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Square-Planar Nickel(II) in an Oxygen-Bridged Dimer

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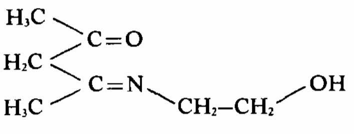
Received July 23, 1969

The structure of the complex of nickel(II) and the dianion of $CH_3-C(O)-CH_2-C(CH_3)=N-CH_2-CH_2-OH$ has been determined by a single-crystal X-ray diffraction study: the ligand (hereafter abbreviated EIA), obtained by the condensation of 2,4-pentanedione and 2-aminoethanol, forms a 1:1 complex with nickel(II). The compound crystallizes as monoclinic crystals ($a = 16.99(2)$ Å, $b = 7.45(1)$ Å, $c = 14.02(2)$ Å, and $\beta = 112.93(4)°$) of space group C2/c with eight formula units (four dimers) per unit cell ($\rho_{obsd.} = 1.61$ g/cm^3; $\rho_{calcd.} = 1.62$ g/cm^3). The structure was solved from Patterson and electron density maps and refined by least-squares methods to a conventional R value of 6.6% for 884 independent, non-zero reflections. The structure consists of oxygen-bridged dimers with square-planar coordination about the nickel; the four-membered nickel-oxygen ring is considerably bent. In the coordination sphere of nickel, the Ni–O bonds vary from 1.81 to 1.88 Å and the Ni–N distance is 1.85 Å.

Introduction

Although a large number of copper(II) compounds are associated into dimers and higher polymers through oxygen bridges, relatively few nickel(II) compounds with oxygen bridges have been reported; dimeric[2] Ni(bdhe)ClO_4 (where bdhe represents the anion of NN-bis-(2-diethylaminoethyl)-2-hydroxyethylamine), trimeric bis(2,4-pentanedionato)nickel(II),[3] tetrameric tetrakis {μ_3-methoxo-2,4-pentanedionatomethanol nickel(II)},[4] and $Ni_6(TFA)_{10}(OH)_2(H_2O)_2$ [5] (where TFA represents the anion of trifluoroacetylacetone) are examples of such compounds for which structure have been reported. Recently, the Schiff's base, I, of acetylacetone and 2-amino-ethanol was reacted with nickel(II) acetate; a complex with the empirical formula Ni(EIA)(CH_3OH), where EIA represents the dianion of I, was isolated[6] from methanol. The green, paramagnetic compound lost methanol readily in a stream of inert gas and the resulting red compound, Ni(EIA), was diamagnetic. A comparison of the properties of the methanolate to those of $[Ni(Acac)(CH_3O)(CH_3OH)]_4$ (Acac is used to represent the anion of 2,4-pentanedione) suggested a similar cubane-type structure;[4] however, the methoxide compound required more severe conditions to remove the methanol and the resulting green compound was paramagnetic. To obtain more information about the coordination of nickel and the association into polymeric units, structure determinations were initiated; the structure of the red, diamagnetic compound, Ni(EIA), is reported in this paper.


I

Experimental Section

Preparation. The method of Jager[6] was used to prepare the methanolate, Ni(EIA)(CH_3OH). To prepare the red, methanol-free compound, Ni(EIA), toluene was refluxed for several hours in a Soxhlet apparatus with anhydrous aluminum oxide in the Soxhlet thimble; the methanolate was added to the toluene in the Soxhlet apparatus and allowed to reflux; the hot solution was filtered and red, needle-like crystals formed on cooling.

Anal. Calcd. for $Ni(C_7H_{11}NO_2)$: C, 42.1; N, 7.0; H, 5.6. Found: C, 42.2; N, 6.9; H, 5.5.

Collection and Reduction of the Intensity Data. A crystal of approximate dimensions 0.1×0.1×0.4 mm was mounted on a glass fiber; optical examination and procession photographs indicated a monoclinic cell; the absence of *hkl* reflections with $h+k = 2n+1$ and the absence of $h0l$ reflections with $l = 2n+1$ indicated space group Cc or C2/c. The space group ambiguity was resolved in favor of C2/c through the Patterson map and the refinement of the structure.

The crystal was transferred to an automated Picker four-circle diffractometer; five reflections were used to refine cell parameters by a least-squares procedure. The cell parameters obtained are $a = 16.99(2)$ Å,[7] $b = 7.45(1)$ Å, $c = 14.02(2)$ Å, $\beta = 112.93(4)°$, and $V = 1634$ Å^3 25°C, molybdenum radiation, $\lambda = 0.7107$ Å).

