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The Crystal Structure of Bis(imidotetramethyldithiodiphosphino-*S*,*S*)nickel(II), a Tetrahedral Complex with an NiS_4 Core

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Bis(imidotetramethyldithiodiphosphino-*S*,*S*)nickel(II), $[SP(CH_3)_2NP(CH_3)_2S]_2Ni$, crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; no. 14) with $a = 15.359\,(13)$, $b = 8.790\,(7)$, $c = 16.160\,(15)$ Å, $\beta = 106.00\,(6)°$, $V = 2097$ Å^3. Observed and calculated densities are 1.40 (5) and 1.454 g cm^{-3} (for $Z = 4$). The use of three-dimensional counter data ($\sin \theta_{\max} = 0.42$, Mo K$\alpha$ radiation) has led to location of all nonhydrogen atoms, the final discrepancy index being $R_F = 7.49\%$ for the 2357 independent nonzero reflections. Discrete molecular units of $[SP(CH_3)_2NP(CH_3)_2S]_2Ni$ are separated by normal van der Waals distances. The central Ni(II) ion is *tetrahedrally* coordinated by four sulfur atoms, the mean Ni–S distance being 2.282 (12) Å. This molecule is the first known tetrahedral complex containing an NiS_4 core.

Introduction

Many experimental attempts have been made to ascertain the factors dictating the stereochemistry of metal(II) chelate complexes. These approaches have typically employed derivatives of bidentate chelate ligands in which the donor atom and/or the degree of molecular crowding may be varied systematically.[2–12] Monomeric sterically unencumbered[9] chelates of nickel(II) with various permutations of ligand donor atoms (N, S, O) have been found to be planar (diamagnetic, $S = 0$), while those which are sterically crowded either are tetrahedral (paramagnetic, $S = 1$) or are involved in a planar $\rightleftharpoons$ tetrahedral equilibrium in solution. Furthermore, all known Ni(II) chelates with four coordinated sulfur atoms are diamagnetic and have been shown to be planar, either from crystallographic studies[13] or by inference from magnetic and optical spectral studies.[14]

Davison and Switkes[15] have recently found that the reaction of $Na^+[SP(CH_3)_2NP(CH_3)_2S^-]$ with $[(C_2H_5)_4N^+]_2[NiCl_4^{2-}]$ in absolute methanol produces the compound bis(imidotetramethyldithiodiphosphino-*S*,*S*)nickel(II), $[SP(CH_3)_2NP(CH_3)_2S]_2Ni$. Magnetic and optical studies are indicative of a tetrahedral stereochemistry. [The complex is paramagnetic, 3.40 BM in the solid state, 3.20 BM in $CHCl_3$ solution; the optical spectrum shows four bands, $\lambda_{\max}$ 14,000, 12,750, 10,700, 8700 cm^{-1} with ϵ 170.7, 240, 55.9, 34.0 l. mol^{-1} cm^{-1} (respectively).]

We have therefore undertaken an X-ray diffraction study of this complex, our results being reported below. An account of the structure at an intermediate stage of refinement has appeared previously.[16]

Unit Cell and Space Group

Crystals of $[SP(CH_3)_2NP(CH_3)_2S]_2Ni$ were supplied by Professor A. Davison and Mrs. E. S. Switkes of the Massachusetts Institute of Technology.

Optical examination and X-ray diffraction data indicated that the crystals belonged to the monoclinic system. Unit cell dimensions,[17] obtained from a least-squares analysis of high-angle zero-level Weissenberg data (Cu Kα_1, λ 1.54051 Å) and calibrated with aluminum ($a = 4.049$ Å) are $a = 15.359\,(13)$ Å, $b = 8.790\,(7)$ Å, $c = 16.160\,(15)$ Å, and $\beta = 106.00\,(6)°$.[17] The systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ are compatible only with the centrosymmetric space group $P2_1/c$ (C_{2h}^5; no. 14). The unit cell volume is 2097 Å^3. The observed density of 1.40 ± 0.05 g cm^{-3} is consistent with that calculated for mol wt 459.14 and $Z = 4$ ($\rho_{\text{calcd}} = 1.454$ g cm^{-3}).

