is approximately 4 standard deviations in the case of $(TiO(acac)_2)_2 \cdot 2C_4H_8O_2$ and 20 standard deviations for $(TiO(acac)_2)_2$, it is felt that this trans effect is real. It should also be noted that a comparison of corresponding Ti–O bond distances in both structures shows that these distances agree to within 1 standard deviation.

The Ti–O bond distances of this study compare with 1.988 and 1.944 Å in rutile,[9] 1.79 and 1.81 Å in $(TiCl(acac)_2)_2 \cdot CHCl_3$,[3] and 1.91, 1.744, and 2.122 Å in $TiCl_2(OC_6H_5)_2$.[10] It is interesting that the short Ti–O bond length does not involve a large oxygen bond angle as it does in the other similar cases of TiO distances of the order of 1.8 Å.

One of the most interesting and still puzzling aspects of this structure is the presence of the solvent molecules in crystal I. Examination of the least-squares planes for the solvent (Table VI) shows that ring 1 is more nearly planar than is ring 2. This is apparently due to a different mechanism of disorder for each dioxane molecule since the occupation factors indicate that the oxygens are nearly equally spread out over the two molecules.

Since the shortest distance from a solvent atom to an atom in the dimer unit is 3.42 Å (C(19)–C(13)), we conclude that the solvent molecules are simply trapped in the spaces between dimer units with little or no chemical bonding. These holes occupied by the solvent molecules are approximately spherical and have a diameter of about 7 Å.

Acknowledgment.—We wish to acknowledge the National Science Foundation for a grant (GP-8301) for partial support of this research. We also wish to thank the Montana State University Computing Center for a grant of computing time.

---

(9) W. H. Baier, *Acta Crystallogr.*, **9**, 515 (1956).

(10) K. Watenpaugh and C. N. Caughlan, *Inorg. Chem.*, **5**, 1782 (1966).

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

The Crystal and Molecular Structure of Chloro(bis{2-[(2-pyridylmethyl)amino]ethyl} disulfide)nickel(II) Perchlorate

By PAUL E. RILEY and KARL SEFF*

Received March 16, 1972

The crystal structure of chloro(bis{2-[(2-pyridylmethyl)amino]ethyl} disulfide)nickel(II) perchlorate, $Ni(C_{16}H_{22}N_4S_2)Cl(ClO_4)$, has been determined by single-crystal X-ray diffraction techniques and was refined by full-matrix least-squares methods to a final conventional R index of 0.058. The deep blue crystals form as rectangular prisms in space group *Pbca* with $a = 24.019$ (8), $b = 14.700$ (4), and $c = 12.439$ (6) Å. The nickel(II) ion is coordinated octahedrally by four nitrogen atoms, a chloride ion, and one sulfur atom of the disulfide group. The two pyridine rings are cis; the two amino groups are cis; and the chloride ion and the coordinating sulfur atom are cis. The octahedral angles are all within 10° of right angles, and the largest deviations can be explained by ring strain. The nickel(II)–sulfur distance, 2.472 (5) Å, is comparable with the sum of the corresponding Pauling covalent radii, 2.43 Å, indicating a strong interaction. Exploratory X-ray photographs and structure factor calculations indicate that $Ni(C_{16}H_{22}N_4S_2)I_2$ and $Ni(C_{16}H_{22}N_4S_2)Br(ClO_4)$ are isostructural with $Ni(C_{16}H_{22}N_4S_2)Cl(ClO_4)$.

Introduction

The breaking of aliphatic disulfide bonds is catalyzed by Ag(I),[1] Hg(II),[2] and Pd(II)[3] by a mechanism in which the –S–S– group first complexes the transition metal ion. An intermediate was isolated in the Pd(II) system which is expected to show disulfide–Pd(II) coordination. Disulfide formation[4,5] has also been postulated in ferredoxin activity, presumably through coordination involving delocalized orbitals.[6,7] A weak Cu(II) cystine complex was reported[8–11] on the basis of anomalous stability constants. The structures of (diethyl disulfide)copper(I) chloride,[12] of a dinuclear cobalt disulfide complex,[13] and of an iridium disulfide complex[14] have been determined crystallographically. Complexes of cystine with Cd, Ni, and Zn have also been postulated.[15]

In the preparation of the Ni(II) complexes, two ligands which differed only by one methylene group per half molecule showed very different behavior[16,17] in the presence of the metal ion. Where five-membered rings formed, the disulfide was stable. Where six-membered rings were expected, the disulfide bond proved to be unstable. The metal ion by itself, then, showed this great selectivity by the nature of the complex it formed with the ligand (substrate). Ample

---

(1) R. Cecil and J. R. McPhee, *Biochem. J.*, **66**, 538 (1957).

(2) F. Challenger, "Aspects of the Organic Chemistry of Sulfur," Butterworth, London, 1959.

(3) T. Boschi, *et al.*, *Inorg. Chem.*, **9**, 532 (1970).

(4) V. Massey and C. Veeger, *Biochim. Biophys. Acta*, **48**, 33 (1961).

(5) E. M. Kosower, *Flavins Flavoproteins, Proc. Symp.*, **8**, 9 (1966).

(6) P. Hemmerich and J. Spence, *ibid.*, **8**, 87 (1966).

(7) C. K. Jørgensen, *Z. Naturwiss.—Med. Grundlagenforsch.*, **2**, 230 (1965).

(8) C. J. Hawkins and D. D. Perrin, *Inorg. Chem.*, **2**, 839 (1963).

(9) O. Dobozy, F. Guba, and T. Mandy, *Chem. Abstr.*, **57**, 172f (1962).

(10) A. Sandell, *Acta Chem. Scand.*, **15**, 190 (1961).

(11) R. M. Tichane and W. E. Bennett, *J. Amer. Chem. Soc.*, **79**, 1293 (1957).

(12) C. I. Brändén, *Acta Chem. Scand.*, **21**, 1000 (1967).

(13) G. Bor and G. Natile, *J. Organometal. Chem.*, C33 (1971).

(14) W. D. Bonds, Jr., and J. A. Ibers, *J. Amer. Chem. Soc.*, **94**, 3415 (1972).

(15) P. Ray and A. Bhaduri, *J. Indian Chem. Soc.*, **27**, 297 (1950).

(16) R. L. Gavino and J. W. Wrathall, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 1968.

(17) R. L. Gavino, Ph.D. Thesis, University of Hawaii, Honolulu, 1971.

precedent[8,18,19] for chelating ring stabilities of this sort exists.

