vents such as benzene, chloroform, and CS_2; however, in the case of $NiS_4C_4H_4$ it is noteworthy that there were no significant changes in infrared spectra under these conditions.

The Crystal and Molecular Structures of the Cis and Trans Isomers of Bis(trichlorogermanyl)tetracarbonylruthenium

By R. Ball and M. J. Bennett*

The crystal and molecular structures of the trans and cis isomers of bis(trichlorogermanyl)tetracarbonylruthenium have been determined. *trans*-$Ru(CO)_4(GeCl_3)_2$ crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 9.152$ (1) Å, $b = 10.025$ (1) Å, $c = 8.399$ (1) Å, $\beta = 94.84$ (1)°, and two molecules per unit cell ($\rho_{obsd} = 2.46$ g cm^{-3}, $\rho_{calcd} = 2.47$ g cm^{-3}). *cis*-$Ru(CO)_4(GeCl_3)_2$ crystallizes in monoclinic space group $P2_1$ with unit cell dimensions $a = 9.759$ (5) Å, $b = 12.608$ (10) Å, $c = 12.878$ (9) Å, $\beta = 91.57$ (10)°, and four molecules per unit cell ($\rho_{obsd} = 2.40$ (2) g cm^{-3}, $\rho_{calcd} = 2.39$ g cm^{-3}). Data were collected using counter methods and the structures were refined using least-squares procedures to give $R = 0.019$ and 0.041 for trans and cis isomers, respectively. Both structures contain discrete molecular species with octahedral coordination of the ruthenium atoms. The chemically different ruthenium–carbon distances in the cis isomer are not significantly different from each other—1.98 Å (trans to $GeCl_3$), 2.00 Å (trans to CO)—or from that observed in the trans isomer, 1.98 Å. The ruthenium–germanium distances are the same in both isomers (2.48 Å). These bond lengths are consistent with the force constant calculations that had suggested an unusual π-bonding ability for the trichlorogermanyl groups in these compounds.

Introduction

Compounds of the type $M(CO)_4(M'X_3)_2$ (where M = Fe, Ru, Os; M' = Si, Ge, Sn; X = Cl, Br, I, alkyl, aryl) have been found to exist as cis and/or trans isomers.[1–6] There are several factors which can affect the relative stability of the cis and trans isomers. A consideration of π-bonding abilities for the ligands CO and $M'X_3$ suggests that any discrepancy (either CO $\gg$ $M'X_3$ or $M'X_3$ $\gg$ CO) would favor the cis isomers. These relative π-bonding abilities would be expected to vary with M, M', and X. The other major factor influencing the preferred geometry involves intramolecular repulsions. Thus the investigations of Stone, *et al.*,[2,5] on trialkyl and triaryl, silyl, and stannyl derivatives of $Ru(CO)_4$, where definite equilibria were established, showed increasing preference for the trans structure as the bulkiness of the $M'R_3$ group increased. However, when X = a halogen in the cis compounds, an additional interaction may be possible but attractive in nature rather than repulsive. This is due to the potential to form intramolecular halogen bridges where the main group IV element increases its coordination number to 5. Thus Graham and Kummer[1] recognized the possible importance of structures I and II for *cis*-$M(M'X_3)_2$ fragments. While the formation of a weak halogen bridge has been demonstrated in bipy(CO)$_3$-$ClMoSnCH_3Cl_2$,[7] as yet there is no direct confirmation that cis $M'X_3$ groups do interact in this way.

I   II
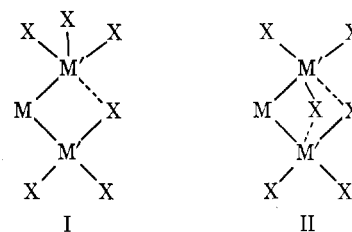
Of particular interest was the synthesis and isolation of both the cis and trans isomers of bis(trichlorogermanyl)tetracarbonylruthenium $(Ru(CO)_4(GeCl_3)_2)$[6] where the spectroscopic studies[5] suggested that the π-acceptor properties of $GeCl_3$ were comparable with those of carbon monoxide. The physical properties of the cis and trans isomers raised the question that the cis and trans isomers might contain intra- and intermolecular halogen to Ge bridge bonding, respectively.[6] The current structural study was undertaken to investigate these features.

Experimental Section

(a) *trans*-$Ru(CO)_4(GeCl_3)_2$.—The white well-formed crystals, as supplied by Dr. W. A. G. Graham and Mr. R. K. Pomeroy, were found to be suitable for an X-ray diffraction study. The preliminary photography—0*kl*, 1*kl*, 2*kl* (Cu Kα Weissenberg) and *h0l*, *hk*0 (Mo Kα precession)—showed the crystals to be monoclinic, and the systematic absences—0*k*0 for $k = 2n + 1$ and *h0l* for $h + l = 2n + 1$—suggested the nonstandard space group $P2_1/n$. The lattice parameters and their estimated standard deviations were obtained at 22° as $a = 9.152$ (1) Å, $b = 10.025$ (1) Å, $c = 8.399$ (1) Å, and $\beta = 94.84$ (1)°, by a least-squares refinement using 2θ values for 12 high-angle reflections that had been accurately centered on a Picker manual four-circle diffractometer (Cu Kα$_1$ radiation, λ 1.54051 Å). The observed density, measured by flotation as 2.46 (2) g cm^{-3}, is in good agreement with that calculated, 2.47 cm^{-3}, for two mole-

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(5) S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 2559 (1969).
(6) R. K. Pomeroy and W. A. G. Graham, in preparation.
(7) M. Elder and D. Hall, *J. Chem. Soc. A*, 245 (1970).

(8) R. Gray and W. A. G. Graham, in preparation.

cules per unit cell. The molecules are required to sit at special positions with site symmetry $\bar{1}$ by these conditions. The faces and dimensions of the study crystal were determined by visual inspection to be (110) 0.19 mm $(\bar{1}\bar{1}0)$, $(1\bar{1}0)$ 0.18 mm $(\bar{1}10)$, $(10\bar{1})$ 0.12 mm $(\bar{1}01)$, and (011) 0.24 mm $(0\bar{1}\bar{1})$—the distances indicate the perpendicular distances separating each pair of centrosymmetrically related faces.

