tainly not have bands at 2035 and 1986 cm^{-1}. The two bands would be shifted perhaps 20–30 cm^{-1} to lower frequency.

These substitution results of Tripathi and Bigorgne[4] are quite interesting, but we do not see how they can be interpreted. They do not seem to be consistent with either a static or a dynamic model of isomers. Our results seem to require a dynamic model of isomerization.

The other point of disagreement between the work of Haas and Sheline[5] and the work of Tripathi and Bigorgne[4] is in the assignment of frequencies. The two sets of workers have different assignments for most of the isomers. Each group's assignments are based on certain assumptions and then the assignment for all isomers of the various compositions are internally consistent from this initial point of departure. Tripathi and Bigorgne[4] have used as their starting point two principal points based on $Fe(CO)(PF_3)_4$. One is a 3:2 ratio of intensities of the two bands, the more intense of which is assigned as equatorial. The other is the presence of PQR branching in the isomer of the monocarbonyl presumed to be the C_{3v} isomer. Haas and Sheline have as their initial assumptions: (1) the A_1 vibration in axial $Fe(CO)(PF_3)_4$ which will occur at higher frequency than in equatorial $Fe(CO)(PF_3)_4$ as an analogy with the frequencies of the two A_1 vibrations in $Fe(CO)_5$, (2) the internal consistency of the calculated and observed frequencies and intensities within their theoretical treatment, and (3) the preliminary solvolysis studies. The complete solvolysis studies and the study of the perfluoroalkyl compounds agree quite well throughout the series of compounds. The first point of Tripathi and Bigorgne[4] assumes complete random positioning of ligands and equal absorptivities of the two A_1 bands. Our experience indicates that neither of these assumptions need be rigorously true.

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The Crystal and Molecular Structure of the Five-Coordinate Complex Chlorotris(*o*-methylthiophenyl)phosphinenickel(II) Perchlorate

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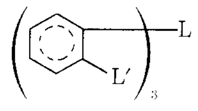
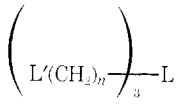
The crystal and molecular structure of chlorotris(*o*-methylthiophenyl)phosphinenickel(II) perchlorate, $[Ni(TSP)Cl][ClO_4]$, has been determined from three-dimensional single-crystal X-ray data collected by standard film techniques. The structure has been refined by least-squares methods to a conventional R factor of 0.090 for 1499 nonzero reflections. The complex crystallizes in space group C2/c of the monoclinic system with a cell of dimensions $a = 22.93 \pm 0.04$, $b = 12.08 \pm 0.03$, $c = 18.21 \pm 0.03$ Å, $\beta = 102.4 \pm 0.1°$, and $V = 4917$ Å^3. An experimental density of 1.57 (4) g/cm^3 is in good agreement with a calculated value of 1.60 g/cm^3 for eight molecules in the unit cell. The $Ni(TSP)Cl^+$ complex possesses a nearly regular trigonal-bipyramidal structure with the three S atoms located in the equatorial positions and the P and Cl atoms at the apices. The Ni–P and Ni–Cl distances are 2.113 (7) and 2.227 (7) Å, respectively. The Ni ion is displaced slightly but significantly out of the plane of the equatorial S atoms toward the apical halogen. The magnitude of this displacement is 0.061 (2) Å. The average Ni–S equatorial distance of 2.267 (7) Å is indicative of only slight metal–sulfur π bonding in the five-coordinate complex.

Introduction



Ia, L = P, L' = $P(C_6H_5)_2$ (QP)
b, L = As, L' = $As(C_6H_5)_2$ (QAS)
c, L = P, L' = $S(CH_3)$ (TSP)
d, L = As, L' = $S(CH_3)$ (TSA)



IIa, L = As, L' = $As(CH_3)_2$, $n = 3$
b, L = P, L' = $As(CH_3)_2$, $n = 3$ (TAP)
c, L = N, L' = $N(CH_3)_2$, $n = 2$ (Me_6tren)

One of the most successful methods employed to synthesize five-coordinate complexes of transition metal ions has involved the use of tetradentate "tripod-type" ligands of general forms I and II. This method has served to produce a number of five-coordinate Ni(II) complexes in which the metal ion is surrounded by a trigonal-bipyramidal array of donor atoms. The first

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(1) (a) Submitted in partial fulfillment of the requirements for the Master of Arts in Teaching Degree, Brown University, 1968. (b) Author to whom correspondence should be sent.

such series of complexes Ni(QP)X$^+$ and Ni(QAS)X$^+$, where X$^-$ = Cl$^-$, Br$^-$, I$^-$, NCS$^-$, CN$^-$, NO_3^-, or ClO_4^-, were reported by Dyer, *et al.*,[2] and were assigned the trigonal-bipyramidal structure on the basis of the close similarities of their electronic spectra with that of the [Pt(QAS)I][$B(C_6H_5)_4$] complex, the structure of which is known from X-ray diffraction studies.[3] Moreover, Dyer, *et al.*,[2] suggested that in these systems the trigonal symmetry of the rigid aryl ligands is imposed on the d^8 metal ions. In studies designed to ensure that the bonding energetics play a major role in determining the structures of the complexes, Benner, *et al.*,[4,5] employed more flexible aliphatic ligands such as tris(3-dimethylarsinopropyl)phosphine (TAP, IIb) thus removing the more stringent steric constraints of the aryl ligands. However, the series of complexes Ni(TAP)X$^+$ (X$^-$ = Cl$^-$, Br$^-$, CN$^-$, SCN$^-$, $SC_2H_5^-$, NO_2^-) was also assigned the trigonal-bipyramidal geometry on the basis of the observed diamagnetism, electronic spectral data, and conductivity measurements.[4] This structural assignment was subsequently confirmed by the structure determination of the complex [Ni(TAP)CN]-[ClO_4] performed by Stevenson and Dahl.[6]

The method of using "tripod-type" chelating agents has also been employed to synthesize a series of spin-triplet five-coordinate Ni(II) complexes with the ligand system employed for this purpose being tris(2-dimethylaminoethyl)amine (Me$_6$tren, IIc).[7] X-Ray structural work by Di Vaira and Orioli has again demonstrated the existence of the trigonal-bipyramidal geometry.[8]

The use of tetradentate ligands with mixed donor atoms, *i.e.*, systems in which the donor atom L differs from the donor atom of L′, allows for the systematic and selective variation of the ligand fields imposed on the metal ions along certain orbital directions.[4,5] Dyer and Meek synthesized the ligands tris(*o*-methylthiophenyl)phosphine (TSP, Ic) and tris(*o*-methylthiophenyl)arsine (TSA, Id) and their complexes in order to examine the effect of the reduced π bonding of the thioethers on the complexes formed.[9] The Ni(TSP)X$^+$ series of complexes are diamagnetic and are assigned the trigonal-bipyramidal structure on the basis of the observed physical properties. The structure determination of the [Ni(TSP)Cl][ClO_4] complex was undertaken to confirm the assumed coordination geometry and to determine accurate structural parameters from which the extent of metal–sulfur π bonding in these systems can be estimated.