Collection and Reduction of X-Ray Data

Intensity data were collected on a 0.01°-incrementing Supper-Pace "Buerger Automated Diffractometer" using a "stationary-background, ω-scan, stationary-background" counting sequence and equiinclination Weissenberg geometry. The apparatus and experimental technique have been described previously.[18] Details specific to the present analysis include the following. (I) MoKα radiation ($\bar{\lambda}$ 0.7107 Å) was used. (ii) The scan angle was chosen as $\omega(hkl) = [1.50 + 0.5/L(hkl)]°$, where $1/L(hkl)$ is the Lorentz factor for the reflection hkl. (iii) The scan speed, $(d\omega/dt)$, was 2°/min. (iv) Initial and final backgrounds, $B_1(hkl)$ and $B_2(hkl)$, were each counted for one-fourth the time

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of the main scan, the count associated with this scan being $C(hkl)$. (v) The stability of the system (within a given level) was monitored by remeasuring a carefully preselected check reflection after every 20 reflections. The maximum deviation was 2% from the mean.

$I(hkl)$, the integrated intensity of the reflection *hkl*, was calculated as $I(hkl) = C(hkl) - 2[B_1(hkl) + B_2(hkl)]$. Reflections were assigned deviations according to the scheme: $I(hkl) > 4900$, $\sigma\{I(hkl)\} = 0.1 \cdot [I(hkl)]$; $I(hkl) < 4900$, $\sigma\{I(hkl)\} = 7.0[I(hkl)]^{1/2}$. Data were rejected on two bases: (i) $B_1(hkl)/B_2(hkl)$ or $B_2(hkl)/B_1(hkl) = 3.0$ (symptomatic of a possible overlap problem); (ii) $I(hkl) \leqslant 3[C(hkl) + 4B_1(hkl) + 4B_2(hkl)]^{1/2}$ (reflection not significantly above background at the 3σ level of significance).

Crystal I ($0.23 \times 0.27 \times 0.34$ mm) was mounted on its *b* axis and used in collecting a total of 3734 reflections in the levels $h(0\text{–}10)l$. [Within each level data are complete to $\sin\theta = 0.42$, save for a few reflections with $\theta \leqslant 4°$ which are shielded from the counter by a lead backstop.] A total of 1422 reflections from the levels $hk(0\text{–}5)$ were collected from crystal II ($0.32 \times 0.24 \times 0.23$ mm) for correlation purposes. All data were corrected for Lorentz and polarization effects and absorption corrections were applied.[19] Transmission factors ranged from 0.74 to 0.86 for data from crystal I and from 0.69 to 0.79 for data from crystal II. All data were placed on a common scale *via* a least-squares procedure;[20] the *R* factor for scaling was 4.52% (based on F^2) for the 1042 overlaps. The resulting 2357 independent nonzero reflections were placed on an absolute scale by means of a Wilson plot.[21]

Unless otherwise stated all subsequent crystallographic computations were performed under the CRYRM system.[22]

Elucidation and Refinement of the Structure

Scattering factors for neutral nickel, sulfur, phosphorus, nitrogen, and carbon were taken from the compilation of Ibers.[23]

The residual minimized during least-squares refinement was $\Sigma w(|F_o|^2 - |F_c|^2)^2$ where $w(hkl) = [\sigma\{F^2(hkl)\}]^{-2}$ and $\sigma\{F^2(hkl)\}$ is derived from $\sigma\{I(hkl)\}$ by appropriate adjustment for Lorentz, polarization, transmission, and scale factors. Discrepancy indices used below are $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|$.[4]

The structure was solved by Sayre's method[24] using a local modification of Long's IBM 7094 program REL.[25] Normalized structure factors, $E(hkl)$, were calculated by the expression

$$E(hkl) = F(hkl)/\epsilon\left\{\sum_{i=1}^{i=N} f^2[i, \theta(hkl)]\right\}^{1/2}$$

where $F(hkl)$ is the structure factor amplitude for the reflection *hkl*, the sum $i = 1 \rightarrow N$ is over all atoms within the unit cell, $f[i, \theta(hkl)]$ is the scattering factor for the *i*th atom at the Bragg angle $\theta(hkl)$, and ϵ adjusts for the degeneracy in $F(hkl)$ for reflections at symmetry locations in reciprocal space. [In space group $P2_1/c$, $\epsilon = 2$ for reflections of classes $h0l$ and $0k0$, and $\epsilon = 1$ for all other reflections.]