The crystal was mounted with a^* coincident with the ϕ axis of the manual diffractometer. Intensity data were collected using Mo Kα radiation to minimize absorption corrections— Mo Kα, $\mu = 58.6$ cm^{-1}; Cu Kα, $\mu = 223$ cm^{-1}. The radiation was monochromated by an oriented graphite crystal (002 reflection) and detected using a scintillation counter with pulse height analyzer tuned to a 97% window. Intensities were measured using the coupled ω-2θ scanning technique with 2θ scanned over the range $2\theta \pm 1.5°$ at a scan speed of $2°$/min. Data were measured to a maximum 2θ limit of 45°. Backgrounds were estimated from a linear interpolation of two 30-sec stationary-crystal, stationary-counter measurements made at the limits of the scan. Six standard reflections were measured periodically during data collection and showed no evidence of decomposition, the deviations being $\pm 1\%$. To provide a guide as to the correctness of the absorption correction, three $h00$ reflections were measured at 10° intervals of ϕ over the range 0–180°. The data were corrected for Lorentz polarization effects and absorption (transmission factor range 0.40–0.45) and were reduced to structure amplitudes with standard deviations estimated using the procedure of Doedens and Ibers[9] with a p factor of 0.03. The ϕ-scan data showed excellent internal consistency ($\sim 1\%$ where counting errors were negligible). Of the 806 independent reflections scanned, 667 were estimated to be significantly above background using the criterion $I/\sigma(I) > 3.0$ where $\sigma(I)$ was calculated from pure counting statistics.

(b) *cis*-Ru(CO)$_4$(GeCl$_3$)$_2$.—The same procedures as used for the trans isomer yielded the following data for the white crystals: preliminary photography—$h0l$, $h1l$, $h2l$ (Cu Kα Weissenberg) and $hk0$, $0kl$ (Mo Kα precession); systematic absences $0k0$ for $k = 2n + 1$, systematic weaknesses hkl for $h + l = 2n + 1$; space group $P2_1$ or $P2_1/m$ approximating to $B2_1$ or $B2_1/m$; lattice parameters at 22° $a = 9.759$ (5) Å, $b = 12.608$ (10) Å, $c = 12.878$ (9) Å, and $\beta = 91.57$ (1)°; observed density 2.40 (2) g cm^{-1} and calculated density 2.39 g cm^{-3} for four molecules in the unit cell; no imposed symmetry; crystal faces and forms identified as $\{101\}$, $\{10\bar{1}\}$, $\{001\}$, $\{010\}$; approximate dimensions $0.12 \times 0.09 \times 0.12$ mm; crystal mounted with b^* coincident with the ϕ axis; Mo Kα absorption, $\mu = 57.8$ cm^{-1}; transmission factor range 0.47–0.65; internal consistency $\pm 3\%$; no decomposition; 1752 reflections scanned—1087 selected on the basis $I/\sigma(I) \geq 2.0$ (a lower standard than used for the trans isomer but this was considered necessary to provide a more suitable number of reflections).

Structure Solution and Refinement

(a) *trans*-Ru(CO)$_4$(GeCl$_3$)$_2$.—$P2_1/n$ is a nonstandard space group and the general positions were derived as x, y, z; $\bar{x}$, $\bar{y}$, $\bar{z}$; $^1/_2 + x$, $^1/_2 - y$, $^1/_2 + z$; $^1/_2 - x$, $^1/_2 + y$, $^1/_2 - z$.

The required symmetry of the molecules ($\bar{1}$) locates the ruthenium atoms at one set of special positions; the set 0, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$ was chosen. A solution for the approximate coordinates of the germanium atom was obtained from a three-dimensional Patterson map. The remaining atoms were located from an observed electron density map computed from structure factors phased by the ruthenium and germanium atoms.

The least-squares refinement of the structural parameters minimized the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(|F_o|)$. Structure factors were calculated using the atomic scattering factors of Cromer and Waber[10] with anomalous scattering[11] of Ru, Ge, and Cl included in the calculated structure factors.[12] Three models were tested: (1) all atoms isotropic—$R_1 = 0.067$, $R_2 = 0.086$ (R_1 defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$; R_2 defined as $\{\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2\}^{1/2})$; (2) Ru, Ge, and Cl anisotropic, C and O isotropic—$R_1 = 0.035$, $R_2 = 0.045$; (3) all atoms anisotropic—$R_1 = 0.028$, $R_2 = 0.038$. The introduction of anisotropic thermal parameters was justified by electron den-

sity difference maps and by the Hamilton statistical test.[13] The poor agreement of several strong reflections ($|F_o| < |F_c|$) suggested that the crystals suffered from extinction and that a correction was desirable. The least-squares program allows extinction corrections to be applied to F_c using the formula of Zachariasen,[14] $F_c' = F_c/[1 + \beta(2\theta)CI]$, where C is a variable parameter. For this study the maximum value of $\beta(2\theta)CI$ appeared to be 0.2, as judged by the worst discrepancies between F_o and F_c. Consideration of crystal size, 2θ range, and total extinction correction suggested that the approximate formula for the extinction correction $(1 + CI)$ was acceptable. The structure was refined to convergence (maximum shift one-fifth of an estimated standard deviation) to give $R_1 = 0.019$ and $R_2 = 0.024$ with $C = 1.06 \times 10^{-6}$. The main effect of including the extinction correction was to increase the thermal parameters. Smaller effects were observed for the fractional coordinates of the carbon and oxygen atoms where the average shift was approximately one standard deviation. No comparable coordinate shifts were observed for the germanium and chlorine atoms. The final value for the standard deviation of an observation of unit weight was 0.91 suggesting that the p factor used in the $\sigma(F)$ calculation was slightly too high. However an analysis of local averages of $w(|F_o| - |F_c|)^2$ for ranges of F_o and (sin θ)/λ suggested that the weighting scheme was acceptable on a relative scale.[15] Structure factor calculations for the rejected data showed no $|F_c|$'s in excess of $1.3|F_{min}|$. Final observed and calculated structure amplitudes are listed in Table I[16] and the atomic parameters are collected in Table II.

