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The Crystal and Molecular Structure of the Adduct of Bis(O,O′-diethyldithiophosphato)nickel(II) with Pyridine

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The crystal and molecular structure of the bis-pyridine adduct of bis(O,O′-diethyldithiophosphato)nickel(II), Ni(dtp)$_2$·2py, has been determined by three-dimensional X-ray analysis. The adduct forms monoclinic crystals, space group P2$_1$/c, a = 8.11 A, b = 17.89 A, c = 9.94 A, β = 104.8°, and z = 2. The molecule has virtually D$_{2h}$-mmm symmetry. The nickel atom occupies a center of symmetry and lies on the plane formed by the four sulfur atoms. Formation of the *trans*-bis-pyridine adduct distorts the chelate rings in Ni(dtp)$_2$ without affecting the coplanarity of the two rings. The Ni–S distance increases, the S–Ni–S angle decreases, and the S–P–S angle increases in comparison with the corresponding values in the Ni(dtp)$_2$ chelate. The distance between the nitrogen atom in the coordinated pyridine molecules and the nickel atom is 2.11 A.

Introduction

Metal chelates in which the metal ion is coordinatively unsaturated can act as electron acceptors and form adducts with neutral molecules which are electron donors. Adduct formation reactions have been found useful for a wide variety of purposes. In a recent study, a tetracoordinated nickel chelate was used as a reference acceptor molecule in the determination of thermodynamic constants for donor–acceptor reactions.[1,2] In certain liquid–liquid extractions of metal chelates, it has often been claimed that the extractability of the metal chelate into an organic phase is increased by the formation of hydrophobic adducts with neutral donor molecules.[3,4] Certain structures that have been postulated for even the simplest metal chelate adducts involved in liquid–liquid extraction have been controversial.[5,6] No attempts have been made, however, to determine the structures of such adducts, probably because of the difficulties experienced in isolating them and because many are unstable in air.

In recent investigations on the behavior of the analytically important ligand, O,O′-diethyldithiophosphoric acid (dtp), and its metal chelates, especially the nickel(II) chelate, in solution, it was observed that the metal–sulfur bond was disrupted in water or other solvents of high dielectric constant.[7,8] An X-ray crystallographic structure determination of the nickel(II) chelate of dtp showed no abnormalities in the structure that could explain this unusual behavior of Ni(dtp)$_2$ in aqueous solution.[9] Although the tetracoordinated chelate, Ni(dtp)$_2$, can be readily isolated from organic solvents, there is little doubt that, in polar solvents, the metal ion is hexacoordinated. It is possible that the solvent molecules that complete the coordination sphere of the metal ion affect the structure of the metal chelate in such a manner that the chelate rings in the resulting adduct are readily disrupted. In order to test this hypothesis, we have prepared Ni(dtp)$_2$·2py, the diadduct of Ni(dtp)$_2$ with pyridine, and have carried out a single-crystal three-dimensional X-ray structure determination on the compound.

Experimental Section

Crystal Data.—Single crystals of the adduct of Ni(dtp)$_2$ with pyridine were prepared by the addition of pyridine to a solution of Ni(dtp)$_2$ in ethanol until the solution changed from purple to pale green. Green, needle-shaped crystals of Ni(dtp)$_2$·2py were obtained in a few hours. On exposure of these crystals to air, pyridine was lost from the complex and the crystals reverted to the original purple color of Ni(dtp)$_2$. The crystals used in the X-ray work were therefore coated with a thin layer of paraffin wax to prevent the loss of pyridine.

Laue symmetry and systematic extinctions of 0k0 reflections with k odd and h0l reflections with l odd showed that the crystals belong to the monoclinic system, space group P2$_1$/c-C$_{2h}^5$. The cell dimensions were determined by superimposing sodium chloride lines on Weissenberg photographs: a = 8.11 ± 0.02 A, b = 17.89 ± 0.02 A, c = 9.94 ± 0.02 A, and β = 104.8°. No density measurements were made because of the instability of the compound. The unit cell contains two molecules and each molecule is required to have a center of symmetry.

Structure Determination and Refinement.—Intensity data (0kl and hk0) were obtained at the beginning of the structure analysis from Weissenberg photographs by means of the multiple-film technique. The approximate positions of two sulfur atoms and one phosphorus atom were obtained from Patterson syntheses. An approximate molecular structure was obtained by successive Fourier syntheses until the R factors for the (0kl) and (hk0) reflections were 0.16 and 0.15, respectively.

Three-dimensional data were obtained with a Buerger automated X-ray diffractometer. The operation of the instrument has been described previously.[9] Cu Kα radiation was used and diffractometer data were collected about the x axis from h = 0 through 5; 1340 independent reflections were obtained. Lorentz and polarization corrections were applied in the usual manner. No absorption or extinction corrections were applied (μr = 0.4). The fine needle-shaped crystals could not be cut into an appropriate shape in order to obtain intensity data around the y and z axes. Interlayer scale factors were therefore determined empirically by a comparison of F_o and F_c values.