Collection and Reduction of the X-Ray Data

A generous supply of the [Ni(TSP)Cl][ClO_4] complex was kindly given to us by Dr. D. W. Meek. Dark blue crystals suitable for single-crystal diffraction studies were grown by slow evaporation of an acetone–methylene chloride solution of the complex. The crystals were examined by optical goniometry and by Weissenberg and precession photography. On the basis of these examinations, the crystals were found to belong to the monoclinic system with a cell of dimensions $a = 22.93 \pm 0.04$, $b = 12.08 \pm 0.03$, $c = 18.21 \pm 0.03$ Å, $\beta = 102.4 \pm 0.1°$, and $V = 4917$ Å^3. Cell constant errors were estimated from measurements made directly on precession photographs taken at ambient room temperature using Mo Kα radiation. No calibrant was employed for these measurements. The observed extinctions, *hkl* for $h + k$ odd and *h*0*l* for *l* odd, are consistent with both the centrosymmetric space group C2/c and the acentric space group Cc. An experimental density of 1.57 (4) g/cm^3 obtained by the flotation method using carbon tetrachloride and iodomethane is in reasonable agreement with a calculated value of 1.60 g/cm^3 for eight molecules in the unit cell. Hence, all atoms would be expected to occupy general positions of either of the two space groups. Our initial assumption of the centrosymmetric space group C2/c appears to be confirmed by the satisfactory agreement ultimately obtained between observed and calculated structure factors.

Intensity data were collected at room temperature by the equiinclination Weissenberg technique using Zr-filtered Mo Kα radiation. The layers *h*0*l* to *h*,10,*l* were recorded on multiple films and the intensities of 2715 independent reflections within the angular range $\theta_{Mo} \leqslant 22°$ were estimated visually using a calibrated intensity strip. The usual Lorentz–polarization factors were then applied to these observed intensities to yield a set of F_o^2 values where F_o is the observed structure factor amplitude. The data were not corrected for absorption because of the smallness of the linear absorption coefficient ($\mu = 13.06$ cm^{-1}) and the average crystal dimensions (0.40 × 0.23 × 0.21 mm), the longest crystal dimension being in the direction of the *c* axis. The F_o values were then brought to an approximate absolute scale through a modification of Wilson's procedure.

Solution and Refinement of the Structure

The positions of the Ni atom and one S atom were determined from a three-dimensional Patterson function.[10] The positional parameters of these atoms, along with isotropic temperature factors assigned to them, were refined through several cycles of least squares. The remaining atoms in the coordination sphere, all of the cation carbon atoms and the perchlorate group, were located in subsequent difference Fourier maps based on phases obtained from previously located atoms.

The complete trial structure was refined by a least-

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(2) G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965).

(3) G. A. Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc.*, 170 (1961).

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(5) G. S. Benner and D. W. Meek, *ibid.*, **6**, 1399 (1967).

(6) D. L. Stevenson and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 3424 (1967).

(7) (a) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); (b) M. Ciampolini and N. Nardi, *ibid.*, **5**, 1150 (1966).

(8) M. Di Vaira and P. L. Orioli, *ibid.*, **6**, 955 (1967).

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(10) The computing for this structure determination was carried out on the IBM 360-50 computer at Brown University. The main programs used in this work include Zalkin's FORDAPER Fourier Program, the Busing–Levy ORFLS least-squares program, the Busing–Martin–Levy ORFFE function and error program, and Johnson's ORTEP thermal ellipsoid plot program. Other local programs were also employed.

TABLE I

FINAL STRUCTURAL PARAMETERS FOR $[Ni(TSP)Cl][ClO_4]$

Atomic Positional and Isotropic Thermal Parameters

Atom	x	y	z	B, Å^2
Ni	0.1991 (1)[a]	0.1463 (2)	−0.2089 (1)	...
S_1	0.1329 (2)	0.0308 (4)	−0.1718 (3)	...
S_2	0.2830 (2)	0.1972 (4)	−0.1282 (3)	...
S_3	0.1647 (2)	0.2102 (5)	−0.3288 (3)	...
P	0.1550 (2)	0.2812 (4)	−0.1705 (3)	...
Cl_1	0.2456 (2)	0.0067 (4)	−0.2521 (3)	...
Cl_2	0.4195 (2)	0.2246 (5)	−0.4003 (3)	...
R_1C_1[b]	0.0985 (7)	0.2288 (15)	−0.1229 (10)	3.6 (4)
R_1C_2	0.0854 (7)	0.1173 (14)	−0.1292 (9)	2.9 (3)
R_1C_3	0.0432 (8)	0.0657 (17)	−0.0929 (11)	4.5 (4)
R_1C_4	0.0107 (8)	0.1364 (17)	−0.0561 (10)	4.2 (4)
R_1C_5	0.0246 (9)	0.2506 (18)	−0.0481 (12)	5.2 (5)
R_1C_6	0.0677 (9)	0.2968 (18)	−0.0799 (11)	4.8 (4)
R_2C_1	0.2074 (7)	0.3637 (16)	−0.1058 (9)	3.6 (4)
R_2C_2	0.2661 (8)	0.3272 (17)	−0.0910 (10)	4.2 (4)
R_2C_3	0.3146 (10)	0.3932 (20)	−0.0485 (12)	5.8 (5)
R_2C_4	0.2985 (9)	0.4889 (18)	−0.0187 (11)	5.0 (5)
R_2C_5	0.2387 (10)	0.5259 (20)	−0.0297 (13)	6.1 (5)
R_2C_6	0.1922 (8)	0.4639 (17)	−0.0741 (10)	4.5 (4)
R_3C_1	0.1177 (7)	0.3650 (15)	−0.2476 (9)	3.2 (3)
R_3C_2	0.1271 (8)	0.3335 (16)	−0.3186 (10)	3.9 (4)
R_3C_3	0.1041 (10)	0.4004 (20)	−0.3827 (13)	5.9 (5)
R_3C_4	0.0697 (8)	0.4943 (17)	−0.3737 (10)	4.6 (4)
R_3C_5	0.0602 (8)	0.5239 (17)	−0.3043 (11)	4.7 (4)
R_3C_6	0.0834 (9)	0.4542 (18)	−0.2409 (11)	4.8 (4)
MC_1	0.0809 (9)	−0.0187 (18)	−0.2581 (11)	5.0 (4)
MC_2	0.3359 (9)	0.2375 (19)	−0.1865 (12)	5.9 (5)
MC_3	0.2277 (10)	0.2588 (20)	−0.3681 (12)	6.0 (5)
O_1	0.4723 (10)	0.2879 (23)	−0.3727 (12)	11.4 (6)
O_2	0.4334 (6)	0.1151 (13)	−0.4230 (8)	6.1 (3)
O_3	0.3954 (10)	0.2883 (21)	−0.4617 (13)	10.9 (6)
O_4	0.3915 (9)	0.2166 (21)	−0.3440 (12)	10.6 (6)