TABLE II

Atomic Parameters for *trans*-Ru(CO)$_4$(GeCl$_3$)$_2$

Atom	x	y	z
Ru(1)	0.0	0.0	0.0
Ge	-0.00568 (5)[a]	0.16971 (5)	0.21377 (6)
Cl(1)	0.01991 (19)	0.37406 (15)	0.14589 (19)
Cl(2)	0.16309 (16)	0.14574 (16)	0.40742 (18)
Cl(3)	-0.20348 (17)	0.16794 (16)	0.33553 (19)
C(1)	-0.2155 (7)	-0.0174 (5)	-0.0066 (6)
C(2)	-0.0264 (5)	0.1386 (5)	-0.1679 (7)
O(1)	-0.3370 (5)	-0.0277 (4)	-0.0119 (5)
O(2)	-0.0426 (5)	0.2161 (4)	-0.2630 (5)

Anisotropic Thermal Parameters[b] ($\times 10^4$) for *trans*-Ru(CO)$_4$(GeCl$_3$)$_2$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	62.9 (9)[a]	54.8 (7)	79.7 (11)	2.8 (6)	8.1 (7)	-1.9 (6)
Ge	88.1 (9)	62.0 (7)	89.7 (11)	0.9 (6)	8.1 (6)	-8.8 (6)
Cl(1)	237 (3)	66.0 (2)	157 (3)	-24 (2)	0 (2)	5 (2)
Cl(2)	137 (2)	145 (2)	133 (3)	13 (2)	42 (2)	-9 (2)
Cl(3)	123 (2)	135 (2)	179 (3)	2 (2)	61 (2)	-32 (2)
C(1)	103 (10)	61 (6)	112 (10)	-3 (6)	10 (7)	5 (6)
C(2)	69 (7)	84 (7)	108 (10)	6 (6)	20 (7)	-25 (7)
O(1)	66 (6)	156 (6)	224 (9)	-92 (5)	8 (6)	24 (6)
O(2)	162 (7)	106 (5)	137 (7)	1 (5)	6 (6)	43 (6)

[a] Numbers in parentheses for the listed parameters are standard deviations and refer to the last digit listed. [b] Temperature factor expressed in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

(b) *cis*-Ru(CO)$_4$(GeCl$_3$)$_2$.—A statistical analysis[17] of the data suggested that the structure was noncentrosymmetric. The space group $P2_1$ was assumed for the initial solution and this was subsequently confirmed by refinement. The asymmetric unit then contained two independent molecules. The Patterson showed a very large vector at $^1/_2$, 0, $^1/_2$ which suggested that the two independent molecules were related by a pseudo B-face centering as previously expected on the basis of systematic weaknesses in the data (hkl for $h + l = 2n + 1$). The approxi-

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(13) W. C. Hamilton, *ibid.*, **18**, 502 (1965).

(14) W. H. Zachariasen, *ibid.*, **16**, 1139 (1963).

(15) D. W. J. Cruickshank in "Computing Methods in Crystallography." J. S. Pollet, Ed., Pergamon Press, London, 1965, p 114.

(16) Structure amplitude listings, Tables I and III, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1806. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(17) I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Crystallogr.*, **19**, 713 (1965).

TABLE IV

Atomic Parameters for *cis*-Ru(CO)₄(GeCl₃)₂

Atom	x	y	z	B, Å²
Ru(1)	0.45282 (24)ᵃ	0.0	0.16628 (18)	b
Ru(2)	−0.03844 (23)	−0.01134 (31)	−0.31807 (19)	b
Ge(1)	0.43687 (33)	−0.02650 (41)	0.35614 (25)	b
Ge(2)	0.48235 (36)	0.19387 (39)	0.18929 (30)	b
Ge(3)	−0.00246 (32)	0.17871 (33)	−0.35153 (25)	b
Ge(4)	−0.00281 (32)	0.01805 (38)	−0.12909 (25)	b
Cl(1)	0.2548 (8)	0.0342 (9)	0.4228 (8)	b
Cl(2)	0.5976 (9)	0.0469 (10)	0.4473 (8)	b
Cl(3)	0.4473 (10)	−0.1869 (10)	0.4036 (8)	b
Cl(4)	0.4308 (10)	0.2726 (9)	0.3290 (7)	b
Cl(5)	0.6820 (10)	0.2498 (10)	0.1583 (11)	b
Cl(6)	0.35670 (12)	0.2863 (9)	0.0795 (8)	b
Cl(7)	0.2057 (9)	0.2321 (8)	−0.3664 (8)	b
Cl(8)	−0.0983 (10)	0.2295 (8)	−0.4967 (7)	b
Cl(9)	−0.0858 (9)	0.2930 (8)	−0.2443 (7)	b
Cl(10)	−0.1693 (9)	0.0831 (9)	−0.0441 (7)	b
Cl(11)	0.0481 (11)	−0.1213 (9)	−0.04150 (8)	b
Cl(12)	0.1586 (10)	0.1263 (9)	−0.0896 (7)	b
C(1)	0.6543 (36)	−0.0193 (34)	0.1854 (27)	6.7 (9)
C(2)	0.2498 (28)	0.0310 (26)	0.1639 (20)	3.7 (7)
C(3)	0.4235 (37)	−0.1534 (33)	0.1528 (29)	6.0 (9)
C(4)	0.4699 (26)	0.0254 (27)	0.0166 (25)	3.9 (7)
C(5)	0.1571 (32)	−0.0319 (29)	−0.3233 (25)	5.2 (8)
C(6)	−0.2293 (32)	0.0204 (32)	−0.3002 (25)	6.1 (9)
C(7)	−0.0642 (24)	−0.0260 (25)	−0.4678 (22)	3.0 (6)
C(8)	−0.0626 (39)	−0.1594 (36)	−0.2874 (31)	7.0 (10)
O(1)	0.7646 (25)	−0.0251 (25)	0.2025 (21)	8.7 (7)
O(2)	0.1416 (22)	0.0451 (18)	0.1632 (15)	5.3 (5)
O(3)	0.4155 (25)	−0.2406 (29)	0.1370 (24)	10.0 (9)
O(4)	0.4799 (19)	0.0376 (19)	−0.0733 (17)	5.4 (5)
O(5)	0.2760 (21)	−0.0373 (20)	−0.3220 (16)	6.2 (6)
O(6)	−0.3427 (21)	0.0450 (18)	−0.2903 (16)	5.3 (5)
O(7)	−0.0759 (20)	−0.0384 (19)	−0.553 (17)	5.3 (5)
O(8)	−0.0772 (24)	−0.2468 (23)	−0.2724 (19)	6.6 (7)