The structure was refined by three-dimensional differential Fourier syntheses. After the first three refinement cycles with isotropic temperature factors, the value of R was 0.180. At this stage interlayer scale factors were calculated and used to obtain

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[1] L. Sacconi, G. Lombardo, and R. Ciafalo, *J. Am. Chem. Soc.*, **82**, 4182 (1960).
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[3] Y. Marcus, *Chem. Rev.*, **63**, 139 (1963).
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[7] P. S. Shetty and Q. Fernando, *J. Inorg. Nucl. Chem.*, **28**, 2873 (1966).
[8] P. S. Shetty and Q. Fernando, *ibid.*, in press.
[9] Q. Fernando and C. D. Green, *ibid.*, **29**, 647 (1967).

a new set of F_o values. Two more refinement cycles reduced R to 0.145. The scale factors were recalculated (the changes in the scale factors were very small) and a new set of F_o values was obtained; two more refinement cycles gave a value of 0.125 for R. In the final refinement, the changes in the atomic coordinates were well within their estimated standard deviations.

Table I gives the final atomic coordinates and temperature factors that were obtained. F_o and F_c are listed in Table II. The scattering factors were obtained from the "International Tables" with the values for nickel corrected for the real part of the dispersion.

TABLE I

ATOMIC COORDINATES × 10^4 [a]

	x	y	z	B, A^2
Ni	0 (0)	0 (0)	0 (0)	3.8 (0.1)
S(1)	2501 (5)	660 (1)	−461 (3)	4.4 (0.1)
S(2)	878 (5)	721 (1)	2221 (3)	4.7 (0.2)
P	2708 (5)	1106 (1)	1401 (3)	4.4 (0.1)
O(1)	2810 (19)	1993 (6)	1380 (12)	7.2 (0.7)
O(2)	4543 (16)	1012 (4)	2429 (11)	5.9 (0.6)
N	1572 (14)	−895 (4)	933 (9)	3.6 (0.4)
C(1)	1405 (36)	2446 (7)	492 (27)	9.2 (1.5)
C(2)	1947 (38)	3224 (9)	671 (19)	8.7 (1.4)
C(3)	5201 (22)	279 (7)	2945 (16)	6.9 (1.0)
C(4)	6928 (32)	374 (11)	3852 (21)	7.8 (1.2)
C(5)	1479 (18)	−1200 (5)	2146 (13)	4.6 (0.6)
C(6)	2384 (31)	−1792 (8)	2723 (18)	6.8 (1.0)
C(7)	3565 (29)	−2131 (8)	2040 (19)	8.4 (1.3)
C(8)	3730 (30)	−1820 (7)	808 (23)	5.8 (0.8)
C(9)	2718 (18)	−1206 (5)	276 (13)	4.7 (0.6)

[a] The formulas given by Cruickshank have been used to calculate the standard deviations given in parentheses: D. W. J. Cruickshank, *Acta Cryst.*, **2,** 65 (1949).

Results

The calculated values of the bond distances and bond angles are given in Tables III and IV, respectively. The projection of the structure down the z axis is shown in Figure 1 and a perspective drawing of the molecule in Figure 2. In the latter figure three planes—(1), (2), and (3)—are also shown which simplify the interpretation of the structure. No weighting factors were used in the calculation of all least-squares planes.

Plane (1) consists of the two pyridine molecules and the nickel atom. The equation of the best least-squares plane (1) is

$$0.597X + 0.635Y + 0.491Y = 0 \qquad \text{plane (1)}$$

(In the equations of best planes, the orthogonal coordinates $X = x$, $Y = y$, and Z directed along z^* are used together with absolute values of the orthogonal coordinates.) The atom C(7) shows the maximum deviation of 0.04 A from this plane. The two sulfur atoms S(1) and S(2′) are 1.81 and 1.95 A, respectively from this plane.

Plane (2) is formed by the two chelate rings and the equation of the best plane through these rings is

$$0.503X - 0.755Y + 0.421Z = 0 \qquad \text{plane (2)}$$

The phosphorus atom shows a maximum deviation of 0.001 A from this plane. Both atoms O(1) and O(2) are 1.16 A from this plane.

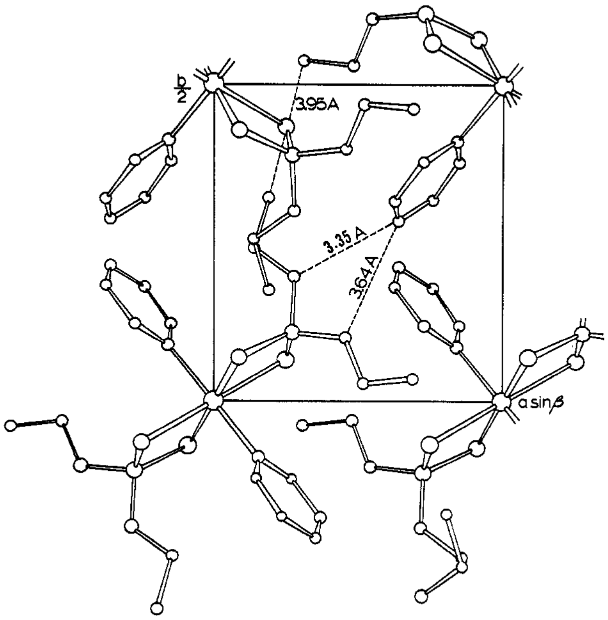

Figure 1.—Projection of the structure of $Ni[S_2P(OC_2H_5)_2]_2 \cdot 2C_5H_5N$ along the z axis.