During an investigation of the chelating ability of some β-mercaptoamines, it was discovered that solutions of Ni(II) complexes of the tridentate ligand 2-[(2-pyridylmethyl)amino]ethanethiol ($C_8H_{12}N_2S$) which were initially red turned blue upon oxidation by air or hydrogen peroxide.[16] Elemental analysis of the deep blue crystals showed the stoichiometry to be of two types[17]

$$\mathrm{Ni(C_{16}H_{22}N_4S_2)X_2} \qquad \mathrm{Ni(C_{16}H_{22}N_4S_2)XY}$$

$$\mathrm{X^- = Br^-, I^-} \qquad \mathrm{X^- = Cl^-, Y^- = ClO_4^-, BF_4^-}$$

$$\mathrm{X^- = Br^-, Y^- = ClO_4^-}$$

The magnetic susceptibility and the electronic spectra of these compounds in the solid state indicate that the nickel ion is octahedrally coordinated throughout. In aqueous solution, all compounds turn red and exhibit identical electronic spectra indicating the existence of the same octahedral cation, probably $[\mathrm{Ni(C_{16}H_{22}N_4S_2)H_2O}]^{2+}$. Furthermore, all of these compounds appear to be 1:2 electrolytes in aqueous solution, in agreement with the formula. The electronic spectra in various nonaqueous solvents show the retention of the coordination observed in the solid state for each complex; therefore cation–solvent interactions are absent, and all cations are probably of the form $[\mathrm{Ni(C_{16}H_{22}N_4S_2)X}]^+$.

Experimental Section

Preliminary X-ray photographs of $\mathrm{Ni(C_{16}H_{22}N_4S_2)I_2}$, $\mathrm{Ni(C_{16}H_{22}N_4S_2)Br(ClO_4)}$, and $\mathrm{Ni(C_{16}H_{22}N_4S_2)Cl(ClO_4)}$ indicated that these materials are isostructural.[20] (This was later confirmed by approximate structure factor calculations.) The crystals of $\mathrm{Ni(C_{16}H_{22}N_4S_2)Cl(ClO_4)}$, which form as deep blue rectangular prisms, were selected for structural study by the equiinclination Weissenberg multiple-film technique. Initial photographs showed the symmetry and systematic absences characteristic of the orthorhombic space group *Pbca*. Unit cell dimensions at 25° as determined by a least-squares refinement of 359 2θ values measured on *hk*0 and *h*0*l* Weissenberg photographs, calibrated with superimposed aluminum powder diffraction lines, are a = 24.031 (3), b = 14.698 (2), and c = 12.461 (2) Å. The assumed value of a for 99.992% pure aluminum powder at 25° is 4.04961 Å. The measured density of 1.587 g cm^{-3} agrees with the calculated value of 1.594 g cm^{-3} for eight formula units per unit cell.

The intensities of 4473 unique reflections (about 90% of the Cu sphere) were estimated visually using two crystals. A crystal with dimensions 0.040 × 0.074 × 0.034 cm was mounted parallel to its b axis (0.074 cm) and *h*0*l* through *h*6*l* intensities were collected using nickel-filtered Cu Kα radiation (λ = 1.5418 Å). A second crystal mounted along its c axis (0.09 cm) with dimensions of 0.040 × 0.043 × 0.090 cm was used to observe layers *hk*0 through *h,k*,10. Lorentz, polarization, extended spot shape, and Cu Kα splitting corrections were applied.[21] An approximate spherical absorption correction (μ = 56.3 cm^{-1}) was made assuming a radius of 0.019 cm for the b-axis crystal and 0.021 cm for the c-axis one. Unobserved reflections were assigned an intensity of $^1/_3 I_{\min}$, the minimum observable intensity. The data were scaled and merged by a modification of the Sparks interlayer scaling program.[22] The structure was determined and refined,[20] but anisotropic least-squares refinement had nearly converged at R = 0.18, and two oxygen atoms remained very poorly defined.

At this time a second data set was collected using a relatively regular crystal with extreme dimensions of 0.010 × 0.010 × 0.014 cm, which had been dipped in liquid nitrogen. A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo Kα radiation (Kα$_1$, λ 0.70926 Å; Kα$_2$, λ 0.71354 Å) and a pulse-height analyzer was used for preliminary experiments and for the collection of diffraction intensities.

The cell constants were determined by a least-squares procedure using the centered angular coordinates of 15 intense reflections with 2θ values up to 22.3°. They are, at 20°, a = 24.019 (8), b = 14.700 (4), and c = 12.439 (6) Å.

Diffraction data were collected by the θ–2θ scan technique at a constant scan rate of 0.5°/min (in 2θ). All 4161 unique lattice points for which $2\theta < 50°$ were examined. The scan range varied from 2.0° at 2θ = 3.3° to 2.3° at 2θ = 50°. A time equal to half of the scan time for each reflection was spent counting background at each end of the scan range. Three check reflections which were measured periodically during data collection showed an average total decrease in intensity of 4%, and an approximate correction for this effect was made.

Standard deviations were assigned according to the formula

$$\sigma(I) = [CT + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$$

where CT is the total integrated count obtained in a scan time of t_c, B_1 and B_2 are the background counts each obtained in time t_b, and $I = CT - 0.5(t_c/t_b)(B_1 + B_2)$. A value of 0.02 was assigned to the empirical parameter p to account for instrument instability.

The net counts were then corrected[23] for Lorentz and polarization effects. An absorption correction (μR = 0.010) was unnecessary. Each of the 1089 reflections for which the net count exceeded 3 times its standard deviation was used in the final refinement of the structure.

Structure Determination

The photographic data set was used to determine the structure by direct methods,[24] using a reiterative application[25] of Sayre's equation, and by Patterson methods. The 444 values of E, the normalized structure factor, greater than 1.50 were used to generate 16 solutions. Of these, the two solutions that were most consistent and converged most rapidly were nearly identical, approximately related by a mirror plane at $x = {}^1/_8$. In both solutions, the z coordinate of Ni(II) was found to be slightly greater than $^1/_4$, and the octahedral environment of the nickel

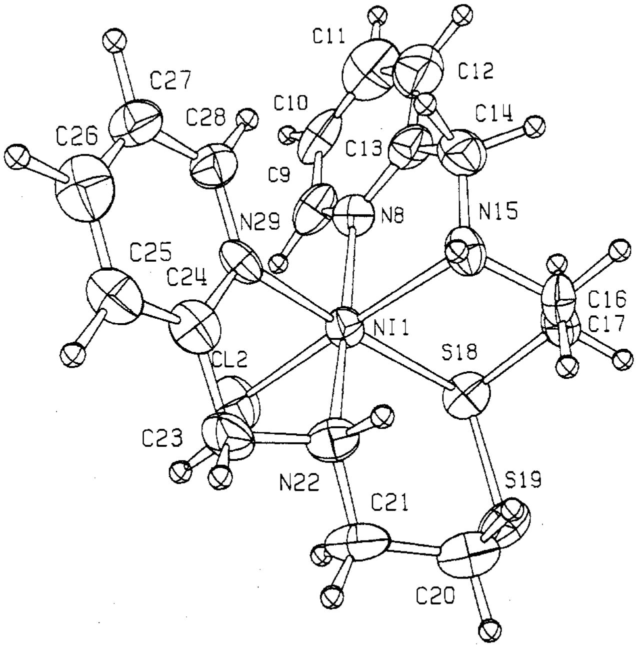

Figure 1.—The chloro(bis{2-[(2-pyridylmethyl)amino]ethyl} disulfide)nickel(II) ion, showing ellipsoids of 50% probability. C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

---

(18) G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 2344 (1952).