Anisotropic Temperature Factors
(×10⁴) for *cis*-Ru(CO)₄(GeCl₃)₂

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru(1)	90 (3)ᵃ	51 (3)	46 (2)	−3 (3)	7 (2)	0 (2)
Ru(2)	90 (3)	38 (3)	47 (2)	2 (3)	8 (2)	2 (2)
Ge(1)	110 (4)	102 (4)	47 (3)	4 (4)	6 (3)	13 (3)
Ge(2)	138 (5)	68 (4)	69 (3)	−30 (4)	18 (3)	−21 (3)
Ge(3)	105 (4)	47 (3)	56 (3)	1 (3)	5 (3)	2 (3)
Ge(4)	118 (4)	66 (4)	48 (3)	14 (14)	7 (3)	6 (3)
Cl(1)	156 (12)	173 (12)	49 (6)	27 (10)	16 (7)	1 (1)
Cl(2)	176 (15)	179 (15)	96 (9)	2 (12)	−75 (10)	−16 (10)
Cl(3)	184 (16)	133 (12)	117 (10)	5 (11)	−18 (10)	52 (10)
Cl(4)	232 (17)	112 (11)	94 (9)	38 (12)	−7 (10)	35 (9)
Cl(5)	179 (17)	124 (13)	301 (19)	−79 (12)	116 (14)	−84 (13)
Cl(6)	330 (21)	79 (10)	101 (10)	−20 (12)	−24 (11)	24 (8)
Cl(7)	131 (12)	91 (10)	135 (10)	10 (10)	26 (8)	11 (8)
Cl(8)	231 (15)	78 (9)	69 (7)	−22 (10)	−26 (8)	32 (7)
Cl(9)	194 (14)	61 (8)	77 (7)	29 (10)	17 (8)	−15 (7)
Cl(10)	188 (15)	135 (10)	65 (8)	29 (11)	22 (8)	−8 (7)
Cl(11)	320 (21)	98 (10)	77 (9)	78 (13)	11 (10)	33 (8)
Cl(12)	167 (21)	143 (10)	81 (9)	25 (12)	41 (10)	0 (8)

ᵃ Numbers in parentheses for the parameters are estimated standard deviations and refer to the last digit listed. ᵇ Anisotropic thermal parameters used.

mation of the structure to the space group $B2_1$ leads to an ambiguity in the solution for the coordinates of the ruthenium and germanium atoms. This ambiguity is simply related to the correct identification of the true and pseudo 2_1 axes. A careful investigation of the Patterson map showed a preference for one solution, but the alternative was also tested in the early stages of refinement. To improve the phasing the calculated positions of the CO groups were introduced into both models. The preferred model refined to $R_1 = 0.28$, and an electron density difference map indicated possible positions for the Cl atoms. The alternate solution proved to be a false minimum that failed to reduce R_1 below 0.35. Even for the correct solution the identification of the chlorine atoms was not quite routine. Semispecial coordinate relationships within each molecule as well as the pseudosymmetry caused several chlorine atoms to refine to false positions. Several difference maps were required before a sensible geometry was achieved and the structure was refined with isotropic temperature factors to $R_1 = 0.071$, $R_2 = 0.077$. The electron density difference maps computed at this stage suggested the use of anisotropic temperature factors, but considering the shortage of data, anistropic refinement was limited

TABLE V

INTRAMOLECULAR GEOMETRY FOR *trans*-Ru(CO)₄(GeCl₃)₂

Bond Distances, Å

Atoms	Dist	Cor distᵃ	Atoms	Dist	Cor distᵃ
Ru–Ge	2.477 (1)ᵇ	2.481 (1)	Ge–Cl(2)	2.160 (2)	2.179 (2)
Ru–C(1)	1.976 (6)	1.980 (6)	Ge–Cl(3)	2.153 (2)	2.171 (2)
Ru–C(2)	1.980 (6)	1.981 (6)	C(1)–O(1)	1.114 (6)	1.154 (7)
Ge–Cl(1)	2.145 (2)	2.166 (2)	C(2)–O(2)	1.115 (6)	1.151 (7)

Bond Angles, Deg

Atoms	Angle	Atoms	Angle
Ge–Ru–C(1)	90.0 (1)	Ru–C(1)–O(1)	179.3 (5)
Ge–Ru–C(2)	89.8 (1)	Ru–C(2)–O(2)	179.3 (5)
C(1)–Ru–C(2)	88.9 (2)	Cl(1)–Ge–Cl(2)	102.7 (1)
Ru–Ge–Cl(1)	117.00 (5)	Cl(1)–Ge–Cl(3)	104.4 (1)
Ru–Ge–Cl(2)	114.33 (5)	Cl(2)–Ge–Cl(3)	102.6 (1)
Ru–Ge–Cl(3)	114.11 (5)		

Selected Intramolecular Contacts, Å

Atoms	Dist	Atoms	Dist
Cl(1)...Cl(2)	3.36	Cl(2)–C(1)′	3.67
Cl(1)...Cl(3)	3.40	Cl(2)–C(2)′	3.67
Cl(2)...Cl(3)	3.37	Cl(3)–C(1)	3.42
Cl(1)–C(2)	3.54		

ᵃ Correction assuming second atom rides on first.[19] ᵇ Standard deviations are given in parentheses and refer to the final digit quoted.

TABLE VI

INTERMOLECULAR NONBONDED CONTACTS
(<3.6 Å) FOR *trans*-Ru(CO)₄(GeCl₃)₂

Atoms	Dist, Å	Symmetry position of second atom
Cl(1)–O(1)	3.42	½ + x, ½ − y, ½ + z
Cl(1)–Cl(1)	3.52	−x, 1 − y, −z
Cl(2)–O(2)	3.45	½ + x, ½ − y, ½ + z
Cl(3)–O(2)	3.35	−½ + x, ½ − y, ½ + z
Cl(3)–C(2)	3.53	−½ + x, ½ − y, ½ + z
Cl(3)–C(1)	3.57	−½ + x, ½ + y, ½ − z
Cl(3)–O(2)	3.60	x, y, 1 + z
O(1)–O(1)	3.06	−1 − x, −y, −z
O(1)–O(2)	3.32	−½ − x, −½ + y, −½ − z

to the heavier atoms, *i.e.*, Ru, Ge, and Cl. This refinement converged to $R_1 = 0.041$, $R_2 = 0.041$. The effects of the polar dispersion error were investigated using the solution x, $\bar{y}$, z, and the refinement converged in this case to $R_1 = 0.042$, $R_2 = 0.042$. A Hamilton[13] statistical test on the data that are sensitive to the change of hand (*i.e.*, $h0l$'s omitted) did show a preference for the first model where the consistency of the Re–Ge distances was better. The formula of Cruickshank and McDonald[18] estimates the error invoked by neglecting the $\Delta f''$ anomalous dispersion term in a polar space group. For the Ru and Ge coordinates along the y coordinate the error between the right and wrong models is estimated to be 0.04 Å which is in good agreement with the average value of 0.03 Å observed.

