Volume 13
Number 11
November 1974

Inorganic Chemistry

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

Crystal and Molecular Structure of an Organic Disulfide Complex: Chloro[bis[2-[(2-pyridylmethyl)imino]phenyl] disulfide]nickel(II) Perchlorate

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Received March 12, 1974

AIC401690

The structure of an organic disulfide complex of Ni(II), chloro[bis[2-[(2-pyridylmethyl)imino]phenyl] disulfide]nickel(II) perchlorate, alternatively named chloro[α,α'-[dithiobis(*o*-phenylenenitrilo)]di-2-picoline]nickel(II) perchlorate or [Ni(py-CH=N-ph-S-S-ph-N=CH-py)Cl](ClO$_4$) where py is α-substituted C_5H_4N and ph is ortho-substituted C_6H_4, has been determined by single-crystal X-ray diffraction techniques using a small crystal and a scintillation counter. After near-full-matrix least-squares refinement using anisotropic temperature factors only for atoms heavier than carbon, the conventional R index converged at 0.058. The brown monoclinic needles form in the space group $P2_1/c$ with a = 16.249 (33) Å, b = 9.558 (11) Å, c = 16.685 (13) Å, β = 100.34 (12)°, and Z = 4. The organic disulfide coordinates to Ni(II) at five of its six octahedral sites, with the sixth site being occupied by a chloride ion. One sulfur atom of the disulfide group is coordinated to Ni(II) at a distance of 2.470 (5) Å. Half of the ligand is nearly planar, retaining its conjugation; the other half is twisted 92 (1)° about its ph–N bond, destroying the conjugation through that bond and causing it to lengthen from 1.430 (14) to 1.49 (2) Å. The S–S bond (2.089 (8) Å), the CSSC torsion angle (55.4 (10)°), and the C–S bonds (1.76 (2) Å) have been altered significantly due to intraligand electronic factors and to the stereochemical requirements of the coordination environment about the Ni(II) ion (the near-right "octahedral" angles range from 76.2 (5) to 101.9 (4)°). A structural trans effect involving the nickel(II)–imine nitrogen bonds has been observed; the bond trans to chloride is longer (2.07 (2) Å) than that trans to a pyridyl nitrogen (2.02 (2) Å). Preliminary Weissenberg photographs indicate that the corresponding tetrafluoroborate salt is isostructural.

Introduction

Disulfide formation[1,2] has been postulated in ferredoxin activity, presumably occurring through coordination involving delocalized orbitals.[3,4] Similar coordination has been suggested for the Ag(I)-,[5] Hg(II)-,[6] and Pd(II)-catalyzed[7] scission of SS bonds. While the effects of organic disulfide-transition metal associations have been observed and the existence of disulfide moiety coordination has been postulated, only recently has it been shown that organic disulfide sulfur coordination actually exists.[8-11] In chloro[bis[2-[(2-pyridylmethyl)amino]ethyl] disulfide]nickel(II) perchlorate,[9] one sulfur atom of the aliphatic disulfide group (-C-S-S-C-) in the pentadentate ligand occupies an octahedral coordination site at the Ni(II) center. The structure of this Ni(II) complex indicates that the disulfide moiety is essentially unaltered by coordination; the SS and CS bond lengths and the CSSC dihedral angle are typical of similar uncoordinated aliphatic disulfides.[12-15]

The report of the synthesis and characterization of Ni(II) and Mn(II) complexes[16] containing another pentadentate disulfide ligand, bis[2-[(2-pyridylmethyl)imino]phenyl] disulfide, alternatively named α,α'-[dithiobis(*o*-phenylenenitrilo)]di-2-picoline, DTPP, presented the opportunity to determine the effect of ligand structure on the stereochemistry of the coordinated CSSC moiety. The more unsaturated and conjugated ligand is expected to impart greater steric effects to the complex and perhaps to alter the disulfide group geometry upon coordination. Of the several samples of Ni(II) and Mn(II) complexes containing this ligand that were provided by Livingstone,[16] crystals suitable for structural studies were present in only one, [Ni(DTPP)-Cl]ClO$_4$.

Experimental Section

Preliminary oscillation and Weissenberg photographs of [Ni(DTPP)Cl]BF$_4$ indicated that it is isostructural with [Ni(DTPP)Cl]ClO$_4$. Each of the several crystals of [Mn(DTPP)Br]Br examined was twinned. A single crystal of [Ni(DTPP)Cl]ClO$_4$, which forms as brown monoclinic needles, of dimensions 1.4 × 0.06 × 0.06 mm was

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selected for further study and mounted so that the needle axis did not coincide with the diffractometer ϕ axis.