(19) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **7**, 795 (1968).

(20) P. E. Riley and K. Seff, *J. Chem. Soc. D*, 194 (1971).

(21) K. Seff, RAWDT computer program instructions, 1966.

(22) W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Crystallogr.*, **13**, 273 (1960).

(23) A. Cristensen, LPCOR computer program, Syntex Instruments, 1970.

(24) J. Karle, *Advan. Struct. Res. Diffr. Methods*, **1**, 55 (1964).

(25) R. E. Long, Ph.D. Thesis, University of California at Los Angeles, 1965, Part III, pp 87–126.

TABLE I

FINAL POSITIONAL PARAMETERS AND THEIR STANDARD DEVIATIONS[a]

	$x, \sigma(x)$	$y, \sigma(y)$	$z, \sigma(z)$
Ni(1)	1651 (1)	1143 (1)	2572 (2)
Cl(2)	1973 (2)	1115 (4)	755 (4)
Cl(3)	−206 (2)	1697 (4)	4194 (5)
O(4)	315 (11)	2076 (23)	4171 (20)
O(5)	−464 (21)	2001 (39)	3475 (58)
O(6)	−474 (13)	1725 (31)	5146 (30)
O(7)	−104 (25)	928 (22)	3869 (56)
N(8)	2441 (7)	1372 (9)	3242 (11)
C(9)	2918 (8)	1401 (11)	2686 (18)
C(10)	3430 (10)	1607 (14)	3197 (26)
C(11)	3411 (11)	1734 (18)	4291 (32)
C(12)	2919 (12)	1668 (16)	4824 (21)
C(13)	2427 (8)	1509 (10)	4324 (14)
C(14)	1877 (8)	1457 (11)	4873 (13)
N(15)	1445 (6)	1028 (10)	4263 (11)
C(16)	1348 (10)	77 (13)	4592 (15)
C(17)	1788 (9)	−573 (11)	4166 (16)
S(18)	1845 (2)	−504 (3)	2722 (4)
S(19)	1209 (2)	−1297 (3)	2177 (4)
C(20)	588 (8)	−630 (15)	2101 (17)
C(21)	627 (9)	266 (13)	1421 (16)
N(22)	833 (7)	1040 (9)	2040 (10)
C(23)	708 (9)	1866 (13)	1448 (17)
C(24)	973 (7)	2697 (13)	1981 (14)
C(25)	754 (8)	3553 (13)	1918 (13)
C(26)	1018 (8)	4265 (12)	2427 (18)
C(27)	1481 (9)	4090 (11)	2996 (14)
C(28)	1698 (8)	3207 (13)	3032 (13)
N(29)	1439 (5)	2512 (8)	2540 (12)
H(9)	2909	1251	1842
H(10)	3808	1670	2727
H(11)	3786	1896	4704
H(12)	2927	1743	5689
H(14A)	1936	1078	5602
H(14B)	1748	2141	5056
H(15)	1087	1380	4368
H(16A)	1348	35	5459
H(16B)	947	−145	4291
H(17A)	2190	−422	4505
H(17B)	1686	−1272	4367
H(20A)	479	−449	2927
H(20B)	265	−1058	1787
H(21A)	901	134	753
H(21B)	214	416	1120
H(22)	644	1053	2767
H(23A)	859	1801	640
H(23B)	259	1959	1434
H(25)	372	3666	1465
H(26)	854	4947	2363
H(27)	1680	4629	3442
H(28)	2086	3085	3454

[a] Values are given × 10^4. See Figures 1 and 2 for the identities of the atoms. The esd is in the units of the least significant digit given for the corresponding parameter. The hydrogen atom coordinates are calculated and not refined.

TABLE II

THERMAL VIBRATION PARAMETERS AND THEIR STANDARD DEVIATIONS[a]

I. Nonhydrogen Temperature Factor =

$$\exp\{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\}$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni(1)	11 (1)	34 (1)	40 (1)	1 (1)	1 (2)	5 (3)
Cl(2)	23 (1)	66 (3)	44 (3)	19 (4)	14 (3)	9 (7)
Cl(3)	13 (1)	54 (3)	87 (4)	8 (3)	−5 (4)	−9 (6)
O(4)	46 (7)	252 (35)	141 (21)	−119 (28)	22 (21)	−85 (45)
O(5)	85 (17)	490 (61)	689 (113)	115 (46)	−226 (75)	712 (131)
O(6)	49 (10)	260 (37)	284 (43)	−22 (31)	145 (36)	−134 (70)
O(7)	142 (28)	117 (24)	632 (126)	−4 (36)	443 (110)	−117 (82)
N(8)	14 (3)	24 (7)	74 (11)	10 (7)	−20 (9)	−17 (16)
C(9)	13 (3)	43 (10)	99 (19)	11 (9)	8 (15)	37 (22)
C(10)	11 (5)	45 (11)	171 (28)	−12 (12)	−17 (20)	40 (29)
C(11)	13 (5)	62 (14)	189 (36)	5 (14)	−64 (25)	20 (40)
C(12)	24 (7)	52 (12)	124 (23)	−17 (15)	−67 (23)	25 (28)
C(13)	19 (5)	18 (8)	51 (13)	−4 (9)	−38 (13)	9 (17)
C(14)	17 (4)	40 (11)	22 (11)	−11 (10)	7 (12)	−20 (16)
N(15)	14 (3)	46 (8)	42 (10)	5 (9)	11 (9)	−32 (17)
C(16)	22 (5)	56 (12)	56 (16)	−39 (14)	−8 (14)	0 (22)
C(17)	27 (6)	37 (9)	72 (14)	2 (12)	3 (14)	52 (19)
S(18)	15 (1)	41 (3)	80 (5)	10 (2)	7 (3)	1 (5)
S(19)	21 (1)	34 (2)	101 (5)	−2 (3)	10 (3)	−26 (6)
C(20)	17 (5)	61 (12)	88 (17)	−13 (12)	−10 (13)	15 (23)
C(21)	17 (5)	48 (11)	91 (19)	5 (11)	−50 (14)	−44 (23)
N(22)	12 (3)	32 (7)	56 (8)	−4 (10)	−9 (10)	−19 (14)
C(23)	16 (5)	44 (12)	61 (17)	16 (12)	−14 (13)	−4 (23)
C(24)	12 (4)	55 (11)	46 (13)	39 (10)	3 (11)	47 (19)
C(25)	13 (4)	50 (11)	59 (14)	11 (11)	−15 (13)	18 (17)
C(26)	23 (4)	43 (8)	55 (13)	24 (10)	−3 (16)	40 (26)
C(27)	26 (5)	26 (10)	48 (12)	−9 (10)	6 (13)	−14 (15)
C(28)	12 (4)	54 (10)	54 (13)	−12 (12)	−5 (12)	25 (20)
N(29)	14 (2)	34 (6)	25 (8)	−3 (6)	0 (10)	−34 (17)

