Structures of Five- and Six-Coordinated Mixed-Ligand Chelates of Nickel(II) Containing Sulfur and Nitrogen Donor Atoms

P. S. Shetty and Quintus Fernando

Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721. *Received January 5, 1970*

Abstract: The structures of the quinoline adduct with bis(diethyldithiophosphinato)nickel(II) and the 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline adducts with bis(O,O′-dimethyldithiophosphato)nickel(II) have been determined by single-crystal X-ray techniques. The nickel atom is hexacoordinated in the 1,10-phenanthroline adduct and pentacoordinated in the quinoline adduct as well as in the 2,9-dimethyl-1,10-phenanthroline adduct. These results suggest that pentacoordinated mixed-ligand complexes of nickel(II) can be obtained by the addition of an appropriate ligand, which may be either monodentate or bidentate, to the planar nickel(II) dithiophosphates or dithiophosphinates.

The addition of monodentate ligands axially to planar tetracoordinated transition metal chelates proceeds in a stepwise manner. A pentacoordinated complex is formed by the addition of the first axial ligand, and the addition of the second ligand results in the formation of a hexacoordinated complex. The structural changes that accompany the introduction of successive axial ligands are reflected in the thermodynamic constants and in the spectral properties of the complexes. In many instances the structure of the intermediate pentacoordinated complex is not known since it cannot be isolated in the solid state and any inferences that are made about its structure from the solution spectra are usually open to question. It is useful therefore, to carry out parallel investigations, wherever possible, on the structures as well as the reflectance and solution spectra of these pentacoordinated intermediates. Compounds that seem to be suited for such studies are the transition metal chelates of dialkyldithiophosphates and dialkyldithiophosphinates. We have found that it is possible to isolate pentacoordinated chelates formed by these ligands and monodentate ligands which add axially to the chelated metal ion. The structure of one such adduct with quinoline as an axial ligand is reported below. The addition of a bidentate ligand to a planar tetracoordinated metal chelate is expected to result in the formation of *cis* adducts. The structure of the *cis* adduct obtained with 1,10-phenanthroline and bis-(O,O′-dimethyldithiophosphato)nickel(II) is reported below. The adduct with 2,9-dimethyl-1,10-phenanthroline was synthesized for purposes of comparison and its structure is also described.

Experimental Section

The adduct of bis(diethyldithiophosphinato)nickel(II) with quinoline, $Ni[S_2P(C_2H_5)_2]_2 \cdot NC_9H_7$ (adduct I), was prepared by the addition of quinoline to a solution of the nickel chelate in diethyl ether until the solution turned brown. Slow evaporation of this solution gave dark brown crystals which were suitable for a structure analysis. The crystals were coated with a thin layer of glue to prevent the loss of quinoline on exposure to air.

Adduct II, $Ni[S_2P(OCH_3)_2]_2 \cdot N_2H_8C_{12}$, was prepared by the addition of a solution of 1,10-phenanthroline in acetone to a solution of bis(O,O′-dimethyldithiophosphato)nickel(II) in a 1:1 mixture of acetone and ethanol, until a green solution was formed. Bright green needle-shaped crystals obtained from this solution were used in the structure determination.

Greenish yellow needle-shaped crystals of adduct III, $Ni[S_2P(OCH_3)_2]_2 \cdot N_2H_{12}C_{14}$, obtained from an ethanol solution containing 2,9-dimethyl-1,10-phenanthroline and bis(O,O′-dimethyldithiophosphato)nickel(II), were found to be suitable for the structure determination.

Table I summarizes the crystal data and the methods used for the structure determination and refinement. Corrections for spot-shape, Lorentz, and polarization factors were applied in the usual manner. No absorption or extinction corrections were made. The atomic scattering factors given in "International Tables for X-ray Crystallography"[1] were used in this work. Correction for the anomalous dispersion of nickel was made by the addition of −3.1 electrons to the scattering factor of nickel and the imaginary part of the dispersion correction was neglected.

The Harker section of a three-dimensional Patterson synthesis calculated from the data obtained for the quinoline adduct (adduct I) showed several possible locations of the Ni–Ni vector. It was decided, therefore, to employ the symbolic addition method as an independent check on the Patterson synthesis. Of the two possible space groups only the space group C2/c is centrosymmetric. An Nz test with the *h*0*l* data indicated that the space group was centrosymmetric. Normalized structure factors (*E* values) were calculated by the program FAME.[2] Despite the presence of several heavy atoms in the molecule it may be concluded from a comparison of the experimental and theoretical values for several functions of *E* that the distribution of intensities is centric and that C2/c is the correct choice of space group. The program FAME calculated a Σ_2 list and also assigned symbols to nine of the largest *E* values that had the greatest number of Σ_2 interactions. The Σ_2 formula was applied by the program MAGIC[2] to 1200 reflections that had the largest *E* values. In the first iteration symbolic signs for 11 new reflections were obtained with a probability >0.99. In each of the subsequent four iterations, 24, 61, 139, and 254 new signs were determined with a probability >0.99 and the total number of reflections whose signs were determined was 498. The reflections, (−6, 6, 25) and (9, 3, 5) were selected as the origin (+) specifying reflections. The symbolic signs for all the 498 reflections were converted to either + or − by the programs LINK and SYMPL.[2] An *E*-map calculated with these 498 reflections revealed the probable positions of the nickel, sulfur, and phosphorus atoms. The correctness of this *E*-map was verified by a comparison with the three-dimensional Patterson synthesis. The structure determination was continued by making use of the usual heavy-atom methods. A comparison of a Fourier synthesis, based on the phases obtained from the position of the nickel atom, with the *E*-map clearly showed that the positions of all the heavy atoms in the *E*-map were correct. All the remaining atoms, with the exception of the hydrogen atoms, were located by successive Fourier and difference Fourier syntheses based on the phases obtained from the position of the heavy atoms.

