be separated mechanically and indexed. In this report we describe the structural details of the violet form of this interesting pair of ruthenium isomers; the orange isomer has been described elsewhere.[5]

Unit Cell and Space Group

Crystals of $(\phi_3P)_2[(CF_3)_2C_2S_2]$Ru(CO), mol. wt. 880.98 gm-mole^{-1}, are orthorhombic with cell parameters $a = 22.394(8)$, $b = 19.107(6)$ and $c = 17.480(5)$ Å. The volume of the unit cell is 7479.4 Å;^{3} $d_0 = 1.56(2)$ gm-cm^{-3} by flotation in aqueous $ZnBr_2$ solution, $d_c = 1.56$ gm-cm^{-3} for $z = 8$ molecules/unit cell. The total number of electrons in the unit cell, F(000) = 3616. The space group was uniquely determined from the absences observed in films (0kl, $k \neq 2n$; h0l, $l \neq 2n$ and hk0, $h \neq 2n$) to be D_{2h}^{15}–Pbca.

EXPERIMENTAL

The crystal chosen for data collection was bound by the {100}, {010} and {001} family of planes and was measured to be 0.20, 0.20 and 0.36 mm, respectively along the [100], [010] and [001] directions. It was mounted on an eucentric goniometer head with the c-axis aligned, approximately, along the ϕ axis of a Picker four-circle diffractometer which was equipped with a high-density graphite monochromator. Data were collected at approximately 21°C using MoK$\bar{\alpha}$ radiation ($\lambda = 0.71069$ Å). The detection system was equipped with a pulse-height analyzer and a pulseshape discriminator and approximately 90% of the diffracted intensity was accepted. Data were collected using the $\theta - 2\theta$ step-scan technique with a take-off angle of 1.9° and each reflection was scanned in steps of $\Delta(2\theta) = 0.03°$. The width of the scan for each reflection was computed from the expression

$$\text{total scan} = 1.80\,(1.0 + 1.0 \tan\theta)$$

and the center of the scanning range was set at the unweighted average value of the Bragg angle corresponding to MoKα_1 and MoKα_2 wavelengths (0.7104 Å). Since partial resolution of the α_1 and α_2 peaks was observed in the upper range of 2θ values explored ($2\theta(\max) \leqslant 52°$) background was taken to be the first and last five points of the scan.

The step scanned data were not smoothed (i.e., they were not fitted to a polynomial) and data from a single form (h, k, l) was collected. A total of 7982 reflections were scanned which included many duplicate records since the data were collected by incrementing the values of $d^*(\min)$ and $d^*(\max)$ and each successive range was made to overlap the previous one by several hundred reflections. Periodic checks on electronic stability and crystal sensitivity to radiation damage were achieved by the use of two standard reflections (7, 1, 7 and 0, 12, 0) which were recorded after every 30 data points. Individual measurements of the two standards did not differ from the mean by more than 3% throughout the entire period of data collection.

For $(\phi_3P)_2[(CF_3)_2C_2S_2]RuCO$ the linear absorption coefficient, μ, is estimated from the sum of atomic absorption coefficients for MoK$\bar{\alpha}$ radiation[6a] to be 6.69 cm^{-1}. An absorption correction[7] was made based on the previous description of the crystal (*vide supra*). The transmission factors ranged from 0.877 to 0.884. The data were corrected for Lorentz and polarization effects but no attempt was made to include the effect of partial polarization of the crystal-monochromatized x-ray beam since the correction for MoKα is small. At this point the entire set of data was placed unto a single scale and this procedure yielded 2386 reflections for which $F_0^2 \geqslant 2\sigma(F_0^2)$, where

$$\sigma(F_0^2) = 1/Lp[(I + B)^2 + (0.05 \times I)^2]^{1/2}$$

with Lp = the Lorentz-polarization factor, I = the total integrated intensity of the peak and B = the time scaled background.[8]

Determination of the Structure

The data for which $2\theta \leqslant 30°$ was used to compute a three-dimensional, sharpened, origin-removed Patterson function from which the approximate coordinates of the Ru, two sulfurs and two phosphorus atoms were deduced. A subsequent series of structure factor calculations and Fourier syntheses provided the missing set of atoms. The scattering curves used in the structure factor calculations were those given by Cromer.[9] The real and imaginary components of the anomalous dispersion corrections were eventually used and those were obtained from the International Tables.[6b] Full-matrix least-squares refinement of the scale factor and of the positional and isotropic thermal parameters of all 53 non-hydrogen atoms gave discrepancy indices of

$$R_1(F_0) = \Sigma\,|\,(\,|F_0| - |F_c|\,)\,|\,/\,\Sigma\,|F_0| = 0.082$$

$$R_2(F_0) = [\Sigma w(F_0 - F_c)^2/\Sigma w F_0^2]^{1/2} = 0.095$$

with an error of fit

$$= [\Sigma w(F_0 - F_c)^2/\Sigma(NO - NV)]^{1/2} = 2.22,$$

where $w(F_0) = 4F_0^2/\sigma^2(F_0^2)$ and NO and NV are the number of observations and the number of variables, respectively.

The non-hydrogen atoms were allowed anisotropic motion while the hydrogen atoms were added in the calculation of the structure amplitudes at fixed, ideal, positions and with isotropic thermal parameters of 5.0 Å^2. Convergence was assumed when the ratio of shift/error was equal to or less than 0.1. At this point the values of $R_1(F_0)$ and of $R_2(F_0)$ were 0.060 and 0.055 with an error of fit of 1.16.

