is not hydrogen bonded to the water but to the coordinated bromide of another molecule.

The coordinated bromide ion shows normal contact distances to the nitrogen atoms; their average of 3.52 Å was compared to the sum of the van der Waals radii[5] of 3.45 Å. The distance Br(1)′–Ni is 2.79 Å which is significantly longer than that found in the octahedral complex tetrapyridinenickel(II) dibromide[6] where the Ni–Br distance was found to be 2.58 Å. The distance is also longer than in the five-coordinate nickel(II) complex $NiBr_2 \cdot triars$[7] (triars = triarsine = $(CH_3)_2As(CH_2)_3As(CH_3)(CH_2)_3As(CH_3)_2$) which is a distorted square-pyramidal, diamagnetic complex of nickel(II) having an Ni–Br distance of 2.69 Å for the apical bromide ion. It should also be noted that the basal plane field strength is enhanced by the short distance Ni–N(1) of 1.81 Å which is about 0.1 Å shorter than the other three normal Ni–N distances of the complex.

The observation that $Ni(CR)Br_2 \cdot H_2O$ is diamagnetic can now be more reasonably explained, especially in the light of the crystal field model calculated for square-pyramidal nickel(II) complexes by Ciampolini.[8] Specifically, it was found that spin pairing is favored by a decrease in the axial field strength and an increase in the basal plane field strength. On the other hand, spin pairing is disfavored by distortion of the metal atom out of the basal plane toward the axial ligand. Apparently in this case, a combination of diminished axial field strength and increased basal plane field strength promotes spin pairing over and above the effect of out-of-plane distortion.

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[6] A. S. Antsyshkina and M. A. Porai-Koshits, *Kristallografiya*, **3**, 676 (1958).

[7] B. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 415 (1960).

[8] M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966).

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Conformations and Crystal Packing. The Crystal and Molecular Structure of *trans*-Bis(2,4-pentanedionato)dipyridinenickel(II), $Ni(AA)_2(py)_2$

BY R. C. ELDER

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The crystal structure of *trans*-bis(2,4-pentanedionato)dipyridinenickel(II), $Ni(AA)_2(py)_2$, was determined by X-ray methods using an automated diffractometer to collect 1641 independent data. The compound crystallizes in the monoclinic space group $P2_1/c$. There are two molecules in the unit cell with $a = 8.321 \pm 0.003$, $b = 9.649 \pm 0.015$, $c = 14.723 \pm 0.025$ Å, and $\beta = 117.06 \pm 0.01°$. The structure was refined by full-matrix least squares to a conventional R factor for nonzero data of 0.050 and wR (all data) of 0.056. The molecule which is required to lie on a center of symmetry has nearly D_{2h} symmetry, with the two pyridine ligands in an eclipsed configuration. All atoms including hydrogen were refined. Packing calculations on this compound and *trans*-$Co(AA)_2(py)_2$, which has a staggered configuration, account for the folding of the acetylacetone ligands and indicate that the configurational differences are the result of crystal forces and not metal–ligand π bonding.

Introduction

The determination of the crystal structure of *trans*-bis(2,4-pentanedionato)dipyridinecobalt(II),[1] $Co(AA)_2(py)_2$, revealed that the two *trans*-pyridine ligands are staggered with respect to one another. Symmetry arguments[2] based on unit cell and space group data indicate that such a configuration is not possible for *trans*-bis(2,4-pentanedionato)dipyridinenickel(II), $Ni(AA)_2(py)_2$, and suggest instead an eclipsed configuration. If $d\pi$–$p\pi$ back-bonding were important in these compounds, the staggered configuration would be ideal, for it makes possible donation from two filled metal d orbitals, one for each pyridine ligand, whereas the eclipsed structure leads only to use of a single metal orbital to form bonds to both pyridine ligands.

Several experiments have been interpreted to show evidence of π bonding between metals and pyridine[3–5] although some of these claims have been disputed[6] and other experiments[7] have been found to show no evidence for π bonding to aromatic heterocycles. This paper reports a single-crystal X-ray analysis which was undertaken to provide detailed information on the structure of $Ni(AA)_2(py)_2$ and the results of a series of packing calculations which were performed to learn if the con-

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[1] R. C. Elder, *Inorg. Chem.*, **7**, 1117 (1968).

[2] J. T. Hashagen and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **87**, 2821 (1965).

[3] P. Ford, D. P. Rudd, R. Gaunder, and H. Taube, *ibid.*, **90**, 1187 (1968).

[4] J. E. Falk, J. N. Phillips, and E. A. Magnusson, *Nature*, **212**, 1531 (1966).

[5] J. deO. Cabral, H. C. A. King, T. M. Shepherd, and E. Koros, *J. Chem. Soc.*, 859 (1966).

[6] D. P. Graddon and E. C. Watton, *Australian J. Chem.*, **18**, 507 (1965).

[7] J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

figurations of these compounds were merely crystal artifacts or if they could be related to π bonding.

Experimental Section

Crystal Preparation.—Characterization of the *trans*-dipyridine adduct of nickel(II) acetylacetonate, $Ni(C_5H_7O_2)_2(C_5H_5N)_2$, has been reported by Hashagen and Fackler. The crystals used in this study were prepared by dissolving anhydrous nickel acetylacetonate ($Ni(AA)_2$) in pyridine (py) at 70°. On cooling, blue crystals precipitated from solution. The needle-shaped crystals were filtered off and washed with pentane. An infrared spectrum of a Nujol mull showed bands characteristic of pyridine and also of acetylacetone coordinated to a first-row transition metal.