The positions of all the atoms except the hydrogen atoms in the 1,10-phenanthroline adduct (adduct II) and in the 2,9-dimethyl-1,10-phenanthroline adduct (adduct III) were obtained by Patterson and Fourier methods.

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

(2) R. B. K. Dewar and A. L. Stone, FAME, MAGIC, LINK, and SYMPL, Fortran Programs for the Application of the Symbolic Addition Method of Karle and Hauptman to Centric Space Groups.

Table I. Results of X-Ray Measurements on Single Crystals of the Three Adducts

	Adduct I $Ni[S_2P(C_2H_5)_2]_2 \cdot NC_9H_7$	Adduct II $Ni[S_2P(OCH_3)_2]_2 \cdot N_2H_8C_{12}$	Adduct III $Ni[S_2P(OCH_3)_2]_2 \cdot N_2H_{12}C_{14}$
Crystal data	$a = 15.61 \pm 0.02$ Å $b = 10.11 \pm 0.02$ Å $c = 29.75 \pm 0.02$ Å $\beta = 101° 17' \pm 30'$ $F(000) = 2064$ $D_{obsd} = 1.402$ g cm^{-3} $D_{calcd} = 1.442$ g cm^{-3} $Z = 8$ Systematic absences hkl, $h + k = 2n + 1$ $h0l$, $h = 2n + 1$, $l = 2n + 1$ Space group C2/c or Cc	$a = 6.61 \pm 0.01$ Å $b = 18.57 \pm 0.02$ Å $c = 18.86 \pm 0.02$ Å $\beta = 100° 10' \pm 30'$ $F(000) = 1136$ $D_{obsd} = 1.610$ g cm^{-3} $D_{calcd} = 1.612$ g cm^{-3} $Z = 4$ Systematic absences $0k0$, $k = 2n + 1$ $h0l$, $l = 2n + 1$ Space group P2$_1$/c	$a = 7.86 \pm 0.01$ Å $b = 14.51 \pm 0.02$ Å $c = 21.79 \pm 0.02$ Å $\beta = 92° 30' \pm 30'$ $F(000) = 1200$ $D_{obsd} = 1.52$ g cm^{-3} $D_{calcd} = 1.55$ g cm^{-3} $Z = 4$ Systematic absences $0k0$, $k = 2n + 1$ $h0l$, $l = 2n + 1$ Space group P2$_1$/c
Method of measurement	Film–Weissenberg [($h0l$ − $h6l$) and ($0kl$ − $1kl$)] Cu Kα radiation (λ 1.5418 Å)	Film–Weissenberg [($hk0$ − $hk4$) and ($0kl$ − $3kl$)] Cu Kα radiation (λ 1.5418 Å)	Film–Weissenberg ($h0l$ − $h0l$) Counter–Weissenberg ($0kl$ − $6kl$) Cu Kα radiation (λ 1.5418 Å)
Number of observations	2720	2570	2990
Solution of phase problem	Direct centric and 3-D Patterson	3-D Patterson	3-D Patterson
Method of refinement	Full-matrix least squares	Full-matrix least squares	Full-matrix least squares
Final $R = \Sigma(\lvert F_o \rvert - F_c\rvert)/\Sigma\lvert F_o \rvert$			
With isotropic temperature factors	13%	13.3%	17.0%
With anisotropic temperature factors	9.1%	9.0%	10.9%
Largest parameter shift	0.003 Å for C(4) in Figure 1	0.003 Å for C(12) in Figure 2	0.0001 Å for C(16) in Figure 3

All three structures were refined by the full-matrix least-squares technique with individual atom isotropic temperature factors. The conventional R values after four refinement cycles are listed in Table I. The refinement was continued with anisotropic temperature factors for all the atoms. The quantity minimized was $\Sigma_{hkl}W(\lvert F_o\rvert - \lvert F_c\rvert)^2$, where $W = 1/(A + B\lvert F_o\rvert + C\lvert F_o\rvert^2)$ and $A = 20.0$, $B = 1.0$, $C = 0.004$. Tables II, III, and IV give the final values of the atomic parameters and their estimated standard deviations. All the refinement cycles for the three structures were calculated by the program ORFLS[3] with a CDC-6400 computer. The program ORFFE[4] was used to calculate all bond distances, bond angles, and their estimated standard deviations in all three structures (Figures 1–3). Although all the anisotropic temperature factors in the three structures are positive definite, they have little signifi-