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[1] Alfred P. Sloan Research Fellow, 1966-1968.

[2] P. Dapporto and L. Sacconi, *Chem. Comm.*, 329 (1969).

[3] J. G. Bullen, R. Mason, and P. P. Pauling, *Inorg. Chem.*, *4*, 456 (1965).

[4] J. A. Bertrand and R. I. Kaplan, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., September, 1967, No. 0-20.

[5] F. A. Cotton and B. H. C. Winquist, *Inorg. Chem.*, *8*, 1304 (1969).

[6] E. G. Jager, Z. *Chem.*, 6, 111 (1966).

[7] Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digits.

Table I. Final Positional and Thermal Parameters for Ni(EIA)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B, Å^2
Ni1	.4570(1)	.1836(2)	.3128(1)	.0022(1)	.0125(2)	.0033(1)	.0002(1)	.0007(1)	—.0001(2)	2.27(3)
O2	.5658(3)	.1200(6)	.3256(4)	.0033(3)	.0088(12)	.0038(4)	.0010(5)	.0005(3)	.0005(6)	2.69(14)
N3	.5007(4)	.2371(9)	.4526(5)	.0033(4)	.0186(23)	.0031(5)	.0017(6)	.0008(4)	.0001(8)	2.28(17)
O4	.3464(3)	.2339(8)	.2876(5)	.0029(3)	.0240(21)	.0042(4)	.0012(5)	.0012(3)	.0003(7)	3.36(16)
C5	.4990(5)	.3029(15)	.6213(5)	.0053(5)	.0023(23)	.0014(5)	.0036(11)	.0010(4)	—.0014(12)	4.05(25)
C6	.4578(6)	.2804(12)	.5061(7)	.0047(6)	.0082(23)	.0049(7)	.0033(8)	.0019(6)	.0026(9)	2.85(21)
C7	.3665(6)	.3046(15)	.4592(7)	.0050(6)	.0161(22)	.0044(7)	.0030(11)	.0018(5)	—.0007(14)	3.76(24)
C8	.3182(6)	.2805(12)	.3569(8)	.0046(6)	.0152(26)	.0046(7)	.0025(9)	.0026(6)	.0026(11)	3.20(23)
C9	.2227(5)	.3140(18)	.3152(6)	.0034(5)	.0453(32)	.0042(6)	.0061(13)	.0013(4)	.0038(16)	5.04(30)
C10	.5952(5)	.2036(12)	.4994(6)	.0024(4)	.0063(18)	.0065(7)	.0006(8)	—.0002(4)	.0006(11)	3.06(21)
C11	.6277(5)	.2162(11)	.4140(6)	.0035(4)	.0091(21)	.0048(6)	—.0010(8)	.0016(5)	.0001(9)	3.31(23)

Anisotropic thermal parameters are expressed in the form $\exp-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$. The B values given in the last column are those obtained in the final isotropic refinement before the anisotropic refinement.

The calculated density of 1.62 g/cm^3 for eight formula units (four dimers) per unit cell agrees well with the observed density of 1.61 g/cm^3 measured by the flotation method using a mixture of carbon tetrachloride and 1,3-diiodopropane.

The X-ray intensity measurements were made, using the same crystal as used for the cell measurements, with molybdenum radiation. The intensities were measured with a scintillation counter mounted 21 cm from the crystal; the intensities were collected by the θ–2θ scan technique with a takeoff angle of 1.6° and a scan rate of 1° min^{-1}. Below $2\theta = 32°$, a symmetrical scan of 1.5° was taken about the calculated position for each reflection; above $2\theta = 32°$, a symmetrical scan of 2° was used. Stationary background counts of 15 and 20 seconds for the 1.5 and 2° scans, respectively, were taken at the beginning (bgdl) and at the end (bgd2) of the scan. Calibrated copper attenuators were used in the collection of data; the attenuators were calibrated by collecting intensities on 30 different reflections of various magnitudes. The threshold point was set so that the counting rate would not exceed 10,000 counts/second. The pulse height analyzer was set for approximately a 90% window, centered on the Mo Kα peak. A total of 1769 reflections were collected, including the equivalent *hk0* and *hk0* reflections which were later averaged. Corrected intensities (CI) were obtained by substracting three times the actual measured background from the total integrated peak count (CT),

$$\mathrm{CI} = \mathrm{CT}-3(\mathrm{bgdl}+\mathrm{bgd2})$$

The factor of three in the calculation arises from the peak scan time being three times as long as the background counting time. The corrected intensities were assigned standard deviations according to the formula[8]