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 measurement of diffraction intensities. The cell constants and their standard deviations were determined by a least-squares treatment of the angular coordinates of 15 independent reflections with 2θ values up to 20°. The program used was written by R. A. Sparks and is part of the diffractometer program library. The temperature was maintained within 1° of 20° throughout. The θ–2θ scan mode was utilized with scan speed variable from 2 to 24° min^{-1} depending upon the peak intensity of the reflection. 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 40°. The intensities of three reflections, which were remeasured after every 100 reflections during data collection, showed no systematic variations, so no decay correction was applied. All reflections ($h0l$) for l odd and ($0k0$) for k odd were systematically absent, uniquely defining the space group as $P2_1/c$.

Standard deviations were assigned to individual reflections according to the formula

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

where ω is the scan rate, CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity $I = \omega(\mathrm{CT} - B_1 - B_2)$. A value of 0.02, appropriate to the instrumentation used, was assigned to the empirical parameter p to account for instrument instability. The weights, w, used in least squares were the reciprocal squares of $\sigma(F_o)$. Of the 2393 symmetry-independent reflections measured, those for which $2\theta < 40°$, 1036 had intensities larger than 3 times their standard deviations, and only these were included in the subsequent calculations, with the exception of $39\bar{2}$ which was apparently mismeasured. The intensities were corrected[17] 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 was not made (μ = 11.7 cm^{-1}); the transmission coefficients are estimated to show a total range of less than 0.015. Extinction corrections were also omitted. The atomic scattering factors[18] for Ni^{2+}, Cl$^-$, Cl^0, S^0, O^0, N^0, C^0, and H (bonded)[19] were used. The first four were modified to account for the real part of the anomalous dispersion correction.[20]

Crystal Data

Chloro[bis[2-[(2-pyridylmethyl)imino]phenyl] disulfide]nickel(II) perchlorate, alternatively named chloro[α,α'-[dithiobis(o-phenylenenitrilo)]di-2-picoline]nickel(II) perchlorate, [Ni(C$_{24}$H$_{18}$N$_4$S$_2$)Cl]ClO$_4$, crystallizes as monoclinic needles in space group $P2_1/c$: a = 16.249 (33) Å, b = 9.558 (11) Å, c = 16.685 (13) Å, β = 100.34 (12)°, V = 2549 (6) Å^3, mol wt 620.2, d_{obsd}(flotation) = 1.59 (3) g cm^{-3}, d_{calcd} = 1.616 g cm^{-3}, Z = 4, $F(000)$ = 1192. Figures in parentheses are estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

Structure Determination

The Ni(II) position was learned from an initial three-dimensional Patterson function. All other nonhydrogen atoms were located in successive cycles of Fourier refinement using the fast-Fourier algorithm.[21] Due to the paucity of data, only atoms heavier than carbon were refined anisotropically. Hydrogen atom positions were calculated[22] assuming that the C–H distance, expected to be foreshortened in a current X-ray diffraction experiment, is 0.95 Å;[23] isotropic thermal parameters, equal to those of the atoms to which they were bonded, were assigned to hydrogens; no hydrogen parameter was refined.

Table I. Final Positional Parameters and Their Standard Deviations[a]

	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)
Ni(1)	3140 (2)	2164 (3)	4042 (1)
Cl(2)	3871 (3)	2887 (6)	5331 (3)
Cl(3)	748 (4)	3862 (7)	1411 (4)
O(4)	1509 (14)	3585 (38)	1150 (13)
O(5)	894 (15)	3832 (31)	2246 (12)
O(6)	142 (18)	2865 (28)	1138 (14)
O(7)	455 (16)	5085 (24)	1053 (19)
S(8)	4090 (3)	132 (5)	4121 (3)
S(9)	3891 (3)	−879 (6)	2993 (3)
N(10)	2445 (8)	730 (15)	4513 (8)
N(11)	2081 (10)	3317 (14)	4095 (8)
N(12)	2719 (9)	1570 (14)	2844 (9)
N(13)	3715 (9)	3591 (14)	3368 (8)
C(14)	3528 (11)	−970 (21)	4689 (11)
C(15)	2744 (11)	−600 (18)	4834 (10)
C(16)	2291 (11)	−1513 (19)	5236 (11)
C(17)	2681 (12)	−2753 (23)	5545 (12)
C(18)	3438 (12)	−3090 (22)	5411 (12)
C(19)	3910 (12)	−2237 (24)	4996 (12)
C(20)	1694 (10)	1100 (19)	4526 (10)
C(21)	1447 (10)	2539 (16)	4286 (9)
C(22)	670 (12)	3112 (22)	4344 (12)
C(23)	566 (13)	4533 (23)	4181 (13)
C(24)	1169 (15)	5312 (25)	4025 (13)
C(25)	1922 (12)	4714 (21)	3973 (12)
C(26)	2795 (12)	−949 (22)	2765 (12)
C(27)	2277 (12)	214 (20)	2658 (11)
C(28)	1439 (15)	123 (24)	2480 (13)
C(29)	1044 (14)	−1231 (26)	2346 (14)
C(30)	1581 (14)	−2360 (23)	2431 (12)
C(31)	2406 (12)	−2298 (22)	2635 (11)
C(32)	2937 (10)	2289 (20)	2306 (10)
C(33)	3459 (11)	3496 (19)	2555 (11)
C(34)	3724 (12)	4446 (20)	2019 (12)
C(35)	4257 (11)	5507 (20)	2318 (11)
C(36)	4537 (10)	5578 (18)	3140 (10)
C(37)	4255 (10)	4646 (18)	3640 (10)
H(38)	1737	−1294	5299
H(39)	2401	−3371	5857
H(40)	3666	−3959	5617
H(41)	4463	−2498	4923
H(42)	1299	461	4686
H(43)	231	2558	4488
H(44)	029	4939	4179
H(45)	1093	6300	3958
H(46)	2353	5298	3841
H(47)	1117	971	2418
H(48)	456	−1350	2215
H(49)	1329	−3260	2336
H(50)	2732	−3130	2694
H(51)	2766	2048	1749
H(52)	3531	4354	1447
H(53)	4440	6173	1963
H(54)	4916	6290	3361
H(55)	4444	4730	4210