Table II. Positional Parameters for the Atoms in the Asymmetric Unit with Their Standard Deviations for Adduct I: $Ni[S_2P(C_2H_5)_2]_2 \cdot NC_9H_7$[a]

Atom	x	y	z
Ni	643 (1)	2342 (2)	1286 (1)
S(1)	1583 (2)	4060 (3)	1086 (1)
S(2)	1472 (2)	2719 (3)	2049 (1)
S(3)	518 (1)	1284 (3)	557 (1)
S(4)	138 (2)	215 (3)	1506 (1)
P(1)	2010 (2)	4211 (3)	1760 (1)
P(2)	−76 (2)	−174 (3)	837 (1)
N	−459 (4)	3446 (8)	1305 (2)
C(1)	1738 (8)	5839 (14)	1976 (4)
C(2)	744 (10)	6117 (19)	1908 (6)
C(3)	3167 (8)	4192 (17)	1868 (5)
C(4)	3573 (18)	4164 (26)	2352 (8)
C(5)	311 (8)	−1815 (13)	722 (4)
C(6)	1293 (8)	−1950 (16)	831 (6)
C(7)	−1225 (6)	−255 (12)	581 (3)
C(8)	−1715 (7)	1060 (14)	590 (4)
C(9)	−758 (6)	3330 (11)	1692 (3)
C(10)	−1487 (7)	4104 (13)	1770 (3)
C(11)	−1883 (7)	4953 (13)	1452 (4)
C(12)	−1585 (6)	5092 (11)	1045 (3)
C(13)	−875 (5)	4292 (10)	969 (3)
C(14)	−601 (6)	4368 (11)	552 (3)
C(15)	−1015 (7)	5169 (12)	211 (3)
C(16)	−1709 (7)	5995 (12)	277 (4)
C(17)	−1992 (7)	5962 (13)	679 (4)

[a] Atomic parameters have been multiplied by 10^4.

Table III. Positional Parameters for the Atoms in the Asymmetric Unit with Their Standard Deviations for Adduct II: $Ni[S_2P(OCH_3)_2]_2 \cdot N_2H_8C_{12}$[a]

Atom	x	y	z
Ni	3842 (3)	2212 (1)	1000 (1)
S(1)	2023 (5)	3228 (2)	1486 (2)
S(2)	5387 (5)	3217 (1)	425 (2)
S(3)	2407 (5)	1213 (1)	1664 (1)
S(4)	6552 (5)	2181 (1)	2093 (1)
P(1)	3605 (5)	3822 (1)	912 (2)
P(2)	4905 (4)	1390 (1)	2387 (1)
O(1)	2039 (16)	4297 (5)	371 (5)
O(2)	4879 (15)	4457 (4)	1353 (6)
O(3)	6144 (11)	656 (4)	2530 (4)
O(4)	4371 (13)	1505 (4)	3182 (4)
N(1)	5247 (12)	1454 (4)	428 (4)
N(2)	1610 (13)	2086 (4)	79 (4)
C(1)	2324 (38)	4643 (14)	−227 (11)
C(2)	6606 (26)	4305 (9)	1876 (9)
C(3)	8106 (19)	636 (7)	3028 (8)
C(4)	3096 (23)	2106 (7)	3306 (7)
C(5)	7137 (15)	1151 (5)	635 (6)
C(6)	7885 (18)	651 (5)	181 (6)
C(7)	6731 (19)	479 (5)	−484 (6)
C(8)	4844 (17)	805 (5)	−702 (5)
C(9)	3555 (22)	667 (6)	−1394 (6)
C(10)	1678 (23)	992 (7)	−1580 (6)
C(11)	923 (17)	1487 (5)	−1099 (5)
C(12)	−952 (19)	1874 (6)	−1264 (6)
C(13)	−1503 (18)	2337 (6)	−778 (7)
C(14)	−211 (16)	2428 (6)	−86 (6)
C(15)	2196 (16)	1626 (5)	−407 (5)
C(16)	4118 (16)	1295 (4)	−216 (5)

[a] Atomic parameters have been multiplied by 10^4.

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(3) W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, A Fortran Crystallographic Least-Squares Program, U. S. Atomic Energy Commission Publication ORNL-TM-305, 1962.

(4) W. R. Busing, K. O. Martin, and H. A. Levy, ORFFE, A Fortran Crystallographic Function and Error Program, U. S. Atomic Energy Commission Publication ORNL-TM-306, 1964.

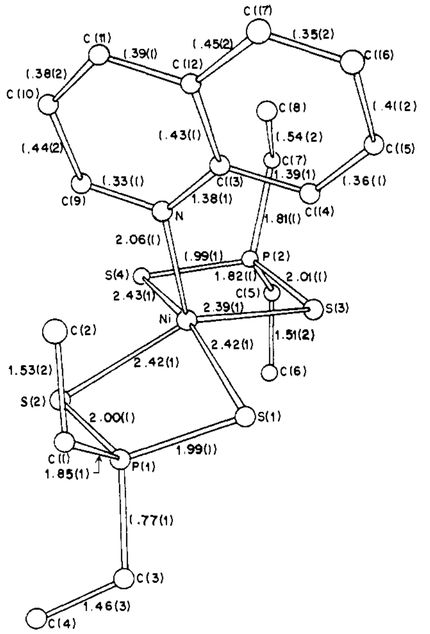

Figure 1. Adduct I. A perspective view of the adduct of Ni-$S_2P(C_2H_5)_2]_2$ with quinoline.