II. Hydrogen (assigned unrefined values)

	B, Å^2		B, Å^2
H(9)	3.56	H(20A)	3.54
H(10)	3.85	H(20B)	3.54
H(11)	6.59	H(21A)	3.74
H(12)	4.31	H(21B)	3.74
H(14A)	3.20	H(22)	2.73
H(14B)	3.20	H(23A)	3.44
H(15)	2.46	H(23B)	3.44
H(16A)	3.41	H(25)	3.73
H(16B)	3.41	H(26)	3.60
H(17A)	4.23	H(27)	3.62
H(17B)	4.23	H(28)	3.00

[a] The b values are × 10^4. See Figures 1 and 2 for the identities of the atoms. The esd is in the units of the least significant digit given for the corresponding parameter.

ion was clear. The Patterson synthesis offered the same two solutions, but without the detail (for instance $z_{Ni} = {}^1/_4$ here) offered by direct methods. Successive structure factor calculations, performed for both (direct methods) solutions, using first the position of the nickel ion only and then including the four remaining heavy atoms (two sulfur atoms, the chloride ion, and the chlorine atom of the ClO_4^- ion) indicated that the most consistent solution was correct. Two cycles of three-dimensional Fourier refinement yielded an $R_1 = (\Sigma|F_o - |F_c||/\Sigma F_o)$ value of 0.24 and revealed the positions of all nonhydrogen atoms except two oxygen atoms of the perchlorate group. These positions were calculated assuming that the anion was tetrahedral. Full-matrix least-squares using isotropic thermal parameters resulted in an R_1 of 0.20, but Cl–O bond lengths ranged from 1.14 to 1.48 Å and thermal parameters for the oxygen atoms ranged from 12 to 28 Å^2. Anisotropic refinement of all but the oxygen (and hydrogen) atoms reduced R_1, but only to 0.18.

At this point, the second data set was carefully collected by counter methods. After least-squares convergence with anisotropic thermal parameters for all nonhydrogen atoms, R_1 decreased to 0.068. A fine-grid Fourier synthesis of the perchlorate anion clearly showed the positions of all but one oxygen atom, O(5), which remained very broad. However, a disordered perchlorate group was not indicated. The positions of all hydrogen atoms, planar and tetrahedral, were calculated[26] assuming C–H bond lengths of 1.08 Å and N–H bond lengths of 1.01 Å. An isotropic temperature factor equal to that of the atom to which it is bonded was assigned to each hydrogen atom. With these 22 hydrogen atoms per molecule included in the calculations, full-matrix least-squares anisotropic refinement of all nonhydrogen atoms converged to a final R_1 index of 0.058. R_2, the weighted R index, $(R_2 = (\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2)^{1/2})$, = 0.061, and the "goodness of fit," or the standard deviation of an observation of unit weight, $((\Sigma w(F_o - |F_c|)^2/(m - s))^{1/2})$, = 0.79. The number of observations used in least-squares is m (1089), and s (262) is the total number of parameters.

In an attempt to better define the poorest oxygen atom, O(5), its position now was calculated so was to best complete the perchlorate group tetrahedron. The relocation of O(5) by about 0.4 Å to this position raised R_1 by 0.013. A difference Fourier synthesis revealed no other peak that could be attributed to O(5). Hydrogen atoms could not be detected at their calculated positions. The largest peak by a factor of two, 0.7 e/Å^3, on a final difference Fourier function (whose standard deviation was 0.11

---

(26) K. Seff, HFIND computer program, University of Hawaii, 1971.

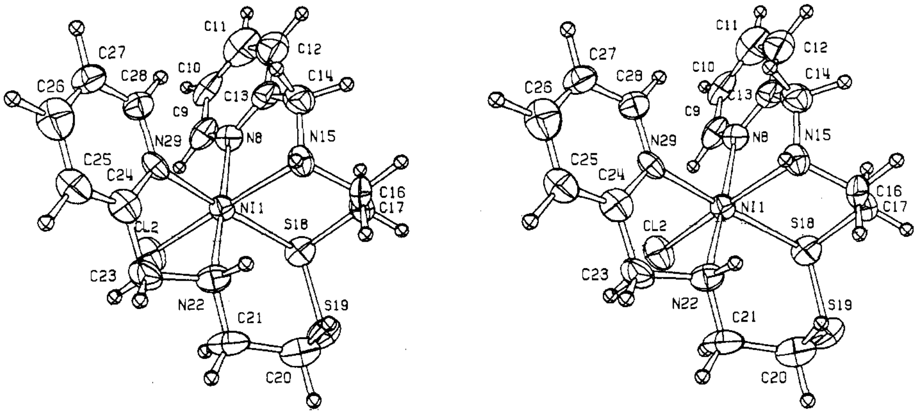

Figure 2.—Stereoview of the chloro(bis{2-[(2-pyridylmethyl)amino]ethyl} disulfide)nickel(II) ion, showing ellipsoids of 50% probability. C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

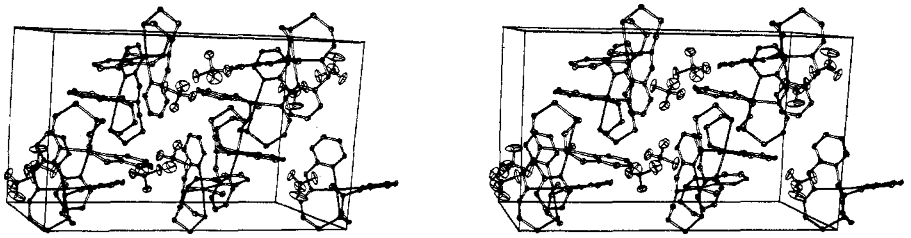

Figure 3.—Stereoview of the packing of chloro(bis{2-[(2-pyridylmethyl)amino]ethyl} disulfide)nickel(II) perchlorate molecules in the unit cell, showing ellipsoids of 15% probability. C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

e/Å^3) was found in the vicinity of Ni(II). It is felt, after working with two independent data sets, that the inability of the anisotropic model to account properly for the large thermal motions of the oxygen atoms of the perchlorate group has substantially elevated the final values of the standard deviations and of the error indices.