[a] Values are given × 10^4. See Figure 1 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.

Near-full-matrix (large block diagonal with approximately half of the structural parameters in each of two blocks) least-squares refinement[24] of all nonhydrogen parameters converged to give the final error indices R_1 = 0.058 and R_2 = 0.063 ($R_1 = (\Sigma|F_o - |F_c||)/\Sigma F_o$; $R_2 = [\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2]^{1/2}$). The "goodness-of-fit," $\{[\Sigma w\cdot(F_o - |F_c|)^2]/(m - s)\}^{1/2}$, is 0.75. The number of observations, m, is 1035, and the number of parameters, s, is 214. In the final cycles of least squares, all shifts in parameters for nonhydrogen atoms were less than 6% of their standard deviations. The largest peak on the final difference Fourier function, whose esd was calculated to be 0.1 e Å^{-3}, was less than 0.5 e Å^{-3} in height. The overdetermination ratio is 4.8.

The positional and thermal parameters of the structures, together with their standard deviations, are presented in Tables I and II.

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Table II. Thermal Vibration Parameters and Their Standard Deviations[a]

I. Atoms Heavier Than Carbon (1-13)[b]
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)	36 (1)	69 (3)	31 (1)	−4 (4)	−2 (2)	−10 (4)
Cl(2)	51 (3)	100 (6)	32 (2)	−9 (8)	−3 (4)	5 (7)
Cl(3)	75 (4)	122 (8)	43 (3)	−45 (10)	4 (5)	−15 (8)
O(4)	93 (13)	748 (90)	77 (11)	200 (56)	84 (20)	181 (50)
O(5)	131 (15)	483 (56)	54 (10)	6 (50)	32 (20)	−70 (40)
O(6)	176 (20)	350 (44)	105 (13)	−324 (54)	49 (25)	−192 (43)
O(7)	125 (17)	190 (35)	195 (22)	84 (40)	−91 (30)	69 (46)
S(8)	33 (2)	79 (6)	48 (3)	12 (7)	2 (4)	−5 (7)
S(9)	49 (3)	99 (7)	51 (3)	9 (7)	32 (4)	−28 (8)
N(10)	26 (7)	93 (20)	21 (6)	41 (19)	−19 (10)	14 (18)
N(11)	65 (9)	68 (20)	18 (6)	46 (21)	8 (12)	−38 (17)
N(12)	32 (7)	62 (18)	43 (7)	−26 (17)	−4 (11)	−30 (19)
N(13)	35 (7)	80 (19)	28 (7)	13 (19)	6 (11)	15 (18)

II. Carbon Atoms (14-37)[c]
Isotropic Thermal Parameters

	B, Å^2		B, Å^2		B, Å^2
C(14)	3.6 (4)	C(22)	4.6 (5)	C(30)	5.4 (5)
C(15)	3.1 (4)	C(23)	5.0 (5)	C(31)	4.4 (4)
C(16)	3.5 (4)	C(24)	5.7 (5)	C(32)	3.5 (4)
C(17)	4.7 (4)	C(25)	4.2 (4)	C(33)	3.5 (4)
C(18)	4.6 (4)	C(26)	4.6 (4)	C(34)	4.2 (4)
C(19)	5.0 (4)	C(27)	3.8 (4)	C(35)	3.9 (4)
C(20)	3.2 (4)	C(28)	5.4 (5)	C(36)	3.0 (4)
C(21)	2.8 (4)	C(29)	5.9 (5)	C(37)	3.2 (4)

[a] See Figure 1 for atom identities. The esd is in the units of the least significant digit given for the corresponding parameter. [b] The *b* values are $\times 10^4$. [c] The hydrogen (atoms 38-55) temperature factors are assigned values equal to those of the carbon atoms to which they are bonded.

