

value of 175°, i.e., nearly square planar. This value is larger than that proposed by Willett et al. (162 ± 5°), who derived their value using the 12,900-cm⁻¹ absorption as the maximum-energy d-d transition and utilizing an absorption vs. distortion graph, which, as noted earlier, uses the maximum d-d absorption for [Pt(NH₃)₄]CuCl₄ as the limiting case of four-coordinate square-planar geometry. The X-ray crystal structures of the four compounds mentioned above are presently under consideration.

Acknowledgment. This work was supported by the Robert A. Welch Foundation; the diffractometer was purchased with funds provided by the National Science Foundation (Grant GP-37028).

Registry No. [C₆H₅CH₂CH(CH₃)NH₂CH₃]₂CuCl₄, 55030-07-4.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC50007J.

References and Notes

- (1) R. L. Harlow, W. J. Wells, III, G. W. Watt, and S. H. Simonsen, *Inorg. Chem.*, **13**, 2106 (1974).
- (2) R. L. Harlow, W. J. Wells, III, G. W. Watt, and S. H. Simonsen, *Inorg. Chem.*, **13**, 2860 (1974).
- (3) D. W. Smith, *J. Chem. Soc. A*, 2529 (1969).
- (4) D. W. Smith, *J. Chem. Soc. A*, 2900 (1970).
- (5) J. Demuynck, A. Veillard, and U. Wahlgren, *J. Am. Chem. Soc.*, **95**, 5563 (1973).
- (6) R. M. Clay, P. Murray-Rust, and J. Murray-Rust, *J. Chem. Soc., Dalton Trans.*, 595 (1973).
- (7) B. Morosin and E. C. Lingafelter, *J. Phys. Chem.*, **65**, 50 (1961).
- (8) M. Bonamico, G. Dessey, and A. Vaciago, *Theor. Chim. Acta*, **7**, 367 (1967).
- (9) J. H. Russell and S. C. Wallwork, *Acta Crystallogr., Sect. B*, **25**, 1961 (1969).
- (10) A. C. Bonamartini, M. Nardelli, C. Palmieri, and C. Pelizzi, *Acta Crystallogr., Sect. B*, **27**, 1775 (1971).
- (11) R. D. Willett and M. L. Larsen, *Inorg. Chim. Acta*, **5**, 175 (1971).
- (12) J. A. McGinney, *J. Am. Chem. Soc.*, **94**, 8406 (1972).
- (13) J. Lamotte-Brasseur, L. Dupont, and O. Dideberg, *Acta Crystallogr., Sect. B*, **29**, 241 (1973).
- (14) J. Lamotte-Brasseur, Doctoral Dissertation, University of Liege, Liege, Belgium, 1973.
- (15) M. R. Caira, G. V. Fazakerley, P. W. Linder, and L. R. Nassimbeni, *Acta Crystallogr., Sect. B*, **30**, 1660 (1974).
- (16) H. P. Calhoun and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 382 (1974).
- (17) J. Lamotte-Brasseur, *Acta Crystallogr., Sect. A*, **30**, 487 (1974).
- (18) R. D. Willett, J. A. Haugen, J. Lebsack, and J. Morrey, *Inorg. Chem.*, **13**, 2510 (1974).
- (19) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
- (20) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
- (21) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- (22) B. Morosin, P. Fallon, and J. S. Valentine, private communication.
- (23) W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, **3**, 841 (1964).
- (24) J. Ferguson, *J. Chem. Phys.*, **40**, 3406 (1964).
- (25) C. Furlani, E. Cervone, F. Calzona, and B. Baldanza, *Theor. Chim. Acta*, **7**, 375 (1967).
- (26) W. Ludwig and M. Textor, *Helv. Chim. Acta*, **54**, 1143 (1971).
- (27) M. Textor, E. Dubler, and H. R. Oswald, *Inorg. Chem.*, **13**, 1361 (1974).
- (28) R. D. Willett, personal communication, 1974.
- (29) R. D. Willett and C. Chow, *Acta Crystallogr., Sect. B*, **30**, 207 (1974).

Contribution from the Chemistry Department,
University of Hawaii, Honolulu, Hawaii 96822

A Structural Trans Effect at Nickel(II). Crystal and Molecular Structure of Bromo[bis(2-((2-pyridylmethyl)amino)ethyl) disulfide]nickel(II) Perchlorate

LARRY G. WARNER, MAVIS M. KADOOKA, and KARL SEFF*

Received January 13, 1975

AIC500305

The crystal and molecular structure of bromo[bis(2-((2-pyridylmethyl)amino)ethyl) disulfide]nickel(II) perchlorate, [Ni(C₁₆H₂₂N₄S₂)Br]ClO₄, has been determined by single-crystal X-ray diffraction techniques using counter methods and has been refined by full-matrix least-squares procedures to a final conventional *R* index of 0.046. The deep blue-violet crystals form as rectangular prisms in the orthorhombic space group *Pbca* with *a* = 23.838 (6), *b* = 14.686 (4), and *c* = 12.823 (2) Å, with eight molecules per unit cell. The nickel(II) ion is coordinated octahedrally by two amine nitrogen atoms, two pyridyl nitrogen atoms, one bromide ion, and one sulfur atom of the disulfide group. It is isostructural with the previously reported chloro compound. The two amine nitrogen atoms, equivalent in the ligand, show different nickel-nitrogen approach distances depending upon whether the trans group is the bromide ion (2.162 (5) Å) or a pyridyl nitrogen atom (2.114 (5) Å). The nickel(II)-sulfur distance, 2.456 (2) Å, is comparable with the sum of the corresponding Pauling covalent radii, 2.43 Å, indicating a strong interaction. Neither the sulfur-sulfur bond, 2.040 (3) Å, nor the CSSC torsion angle, 85°, has been modified by coordination to Ni(II). The precision of this work is approximately 3 times that reported for the corresponding chloro compound and great enough to indicate clearly a structural trans effect.

Introduction

The trans effect has been discussed, both kinetically and structurally, for an increasing number of transition metals, beginning with square-planar Pt(II)¹ and octahedral Co(III).¹⁻⁴ More recently, as new physical methods for studying rapid-exchange processes have been introduced and as crystallographic results have become more precise, trans effects and general labilizing effects have been noted for other ions, such as Ru(II)⁵ and Co(II).⁶

Octahedral Ni(II) has been the object of kinetic and thermodynamic study^{7,8} and its ligand substitution behavior has been comprehensively reviewed.⁹⁻¹² In no case has a specific structural or kinetic trans effect been discussed, al-

though general labilizing effects consistent with the trans-directing sequence are reported.