An electron density difference map based on the final parameters contained no residual peaks greater than 0.6 e/Å³, and these peaks could be assigned to the anisotropic motion of the carbonyl moieties. The final standard deviation for an observation of unit weight was 1.09. The experimental weighting scheme satisfied, within acceptable limits, Cruickshank's criterion,[15] and a comparison of the final observed and calculated structure amplitudes suggested that a correction for extinction was unnecessary. An investigation of the correlation matrix from the final least-squares refinement revealed that the largest correlation coefficient between equivalent parameters of the two independent molecules of the asymmetric unit was 0.12. Structure factor calculations using the rejected data showed no reflections for which $|F_c|$ exceeded $1.6|F_{min}|$. The final observed and calculated structure amplitudes are listed in Table III[16] and the final atomic parameters are collected in Table IV.

Major computer programs used in these analyses are local modifications of SFLS5 by C. T. Prewitt, GONO9 by W. C. Hamilton, FORDAP by A. Zalkin, ORFFE by W. A. Busing and H. A.
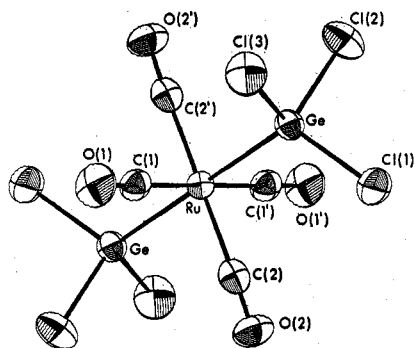
(18) D. W. J. Cruickshank and W. S. McDonald, *Acta Crystallogr.*, **23**, 9 (1967).

Figure 1.—A perspective view of a *trans*-Ru(CO)$_4$(GeCl$_3$)$_2$ molecule with ellipsoids drawn at the 50% probability level. Primed atoms are related by the center of symmetry.

Figure 2.—The RuC$_4$(GeCl$_3$)$_2$ framework of the trans isomer as viewed down the Ge–Ru–Ge axis to demonstrate the relative orientations of the RuC$_4$ and GeCl$_3$ fragments.

TABLE VII
SELECTED INTRAMOLECULAR DISTANCES (Å)

(i) Bond Lengths

Atoms	Uncor dist	Cor dist[a]	Atoms	Uncor dist	Cor dist[a]
Ru(1)–Ge(1)	2.477 (4)[b]	2.487 (5)	Ru(2)–Ge(3)	2.461 (4)	2.466 (5)
Ru(1)–Ge(2)	2.478 (5)	2.488 (6)	Ru(2)–Ge(4)	2.477 (5)	2.484 (5)
Ge(1)–Cl(1)	2.11 (1)	2.18 (1)	Ge(3)–Cl(7)	2.15 (1)	2.19 (1)
Ge(1)–Cl(2)	2.14 (1)	2.19 (1)	Ge(3)–Cl(8)	2.16 (1)	2.19 (1)
Ge(1)–Cl(3)	2.14 (1)	2.18 (1)	Ge(3)–Cl(9)	2.17 (1)	2.19 (1)
Ge(2)–Cl(4)	2.13 (1)	2.17 (1)	Ge(4)–Cl(10)	2.15 (1)	2.18 (1)
Ge(2)–Cl(5)	2.12 (1)	2.20 (1)	Ge(4)–Cl(11)	2.14 (1)	2.19 (1)
Ge(2)–Cl(6)	2.18 (1)	2.22 (1)	Ge(4)–Cl(12)	2.14 (1)	2.17 (1)
Ru(1)–C(1)	1.99 (4)	2.03 (4)	Ru(2)–C(5)	1.93 (3)	1.96 (4)
Ru(1)–C(2)	2.02 (3)	2.04 (4)	Ru(2)–C(6)	1.92 (3)	1.96 (4)
Ru(1)–C(3)	1.96 (4)	2.00 (5)	Ru(2)–C(7)	1.95 (3)	1.97 (4)
Ru(1)–C(4)	1.97 (3)	1.99 (4)	Ru(2)–C(8)	1.92 (4)	1.97 (4)
C(1)–O(1)	1.10 (3)	...	C(5)–O(5)	1.16 (3)	...
C(27)–O(2)	1.07 (3)	...	C(6)–O(6)	1.16 (3)	...
C(3)–O(3)	1.12 (3)	...	C(7)–O(7)	1.14 (3)	...
C(4)–O(4)	1.17 (3)	...	C(8)–O(8)	1.13 (4)	...

(II) Nonbonded Contacts

Atoms	Dist	Atoms	Dist	Atoms	Dist
Cl(1)–Cl(2)	3.36	Cl(11)–Cl(12)	3.37	C(1)–C(2)	2.88
Cl(1)–Cl(3)	3.38	Cl(2)–Cl(4)	3.60	C(1)–C(3)	2.84
Cl(2)–Cl(3)	3.33	Cl(1)–C(2)	3.33	C(1)–C(4)	2.84
Cl(4)–Cl(5)	3.35	Cl(2)–C(2)	3.53	C(2)–C(4)	2.91
Cl(4)–Cl(6)	3.28	Cl(5)–C(1)	3.42	C(3)–C(4)	2.90
Cl(5)–Cl(6)	3.34	Cl(6)–C(2)	3.56	C(5)–C(7)	2.81
Cl(7)–Cl(8)	3.37	Cl(6)–C(4)	3.57	C(5)–C(8)	2.73
Cl(7)–Cl(9)	3.38	Cl(7)–C(5)	3.41	C(6)–C(7)	2.79
Cl(8)–Cl(9)	3.35	Cl(8)–C(7)	3.26	C(6)–C(8)	2.79
Cl(10)–Cl(11)	3.34	Cl(11)–C(8)	3.35	C(6)–C(8)	2.87
Cl(10)–Cl(12)	3.31	Cl(12)–C(5)	3.61		

[a] Second atom assumed to ride on first.[19] [b] Standard deviations are given in parentheses.

Levy,[19] ORTEP by C. K. Johnson, and MIXG2 by D. P. Shoemaker.