The positional and thermal parameters obtained from the last cycle of least-squares refinement, together with the estimated standard deviations for each of these quantities are given in Table I. A table listing the observed structural amplitudes and their calculated values is available from the authors upon request. Interatomic distances and angles and their estimated standard deviations (which include the effect of estimated errors in the lattice parameters) are given in Tables IIA and IIB. The equations of planes determined by least-squares procedures and

TABLE I

Positional and thermal parameters. The positional and thermal parameters of the Ru, P and S atoms were multiplied by 10^5 while those of the other atoms were multiplied by 10^4. The estimated standard deviations are given in parentheses and the form of the thermal ellipsoid used was $\exp-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	35478(4)	00901(3)	22253(4)	00111(2)	00131(2)	00172(2)	-00004(2)	00006(2)	-00006(2)
S1	28785(12)	-03113(12)	13305(4)	00139(8)	00169(8)	00232(9)	00000(6)	-00019(7)	00021(7)
S2	42433(12)	-05851(13)	16141(14)	00144(8)	00193(9)	00224(10)	00045(6)	-00021(7)	-00033(7)
P1	41971(12)	01463(13)	32810(13)	00134(8)	00166(8)	00180(9)	-00023(6)	-00009(7)	-00010(7)
P2	35199(12)	11966(12)	17482(14)	00139(8)	00153(7)	00203(9)	-00018(7)	00001(8)	00009(7)
O	2519(4)	0219(4)	3293(4)	0027(2)	0064(4)	0021(2)	-0004(3)	0010(2)	-0010(3)
C1	2906(5)	0222(5)	2874(5)	0023(3)	0031(4)	0007(3)	-0003(3)	-0009(3)	-0009(3)
C2	1116(4)	4066(4)	0834(5)	0012(3)	0010(3)	0019(4)	-0004(2)	0004(3)	-0008(3)
C3	1700(4)	4213(4)	0696(5)	0015(3)	0012(3)	0015(4)	0001(2)	0006(3)	0007(3)
C4	0722(5)	3697(5)	0301(7)	0024(5)	0021(4)	0051(6)	-0006(3)	0032(4)	-0010(4)
C5	2045(5)	3915(6)	0005(6)	0015(4)	0035(4)	0041(6)	-0005(3)	-0001(4)	-0002(4)
F1	0976(4)	3148(4)	-0026(5)	0040(3)	0051(3)	0091(5)	-0005(2)	-0002(3)	-0041(3)
F2	0247(4)	3421(4)	0645(4)	0040(3)	0060(3)	0058(4)	-0022(3)	0009(3)	-0029(3)
F3	0484(4)	0947(4)	4729(4)	0054(3)	0046(3)	0052(3)	0016(2)	-0031(3)	-0008(3)
F4	2540(3)	0723(4)	4919(4)	0025(2)	0085(4)	0043(3)	0008(2)	0017(2)	0022(3)
F5	2176(3)	1742(4)	5074(4)	0040(3)	0038(3)	0062(4)	-0014(2)	0017(2)	0013(2)
F6	1749(3)	0976(4)	4363(4)	0033(2)	0076(3)	0030(3)	0000(2)	0007(2)	0013(3)
C6	2845(5)	1729(5)	1930(5)	0025(4)	0019(3)	0015(4)	0008(3)	0004(3)	-0004(3)
C7	2294(5)	1405(6)	1997(6)	0013(4)	0036(4)	0042(5)	0004(3)	0005(3)	-0002(4)
C8	1766(6)	1787(6)	2057(6)	0028(4)	0032(4)	0031(5)	0018(4)	0005(3)	-0004(4)
C9	1809(6)	2518(7)	2065(7)	0022(4)	0062(6)	0041(6)	0020(4)	0005(4)	-0007(5)
C10	2369(7)	2852(6)	1996(8)	0034(5)	0031(4)	0089(8)	0027(4)	-0014(5)	-0004(5)
C11	2892(5)	2461(6)	1920(6)	0024(4)	0027(4)	0045(5)	0008(3)	-0009(4)	0014(4)
C12	3527(5)	1172(4)	0695(6)	0023(3)	0015(3)	0018(4)	-0003(3)	0001(3)	-0005(3)
C13	3981(5)	0771(4)	0332(5)	0028(4)	0006(3)	0023(4)	-0015(2)	0006(3)	-0005(3)
C14	3969(5)	00743(5)	-0453(5)	0031(4)	0023(4)	0014(4)	-0012(3)	0004(3)	0004(3)
C15	3568(6)	1090(6)	-0889(6)	0028(5)	0047(5)	0023(5)	-0016(4)	-0003(4)	-0002(3)
C16	3129(6)	1477(7)	-0519(7)	0025(4)	0060(6)	0034(6)	0001(4)	-0004(4)	0005(4)
C17	3105(5)	1523(6)	0271(6)	0022(4)	0052(5)	0011(4)	-0003(3)	-0011(3)	0006(4)
C18	4142(5)	1779(4)	2011(6)	0018(3)	0017(3)	0032(5)	0000(2)	0003(3)	0001(3)
C19	4645(5)	1826(5)	1543(6)	0014(3)	0029(4)	0044(5)	0002(3)	-0008(3)	0006(4)
C20	5108(6)	2275(6)	1749(7)	0029(4)	0033(5)	0045(5)	-0007(4)	-0006(4)	-0004(4)
C21	5064(6)	2692(6)	2394(7)	0035(4)	0034(4)	0042(6)	-0004(4)	-0024(4)	0007(4)
C22	4551(6)	2446(6)	2885(7)	0034(5)	0027(4)	0037(6)	-0007(3)	-0008(4)	0014(4)
C23	4097(5)	2179(6)	2665(5)	0036(4)	0017(3)	0011(4)	-0002(3)	0002(3)	0001(3)
C24	4986(4)	-0081(5)	3128(5)	0009(3)	0032(4)	0018(3)	0000(3)	0002(2)	-0007(3)
C25	5277(5)	-0577(5)	3566(6)	0014(3)	0023(4)	0034(5)	0004(3)	-0008(3)	-0008(3)
C26	5880(6)	-0697(6)	3433(6)	0020(4)	0042(5)	0038(5)	-0003(3)	0008(4)	-0002(4)
C27	6176(5)	-0333(6)	2880(8)	0006(3)	0030(4)	0071(7)	0002(3)	-0014(4)	-0017(4)
C28	5882(5)	0157(6)	2427(6)	0002(3)	0045(5)	0040(5)	-0001(3)	0002(3)	-0008(4)
C29	5287(5)	0279(6)	2555(5)	0011(3)	0044(5)	0020(4)	-0015(3)	0005(3)	0004(3)
C30	3941(4)	-0536(5)	3959(5)	0003(3)	0021(3)	0029(4)	0005(2)	-0006(3)	0006(3)
C31	3870(5)	-0393(5)	4738(5)	0020(3)	0026(4)	0018(3)	-0007(3)	-0005(3)	0005(3)
C32	3655(5)	-0906(6)	5220(7)	0022(4)	0033(4)	0043(5)	-0009(3)	0009(3)	0008(4)
C33	3494(4)	-1558(5)	4926(6)	0010(3)	0032(4)	0041(5)	0001(3)	0002(3)	0015(4)
C34	3574(5)	-1685(5)	4155(6)	0018(3)	0028(4)	0036(5)	0010(3)	0001(3)	0006(3)
C35	3782(5)	-1171(5)	3662(6)	0032(4)	0008(3)	0038(5)	0000(3)	-0007(3)	0002(3)
C36	4250(5)	0918(4)	3902(5)	0013(3)	0015(3)	0025(4)	0007(2)	0005(3)	0004(3)
C37	3717(5)	1201(5)	4140(6)	0024(4)	0019(3)	0026(4)	-0013(3)	0006(3)	-0011(3)
C38	3727(6)	1789(5)	4635(7)	0031(4)	0018(3)	0039(5)	-0005(3)	0006(4)	-0006(3)
C39	4258(5)	2053(6)	4888(7)	0034(5)	0026(4)	0045(6)	0004(3)	0004(4)	-0005(4)
C40	4794(6)	1755(5)	4653(6)	0039(5)	0019(4)	0034(5)	-0008(3)	-0011(4)	-0004(4)
C41	4803(4)	1175(5)	4160(6)	0009(3)	0031(4)	0027(4)	-0015(3)	-0005(3)	0005(3)