Previous work in this laboratory on the crystal structure of chloro[bis(2-((2-pyridylmethyl)amino)ethyl) disulfide]nickel(II) perchlorate,¹³ [Ni(PMS)Cl]ClO₄, and that of chloro[α,α'-dithiobis(o-phenylenenitrilo)di-2-picoline]nickel(II) perchlorate,¹⁴ [Ni(DTPP)Cl]ClO₄, indicated a structural trans effect, but in a marginally significant manner. The nitrogen atom trans to the chloride ion was found to be further from Ni(II) than was a second nitrogen atom equivalent to the first in the uncoordinated ligand. In the first complex,¹³ [Ni(PMS)Cl]ClO₄, the difference in amino nitrogen bond lengths to Ni(II) was 0.086 (21) Å; in the second case,¹⁴ [Ni(DT-

PP)Cl]ClO₄, the difference involving imino nitrogen atoms was 0.051 (21) Å.

Another lesser trans effect was suggested by these two structures. The pyridyl nitrogen atoms trans to an amine or imine nitrogen showed insignificantly but consistently longer bonds to Ni(II) than did the pyridyl nitrogen atoms trans to sulfur. For the amines,¹³ the difference was 0.023 (21) Å, and for the imines¹⁴ it was 0.033 (21) Å.

The bromide ion is expected to be somewhat more inductive than the chloride and to give a somewhat larger trans effect.¹ To allow a more precise observation and more careful discussion of this effect, the crystal structure of bromo[bis(2-((2-pyridylmethyl)amino)ethyl) disulfide]nickel(II) perchlorate, [Ni(PMS)Br]ClO₄, was carefully determined.

Experimental Section

Ethylene monothiocarbonate and 2-methylaminopyridine were obtained from Aldrich Chemical Co. and Eastman Kodak Co., respectively. Reagent grade NiBr₂ was obtained from G. Frederick Smith Chemical Co., and LiClO₄·3H₂O, from Apache Chemicals. All other chemicals were of reagent grade quality. The laser-Raman (excitation at 5145 Å) and infrared spectra were obtained using the Cary 82 and Beckman IR-10 instruments, respectively. Elemental analysis was performed by Galbraith Laboratories.

Preparation of Bis[2-((2-pyridylmethyl)amino)ethyl] Disulfide, pyCH₂NHCH₂CH₂SSCH₂CH₂NHCH₂py, PMS. A 92.4-g (0.85-mol) sample of 2-methylaminopyridine (distilled) was dissolved in 150 ml of toluene (distilled over Na) and brought to reflux. Ethylene monothiocarbonate (47 g, 0.45 mol) dissolved in 50 ml of anhydrous toluene was added dropwise to the refluxing solution over a 15-min period. Refluxing continued for 3 hr using a very efficient condenser to avoid loss of ethylene monothiocarbonate. The reaction mixture was then allowed to cool overnight. The product 2-(2'-picolylamine)ethanethiol was distilled between 101 and 103°, after both toluene and excess 2-methylaminopyridine had distilled over. This procedure is a modification¹⁵ of that reported by Reynolds et al.¹⁶

Iodine (0.13 g, 0.0005 mol) dissolved in 50% aqueous ethanol was added dropwise with stirring to an aqueous solution of 2-(2'-picolylamine)ethanethiol (0.17 g, 0.001 mol). The pH was then adjusted to 8-9 with 10% Na₂CO₃, and the solution was extracted with chloroform. The chloroform was evaporated leaving an oil which was dissolved in ethanol and filtered to remove insoluble salts. The ethanol was removed by vacuum evaporation. This ethanol treatment was repeated several times, and a dry viscous oil of low analytical purity was obtained.

Preparation of Bromo[bis(2-((2-pyridylmethyl)amino)ethyl) disulfide]nickel(II) Perchlorate, Ni(pyCH₂NHCH₂CH₂SSCH₂CH₂NHCH₂py)BrClO₄, [Ni(PMS)Br]ClO₄. Following the procedure of Gavino,¹⁵ a 0.82-g (0.0025-mol) sample of the above oil, PMS, dissolved in 10 ml of ethanol was added to a 10% aqueous solution of NiBr₂ (0.68 g or 0.0025 mol in 55 ml). A 0.40-g (0.0025-mol) sample of LiClO₄·3H₂O dissolved in ca. 15 ml of 50% aqueous ethanol was then added. Intensely blue-violet crystals formed from the resulting blue solution by slow evaporation. The infrared spectrum of this complex is very similar to that of [Ni(PMS)Cl]ClO₄. Anal. Calcd for [Ni(C₁₆H₂₂N₄S₂)Br]ClO₄: Ni, 10.25; C, 33.56; H, 3.87; Br, 13.95; Cl, 6.19. Found: Ni, 10.15; C, 34.22; H, 3.94; Br, 13.99; Cl, 6.26.

Diffraction Work. Preliminary X-ray photographs of [Ni(PMS)Br]ClO₄ and approximate structure factor calculations indicated that it is isostructural with [Ni(PMS)Cl]ClO₄¹³ and [Ni(PMS)I]I. A single crystal, a rectangular prism with extreme dimensions of 0.22 × 0.11 × 0.47 mm, was selected for further study and was mounted nearly along its long axis, so that this axis did not coincide with the diffractometer ϕ axis. Systematic absences characteristic of the orthorhombic space group *Pbca* were observed (h k 0, $h = 2n$; h 0 l , $l = 2n$; 0 k l , $k = 2n$).

A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo K α radiation (K α ₁, λ 0.70926 Å; K α ₂, λ 0.71354 Å) and a pulse-height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants and their standard deviations were determined by a least-squares treatment of the angular coordinate of 15 independent reflections with 2θ values up to 22°. The program used was written by R. A. Sparks and is part of the diffractometer program library.