Anisotropic Thermal Parameters

Atom	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.00151 (5)	0.0059 (2)	0.00317 (9)	0.00024 (9)	0.00056 (5)	−0.0003 (1)
S_1	0.00163 (10)	0.0064 (4)	0.00295 (18)	−0.0001 (2)	0.0004 (1)	−0.0001 (2)
S_2	0.00173 (11)	0.0073 (5)	0.00428 (21)	0.0002 (2)	−0.0002 (1)	0.0006 (3)
S_3	0.00275 (13)	0.0077 (5)	0.00256 (17)	0.0004 (2)	0.0008 (1)	0.0001 (2)
P	0.00146 (10)	0.0055 (4)	0.00270 (18)	0.0001 (2)	0.0004 (1)	−0.0001 (2)
Cl_1	0.00213 (12)	0.0078 (5)	0.00495 (24)	0.0006 (2)	0.0014 (1)	−0.0009 (3)
Cl_2	0.00287 (14)	0.0087 (5)	0.00328 (20)	0.0004 (2)	0.0010 (1)	0.0010 (3)

[a] The numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. [b] The carbon atoms are numbered as follows: (1) ring 1 (R_1) bridges the P and S_1 atoms, ring 2 (R_2) bridges the P and S_2 atoms, etc.; (2) carbon 1 (C_1) of each phenyl ring is bound to P and carbon 2 (C_2) of each phenyl ring is bound to S with the remaining carbon atoms numbered in sequence; (3) MC_1 is the methyl group bound to S_1, etc. [c] The form of the anisotropic thermal ellipsoid is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

squares procedure. The function minimized was $\Sigma w(F_o - F_c)^2$, where the weights w were assigned in the following way: $I < 5$, $w = I/5$; $5 \leqslant I \leqslant 140$, $w = 1$; $I > 140$, $w = 140/I$, where I is the average raw intensity of the reflection. The neutral atom scattering factors as tabulated by Ibers[11] were used. The anomalous parts of the Ni, Cl, S, and P scattering factors were obtained from Cromer's tabulation[12] and were included in the calculated structure factors.[13]

In the initial round of calculations, all atoms were assigned individual isotropic temperature factors. This refinement of 139 positional, scale, and thermal parameters converged to a conventional R factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.108 and a weighted R factor R' ($R' = (\Sigma w(F_o - F_c)^2/\Sigma w F_o^2)^{1/2}$) of 0.118 for 1508 nonzero reflections. A difference Fourier based on this refinement provided evidence for some anisotropic thermal motion of the heavy atoms. After the elimination of several incorrectly indexed reflections, a final refinement was carried out in which the Ni, Cl, S, and P atoms were allowed to vibrate anisotropically while all other atoms were restricted to isotropic thermal motion. This refinement of 163 positional and thermal parameters, in which the individual level scale factors were not varied, converged to final values of 0.090 and 0.094 for the conventional and weighted R factors, respectively. A difference Fourier based on this partial anisotropic refinement showed no peaks higher than 0.41 e$^-$/Å^3 or 25% of the height of a carbon atom in

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(11) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1965, Table 3.3.1A.

(12) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

(13) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

Table II

Observed and Calculated Structure Factor Amplitudes (in electrons × 10) for [Ni(TSP)Cl][ClO$_4$]