Sayre's equation was applied to the 159 reflections with $E > 1.5$. Seven reflections with high *E*'s were chosen as the starting set; three of appropriate parity [ugg, gug, ggu (u = ungerade, g = gerade)] were arbitrarily assigned positive signs and thus uniquely define the origin of the unit cell. The remaining four reflections gave 16 possible permutations of signs; one of these led to the phasing of the remaining 152 reflections in only three iteration cycles and had the highest consistency index, $C = 0.945$. [The consistency index, *C*, is defined as

$$C = \left\langle \left|E_h \sum_{h=h_1+h_2} E_{h_1}E_{h_2}\right| \right\rangle \Big/ \left\langle |E_h| \sum_{h=h_1+h_2} |E_{h_1}|\,|E_{h_2}| \right\rangle$$

where sums are over all pairs of reflections h_1 and h_2 for which $h = h_1 + h_2$ and where $\langle\,\rangle$ means the average over all values of *h*.] An *F* map calculated from these 159 phased reflections clearly showed[26] the NiS_4P_4 fragment of the molecule. A three-dimensional difference-Fourier synthesis phased by these nine atoms and now using all 2357 reflections ($R_F = 29.5\%$) yielded the positions of the remaining two nitrogen atoms and eight carbon atoms. Four cycles of full-matrix least-squares refinement of positional and isotropic thermal parameters led to convergence at $R_F = 12.16\%$, $R_{wF^2} = 7.40\%$. A further three cycles of refinement of positional and *an*isotropic thermal parameters, along with a correction for secondary extinction,[27] led to convergence, $(\Delta/\sigma)_{\max} \approx 0.2$ at $R_F = 7.49\%$ and $R_{wF^2} = 3.52\%$. The final value for the secondary extinction correction (χ) was 1.823×10^{-6} where $\{F^2(\text{corrected})\} = \{F^2(\text{uncorrected})\}/[1 + \chi\beta F^2(\text{uncorrected})]$ and $\beta = (1 + \cos^4 2\theta)/[(\sin 2\theta)(1 + \cos^2 2\theta)]$.

TABLE I

FINAL ATOMIC COORDINATES, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*
Ni	0.73097 (10)	0.43864 (14)	0.18994 (11)
S(1)	0.72593 (20)	0.18421 (28)	0.20767 (22)
S(2)	0.64534 (20)	0.50088 (29)	0.05803 (22)
S(3)	0.89063 (23)	0.48892 (37)	0.21254 (23)
S(4)	0.68840 (23)	0.57347 (42)	0.28774 (28)
P(1)	0.61635 (20)	0.11718 (31)	0.11311 (22)
P(2)	0.65024 (20)	0.31375 (28)	−0.01328 (22)
P(3)	0.94193 (20)	0.47106 (30)	0.34223 (22)
P(4)	0.80053 (23)	0.65548 (30)	0.37269 (24)
N(1)	0.61800 (65)	0.16032 (89)	0.01851 (65)
N(2)	0.88528 (64)	0.54495 (96)	0.40008 (59)
C(1)	0.61414 (97)	−0.08878 (121)	0.12067 (96)
C(2)	0.51197 (84)	0.18968 (155)	0.13273 (82)
C(3)	0.57872 (97)	0.35308 (126)	−0.12136 (81)
C(4)	0.76405 (78)	0.29138 (129)	−0.02572 (93)
C(5)	0.95452 (84)	0.26794 (117)	0.37318 (83)
C(6)	1.05372 (77)	0.56128 (149)	0.36889 (109)
C(7)	0.76696 (98)	0.69952 (155)	0.46665 (89)
C(8)	0.83025 (104)	0.83822 (111)	0.32963 (109)

Peak heights on a final "observed" Fourier map were as follows: Ni, 56.0 e⁻; S, 24.0–32.0 e⁻; P, 28.0–31.4 e⁻; N, 9.2–10.1 e⁻; C, 6.1–7.4 e⁻. A final *difference*-Fourier synthesis showed no significant features, nor

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(19) Using the IBM 360 program IMBIBE, by J. Wormald.