$$\sigma(\mathrm{I}) = [\mathrm{CT}+0.25(t_c/t_b)^2(\mathrm{bgdl}+\mathrm{bgd2})]^{1/2}$$

where t_c is the scan time and t_b is the counting time of each background (either bgdl or bgd2). A total of 884 reflections were accepted as statistically above background on the basis that $\sigma(\mathrm{I})/\mathrm{CI}$ be less than 0.18. The intensities were corrected for Lorentz and polarization effects but were not corrected for absorption (calculated linear absorption coefficient, μ, is 23.1 cm^{-1}); for the 0*k*0 reflections, rotation around Φ did not cause more than 5% variation in intensity. Periodic checks of a standard reflections showed no significant variation.

Solution and refinement of Structure

Computations were carried out on the Burroughs 5500 computer and on the Univac 1108 computer; programs employed included modified versions of F. L. Carter's program for calculating diffractometer settings, Zalkin's FORDAP Fourier summation program, the Busing-Martin-Levy ORFLS and ORFFE least-squares and function and error programs, and various locally written programs.

A three-dimensional Patterson function was calculated using the 884 unique reflections. The distribution of peaks on the Patterson map was consistent with the centrosymmetric space group, C2/c.

Positions for the nickel atoms and for the atoms coordinated to nickel were obtained from the Patterson function; a subsequent electron calculation phased on these atoms revealed the positions of all carbon atoms. After one cycle of least-squares refinement of the scale factor alone, a second cycle varying scale factor and atomic coordinates, and four further cycles in which scale factor, coordinates, and isotropic temperature factors were allowed to vary, the refinement converged to a conventional R_1 value $(\Sigma||F_o|-|F_c||/\Sigma|F_o|)$ of 0.079. At this point with all reflections weighted at unity, the value of R_2 $(\{\sum_i w_i(|F_o|-|F_c|)^2/\sum_i w_i(|F_o|)^2\}^{1/2})$ was 0.084. After further refinement with anisotropic temperature factors and a weighting scheme based on counting statistics ($w_i = 4(\mathrm{CI})/\sigma(\mathrm{I})^2$, values of 0.079 and 0.044 were obtained for R_1 and R_2 respectively. A difference electron density map at this point revealed peaks for ten of the eleven hydrogen atoms of the ligand; a position was calculated for the eleventh hydrogen— the one attached to the C7 carbon— assuming a C–H distance of 1.06 Å. All hydrogen atoms were introduced into the structure factor calculations at the coordinates listed in Table V, and each hydrogen atom was

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[8] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

Table II. Observed and Calculated Structure Factors (Electrons) for Ni(EIA)