H	L	FOBS	FCAL
*******K= 0******			
0	0	0	11367
0	6	275	235
0	8	176	106
0	10	170	97
0	12	212	224
0	14	613	532
2	6	358	287
2	8	605	539
2	10	317	267
2	12	275	180
2	14	163	199
2	18	191	177
4	6	2137	2222
4	8	1112	1053
4	12	455	543
4	14	654	581
4	16	181	169
6	0	1007	1121
6	2	223	350
6	4	429	476
6	6	2296	2345
6	8	2458	2426
8	0	660	623
8	4	450	432
8	6	253	189
8	8	823	783
8	10	712	713
8	12	325	276
8	14	423	394
10	0	419	450
10	4	324	406
10	8	761	793
10	12	854	766
10	14	446	468
12	2	381	450
12	4	159	159
12	6	207	197
12	8	180	186
12	10	217	164
12	12	307	270
12	14	483	543
14	0	573	492
14	2	312	319
14	6	91	125
14	8	255	265
14	10	247	205
16	2	536	513
16	4	207	213
16	8	493	478
18	0	466	457
18	8	187	195
20	0	200	230
20	2	613	601
20	4	569	495
22	0	372	365
22	2	436	445
22	4	427	395
-2	6	832	839
-2	8	384	424
-2	10	175	141
-2	12	83	75
-2	14	302	297
-2	18	240	183
-4	6	235	281
-4	8	314	290
-4	10	252	175
-4	12	805	795
-4	14	311	279
-4	16	293	278
-4	18	529	475
-6	4	139	223
-6	6	986	1119
-6	8	365	413
-6	14	223	223
-6	16	510	485
-6	18	707	783
-8	2	206	231
-8	4	123	99
-8	6	1210	1116
-8	10	988	1015
-8	12	829	747
-8	14	537	511
-8	16	467	369
-8	18	309	221
-10	2	470	529
-10	4	683	650
-10	6	1109	1120
-10	8	510	510
-10	10	859	859
-10	12	1067	1143
-10	14	599	612
-10	16	203	164
-12	2	353	396
-12	4	344	261
-12	6	383	497
-12	8	693	656
-12	10	1081	1109
-12	12	899	873
-12	16	207	179
-12	18	191	133
-14	2	333	276
-14	4	1325	1283
-14	6	587	634
-14	8	644	657
-14	10	352	322
-14	12	133	192
-14	16	106	79
-16	2	1063	1008
-16	4	1093	1213
-16	6	816	789
-16	8	239	236
-16	10	210	180
-16	14	207	110
-18	2	478	477
-18	4	798	798
-18	6	544	520
-18	8	177	206
-20	10	275	179
*******K= 1******			
1	5	475	392
1	6	314	324
1	8	340	359
1	9	515	519
1	14	307	320
1	15	416	402
3	4	250	299
3	5	557	472
3	6	810	741
3	7	758	718
3	8	804	797
3	9	972	919
3	10	222	238
3	11	148	130
3	12	330	299
3	13	462	434
5	2	267	358
5	3	381	305
5	4	632	596
5	5	674	539
5	6	613	536
5	7	531	463
5	8	202	151
5	9	640	602
5	10	367	401
5	11	280	309
5	12	277	245
5	15	128	121
5	17	292	297
7	0	506	480
7	1	235	153
7	2	244	170
7	3	746	841
7	4	855	868
7	5	842	826
7	6	455	404
7	7	626	626
7	8	595	541
7	11	278	321
7	12	144	159
7	13	594	547
7	14	175	166
7	15	208	274
7	16	216	186
9	0	235	260
9	3	650	664
9	4	467	506
9	5	1002	1017
9	7	442	469
9	9	182	271
9	10	304	363
9	11	166	119
9	12	150	89
9	13	256	281
9	14	264	281
9	15	292	328
11	1	171	188
11	2	485	506
11	3	267	171
11	4	188	193
11	5	159	103
11	6	330	330
11	7	217	220
11	8	111	92
11	9	230	257
11	11	276	304
11	12	310	393
11	13	161	158
11	14	136	148
13	0	415	377
13	2	333	345
13	3	390	431
13	4	911	922
13	5	273	280
13	6	351	354
13	7	467	473
13	9	343	371
13	11	292	378
15	0	207	240
15	2	270	209
15	4	292	289
15	5	115	174
15	6	187	245
15	7	227	246
15	9	91	88
15	11	235	313
17	0	190	211
17	1	140	163
17	2	211	250
17	4	543	526
17	5	550	355
17	7	91	61
17	8	132	154
17	9	191	190
17	10	219	222
19	0	243	247
19	1	260	285
19	3	195	240
19	4	222	247
19	5	244	276
19	6	133	212
21	0	259	298
21	2	205	231
21	3	268	278
21	5	293	270
23	1	310	313
-1	5	385	324
-1	6	450	446
-1	9	502	417
-1	10	179	207
-1	11	507	495
-1	13	110	145
-1	14	287	274
-1	15	120	158
-1	16	177	186
-1	18	96	176
-3	5	1236	1261
-3	6	430	372
-3	10	149	141
-3	11	122	118
-3	12	165	185
-3	13	155	159
-3	16	208	242
-3	17	354	383
-3	18	134	193
-3	19	402	385
-5	4	615	613
-5	5	441	545
-5	6	75	57
-5	7	583	563
-5	9	774	794
-5	10	116	108
-5	11	122	91
-5	12	167	219
-5	14	404	393
-5	15	393	380
-5	16	176	189
-5	17	339	354
-7	1	1076	1122
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-20	7	336	316
-20	9	343	380
*******K= 7******			
1	1	60	110
1	2	314	330
1	3	249	322
1	4	846	862
1	5	116	151
1	6	521	509
1	8	207	224
1	9	335	352
1	10	165	234
1	11	123	158
3	0	631	636
3	1	258	258
3	2	945	852
3	4	180	179
3	5	175	144
3	6	598	600
3	7	209	197
3	8	194	189
3	9	302	265
3	10	318	319
3	12	392	345
5	0	560	534
5	1	266	282
5	2	787	810
5	4	966	853
5	5	320	326
5	8	330	375
5	10	287	329
5	12	455	451
7	0	667	602
7	1	429	371
7	2	614	578
7	4	597	546
7	5	514	446
7	6	658	583
7	7	198	223
7	10	227	221
7	12	201	194
9	0	323	316
9	3	276	243
9	8	519	531
11	2	356	353
11	3	348	308
11	6	251	244
11	7	283	300
11	8	409	367
11	10	353	336
13	0	118	161
13	1	207	167
13	2	210	224
13	3	248	281
13	6	355	375
13	8	202	275
15	0	361	393
15	1	129	229
15	3	232	155
17	0	617	400
17	2	428	418
19	1	210	199
-1	2	495	569
-1	3	279	268
-1	4	873	889
-1	5	244	221
-1	6	592	662
-1	9	337	132
-1	12	180	70
-3	1	171	217
-3	3	132	191
-3	4	200	237
-3	6	358	337
-3	7	570	625