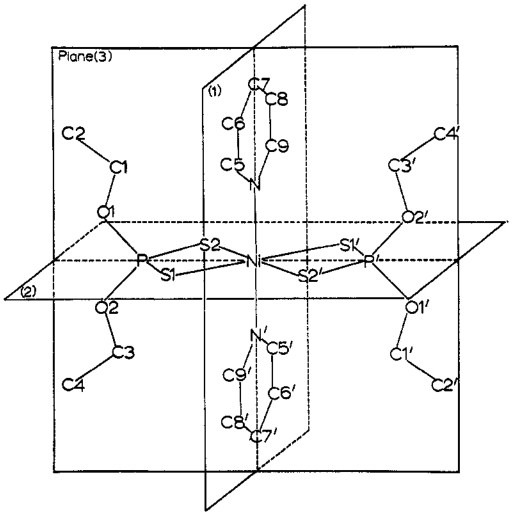

Figure 2.—Molecular structure and numbering scheme of $Ni[S_2P(OC_2H_5)_2]_2 \cdot 2C_5H_5N$.

The group of atoms C(2), C(1), O(1), P, O(2), C(3), and C(4), together with the centrosymmetrically related atoms (which are primed in Figure 2) and the nickel atom constitute plane (3). Its equation is

$$-0.622X + 0.050Y + 0.781Z = 0 \qquad \text{plane (3)}$$

The atoms with the largest deviations from this plane are C(7), C(2), and C(3), and the deviations are 0.14, 0.09, and 0.08 A, respectively. The atoms S(1) and S(2) are 1.62 and 1.64 A from this plane.

The angles between planes (1), (2), and (3) are: 88.4° (between planes (1) and (2)), 88.8° (between planes (2) and (3)), and 87.5° (between planes (1) and (3)). Hence, the symmetry of the molecule approximates to D_{2h}-mmm within the limits of error. This was confirmed by the calculation of the distances of the atoms O(1), C(1), C(2), and the mirror-related atoms O(2′), O(3′), and C(4′) from plane (1); the distances of the atoms O(1), C(1), C(2), and the mirror-