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(26) It should be noted that the corresponding *E* map was not readily interpretable.

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TABLE II

ANISOTROPIC THERMAL PARAMETERS[a] ($\times 10^5$), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	363 (08)	847 (19)	383 (09)	−202 (20)	7 (13)	−107 (22)
S(1)	417 (16)	1000 (37)	356 (18)	−248 (40)	−72 (28)	263 (43)
S(2)	476 (17)	779 (33)	384 (17)	119 (39)	205 (29)	86 (44)
S(3)	447 (17)	1879 (50)	343 (17)	−668 (48)	269 (28)	−244 (54)
S(4)	466 (19)	2005 (56)	666 (27)	261 (54)	298 (38)	−578 (67)
P(1)	387 (16)	1029 (39)	269 (16)	−357 (41)	85 (27)	242 (44)
P(2)	401 (16)	848 (35)	276 (16)	−27 (39)	292 (26)	131 (42)
P(3)	304 (15)	1052 (39)	341 (17)	−70 (38)	203 (27)	−121 (44)
P(4)	542 (19)	913 (39)	370 (19)	438 (43)	143 (32)	−198 (45)
N(1)	536 (59)	1105 (127)	232 (50)	−351 (134)	21 (90)	288 (136)
N(2)	552 (57)	1492 (141)	122 (43)	475 (146)	135 (84)	−192 (136)
C(1)	871 (98)	1009 (151)	487 (85)	−1196 (196)	−389 (146)	101 (194)
C(2)	476 (72)	3058 (290)	178 (60)	452 (226)	320 (114)	26 (226)
C(3)	828 (94)	1551 (184)	158 (57)	−109 (209)	134 (122)	191 (181)
C(4)	402 (67)	1818 (198)	601 (85)	374 (184)	465 (127)	1151 (220)
C(5)	755 (81)	921 (144)	289 (62)	331 (181)	400 (120)	398 (174)
C(6)	279 (58)	2279 (238)	794 (108)	−874 (197)	−36 (131)	180 (276)
C(7)	813 (97)	2959 (276)	287 (70)	1329 (255)	222 (137)	−1100 (232)
C(8)	1022 (115)	780 (149)	613 (100)	127 (198)	97 (177)	70 (202)

[a] The anisotropic thermal parameter is defined as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

did it suggest positions for the 24 hydrogen atoms of the methyl groups. The structure was thus considered to be correct and complete.[28]

Atomic coordinates are collected in Table I. Anisotropic thermal parameters are listed in Table II; the magnitudes of principal axes of the associated vibrational ellipsoids are given in Table III, their orientations being depicted[29] in Figure 1.

TABLE III

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (IN Å) ALONG THE PRINCIPAL AXES OF THE ATOMIC VIBRATION ELLIPSOIDS[a]

Atom	$[\overline{U^2}_{\mathrm{maj}}]^{1/2}$	$[\overline{U^2}_{\mathrm{med}}]^{1/2}$	$[\overline{U^2}_{\mathrm{min}}]^{1/2}$
Ni	0.245	0.201	0.163
S(1)	0.271	0.184	0.177
S(2)	0.233	0.218	0.172
S(3)	0.294	0.200	0.191
S(4)	0.322	0.251	0.212
P(1)	0.246	0.181	0.160
P(2)	0.214	0.191	0.159
P(3)	0.214	0.193	0.180
P(4)	0.271	0.211	0.163
N(1)	0.275	0.196	0.153
N(2)	0.281	0.210	0.114
C(1)	0.395	0.221	0.130
C(2)	0.351	0.224	0.126
C(3)	0.311	0.247	0.134
C(4)	0.336	0.199	0.174
C(5)	0.293	0.208	0.146
C(6)	0.351	0.295	0.137
C(7)	0.409	0.255	0.102
C(8)	0.360	0.266	0.174

[a] The orientations of the atomic vibration ellipsoids are illustrated in Figure 1.