H	K	FO	FC
L= 0			
4	0	31	29
6	0	29	28
8	0	28	27
10	0	52	52
12	0	39	39
14	0	16	16
3	1	24	21
7	1	32	31
9	1	22	23
11	1	21	21
13	1	10	10
0	2	205	210
2	2	73	69
4	2	19	17
6	2	36	36
10	2	29	28
12	2	24	25
14	2	12	12
1	3	76	76
3	3	44	43
7	3	36	37
9	3	33	36
11	3	39	41
13	3	22	23
0	4	27	24
2	4	8	7
6	4	27	27
8	4	17	16
10	4	10	9
1	5	32	34
3	5	22	19
5	5	9	1
7	5	10	8
9	5	13	11
11	5	23	23
13	5	17	17
0	6	25	21
2	6	23	23
4	6	13	13
8	6	13	10
10	6	18	17
12	6	20	17
14	6	15	13
3	7	10	1
0	8	22	22
2	8	16	16
4	8	11	5
8	8	11	3
10	8	13	9
12	8	17	13
14	8	14	11
1	9	11	4
13	9	13	7
2	10	11	6
L= 1			
H	K	FO	FC
-13	1	21	20
-11	1	43	46
-9	1	94	93
-7	1	55	56
-5	1	32	30
-3	1	13	15
3	1	15	12
5	1	24	24
7	1	48	46
9	1	36	35
11	1	38	39
13	1	34	35
-14	2	13	10
-12	2	24	23
-10	2	48	46
-8	2	46	46
-6	2	32	30
-4	2	20	16
-2	2	104	111
0	2	81	84
2	2	65	63
4	2	28	28
6	2	17	17
8	2	16	17
10	2	27	25
12	2	25	25
14	2	15	15
-9	3	20	18
-7	3	8	8
-3	3	23	20
-1	3	13	11
1	3	42	40
5	3	24	25
7	3	39	41
9	3	9	6
11	3	16	16
13	3	14	13
-14	4	16	14
-12	4	23	24
-10	4	36	37
-8	4	28	29
-6	4	21	23
-4	4	11	10
-2	4	71	71
0	4	61	60
2	4	50	47
4	4	36	38
6	4	29	32
10	4	27	28
12	4	30	31
14	4	20	21
-13	5	12	11
-11	5	20	18
-9	5	21	21
-7	5	17	14
-5	5	9	4
-3	5	19	19
-1	5	19	19
1	5	19	19
3	5	27	27
7	5	15	17
9	5	11	8
11	5	11	8
13	5	13	11
-12	6	10	8
-10	6	11	9
-2	6	25	28
0	6	18	17
2	6	13	8
4	6	15	14
6	6	16	19
10	6	14	13
12	6	16	14
14	6	11	10
-13	7	14	12
-11	7	18	18
-9	7	21	23
-7	7	15	13
-5	7	11	4
-3	7	11	8
-1	7	15	14
1	7	23	21
3	7	26	24
5	7	14	12
11	7	17	14
13	7	20	19
2	8	11	11
-9	9	12	12
1	9	14	9
13	9	12	9
2	10	14	11
4	10	12	10
L= 2			
H	K	FO	FC
-12	0	36	36
-10	0	68	67
-8	0	117	120
-6	0	50	50
-4	0	13	10
-2	0	29	29
0	0	42	38
2	0	35	33
4	0	64	62
6	0	38	39
10	0	39	39
12	0	19	21
14	0	22	23
-11	1	31	30
-9	1	38	37
-7	1	33	34
-5	1	7	5
-1	1	54	53
1	1	16	24
3	1	25	21
5	1	20	20
11	1	13	12
13	1	11	8
-12	2	16	17
-10	2	33	33
-8	2	71	68
-6	2	31	30
-4	2	10	8
-2	2	44	42
0	2	14	9
2	2	19	20
4	2	34	32
6	2	36	37
10	2	30	30
12	2	16	17
14	2	17	16
-13	3	18	17
-11	3	47	48
-9	3	60	59
-7	3	54	55
-5	3	30	29
-1	3	70	69
1	3	51	51
3	3	57	56
5	3	52	54
7	3	24	24
9	3	9	9
11	3	31	30
13	3	20	20
-10	4	12	12
-4	4	12	9
-2	4	41	39
0	4	21	22
2	4	18	19
4	4	17	13
6	4	10	13
10	4	14	10
-13	5	10	12
-11	5	25	26
-9	5	31	32
-7	5	28	28
-5	5	25	24
-3	5	11	10
-1	5	27	25
1	5	26	27
3	5	39	42
5	5	55	52
7	5	22	24
11	5	28	27
13	5	17	13
-12	6	14	12
-10	6	18	20
-8	6	27	25
-6	6	19	19
-2	6	15	11
0	6	22	20
2	6	33	35
4	6	39	39
6	6	16	14
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14	6	16	13
-5	7	10	4
5	7	11	17
11	7	12	10
-12	8	11	7
-8	8	15	16
-6	8	12	11
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4	8	27	26
6	8	15	15
14	8	13	10
1	9	12	9
3	9	13	8
5	9	13	4
L= 3			
H	K	FO	FC
-11	1	29	29
-9	1	61	60
-7	1	66	66
-5	1	38	36
-3	1	14	14
-1	1	36	34
1	1	69	67
3	1	55	53
5	1	44	44
7	1	35	33
9	1	9	5
13	1	10	6
-12	2	14	13
-10	2	53	51
-8	2	52	50
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-4	2	38	36
-2	2	26	21
0	2	18	16
2	2	46	44
4	2	29	28
6	2	30	31
8	2	14	13
10	2	10	8
14	2	14	14
-9	3	12	12
-7	3	22	23
-5	3	14	12
-3	3	22	22
-1	3	32	31
1	3	25	25
3	3	19	23
5	3	15	15
7	3	13	13
9	3	16	13
11	3	11	7
-10	4	43	42
-8	4	50	51
-6	4	47	50
-4	4	53	55
-2	4	36	35
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2	4	40	51
4	4	49	51
6	4	39	41
8	4	14	11
12	4	17	13
14	4	19	17
-11	5	10	5
-9	5	15	12
-7	5	18	15
-5	5	19	19
-3	5	8	2
-1	5	15	16
1	5	11	11
3	5	24	21
5	5	28	26
7	5	14	11
9	5	15	11
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-4	6	30	32
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2	6	21	24
4	6	26	30
6	6	18	19
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7	7	15	15
-7	9	11	9
3	9	15	18
5	9	15	15
4	10	13	6
6	10	12	7
L= 4			
H	K	FO	FC
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-12	0	8	5
-10	0	33	32
-8	0	83	83
-6	0	68	67
-4	0	71	72
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0	0	10	11
2	0	47	49
4	0	27	29
6	0	43	42
8	0	64	64
10	0	15	14
14	0	17	18
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1	1	8	6
3	1	19	18
5	1	14	14
7	1	24	23
9	1	22	21
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1	3	23	21
3	3	49	48
5	3	39	37
7	3	41	42
9	3	36	35
11	3	21	19
0	4	15	15
2	4	25	26
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-11	5	12	15
-9	5	22	22
-7	5	29	32
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-1	5	11	12
1	5	22	24
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4	6	21	22
6	6	20	21
8	6	13	14
-11	7	11	10
-3	7	14	12
-8	8	16	14
-6	8	23	25
-4	8	22	24
4	8	16	16
6	8	14	14
-7	9	12	9
-5	9	11	13
L= 5			