TABLE II

LIST OF F_0 VALUES ON AN ABSOLUTE SCALE

H	K	L	10FO	10FC
0	0	4	[illegible]	513
0	0	6	[illegible]	91
0	0	8	[illegible]	151
0	1	1	[illegible]	[illegible]
0	1	2	333	[illegible]
0	1	3	254	[illegible]
0	1	4	277	[illegible]
0	1	5	391	374
0	1	6	153	[illegible]
0	1	9	130	106
0	1	10	47	64
0	1	11	73	91
0	2	0	753	902
0	2	1	482	514
0	2	2	197	217
0	2	3	555	647
0	2	4	498	494
0	2	5	460	504
0	2	6	101	100
0	2	7	174	229
0	2	8	114	110
0	2	9	91	129
0	2	10	54	34
0	3	1	55	46
0	3	2	302	282
0	3	3	791	824
0	3	4	661	774
0	3	5	310	292
0	3	6	116	167
0	3	8	125	123
0	3	9	29	49
0	3	10	61	73
0	4	0	335	453
0	4	1	969	941
0	4	2	500	573
0	4	3	659	787
0	4	4	273	235
0	4	5	49	49
0	4	6	174	210
0	4	7	166	231
0	4	10	96	119
0	5	1	316	339
0	5	2	361	353
0	5	3	462	468
0	5	4	217	236
0	5	5	75	64
0	5	6	43	64
0	5	7	222	221
0	5	8	139	156
0	5	11	122	151
0	6	0	597	612
0	6	2	401	369
0	6	3	169	188
0	6	6	245	260
0	12	7	117	90
0	12	9	72	104
0	12	10	51	49
0	13	1	147	157
0	13	2	114	72
0	13	3	269	239
0	13	4	49	82
0	13	5	193	186
0	13	6	91	79
0	13	7	107	112
0	13	8	75	98
0	13	9	62	63
0	14	0	39	90
0	14	2	161	147
0	14	3	75	70
0	14	4	301	304
0	14	5	148	147
0	14	7	83	67
0	15	1	243	249
0	15	2	122	103
0	15	3	142	149
0	15	5	178	193
0	15	6	115	109
0	15	7	35	54
0	15	9	54	34
0	16	0	302	304
0	16	2	206	162
0	16	3	129	145
0	16	4	185	172
0	16	5	67	90
0	17	1	209	213
0	17	2	28	56
0	17	3	106	72
0	17	4	55	65
0	17	5	100	96
0	17	7	69	52
0	17	8	61	75
0	18	0	159	152
0	18	2	96	88
0	18	3	101	104
0	18	4	44	28
0	18	6	72	65
0	18	7	52	51
0	19	1	92	77
0	19	4	66	80
0	19	6	60	65
0	20	1	42	52
0	20	2	52	72
0	20	5	71	70
0	21	2	75	52
0	22	0	64	74
0	22	2	55	49
1	0	2	777	795
-1	0	2	1923	1671
-1	3	7	65	76
1	3	8	59	61
-1	3	8	79	67
1	3	9	166	172
-1	3	10	165	213
1	4	0	136	251
1	4	1	539	602
-1	4	1	686	657
1	4	2	791	828
-1	4	2	242	179
1	4	3	59	67
-1	4	3	392	394
-1	4	4	365	366
1	4	4	172	166
-1	4	5	86	48
1	4	5	129	127
1	4	6	103	80
-1	4	6	249	265
1	4	7	111	119
-1	4	7	119	157
1	4	8	172	170
-1	4	8	135	117
1	4	11	53	71
-1	4	11	[illegible]	[illegible]
0	6	7	55	51
0	6	8	96	77
0	6	9	67	91
0	6	10	92	124
0	7	1	261	243
0	7	2	267	294
0	7	3	339	347
0	7	4	58	35
0	7	5	54	55
0	7	6	79	116
0	7	7	326	349
0	7	8	96	93
0	7	11	105	112
0	8	0	182	211
0	8	1	254	239
0	8	2	218	213
0	8	3	90	169
0	8	5	61	50
0	8	6	330	351
0	8	8	171	203
0	8	9	27	99
0	8	10	75	64
0	9	1	460	379
0	9	2	97	70
0	9	3	139	132
0	9	4	377	380
0	9	5	108	62
0	9	6	55	40
0	9	7	253	292
0	9	8	91	92
0	9	9	99	105
0	9	10	67	77
0	9	11	44	39
0	10	1	79	55
0	10	2	51	37
0	10	3	468	512
0	10	6	159	134
0	10	6	170	182
0	10	9	36	41
0	10	10	55	42
0	11	1	271	275
0	11	2	198	193
0	11	4	173	211
0	11	5	74	16
0	11	6	198	188
0	11	7	104	85
0	11	8	206	208
0	11	9	66	88
0	12	0	192	204
0	12	1	125	92
0	12	2	202	175
0	12	3	166	200
0	12	4	243	264
0	12	5	128	85
1	0	4	622	674
-1	0	4	110	121
1	0	6	321	351
-1	0	6	119	166
1	0	8	198	185
-1	0	10	140	199
1	1	1	135	182
-1	1	1	1355	1375
1	1	2	465	383
-1	1	2	41	98
1	1	3	469	423
-1	1	3	393	350
1	1	4	232	216
-1	1	4	301	334
-1	1	5	203	191
1	1	5	569	611
1	1	6	199	217
-1	1	6	37	43
1	1	7	129	158
-1	1	7	206	247
-1	1	8	64	96
1	1	9	164	149
-1	1	9	214	239
1	1	10	46	69
-1	1	10	96	134
1	2	0	430	526
1	2	1	137	166
-1	2	1	506	485
1	2	2	414	440
1	2	3	448	438
-1	2	3	364	374
1	2	4	596	598
-1	2	4	41	55
1	2	5	66	71
1	2	6	232	251
1	2	7	127	163
-1	2	7	84	103
1	2	8	224	231
-1	2	10	111	123
1	2	11	81	112
-1	2	11	130	168
1	3	0	484	564
1	3	1	1297	1465
-1	3	1	92	132
1	3	2	362	324
-1	3	2	212	178
1	3	3	361	331
-1	3	4	408	404
1	3	4	58	59
-1	3	5	296	312
1	3	5	207	201
1	3	6	146	133
-1	3	6	88	84
1	3	7	95	91
-1	6	7	87	109
-1	6	8	239	261
1	6	10	60	60
1	7	0	187	206
1	7	1	401	438
-1	7	1	35	4
1	7	2	439	459
-1	7	2	41	30
1	7	3	21	7
-1	7	3	610	570
-1	7	4	216	245
1	7	4	141	142
-1	7	5	278	296
1	7	6	40	29
-1	7	6	95	73
1	7	7	29	16
-1	7	7	412	417
1	7	8	136	153
-1	7	8	53	49
1	7	9	27	62
-1	7	9	68	87
1	7	11	56	64
-1	7	11	56	68
1	8	0	123	84
1	5	0	441	527
1	5	1	426	464
-1	5	1	121	146
-1	5	1	109	146
1	5	2	353	330
1	5	3	377	384
-1	5	3	423	377
-1	5	4	662	724
1	5	4	195	205
-1	5	5	314	326
1	5	5	34	32
1	5	6	71	64
-1	5	6	233	261
1	5	7	165	139
-1	5	7	334	398
1	5	8	167	172
-1	5	10	141	121
1	5	11	50	55
1	6	0	92	86
1	6	1	570	610
-1	6	1	59	38
1	6	2	463	447
-1	6	2	363	290
-1	6	3	420	413
-1	6	4	572	554
1	6	4	149	153
1	6	5	196	221
1	6	6	146	120
-1	6	6	323	357
1	6	7	179	198
-1	9	9	137	153
-1	9	10	89	65
1	10	1	318	350
-1	10	1	234	226
1	10	2	59	56
-1	10	2	689	691
1	10	3	44	27
-1	10	3	369	377
-1	10	4	115	121
1	10	4	86	30
-1	10	5	195	195
1	10	5	330	322
1	10	6	176	160
1	10	6	122	160
1	10	7	176	160
-1	10	7	128	135
1	10	8	40	21
-1	10	8	117	134
-1	10	10	80	100
1	11	0	190	214
-1	11	1	349	345