TABLE II
Interatomic distances, angles and least-square planes.

A. Bond Distances in Å

Ru - S1	2.298(3)
Ru - S2	2.287(3)
Ru - P1	2.353(3)
Ru - P2	2.274(3)
Ru - C1	1.849(11)

C1 - O1	1.133(11)	F1 - C4	1.326(11)
S1 - C3	1.717(10)	F2 - C4	1.330(11)
S2 - C2	1.721(9)	F3 - C4	1.317(13)
C2 - C3	1.358(12)	F4 - C5	1.314(11)
C2 - C4	1.467(14)	F5 - C5	1.295(11)
C3 - C5	1.542(13)	F6 - C5	1.319(11)
P1 - C24	1.837(10)	P2 - C6	1.853(11)
P1 - C30	1.853(10)	P2 - C12	1.842(9)
P1 - C36	1.833(9)	P2 - C18	1.835(10)
C24 - C25	1.381(12)	C6 - C7	1.382(13)
C25 - C26	1.389(12)	C7 - C8	1.387(14)
C26 - C27	1.361(15)	C8 - C9	1.398(15)
C27 - C28	1.388(14)	C9 - C10	1.410(17)
C28 - C29	1.379(14)	C10 - C11	1.392(14)
C29 - C24	1.389(12)	C11 - C6	1.406(13)
C30 - C31	1.397(12)	C12 - C13	1.422(13)
C31 - C32	1.376(13)	C13 - C14	1.373(12)
C32 - C33	1.393(14)	C14 - C15	1.384(15)
C33 - C34	1.381(14)	C15 - C16	1.387(16)
C34 - C35	1.385(13)	C16 - C17	1.384(14)
C35 - C30	1.371(12)	C17 - C12	1.375(13)
C36 - C37	1.376(12)	C18 - C19	1.401(13)
C37 - C38	1.415(13)	C19 - C20	1.394(14)
C38 - C39	1.372(15)	C20 - C21	1.385(16)
C39 - C40	1.390(15)	C21 - C22	1.431(16)
C40 - C41	1.403(13)	C22 - C23	1.411(13)
C41 - C36	1.406(12)	C23 - C18	1.381(12)

B. Angles in Degrees

Ru - C1 - O	171.8(9)	P1 - Ru - P2	105.2(1)
Ru - P1 - C24	118.0(3)	P1 - Ru - S1	162.3(1)

TABLE II (continued)

B. Angles in Degrees

Ru - P1 - C30	106.1(3)	P1 - Ru - S2	88.3(1)
Ru - P1 - C36	122.8(3)	P1 - Ru - C1	89.6(3)
Ru - P2 - C6	118.0(3)	P2 - Ru - S1	92.5(1)
Ru - P2 - C12	110.1(3)	P2 - Ru - S2	111.8(1)
Ru - P2 - C18	116.8(3)	P2 - Ru - C1	94.3(3)
Ru - S1 - C3	105.0(3)	S1 - Ru - S2	86.5(1)
Ru - S2 - C2	105.7(3)	S1 - Ru - C1	87.5(3)
		S2 - Ru - C1	153.2(3)
S1 - C3 - C2	121.6(4)	S2 - C2 - C3	120.7(3)
S1 - C3 - C5	115.3(4)	S2 - C2 - C4	114.0(3)
C3 - C5 - F4	108.6(9)	C2 - C4 - F1	112.9(9)
C3 - C5 - F5	113.5(9)	C2 - C4 - F2	112.5(9)
C3 - C5 - F6	110.8(9)	C2 - C4 - F3	118.6(9)
F4 - C5 - F5	109.1(3)	F1 - C4 - F2	102.9(9)
F4 - C5 - F6	104.1(3)	F1 - C4 - F3	105.0(9)
F5 - C5 - F6	110.3(3)	F2 - C4 - F3	103.4(9)
C5 - C3 - C2	122.9(4)	C4 - C2 - C3	124.7(5)
C6 - P2 - C12	101.1(4)	C24 - P1 - C30	103.0(4)
C6 - P2 - C18	104.1(5)	C24 - P1 - C36	102.5(5)
C12 - P2 - C18	105.0(4)	C30 - P1 - C36	101.8(4)
P1 - C24 - C25	122.4(8)	P2 - C6 - C7	119.8(7)
P1 - C24 - C29	116.9(8)	P2 - C6 - C11	118.8(9)
P1 - C30 - C31	121.6(7)	P2 - C12 - C13	117.8(8)
P1 - C30 - C35	117.5(8)	P2 - C12 - C17	121.5(8)
P1 - C36 - C37	116.2(7)	P2 - C18 - C19	120.3(8)
P1 - C36 - C41	121.8(7)	P2 - C18 - C23	119.3(8)
C7 - C6 - C11	121(1)	C29 - C24 - C25	121(1)
C6 - C7 - C8	121(1)	C24 - C25 - C26	119(1)
C7 - C8 - C9	118(1)	C25 - C26 - C27	121(1)
C8 - C9 - C10	120(1)	C26 - C27 - C28	121(1)
C9 - C10 - C11	121(1)	C27 - C28 - C29	119(1)
C10 - C11 - C6	118(1)	C28 - C29 - C24	120(1)
C17 - C12 - C13	121(1)	C35 - C30 - C31	121(1)
C12 - C13 - C14	119(1)	C30 - C31 - C32	120(1)
C13 - C14 - C15	121(1)	C31 - C32 - C33	120(1)
C14 - C15 - C16	119(1)	C32 - C33 - C34	119(1)