-3	10	248	184
-5	3	356	333
-5	8	206	258
-5	10	199	171
-5	12	406	428
-5	14	485	460
-7	1	118	164
-7	2	84	75
-7	3	148	104
-7	4	284	308
-7	5	408	433
-7	7	204	127
-7	8	185	197
-7	9	286	279
-7	10	322	274
-7	12	258	247
-7	13	134	119
-9	1	269	275
-9	3	458	514
-9	4	196	226
-9	6	317	293
-9	7	432	464
-9	8	512	593
-9	9	255	305
-9	10	236	294
-11	2	410	401
-11	4	241	260
-11	5	263	354
-11	6	735	785
-11	8	266	301
-11	14	291	292
-11	15	213	67
-13	1	373	401
-13	3	239	227
-13	4	409	430
-15	1	322	313
-15	2	309	290
-15	8	267	260
-15	10	460	434
-15	12	359	255
-17	8	447	482
-17	10	414	425
*******K= 8******			
0	2	203	281
0	3	559	553
0	4	384	411
0	7	621	594
2	1	500	531
2	2	628	596
2	5	1031	981
2	9	509	485
2	11	307	316
4	2	420	379
4	3	770	924
4	5	737	702
4	6	484	650
4	7	373	366
4	9	153	163
4	10	161	165
4	11	239	271
6	0	241	208
6	1	353	336
6	2	454	403
6	3	166	118
6	8	387	355
6	9	632	526
6	10	168	226
6	11	269	341
6	12	130	127
8	1	226	200
8	2	322	319
8	3	804	676
8	4	193	181
8	7	220	224
8	8	322	300
8	9	444	436
8	10	427	402
8	11	463	483
10	0	134	157
10	1	296	277
10	2	99	143
10	3	102	160
10	5	248	325
10	9	219	210
10	10	262	227
12	0	105	154
12	1	213	175
12	4	255	238
14	1	200	123
14	2	235	191
14	3	240	239
16	0	276	278
16	1	176	159
16	3	182	158
18	0	296	296
18	1	189	210
-2	1	149	196
-2	3	202	275
-2	4	274	317
-2	5	594	614
-2	6	162	177
-2	9	372	378
-4	1	255	317
-4	3	590	632
-4	8	230	292
-6	1	337	333
-6	7	355	362
-6	9	395	425
-6	11	254	245
-6	14	259	282
-8	1	309	306
-8	2	167	197
-8	3	120	101
-8	4	151	139
-8	5	227	235
-8	6	359	392
-8	7	237	236
-8	9	151	183
-8	12	271	329
-8	13	490	413
-8	14	227	243
-10	1	188	190
-10	3	273	274
-10	4	135	138
-10	8	283	231
-10	9	111	145
-10	10	231	209
-10	11	347	393
-10	14	273	141
-12	1	473	509
-12	3	207	264
-12	5	150	217
-12	6	343	308
-12	7	368	347
-12	8	361	336
-12	9	550	550
-12	10	171	214
-12	11	283	291
-14	4	286	325
-14	5	277	298
-14	6	232	243
-14	7	619	558
-14	8	247	320
-14	9	500	519
-14	10	293	237
-16	1	173	222
-16	2	303	328
-16	3	243	252
-16	5	347	356
-16	6	124	134
-16	7	126	190
-16	8	181	232
-18	1	262	284
-18	2	185	204
-18	3	291	335
*******K= 9******			
1	2	264	321
1	3	259	324
1	4	496	532
1	5	494	474
1	6	118	180
1	7	369	404
3	1	529	555
3	2	394	378
3	3	203	252
3	4	184	164
3	6	177	170
3	7	164	172
3	9	238	240
3	10	261	305
5	1	661	596
5	2	530	467
5	3	290	246
5	4	485	490
5	8	237	262
5	9	223	197
5	10	202	174
5	11	297	355
7	0	137	169
7	1	461	398
7	2	119	155
7	3	124	151
7	5	168	73
7	6	214	246
7	7	279	310
7	10	212	232
9	0	180	94
9	1	532	490
9	6	155	108
9	7	255	251
9	8	237	236
9	9	246	265
11	1	256	273
11	2	218	212
11	5	161	84
11	7	210	254
13	0	155	108
13	1	381	340
13	4	168	183
13	5	172	168
15	8	148	173
15	1	395	383
15	3	305	273
-1	3	330	361
-1	4	114	153
-1	5	553	550
-1	6	393	397
-1	7	302	284
-1	8	95	146
-1	10	366	390
-1	11	196	162
-3	1	248	290
-3	4	137	145
-3	7	477	407
-3	8	164	129
-3	10	184	237
-3	11	225	288
-5	3	366	336
-5	4	244	240
-5	7	262	230
-5	8	315	335
-5	10	152	132
-5	11	196	223
-5	12	168	168
-5	13	346	387
-7	1	135	138
-7	2	310	311
-7	4	265	275
-7	5	296	351
-7	6	157	161
-7	7	135	88
-7	10	278	273
-7	11	332	322
-7	13	177	205
-9	1	501	459
-9	3	127	130
-9	4	183	184
-9	5	406	373
-9	6	138	139
-9	7	373	367
-9	8	335	277
-9	9	357	400
-9	10	114	113
-9	11	118	96
-11	2	195	163
-11	3	172	133
-11	4	142	114
-11	5	462	434
-11	6	263	239
-11	7	352	328
-11	8	157	166
-13	1	284	265
-13	2	261	234
-13	3	293	329
-13	4	229	246
-13	5	353	388
-13	6	112	136
-13	8	232	208
-13	9	128	155
-13	10	124	149
-15	1	308	322
-15	2	232	229
*******K= 10******			
0	4	217	274
0	5	147	84
0	8	262	277
0	9	191	182
0	10	207	278
2	1	116	134
2	2	257	316
2	3	223	216
2	4	266	233
2	8	137	123
2	9	205	179
2	10	108	165
4	1	248	263
4	2	251	193
4	4	110	114
4	5	471	457
6	0	237	233
6	1	74	106
6	2	167	221
6	3	302	252
8	0	122	145
8	1	269	266
8	2	152	134
8	3	255	246
8	6	179	146
10	0	345	383
10	2	264	246
10	3	200	184
10	4	281	288
10	5	382	356
10	6	157	127
12	0	381	384
12	2	338	369
12	3	244	243
12	4	159	164
-2	2	151	160
-2	3	177	238
-2	4	141	189
-2	5	248	270
-2	6	330	297
-2	9	327	168
-4	1	81	120
-4	2	389	456
-4	3	313	346
-4	4	291	302
-4	6	368	349
-4	8	405	422
-4	10	209	199
-6	1	141	169
-6	2	348	374
-6	3	128	143
-6	4	337	282
-6	6	450	482
-6	8	366	300
-6	10	238	197
-6	11	112	124
-8	1	183	169
-8	2	441	468
-8	3	308	304
-8	4	403	415
-8	6	159	178
-8	8	284	228
-8	11	255	215
-10	1	92	7
-10	2	449	497
-10	4	188	182
-10	5	193	110
-10	10	161	44
-12	2	227	248
-12	5	233	226
-12	6	213	223
-12	7	295	322
-12	8	254	244
-14	3	271	262
-14	5	252	238