1	11	2	230	233
-1	11	2	75	78
1	11	3	117	64
-1	11	3	213	231
-1	11	4	431	457
1	11	4	292	270
-1	11	5	140	134
1	11	5	158	124
1	11	6	67	38
-1	11	6	194	199
1	11	7	121	126
-1	11	7	74	16
1	11	8	156	166
-1	11	8	51	75
1	11	9	40	59
-1	11	9	66	74
1	11	10	29	42
-1	11	10	61	45
1	12	0	373	363
1	12	1	409	402
-1	12	1	143	123
1	12	2	250	212
1	12	3	137	104
-1	12	3	460	441
-1	12	4	210	203
1	12	4	87	104
1	12	5	126	128
1	12	6	51	43
-1	12	6	105	83
1	12	7	228	201
-1	12	7	139	149
1	12	8	118	136
-1	12	9	58	44
-1	17	4	135	119
1	17	4	82	44
1	17	5	150	154
-1	17	6	103	85
1	17	7	64	55
1	18	1	131	139
1	18	2	28	43
-1	18	2	121	112
-1	18	3	75	62
1	18	4	133	108
-1	18	5	77	59
1	18	6	93	100
1	18	7	60	61
1	19	0	108	125
-1	19	1	62	63
1	19	2	54	60
1	19	3	86	52
-1	19	3	158	130
1	19	5	72	67
-1	19	5	49	49
1	20	1	112	115
-1	20	1	96	87
1	20	2	74	90
-1	20	2	176	132
-1	20	2	147	132
1	20	3	43	23
1	21	0	148	117
1	21	1	62	74
-1	21	3	112	119
-1	21	4	50	39
1	22	2	79	73
2	0	2	434	393
2	0	4	685	622
-2	0	4	746	798
2	0	6	146	167
2	0	8	217	230
2	0	10	137	123
2	0	10	119	123
-2	0	10	214	289
2	1	1	670	702
2	1	2	135	136
2	1	3	407	396
2	1	4	318	292
-2	1	4	60	43
2	1	5	93	100
-2	1	5	426	403
2	1	6	163	180
-2	1	6	305	366
2	1	7	69	82
2	1	8	74	81
2	1	9	215	210
-2	1	9	163	176
-2	1	11	115	179
2	2	1	146	162
1	8	1	196	158
-1	8	1	109	51
1	8	2	319	285
-1	8	2	713	692
1	8	3	171	184
-1	8	3	64	6
-1	8	4	225	216
1	8	4	90	104
1	8	6	104	82
-1	8	6	322	322
1	8	7	112	121
1	8	8	114	126
-1	8	8	224	248
1	8	9	66	40
-1	8	10	114	113
-1	8	11	44	84
1	9	0	310	334
1	9	1	111	101
-1	9	1	679	585
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-4	9	9	154	176
-4	9	10	24	48
4	10	0	227	190
4	14	6	53	41
-4	14	6	141	139
-4	14	8	76	105
4	15	1	115	85
-4	15	1	268	256
-4	15	2	103	86
4	15	3	199	203
-4	15	3	163	137
4	15	4	92	89
-4	15	5	135	108
-4	15	6	39	63
4	16	0	134	135
4	16	1	102	97
-4	16	1	74	86
4	16	2	148	137
-4	16	2	221	221
-4	16	4	29	47
-4	16	5	58	32
-4	16	6	68	77
4	17	1	126	120
-4	17	1	190	183
4	17	2	151	132
-4	17	3	97	114
4	17	4	52	43
-4	17	4	54	73
-4	17	5	36	27
4	18	0	140	147
4	18	1	87	69
-4	18	1	45	56
4	18	2	57	39
-4	18	2	126	108
-4	18	5	112	118
4	19	1	103	93
-4	19	1	99	69
4	19	3	47	39
-4	19	4	81	63
4	20	0	47	50
-4	21	1	48	56
5	0	2	353	390
5	0	4	308	321
5	0	6	204	193
-5	0	10	100	155
5	1	2	213	194
5	1	3	349	386
5	1	5	139	156
5	1	7	150	133
-5	1	9	52	108
-5	1	11	107	113
5	2	0	30	36
5	2	2	248	282
5	2	3	165	129
5	2	4	159	179
5	2	6	109	125
-5	2	8	51	4
5	10	5	95	82
-5	10	7	53	119
-5	10	8	136	133
-5	10	9	60	49
-5	11	1	75	165
5	11	2	168	153
5	11	3	228	187
5	11	4	153	125
-5	11	6	55	95
5	11	6	136	109
-5	11	7	75	66
-5	11	8	132	176
-5	11	9	72	68
5	12	0	125	124
5	12	1	60	36
5	12	2	243	216
5	12	3	132	197
-5	12	4	66	96
5	12	4	65	61
-5	12	5	94	146
-5	12	6	93	137
-5	12	7	68	70
5	13	0	53	45
5	13	1	191	153
4	10	1	199	218
-4	10	1	294	326
4	10	2	30	17
-4	10	2	109	63
4	10	3	53	62
-4	10	3	86	73
4	10	4	83	45
-4	10	5	152	178
4	10	6	145	142
-4	10	6	129	121
4	10	7	95	96
-4	10	7	31	65
4	10	8	78	53
-4	10	8	222	239
-4	10	9	55	105
-4	11	1	101	72
4	11	2	310	306
-4	11	2	199	184
-4	11	3	115	84
4	11	4	150	118
-4	11	4	172	180
4	11	5	136	106
-4	11	5	96	78
4	11	6	83	104
4	11	7	71	71
-4	11	7	166	150
-4	11	10	52	65
4	12	1	261	267
-4	12	1	177	179
4	12	2	153	165
-4	12	2	43	32
4	12	3	62	83
-4	12	3	168	153
4	12	4	222	183
-4	12	4	107	87
-4	12	5	169	168
-4	12	6	192	164
4	12	7	65	72
-4	12	9	76	93
-4	12	10	37	52
-4	13	1	128	133
4	13	2	125	151
-4	13	2	62	67
4	13	3	324	304
-4	13	3	112	88
-4	13	4	163	169
-4	13	5	192	191
4	13	6	59	49
4	14	2	266	263
-4	14	2	298	280
4	14	4	121	121
-4	14	4	98	74
4	14	5	63	42
-4	14	5	118	101
5	2	8	60	78
-5	2	10	66	59
-5	2	11	66	100
-5	3	1	170	207
5	3	2	77	64
5	3	3	105	118
5	3	4	104	113
5	3	5	59	73
5	3	6	68	77
5	3	7	129	118
5	3	8	76	34
-5	3	11	67	73
5	4	0	198	278
-5	4	1	388	408
-5	4	2	52	29
5	4	2	204	192
5	4	3	163	181
5	4	4	65	66
5	4	6	79	51
5	4	8	132	118
-5	4	11	61	47
-5	5	1	109	127
-5	5	2	102	106
5	5	2	99	111
5	5	3	58	52
5	5	4	114	123
5	5	5	90	52
5	5	6	108	109
-5	5	9	63	46
-5	6	1	174	188
-5	6	2	76	76
5	6	3	157	176
-5	7	2	89	111
5	7	2	283	286
5	7	3	139	162
5	7	5	96	69
5	7	7	60	58
-5	7	9	136	160
5	8	2	123	159
5	8	3	97	60
5	8	4	76	36
-5	8	8	132	202
-5	8	10	85	86
5	9	1	45	17
5	9	2	89	35
5	9	4	103	66
5	9	5	144	107
5	9	6	87	71
5	9	7	74	59
-5	9	8	76	93
-5	9	9	144	202
5	10	1	49	53
5	10	3	185	187
5	10	4	142	97
-5	13	3	51	61
5	13	3	186	174
5	13	4	78	80
-5	13	7	111	120
-5	13	8	84	80
5	14	0	60	46
5	14	2	181	186
-5	14	6	105	120
5	15	1	99	62
5	15	3	112	108
-5	15	4	70	50
-5	15	6	71	23
-5	16	2	66	64
5	16	2	94	80
5	16	3	143	93
-5	16	5	68	73
-5	16	6	66	19
5	17	0	62	15
-5	17	1	59	40
-5	18	1	78	76