Discussion

trans-Ru(CO)$_4$(GeCl$_3$)$_2$ has the expected octahedral configuration and a perspective view is shown in Figure 1. There are no intermolecular chlorine bridges and indeed all the intermolecular contacts are consistent with a normal molecular crystal. The orientations of the GeCl$_3$ groups with respect to the Ru(CO)$_4$ fragment are close to the idealized geometry calculated assuming a 12-fold minimum potential barrier. Figure 2 shows a view of the molecule down the Ge–Ru–Ge axis. Details of the intramolecular geometry are listed in Table V and selected intermolecular contacts in Table VI.

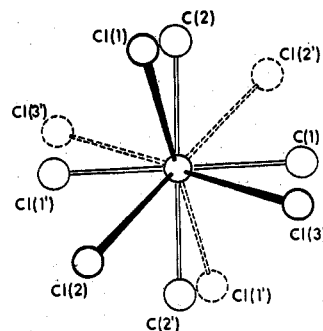The cis isomer also has an octahedral coordination but the ligand–metal–ligand angles show considerably

(19) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).

TABLE VIII
INTRAMOLECULAR ANGLES (DEG) OF *cis*-Ru(CO)$_4$(GeCl$_3$)$_2$[a]

Atoms	Angle	Atoms	Angle
Ge(1)–Ru(1)–Ge(2)	91.5 (2)	Ge(3)–Ru(2)–Ge(4)	90.5 (1)
Ge(1)–Ru1)–C(1)	87 (1)	Ge(3)–Ru(2)–C(5)	89 (1)
Ge(1)–Ru(1)–C(2)	87 (1)	Ge(3)–Ru(2)–C(6)	88 (1)
Ge(1)–Ru(1)–C(3)	87 (1)	Ge(3)–Ru(2)–C(7)	88 (1)
Ge(1)–Ru(1)–C(4)	178 (1)	Ge(3)–Ru(2)–C(8)	178 (1)
Ge(2)–Ru(1)–C(1)	90 (1)	Ge(4)–Ru(2)–C(5)	87 (1)
Ge(2)–Ru(1)–C(2)	86 (1)	Ge(4)–Ru(2)–C(6)	88 (1)
Ge(2)–Ru(1)–C(3)	178 (1)	Ge(4)–Ru(2)–C(7)	177 (1)
Ge(2)–Ru(1)–C(4)	87 (1)	Ge(4)–Ru(2)–C(8)	88 (1)
C(1)–Ru(1)–C(2)	173 (1)	C(5)–Ru(2)–C(6)	174 (2)
C(1)–Ru(1)–C(3)	92 (2)	C(5)–Ru(2)–C(7)	93 (1)
C(1)–Ru(1)–C(4)	92 (1)	C(5)–Ru(2)–C(8)	90 (2)
C(2)–Ru(1)–C(3)	93 (1)	C(6)–Ru(2)–C(7)	93 (2)
C(2)–Ru(1)–C(4)	94 (1)	C(6)–Ru(2)–C(8)	93 (2)
C(3)–Ru(1)–C(4)	95 (1)	C(7)–Ru(2)–C(8)	96 (2)
Ru(1)–Ge(1)–Cl(1)	115.1 (3)	Ru(2)–Ge(3)–Cl(7)	117.3 (3)
Ru(1)–Ge(1)–Cl(2)	114.7 (3)	Ru(2)–Ge(3)–Cl(8)	112.3 (3)
Ru(1)–Ge(1)–Cl(3)	114.2 (3)	Ru(2)–Ge(3)–Cl(9)	118.5 (3)
Ru(1)–Ge(2)–Cl(4)	122.1 (4)	Ru(2)–Ge(4)–Cl(10)	118.1 (3)
Ru(1)–Ge(2)–Cl(5)	114.2 (4)	Ru(2)–Ge(4)–Cl(11)	114.8 (3)
Ru(1)–Ge(2)–Cl(6)	112.8 (3)	Ru(2)–Ge(4)–Cl(12)	114.4 (3)
Cl(1)–Ge(1)–Cl(2)	103.3 (4)	Cl(7)–Ge(3)–Cl(8)	102.5 (4)
Cl(1)–Ge(1)–Cl(3)	105.1 (4)	Cl(7)–Ge(3)–Cl(9)	102.7 (4)
Cl(2)–Ge(1)–Cl(3)	103.1 (4)	Cl(8)–Ge(3)–Cl(9)	101.1 (4)
Cl(4)–Ge(2)–Cl(5)	104.1 (4)	Cl(10)–Ge(4)–Cl(11)	102.3 (4)
Cl(4)–Ge(2)–Cl(6)	99.1 (4)	Cl(10)–Ge(4)–Cl(12)	101.4 (4)
Cl(5)–Ge(2)–Cl(6)	101.7 (5)	Cl(11)–Ge(4)–Cl(12)	103.9 (4)
Ru(1)–C(1)–O(1)	174 (4)	Ru(2)–C(5)–O(5)	175 (3)
Ru(1)–C(2)–O(2)	178 (3)	Ru(2)–C(6)–O(6)	176 (3)
Ru(1)–C(3)–O(3)	173 (4)	Ru(2)–C(7)–O(7)	178 (4)
Ru(1)–C(4)–O(4)	178 (3)	Ru(2)–C(8)–O(8)	177 (3)

[a] Standard deviations are in parentheses and refer to the last digit quoted.

greater deviations from 90° than those in the trans isomer. There is no intramolecular chlorine bridge between germanium atoms in either molecule of the asymmetric unit. Selected intramolecular distances and angles are collected in Tables VII and VIII, respectively. A selection of intermolecular contacts is given in Table IX since these distances are pertinent to the discussion of the geometry of the trichlorogermanyl groups (*vide infra*). The two independent molecules differ only in the relative orientations of their trichlorogermanyl groups and a perspective view of one of the molecules is shown in Figure 3. The slight differences of orientation of the trichlorogermanyl groups is shown in Figure 4 where the RuGe$_2$-Cl$_6$ skeletons are viewed down their Ge–Ru axes. The precision of the parameters of the cis isomer is the limiting factor in a comparison of the two structures. The