TABLE II (continued)

C15 - C16 - C17	122(1)	C33 - C34 - C35	122(1)
C16 - C17 - C12	119(1)	C34 - C35 - C30	119(1)
C23 - C18 - C19	120(1)	C41 - C36 - C37	122(1)
C18 - C19 - C20	119(1)	C36 - C37 - C38	119(1)
C19 - C20 - C21	121(1)	C37 - C38 - C39	120(1)
C20 - C21 - C22	121(1)	C38 - C39 - C40	120(1)
C21 - C22 - C23	117(1)	C39 - C40 - C41	121(1)
C22 - C23 - C18	122(1)	C40 - C41 - C36	118(1)

C. Least-Squares Planes and Deviations of Selected Atoms from These Planes.

(1) Plane Defined by S1, S2 and P1

$0.2185x + 0.8829y - 0.4156z = -0.0829$

Ru	0.354	C1	-0.210

Planes

(2) Plane Defined by Ru, S1 and S2

$0.2284x + 0.7697y - 0.5961z = -0.3714$

C2	0.114	C4	0.334
C3	0.176	C5	0.282

(3) Plane Defined by S1, S2, C2 and C3

$0.2275x + 0.8264y - 0.5151z = -0.2190$

Ru	0.165	C3	0.030
S1	-0.004	C4	0.074
S2	0.004	C5	0.007
C2	-0.030		

(4) Plane Defined by Atoms Ru, S1, S2, C2, C3, C4 and C5

$0.2251x \quad 0.7987y - 0.5580z = -0.2472$

Ru	0.003	C3	0.031
S1	-0.074	C4	0.127
S2	-0.080	C5	0.077
C2	-0.035		

Planes

(5) Plane Through C6---C11

$-0.0977x + 0.0059y - 0.9952z = -3.9549$

C6	-0.004	C9	-0.007
C7	-0.005	C10	-0.002
C8	0.011	C11	0.007

TABLE II (continued)

(6) Plane Through C12---C17

$0.5906x + 0.8065y - 0.0279z = 6.4398$

C12	-0.001	C15	-0.003
C13	-0.001	C16	0.001
C14	0.003	C17	0.001

(7) Plane Through C18---C23

$-0.4373x + 0.7270y - 0.5294z = -3.4469$

C18	0.002	C21	0.013
C19	0.007	C22	0.004
C20	-0.015	C23	-0.004

(8) Plane Through C24---C29

$-0.2346x - 0.7112y - 0.6627z = -6.1220$

C24	-0.009	C27	-0.008
C25	0.006	C28	0.004
C26	0.003	C29	0.005

(9) Plane Through C30---C35

$-0.9312x + 0.3254y - 0.1644z = -9.6795$

C30	-0.009	C33	0.009
C31	0.004	C34	-0.015
C32	-0.004	C35	0.014

(10) Plane Through C36---C41

$0.0267x + 0.6179y - 0.7858z = -4.0350$

C36	0.011	C39	-0.001
C37	-0.010	C40	0.002
C38	0.005	C41	-0.006

D. Angles Between Planes

Plane 1	Plane 2	Angle in Degrees
2	3	5.67
5	6	91.44
5	7	54.98
6	7	69.95
8	9	84.49
8	10	85.69
9	10	72.21

TABLE II (continued)

E. Selected Inter and Intramolecular Contacts Shorter than 4.00 Å.

Ru -	H35	3.08	Ru -	H37	3.54
	H7	3.28		H29	3.56
	H13	3.33		H10	3.94
S1 -	H10	2.85	S1 -	H27	3.24
	H7	2.91		H13	3.73
S2 -	H13	2.72	S2 -	H9	3.55
	H35	3.07		H14	3.62
	H21	3.17		H22	3.96
	H29	3.18			
F1 -	H20	2.84	F1 -	H34	2.94
	H33	2.84		H19	3.50
	H40	2.93		H9	3.93
F2 -	H22	2.59	F2 -	H21	3.28
	H40	2.94		H13	3.71
	H14	3.00		H9	3.90
	H39	3.27		H20	3.91
	H19	3.28			
F3 -	H19	2.56	F3 -	H14	3.29
	H14	2.85		H20	3.31
	H13	2.88		H28	3.54
	H13*	3.28		H29	3.63

* At a different symmetry position from the previous one

F4 -	H37	2.51	F4 -	H31	3.47
	H38	3.03		H26	3.90
F5 -	H38	2.70	F5 -	H10	3.39
	H33	2.80		H37	3.53
	H34	3.23		H16	3.62
	H17	3.24			
F6 -	H28	3.04	F6 -	H37	3.63
	H14	3.63		H34	3.69

the distances of atoms from these planes are given in Table IIC. Angles between the normals of selected pairs of planes are given in Table IID and inter- and intramolecular contacts shorter than 4.00 Å are listed in Table IIE.

The following programs were used during this study: PROCH (initial processing of the raw data); DATAPH (Lorentz-polarization and absorption corrections); ESORTH (sorting and averaging); JIMDAP (a local version of the Fourier summation program originally written by A. Zalkin); LINUS (a local modification of the Busing, Martin and Levy ORFLS least-squares program);[10] ORFEE (function and error);[11] and ORTEP (C. Johnson's molecular plotting program).[12]

Description of the Structure

The violet isomer of $(\phi_3P)_2[(CF_3)_2C_2S_2]RuCO$, hereafter referred to as (I), contains an approximately square-pyramidally coordinated Ru atom. The base of the square pyramid is defined by a triphenylphosphine phosphorus, a carbonyl carbon and the two sulfurs of a bidendate perfluoromethyldithiolene moiety. The metal lies above the basal plane of the ligands and the coordination polygon is irregular as a result of the fact that the Ru–C bond is about 0.5 Å shorter than the approximately equidistant sulfur and phosphorus ligands. Some distortion from regularity also appears to result from steric hindrance between the basal plane triphenylphosphine and the perfluoromethyldithiolene ligand.