The full-matrix least-squares program used[27] minimizes $\Sigma w \cdot (\Delta|F|)^2$, and the weights used were the reciprocal squares of σ, the standard deviation of each observation. The scattering factors used were the following: Ni$^+$,[28] Cl$^-$,[29] Cl^0,[29] S^0,[29] C(valence),[30] O^0,[30] N^0,[31] and H^0 (bonded);[32] the first four of these were modified using the real part of the anomalous dispersion correction.[33] In the final cycles of least-squares refinement, further convergence was not observed. About 90% of the positional shifts were less than half of their esd's. The remainder were less than 1.01 esd's, and were associated with the perchlorate group and atoms near it or whose hydrogen atoms are near it (see Table V), namely C(10), C(11), C(20), C(24), C(25), and N(29).

A listing of observed and calculated structure factors obtained by counter methods is available.[34] The final positional and thermal parameters are listed in Tables I and II, respectively.

Crystal and Molecular Structure

The octahedral nickel(II) ion (Figures 1 and 2) is located near the center of an approximately planar group consisting of the chloride ion, the two (cis) amino nitrogen atoms, and one pyridyl nitrogen atom. The remainder of this pyridine ring lies essentially in this plane (Table III, planes 1 and 5). The second

TABLE III
DEVIATIONS OF ATOMS FROM LEAST-SQUARES PLANES (Å × 10^3)[a]

Atoms	Plane no. 1	2	3	4	5
Ni(1)	−61	105	**−18**	**−69**	**−9**
Cl(2)	−247		**13**		**23**
N(8)	**−3**	−306		**29**	**−121**
C(9)	**14**				−74
C(10)	**−18**				−227
C(11)	**−6**			411	−365
C(12)	**21**				−363
C(13)	**−7**				−273
C(14)					−304
N(15)	345		**120**		**189**
C(16)			−258		
C(17)			373		
S(18)		423	**−19**	**−2**	
N(22)	−285	663		**14**	**−82**
C(23)				−596	
C(24)		**−2**		−231	
C(25)		**2**		−148	
C(26)		**−5**	−558	194	
C(27)		**11**		467	
C(28)		**−11**		356	
N(29)		**4**	**−97**	**28**	
q_a	1397	−5461	9317	−3547	1008
q_b	−9792	−1730	2029	−236	−9942
q_c	1474	8197	3014	9347	383
D	−0.559	+0.060	+5.018	+1.612	−1.139
δ	13	7	70	36	107

[a] Boldface 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 (×10^4), q, are with respect to a, b, and c. The rms deviation (Å × 10^3) of the boldface atoms from the plane is δ. D is the distance (in Å) from the plane to the origin.

---

[27] P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, UCLALS4, American Crystallographic Association Program Library (old) No. 317, modified.

[28] R. E. Watson and A. J. Freeman, *Acta Crystallogr.*, **14**, 27 (1961).

[29] B. Dawson, *ibid.*, **13**, 403 (1960).

[30] J. A. Hoerni and J. A. Ibers, *ibid.*, **7**, 744 (1954).

[31] J. Berghuis, *et al.*, *ibid.*, **8**, 478 (1955).

[32] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3178 (1965).

[33] C. H. Dauben and D. H. Templeton, *Acta Crystallogr.*, **8**, 841 (1955).

[34] A listing of structure factor amplitudes will appear immediately 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 Street, N.W., Washington, D. C. 20036, by referring to code number INORG-72-2993. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE IV

MOLECULAR DIMENSIONS AND ESD'S[a]

I. Bond Lengths (Å)

Atoms	Distance	Atoms	Distance
Ni(1)–Cl(2)	2.389 (5)	C(23)–N(22)	1.45 (2)
Ni(1)–S(18)	2.472 (5)	C(9)–C(10)	1.42 (3)
S(18)–S(19)	2.039 (7)	C(10)–C(11)	1.37 (5)
Ni(1)–N(8)	2.099 (17)	C(11)–C(12)	1.36 (4)
Ni(1)–N(15)	2.167 (14)	C(12)–C(13)	1.35 (3)
Ni(1)–N(22)	2.081 (15)	C(24)–C(25)	1.37 (3)
Ni(1)–N(29)	2.076 (12)	C(25)–C(26)	1.38 (3)
C(17)–S(18)	1.80 (2)	C(26)–C(27)	1.34 (3)
C(20)–S(19)	1.79 (2)	C(27)–C(28)	1.40 (3)
C(9)–N(8)	1.34 (3)	C(13)–C(14)	1.49 (3)
C(13)–N(8)	1.36 (2)	C(16)–C(17)	1.52 (3)
C(24)–N(29)	1.35 (2)	C(20)–C(21)	1.57 (3)
C(28)–N(29)	1.34 (2)	C(23)–C(24)	1.53 (3)
C(14)–N(15)	1.43 (2)	Cl(3)–O(4)	1.37 (3)
C(16)–N(15)	1.48 (2)	Cl(3)–O(5)	1.18 (6)
C(21)–N(22)	1.46 (2)	Cl(3)–O(6)	1.35 (4)
		Cl(3)–O(7)	1.22 (4)

II. Bond Angles (deg)

Atoms	Angle	Atoms	Angle
Cl(2)–Ni(1)–N(8)	94.9 (4)	Ni(1)–N(15)–C(16)	112.3 (12)
N(8)–Ni(1)–N(15)	80.4 (6)	N(15)–C(16)–C(17)	112.8 (16)
N(15)–Ni(1)–N(22)	95.0 (5)	C(16)–C(17)–S(18)	111.4 (15)
N(22)–Ni(1)–Cl(2)	90.2 (4)	C(17)–S(18)–Ni(1)	96.7 (7)
Cl(2)–Ni(1)–S(18)	89.7 (2)	C(17)–S(18)–S(19)	104.0 (6)
Cl(2)–Ni(1)–N(29)	94.5 (4)	Ni(1)–S(18)–S(19)	113.2 (3)
N(29)–Ni(1)–N(22)	80.3 (5)	S(18)–S(19)–C(20)	109.2 (8)
N(22)–Ni(1)–S(18)	97.5 (4)	S(19)–C(20)–C(21)	116.1 (14)
S(18)–Ni(1)–N(8)	87.5 (4)	C(20)–C(21)–N(22)	113.0 (16)
N(8)–Ni(1)–N(29)	94.3 (6)	C(21)–N(22)–Ni(1)	123.0 (12)
N(15)–Ni(1)–S(18)	83.9 (4)	C(21)–N(22)–C(23)	108.3 (15)
N(15)–Ni(1)–N(29)	92.2 (5)	Ni(1)–N(22)–C(23)	107.2 (11)
Cl(2)–Ni(1)–N(15)	172.2 (4)	N(22)–C(23)–C(24)	111.3 (15)
N(8)–Ni(1)–N(22)	172.8 (6)	C(23)–C(24)–C(25)	123.5 (17)
N(29)–Ni(1)–S(18)	175.3 (4)	C(23)–C(24)–N(29)	114.1 (15)
C(13)–N(8)–C(9)	121.8 (14)	C(24)–N(29)–Ni(1)	114.2 (10)
N(8)–C(9)–C(10)	121.2 (16)	Ni(1)–N(29)–C(28)	127.9 (11)
C(9)–C(10)–C(11)	116.4 (19)	C(28)–N(29)–C(24)	117.8 (14)
C(10)–C(11)–C(12)	120.1 (26)	N(29)–C(24)–C(25)	122.4 (16)
C(11)–C(12)–C(13)	123.2 (26)	C(24)–C(25)–C(26)	119.8 (17)
C(12)–C(13)–N(8)	117.2 (15)	C(25)–C(26)–C(27)	118.6 (17)
Ni(1)–N(8)–C(9)	125.0 (14)	C(26)–C(27)–C(28)	120.2 (19)
Ni(1)–N(8)–C(13)	113.2 (10)	C(27)–C(28)–N(29)	121.2 (17)
N(8)–C(13)–C(14)	117.9 (13)	O(4)–Cl(3)–O(5)	108 (3)
C(12)–C(13)–C(14)	124.9 (19)	O(4)–Cl(3)–O(6)	116 (2)
C(13)–C(14)–N(15)	115.0 (14)	O(4)–Cl(3)–O(7)	101 (2)
C(14)–N(15)–Ni(1)	108.4 (10)	O(5)–Cl(3)–O(6)	114 (4)
C(14)–N(15)–C(16)	112.6 (13)	O(5)–Cl(3)–O(7)	102 (3)
		O(6)–Cl(3)–O(7)	114 (3)