H	K	FO	FC
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-9	1	21	20
-7	1	19	20
-5	1	32	33
-3	1	54	52
-1	1	50	48
1	1	45	40
3	1	30	29
5	1	41	41
7	1	78	78
9	1	69	69
11	1	17	16
-14	2	15	16
-12	2	16	16
-8	2	24	22
-6	2	28	30
-4	2	24	22
-2	2	50	50
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4	2	13	11
6	2	40	39
8	2	37	36
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12	2	10	4
14	2	11	6
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-9	3	9	9
-7	3	11	8
-5	3	16	16
-3	3	21	22
1	3	38	36
3	3	26	27
5	3	13	11
7	3	28	28
9	3	22	22
-14	4	21	22
-12	4	23	24
-8	4	30	33
-6	4	39	41
-4	4	35	38
-2	4	46	48
0	4	14	13
4	4	16	19
6	4	36	36
8	4	30	30
10	4	23	23
-9	5	9	2
-7	5	15	14
-5	5	21	21
-3	5	20	18
-1	5	16	16
1	5	16	17
5	5	13	14
7	5	11	7
9	5	10	8
-14	6	12	11
-12	6	15	11
-8	6	15	19
-6	6	15	16
-4	6	13	14
-2	6	15	17
6	6	13	13
8	6	10	11
10	6	11	7
-13	7	14	11
-7	7	19	21
-5	7	28	29
-3	7	25	24
-1	7	15	12
5	7	17	15
7	7	15	15
9	7	14	12
-6	8	11	9
-4	8	13	9
-5	9	13	13
-3	9	12	11
-6	10	14	13
-4	10	13	11
L= 6			
H	K	FO	FC
-14	0	40	39
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-10	0	11	15
-8	0	8	1
-6	0	24	15
-4	0	77	76
-2	0	103	106
0	0	91	89
2	0	15	14
6	0	37	37
8	0	71	71
10	0	37	37
12	0	12	13
-11	1	12	13
-5	1	13	13
-3	1	33	34
-1	1	34	33
1	1	22	27
5	1	16	16
7	1	27	29
9	1	16	16
11	1	12	10
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0	2	44	42
6	2	19	17
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10	2	27	19
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-11	3	23	23
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-5	3	36	38
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-1	3	51	52
1	3	34	34
5	3	26	26
7	3	46	50
9	3	27	28
11	3	17	18
0	4	10	10
2	4	13	12
6	4	11	9
-13	5	13	12
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-3	5	34	36
-1	5	23	23
1	5	10	6
5	5	14	16
7	5	26	28
9	5	12	13
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-4	6	25	24
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0	6	18	17
6	6	16	13
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10	6	13	12
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-6	8	12	10
-4	8	18	17
-2	8	17	17
0	8	14	10
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-5	9	12	10
-3	9	12	6
-1	9	11	6
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-11	1	35	36
-9	1	23	22
-5	1	33	33
-3	1	83	81
-1	1	89	90
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-1	3	18	19
1	3	12	14
3	3	12	11
5	3	13	14
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-4	6	17	19
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0	6	10	5
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-9	7	11	8
-5	7	14	12
-3	7	18	19
-1	7	19	20
1	7	16	12
11	7	14	13
-1	9	11	8
1	9	12	5
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-8	0	17	18
-4	0	36	36
-2	0	43	44
0	0	64	66
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8	0	19	19
10	0	24	26
12	0	18	21
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-9	1	22	21
-7	1	10	12
-5	1	12	12
-3	1	28	26
-1	1	40	38
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3	1	15	14
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-4	6	11	7
-2	6	12	13
0	6	19	19
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10	6	13	13
12	6	15	14
-5	7	10	5
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-10	8	13	14
-8	8	12	8
0	8	12	9
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-11	1	54	54
-9	1	42	40
-7	1	8	7
-5	1	13	14
-3	1	29	29
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-7	7	12	10
1	7	19	20
3	7	19	23
5	7	11	13
3	9	12	12
2	10	12	6
L=10			
	K	FO	FC
-12	0	39	41
-10	0	51	51
-8	0	46	46
-6	0	50	50
-4	0	26	26
-2	0	31	31
0	0	37	37
2	0	22	20
4	0	28	31
6	0	15	15
10	0	12	9
14	0	15	15
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-7	1	16	17
-5	1	9	7
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1	1	15	11
3	1	10	7
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2	8	14	14
4	8	14	15
4	10	13	3
L=11			
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3	1	13	8
5	1	30	30
2	2	15	16
4	2	16	16
-5	3	29	30
5	3	14	11
0	4	15	15
2	4	20	23
4	4	19	21
L=12			
H	K	FO	FC
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-2	0	12	7
4	0	28	32
-1	1	13	9
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3	3	17	19
5	3	21	20
-5	5	17	18
-3	5	15	11
3	5	15	16
5	5	16	16
L=13			
H	K	FO	FO
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-3	1	34	34
-1	1	19	19
3	1	12	7
5	1	18	18
-4	2	20	18
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-4	4	21	20
-2	4	20	19
4	4	16	14
-5	5	13	12
-3	5	12	9
-1	5	13	10