The phenyl rings on each phosphorus are disposed so as to minimize intramolecular contacts with one another. The CF_3 groups are arranged such that intramolecular fluorine contacts are minimized, as is the case in a number of other studies of perfluorodithiete derivatives.[5,13] In each molecule there are a number of phenyl hydrogens which are oriented towards the metal atom, as shown in Figure 2. The nearest *inter-* or *intra*molecular contact is the *intra*-molecular contact between Ru and H(35); however, the distance is quite large (3.08 Å) and exceeds the sum of van der Waals' distances by 0.5 Å. Thus, unlike $(\phi_3P)_3RuCl_2$, where La Placa and Ibers[14] found a quasi-octahedral array of ligands about the Ru atom as a result of a short Ru–H *intra*molecular contact, molecule (I) is a genuine example of five-coordination for the Ru atom. In (I) there are other *intra-* and *inter*molecular Ru–H contacts which are shown in Figure 2 but all of these are longer than the Ru–H(35) contact. The packing of the molecules is such that the axial triphenylphosine of one molecule is directly below the basal plane of the adjacent molecules (see for instance the location of C(10) in Figure 1 and the Ru–H(10) contact shown in Figure 2). The arrangement of the molecules in the unit cell is shown in Figure 3.

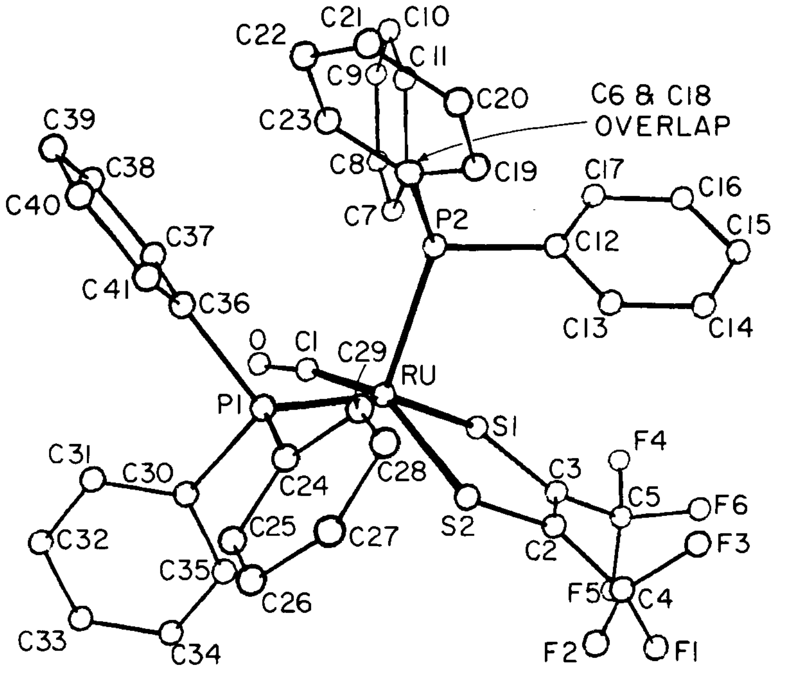


FIGURE 1 The molecular configuration of $[(CF_3)_2C_2S_2](\phi_3P)_2RuCO$. In this figure we show the numbering system employed in the structural refinement. For the sake of clarity the hydrogen atoms were omitted and the thermal parameters of the carbon atoms were made spherical and of arbitrarily convenient size.

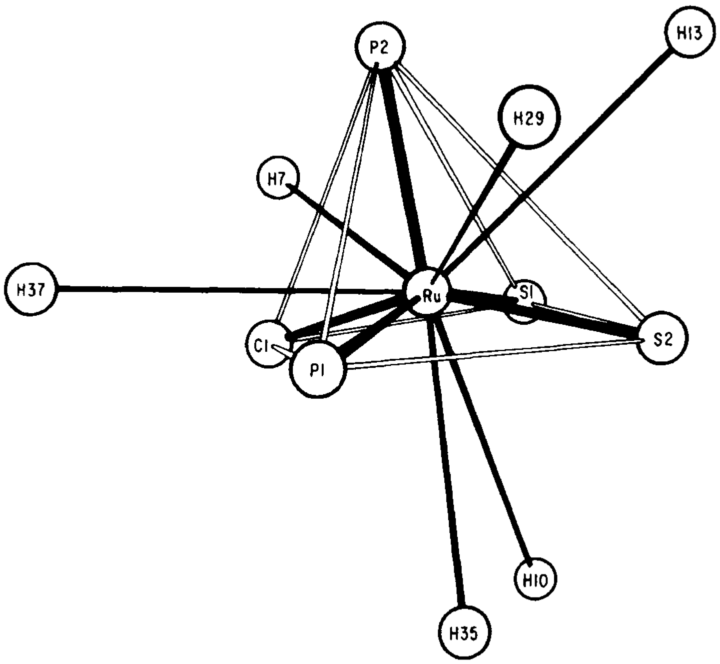


FIGURE 2 Atoms surrounding the Ru atom. This Figure includes all the nearest contacts up to a sphere of 4.0 Å radius centered at the Ru atom. The hydrogen atoms are at the following distances from the Ru: H(35) = 3.10, H(7) = 3.22, H(13) = 3.34, H(29) = 3.52, H(37) = 3.60 and H(10) = 3.93 Å. The numbering system is such that each hydrogen atom has been assigned the number of the carbon atom to which it is attached. The two hydrogens below the ruthenium, H(35) and H(10), are intra and an intermolecular contact, respectively.