III. Some Dihedral Angles (deg)

Atoms	Angle
C(17)–S(18)–S(19)–C(20)	86
Ni(1)–S(18)–S(19)–C(20)	17
N(8)–C(13)–C(14)–N(15)	16
C(12)–C(13)–C(14)–N(15)	163
N(22)–C(23)–C(24)–C(25)	151
N(22)–C(23)–C(24)–N(29)	28
N(15)–C(16)–C(17)–S(18)	55

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

pyridine ring (Table III, plane 2) is approximately normal to and "above" this plane, while trans to this pyridyl nitrogen atom and "below" the plane is the coordinated sulfur atom.

All angles about Ni(II) are within 5.5° of 90° (see Table IV) except the intrachelate angles. The five-membered rings form angles of 80.3 (5), 83.9 (4), and 80.4 (6)° which agree with values reported for similar nickel(II) complexes. (The corresponding angles in the bis[di(2-aminoethyl)amine]nickel(II) ion average 81.6 (10)°.[35]) A larger angle, 97.5 (4)°, observed for the six-membered chelate ring, is somewhat greater than the mean value (91.4 (8)°) found in bis[di-(3-aminopropyl)amine]nickel(II) perchlorate.[35]

The Ni(II)–Cl bond length is 2.389 (5) Å. In the octahedral complexes tetrapyridinenickel dichloride[36] and dichlorotetrakis(trimethylenethiourea)nickel(II),[37] the corresponding distances are 2.382 (5) and 2.413 (5) Å.

Two types of nitrogen ligands coordinate the nickel(II) ion: pyridine nitrogen atoms at distances of 2.099 (17) and 2.076 (12) Å and amino nitrogen atoms at distances of 2.081 (15) and 2.167 (14) Å. The mean bond length of 2.106 (21) Å is typical of previously reported (average) octahedral Ni(II)–N distances: bisperchloratotetrakis(3,5-dimethylpyridine)nickel(II) (2.093 (2) Å),[38] *trans*-bis(acetylacetonato)dipyridinenickel(II) (2.112 (5) Å),[39] the pyridine adduct of bis(diphenyldithiophosphinato)nickel(II) (2.083 (13) Å),[40] 2,2′,2″-triaminotriethylaminenickel(II) dithiocyanate (2.13 (1) Å, for amino nitrogen atoms only),[41] tris(ethylenediamine)nickel(II) sulfate (2.124 (6) Å),[42] and bis[2,2′-iminobis(acetamidoxime)]nickel (II) chloride dihydrate (2.115 (2) Å, for the amino atom).[43] Although the Ni(II)–N(22) distance (2.081 Å) is equivalent within one standard deviation of the average Ni(II)–N (pyridine) distance (2.088 (12) Å), the Ni(II)–N(15) distance (2.167 Å) appears to be significantly longer (by 4.4σ) than the mean Ni(II)–N distance in this complex. Ligand N(15) is trans to Cl(2) and kinetic studies[44] have shown that chloride ions can labilize trans amino groups. Although this may be consistent with the longer Ni(II)–N(15) bond, no evidence for such a chloride trans influence is provided by structural studies of metal complexes with similar ligands. For example, differences among the four Pt–N bonds of *cis*-dichlorobis(ethylenediamine)platinum(IV) chloride [45] are not significant. In the planar anion $[PtNH_3Cl_3]^-$,[46] the three Pt–Cl distances agree within one standard deviation and the Pt–N distance agrees with the distances observed in both *cis*- and *trans*-$Pt(NH_3)_2Cl_2$. (The Pt–Cl bond lengths for these isomers are equivalent also.)[47] The Co–N bonds trans to the chloride ions in the octahedral cations chlorotetraethylenepentaminecobalt(III)[48] and α-amminechlorotriethylenetetramine)cobalt(III)[49] are less than one standard deviation from the mean Co–N distances in each cation.

Apparently the greater length of the Ni(II)–N(15) bond can be attributed to cumulative chelate ring

---

(35) S. Biagini and M. Cannas, *J. Chem. Soc. A*, 2398 (1970).

(36) M. A. Porai-Koshits, *Tr. Inst. Kristallogr. Acad. Nauk SSSR*, **10**, 117 (1954).

(37) H. Luth and M. R. Truter, *J. Chem. Soc. A*, 1879 (1968).

(38) F. Madaule-Aubry and G. M. Brown, *Acta Crystallogr., Sect. B*, **24**, 745 (1968).

(39) R. C. Elder, *Inorg. Chem.*, **7**, 2316 (1968).

(40) P. Porta, A. Sgamellotti, and N. Vinciguerra, *ibid.*, **10**, 541 (1971).

(41) P. D. Cradwick and D. Hall, *Acta Crystallogr., Sect. B*, **26**, 1384 (1970).

(42) M. U. Haque, C. N. Caughlan, and K. Emerson, *Inorg. Chem.*, **9**, 2421 (1970).

(43) D. L. Cullen and E. C. Lingafelter, *ibid.*, **9**, 1865 (1970).

(44) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

(45) C. F. Liu and J. A. Ibers, *Inorg. Chem.*, **9**, 773 (1970).

(46) Y. P. Jeannin and D. R. Russell, *ibid.*, **9**, 778 (1970).