this structure. It should be noted that in the final refinement, 21 carbon atoms and 4 oxygen atoms, representing a reasonable fraction of the scattering power in the asymmetric unit, were restricted to isotropic thermal motion.

The parameters obtained in this final round of calculations are taken as the final parameters of the [Ni(TSP)Cl][ClO$_4$] structure and are given in Table I. Standard deviations as obtained from the inverse matrix are also given. In Table II, the values of F_o and $|F_c|$ (in electrons × 10) are given for the 1499 nonzero reflections used in the final refinement. The $|F_c|$ values for the unobserved reflections are omitted from Table II since none of the intensities calculated for the unobserved but accessible reflections exceeds the minimum observable intensity value.

Description of the Structure

The structure described by the unit cell constants, the symmetry operations of the space group, and the atomic parameters of Table I consists of the packing of discrete five-coordinate Ni(TSP)Cl$^+$ cations and tetrahedral ClO_4^- anions. No unusual intermolecular contacts are noted in the structure and the closest Ni-Ni distance is 8.93 Å. Figure 1 is a stereoscopic view of the packing of the $[Ni(TSP)Cl][ClO_4]$ molecules in the crystal.

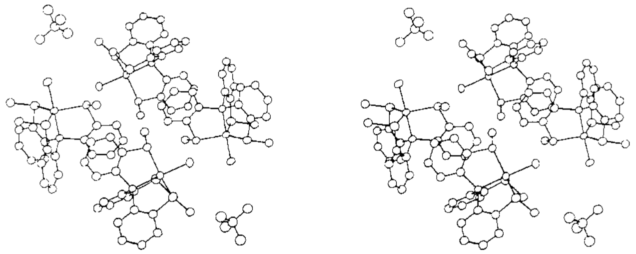

Figure 1.—These drawings present a view of the packing of the $[Ni(TSP)Cl][ClO_4]$ complex about the center of symmetry at the origin (0, 0, 0). The drawings constitute a stereo pair and may be viewed with a hand viewer.

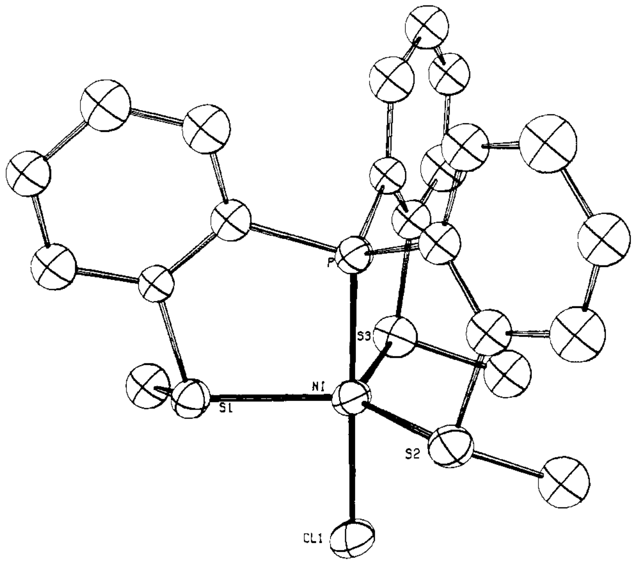

Figure 2.—A perspective drawing of the $Ni(TSP)Cl^+$ complex. The thermal ellipsoids have been scaled to 35% probability distributions.

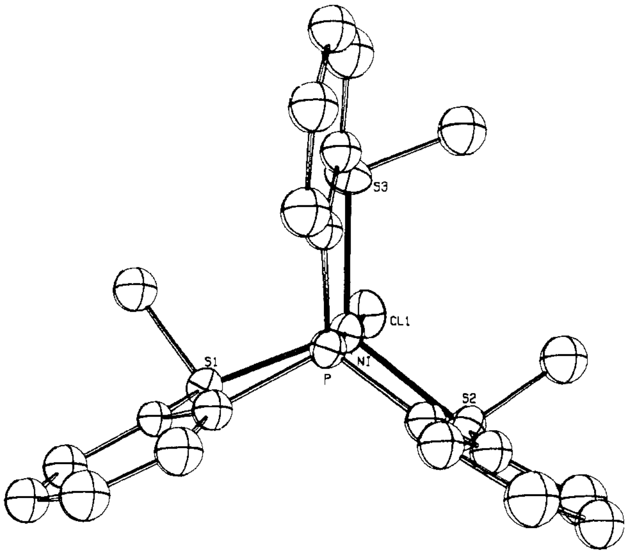

Figure 3.—A perspective drawing of the $Ni(TSP)Cl^+$ complex down the "pseudo-three-fold axis" of the trigonal bipyramid. The orientation of the methyl groups is clearly shown. The thermal ellipsoids have been scaled to 35% probability distributions.

Table III[a]

Principal Intramolecular Distances (Å) and Angles (deg)

Distances		Angles	
	Cation		
Ni–S_1	2.269 (6)	S_1–Ni–S_2	120.6 (2)
Ni–S_2	2.242 (8)	S_1–Ni–S_3	112.1 (3)
Ni–S_3	2.290 (7)	S_2–Ni–S_3	127.1 (3)
Ni–Cl	2.227 (7)	P–Ni–S_1	88.7 (3)
Ni–P	2.113 (7)	P–Ni–S_2	88.6 (2)
P–R_1C_1	1.82 (2)	P–Ni–S_3	88.0 (2)
P–R_2C_1	1.79 (2)	P–Ni–Cl_1	178.5 (3)
P–R_3C_1	1.79 (2)	Cl_1–Ni–S_1	92.4 (3)
S_1–R_1C_2	1.80 (2)	Cl_1–Ni–S_2	91.7 (2)
S_2–R_2C_2	1.78 (2)	Cl_1–Ni–S_3	90.7 (2)
S_3–R_3C_2	1.75 (2)	Ni–P–R_1C_1	109.3 (6)
S_1–MC_1	1.86 (2)	Ni–P–R_2C_1	110.1 (6)
S_2–MC_2	1.84 (2)	Ni–P–R_3C_1	111.0 (6)
S_3–MC_3	1.84 (2)	R_1C_1–P–R_2C	109.0 (8)
R_1C_1–R_1C_2	1.38 (2)	R_1C_1–P–R_3C_1	107.5 (8)
R_2C_1–R_2C_2	1.39 (2)	R_2C_1–P–R_3C_1	109.9 (9)
R_3C_1–R_3C_2	1.41 (2)	Ni–S_1–R_1C_2	106.1 (6)
		Ni–S_1–MC_1	107.2 (7)
		R_1C_2–S_1–MC_1	102.3 (8)
		Ni–S_2–R_2C_2	105.3 (6)
		Ni–S_2–MC_2	105.9 (7)
		R_2C_2–S_2–MC_2	102.1 (10)
		Ni–S_3–R_3C_2	105.2 (6)
		Ni–S_3–MC_3	109.9 (7)
		R_3C_2–S_3–MC_3	102.4 (10)
	Anion		
Cl_2–O_1	1.43 (2)	O_1–Cl–O_2	112 (1)
Cl_2–O_2	1.44 (2)	O_1–Cl–O_3	99 (1)
Cl_2–O_3	1.37 (2)	O_1–Cl–O_4	106 (1)
Cl_2–O_4	1.32 (2)	O_2–Cl–O_3	111 (1)
		O_2–Cl–O_4	109 (1)
		O_3–Cl–O_4	120 (1)

[a] The labeling system used is described in footnote *b* of Table I and errors in the least significant digits are given in parentheses.