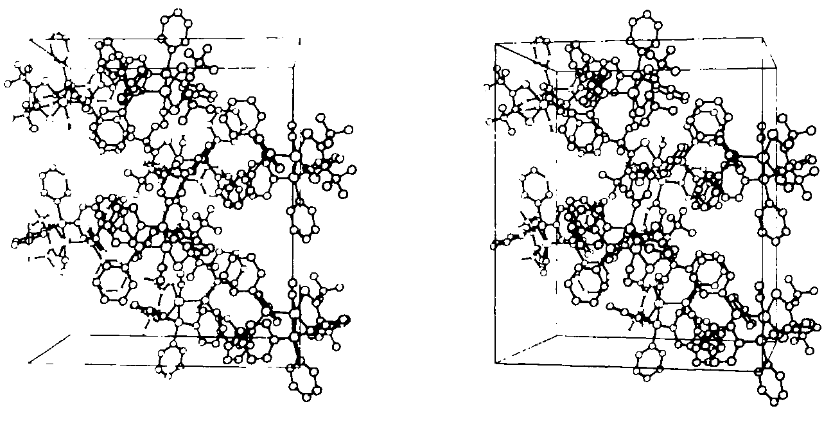


FIGURE 3 Packing diagram of the molecules in the violet isomer of $(\phi_3P)_2[(CF_3)_2C_2S_2]_2RuCO$. The vertical axis is the y-axis, and the horizontal axis is the x-axis of the right-handed cell. This is a stereoscopic pair.

DISCUSSION

The Triphenylphosphines

The carbon atoms of the six phenyl rings, which were refined individually, show the expected planar, hexagonal geometry. For each of the six rings the largest deviation from planarity was given by C7(0.11 Å), C14 and C15(0.003 Å), C20(0.015 Å), C24(0.009 Å), C34(0.015) and C36(0.011 Å), while the largest deviation from hexagonal geometry is represented by the C–C–C angle of 117(1)° at C22. The average of the thirty-six C–C distances is

1.389(12) Å which compares favorably with the value of 1.397(1) Å Stoicheff found[15] for gaseous benzene and the value of 1.392(4) Å for crystalline benzene obtained from X-ray data by Cox, Cruikshank and Smith.[16] Our data was not corrected for libration of the rings, as recommended by Cruikshank[17a] and by Schomaker and Trueblood.[17b]

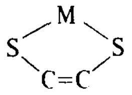
The P–C distances for the triphenylphosphine groups have an average value of 1.842(10) Å. The average value of the P–C–C angles is 119.5(7)°, C–P–C angles have an average value of 102.9(4)° while the Ru–P–C angles have an average value of 115.3(3)°. These angles indicate a 3m idealized point group symmetry at the phosphorus atom. The C–P–C angles are intermediate between those found in $(CH_3)_3P$[18] and $(CH_3)_3PO$,[19] where the average angles are 98.6° and 106.0° respectively. In ϕ_3P itself[20] the average C–P–C angle is 103.0(2). The average P–C distance of 1.842(10) Å in (I) compares with values of 1.848(5) Å in $(\phi_3P)_3RuCl_2$,[21] 1.858(20) Å in Ru_2Cl_5–$(PBu_3^n)_4$,[22] 1.81(1) Å in $IrO_2Cl(CO)(P\phi_3)_2^5$ and similar values in related complexes[23–28] which involve other metals as well. The P–C distances are 1.846(3) and 1.828(3) Å in $P(CH_3)_3$ and $P(C_6H_5)_3$ respectively.[18,20] Thus, to the extent of the precision with which the P–C bond is known, there is relatively little change in the length of these bonds despite (a) the change from aryl to alkyl phosphine, (b) the change in the central metal, (c) the significant change in Ru–P distance in some of these complexes (*vide infra*). Thus, coordination of a trialkyl or aryl phosphine to various transition metals introduces little change in the P–C geometry of the ligand.

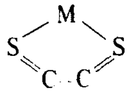
In (I) the ruthenium-phosphorus bond lengths are 2.353(3) Å (equatorial) and 2.274(3) Å (axial). In $(\phi_3P)_3RuCl_2$,[21] where a quasi-octahedral coordination geometry exists for the Ru(II) atom, the axial Ru–P distance is 2.230(8) Å while the two equatorial distances are 2.374(6) Å and 2.412(6) Å. For the octahedrally coordinated ruthenium atoms in $Ru_2Cls(PBu_3^n)_4$,[22] $[Ru_2Cl_3(Et_2\phi P)_6]$ $[RuCl_3(Et_2\phi P)_3]$[27] and in $Ru_2Cl_4(Et_2\phi P)_5$[28] the average Ru–P distances are 2.329(5) Å, 2.298(6) and 2.318(7) Å, respectively. In the apparent five coordinate ruthenium complex $[RuCl(NO)_2$-$(P(C_6H_5)_3)_2][PF_6]$,[29] the Ru–P distances are 2.432(5) and 2.424(5) Å.

The axial contraction of the Ru–P bond observed in (I) [2.274(3) vs 2.353(3) Å; $\Delta = n(\sigma_1^2 + \sigma_2^2),^{1/2}$ or n = 18.6] is more pronounced in $(\phi_3P)_3RuCl_2$,[21] where the axial Ru–P bond length is 2.230(8) Å and the two basal Ru–P distances are 2.374(6) and 2.412(6) Å. Shortening may be atrributed to steric effects or may result from a strong axial π-bond in square pyramidal metal complexes as has been suggested by Ballhausen and Gray.[30] On the other hand, in the complexes $Ru_2Cl_4(Et_2\phi P)_5$[28] and $[Ru_2Cl_3(Et_2\phi P)_6][RuCl_3(Et_2\phi P)_3]$,[27] both containing octahedral Ru, differences in Ru–P bond lengths have been attributed to steric effects. For the case of three *fac* diethylphenyl phosphine groups,[28] the Ru–P bond lengths are longer than those for bonds between ruthenium and a different phosphine ligand, within the same molecule,[28] having less steric hindrance. In (I) the angles P(axial)–Ru–P(basal) and P(axial)–Ru–S2 are 105.18(9) and 111.81(10)° respectively while the angles P(axial)–Ru–S1 and P(axial–Ru–Cl, which involve less sterically hindered atoms, are 92.46(9) and 94.5(3)°, respectively. Thus, steric hinderance appears to have caused an increase in the P–Ru–ligand angle and the Ru–P distance. A similar effect has been observed in $[Ru_2Cl_3(Et_2\phi P)_6]$-$[RuCl_3(Et_2\phi P)_3]$.[27] Finally, in $Ru_2Cl_5(PBu_3^n)_4$[22] a similar, but lesser, crowding has been observed with n-butyl groups which leads to a P–Ru–P angle of 102° for the two *cis* trialkyl phosphine ligands and a shorter average Ru–P bond length of 2.329(5) Å than that found for a Ru atom in a similar environment but bonded to a triaryl phosphine.[21] In conclusion, it seems that an axial bond shortening due to strong π-bonding is not a general phenomenon of square-pyramidal configurations of transition metals since a review of such systems shows that less than half exhibit axial shortening.[31] Rather, it would appear that steric effects and phosphine substituent effects (alkyl *versus* aryl) play a primary role in the determination of Ru–P bond lengths in these five and six coordinated ruthenium complexes.