related atoms O(2), C(3), and C(4) from plane (2); and the distances of the atoms C(5), C(6), and the mirror related atoms C(8) and C(9) from plane (3).

Further least-squares planes were calculated through selected portions of the molecule. The equation of the plane formed by the pyridine ring is

$$0.611X + 0.611Y + 0.504Z = 0$$

The nitrogen atom of the pyridine ring shows a maximum deviation of 0.01 A from this plane. The carbon atoms C(3′) and C(1) are 3.73 and 3.65 A from this plane.

The equation of the plane formed by the atoms C(1), O(1), P, O(2), and C(3) is

$$-0.634X + 0.062Y + 0.771Z = 0.002$$

The atoms with the largest deviations from this plane are O(2), with a deviation of 0.03 A, and the two terminal carbon atoms C(2) and C(4), with deviations of 0.04 and 0.04 A.

Discussion

In Ni(dtp)$_2$, the nickel–sulfur bond distance is 2.21 A, which is the value expected for a tetracoordinated, planar, diamagnetic complex of nickel(II). In the hexacoordinated paramagnetic compound, Ni(dtp)$_2\cdot$2py, the nickel–sulfur distance is increased to 2.49 A. In other nickel(II) complexes with similar octahedral configurations, the nickel–sulfur bond lengths lie between 2.4 and 2.6 A; *e.g.*, 2.46 A in [Ni(thiourea)$_4$]Cl$_2$,[10] and an average value of 2.54 A in Ni(thiourea)$_2$(NCS)$_2$.[11]

The formation of the bis-pyridine adduct of Ni(dtp)$_2$

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TABLE III

BOND DISTANCES IN $Ni(dtp)_2 \cdot 2py$ (ESD'S IN ÅNGSTROMS; LATTICE ERRORS HAVE BEEN TAKEN INTO ACCOUNT IN THE CALCULATIONS OF THE ESD'S)

Ni–S(1)	2.49	(0.01)
Ni–S(2)	2.50	(0.01)
Ni–N	2.11	(0.01)
S(1)–P	1.98	(0.01)
S(2)–P	1.99	(0.01)
P–O(1)	1.59	(0.01)
P–O(2)	1.58	(0.01)
O(1)–C(1)	1.49	(0.03)
O(2)–C(3)	1.46	(0.02)
C(1)–C(2)	1.46	(0.02)
C(3)–C(4)	1.47	(0.03)
N–C(5)	1.34	(0.02)
N–C(9)	1.38	(0.02)
C(5)–C(6)	1.33	(0.02)
C(8)–C(9)	1.39	(0.02)
C(6)–C(7)	1.44	(0.03)
C(8)–C(7)	1.38	(0.03)