Standard deviations were calculated from the inverse normal equations matrix, ignoring the standard deviations of the cell parameters.

Discussion

The organic disulfide within the complex chloro[bis[2-[(2-pyridylmethyl)imino]phenyl] disulfide]nickel(II) perchlorate, [Ni(DTPP)Cl](ClO$_4$), functions as a pentadentate ligand. The Ni(II) ion resides in a six-coordinate environment (NiN$_4$SCl) consisting of two cis pyridyl nitrogen atoms, two cis imine nitrogen atoms, one disulfide sulfur atom, and a chloride ion (see Figure 1[25]). The half of the organic disulfide ligand from N(11) through S(8) occupies three consecutive "equatorial" octahedral coordination sites. The conjugation from the pyridyl group containing N(11) through the imine C(20)-N(10) to the phenyl group C(14)-C(19) is maintained, although a small departure from strict planarity is apparent (see Figures 1-3 and Table III). The conjugation in the other half of the disulfide ligand S(9)-N(13) is broken by a 92 (1)° rotation of the phenyl ring C(26)-C(31) relative to the imine group N(12)-C(32). The imine nitrogen N(12) is coordinated "above" the plane of the first half of the ligand and Ni(II) ion, while the pyridyl nitrogen N(13) is coordinated in the plane and occupies the fourth "equatorial" coordination site. The chloride ion occupies the "axial" site "below" this plane and trans to the imine nitrogen N(12). One sulfur atom, S(9), remains uncoordinated.

The N(12)-C(27) bond is 1.487 (23) Å in length (Table IV) and is nearly a pure N(sp^2)-C(sp^2) σ bond. In contrast, the N(10)-C(15) bond length, which would be equivalent in the uncoordinated ligand, is 1.430 (14) Å and has appreciable π character. The adjacent bonds at the imine nitrogen atoms are also not equivalent and are altered in the opposite sense: N(10)-C(20) is longer (1.27 (2) Å) than N(12)-C(32) (1.23 (2) Å). This is consistent with the disruption of conjugation around N(12).

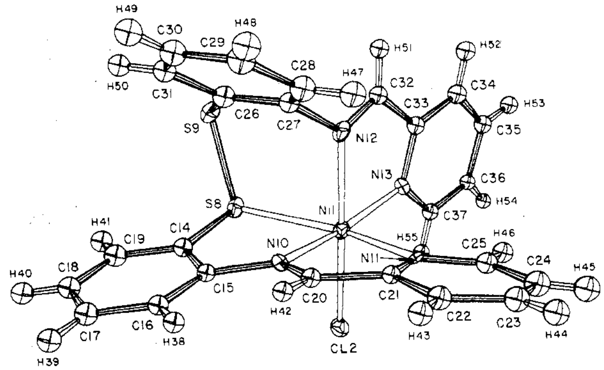

Figure 1. Stereochemistry of the [Ni(DTPP)Cl]$^+$ ion. The ClO$_4^-$ group is omitted. Ellipsoids of 15% probability are shown.[25]

The coordination configuration or "wrap" of the pentadentate disulfide ligand is nearly as suggested by Livingstone and Nolan[16] and found in the very similar complex chloro[bis[2-[(2-pyridylmethyl)amino]ethyl] disulfide]nickel(II) perchlorate,[9] [Ni(PMS)Cl]ClO$_4$. The major difference is that the first two nitrogen atoms (N(11) and N(10)) and the first sulfur atom (S(8)) along the ligand chain coordinate "equatorially" in the complex reported herein, [Ni(DTPP)Cl]$^+$, while the first two nitrogen atoms and the second sulfur atom along the ligand chain coordinate in [Ni(PMS)Cl]$^+$; that is, in the only equatorial sequence, the alternate sulfur atom is coordinated. Presumably the opportunity for conjugation in [Ni(DTPP)Cl]$^+$ and the different steric requirements of the ligand have redirected its coordination configuration to the one observed, even though a great deal of strain is produced as is indicated by the range of near-right octahedral angles (from 76.2 (5) to 101.9 (4)°) and by the deviations of the coordinating atoms from planes 5, 6, and 7 in Table III. The five-membered chelate ring involving N(10)-C(15)-C(14)-S(8) assists in the maintenance of the planarity of the "equatorial" half of the ligand, while the