The Dithiolene Ligand

The $S_2C_2C_2$ fragment of the dithiolene ligand is essentially planar, as are similar fragments in other perfluoromethyldithietene metal complexes.[32–35] The C–S bond distances are 1.717(10) and 1.721(9) Å which should be compared with the values of 1.65–1.66 Å for C–S double bonds in tetraethylthiuramdisulfide[36] and in allylthiourea[37] and the values of 1.87–1.89 Å for C–S single bonds in gliotoxin[38] and diglycylcystein.[39] The ethylenic C–C distance of 1.358(12) Å is quite close to the value expected for a double bond; thus, the S–C–C–S fragment exhibits those structural characteristics associated with the dithiol form (a) of the ligand as found in such complexes as $[n\text{-}Bu_4N]_2[Fe(S_2C_2\{CF_3\}_2)_2]_2$[32]


(a)


(b)

and in $[n\text{-}Bu_4N][\phi_3POFe(S_2C_2\{CF_3\}_2)_2]$[32] and in contrast with the more dithioketonic form of the ligand found in $\phi_3AsFe(S_2C_2\{CF_3\}_2)_2$[13a] and in $[Co(S_2C_2\{CF_3\}_2)_2]_2$.[33] Some delocalization of charge is very likely to occur in all of these complexes but a valence bond description of the sulfur ligand in the Ru complex would involve a greater contribution from (a) than from (b).

The (ethylenic C)–(perfluoromethyl carbon) distances of 1.542(13) and 1.467(14) Å compare favorably with similar distances in related complexes,[32–35] as do the C–F distances and angles. The fluorine atoms of the perfluoromethyl groups, particularly those associated with C4, exhibit the considerable torsional motional characteristics observed for these moieties in related complexes.[32–35] The F . . . H non-bonded contacts for F4, F5 and F6 are stronger than those for F1, F2 and F3 (see Table III). Therefore, the librational motion exhibited at C5(F4, F5, F6) is less than that for group C4(F1, F2, F3). This effect is reflected in the values of the r.m.s. amplitudes of thermal motion for the fluorine atoms which are smaller for the first group (see Table I). A similar effect has been observed in other metal complexes containing perfluoromethyldithietene ligands.[13,32–35] The extent of the librational motion in most of these complexes is sufficiently large that the ellipsoidal, individual, thermal motional model is not adequate to describe the motion of the fluorine atoms of the CF_3 groups. A final difference map computed at the completion of refinement revealed no significant residual electron density in the region of the ruthenium atom, the carbonyl ligand or the atoms of the two phosphine ligands, which suggests that the use of this model for the thermal motion of the CF_3 groups has no adverse effect on the geometry of the other portions of the molecule.

TABLE III
Comparison of bond distances and angles in the orange and violet isomers.

Bonds (Å)	Violet	Orange
Ru-P (Apical)	2.274(2)	-
(Axial)	2.353(3)	2.381(2) 2.397(2)
Ru-S	2.286(2) 2.335(2)	2.287(3) 2.298(3)
Ru-C (Axial)	1.849(11)	-
(Apical)	-	1.827(10)
Angles (deg)		
S-Ru-S	86.5(1)	85.1(1)
S-Ru-P	88.3(1)	84.0(1)
P-Ru-C	89.6(3)	-
P-Ru-P	-	100.8(1)
C-Ru-S	87.5(3)	-
P(1)-Ru-S(1)	-	85.8(1)
Ru-C-O	172(1)	174(1)

The Ru–C–O Fragment

The Ru–C distance of 1.849(11) Å is shorter than the values 1.861(15), 1.91(2), 1.92(4), 1.89(1), 1.93(3), and 2.05(5) for the complexes $[(CH_3)_3C_{10}H_5]Ru(CO)_9$,[40] $Ru_3(CO)_{12}$,[41] $Ru_6(CO)_{14}[C_6H_3(CH_3)_3]$,[42] $[(CH_3)_3Sn(CO)_3RuSn(CH_3)_2]$,[43] $[(CO)_3RuBr_2]_2$[44] and $Ru_6(CO)_{17}C$[45] respectively. A useful comparison can be made with *cis*-(diethylenetriammine) tricarbonylmolybdenum, for which the (Mo–C bond order) vs. (bond length) has been calculated.[46] When the same curve is used, scaled by the difference in Mo(0) radius versus Ru(II) radius,[6c] the Ru–C bond order is estimated to be approximately 2 and the C–O bond length of 1.133(11) Å may also be regarded as a double bond. Therefore, the metal–carbon–oxygen system appears to be best represented by the form Ru=C=O. This configuration is consistent with the observation by Blach and Miller[4] that the carbonyl group is relatively inert to substitution.

Comparison of Orange and Violet Isomers

A comparison of some significant parameters in the coordination spheres of the two isomers is shown in Table III. In the orange isomer the base of the square pyramid is formed by two phosphorus and two sulphur atoms of the coordinating ligands while the apical position is occupied by the carbonyl carbon atom.[5] The ruthenium atom is situated 0.34 Å above the basal plane. In the violet isomer the carbonyl and one of the tri-phenyl phosphine groups have interchanged positions. However, the ruthenium atom remains about the same distance (0.35 Å) above the basal plane formed by the two sulfur atoms and one phosphorus atom while the carbon atom is 0.21 Å below this plane. A significant shortening of the Ru–P bond distance accompanies the change from axial to apical position. Similarly the Ru–C bond distance increases in the axial versus apical position but the larger error in this bond distance does not allow a firm conclusion on this point. Bond angles about the base of the pyramid are given in Table III starting with S(1) and proceeding clockwise around the base. As discussed previously[5] crowding of the two adjacent triphenyl phosphine ligands results in a large P–Ru–P angle relative to other angles in the base. However, when the carbonyl group replaces the phosphine a much smaller angle results and all the ligand–metal–ligand angles fall into a narrow range. Finally, it should be noted that in the orange isomer the carbonyl group tilts towards the phosphine ligands and away from the sulfur atoms. In the violet isomer the apical phosphorus tilts towards a position roughly half way between S(1) and the carbonyl group.