Table I. Final Positional Parameters and Their Standard Deviations^a

	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)
Ni(1)	1626.4 (0.3)	1121.2 (0.5)	2550.6 (0.6)
Br(2)	1983.2 (0.4)	1067.4 (0.5)	681.6 (0.5)
Cl(3)	-212 (1)	1702 (1)	4160 (2)
O(4)	270 (3)	2218 (6)	4135 (6)
O(5)	-502 (6)	1776 (9)	3371 (12)
O(6)	-492 (4)	1846 (8)	5010 (10)
O(7)	-26 (4)	853 (6)	4147 (10)
N(8)	2402 (2)	1347 (3)	3228 (4)
C(9)	2901 (4)	1412 (4)	2742 (6)
C(10)	3393 (3)	1598 (5)	3258 (8)
C(11)	3382 (4)	1711 (5)	4315 (8)
C(12)	2886 (4)	1651 (5)	4828 (7)
C(13)	2391 (3)	1470 (4)	4275 (5)
C(14)	1846 (3)	1462 (4)	4801 (5)
N(15)	1397 (2)	998 (3)	4176 (4)
C(16)	1287 (3)	59 (5)	4506 (5)
C(17)	1739 (3)	-583 (4)	4120 (5)
S(18)	1827 (1)	-513 (1)	2708 (1)
S(19)	1200 (1)	-1312 (1)	2129 (2)
C(20)	574 (3)	-637 (5)	2053 (6)
C(21)	590 (3)	227 (5)	1413 (6)
N(22)	791 (2)	1021 (3)	2016 (4)
C(23)	673 (3)	1873 (5)	1442 (5)
C(24)	948 (3)	2668 (4)	1944 (5)
C(25)	738 (3)	3545 (5)	1841 (5)
C(26)	1013 (4)	4248 (5)	2316 (6)
C(27)	1485 (4)	4077 (4)	2881 (6)
C(28)	1683 (3)	3194 (4)	2948 (5)
N(29)	1412 (2)	2491 (3)	2492 (4)
H(9)	290 (2)	132 (3)	200 (4)
H(10)	375 (2)	163 (3)	288 (4)
H(11)	374 (3)	189 (4)	472 (5)
H(12)	286 (3)	183 (5)	564 (6)
H(14A)	188 (3)	117 (4)	549 (5)
H(14B)	175 (2)	206 (4)	493 (5)
H(15)	109 (2)	135 (3)	428 (4)
H(16A)	126 (2)	4 (3)	530 (3)
H(16B)	91 (2)	-8 (3)	425 (4)
H(17A)	207 (2)	-41 (4)	437 (4)
H(17B)	167 (2)	-122 (4)	430 (4)
H(20A)	47 (2)	-53 (4)	277 (4)
H(20B)	25 (2)	-107 (3)	181 (4)
H(21A)	85 (2)	13 (4)	85 (4)
H(21B)	21 (2)	32 (4)	111 (4)
H(22)	59 (2)	100 (3)	255 (4)
H(23A)	84 (2)	176 (3)	72 (4)
H(23B)	29 (2)	205 (4)	131 (4)
H(25)	42 (2)	363 (3)	148 (4)
H(26)	89 (2)	480 (4)	232 (5)
H(27)	171 (3)	452 (4)	322 (5)
H(28)	203 (2)	302 (3)	333 (3)

^a Values for nonhydrogen atoms are given $\times 10^4$; values for hydrogen atoms are given $\times 10^3$. See Figures 2 and 3 for the identities of the atoms. The esd is in the units of the least significant digit given for the corresponding parameter.

The temperature was maintained within 1° of 20° throughout. The θ - 2θ scan mode was used with a scan rate (ω) in 2θ of 0.5° min⁻¹. The total background counting time, equal to the scan time, was equally spent at each end of the scan range, which varied from 2.0° at low 2θ to 2.3° at 50°, that is, from 1° below the K α ₁ maximum to 1° above the K α ₂ position, in 2θ . The intensities of three reflections, which were remeasured after every hundred during data collection, showed a small average decrease in intensity of 2%, for which the appropriate correction was applied.

Standard deviations were assigned to individual reflections according to the formula

$$\sigma(I) = [\omega^2(CT + B_1 + B_2) + (pI)^2]^{1/2}$$

where CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity $I = \omega(CT - B_1 - B_2)$. A value of 0.02, appropriate to the instrumentation used, was assigned to the empirical parameter p .¹⁷ The weights, w , used in least-squares were the reciprocal squares of $\sigma(F_o)$. Of the 4477 symmetry-independent re-

Table II. Thermal Vibrational Parameters and Their Standard Deviations^a

1. Nonhydrogen Atoms						
$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$						
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni(1)	15.6 (0.2)	33.9 (0.4)	44.3 (0.5)	3.4 (0.5)	2.8 (0.5)	4.5 (0.8)
Br(2)	29.7 (0.2)	62.3 (0.4)	50.5 (0.5)	11.6 (0.5)	21.3 (0.5)	6.2 (0.8)
Cl(3)	18.7 (0.5)	51 (1)	86 (2)	6 (1)	-7 (2)	4 (2)
O(4)	55 (3)	165 (7)	158 (8)	-92 (7)	45 (7)	-66 (11)
O(5)	119 (6)	278 (14)	438 (23)	39 (15)	-364 (22)	59 (28)
O(6)	63 (3)	264 (12)	349 (17)	-73 (11)	193 (14)	-319 (24)
O(7)	63 (3)	100 (6)	498 (21)	44 (7)	118 (14)	99 (18)
N(8)	15 (2)	32 (3)	66 (4)	-2 (3)	2 (4)	17 (5)
C(9)	18 (2)	42 (4)	95 (7)	0 (4)	7 (6)	20 (8)
C(10)	13 (2)	38 (4)	149 (9)	-5 (4)	13 (7)	43 (10)
C(11)	24 (2)	55 (5)	132 (10)	-14 (6)	-38 (9)	30 (11)
C(12)	22 (2)	56 (5)	98 (7)	-11 (5)	-24 (7)	7 (9)
C(13)	17 (2)	30 (3)	74 (5)	-7 (4)	-12 (6)	25 (7)
C(14)	24 (2)	57 (4)	54 (5)	-14 (5)	-10 (5)	-4 (7)
N(15)	18 (1)	43 (3)	51 (4)	2 (3)	5 (4)	16 (6)
C(16)	27 (2)	53 (4)	54 (5)	-24 (5)	0 (5)	19 (7)
C(17)	29 (2)	42 (4)	75 (6)	-3 (5)	-13 (6)	34 (8)
S(18)	18.4 (0.4)	36.4 (0.8)	80 (2)	7 (1)	6 (1)	5 (2)
S(19)	27.2 (0.6)	37 (1)	89 (2)	-5 (1)	4 (2)	-20 (2)
C(20)	24 (2)	60 (5)	91 (6)	-26 (5)	-2 (6)	-20 (9)
C(21)	23 (2)	60 (5)	87 (7)	-4 (5)	-26 (6)	-20 (9)
N(22)	19 (1)	43 (3)	63 (4)	1 (4)	-8 (4)	-6 (6)
C(23)	22 (2)	64 (5)	75 (6)	16 (5)	-17 (6)	25 (9)
C(24)	16 (2)	41 (4)	55 (5)	13 (4)	9 (5)	6 (7)
C(25)	19 (2)	61 (4)	68 (6)	28 (5)	-2 (5)	10 (8)
C(26)	29 (2)	43 (4)	78 (6)	29 (5)	15 (6)	9 (8)
C(27)	35 (2)	34 (4)	75 (6)	4 (5)	2 (6)	2 (7)
C(28)	26 (2)	39 (4)	59 (5)	5 (5)	-4 (5)	13 (7)
N(29)	17 (1)	35 (2)	52 (4)	9 (3)	-5 (4)	8 (6)