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(25) C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

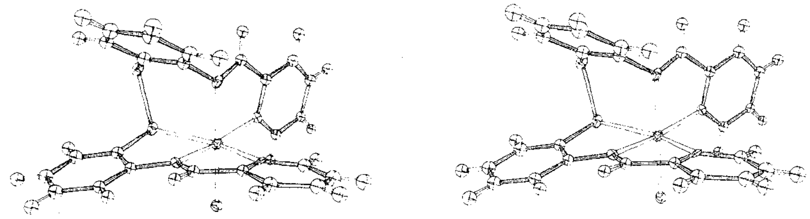

Figure 2. Stereoview[25] of the [Ni(DTPP)Cl]$^+$ ion, as described in the caption to Figure 1.

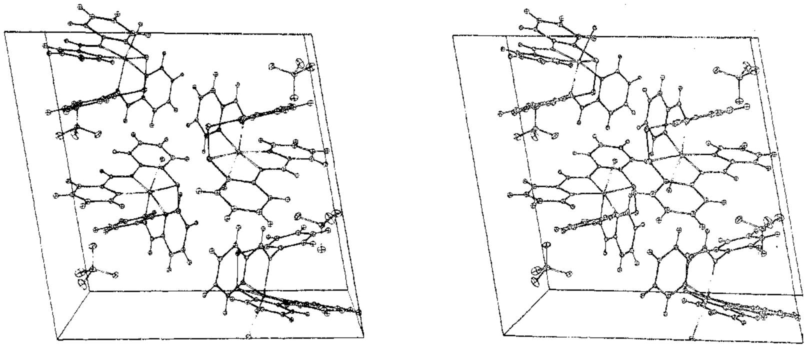

Figure 3. Stereoview[25] of the structure, illustrating the arrangement of the ions within the unit cell. Ellipsoids of 5% probability are used. The view is approximately into *b* with *a* horizontal and *c* nearly vertical in the plane of the page.

Table III. Deviations of Atoms from Least-Squares Planes (Å × 10^3)[a]

Atoms	1	2	3	4	5	6	7
Ni(1)	316		−40	181	*35*	*−79*	*94*
Cl(2)				105	*−17*	*−47*	
S(8)	−68		−45			*38*	*14*
S(9)		−38				−275	
N(10)	45		279		*47*		*13*
N(11)	455		*−8*			*527*	*45*
N(12)		61		−41	*−172*	*−439*	*−167*
N(13)		461	−704	*5*	*106*		
C(14)	*−14*						229
C(15)	*20*						196
C(16)	*−22*						283
C(17)	*14*						517
C(18)	*−2*						565
C(19)	*4*						449
C(20)	−8		185				−192
C(21)	117		*4*				−204
C(22)	126		*9*				−296
C(23)			*−24*				−143
C(24)			*12*				143
C(25)			*7*				225
C(26)		*11*				764	
C(27)		*−18*		−306	−584	607	
C(28)		*15*			303		
C(29)		*3*			−149		
C(30)		*−14*					
C(31)		*3*					
C(32)		−948		−106	−104		
C(33)		−790		*−7*	132		
C(34)				*−4*	295		
C(35)				*16*	436		
C(36)				*−12*	370		
C(37)				*2*	228		
$q_{b \times c}$	2495	−2384	1455	−7995	−7295	−6846	2745
q_b	4507	−453	1811	5962	6834	−5658	3166
q_c	8571	9701	9726	724	288	4595	9080
D	7.273	3.549	7.440	−1.577	−1.269	−0.706	7.653
δ	15	12	12	9	86	283	81

[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 (× 10^4), q, are with respect to orthogonalized axes. 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. See Figure 1 to identify the planes.

resulting six-membered chelate ring involving the other half of the ligand, S(8)-S(9)-C(26)-C(27)-N(12), allows a minimum of strain about the "axial" imino function, C(27)-N(12)-C(32). Coordination of S(8) rather than S(9) and the resulting five-membered chelate ring involving the "axial" imino function would have generated significantly more strain than that observed.