TABLE IV

BOND ANGLES (DEGREES) IN $Ni(dtp)_2 \cdot 2py$ (ESD'S IN DEGREES)

S(1)–Ni–S(2)	81.7	(0.1)
S(1)–Ni–N	90.7	(0.3)
S(2)–Ni–N	90.0	
Ni–S(1)–P	84.2	
Ni–S(2)–P	83.7	(0.2)
S(1)–P–S(2)	110.4	(0.3)
S(1)–P–O(1)	112.5	
S(2)–P–O(1)	113.4	
S(1)–P–O(2)	113.7	(0.6)
S(2)–P–O(2)	112.0	
O(1)–P–O(2)	94.0	(0.7)
P–O(1)–C(1)	121.1	(1.5)
P–O(2)–C(3)	121.4	
O(1)–C(1)–C(2)	106.6	(2.2)
O(2)–C(3)–C(4)	108.5	
C(5)–N–C(9)	117.4	(1.2)
N–C(5)–C(6)	124.0	(1.7)
N–C(9)–C(8)	122.7	
C(5)–C(6)–C(7)	119.4	(2.0)
C(9)–C(8)–C(7)	118.2	
C(6)–C(7)–C(8)	118.2	(2.0)

not only increases the nickel–sulfur bond distance, but also causes significant variations in the bond angles in the chelate ring. The S–Ni–S angle in $Ni(dtp)_2$ is decreased from 88 to 81.7° in $Ni(dtp)_2 \cdot 2py$; the S–P–S angle is increased from 103° in $Ni(dtp)_2$ to 110.4° in the adduct. It is possible to interpret these results on the basis of a simple electrostatic model. Adduct formation reduces the net positive charge on the nickel atom and increases the net negative charge on the sulfur atoms. The latter effect results in an increase in the S–P–S angle while the former effect lengthens the Ni–S distance and decreases the S–Ni–S angle. It is conceivable that if these effects become more pronounced, the chelate ring will be disrupted. The disruption of the chelate rings in $Ni(dtp)_2$ in aqueous solutions is probably brought about by water molecules that form strong coordinate bonds with the nickel atom thereby causing the Ni–S distance and the S–P–S angle to increase to such an extent that the Ni–S bonds are disrupted.

It has been shown recently by X-ray analysis that in the complex, $Te[(CH_3O)_2PS_2]$, the ligand, O,O′-dimethyldithiophosphate, is monodentate.[12] Nevertheless, with the exception of the bond angles around the phosphorus atom, the bond angles and bond lengths in the rest of the ligand do not deviate significantly from the corresponding values found in the chelate, $Ni(dtp)_2$, or its adduct, $Ni(dtp)_2 \cdot 2py$. In the tellurium complex the S–P–S angle is 106.9° and the O–P–O angle is 100.6°, whereas in the adduct, $Ni(dtp)_2 \cdot 2py$, these angles are 110.4 and 94.0°, respectively. The repulsion between the pyridine molecules and the methylene groups is probably responsible for the large decrease in the O–P–O angle in $Ni(dtp)_2 \cdot 2py$. The proximity of the methylene groups to the plane formed by the pyridine molecule is apparent from the distances of the carbon atoms C(1) and C(3′) from this plane. These distances (3.62 and 3.78 A, respectively) are slightly smaller than the sum of the van der Waals radii of the two groups, 2.0 A for the methylene group and 1.85 A for the half-thickness of an aromatic group.

The P–O–C angles (121.1 and 121.4°) in the adduct compare well with the values for the corresponding angles (119 and 122°) found in dibenzilphosphoric acid[13] and in the tellurium complex (120.8°).[12] The P–O distances in the adduct (1.58 and 1.59 A) are very similar to those found in the tellurium complex (1.57 and 1.59 A),[12] in L-serine phosphate[14] (1.608 A), and in $Ni(dtp)_2$ (1.63 A).[9] The P–S bond distances are slightly larger than the average value of 1.97 A that has been found in $Ni(dtp)_2$, but the differences are not significant. The O–C distances in the adduct (1.46 and 1.4 A), in dibenzilphosphoric acid[13] (1.464 and 1.465 A), and in L-serine phosphate (1.466 A)[14] agree within experimental error. The two independently measured bond lengths, C(1)–C(2), in the adduct show fair agreement, but are significantly shorter than the accepted value for a C–C single bond. This is attributable to experimental errors; for example, no attempt was made to correct errors caused by rotation–oscillation effects.[15]

The shortest intermolecular distance was found to be 3.35 A, between an oxygen atom and the C(7) carbon atom in pyridine. The broken lines in Figure 1 connect the methyl groups and the atoms closest to them.