2. Hydrogen Atoms			
	$B, \text{Å}^2$	$B, \text{Å}^2$	$B, \text{Å}^2$
H(9)	3 (1)	H(15)	5 (1)
H(10)	4 (1)	H(16A)	3 (1)
H(11)	8 (2)	H(16B)	3 (1)
H(12)	10 (2)	H(17A)	6 (2)
H(14A)	6 (2)	H(17B)	5 (1)
H(14B)	5 (1)	H(20A)	5 (1)
		H(20B)	4 (1)
		H(21A)	5 (1)
		H(21B)	5 (1)
		H(22)	5 (1)
		H(23A)	4 (1)
		H(23B)	4 (1)
		H(25)	4 (1)
		H(26)	7 (2)
		H(27)	7 (2)
		H(28)	3 (1)

^a The β 's are $\times 10^4$. See Figures 2 and 3 for the identities of the atoms. The esd is in the units of the least significant digit given for the corresponding parameter.

flections measured, all those for which $2\theta < 50^\circ$, 2329 had intensities larger than 3 times their standard deviations, and only these were included in subsequent calculations, with the exception of 040 which apparently suffered badly from extinction. The intensities were corrected¹⁸ for Lorentz and polarization effects; the contribution of the monochromator crystal was calculated assuming it to be half-perfect and half-mosaic in character. An absorption correction ($\mu = 30.78 \text{ cm}^{-1}$) was applied¹⁹ which approximated the crystal shape by a $6 \times 6 \times 6$ grid;²⁰ the calculated transmission coefficients ranged from 0.596 to 0.641.

Crystal Data. Bromo[bis(2-((2-pyridylmethyl)amino)ethyl) disulfide]nickel(II) perchlorate, $[\text{Ni}(\text{C}_{16}\text{H}_{22}\text{N}_4\text{S}_2)\text{Br}]\text{ClO}_4$, crystallized in space group *Pbca*, with $a = 23.838$ (6) Å, $b = 14.686$ (4) Å, $c = 12.823$ (2) Å, $V = 4489$ (2) Å³, mol wt 544.56, $d_{\text{obsd}}(\text{floatation}) = 1.686 \text{ g cm}^{-3}$, $d_{\text{calcd}} = 1.694 \text{ g cm}^{-3}$, $Z = 8$, and $F(000) = 2320$. Figures in parentheses are estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

Structure Refinement. Beginning with the positional and anisotropic thermal parameters of the 29 nonhydrogen atoms of the isostructural $[\text{Ni}(\text{PMS})\text{Cl}]\text{ClO}_4$,¹³ the structure was refined²¹ by full-matrix least-squares methods. After near convergence, the positions of all hydrogen atoms were calculated²² and refined with isotropic thermal parameters. Final cycles with all parameters varying converged to give the final error indices $R_1 = 0.046$ and $R_2 = 0.045$ ($R_1 = (\sum |F_o - |F_c||) / \sum F_o$; $R_2 = [\sum w(F_o - |F_c|)^2 / \sum wF_o^2]^{1/2}$). The "goodness of fit", $[\sum w(F_o - |F_c|)^2 / (m - s)]^{1/2}$, is 2.46. The number of observations used in least squares, m , is 2328, and the number of parameters, s , is 350. In the final cycle of refinement, all shifts in the positional parameters were less than 6% of their esd's, and the largest shift in a thermal parameter was 8% of its esd for the nonhydrogen atoms. For the hydrogen atoms, these values were 19% and 15%, respectively.

These largest shifts were oscillatory and were associated with the perchlorate oxygens and other atoms near them. (See Figures 1 and 2, and note that the thermal parameters of the perchlorate oxygen atoms are very large.) Six of the largest peaks on the final difference Fourier function,²³ whose esd was calculated to be 0.1 e Å^{-3} , were $0.4\text{--}0.6 \text{ e Å}^{-3}$ in height and were located very close to the perchlorate ion. Two other peaks at 0.5 e Å^{-3} are located about 1 Å from Ni(II) and Br⁻, respectively.

Atomic scattering factors²⁵ for Ni⁺, Br⁻, Cl⁰, S⁰, O⁰, N⁰, C⁰, and H (bonded)²⁶ were used. The first four were modified to account for the real part of the anomalous dispersion correction.²⁷ The final positional and thermal parameters, together with their standard deviations, are presented in Tables I and II. Standard deviations were calculated from the inverse normal-equations matrix, ignoring the standard deviations of the cell parameters.

Discussion

The molecular geometry presented in Table III and the least-squares planes described in Table IV are similar to those previously reported and discussed for $[\text{Ni}(\text{PMS})\text{Cl}]\text{ClO}_4$.¹³ The crystallographic results indicate again that the geometry of the disulfide group has not been altered by coordination to Ni(II); the SS bond length is 2.040 (3) Å, and the CSSC torsion angle (see Figures 2 and 3) is 85° , as compared to the less precise values of 2.039 (7) Å and 86° , respectively, for $[\text{Ni}(\text{PMS})\text{Cl}]\text{ClO}_4$.¹³

The Raman spectrum of $[\text{Ni}(\text{PMS})\text{Br}]\text{ClO}_4$ exhibits a moderately strong $\nu(\text{SS})$ absorption band at 501 cm^{-1} , as does $[\text{Ni}(\text{PMS})\text{Cl}]\text{ClO}_4$. Uncomplexed or unaltered (by CSSC torsion angle strain, for example) aliphatic disulfides exhibit

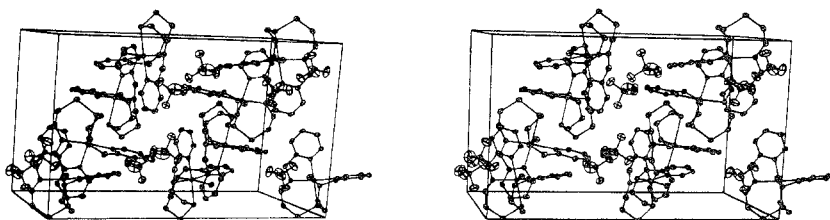


Figure 1. Stereoview²⁴ of the crystal structure of [Ni(PMS)Br]ClO₄, bromo[bis(2-(2-pyridylmethyl)amino)ethyl] disulfide]nickel(II) perchlorate, in the unit cell, showing ellipsoids of 15% probability. Hydrogen atoms have been omitted for clarity.