The Ni-S distance of 2.470 (5) Å is in excellent agreement with that of 2.472 (5) Å which has been observed[9] in [Ni(PMS)Cl]$^+$ and with similar distances found in octahedral nickel(II) complexes containing thiourea-type ligands (2.443 (8)-2.55 Å)[26-29] and dithiophosphinato ligands (2.482 (4)-2.50 (1) Å).[30,31] This distance indicates a strong nickel(II)-disulfide sulfur bonded interaction and can be compared with the copper(I)-disulfide sulfur bond lengths found in chloro(diethyl disulfide)copper(I)[8] (2.34 (1) and 2.40 (1) Å), *cyclo*-di-μ-[bis[2-(*N*,*N*′-dimethylamino)ethyl] disulfide]-dicopper(I) tetrafluoroborate[10] (2.288 (6)-2.326 (6) Å), and [bis[2-(2-pyridyl)ethyl] disulfide]copper(I) perchlorate[11] (2.318 (1) and 2.325 (1) Å). At 3.057 (10) and 3.138 (9) Å the Cu^{II}-S distances in bis[(D-penicillamine disulfide)-copper(II)] nonahydrate[32] represent no more than weak interactions.

The Ni-Cl bond distance of 2.365 (5) Å is short in comparison with the corresponding bond in the very similar complex,[9] [Ni(PMS)Cl]$^+$. It falls below the range of 2.38-2.53 Å that has been reported[29,33] and appears to be the shortest that has been observed for octahedral Ni(II) complexes.

Two types of unsaturated nitrogen ligands are coordinated to the nickel(II): pyridyl and imine nitrogen atoms. The mean Ni-N bond length of 2.061 (15) Å (see Table IV) falls well within the range of 2.00-2.16 Å that has been reported

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Table IV. Molecular Dimensions and Esd's[a]

I. Bond Lengths, Å

Atoms	Distance	Atoms	Distance
Ni(1)–Cl(2)	2.365 (5)	C(23)–C(24)	1.29 (3)
Ni(1)–S(8)	2.470 (5)	C(24)–C(25)	1.37 (2)
Ni(1)–N(10)	2.022 (14)	C(33)–C(34)	1.40 (3)
Ni(1)–N(12)	2.073 (15)	C(34)–C(35)	1.37 (3)
Ni(1)–N(11)	2.058 (15)	C(35)–C(36)	1.37 (2)
Ni(1)–N(13)	2.091 (14)	C(36)–C(37)	1.36 (2)
S(8)–S(9)	2.089 (8)	C(14)–C(15)	1.39 (2)
S(8)–C(14)	1.775 (19)	C(15)–C(16)	1.39 (2)
S(9)–C(26)	1.755 (20)	C(16)–C(17)	1.40 (3)
N(10)–C(15)	1.430 (14)	C(17)–C(18)	1.33 (3)
N(12)–C(27)	1.487 (23)	C(18)–C(19)	1.39 (3)
N(10)–C(20)	1.27 (2)	C(19)–C(14)	1.41 (3)
N(12)–C(32)	1.23 (2)	C(26)–C(27)	1.39 (3)
N(11)–C(21)	1.35 (2)	C(27)–C(28)	1.34 (3)
N(11)–C(25)	1.37 (2)	C(28)–C(29)	1.44 (3)
N(13)–C(33)	1.35 (2)	C(29)–C(30)	1.38 (3)
N(13)–C(37)	1.36 (2)	C(30)–C(31)	1.32 (3)
C(20)–C(21)	1.47 (3)	C(31)–C(26)	1.44 (3)
C(32)–C(33)	1.45 (3)	Cl(3)–O(4)	1.41 (2)
C(21)–C(22)	1.40 (3)	Cl(3)–O(5)	1.37 (2)
C(22)–C(23)	1.39 (3)	Cl(3)–O(6)	1.39 (3)
		Cl(3)–O(7)	1.36 (3)

II. Selected Dihedral Angles, Deg

Atoms	Angle	Atoms	Angle
C(14)–S(8)–S(9)–C(26)	55.4	Ni(1)–S(8)–S(9)–C(26)	45.8
C(19)–C(14)–S(8)–S(9)	78.4	Ni(1)–N(12)–C(27)–C(26)	75.2
C(15)–C(14)–S(8)–S(9)	102.1	Ni(1)–N(12)–C(27)–C(28)	98.4
C(31)–C(26)–S(9)–S(8)	121.5	Ni(1)–N(10)–C(15)–C(16)	172.7
C(27)–C(26)–S(9)–S(8)	62.3	Ni(1)–N(10)–C(15)–C(14)	9.9
C(19)–C(14)–S(8)–Ni(1)	170.9	Ni(1)–S(8)–C(14)–C(19)	170.9
C(15)–C(14)–S(8)–Ni(1)	8.6	Ni(1)–S(8)–C(14)–C(15)	8.6