(47) G. H. W. Milburn and M. R. Truter, *J. Chem. Soc. A*, 1609 (1966).

(48) M. R. Snow, *J. Amer. Chem. Soc.*, **92**, 3610 (1970).

(49) M. Dwyer and I. E. Maxwell, *Inorg. Chem.*, **9**, 1459 (1970).

strain. This bond is the common link of two adjacent five-membered chelate rings, both of which are strained. One ring, resulting from the coordination of N(15) and S(18) to Ni(II), has two long (but normal) bonds, (excluding Ni(II)–N(15)): Ni(II)–S(18), 2.47 Å; and C(17)–S(18), 1.80 Å. Stereomodels indicate that, as a consequence of these two bonds, considerable distortion of the internal ring angle(s) at C(17) and/or S(18) is required for N(15) to approach Ni(II) in the coordination plane which is approximately normal to the Ni(II)–S(18) bond. The C(16)–C(17)–S(18) angle is normal (111.4 (15)°), but the Ni(II)–S(18)–C(17) angle is 96.7 (7)°, a deviation of 18σ from the unstrained tetrahedral value. (This ability of the large, polarizable sulfur atom to relieve chelate strain by bond angle distortion has been observed and discussed for an octahedral iron(II) complex.[50]) In addition, the deviation of N(15) from its least-squares coordination plane (Table III, plane 5) by 0.19 Å (more than any other ligand atom) attests to the strain at this position.

The adjoining chelate ring is constituted in part by two atoms of a planar pyridine ring, N(8) and C(13). As a result, this chelate ring (N(8), C(13), C(14), N(15), Ni(II)) is somewhat rigid (as is the analogous ring formed by atoms N(22), C(23), C(24), N(29), Ni(II)). Models show that this rigidity strains all chelate ring bonds formed at N(15) and further distorts the angle at S(18).

The bond between Ni(II) and the other amino atom, N(22), is less strained than the Ni(II)–N(15) bond, probably because it is common to a five-membered ring and a six-membered ring (atoms S(18), S(19), C(20), C(21), N(22), Ni(II)). Although the six-membered ring has three long bonds (Ni(II)–S(18), S(18)–S(19), S(19)–C(20)) in addition to the Ni(II)–N(22) bond, it is considerably more flexible than a five-membered ring. Thus, unlike the five-membered ring with which it shares the Ni(II)–S(18) bond, the six-membered ring is free to twist and pucker to such an extent that N(22) can make an unrestrained approach to Ni(II).

The extent of ring puckering is indicated by the deviations of the uncoordinated ring atoms from the plane defined by the nickel(II) ion and the two coordinated atoms. Atoms S(19), C(20), and C(21) of the six-membered ring are unsymmetrically skewed about the S(18)–Ni(II)–N(22) plane, at distances of −0.17, 0.23, and −0.58 Å, respectively. Coordination of N(15) and S(18) to Ni(II) yields a five-membered ring displaying a nearly symmetrical-skew conformation; atoms C(16) and C(17) are −0.41 and 0.28 Å from the N(15)–Ni(II)–S(18) plane. In contrast, the two rigid chelate rings formed with the pyridyl and amino atoms are less puckered. Atoms C(13) and C(14) are 0.25 and 0.45 Å "above" the N(8)–Ni(II)–N(15) plane, and atoms C(23) and C(24) are −0.68 and −0.31 Å from the N(22)–Ni(II)–N(15) plane, and therefore lie "below" it with respect to the origin. The latter ring, which is more puckered and probably less strained,[51] has only one calculated intramolecular hydrogen–hydrogen separation which may be significantly shorter than 2.4 Å,[52] the sum of the van der Waals radii. This involves atoms H(20A) and H(22) which, at calculated tetrahedral positions, are 2.2 Å apart. In the other ring, the distances between atoms H(14A) and H(16A) and atoms H(14B) and H(15) are both determined to be 2.1 Å. This is a consequence of the greater planarity of this ring. The only other short intramolecular interhydrogen distances are 2.3 Å in length and are from H(21B) to H(20B) and H(23B) and from H(22A) to H(23B).

Dihedral angles at the intersection of the planes described by one nitrogen atom and the two carbon atoms, and the two carbon atoms and the other nitrogen atom, in ethylenediamine complexes range from 45 to 58°.[43] The values of these angles in this complex are the following (atoms in plane 1, atoms in plane 2, angle): N(8)–C(13)–C(14), N(15)–C(14)–C(13), 16°; N(15)–C(16)–C(17), S(18)–C(17)–C(16), 55°; N(22)–C(23)–C(24), N(29)–C(24)–C(23), 28°. The corresponding angles for the two five-membered rings of the bis[2,2′-iminobis(acetamidoxime)]nickel(II) cation are 14.5 and 17.5°.[43] The saturated five-membered ring, then, has a larger dihedral angle as is found in ethylenediamine complexes, and the two unsaturated rings have appropriately smaller angles.

The distances between coordinated atoms of the chelate rings, referred to as "bite" distances, are the following: N(8)–N(15), 2.76; N(22)–N(29), 2.68; N(15)–S(18), 3.11; and S(18)–N(22), 3.43 Å.

The most significant feature of this structure is the nickel(II)–disulfide interaction. Since the sum of the Pauling covalent radii for octahedral nickel(II) and a singly bonded sulfur atom is 2.43 Å,[53] the Ni(II)–S(18) distance of 2.472 (5) Å indicates a strong bonded interaction. (The larger initial data set had indicated a Ni(II)–S(18) distance of 2.468 (3) Å.)[20] In (diethyl disulfide)copper(I) chloride,[12] the Cu–S distances are 2.34 and 2.40 Å, also surprisingly short. The Ni–S distance of 2.462 (4) Å reported in dichlorotetrakis(thiourea)nickel(II)[54] as well as the two distances of 2.465 (5) and 2.491 (5) Å found in dichlorotetrakis(trimethylenethiourea)nickel(II)[37] agree well with the bond length reported here. In the octahedral complex $\mathrm{Ni[S_2P(C_6H_5)_2]_2\cdot 2py}$ (py = pyridine), the Ni(II)–S bonds are 2.482 (4) and 2.523 (2) Å.[40] The average Ni(II)–S bonds in planar tetrakis(2-aminoethanethiol)trinickel(II) chloride are much shorter, 2.212 (3) and 2.155 (3) Å.[55] Planar coordination of Ni(II) by the disulfide group of a trithioperoxy acid salt[56] is of similar length (2.13 Å).

The geometry of the C–S–S–C linkage is unaffected by its coordination to Ni(II). The S–S interatomic distance (2.039 (7) Å) agrees with the corresponding length in L-cystine[57] (2.032 (3) Å) and those found in several organic disulfides[58] (2.03–2.05 Å). In (diethyl disulfide)copper(I) chloride[12] the S–S bond length is

---

(50) D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, **9**, 2775 (1970).