assigned the isotropic temperature factor of the adjacent carbon; further refinement of all parameters except hydrogen coordinates and hydrogen temperature factors converged to $R_1 = 0.066$ and $R_2 = 0.034$. In the final cycle of refinement, there was no parameter shift greater than 1/10 of one esd. A final difference Fourier had no positive maxima greater than 0.5 e/Å.[3]

In the structure factor calculations, the scattering factors tabulated by Ibers[9] were employed for all atoms.

The positional and thermal parameters derived from the last cycle of least-squares refinement are presented in Table I; the observed and calculated structure factors for the 884 reflections are given in Table II.

Description of the Structure

The molecular structure is shown in Figure 1; Table III presents selected intramolecular distances and angles. The structure consists of discrete dimers; a two-fold axis relates the two halves of each dimer.

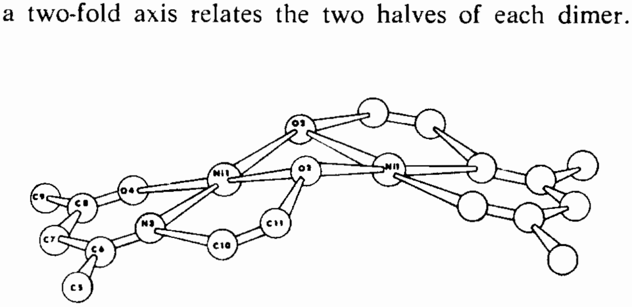

Figure 1. A perspective drawing of the molecular structure of Ni(EIA).

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[9] J. A. Ibers in « International Tables for X-Ray Crystallography », Vol, 3, The Kynoch Press, Birmingham, England, 1962.

The four-membered ring of nickel and oxygen is distinctly bent; the dihedral angle between the two Ni–O–Ni planes of the ring is 43° and the dihedral angle between the two O–Ni–O planes of the ring is 39°.

Table III. Intramolecular Distances, and angles for Ni(EIA)