Table III. Molecular Dimensions and Esd's^a

		1. Bond Lengths, Å					
Ni(1)-Br(2)	2.544 (1)	C(16)-N(15)	1.465 (8)	C(23)-C(24)	1.486 (10)	C(17)-H(17A)	0.90 (6)
Ni(1)-S(18)	2.456 (2)	C(21)-N(22)	1.480 (9)	Cl(3)-O(4)	1.378 (8)	C(17)-H(17B)	0.98 (5)
S(18)-S(19)	2.040 (3)	C(23)-N(22)	1.479 (9)	Cl(3)-O(5)	1.230 (15)	C(20)-H(20A)	0.97 (6)
Ni(1)-N(8)	2.070 (5)	C(9)-C(10)	1.375 (12)	Cl(3)-O(6)	1.294 (13)	C(20)-H(20B)	1.04 (5)
Ni(1)-N(15)	2.162 (5)	C(10)-C(11)	1.365 (15)	Cl(3)-O(7)	1.324 (9)	C(21)-H(21A)	0.96 (5)
Ni(1)-N(22)	2.112 (5)	C(11)-C(12)	1.356 (14)	C(9)-H(9)	0.96 (5)	C(21)-H(21B)	0.99 (5)
Ni(1)-N(29)	2.077 (5)	C(12)-C(13)	1.402 (12)	C(10)-H(10)	0.98 (5)	N(22)-H(22)	0.84 (5)
C(17)-S(18)	1.826 (7)	C(24)-C(25)	1.387 (10)	C(11)-H(11)	1.03 (6)	C(23)-H(23A)	1.02 (5)
C(20)-S(19)	1.793 (8)	C(25)-C(26)	1.366 (11)	C(12)-H(12)	1.07 (7)	C(23)-H(23B)	0.97 (5)
C(9)-N(8)	1.344 (10)	C(26)-C(27)	1.361 (12)	C(14)-H(14A)	0.99 (6)	C(25)-H(25)	0.91 (5)
C(13)-N(8)	1.355 (9)	C(27)-C(28)	1.383 (9)	C(14)-H(14B)	0.92 (6)	C(26)-H(26)	0.87 (6)
C(24)-N(29)	1.335 (8)	C(13)-C(14)	1.465 (11)	N(15)-H(15)	0.90 (5)	C(27)-H(27)	0.96 (6)
C(28)-N(29)	1.351 (8)	C(16)-C(17)	1.514 (10)	C(16)-H(16A)	1.02 (4)	C(28)-H(28)	0.99 (4)
C(14)-N(15)	1.501 (9)	C(20)-C(21)	1.512 (10)	C(16)-H(16B)	0.98 (5)		
		2. Bond Angles, Deg					
Br(2)-Ni(1)-N(8)	95.8 (1)	Ni(1)-N(15)-C(16)	113.7 (4)	O(5)-Cl(3)-O(7)	105.1 (9)	H(17B)-C(17)-S(18)	108 (3)
N(8)-Ni(1)-N(15)	80.5 (2)	N(15)-C(16)-C(17)	111.4 (6)	O(6)-Cl(3)-O(7)	109.7 (8)	S(19)-C(20)-H(20A)	104 (3)
N(15)-Ni(1)-N(22)	93.9 (2)	C(16)-C(17)-S(18)	111.8 (5)	N(8)-C(9)-H(9)	117 (3)	H(20A)-C(20)-C(21)	113 (3)
N(22)-Ni(1)-Br(2)	90.4 (2)	C(17)-S(18)-Ni(1)	96.5 (3)	H(9)-C(9)-C(10)	120 (3)	H(20A)-C(20)-H(20B)	101 (4)
Br(2)-Ni(1)-S(18)	89.0 (1)	C(17)-S(18)-S(19)	104.1 (2)	C(9)-C(10)-H(10)	121 (3)	S(19)-C(20)-H(20B)	107 (3)
Br(2)-Ni(1)-N(29)	94.5 (2)	Ni(1)-S(18)-S(19)	112.9 (1)	H(10)-C(10)-C(11)	120 (3)	H(20B)-C(20)-C(21)	112 (3)
N(29)-Ni(1)-N(22)	79.8 (2)	S(18)-S(19)-C(20)	108.2 (3)	C(10)-C(11)-H(11)	121 (4)	C(20)-C(21)-H(21A)	108 (3)
N(22)-Ni(1)-S(18)	98.2 (2)	S(19)-C(20)-C(21)	118.2 (6)	H(11)-C(11)-C(12)	119 (4)	H(21A)-C(21)-N(22)	107 (3)
S(18)-Ni(1)-N(8)	87.0 (2)	C(20)-C(21)-N(22)	112.6 (6)	C(11)-C(12)-H(12)	120 (4)	H(21A)-C(21)-H(21B)	108 (5)
S(18)-Ni(1)-N(29)	94.6 (2)	C(21)-N(22)-Ni(1)	122.0 (4)	H(12)-C(12)-C(13)	120 (4)	C(20)-C(21)-H(21B)	108 (3)
N(15)-Ni(1)-S(18)	83.6 (2)	C(21)-N(22)-C(23)	110.2 (5)	C(13)-C(14)-H(14A)	111 (4)	H(21B)-C(21)-N(22)	113 (3)
N(15)-Ni(1)-N(29)	93.1 (2)	Ni(1)-N(22)-C(23)	106.3 (4)	H(14A)-C(14)-N(15)	109 (3)	C(21)-N(22)-H(22)	102 (4)
Br(2)-Ni(1)-N(15)	171.8 (1)	N(22)-C(23)-C(24)	111.5 (6)	H(14A)-C(14)-H(14B)	106 (5)	H(22)-N(22)-Ni(1)	106 (4)
N(8)-Ni(1)-N(22)	172.0 (2)	C(23)-C(24)-C(25)	121.9 (6)	C(13)-C(14)-H(14B)	107 (4)	C(22)-N(22)-C(23)	109 (4)
N(29)-Ni(1)-S(18)	176.0 (2)	C(23)-C(24)-N(29)	116.1 (6)	H(14B)-C(14)-N(15)	111 (4)	N(22)-C(23)-H(23A)	104 (3)
C(13)-N(8)-C(9)	117.8 (5)	C(24)-N(29)-Ni(1)	114.4 (4)	C(14)-N(15)-H(15)	103 (3)	H(23A)-C(23)-C(24)	110 (3)
N(8)-C(9)-C(10)	123.1 (8)	Ni(1)-N(29)-C(28)	127.3 (4)	H(15)-N(15)-Ni(1)	107 (3)	H(23A)-C(23)-H(23B)	105 (4)
C(9)-C(10)-C(11)	119.0 (6)	C(28)-N(29)-C(24)	118.3 (5)	H(15)-N(15)-C(16)	111 (3)	N(22)-C(23)-H(23B)	119 (3)
C(10)-C(11)-C(12)	119.4 (7)	N(29)-C(24)-C(25)	122.0 (6)	N(15)-C(16)-H(16A)	109 (3)	H(23B)-C(23)-C(24)	107 (3)
C(11)-C(12)-C(13)	119.9 (7)	C(24)-C(25)-C(26)	119.1 (7)	H(16A)-C(16)-C(17)	111 (3)	C(24)-C(25)-H(25)	119 (3)
C(12)-C(13)-N(8)	120.7 (6)	C(25)-C(26)-C(27)	119.6 (7)	H(16A)-C(16)-H(16B)	106 (4)	H(25)-C(25)-C(26)	122 (3)
Ni(1)-N(8)-C(9)	127.3 (4)	C(26)-C(27)-C(28)	119.3 (7)	N(15)-C(16)-H(16B)	105 (3)	C(25)-C(26)-H(26)	123 (4)
Ni(1)-N(8)-C(13)	114.8 (4)	C(27)-C(28)-N(29)	121.8 (6)	H(16B)-C(16)-C(17)	114 (3)	H(26)-C(26)-C(27)	117 (4)
N(8)-C(13)-C(14)	118.2 (5)	O(4)-Cl(3)-O(5)	113.7 (8)	C(16)-C(17)-H(17A)	110 (4)	C(26)-C(27)-H(27)	126 (4)
C(12)-C(13)-C(14)	121.0 (7)	O(4)-Cl(3)-O(6)	111.0 (7)	H(17A)-C(17)-S(18)	104 (4)	H(27)-C(27)-C(28)	115 (4)
C(13)-C(14)-N(15)	113.0 (6)	O(4)-Cl(3)-O(7)	103.8 (6)	H(17A)-C(17)-H(17B)	110 (5)	C(27)-C(28)-H(28)	124 (3)
C(14)-N(15)-Ni(1)	107.2 (4)	O(5)-Cl(3)-O(6)	112.9 (9)	C(16)-C(17)-H(17B)	114 (3)	H(28)-C(28)-N(29)	115 (3)
C(14)-N(15)-C(16)	113.6 (5)						
		3. Some Dihedral Angles, Deg					
C(17)-S(18)-S(19)-C(20)	85	N(8)-C(13)-C(14)-N(15)	20	N(22)-C(23)-C(24)-C(25)	154	N(15)-C(16)-C(17)-S(18)	55
Ni(1)-S(18)-S(19)-C(20)	19	C(12)-C(13)-C(14)-N(15)	163	N(22)-C(23)-C(24)-N(29)	27		