(51) E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

(52) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

(53) Reference 52, pp 246 and 249.

(54) A. Lopez-Castro and M. R. Truter, *J. Chem. Soc.*, 1309 (1963).

(55) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **9**, 1878 (1970).

(56) D. C. Fries and J. P. Fackler, Jr., *J. Chem. Soc. D*, 276 (1971).

(57) B. M. Oughton and P. M. Harrison, *Acta Crystallogr.*, **12**, 396 (1959).

(58) R. Rahman, S. Safe, and A. Taylor, *Quart. Rev., Chem. Soc.*, **24**, 208 (1970).

Table V

Some Nonbonded Interatomic Distances (Å)[a]

(*x*, *y*, *z*)[b]	O(4)···H(15)	2.13
	O(4)···H(22)	2.44
	O(7)···H(22)	2.27
	O(5)···H(22)	3.13
	O(5)···H(23B)	3.08
	O(7)···H(16B)	3.02
	O(7)···H(20A)	2.73
	O(4)···N(15)	3.12
	O(4)···N(22)	3.30
	O(4)···C(24)	3.28
	O(4)···N(29)	3.44
	O(7)···N(22)	3.20
	O(7)···H(15)	3.00
(−*x*, −*y*, −*z*)	O(6)···C(16)	3.40
	O(6)···H(16B)	2.68
	O(6)···H(17B)	3.05
	O(6)···H(20A)	3.04
(1/2 + *x*, 1/2 − *y*, −*z*)	O(6)···H(11)	2.70
(1/2 − *x*, 1/2 + *y*, *z*)	C(10)···S(19)	3.44
	C(11)···H(17B)	2.94
	H(10)···S(19)	3.06
	H(26)···H(10)	2.70
	H(27)···C(9)	2.93
	H(27)···C(10)	2.94
(−*x*, 1/2 + *y*, 1/2 − *z*)	O(5)···S(19)	3.18
	O(5)···H(20B)	2.91
	H(25)···H(20A)	2.54
	H(25)···H(20B)	2.69
	H(26)···O(7)	2.77
	C(25)···H(20B)	2.98
	H(25)···C(20)	3.09
(*x*, 1/2 − *y*, 1/2 + *z*)	O(4)···C(23)	3.37
	O(4)···H(23A)	2.79
	O(4)···H(23B)	3.16
	O(4)···H(25)	3.06
	O(6)···H(23B)	3.07
	O(6)···H(25)	2.67
	H(14B)···Cl(2)	2.76
	H(16A)···H(26)	2.65
	H(27)···Cl(2)	3.16
	H(28)···Cl(2)	3.10
	H(14B)···C(24)	3.04
	H(16A)···C(26)	2.77
(1/2 − *x*, −*y*, 1/2 + *z*)	H(11)···S(19)	3.20
	H(12)···S(18)	3.16
	H(12)···S(19)	2.86
	H(17A)···Cl(2)	2.74
(1/2 + *x*, *y*, 1/2 − *z*)	H(10)···O(5)	2.35

[a] All *inter*molecular or *inter*ionic distances less than the following are given: H···H, 2.7; H···nonH, 3.1; nonH···nonH, 3.5 Å. [b] The first atom of each pair has coordinates as given in Table I. The second atom is related to the one in Table I by the symmetry operation given in the subheading.

2.04 (2) Å also. A somewhat longer distance, 2.066 (6) Å, is observed for a nonaliphatic S–S bond in disulfurbis(bis(diphenylphosphino)ethane)iridium(I).[14] The disulfide dihedral angle (86°) is near the expected value of 90° and within the range[58] (74–105°) found for organic disulfides. The C–S interatomic distances average 1.80 (1) Å, in agreement with the value (1.81 (1) Å) commonly reported[59] for the carbon–sulfur single bond.

The average C–C and C–N distances in the pyridine rings, 1.37 (1) and 1.35 (1) Å, respectively, are equivalent to the corresponding averages of 1.383 (10) and 1.346 (10) Å found in 2-(2′,4′-dinitrobenzyl)pyridine[60] and 1.380 (12) and 1.349 (10) Å in 1-phenyl-2-(2-pyridyl)ethanedione-1,2.[61] The variation in bond angles about the two pyridine rings is also in agreement with the observed trends in these latter two structures. Table III presents the best least-squares planes, and the displacements of atoms from these planes, for these and other approximately planar groupings. (All atoms used to define the planes were weighted equally.)

The C–C single bonds are of two types. The two bonds (C(13)–C(14) and C(23)–C(24)) connecting the pyridine rings to the amino nitrogen atoms average 1.51 (2) Å, in good agreement with the average of 1.515 (7) Å found in 2-(2′,4′-dinitrobenzyl)pyridine. The bonds which in turn link the amino nitrogen atoms to the disulfide group (C(16)–C(17) and C(20)–C(21)) average 1.54(3) Å, and agree with the accepted carbon–carbon single bond distance of 1.541 (3) Å.[59]

The large thermal motion of the perchlorate ion is apparent from an examination of Figure 3 and Table II. These motions are responsible for the severe foreshortening effect exhibited by some of the chlorine–oxygen bonds so that even the longest perchlorate bond length of 1.37 (3) Å for Cl(3)–O(4) compares poorly with the value of 1.43 (1) Å reported for well-defined perchlorate ions such as the one found in bis(*m*-xylene)silver perchlorate.[62] The observed bond angles (101–116°) fall within the wide range generally found for perchlorate anions (96–117°).[63] Of the four oxygen atoms, only O(6) fails to participate in a short nonbonded interaction. O(4), the best-defined oxygen atom, is 2.13 Å from H(15) and 2.44 Å from H(22). O(7) and H(22) are 2.27 Å apart (see Table V). At a distance of 3.18 Å, O(5) and the uncoordinated sulfur atom, S(19), are somewhat closer than the sum of the van der Waals radii, 3.25 Å.[52] This correlates with the particularly large amplitudes of motion exhibited by O(5).

Acknowledgments.—This work was supported by the U. S. Army Research Office—Durham. We are indebted to Drs. J. W. Wrathall and R. L. Gavino for supplying the crystals, to John R. Ruble and Linda L. Y. Chun for their assistance, to the University of Hawaii Computing Center, and to Dr. Arild Christensen of Syntex Analytical Instruments for the collection of an intermediate data set.

---

(59) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 276.

(60) K. Seff and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **24**, 1406 (1968).

(61) T. Ashida, S. Hirokawa, and Y. Okaya, *Acta Crystallogr.*, **21**, 506 (1966).

(62) I. F. Taylor, Jr., E. A. Hall, and E. L. Amma, *J. Amer. Chem. Soc.*, **91**, 5745 (1969).

(63) B. N. Figgis, L. G. B. Wadley, and J. Graham, *Acta Crystallogr., Sect. B*, **28**, 187 (1972).