The $Ni(TSP)Cl^+$ complex possesses a nearly regular trigonal-bipyramidal geometry with the three S atoms located in the equatorial positions and the P and Cl atoms located at the apices. Perspective drawings of the $Ni(TSP)Cl^+$ complex are shown in Figures 2 and 3 and all important intramolecular bond distances and angles are tabulated in Table III. Although obviously trigonal bipyramidal, the complex exhibits distortions from perfect trigonal symmetry, primarily as the result of the positions of the S-bonded methyl groups. The orientations of the methyl groups which are clearly shown in Figure 3 prevent the molecule from possessing a C_3 symmetry axis. In addition, nonbonded repulsions between MC_2 and MC_3 apparently result in the opening of the S_2–Ni–S_3 bond angle to 127.1° from the idealized trigonal-bipyramidal value of 120° and a closing of the S_1–Ni–S_3 bond angle to 112.1°. The average Ni–S equatorial bond distance is 2.267 Å with an estimated standard deviation of 0.007 Å while the two apical bond distances are 2.113 (7) and 2.227 (7) Å for the Ni–P and Ni–Cl bonds, respectively. The P–Ni–Cl bond angle of

178.5° lies almost within experimental range of the idealized trigonal-bipyramidal value of 180° and indicates the approximate linearity of the P, Ni, and Cl atoms.

The Ni atom is located significantly out of the plane of the three S atoms in the direction of the apical Cl by 0.061 (2) Å. The equation of the best weighted least-squares plane[14] through the atoms Ni, S_1, S_2, and S_3 is

$$12.55x - 9.28y - 8.04z = 2.80 \text{ (monoclinic coordinates)}$$

and the deviations of these four atoms from this plane are 0.024 (2), −0.033 (5), −0.044 (5), and −0.035 (5) Å, respectively. The average P–Ni–S and Cl–Ni–S bond angles reflect the displacement of the Ni out of the equatorial plane, the former value being 88.4° and the latter value being 91.6°.

Other important distances are the average P–C distance of 1.80 (2) Å, the average S–C (phenyl ring) distance of 1.78 (2) Å, and the average S–C (methyl group) distance of 1.85 (2) Å. The bridging phenyl rings of the TSP ligand are all planar within experimental error. However, slight deviations are noted in the coplanarity of the chelate rings with their associated phenyl rings. Although significant, these deviations are quite small, as illustrated in Figure 3, and probably result from simple packing considerations. The carbon–carbon phenyl ring distances are given in Table IV.

TABLE IV

CARBON–CARBON PHENYL RING DISTANCES (Å)

R_1C_1–R_1C_2	1.38 (2)	R_2C_1–R_2C_2	1.39 (2)	R_3C_1–R_3C_2	1.41 (2)
R_1C_2–R_1C_3	1.43 (2)	R_2C_2–R_2C_3	1.45 (3)	R_3C_2–R_3C_3	1.42 (3)
R_1C_3–R_1C_4	1.40 (2)	R_2C_3–R_2C_4	1.36 (3)	R_3C_3–R_3C_4	1.41 (3)
R_1C_4–R_1C_5	1.41 (3)	R_2C_4–R_2C_5	1.41 (3)	R_3C_4–R_3C_5	1.38 (2)
R_1C_5–R_1C_6	1.37 (3)	R_2C_5–R_2C_6	1.41 (3)	R_3C_5–R_3C_6	1.43 (3)
R_1C_6–R_1C_1	1.42 (2)	R_2C_6–R_2C_1	1.42 (3)	R_3C_6–R_3C_1	1.35 (2)
Av	1.402	Av	1.407	Av	1.400

The ClO_4^- group is distorted somewhat from its expected tetrahedral geometry. The relatively high-temperature factors of O_1, O_3, and O_4 appear to be indicative of slight torsional motion of the perchlorate group about the Cl–O_2 axis. The average Cl–O distance is 1.39 Å. The bond distances and angles for the anion are given in Table III.

Discussion

A comparison of the structure of the [Ni(TSP)Cl]-[ClO_4] complex with those found for other related systems yields several interesting facts which can be of help in evaluating the electronic structures and bonding in d^8 five-coordinate complexes. Particularly relevant is a comparison of the two complexes $Ni(TSP)Cl^+$ and $Ni(TAP)CN^+$. In the former, the Ni–P apical bond distance is 2.113 Å, whereas in the latter, the corresponding distance is 2.206 Å.[6] The significant difference between these two values is attributable to the differences in the two *trans* ligands, Cl^- being a weak-field ligand not capable of significant π bonding as opposed to the strong-field CN^- ion which is capable of extensive metal–ligand π bonding. Thus, it appears that in the $Ni(TAP)CN^+$ complex the metal–ligand back-bonding involving the apical P atom is greatly reduced and the Ni–P bond length is almost 0.1 Å longer than in the $Ni(TSP)Cl^+$ complex.

In the $Ni(TSP)Cl^+$ complex, the metal is located significantly out of the equatorial plane in the direction of the Cl^- ligand. However, in the $Ni(TAP)CN^+$ complex, the Ni atom lies out of the equatorial plane in the direction of the apical P atom.[6] The displacement of the metal out of the equatorial plane is also observed in the other structurally known d^8 five-coordinate complexes containing "tripod-type" ligands—[Pt(QAS)I]-[$B(C_6H_5)_4$][3] and [$Ni(Me_6tren)Br$]Br[8]—and in each of these structures the metal is displaced in the direction of the apical halide ion. While no unambiguous conclusions can be drawn from these results, it is quite possible that the direction of displacement depends solely on the size of the chelate ring being formed. If five-membered chelate rings are formed, such as in Ni-$(TSP)Cl^+$, the displacement is toward the halogen, while if six-membered chelate rings are formed, such as in $Ni(TAP)CN^+$, the displacement is toward the apical atom of the tripod ligand.