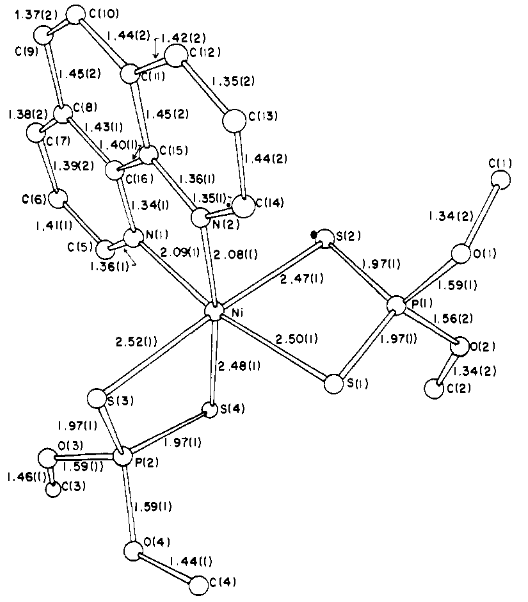

Figure 2. Adduct II. A perspective view of the adduct of Ni-$[S_2P(OCH_3)_2]_2$ with 1,10-phenanthroline.

cance unless absorption corrections are made and all the hydrogen atoms are located in each of the three structures.[5]

Results and Discussion

The structure of adduct I consists of discrete molecules of $Ni[S_2P(C_2H_5)_2]_2 \cdot NC_9H_7$ as shown in Figure 1. The coordination polyhedron around the nickel atom is an approximate square pyramid. Four sulfur atoms form the base of the pyramid and the apex is occupied by the nitrogen atom of the quinoline molecule. The four sulfur atoms lie in approximately one plane and the nickel atom lies 0.52 Å above the best plane passing through these four atoms. The sixth coordination position of the nickel atom can therefore be occupied only by a small molecule and the approach of a second quinoline molecule, *trans* to the first, would be sterically hindered.

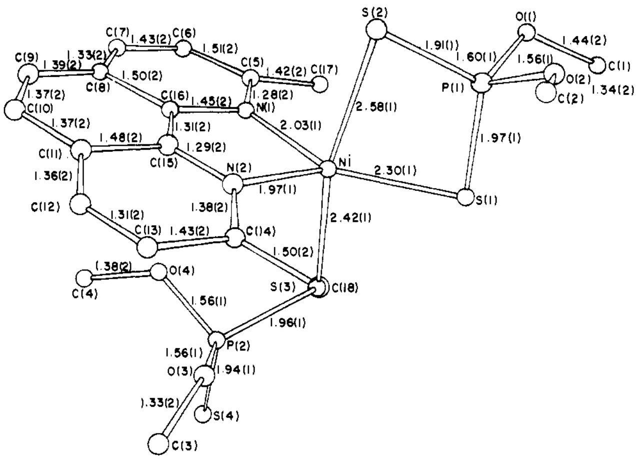

Figure 3. Adduct III. A perspective view of the adduct of Ni-$[S_2P(OCH_3)_2]_2$ with 2,9-dimethyl-1,10-phenanthroline.

Table IV. Positional Parameters for the Atoms in the Asymmetric Unit with Their Standard Deviations for Adduct III: $Ni[S_2P(OCH_3)_2]_2 \cdot N_2H_{12}C_{14}$[a]

Atom	*x*	*y*	*z*
Ni	1956 (2)	990 (1)	1439 (1)
S(1)	1780 (6)	2570 (3)	1380 (1)
S(2)	594 (4)	1118 (2)	342 (1)
S(3)	3523 (4)	1239 (2)	2405 (1)
S(4)	4857 (4)	283 (2)	3725 (1)
P(1)	936 (4)	2396 (2)	524 (1)
P(2)	3321 (3)	242 (2)	3006 (1)
O(1)	2189 (13)	2820 (6)	39 (4)
O(2)	−652 (16)	3012 (8)	368 (7)
O(3)	1400 (14)	258 (11)	3157 (5)
O(4)	3498 (15)	−650 (7)	2616 (4)
N(1)	3233 (11)	−148 (8)	1180 (4)
N(2)	288 (11)	66 (7)	1696 (4)
C(1)	2798 (25)	3744 (12)	137 (8)
C(2)	−2289 (22)	2907 (16)	507 (11)
C(3)	520 (21)	7 (11)	3637 (7)
C(4)	3830 (21)	−1529 (11)	2830 (7)
C(5)	4667 (18)	−217 (12)	930 (5)
C(6)	5416 (17)	−1153 (11)	803 (6)
C(7)	4380 (20)	−1917 (13)	965 (7)
C(8)	2820 (21)	−1873 (13)	1173 (7)
C(9)	1720 (22)	−2576 (9)	1326 (7)
C(10)	174 (22)	−2423 (11)	1578 (8)
C(11)	−352 (18)	−1561 (10)	1737 (6)
C(12)	−1799 (18)	−1347 (12)	2028 (6)
C(13)	−2257 (18)	−512 (11)	2180 (7)
C(14)	−1169 (14)	225 (10)	2008 (5)
C(15)	706 (16)	−765 (9)	1561 (5)
C(16)	2158 (16)	−933 (8)	1310 (5)
C(17)	5588 (16)	596 (13)	807 (6)
C(18)	−1575 (18)	1204 (10)	2172 (7)

[a] Atomic parameters have been multiplied by 10^4.