TABLE IX
SELECTED (<3.6 Å) INTERMOLECULAR CONTACTS
FOR *cis*-$Ru(CO)_4(GeCl_3)_2$

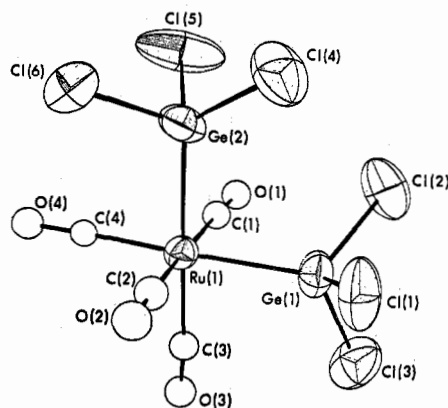| Atoms	Dist, Å	Position of second atom
Cl(1)–O(5)	3.41	$x, y, 1 + z$
Cl(1)–O(7)	3.38	$x, y, 1 + z$
Cl(2)–O(6)	3.41	$1 + x, y, 1 + z$
Cl(2)–O(7)	3.36	$1 + x, y, 1 + z$
Cl(4)–O(6)	3.57	$-x, +y, -z$
Cl(4)–O(8)	3.52	$-x, +y, -z$
Cl(5)–O(5)	3.43	$1 - x, +y, -z$
Cl(6)–O(4)	3.55	$1 - x, +y, -z$
Cl(7)–O(7)	3.31	$-x, +y, -1 - z$
Cl(8)–O(7)	3.44	$-x, +y, -1 - z$
Cl(8)–O(8)	3.49	$-x, +y, -1 - z$
Cl(9)–O(2)	3.39	$-x, +y, -z$
Cl(9)–O(3)	3.56	$-x, y, -z$
Cl(10)–O(1)	3.53	$-1 + x, y, z$
Cl(10)–O(3)	3.46	$-x, +y, -z$
Cl(10)–O(4)	3.48	$-1 + x, y, z$
Cl(11)–O(2)	3.47	x, y, z
Cl(12)–O(4)	3.33	x, y, z
Cl(1)–C(5)	3.53	$x, y, 1 + z$
Cl(1)–C(7)	3.54	$x, y, 1 + z$
Cl(2)–C(7)	3.57	$1 + x, y, 1 + z$
Cl(8)–C(7)	3.50	$-x, +y, -1 - z$
Cl(8)–C(8)	3.52	$-x, +y, -1 - z$
Cl(9)–C(2)	3.57	$-x, +y, -z$
Cl(9)–C(9)	3.60	$-x, +y, -z$
Cl(12)–C(2)	3.57	x, y, z
Cl(12)–C(4)	3.53	x, y, z
Cl(6)–Cl(12)	3.51	x, y, z
Cl(7)–Cl(3)	3.58	$1 - x, +y, -z$
Cl(5)–Cl(11)	3.47	$1 - x, +y, -z$
O(1)–O(7)	3.45	$1 + x, y, 1 + z$
O(4)–O(6)	3.33	$1 + x, y, z$
C(2)–O(8)	3.57	$-x, +y, -z$
O(6)–O(3)	3.43	$-x, +y, -z$

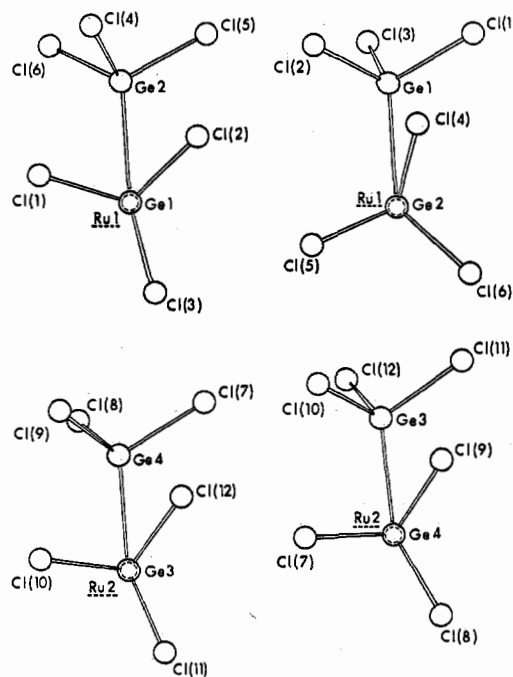Figure 3.—A perspective view of one of the *cis*-$Ru(CO)_4$-$(GeCl_3)_2$ molecules with ellipsoids drawn at the 50% probability level.

Figure 4.—Views of the $Ru(GeCl_3)_2$ frameworks on the cis isomer for the two independent molecules down each of the Ge–Ru axes.

noncentrosymmetric space group and the shortage of data due to generally higher thermal parameters and pseudosymmetry all combine to make this structure much less reliable than that of the trans isomer. The internal consistency of the four ruthenium–germanium bond distances is not that expected from the standard deviations as calculated by ORFFE and a systematic error in the data is indicated. However, the twelve germanium–chlorine and eight ruthenium–carbon distances appear to be consistent with the standard deviations as calculated.

In both structures the trichlorogermanyl groups appear to undergo considerable oscillation about the ruthenium–germanium axes and this effect is more pronounced in the cis isomer. Any quoted germanium–chlorine distances are then considerably less reliable than the standard deviations might suggest. The germanium atoms show considerable angular deviations from a perfect tetrahedral geometry—average Ru–Ge–Cl 115.7° (trans), 115.2° (cis); average Cl–Ge–Cl 103.2° (trans), 102.5° (cis). This pattern is identical with that observed in trichlorosilyl derivatives.[20] A survey of the intermolecular contacts of both structures show several chlorine–chlorine and carbon–chlorine contacts at approximately 3.5 Å, and at this distance these interactions must be attractive in nature. In the cis isomer all intergroup carbon–chlorine and chlorine–

chlorine contacts are ≥ 3.5 Å and in the trans isomer there is one carbon–chlorine contact of 3.42 Å that is less than this value. The typical intragroup chlorine–chlorine contact at 3.35 Å certainly does not reflect a balance of intra-$GeCl_3$ and interligand forces and the observed distortions from a tetrahedral geometry appear to be an inherent property of the trichlorogermanyl group. While the trichlorogermanyl and silyl groups are very similar in their angular behavior, there is an obvious difference in bond lengths. Thus the germanium–chlorine distances at ~2.18 Å are close to the covalent radius sum[21] (2.21 Å) while the silicon–chlorine bond lengths (2.05 Å) are considerably shorter than the covalent radius sum (2.16 Å). These observations are in accord with the trend observed by Griffiths and McAfee.[22]

(20) L. Manojlovic-Muir, K. W. Muir, and J. A. Ibers, *Inorg. Chem.*, **9**, 447 (1970).