Description of the Molecular Structure

Interatomic distances with their estimated standard deviations (esd's) are collected in Table IV; bond angles (with esd's) are shown in Table V.

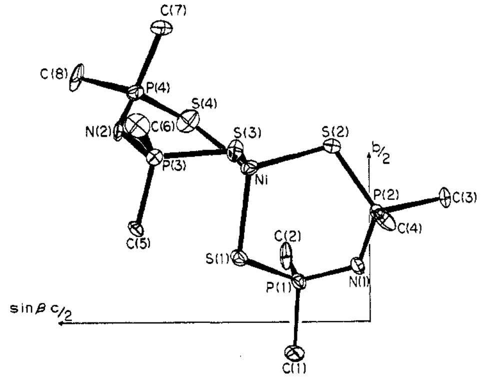

Figure 1.—The $[SP(CH_3)_2NP(CH_3)_2S]_2Ni$ molecule, viewed down *a* (OTLIPS diagram,[29] showing the 68% probability envelopes for the atomic vibration ellipsoids.).

TABLE IV

INTERATOMIC DISTANCES (Å), WITH ESTIMATED STANDARD DEVIATIONS[a]

Atoms	Dist	Atoms	Dist
Ni–S(1)	2.270 (3)	Ni–S(3)	2.296 (3)
Ni–S(2)	2.285 (3)	Ni–S(4)	2.277 (4)
		Av	2.282 (12)[b]
S(1)–P(1)	2.024 (4)	S(3)–P(3)	2.031 (4)
S(2)–P(2)	2.021 (4)	S(4)–P(4)	2.017 (5)
		Av	2.023 (6)[b]
P(1)–N(1)	1.581 (10)	P(3)–N(2)	1.581 (9)
P(2)–N(1)	1.570 (9)	P(4)–N(2)	1.586 (9)
		Av	1.580 (7)[b]
P(1)–C(1)	1.815 (14)	P(3)–C(5)	1.849 (12)
P(1)–C(2)	1.831 (13)	P(3)–C(6)	1.831 (14)
P(2)–C(3)	1.822 (13)	P(4)–C(7)	1.775 (14)
P(2)–C(4)	1.824 (13)	P(4)–C(8)	1.856 (15)
		Av	1.825 (25)[b]

[a] Esd's for individual bond lengths are those obtained from the least-squares process *via* the matrix inverse to the normal equation matrix. [b] Esd's for average bond lengths are calculated from the equation

$$\sigma = \left\{\left[\sum_{i=1}^{i=N}(\chi_i - \bar{\chi})^2/(N-1)\right]\right\}^{1/2}$$

where χ_i is the *i*th bond length and $\bar{\chi}$ is the mean of the N equivalent bond lengths.

As was predicted from magnetic and spectral data[15] (*vide supra*), the $[SP(CH_3)_2NP(CH_3)_2S]_2Ni$ molecule contains a nickel(II) center which is tetrahedrally coordinated to four sulfur atoms. This molecule is the first example of a d^8 Ni(II) complex with a *tetrahedral*

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(28) Tables of observed and calculated structure factor amplitudes have been deposited as Document No. NAPS-01222 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and remitting $6.50 for photoprints or $2.00 for microfiche. Advance payment is required. Make checks or money order payable to CCMIC–NAPS.

(29) The atomic vibration ellipsoids were drawn using OTLIPS, an IBM 1620/CALCOMP program written by Dr. P. H. Bird.