The bond distances and bond angles together with their estimated standard deviations are shown in Figure 1 and Table V. The Ni–S distances are equal (average, 2.41 Å) and lie within the range of values found for

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(5) Structure factor tables and temperature factor tables have been deposited as Document No. NAPS-00916 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 by remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

Table V. Bond Angles and Their Standard Deviations (in deg) for Adduct I: $Ni[S_2P(C_2H_5)_2]_2 \cdot NC_9H_7$

Ni–S(1)–P(1)	84.8 (0.2)
S(1)–Ni–S(2)	83.0 (0.1)
Ni–S(2)–P(1)	84.7 (0.1)
S(1)–Ni–S(3)	92.6 (0.1)
S(2)–Ni–S(4)	91.7 (0.1)
N–Ni–S(4)	98.9 (0.2)
N–Ni–S(3)	110.3 (0.3)
N–Ni–S(2)	100.7 (0.3)
N–Ni–S(1)	99.7 (0.3)
S(1)–P(1)–C(3)	108.2 (0.6)
S(1)–P(1)–S(2)	106.8 (0.2)
P(1)–C(3)–C(4)	114.3 (1.4)
P(1)–C(1)–C(2)	114.2 (1.0)
C(1)–P(1)–C(3)	104.1 (0.7)
C(1)–P(1)–S(2)	112.1 (0.4)
Ni–S(3)–P(2)	85.2 (0.2)
Ni–S(4)–P(2)	84.6 (0.2)
S(4)–Ni–S(3)	82.8 (0.2)
S(3)–P(2)–S(4)	105.5 (0.2)
S(3)–P(2)–C(5)	113.2 (0.4)
P(2)–C(5)–C(6)	113.7 (1.0)
S(4)–P(2)–C(7)	112.8 (0.4)
P(2)–C(7)–C(8)	114.3 (0.7)
C(7)–P(2)–C(5)	102.7 (0.5)
S(3)–P(2)–C(5)	113.2 (0.4)
P(2)–C(5)–C(6)	113.7 (1.0)
Ni–N–C(13)	126.4 (0.5)
Ni–N–C(9)	114.4 (0.7)
C(9)–N–C(13)	119.1 (0.8)
N–C(9)–C(10)	121.1 (0.9)
C(9)–C(10)–C(11)	120.4 (0.9)
C(10)–C(11)–C(12)	119.6 (1.0)
C(11)–C(12)–C(17)	123.0 (1.0)
C(11)–C(12)–C(13)	119.1 (0.9)
C(12)–C(13)–N	120.5 (0.7)
C(17)–C(12)–C(13)	117.7 (0.8)
C(12)–C(17)–C(16)	120.5 (1.0)
C(12)–C(13)–C(14)	119.7 (0.8)
C(13)–C(14)–C(15)	121.0 (0.9)
C(14)–C(15)–C(16)	120.9 (1.0)
C(15)–C(16)–C(17)	120.1 (1.0)

high-spin nickel complexes.[6] The P–S distances are equal (average, 2.00 Å) and are identical with the P–S distances in the tetracoordinated chelate bis(diethyldithiophosphinato)nickel(II).[7] The Ni–N distance (2.06 Å) is slightly shorter than the Ni–N distance of 2.11 Å in the hexacoordinated adduct of bis(O,O′-diethyldithiophosphato)nickel(II) with pyridine[8] but slightly longer than the Ni–N distance of 2.00 Å in the pentacoordinated adduct of bis(O,O′-dimethyldithiophosphato)nickel(II) with 2,9-dimethyl-1,10-phenanthroline in adduct III. The rest of the bond lengths in the molecule (P–C and C–C distances) assume normal values.

The atoms in the quinoline molecule lie in one plane; the nickel atom deviates from this plane by 0.085 Å. The angle between the plane of the quinoline molecule and the plane of the four sulfur atoms is 84°. All intermolecular contacts were found to be greater than 3.5 Å. The shortest van der Waals distance was 3.61 Å between C(3) and S(4).