Intramolecular Distances, Å Atoms	 Distance	Bond Angles, Deg. Atoms	 Angle
Ni1—Ni1′	2.690(4)	Ni1—O2—Ni1′	92.2(2)
Ni1—O2	1.849(6)	O2—Ni1—O2	80.4(3)
Ni1—O2′	1.884(6)	O2—Ni1—N3	88.8(3)
Ni1—N3	1.849(7)	O2′—Ni1—O4	94.0(3)
Ni1—O4	1.812(6)	N3—Ni1—O4	96.9(3)
O2—C11	1.464(8)	Ni1—O2—C11	108.5(4)
O4—C8	1.288(9)	Ni1′—O2—C11	122.8(4)
N3—C6	1.276(9)	N3—C10—C11	107.7(7)
N3—C10	1.50(1)	O2—C11—C10	106.1(6)
C5—C6	1.50(1)	Ni1—N3—C10	110.3(6)
C6—C7	1.44(1)	C10—N3—C6	123.0(7)
C7—C8	1.36(1)	Ni1—N3—C6	126.4(6)
C8—C9	1.52(1)	N3—C6—C7	121.5(8)
C10—C11	1.50(1)	C6—C7—C8	124.5(8)
		C7—C8—O4	125.6(8)
		Ni1—O4—C8	124.8(5)
		O4—C8—C9	114.3(8)
		C7—C8—C9	120.1(9)
		N3—C6—C5	121.9(8)
		C5—C6—C7	116.6(8)

Dihedral Angles, Deg. Atoms	 Angle
Ni1—O2—Ni1′ Ni1—C11—O2	54.3(5)
Ni1—O2—Ni1′ Ni1′—O2—C11	66.2(6)
Ni1—N3—O4 C6—C7—C8	2.5(12)
Ni1—O2—Ni1′ Ni1—O2—Ni1′	43.0(4)
O2—Ni1—O2′ O2—Ni1′—O2′	38.8(4)

Table IV. Equations of Atomic Planes and Distances(A) of Atoms from these Planes

(a) Equation of the Least-Squares Plane[a] of the Coordination Sphere (Ni1, O2, O2′, N3, O4):

$$0.253X+0.947Y-0.197Z = 2.030$$

Ni1	−0.001	O2′	0.015	O4	−0.014
O2	−0.014	N3	0.014		

(b) Equations of the Least-Squares Plane[a] of the Six-membered Ring Carbon Atoms (C5, C6, C7, C8, C9):

$$0.190X+0.971Y-0.145Z = 2.036$$

C5	−0.010	C7	0.017	C9	−0.005
C6	0.004	C8	−0.006		

[a] Direction cosines of the plane refer to the orthogonal axis system. A, b, c*; all atoms weighted at unity.

The coordination around nickel is planar; for the nickel and the four coordinated atoms, the greatest distance of any atom from their least-squares plane, Table IV, is 0.01 Å. The bond angles at nickel vary from 80.4° for the O–Ni–O angle of the four-membered ring to 96.9° for the O–Ni–N angle of the six-membered ring; the O–Ni–N angle in the five-membered chelate ring is 88.8° and the non-cyclic O–Ni–O angle is 94.0°. The Ni–O bond lengths are 1.81 for the oxygen of the six-membered ring, 1.85 for the oxygen common to the four- and five-membered rings, and 1.88 for the oxygen of the four-membered ring; the Ni–N distance is 1.85 Å. The molecules are packed together in such a way that the closest intermolecular approach to the nickel atom is by a methyl group (3.9 Å).

Table V.

Atom	Adjacent Carbon Atom	x	y	z
H1	C5	.57	.40	.63
H2	C5	.54	.17	.67
H3	C5	.49	.38	.67
H4	C7	.334	.340	.508
H5	C9	.20	.26	.37
H6	C9	.20	.46	.27
H7	C9	.62	.32	.55
H8	C10	.60	.06	.51
H9	C10	.64	.36	.39
H10	Cl1	.68	.12	.42
H11	Cl1	.19	.26	.25

The coordination around the bridging oxygen is pyramidal with bond angles of 92.2, 108.5, and 122.8°; dihedral angles between the Ni–O–Ni plane and the two Ni–O–C planes are 54° (for the nickel within the same five-membered chelate ring) and 66°.

The carbons within the six-membered ring and the methyl carbons on the six-membered ring are essentially planar with none of the atoms deviating more than 0.02 Å from their least-squares plane, Table IV; the dihedral angle between the carbon plane and the O–Ni–N plane of the same chelate rings is only 2°. Although there is a difference (1.44, 1.36 Å) between the two C–C bond distances within the six-membered chelate ring, both distances are considerably less than the normal C–C single-bond distance (1.54 Å). As a further indication of delocalization within the ring, the C–O (1.29 Å) and C–N (1.28 Å) distances of this ring are significantly shorter than the C–O (1.46 Å) and C–N (1.50 Å) distances of the five-membered ring.

Although hydrogen atoms were not refined, the observed positions of the hydrogens on the five-membered ring indicate that the hydrogens are staggered by about 30°.