^a The esd is in the units of the least significant digit given for the corresponding parameter.

$\nu(\text{SS})$ bands at 506–512 cm^{-1} .²⁸ The small shift of this band to lower energy can be associated with the coordination of the disulfide group.²⁸ It appears that the spectral change is a more sensitive indicator of the electronic perturbation of the disulfide link than are the crystallographic results.

The Raman spectra of both [Ni(PMS)Br]ClO₄ and [Ni(PMS)Cl]ClO₄ exhibit bands of medium intensity at 617, 645, and 655 cm^{-1} . These bands are tentatively assigned to $\nu(\text{CS})$.^{29–31} The multiplicity within this region may be indicative of the asymmetric coordination of the CSSC moiety.

In the present work a consistent and interpretable pattern of Ni(II) to N distances appears. Where pyridine nitrogen atoms are involved, the consistent bond lengths of 2.072 (5)

and 2.077 (5) Å are observed, to N(8) and N(29), respectively. Noticeably shorter Ni(II)-N bonds to pyridyl nitrogen atoms, as compared to amine nitrogens, are expected, perhaps, because of the opportunity for π bonding from d orbitals of Ni(II) to empty low-lying π^* orbitals of the pyridyl group. (See ref 14 for a brief discussion of this effect.) Appropriately longer then, by 0.040 (6) Å, is the 2.114 (5) Å distance from Ni(II) to the amine nitrogen atom, N(22). Inconsistently longer is the Ni(II)-N(15) distance, 2.162 (5) Å. However, N(15) is trans to Br⁻ (see Figure 2), and the increase in bond length of 0.048 (7) Å is interpreted as a structural trans effect, observed with respect to the intramolecular Ni(II)-N(22) standard. See Table V.

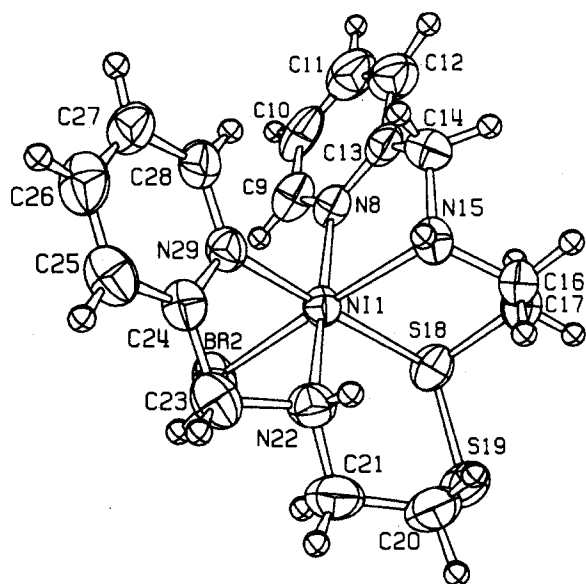


Figure 2. $[\text{Ni}(\text{PMS})\text{Br}]^+$, the bromo[bis(2-((2-pyridylmethyl)amino)ethyl) disulfide]nickel(II) complexed cation, showing ellipsoids of 50% probability.²⁴

Similar bond elongations, 0.086 (21) Å found in the corresponding chloro compound¹³ and 0.051 (21) Å in $[\text{Ni}(\text{DTPP})\text{Cl}]\text{ClO}_4$ ¹⁴ involving imino nitrogen atoms and a chloride ion, have been reported.