Several factors govern the ease of addition of axial ligands to planar metal chelates. Among the more important factors are the extent to which the metal in the planar metal chelate is coordinatively unsaturated, the basicity of the axial ligand, inductive effects of substituents on the chelate ring, and steric and solvation effects. It has been established that certain structural changes occur in the chelate ring system when axial ligands are added to the metal ion. This may well be a more general phenomenon than has been suspected hitherto. One striking example of the structural changes that do occur is illustrated by a comparison of the planar nickel chelate, bis(O,O′-diethyldithiophosphato)nickel(II), with the octahedral complex formed when two pyridine molecules are added axially and in *trans* positions.[8] The most significant changes occur in the chelate ring in which the Ni–S distances and the S–P–S angles are increased. It is not possible, however, to determine the structural changes that occur when only one pyridine molecule is added to form a pentacoordinated complex, since such a complex cannot be isolated as a solid. It may be speculated from the thermodynamic data available that the two chelate rings are no longer coplanar and that the nickel atom is above the plane of the four bonding sulfur atoms. Coplanarity of the two chelate rings is achieved by the addition of a second axial pyridine molecule, but at the expense of a greater distortion in the chelate ring; the Ni–S distances and the S–P–S angles show a further increase. That the foregoing explanation is probably correct can be deduced from the structure of the pentacoordinated quinoline adduct reported in this study. It is noteworthy that the increases in the Ni–S distances and the S–P–S angles in the compound reported here are not as large as the corresponding values in the hexacoordinated pyridine adduct. Hexacoordination therefore should result in a further increase in the Ni–S distance and in the S–P–S angle. It must be emphasized, however, that the above inferences are only qualitative, since the inductive effects of the ethoxy groups and the ethyl groups in the two complexes are not identical.

The addition of an axial ligand cannot only affect the metal chelate to which the ligand is added but can also affect the ligand itself. In this work the axial addition of quinoline to the central nickel ion is tantamount to reducing the electron availability on the coordinated nitrogen atom. Despite this it is of interest that the bond distances in the quinoline molecule show the same type of behavior that is observed in the absence of such an effect on the nitrogen atom. Unfortunately, the large standard deviations of the C–C bonds in the quinoline molecule preclude a discussion of this effect on a more quantitative basis.

The structure of adduct II consists of discrete molecules of 1,10-phenanthrolinebis(O,O′-dimethyldithiophosphato)nickel(II) as shown in Figure 2 and Table VI. As expected, the nitrogen atoms of the bidentate ligand, 1,10-phenanthroline, occupy *cis* positions in the hexacoordinated nickel complex. The four Ni–S distances are approximately equal; their average of 2.49 Å is in the range of Ni–S distances found in high-spin nickel complexes.[6,8] The Ni–N distances (2.08 and 2.09 Å) agree with the Ni–N distances found in related hexacoordinated nickel complexes[8] and are slightly longer than the corresponding distances in pentacoordinated nickel complexes. All other bond distances are normal. The bond angles in the chelate ring are similar to the values found previously in the hexacoordinated adducts

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

(7) P. S. Shetty and Q. Fernando, *Acta Crystallogr., Sect. B*, **25**, 1294 (1969).

(8) S. Ooi and Q. Fernando, *Inorg. Chem.*, **6**, 1558 (1967).

Table VI. Bond Angles and Their Standard Deviations (deg) for Adduct II: $Ni[S_2PO(CH_3)_2]_2 \cdot N_2H_8C_{12}$

S(1)–Ni–S(2)	81.6 (0.2)
S(2)–Ni–N(2)	90.3 (0.2)
N(2)–Ni–N(1)	78.9 (0.3)
N(1)–Ni–S(3)	90.1 (0.2)
S(3)–Ni–S(4)	81.3 (0.1)
N(1)–Ni–S(4)	95.3 (0.2)
N(2)–Ni–S(2)	90.3 (0.2)
N(1)–Ni–S(2)	91.5 (0.2)
Ni–S(2)–P(1)	84.2 (0.2)
S(2)–P(1)–S(1)	110.8 (0.2)
P(1)–S(1)–Ni	83.4 (0.2)
S(2)–P(1)–O(1)	113.1 (0.4)
S(1)–P(1)–O(2)	114.2 (0.4)
O(1)–P(1)–O(2)	98.6 (0.6)
P(1)–O(1)–C(1)	129.4 (1.3)
P(1)–O(2)–C(2)	120.5 (0.9)
Ni–S(4)–P(2)	84.1 (0.1)
Ni–S(3)–P(2)	83.0 (0.1)
S(3)–P(2)–S(4)	111.6 (0.2)
S(3)–P(2)–O(3)	108.5 (0.3)
S(4)–P(2)–O(4)	112.7 (0.4)
O(3)–P(2)–O(4)	98.3 (0.4)
P(2)–O(3)–C(3)	120.2 (0.7)
P(2)–O(4)–C(4)	118.8 (0.7)
Ni–N(1)–C(5)	126.8 (0.6)
Ni–N(1)–C(16)	112.9 (0.6)
Ni–N(2)–C(14)	127.7 (0.7)
Ni–N(2)–C(15)	112.9 (0.6)
C(15)–N(2)–C(14)	119.4 (0.9)
N(2)–C(14)–C(13)	121.2 (1.0)
N(2)–C(15)–C(16)	117.2 (0.8)
N(2)–C(15)–C(11)	122.1 (0.9)
C(14)–C(13)–C(12)	120.1 (1.1)
C(13)–C(12)–C(11)	120.2 (1.1)
C(12)–C(11)–C(15)	117.0 (1.0)
C(12)–C(11)–C(10)	124.8 (1.0)
C(11)–C(15)–C(16)	120.7 (0.9)
C(11)–C(10)–C(9)	121.3 (1.0)
C(10)–C(9)–C(8)	121.0 (1.0)
C(9)–C(8)–C(7)	123.1 (1.0)
C(9)–C(8)–C(16)	118.6 (1.0)
C(8)–C(7)–C(6)	119.4 (1.0)
C(8)–C(16)–N(1)	121.5 (0.9)
C(7)–C(8)–C(16)	118.4 (0.9)
C(7)–C(6)–C(5)	120.4 (1.0)
C(5)–N(1)–C(16)	120.3 (0.8)
C(6)–C(5)–N(1)	120.0 (1.0)