TABLE V

BOND ANGLES (DEG), WITH ESTIMATED STANDARD DEVIATIONS

Atoms	Angle	Atoms	Angle
S(1)-Ni-S(2)	107.3 (1)	S(2)-Ni-S(3)	117.0 (1)
S(1)-Ni-S(3)	106.8 (1)	S(2)-Ni-S(4)	106.0 (1)
S(1)-Ni-S(4)	111.5 (1)	S(3)-Ni-S(4)	108.4 (1)
		Av	109.5 (4.1)
Ni-S(1)-P(1)	106.0 (2)	Ni-S(3)-P(3)	103.8 (2)
Ni-S(2)-P(2)	103.0 (2)	Ni-S(4)-P(4)	105.5 (2)
		Av	104.6 (1.4)
S(1)-P(1)-N(1)	115.4 (4)	S(3)-P(3)-N(2)	117.3 (4)
S(2)-P(2)-N(1)	116.6 (4)	S(4)-P(4)-N(2)	116.9 (4)
		Av	116.6 (0.8)
P(1)-N(1)-P(2)	127.7 (6)	P(3)-N(2)-P(4)	129.0 (6)
		Av	128.4 (0.9)
S(1)-P(1)-C(1)	105.5 (5)	S(3)-P(3)-C(5)	109.4 (4)
S(1)-P(1)-C(2)	110.7 (5)	S(3)-P(3)-C(6)	106.4 (5)
S(2)-P(2)-C(3)	106.6 (5)	S(4)-P(4)-C(7)	105.4 (5)
S(2)-P(2)-C(4)	109.7 (4)	S(4)-P(4)-C(8)	107.9 (5)
		Av	107.6 (2.1)
N(1)-P(1)-C(1)	108.0 (6)	N(2)-P(3)-C(5)	105.7 (5)
N(1)-P(1)-C(2)	109.4 (6)	N(2)-P(3)-C(6)	108.4 (6)
N(1)-P(2)-C(3)	108.3 (6)	N(2)-P(4)-C(7)	107.7 (6)
N(1)-P(2)-C(4)	110.0 (6)	N(2)-P(4)-C(8)	111.5 (6)
		Av	108.6 (1.7)
C(1)-P(1)-C(2)	107.6 (6)	C(5)-P(3)-C(6)	109.5 (6)
C(3)-P(2)-C(4)	104.9 (6)	C(7)-P(4)-C(8)	106.9 (7)
		Av	107.2 (1.9)

TABLE VI

LEAST-SQUARES PLANES IN THE $[SP(CH_3)_2NP(CH_3)_2S]_2Ni$ MOLECULE[a-c]

Atom	Dev, Å	Atom	Dev, Å
Plane A: $0.8947X - 0.1635Y - 0.4157Z - 7.542 = 0$			
Ni*	0.0	N(1)	+0.527
S(1)*	0.0	C(1)	−0.235
S(2)*	0.0	C(2)	−2.165
P(1)	−0.422	C(3)	+1.170
P(2)	+1.081	C(4)	+2.807
Plane B: $-0.0497X + 0.7678Y - 0.6387Z - 0.553 = 0$			
Ni*	0.0	N(2)	−1.433
S(3)*	0.0	C(5)	−3.094
S(4)*	0.0	C(6)	−1.149
P(3)	−1.414	C(7)	−0.945
P(4)	−0.356	C(8)	1.272

[a] Planes are defined in Cartesian coordinates (X, Y, Z), which are related to the monoclinic fractional cell coordinates (x, y, z) by the transformations $X = xa + zc \cos \beta$, $Y = yb$, and $Z = zc \sin \beta$. [b] Planes are calculated using unit weights for atoms marked with an asterisk. [c] The interplanar angle AB is 84.4°.

NiS_4 core. Individual nickel–sulfur bond distances range from 2.270 (3) to 2.296 (3) Å, averaging 2.282 (12) Å. This is significantly longer than the corresponding distances (2.10–2.24 Å)[13] found in nickel(II) chelate complexes containing a *square-planar* center.