III. Bond Angles, Deg

Atoms	Angle	Atoms	Angle
Cl(2)–Ni(1)–S(8)	88.5 (2)	N(11)–C(21)–C(20)	113.3 (14)
Cl(2)–Ni(1)–N(10)	94.0 (4)	N(13)–C(33)–C(32)	113.6 (16)
Cl(2)–Ni(1)–N(11)	95.3 (4)	N(11)–C(21)–C(22)	122.5 (15)
Cl(2)–Ni(1)–N(12)	169.0 (4)	N(13)–C(33)–C(34)	121.7 (16)
Cl(2)–Ni(1)–N(13)	95.7 (4)	C(20)–C(21)–C(22)	123.7 (15)
S(8)–Ni(1)–N(10)	80.4 (4)	C(32)–C(33)–C(34)	124.6 (16)
S(8)–Ni(1)–N(11)	159.7 (4)	N(11)–C(25)–C(24)	123.1 (18)
S(8)–Ni(1)–N(12)	86.1 (4)	N(13)–C(37)–C(36)	123.5 (15)
S(8)–Ni(1)–N(13)	101.9 (4)	C(21)–C(22)–C(23)	116.7 (17)
N(10)–Ni(1)–N(11)	79.4 (5)	C(22)–C(23)–C(24)	122.2 (21)
N(10)–Ni(1)–N(12)	94.5 (5)	C(23)–C(24)–C(25)	119.4 (21)
N(10)–Ni(1)–N(13)	170.2 (5)	C(33)–C(34)–C(35)	119.9 (17)
N(11)–Ni(1)–N(12)	93.1 (6)	C(34)–C(35)–C(36)	118.4 (17)
N(11)–Ni(1)–N(13)	97.6 (5)	C(35)–C(36)–C(37)	119.8 (16)
N(12)–Ni(1)–N(13)	76.2 (5)	N(10)–C(20)–C(21)	118.1 (15)
O(4)–Cl(3)–O(5)	108.0 (14)	N(12)–C(32)–C(33)	117.8 (16)
O(4)–Cl(3)–O(6)	112.4 (17)	S(8)–C(14)–C(15)	121.3 (13)
O(4)–Cl(3)–O(7)	106.5 (16)	S(9)–C(26)–C(27)	124.5 (15)
O(5)–Cl(3)–O(6)	107.5 (16)	N(10)–C(15)–C(16)	124.4 (15)
O(5)–Cl(3)–O(7)	116.6 (16)	N(12)–C(27)–C(28)	122.3 (16)
O(6)–Cl(3)–O(7)	105.9 (15)	S(8)–C(14)–C(19)	117.9 (14)
Ni(1)–S(8)–S(9)	108.0 (3)	S(9)–C(26)–C(31)	118.0 (15)
Ni(1)–S(8)–C(14)	96.8 (6)	N(10)–C(15)–C(14)	115.0 (15)
S(9)–S(8)–C(14)	101.2 (7)	N(12)–C(27)–C(26)	114.4 (15)
S(8)–S(9)–C(26)	101.5 (7)	C(14)–C(15)–C(16)	120.5 (16)
Ni(1)–N(10)–C(15)	124.9 (10)	C(15)–C(16)–C(17)	117.8 (16)
Ni(1)–N(12)–C(27)	120.2 (11)	C(16)–C(17)–C(18)	121.0 (18)
Ni(1)–N(10)–C(20)	114.9 (11)	C(17)–C(18)–C(19)	123.6 (19)
Ni(1)–N(12)–C(32)	117.5 (12)	C(18)–C(19)–C(14)	116.0 (17)
C(15)–N(10)–C(20)	120.2 (14)	C(19)–C(14)–C(15)	120.8 (16)
C(27)–N(12)–C(32)	121.7 (15)	C(26)–C(27)–C(28)	123.0 (18)
Ni(1)–N(11)–C(21)	113.2 (10)	C(27)–C(28)–C(29)	119.8 (19)
Ni(1)–N(13)–C(33)	114.2 (11)	C(28)–C(29)–C(30)	115.5 (20)
Ni(1)–N(11)–C(25)	130.8 (12)	C(29)–C(30)–C(31)	125.8 (20)
Ni(1)–N(13)–C(37)	128.9 (11)	C(30)–C(31)–C(26)	118.5 (18)
C(21)–N(11)–C(25)	116.1 (14)	C(31)–C(26)–C(27)	117.4 (17)
C(33)–N(13)–C(37)	116.6 (14)		

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

for octahedral nickel(II)-unsaturated nitrogen (pyridyl, imine, and oxime) distances[9,30,31,33-37] but is approximately 3σ shorter than the mean value (2.11 (2) Å) found in the very similar complex[9] [Ni(PMS)Cl]$^+$, which has saturated as well as unsaturated nitrogen donor atoms. A number of authors[38-40] have interpreted related results in terms of π bonding between transition metals and unsaturated nitrogen ligands; however, some of these claims have been disputed,[41] and other authors have reported no evidence for such bonding[42] or have suggested that the observed phenomena are associated with alternate effects.[34] Such π bonding could account, at least in part, for the short Ni-Cl distance by facilitating the delocalization of antibonding electron density from the metal ion.