Table VII. Bond Angles and Their Standard Deviations (deg) for Adduct III: $Ni[S_2P(OCH_3)_2]_2 \cdot N_2H_{12}C_{14}$

Ni–S(1)–P(1)	86.6 (0.2)
S(1)–Ni–S(2)	81.7 (0.1)
S(1)–Ni–S(3)	85.8 (0.1)
S(2)–Ni–N(1)	89.5 (0.3)
N(1)–Ni–N(2)	82.4 (0.4)
N(2)–Ni–S(3)	100.0 (0.3)
N(2)–Ni–S(1)	130.2 (0.3)
N(2)–Ni–S(2)	93.0 (0.3)
Ni–S(2)–P(1)	80.2 (0.1)
S(1)–P(1)–S(2)	111.1 (0.2)
S(1)–P(1)–O(2)	111.5 (0.6)
P(1)–O(2)–C(2)	130.6 (1.4)
O(2)–P(1)–O(1)	98.3 (0.7)
P(1)–O(1)–C(1)	118.2 (1.0)
O(1)–P(1)–S(2)	108.8 (0.4)
Ni–S(3)–P(2)	114.7 (0.2)
S(3)–P(2)–O(3)	103.7 (0.5)
S(3)–P(2)–S(4)	116.9 (0.2)
S(3)–P(2)–O(4)	103.7 (0.4)
O(4)–P(2)–S(4)	113.5 (0.4)
P(2)–O(3)–C(3)	134.7 (1.2)
C(4)–O(4)–P(2)	127.2 (1.0)
Ni–N(1)–C(5)	129.8 (1.1)
N(1)–C(5)–C(17)	118.9 (1.5)
N(1)–C(5)–C(6)	120.4 (1.4)
N(1)–C(16)–C(8)	117.8 (1.2)
N(1)–C(16)–C(15)	117.4 (1.0)
C(17)–C(15)–C(6)	120.6 (1.3)
C(5)–C(6)–C(7)	114.9 (1.2)
C(6)–C(7)–C(8)	126.3 (1.7)
C(7)–C(8)–C(16)	116.5 (1.7)
C(7)–C(8)–C(9)	129.9 (1.8)
C(8)–C(9)–C(10)	123.4 (1.6)
C(8)–C(16)–C(15)	124.8 (1.2)
C(9)–C(10)–C(11)	122.1 (1.5)
C(10)–C(11)–C(12)	126.4 (1.5)
C(10)–C(11)–C(15)	117.9 (1.5)
C(11)–C(15)–C(16)	118.1 (1.3)
C(11)–C(12)–C(13)	124.9 (1.4)
C(15)–C(11)–C(12)	115.6 (1.3)
C(12)–C(13)–C(14)	116.8 (1.4)
C(11)–C(15)–N(2)	121.2 (1.3)
C(15)–N(2)–C(14)	119.8 (1.0)
C(13)–C(14)–C(18)	120.6 (1.2)
C(13)–C(14)–N(2)	121.6 (1.3)
C(18)–C(14)–N(2)	117.8 (1.0)

bispyridinebis(O,O′-diethyldithiophosphato)nickel(II),[8] and 2,2′-dipyridylbis(O,O′-dimethyldithiophosphato)nickel(II).[9] The shortest intermolecular distance is 3.29 Å between C(4) and C(11). All other intermolecular contacts are greater than 3.51 Å.

The phenanthroline molecule and the nickel atom lie in approximately one plane. Atom C(6) shows a maximum deviation of 0.045 Å from this plane. The atoms Ni, S(2), P(1), and S(1) are in the same plane and the atom P(1) shows a deviation of 0.11 Å from the plane. The atom P(2) has a maximum deviation of 0.013 Å from the plane formed by the four atoms Ni, S(3), P(2), and S(4). Hence the three chelate rings form three planes which are approximately at right angles to each other. The structure of adduct III consists of discrete molecules of 2,9-dimethyl-1,10-phenanthrolinebis(O,O′-dimethyldithiophosphato)nickel(II) as shown in Figure 3 and Table VII. One of the dithiophosphato ligands in this complex is bidentate and the other dithiophosphato ligand is monodentate. Both nitrogen atoms in the phenanthroline molecule are coordinated to the nickel atom. Hence, the nickel atom is pentacoordinated in this compound and the coordination polyhedron is a distorted tetragonal pyramid. Three sulfur atoms and a nitrogen atom, S(1), S(2), S(3), and N(1), form the base and the apex is occupied by the nitrogen atom N(2). The four atoms Ni, S(2), S(3), and N(1) lie approximately in a plane, and the nickel atom lies 0.18 Å above the best plane through these four atoms. The atom S(1) is at a distance of 0.9 Å below this plane. Therefore, the structure could also be described as a distorted trigonal bipyramid in which the atoms S(2), S(3), and N(1) are equatorial and the atoms N(2) and S(1) apical. This structure is another example of a pentacoordinated nickel complex with a coordination polyhedron that is intermediate between a tetragonal pyramid and trigonal bipyramid. Mair, Powell, and Henn[10] described the structure of a similar pentacoordinated nickel complex that was obtained with the tridentate ligand, bis(3-dimethylarsinopropyl)methylarsine.