There are slight irregularities in the coordination tetrahedron. *Intra*ligand angles are S(1)–Ni–S(2) = 107.3 (1)° and S(3)–Ni–S(4) = 108.4 (1)°, while *inter*ligand angles (in order of increasing size) are S(2)–Ni–S(4) = 106.0 (1)°, S(1)–Ni–S(3) = 106.8 (1)°, S(1)–Ni–S(4) = 111.5 (1)°, and S(2)–Ni–S(3) = 117.0 (1)°. [The difference between the smallest and greatest angle is 11.0°, or about 78σ, indicating that the distortions are real.] Deviations of S–Ni–S bond angles from the true tetrahedral value of 109.5° are not consistent with a simple Jahn–Teller[30] "tetragonal elongation" from T_d to D_{2d} symmetry as predicted for d^8 complexes.[31] Rather, the molecule distorts such that one chelate ring is twisted away from orthogonality to the other, the dihedral angle between [S(1)–Ni–S(2)] and [S(3)–Ni–S(4)] planes now being 84.4° (see Table VI).

It should be emphasized that the tetrahedral stereochemistry about the nickel(II) atom is not the result of steric crowding. As may clearly be seen in Figure 1, there are no close intramolecular interactions between the two imidotetramethyldithiodiphosphinate ligands, nor are any anticipated for this compound, even in a *planar* geometry. Davison and Switkes have shown that the ligand field spectra of planar $[SP(CH_3)_2NP(CH_3)_2S]_2M$ species (M = Pd(II), Pt(II)) are not appreciably different from those of other

$$[S^\frown S]_2M$$

complexes,[15] suggesting that $SP(CH_3)_2NP(CH_3)_2S^-$ does not have an abnormally weak ligand field. The existence of $[SP(CH_3)_2NP(CH_3)_2S]_2Ni$ as a *tetrahedral* rather than as a *square-planar* species is not understood at the present time.

The average phosphorus–sulfur distance of 2.023 (6) Å is significantly lower than the single-bond value of 2.14 Å (from the appropriate Pauling covalent radii, 1.10 Å for P, 1.04 Å for S)[32] and is intermediate between the P—S (2.08–2.19 Å) and P=S (1.94 Å) bond lengths found in P_4S_5.[33]

The average phosphorus–nitrogen distance of 1.580 (7) Å is shorter than the accepted P—N single σ-bond distance of 1.78 Å[34] and may be compared with values in various trimeric phosphonitrilic halides and *pseudo*-halides, *viz.*, 1.58 (5) Å in $P_3N_3(NCS)_6$,[35] 1.58 (3) Å in $P_3N_3Br_6$,[36] 1.570 Å (corrected for thermal motion) in $P_3N_3F_6$,[37] and 1.59 Å in $P_3N_3Cl_6$.[38] Similar values are found in tetrameric phosphonitrilic derivatives[39] and in $[(C_6H_5)_2(NH_2)P{=\!=}N{=\!=}P(NH_2)(C_6H_5)_2{}^+]Cl^-$, where P=N = 1.57 and 1.58 Å.[40]

The $SP(CH_3)_2NP(CH_3)_2S^-$ ligand may thus correctly be written in the delocalized form

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The phosphorus atoms are each in approximately tetrahedral environments, average bond angles being S–P–N = 116.6°, S–P–C = 107.6°, and C–P–C = 107.2°. The mean P^V–CH_3 bond distance of 1.825 (25) Å is not significantly different from the P^{III}–CH_3 distance of 1.841 (3) Å in trimethylphosphine.[41]

The two six-membered chelate rings are markedly nonplanar but have different conformations. Thus

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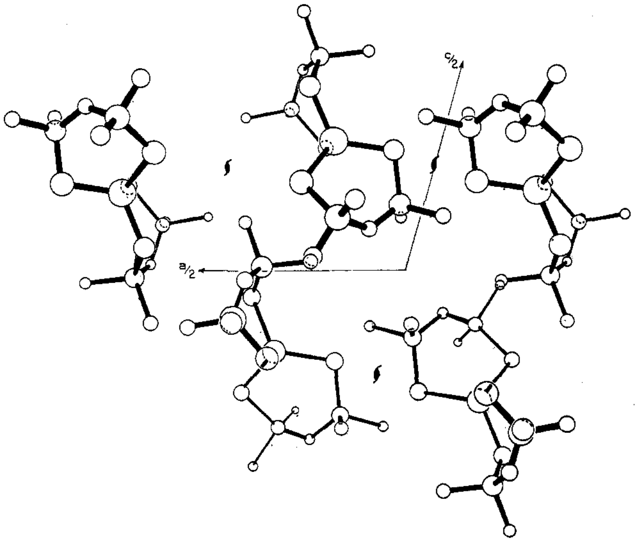