The relatively important question of metal–thioether π bonding is one that can be dealt with by an examination of the Ni–S distances found in other structural studies. The observed Ni–S distance of 2.267 Å is significantly shorter than the Ni–S distances of 2.4–2.6 Å found in thiourea complexes in which the sulfur atoms formally serve as neutral donor atoms (2.45 Å in $Ni(SC(NH_2)_2)_4Cl_2$;[15] 2.51 and 2.57 Å in $Ni(SC(NH_2)_2)_2(NCS)_2$;[16] 2.45 and 2.49 Å in $Ni(etu)_4Cl_2$[17]). However, in each of the thiourea complexes, the metal is six-coordinate and the complex possesses a spin triplet ground state. The average Ni–S distance of 2.267 Å in diamagnetic $Ni(TSP)Cl^+$ lies close to values found in the structures of the 1,1-dithiolato complexes such as the 2.23-Å distance in the $Ni(S_2COC_2H_5)_2$ complex[18] and the 2.233-Å value reported for the dithiophosphate structure $Ni(S_2P(OC_2H_5)_2)_2$.[19] In the 1,1-dithiolato ligand systems, the sulfur atoms possess a formal negative charge of −0.5 and are capable of participating in limited metal–ligand π bonding. The Ni–S value in $Ni(TSP)Cl^+$ is quite significantly longer than the distances of 2.10, 2.15, and 2.17 Å found for the four-coordinate 1,2-dithiolato complexes $Ni(S_2C_2(C_6H_5)_2)_2$,[20] $Ni(S_2C_2(CN)_2)_2^-$,[21] and $Ni(S_2C_2(CN)_2)_2^{2-}$,[22] in which more extensive π-bonding interactions exist between Ni and S atoms. Lopez-Castro and Truter[15] have suggested the existence of two very different bonding radii for Ni^{2+} depending upon the coordination number and

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the spin ground state of the complex. Whereas the generally accepted Ni^{2+} octahedral spin-triplet radius is 1.39 Å,[23] the low-spin radius of Ni^{2+} in square-planar complexes is probably around 1.18–1.20 Å. Therefore, the 2.267-Å value which we observe in $Ni(TSP)Cl^+$ is slightly longer than but in reasonable agreement with a calculated Ni–S bond distance of 2.22–2.24 Å using the proper covalent radii. We are therefore led to believe that there is minimal metal–sulfur π bonding in complexes of this type containing coordinated thioethers. This conclusion is affirmed by the recent structure determination of the related complex $Ni(DSP)I_2$ (DSP = bis(*o*-methylthiophenyl)phenylphosphine) by Meek and Ibers in which a value of 2.19 Å is observed for the basal Ni–S distance.[24] In addition, an examination of the bond distances and angles around the sulfur atoms in $Ni(TSP)Cl^+$ clearly indicates an approximate sp^3 hybridization for the coordinated thioether which is entirely consistent with the notion of very limited metal–sulfur π bonding. Any arguments which suggest the existence of considerable metal–sulfur π bonding must rely on *extensive* involvement of the vacant sulfur 3d orbitals which, although possible, does not seem likely.

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The Crystal Structure of Trichloroamminebis(triphenylphosphine)osmium(III), $OsCl_3(NH_3)(P(C_6H_5)_3)_2$

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The yellow-orange product obtained from the reaction of oxotrichlorobis(triphenylphosphine)osmium(V) with hydrazine dihydrochloride in refluxing ethanol–water solutions and recrystallized from acetonitrile is shown, on the basis of a diffraction study, to be trichloroamminebis(triphenylphosphine)osmium(III), $OsCl_3(NH_3)(P(C_6H_5)_3)_2$. The crystal structure has been determined from three-dimensional X-ray data collected by counter methods and has been refined using least-squares techniques to a final *R* factor, on *F*, of 3.2% for the 1554 independent reflections above background. The material crystallizes in the monoclinic space group C_{2h}^6-I2/a in a cell of dimensions $a = 22.429$ (8), $b = 9.519$ (3), $c = 15.852$ (5) Å, and $\beta = 102.80$ (2)°. The density of 1.69 g/cm^3 calculated for four formula units in the cell agrees well with the observed density of 1.68 ± 0.01 g/cm^3. The well-separated individual molecules are required crystallographically to possess C_2 symmetry. Imposition of C_2 symmetry requires that the ammine hydrogens be disordered, and an NH_3 group freely rotating about the Os–N bond was used as an approximation to this disorder. The configuration about the osmium atom is distorted octahedral with P atoms *trans* to one another and Cl atoms *trans* to one another in the basal plane and with the third Cl atom at the one vertex and the ammine group at the other. The only large deviation from an ideal octahedral configuration is a movement of the Cl atoms *cis* to N toward the nitrogen atom. The Os–N distance is 2.136 (9) Å, and the Os–P distance is 2.411 (2) Å. The Os–Cl distance *cis* to the N atom is not significantly different from the Os–Cl distance *trans* to the N atom, and the mean value of these distances is 2.362 (1) Å. The geometric details on this molecule are compared with previous results on aryl- and alkylimino complexes of Re and found to be explicable in terms of intramolecular nonbonded interactions.

Introduction

From a series of studies of closely related compounds containing metal–nitrogen multiple bonds[1–5] we concluded[5] that in these cases the variations in metal–ligand bond distances and in distortions about the central metal may be most easily understood in terms of nonbonded intramolecular interactions. In the course of attempts to prepare the nitrido complex $OsNCl_3(P(C_6H_5)_3)_2$, the phosphine analog of the $OsNCl_5^{2-}$ ion, Chatt and Paske[6] separated a paramagnetic compound of nearly the correct composition which exhibited N–H stretching bands in the infrared region of the spectrum. Although a dimeric complex is a possibility (*cf.* $(NH_3)_5RuNNRu(NH_3)_5^{4+}$ [7]), the most probable formulation of the compound was thought to be either $OsCl_3(NH)(P(C_6H_5)_3)_2$ or $OsCl_3(NH_3)(P(C_6H_5)_3)_2$. The present

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