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The bond distances and bond angles with their estimated standard deviations are shown in Figure 3. The three nickel–sulfur distances are unequal and they are all significantly greater than the nickel–sulfur distance, 2.20 Å, that is usually found in low-spin nickel complexes. In high-spin nickel complexes the nickel–sulfur distance lies between 2.4 and 2.6 Å.[6] The Ni–S(2) and the Ni–S(3) distances are well within this range; the Ni–S(1) distance, however, is significantly smaller.

Although in general, the mechanisms of reactions that take place in solution cannot be deduced from structural data, it is reasonable to assume that the pentacoordinated intermediate did exist in solution if it could be isolated in the solid state. Hence it can be speculated that the following mechanism is involved in the formation of the mixed ligand complex. The bidentate ligand, 2,9-dimethyl-1,10-phenanthroline, approaches the planar nickel chelate in an axial direction and coordination of one of the nitrogen atoms disrupts a chelate ring to allow the second nitrogen atom to coordinate in *cis* position. The free sulfur atom, however, does not occupy the sixth coordination position. The reasons for this unexpected behavior will be sought by carrying out further work with a series of substituted 1,10-phenanthrolines and other substituted bidentate ligands such as 2,2′-dipyridyl.

The nickel–nitrogen distances are approximately equal to the nickel–nitrogen distances (2.07 and 2.11 Å) found in the hexacoordinated compound, 2,2′-dipyridylbis(O,O′-dimethyldithiophosphato)nickel(II)[9] and bispyridinebis(O,O′-diethyldithiophosphato)nickel(II).[8] All other interatomic distances in the molecule do not differ significantly from the distances reported for similar molecules. The nickel–sulfur bond lengthening and the chelate ring distortion are similar to those which occur on the addition of an axial ligand to planar metal chelates. The decrease in the S(1)–Ni–S(2) angle and the concomitant increase in the S(1)–P(1)–S(2) angle are of the same order of magnitude as those found when two pyridine molecules were added axially to the planar chelate, bis(O,O′-diethyldithiophosphato)nickel(II).[8] The shortest intermolecular distance observed was 3.39 Å, between C(12) and C(6); all other intermolecular contacts were greater than 3.5 Å. All the atoms in the 2,9-dimethyl-1,10-phenanthroline molecule together with the nickel atom lie in approximately the same plane. The atom C(9) shows a maximum deviation of 0.13 Å from this plane. Unfortunately the accuracy of this structure determination does not warrant any discussion of structural changes in the phenanthroline molecule that may have resulted from coordination to the nickel atom. The high temperature factors and their large standard deviations (which were anticipated from the absence of the high angle reflections in the Weissenbergh photographs) contributed to the low accuracy of this structure determination.

One of the most interesting features in this complex is that although three of the five donor atoms are sulfur atoms, the complex has a magnetic moment of 3.2 BM. The interpretation of the d-d transitions in this compound and related mixed-ligand complexes obtained with other substituted 1,10-phenanthrolines and 2,2′-dipyridyls should be of interest.

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Methylarsaoxanes. Structural Chemistry of Cacodyl Oxide and Arsenosomethane in the Liquid State

Heinrich C. Marsmann and John R. Van Wazer[1]

Contribution from the Central Research Department, Monsanto Company, St. Louis, Missouri, and the Chemistry Department of Vanderbilt University, Nashville, Tennessee 37202. *Received October 18, 1969*

Abstract: Nuclear magnetic resonance data indicate that the oxygen in cacodyl oxide, $(CH_3)_2AsOAs(CH_3)_2$, is in the bridging position and, on dissolution in organic solvents, crystalline arsenosomethane, CH_3AsO, is shown to form a mixture of species in which the tetrameric and trimeric cyclics predominate. Arsenosomethane and cacodyl oxide react immediately in solution or as a neat liquid to give equilibrium mixtures containing compounds of the type $CH_3[As(CH_3)O]_nAs(CH_3)_2$ for $n \geq 2$. The controlling equilibrium constants are reported. Arsenosomethane also reacts with methyldibromoarsine to give compounds of the type $Br[As(CH_3)O]_nAs(CH_3)Br$. However, arsenosomethane does not react with dimethylbromoarsine because the equilibrium for redistribution of bromine and bridging oxygen atoms between the $CH_3As<$ and $(CH_3)_2As-$ is shifted strongly toward the placement of the bromine on the dimethylarsino group.

The methyl-substituted oxides of arsenic are among the oldest organometallic compounds. Cacodyl oxide, $(CH_3)_2AsOAs(CH_3)_2$, was first prepared in 1760 as part of a mixture[2] and its isolation and elemental composition were first demonstrated by Bunsen[3] in

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[1] To whom reprint requests should be sent at Vanderbilt University.

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