Discussion of the Structure

The structure is very similar to that found[10] for the d^8 rhodium(I) dimer, $[Rh(CO)_2Cl]_2$; the rhodium complex has a dihedral angle of 56° between the two Cl–Rh–Cl planes while $[Ni(EIA)]_2$ has a dihedral angle of 39° between the two O–Ni–O. Both complexes have planar coordination about the metal and both are diamagnetic. The cause of the dihedral angle in the nickel dimer appears to be related to the steric limitations of the ligand; however, no ana-

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[10] L. F. Dahl, C. Martell, and D. L. Wampler, *J. Amer. Chem. Soc.*, 83, 1761 (1961).

logous steric limitations are present in the complex of rhodium(I). As suggested for the rhodium dimer, the dihedral angle may be related to direct metal-metal interactions; however, the nickel-nickel distance, 2.69 Å, is greater than that in nickel metal, 2.50 Å, or that in nickel arsenide, 2.52 Å.

The structure is distinctly different from that found for the copper(II) complex of the Schiff's base formed from acetylacetone and 3-aminopropanol, Cu(PIA)[11] where PIA represents the dianion of $CH_3-C(O)-CH_2-C(CH_3)=N-(CH_2)_3-OH$. Although dimeric, Cu(PIA) contains a four-membered copper-oxygen ring which is completely planar and the coordination around the bridging oxygens is completely planar; π-bonding, involving the copper d_{xz}, d_{yz} orbitals and the oxygen p_z orbitals, appears to be important in Cu(PIA). Nickel(II), with one less electron per metal, would be expected to show even stronger π-bonding since the highest energy electrons in the copper structure are assumed to occupy π^* orbitals. However, the steric limitations of the 2-aminoethanol ligand prevent such a planar arrangement- the Ni–O–C angle within the five-membered ring would have to be at least 120° to give a planar arrangement of Ni1, Ni1′, and C11 about O2. The value found for the Ni1–O2–C11 angle, 109°, is indicative of sp^3 hybridization of the oxygen orbitals.

Even though sp^3 hybridization of the oxygen orbitals prevents planar coordination about the bridging oxygen, it should be possible for the metal-oxygen ring to be planar. In $[Ni(bdhe)]_2^{2+}$, in which the coordination about nickels is trigonal-bipyramidal, the nickel-oxygen four-membered ring is planar; however, construction of a molecular model shows that, with EIA, square-planar coordination around nickel and a planar nickel-oxygen ring would create considerable strain within the chelate ring. For a square-planar d^8 system, there is a large ligand-field stabilization and the strain is relieved by bending the four-membered ring rather than altering the coordination.

In the corresponding copper(II) complex, Cu(EIA),[12] the metal-oxygen four-membered ring shows much less bending than in the nickel compound (the dihedral angle between the Cu–O–Cu planes is only 13°); however, the coordination around copper is no longer square-planar the nitrogen has moved considerably out of the plane which includes the copper and the bridging oxygens. In addition, two of the copper « dimers » are joined by Cu–O bonds to form a cubane-type of complex in which the copper is five-coordinate.

The nature of the 1:1 adduct by Ni(EIA) and methanol is of considerable interest but the crystals are unstable and several attempts to collect diffraction data have been unsuccessful. The adduct could be formed by the addition of methanol perpendicular to the coordination plane of the nickel to give square-pyramidal coordination about nickel, retaining the dimeric structure; the coordination of methanol could also produce a dimer with trigonal-bipyramidal coordination about nickel, similar to that in $[Ni(bdhe)]_2^{2+}$. The relatively weak field associated with oxygen ligands could produce a high-spin five-coordinate complex consistent with observations. An alternate possibility would be the addition of methanol in the same way, accompanied by the association of dimers into tetramers with a cubane-type structure; this type of structure has been found for $Ni(Acac)(CH_3O)(CH_3OH)$[4] and for Cu(EIA).[12] The similarity of properties of $Ni(EIA)(CH_3OH)$ and the methoxide complex favor such a structure, but the ease with which the compound reversibly adds methanol makes the tetrameric structure questionable. Further attempts are being made to collect diffraction data on the methanolate crystals.

Acknowledgments. This work was supported by NSF Grants GP-7406 and GP-8475. Funds from the Quality Improvement Program of the State of Georgia for the purchase of X-ray diffraction equipment are gratefully acknowledged; the help of the Rich Electronic Computer Center of Georgia Institute of Technology with computations is appreciated.

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(11) J. A. Bertrand and J. A. Kelley, to be published.

(12) J. A. Bertrand, J. A. Kelley, and C. E. Kirkwood, *Chem. Comm.*, 1329 (1968).