These two previous structures^{13,14} had suggested, but only weakly, that the disulfide group is a weaker trans-labilizing agent than either imine or amine. In the present work, the two Ni(II) to N(pyridyl) bond lengths are 2.072 (5) Å trans to the amine nitrogen atom, N(22), and 2.077 (5) Å trans to the coordinated disulfide group. Accordingly, this potential trans effect involving the disulfide is dismissed.

An inspection of the structures of $[\text{Ni}(\text{PMS})\text{Br}]\text{ClO}_4$ and $[\text{Ni}(\text{PMS})\text{Cl}]\text{ClO}_4$ reveals that the long Ni(II)-N(amine) bond is the one shared between two nearly orthogonal five-membered rings, so that logically its length could be attributed to strain as well as to electronic effects. The other Ni(II)-N(amine) bond is shared between a five- and a six-membered ring and appears to be less strained. However,

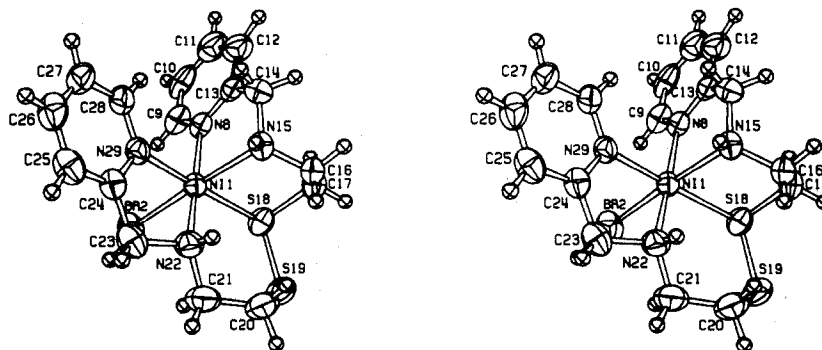


Figure 3. Stereoview²⁴ of $[\text{Ni}(\text{PMS})\text{Br}]^+$, the bromo[bis(2-((2-pyridylmethyl)amino)ethyl) disulfide]nickel(II) complexed cation, showing ellipsoids of 50% probability.

Table V. Coordination Sphere Trans-Pair Bond Lengths (Å)

	$[\text{Ni}(\text{PMS})\text{Br}]^+$ trans to		$[\text{Ni}(\text{PMS})\text{Cl}]^+{}^a$ trans to		$[\text{Ni}(\text{DTPP})\text{Cl}]^+{}^b$ trans to	
	Br ⁻	Pyridyl	Cl ⁻	Pyridyl	Cl ⁻	Pyridyl
Ni-N(amine)	2.162 (5)	2.114 (5)	2.167 (14)	2.081 (15)	2.073 (15)	2.022 (14)
Ni-N(imine)						
Δ/σ		6.8		4.2		2.5

^a Reference 13. ^b Reference 14.

Table IV. Deviations of Atoms from Least-Squares Planes (Å × 10³)^a

Atoms	Plane no.				
	1	2	3	4	5
Ni(1)	-60	50	-11	-71	-17
Br(2)	-171		2		4
N(8)	1	-301		51	-119
C(9)	2				-135
C(10)	-6				-257
C(11)	4			480	-346
C(12)	3				-333
C(13)	-4				-223
C(14)					-297
N(15)	310		104		232
C(16)			-297		
C(17)			342		
S(18)		270	-14	-6	
N(22)	-300	605		24	-101
C(23)				-586	
C(24)		0		-254	
C(25)		-3		-221	
C(26)		-1	-483	82	
C(27)		9		350	
C(28)		-10		285	
N(29)		4	-81	2	
Other Parameters					
<i>q</i> _a	1478	-5521	9247	-3664	958
<i>q</i> _b	-9803	-1327	2123	-224	-9937
<i>q</i> _c	1308	8232	3160	9302	581
<i>D</i>	-0.553	+0.284	+4.979	+1.656	-1.058
δ	4	6	59	41	125

^a Italic deviations indicate the atoms used to define the least-squares plane. A negative deviation from a plane indicates that the atom with the coordinates given in Table I lies between that plane and the origin. The direction cosines (× 10⁴), *q*, are with respect to *a*, *b*, and *c*. The rms deviation (Å × 10³) of the italic atoms from the plane is δ . *D* is the distance (in Å) from the plane to the origin.

in $[\text{Ni}(\text{DTPP})\text{Cl}]\text{ClO}_4$,¹⁴ the longer Ni(II)-N(imine) bond is involved with larger rings than the shorter, and it appears that only the electronic trans effect argument is consistent with the results. If strain was the correct explanation, then the most strained complexed ion of this series, $[\text{Ni}(\text{DTPP})\text{Cl}]^+$, should have a different order to its long and short Ni(II)-N(imine) bonds, and a greater difference than is observed. For this reason, in part, the electronic trans argument is preferred.

The Ni(II)-S coordinative covalent distance, 2.456 (2) Å, is comparable with the sum of the corresponding Pauling covalent radii,³² 2.43 Å, indicating a strong interaction. The corresponding distance in [Ni(PMS)Cl]ClO₄ was found to be 2.472 (5) Å.¹³

The octahedral Ni(II) to Br⁻ distance, 2.544 (1) Å, is also approximately the sum of the corresponding Pauling covalent radii,³² 2.50 Å, and is close to the reported values of 2.606 (3) Å in dibromodiaquo(*N,N,N',N'*-tetramethyl-*o*-phenylenediamine)nickel(II),³³ 2.635 (5) Å in dibromotetrakis(1,8-naphthyridine)dinickel(II) tetraphenylborate,³⁴ and 2.54 Å in *trans*-dibromobis(acetylacetonate)nickel(II).³⁵

The pattern of closest nonbonded contacts is similar to that already discussed for the isostructural [Ni(PMS)Cl]ClO₄.¹³ The best defined oxygen, O(4), is 2.29 Å from an amino hydrogen atom, H(15); and O(7), next best defined according to the thermal foreshortening of its Cl-O bond length, is 2.39 Å from the other amino hydrogen atom, H(22). See Figure 1. The remaining perchlorate oxygen atoms do not participate in such close approaches.