When all nickel(II)-donor atom bond distances are considered in trans pairs (see Table V), a structural trans effect seems apparent. Considering the nickel(II)-imine nitrogen atom distances, it is seen that the one trans (Ni(1)-N(12)) to the chloride ion is longer (2.073 (15) Å) than the one trans (Ni(1)-N(10)) to the pyridyl nitrogen N(13) (2.022 (14) Å) ($\Delta/\sigma = 3.4$). A nearly identical effect has been observed in the very similar complex[9] [Ni(PMS)Cl]$^+$ (see Table V). The longest Ni^{II}-N bond which is trans to Cl$^-$ in the latter complex has been attributed to "cumulative chelate ring strain."[9] However, the apparent differences in the chelate ring conformations and in the resulting strain between [Ni(DTPP)Cl]$^+$ and [Ni(PMS)Cl]$^+$ suggest the need for an additional or alternative explanation.

The trans effect is well documented kinetically[43,44] and spectroscopically,[44-46] but less so structurally, particularly with regard to the trans influence of chloride[47-52] and the

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

	$[Ni(DTPP)Cl]^+$		$[Ni(PMS)Cl]^{+\ 9}$	
	Trans to Cl^-	Trans to pyridyl		
Ni–N(imine)	2.073 (15)	2.022 (14)		
			Trans to Cl^-	Trans to pyridyl
Ni–N(amine)			2.167 (14)	2.081 (15)
	Trans to imine	Trans to sulfur	Trans to amine	Trans to sulfur
Ni–N(pyridyl)	2.091 (14)	2.058 (15)	2.099 (17)	2.076 (12)

general trans effect in octahedral complexes.[44,53] We propose that the lengthening of the Ni–N bond that is trans to the chloride ion in both of these complexes (see Table V) represents a structural trans effect. This lengthening is consistent with chloride destablization of a trans group *via* the σ-inductive mechanism[43,44,54] that has been proposed to account for the trans ground-state effects observed nonkinetically, as well as for some of the kinetically observed effects.

Considering the nickel–pyridyl nitrogen distances (see Tables IV and V), it is seen that the one trans (Ni(1)–N(13)) to the imine nitrogen (N(10)) is longer (2.091 (14) Å) than the one trans (Ni(1)–N(11)) to the sulfur S(8) (2.058 (15) Å). The small difference in these bond lengths ($\Delta/\sigma = 2.2$) precludes further discussion of this effect. However, it is interesting that again a nearly identical effect has been observed in the very similar complex[9] $[Ni(PMS)Cl]^+$ (see Table V), even though the "wrap" of the ligand is different.

The CSSC torsion angle of 55.4 (10)° is appreciably less than 90° where lone pair–lone pair repulsions between the sulfur atoms would be minimized and favorable dπ overlap would be maximized. Actually, this distortion would be facilitated by the removal or polarization of the lone-pair electrons by complexation, allowing the dihedral angle to deviate from 90° with a diminished increase in the potential energy of the SS bond.[55-57] Nevertheless, this small angle, apparently required of the ligand upon coordination, would be expected to lead to a 0.04-Å increase, or somewhat less on the basis of the argument just presented, in the length of the SS bond.[12] The structure of 2,2′-diaminodiphenyl disulfide,[58] as compared to the structures of diphenyl disulfide[59] and dibenzyl disulfide,[60] indicates that electronic factors are operative[61] which cause the CS bond to decrease to 1.76 Å and the SS bond to increase to 2.06 Å; the same situation appears to occur here in $[Ni(DTPP)Cl]^+$ where (2-pyridylmethyl)imino groups ($-N{=}C-C_5H_4N$) replace the amines. Combining the above considerations satisfactorily accounts for the geometry of the CSSC group.

As was the case in $[Ni(PMS)Cl]^+$,[9] the CSSC group appears to be unaffected by coordination to Ni(II), except for the sterically induced alteration of the dihedral angle and the resulting effect on the bond lengths. In contrast, metal dπ to sulfur dπ back-bonding appears to affect the geometry of the disulfide moiety in several copper(I)–aliphatic disulfide complexes.[10,11]

Acknowledgments. This work was supported by the National Institutes of Health (Grant No. GM-18813-01). We are indebted to Stanley E. Livingstone at the University of New South Wales, Kensington, Australia, for the crystals used in this work, and to the University of Hawaii Computing Center.

Registry No. $[Ni(DTPP)Cl](ClO_4)$, 52152-13-3.

Supplementary Material Available. A listing of structure factor amplitudes (×10) for $[Ni(DTPP)Cl]ClO_4$ 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 $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2529.

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