Figure 2.—Packing of $[SP(CH_3)_2NP(CH_3)_2S]_2Ni$ molecules within the unit cell, viewed down "*b*."

atoms P(1), N(1), and P(2) lie −0.422, +0.527, and +1.081 Å (respectively) from plane A [defined by Ni, S(1), S(2); see Table VI], whereas atoms P(3), N(2), and P(4) are displaced by −1.414, −1.433, and −0.356 Å from plane B.

The Crystal Structure

Intermolecular contacts less than 3.5 Å all involve hydrogen atoms (which were not located in this crystallographic analysis). However, it is clear that the crystal contains independent units of $[SP(CH_3)_2NP(CH_3)_2S]_2Ni$, separated by normal van der Waa's distances. Packing of molecules within the unit cell is shown in Figure 2.

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The Crystal and Molecular Structure of Dichloronitrosylbis(triphenylphosphine)iridium, $IrCl_2(NO)(P(C_6H_5)_3)_2$

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The structure of dichloronitrosylbis(triphenylphosphine)iridium, $IrCl_2(NO)(P(C_6H_5)_3)_2$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the space group C_{2h}^6-$I2/a$ of the monoclinic system with four molecules in a unit cell of dimensions $a = 15.851$ (4), $b = 9.624$ (3), $c = 22.050$ (6) Å, $\beta = 104.6$ (3)°. The observed and calculated densities are 1.66 (±0.02) and 1.67 g/cm³. Least-squares refinement of the structure has led to a final value of the conventional R factor (on F) of 0.032 for the 1338 reflections having $F^2 > 3\sigma(F^2)$. The structure consists of well-separated discrete molecules. There is a crystallographically imposed twofold axis on the molecule and the geometry around the iridium atom is approximately square-pyramidal with the nitrogen atom of the nitrosyl group occupying the apical position. Despite the fact that the oxygen and nitrogen atoms are disordered about the twofold axis an iridium–nitrogen–oxygen bond angle of 123 (2)° may be derived from the data. Important bond lengths in the molecule are as follows: Ir–Cl, 2.348 (2); Ir–P, 2.367 (2); Ir–N, 1.94 (2); N–O, 1.03 (2) Å. This complex provides another example of the nitrosyl ligand coordinated to iridium in a nonlinear fashion. The bonding in this complex is rationalized in terms of a qualitative molecular orbital scheme, and the complex is described formally as an NO^- complex of iridium(III).

Introduction

X-Ray structural studies of $[IrX(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$ (X = Cl or I)[1,2] showed that in each compound the metal–nitrosyl geometry was very different from that previously observed in reliable structural determinations of transition metal–nitrosyl complexes. The metal–nitrogen–oxygen bond angles are approximately 120° in the iridium complexes in contrast to the approximately 180° bond angle usually observed for nitrosyl complexes. The complexes with linear metal–nitrogen–oxygen bond angles have been formulated as complexes of NO^+, because they show properties and geometries similar to those of analogous carbonyl complexes. Hodgson, *et al.*,[1] suggested that in the complexes $[IrX(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$, which were prepared from the reaction of $NO^+BF_4^-$ with $IrX(CO)(P(C_6H_5)_3)_2$, the NO^+ ion was acting as a Lewis acid accepting two electrons from the metal d_{z^2} orbital into an empty sp^2 hybrid orbital on the nitrogen atom. However, the complex $[CoCl(NO)(en)_2][ClO_4]$ (en = ethylenediamine), which was prepared from nitric oxide[3] and which also has the nitrosyl ligand coordinated in a nonlinear fashion,[4] has been formulated as a complex of NO^-. These formulations (Figure 1) are equivalent and represent two of the canonical forms which may be used to describe the bonding in these ions.

The structural determinations of the complexes $[IrX(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$ (X = Cl or Br)[1,2] prompted us to study other iridium complexes which might have the nitrosyl ligand coordinated in a bent

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