Acknowledgment. This work was supported by the National Institutes of Health (Grant No. GM-18813-03). We are also indebted to the University of Hawaii Computing Center.

Registry No. [Ni(PMS)Br]ClO₄, 55267-64-6.

Supplementary Material Available. A listing of the structure factor amplitudes (×10) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC500305.

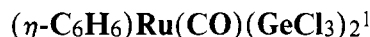
References and Notes

- (1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967.
- (2) J. M. Pratt and R. G. Thorpe, *Adv. Inorg. Chem. Radiochem.*, **12**, 375 (1969).

- (3) R. C. Elder and M. Trkula, *J. Am. Chem. Soc.*, **96**, 2635 (1974).
- (4) R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *Inorg. Chem.*, **12**, 2690 (1973).
- (5) F. C. March and G. Ferguson, *Can. J. Chem.*, **49**, 3590 (1971).
- (6) P. E. Hoggard, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **10**, 959 (1971).
- (7) A. G. Desai, N. W. Dodgen, and J. P. Hunt, *J. Am. Chem. Soc.*, **92**, 798 (1970).
- (8) S. Funahashi and M. Tanaka, *Inorg. Chem.*, **8**, 2159 (1969).
- (9) R. G. Wilkins, *Acc. Chem. Res.*, **3**, 408 (1970).
- (10) D. N. Hague, *Inorg. React. Mech.*, **2**, 196 (1972).
- (11) R. G. Wilkins, *Pure Appl. Chem.*, **33**, 583 (1973).
- (12) A. Peloso, *Coord. Chem. Rev.*, **10**, 123 (1973).
- (13) P. E. Riley and K. Seff, *Inorg. Chem.*, **11**, 2993 (1972).
- (14) L. G. Warner, T. Ottersen, and K. Seff, *Inorg. Chem.*, **13**, 2529 (1974).
- (15) R. L. Gavino, private communication, 1971.
- (16) D. D. Reynolds, M. K. Massad, D. L. Fields, and D. L. Johnson, *J. Org. Chem.*, **26**, 5109 (1961).
- (17) S. W. Peterson and H. A. Levy, *Acta Crystallogr.*, **10**, 70 (1957).
- (18) T. Ottersen, LP-73 computer program, University of Hawaii, 1973.
- (19) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).
- (20) T. Dahl, ABCO computer program, Chemistry Department, University of Oslo, modified by T. Ottersen, 1973.
- (21) P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, UCLASLS4, American Crystallographic Association Library (old) No. 317; modified by K. S., 1972.
- (22) K. Seff, HFIND computer program, University of Hawaii, 1971.
- (23) C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "ALFF, Ames Laboratory Fast Fourier", Iowa State University, 1971; modified by K.S., 1973.
- (24) C. K. Johnson, "ORTEP", Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
- (25) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968).
- (26) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- (27) C. H. Dauben and D. H. Templeton, *Acta Crystallogr.*, **8**, 841 (1955).
- (28) L. G. Warner, T. Ottersen, and K. Seff, *Inorg. Chem.*, **13**, 2819 (1974), and references therein.
- (29) B. Schrader, *Angew. Chem., Int. Ed. Engl.*, **12**, 884 (1973).
- (30) E. J. Bastian and R. B. Martin, *J. Phys. Chem.*, **77**, 1129 (1973).
- (31) H. E. Van Wart, A. Lewis, H. A. Scheraga, and F. D. Saeva, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 2619 (1973).
- (32) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, pp 246 and 249.
- (33) G. Bombieri, E. Forsellini, G. Bandoli, L. Sindellari, R. Graziani, and C. Panattoni, *Inorg. Chim. Acta*, **2**, 27 (1968).
- (34) D. Gatteschi, C. Mealli, and L. Sacconi, *J. Am. Chem. Soc.*, **95**, 2736 (1973).
- (35) S. Koda, S. Ooi, H. Kuroya, I. Isobe, Y. Nakamura, and S. Kawaguchi, *J. Chem. Soc., Chem. Commun.*, 1321 (1971).

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta T6G 2E1, Canada

Organometallic Compounds with Metal-Metal Bonds. XXI. Crystal and Molecular Structure of (η -Benzene)carbonylbis(trichlorogermyl)ruthenium,



L. Y. Y. CHAN and W. A. G. GRAHAM*

Received January 23, 1975

AIC500599

The structure of (η -C₆H₆)Ru(CO)(GeCl₃)₂ has been determined by single-crystal X-ray techniques. The compound crystallizes in the orthorhombic *Pnma* space group with four molecules in the unit cell of dimensions $a = 14.3071$ (6), $b = 13.2024$ (6), and $c = 8.3497$ (5) Å. Intensity data were collected by counter methods and the 720 observed independent reflections were refined using full-matrix least-squares procedures to a final *R* factor of 3.9%. The molecule has a "piano stool" geometry with a crystallographic mirror plane passing through the ruthenium atom, the carbonyl group, and two carbon atoms of the benzene ring and therefore has an eclipsed conformation when viewed perpendicular to the ring. The benzene ring is planar and all ruthenium-ring carbon distances are equal at 2.29 (1) Å. The ruthenium-germanium distance is 2.408 (2) Å.

Introduction

Recent synthetic work in this laboratory has made available complexes of the type (arene)Ru(CO)(GeCl₃)₂ (arene = benzene, toluene, *o*-, *m*-, and *p*-xylene, mesitylene).¹ A structural investigation of a representative of these compounds was of interest from several points of view. The first was a comparison with the known structures of *cis*- and *trans*-

Ru(CO)₄(GeCl₃)₂.² The second was the relation to the extensively studied³⁻⁷ arenechromium tricarbonyl compounds, with respect particularly to the symmetry maintained in the aromatic ring, and its conformation relative to the three ligands making up the opposite face of the idealized octahedron. Finally, the report⁸ of slightly nonplanar arene rings in the complexes (arene)Ru[PCH₃(C₆H₅)₂]Cl₂ suggested that other