(21) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(22) J. E. Griffiths and K. B. McAfee, *Proc. Chem. Soc., London*, 456 (1961).

This discussion of the trichlorogermanyl groups shows that the chlorine atoms do not provide a source of steric repulsion in the cis isomer although the small deviation (1.1°) from 90° of the angles C(1)–Ru–C(2) and C(1)–Ru–C(2') in the trans isomer may result from carbon–chlorine contacts. The major angular deformations from an octahedral geometry for the $RuGe_2C_4$ skeleton of the cis isomer appear to be due to the differences in carbon–carbon, carbon–germanium, and germanium–germanium repulsion within the immediate coordination sphere. The average ruthenium–carbon and ruthenium–germanium distances are collected in Table X, where a totally optimistic view has

TABLE X

Atoms	Trans ligand	Isomer	Distance,[a] Å
Ru–Ge	$GeCl_3$	Trans	2.481 (1)
Ru–Ge	CO	Cis	2.481 (6)
Ru–C	CO	Trans	1.980 (4)
Ru–C	CO	Cis	2.00 (1)
Ru–C	$GeCl_3$	Cis	1.98 (1)

[a] Values with riding correction are used. Standard deviations are given in parentheses and refer to the last digit quoted.

been taken with regard to the standard deviations of the averages concerned, $\sigma(av) = (1/\Sigma_i 1/\sigma_i^2)^{1/2}$. While the cis isomer has its own internal calibration for ruthenium–carbon distances, it cannot provide the comparison for the ruthenium–germanium distances which might provide the more sensitive indicator of

the trans ligand effects simply because these distances should be the most precise determined in each structure. However, in this respect it should be remembered that the manganese–manganese distances in $Mn_2(CO)_{10}$[23] and $Mn_2(CO)_8(P(C_2H_5)_3)_2$[24] are not significantly different despite the difference in trans ligand. The ruthenium–germanium distances are the same and are not significantly different from the value (2.47 Å) reported for $(Ru(CO)_3Ge(CH_3)_2)_2$.[25] The average ruthenium–carbon distances show no significant difference even when the totally optimistic view is taken in the calculation of their standard deviations. The values are higher than those previously[26-29] reported for ruthenium–carbon distances in carbonyl derivatives. This may be due to the corrections for thermal motion used in this structure and the proposed high π-bonding ability of the trichlorogermanyl groups in these compounds.

(23) L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963).
(24) M. J. Bennett and R. Mason, *J. Chem. Soc. A*, 75 (1968).
(25) J. Howard, S. A. R. Knox, F. G. A. Stone, and P. Woodward, *J. Chem. Soc. D*, 1477 (1970).
(26) (a) E. R. Corey, Ph.D. Thesis, University of Wisconsin, 1963; (b) R. Mason and A. I. M. Rae, *J. Chem. Soc. A*, 778 (1968).
(27) S. Merlino and G. Montagnoli, *Acta Crystallogr., Sect. B*, **24**, 424 (1968).
(28) M. Elder and D. Hall, *J. Chem. Soc. A*, 245 (1970).
(29) S. F. Watkins, *ibid.*, 1552 (1969).

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Structural Studies on Clathro Chelate Complexes. I. Trigonal-Prismatic Coordination of d⁸ Nickel(II) in Crystalline [Fluoroborotris(2-aldoximo-6-pyridyl)phosphine]nickel(II) Tetrafluoroborate

BY MELVYN ROWEN CHURCHILL* AND ARTHUR H. REIS, JR.

[Fluoroborotris(2-aldoximo-6-pyridyl)phosphine]nickel(II) tetrafluoroborate, [{FB(ONCHC₅H₃N)₃P}Ni⁺][BF₄⁻], crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; no. 14) with $a = 13.296$ (20), $b = 17.857$ (35), $c = 10.580$ (10) Å, $\beta = 108.68$ (5)°, and $Z = 4$. Observed and calculated densities are 1.65 (5) and 1.58 g cm⁻³. The use of three-dimensional counter data (sin $\theta_{max} = 0.80$; Cu Kα radiation) has led to the location of all atoms (including hydrogens), the final discrepancy index being $R_F = 7.32\%$ for the 1781 symmetry-independent nonzero reflections. The cation is only slightly distorted from idealized C_{3v} symmetry. The central nickel(II) atom is coordinated to six nitrogen atoms, mean distances being Ni–N(aldoximo) = 2.030 (21) and Ni–N(pyridyl) = 2.043 (20) Å. The coordination sphere of the nickel atom defines a slightly tapered trigonal prism, in which N(aldoximo)···N(aldoximo) = 2.648 (11)–2.716 (12), N(pyridyl)··· N(pyridyl) = 2.836 (11)–2.869 (11), and the aldoximo-pyridyl chelate "bite," N(aldoximo)···N(pyridyl), ranges from 2.521 (11) to 2.544 (12) Å. In addition, the triangle defined by the three aldoximo nitrogen atoms is rotated by ~1.6° relative to that defined by the three pyridyl nitrogens. However, deviations from an idealized trigonal-prismatic coordination of nickel(II) are relatively small.

Introduction

Trigonal-prismatic coordination of molybdenum(IV) and tungsten(IV) in the layer structures MoS_2 and WS_2 was reported by Dickinson and Pauling in 1923,[1] but more than 40 years was to elapse before this unusual coordination geometry was detected in a discrete molecular species.[2] Trigonal-prismatic coordination

of transition metal ions by sulfur- and selenium-containing chelate ligands is now well established, as is exemplified by recent crystallographic studies on Re-$(S_2C_2Ph_2)_3$,[2,3] $Mo(S_2C_2H_2)_3$,[4] $V(S_2C_2Ph_2)_3$,[5,6] and Mo-

(2) R. Eisenberg and J. A. Ibers, *ibid.*, **87**, 3776 (1965).
(3) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **5**, 411 (1966).
(4) A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Amer. Chem. Soc.*, **87**, 5798 (1965).
(5) R. Eisenberg, E. I. Stiefel, R. S. Rosenberg, and H. B. Gray, *ibid.*, **88**, 2874 (1966).
(6) R. Eisenberg and H. B. Gray, *Inorg. Chem.*, **6**, 1844 (1967).

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(1) R. G. Dickinson and L. Pauling, *J. Amer. Chem. Soc.*, **45**, 1466 (1923).