The nickel–nitrogen bond in the adduct does not have any double-bond character and the bond distance (2.11 A) agrees well with the distances found in $[Ni(en)_3](NO_3)_2$ (2.120 A)[16] and in $NiYH_2 \cdot H_2O$ (2.08 and 2.03 A),[17] where Y = EDTA. Appreciably shorter nickel–nitrogen distances have been found in bis(salicylaldimine)nickel(II) (1.84 A), in bis(N-methylsalicylaldimine)nickel(II) (1.90 A),[18] and in biacetylbis-

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(mercaptoethylimine)nickel(II) (1.85 and 1.86 A).[19] Undoubtedly, the nickel–nitrogen bonds in these compounds have double-bond character.

The accuracy of this structure determination was not sufficiently high to detect any structural changes in the pyridine molecule that could be attributed to coordination with the nickel atom.

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Electronic and Circular Dichroism Spectra of Polynuclear 2-Aminoethanethiol Complexes[1]

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The cations hexakis(2-aminoethanethiolo)tricobalt(III) and hexakis(2-aminoethanethiolo)dicobalt(III)zinc(II) have been prepared in *meso* and optically active forms. The electronic and circular dichroism (CD) spectra are reported for the optical isomers. Only the terminal cobalt(III) ions contribute to the visible CD spectrum of the heterometallic complex ion. This spectrum was subtracted from that for the tricobalt(III) complex to obtain the CD spectrum of the central cobalt. Opposite configurations about the central and terminal cobalt ions are assigned from the CD spectra.

Werner's verification of his octahedral stereochemical model for coordination compounds by resolving the completely inorganic complex $[\mathrm{Co}((\mathrm{OH})_2(\mathrm{NH}_3)_4\mathrm{Co})_3]^{6+}$ climaxed the preparation and resolution of numerous cobalt(III) complexes including several novel binuclear $[(\mathrm{en})_2\mathrm{Co}\overset{\mathrm{X}}{\underset{\mathrm{Y}}{<>}}\mathrm{Co}(\mathrm{en})_2]^{n+}$ species. These binuclear complexes may be considered as combinations of two discrete monomeric compounds. If each of the latter is optically active, the binuclear product will exist in optically active and *meso* isomers.

Mathieu[2] examined Werner's $[(\mathrm{en})_2\mathrm{Co}\overset{\mathrm{X}}{\underset{\mathrm{Y}}{<>}}\mathrm{Co}(\mathrm{en})_2]^{n+}$ binuclear complexes, concluding that the absolute configurations of the polynuclear complexes were inaccessible from either the ORD or CD measurements. Recently, Garbett and Gillard[3] have reexamined the optical properties of some of these compounds and their monomeric derivatives. By comparing the binuclear compound $[(\mathrm{en})_2(\mathrm{NH}_3)\mathrm{Co}(\mathrm{NH}_2)\text{-}\mathrm{Co}(\mathrm{NH}_3)(\mathrm{en})_2]^{5+}$ with the products of its reaction with HCl, $[\mathrm{Co}(\mathrm{en})_2\mathrm{NH}_3\mathrm{Cl}]^{2+}$ and $[\mathrm{Co}(\mathrm{en})_2(\mathrm{NH}_3)_2]^{3+}$, these authors established that the L configuration of the binuclear complex corresponds to the combination of two monomeric units of L configuration.

There has been little work reported on the optical properties of new polynuclear complexes since Werner's classic work of 1915. Indeed, even the completely inorganic complex prepared by Werner is, by that author's account, too unstable to lend itself easily to more detailed study. We are reporting the results of an examination of the electronic spectra, circular dichroism, and optical rotatory dispersion of hexakis-(2-aminoethanethiolo)tricobalt(III) bromide (Figure 1), the synthesis of which was first reported by Busch and Jicha.[4]

Experimental Section

Commercially available salts and solvents of CP grade or better were used without further purification.

Preparation of Hexakis(2-aminoethanethiolo)tricobalt(III) Bromide, $[\mathrm{Co}(\mathrm{Co}(\mathrm{H_2NCH_2CH_2S})_3)_2]\mathrm{Br}_3$.—The procedures given by Busch and Jicha[4] were employed, giving identical products by either route. *Anal.* Calcd for $[\mathrm{Co}_3(\mathrm{H_2NCH_2CH_2S})_6]\mathrm{Br}_3$: C, 16.50; H, 4.58; N, 10.60; Br, 27.45. Found: C, 16.37; H, 4.40; N, 9.77; Br, 27.20.

Resolution of the Hexakis(2-aminoethanethiolo)tricobalt(III) Cation, $[\mathrm{Co}_3(\mathrm{H_2NCH_2CH_2S})_6]^{3+}$.—Three grams of silver antimony *d*-tartrate (0.0075 mole) suspended in 100 ml of water was added to a solution of 8.4 g (0.01 mole) of hexakis(2-aminoethanethiolo)tricobalt(III) bromide in 500 ml of water at 65°. The solution was heated with stirring for 0.5 hr and then filtered to remove the silver bromide. The filtrate was concentrated to about 300 ml, whereupon the mixed *meso*- and (−)-hexakis(2-aminoethanethiolo)tricobalt(III) antimonyl tartrates (the sign of the major CD peak in the low-energy absorption band is given) began to crystallize from the solution. Methanol (500 ml) was added and the mixture allowed to stand for several hours. The antimonyl tartrates were filtered and an excess of potassium iodide (10 g) was added to the filtrate to precipitate *meso*- and

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[1] This work was supported by a research grant (GM-10829-08) from the Division of General Medical Studies, Public Health Service.

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