There is no sixth ligand about the ruthenium atom in the solid. Two hydrogen atoms are in the region of the sixth (octahedral) coordination site but the distances to H35 and to H10 are longer by at least 0.5 Å than van der Waals' distances. These hydrogen atoms belong to carbon atoms 35 and 10 and they represent intra and intermolecular contacts, respectively, for the Ru atom. It is interesting to note that the recystallization of the violet form from a polar solvent such as acetonitrile leads exclusively to the orange form. This seems to indicate an attack at the open sixth position of the violet form, molecular rearrangement, solvent elimination and formation of the orange form. It is found that the black crystals of $(\phi_3P)_3RuCl_2$, which formally also contains a Ru(II) ion with a square-pyramidal coordination geometry and a hydrogen atom blocking the sixth coordination site, undergo a rapid color change in dilute solutions.[14]

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REFERENCES AND NOTES

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4. J. S. Miller and A. Balch, *Inorg. Chem.*, **10**, 1410 (1971).
5. J. S. Ricci, Jr. A. Clearfield and I. Bernal, *J. Cryst. Mol. Structure*, **4**, 43 (1974).
6. *International Tables for X-Ray Crystallography*, The Kynoch Press, Birmingham, England, 1967. (a) Vol. III, p. 162; (b) Vol. III, p. 215; (c) Vol. III, p. 257.
7. W. H. Zachariasen, *Acta Cryst.*, **23**, 558 (1967); P. Coppens and W. C. Hamilton, *Acta Cryst.*, **A26**, 71 (1970).
8. P. W. R. Corfield, R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
9. D. T. Cromer, private communication.
10. W. R. Busing, K. O. Martin and H. Levy, *ORFLS, A Fortran Crystallographic Least-Squares Program*, ORNL–TM–305, Oak Ridge National Laboratory, 1962.
11. W. R. Busing, K. O. Martin and H. Levy, *ORFFE, A. Fortran Crystallographic Function and Error Program*, ORNL-TM-306, Oak Ridge National Laboratory, 1962.
12. C. K. Johnson, *ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*, ORNL-3794 Revised, Oak Ridge National Laboratory, 1965.
13. (a) E. F. Epstein and I. Bernal, *J. Organometal Chem.*, submitted, and references therein.
    (b) J. A. Herman and R. M. Wing, *J. Organometal Chem.*, **63**, 441 (1973).
14. S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).
15. B. P. Stoicheff, *Can. J. Phys.*, **32**, 339 (1954).
16. E. G. Cox, D. W. J. Cruickshank and J. A. S. Smith, *Proc. Royal Soc.*, **A247**, 1 (1958).
17. (a) D. W. J. Cruickshank, *Acta Cryst.*, **9**, 754, 757 (1956);
    (b) V. Schomaker and K. N. Trueblood, *Acta Cryst.*, **B24**, 63 (1968).
18. L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, **32**, 512 (1960).
19. H. K. Wang, *Acta Chem. Scand.*, **19**, 879 (1965).
20. J. J. Daly, *J. Chem. Soc.*, 3799 (1964).
21. S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).
22. G. Chioccola and J. J. Daly, *J. Chem. Soc.* (A), 1981 (1968).
23. S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 2581 (1965).
24. G. G. Messmer and E. L. Amma, *Inorg. Chem.*, **5**, 1775 (1966).
25. G. G. Messmer, E. L. Amma and J. A. Ibers, *Inorg. Chem.*, **6**, 725 (1967).
26. R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).
27. K. A. Raspin, *J. Chem. Soc.* (A), 461 (1969).
28. N. W. Alcock and K. A. Raspin, *J. Chem. Soc.* **(A)**. 2108 (1968).
29. C. G. Pierpont, D. G. VanDerveer, W. Durland and R. Eisenberg, *J. Am. Chem. Soc.*, **92**, 4760 (1970).
30. C. J. Balhausen and H. B. Gray, *Inorg. Chem.*, **2**, 426 (1963).
31. J. S. Wood, *Progress in Inorganic Chemistry*, J. S. Lippard, Ed., Interscience, New York, 1972, pp. 227–486.

32. E. F. Epstein and I. Bernal, *Chem. Commun.*, 136 (1970).
33. J. H. Ennemark and W. N. Lipscomb, *Inorg. Chem.*, **4**, 1729 (1965).
34. R. D. Schmitt, R. M. Wing and A. H. Maki, *J. Am. Chem. Soc.*, **91**, 4394 (1969).
35. J. H. Ennemark and J. A. Ibers, *Inorg. Chem.*, **11**, 2636 (1968).
36. I. L. Karle, J. A. Estlin and K. Britts, *Acta Cryst.*, **22**, 273 (1967).
37. K. S. Dragonette and I. L. Karle, *Acta Cryst.*, **19**, 978 (1965).
38. J. Fridrichsons and A. McL. Mathieson, *Acta Cryst.*, **23**, 439 (1967).
39. M. O. Chaney and L. K. Steinrauf, *Acta Cryst.*, **B24**, 1564 (1968).
40. M. R. Churchill, K. Gold and P. H. Bird, *Inorg. Chem.*, 8, 1956 (1969).
41. R. Mason and I. M. Rae, *J. Chem. Soc.*, (A), 778 (1968).
42. R. Mason and W. R. Robinson, *Chem. Commun.*, 468 (1968).
43. S. F. Watkins, *J. Chem. Soc.*, (A), 1552 (1969).
44. S. Merlino and G. Montagnoli, *Acta Cryst.*, **B24**, 424 (1968).
45. A. Sirigu, M. Bianchi and E. Benedetti, *Chem. Commun.*, 596 (1969).
46. F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 314 (1965).