The compound crystallizes in the monoclinic system. Cell constants and their estimated standard deviations determined by least-squares analysis of data obtained on a Philips PAILRED automated diffractometer using crystal-monochromated molybdenum radiation (λ_{α_1} 0.70926, λ_{α_2} 0.71354 Å) are $a = 8.321 \pm 0.003$, $b = 9.649 \pm 0.015$, $c = 14.723 \pm 0.025$ Å, $\beta = 117.06 \pm 0.01°$, and $V = 1052.7$ Å^3. Previously reported values are $a = 8.28$, $b = 9.57$, $c = 14.65$ Å, and $\beta = 116.83°$. On the basis of systematic absences observed on precession photographs (*h0l*, *h1l*, *hk0*, *hk1* films; absences *h0l*, $l = 2n + 1$; 0*k*0, $k = 2n + 1$), the space group[8] is $P2_1/c$. As was previously noted, there are two molecules in the unit cell and the metal atoms are thus required to lie on centers of symmetry. This confirms that the compound is the *trans*-dipyridine adduct.

Intensity Data Collection.[9]—The needle growth is in the *a* direction. In order to mount a crystal to rotate about the *b* axis, a needle was cleaved perpendicular to *a* to give a diamond-shaped plate with short diagonal (0.3 mm) coincident with *b*; the long diagonal was 0.4 mm and the plate was 0.2 mm thick. The crystal was mounted on a glass fiber with epoxy cement. The value of the linear absorption coefficient for the compound with molybdenum radiation was 9 cm^{-1}. The maximum absorption error in the intensity measurements was less than 10% with such a crystal. Alignment was checked by measuring the intensity of the 020 reflection while the crystal was rotated through 360°. The 106 reflection was used as a monitor peak throughout data collection. The intensity of the monitor peak decreased approximately 10% over the 2-week period of data collection. Since alignment checks on the 020 reflection, which were performed after every second layer was collected, indicated no alignment problems, this decrease was assumed to result from crystal decomposition. In an effort partially to correct[10] for the effects of decomposition, the data were collected in order from the zero level increasing through the tenth level, the crystal was then rotated by 180°, and levels were collected from the tenth decreasing to the zero level. The data from the two forms were averaged after processing for Lp factors and backgrounds to yield the final set. Reflections with a counting error of less than 0.5 were considered nonzero and given a standard deviation of 1.0 in subsequent least-squares refinement. Those with counting errors greater than 0.5 were considered zero and given a standard deviation of 2.5. The R_{sym} factor[11] was 3.5%. After averaging there were 1641 reflections measured with $2\theta < 48°$; of these, 734 were nonzero and 907 were zero. Ninety-nine of the zero class reflections had zero or negative corrected intensities. The structure factors for these reflections were set arbitrarily to 0.98, approximately 40% of the mean value of all reflections in the zero class. Calculations were made using local variants of known programs[12] on an IBM 7094 computer. The scattering curves used were those for Ni$^+$, O, N, C, and H as tabulated by Ibers.[13]

Determination of the Structure

If the two nickel atoms are chosen to lie on position 2a of the space group $P2_1/c$ (*i.e.*, 0, 0, 0; 0, $^1/_2$, $^1/_2$), then for the class of reflections *hkl* where $k + l = 2n$ the metal contribution will have a positive sign. On the assumption that the metal contribution was dominant, an electron density synthesis was carried out using this subset of the nonzero reflections with positive signs. Positions for all nonhydrogen atoms in the cell were determined from this map. A structure factor calculation using a least-squares-adjusted scale factor for the 734 nonzero reflections gave an R factor[14] of 23%. Full-matrix least-squares refinement was used with corrections for both real and imaginary parts of the anomalous dispersion of the nickel atoms ($f = f_0 + \Delta f' + i\Delta f''$, where $\Delta f' = 0.4$ and $\Delta f'' = 1.0$ electron[15]) and also a one-parameter correction[16] for extinction. This correction which is applied to F_o is varied by least squares. Ten cycles of refinement varying positional parameters and isotropic temperature factors converged to $wR' = 10.0\%$ for the 890 reflections with largest structure factors. The six aromatic hydrogen atoms were found on a difference Fourier map calculated at this stage. The positions of the six methyl hydrogen atoms were not determined with certainty. Refinement was continued using anisotropic temperature parameters for all nonhydrogen atoms. The six hydrogen atoms were kept fixed with isotropic temperature parameters of 4.0 Å^2. After two cycles, the values of wR and wR' were, respectively, 7.10 and 6.03%. A difference Fourier map indicated clearly the positions for five of the six methyl hydrogen atoms. These five hydrogen atoms were added to the structure factor calculation and least-squares refinement continued for two more cycles to give $wR = 6.17\%$ and $wR' = 5.17\%$. The position of the last hydrogen atom, H_3C_1, was calculated using a bond length of 1.0 Å and tetrahedral angles. Two additional cycles of refinement were then done varying all parameters except the hydrogen isotropic temperature factors. This gave a final $wR = 5.57\%$ and $wR' = 4.41\%$. The structure factor calculation before variation of hydrogen atom positions and after the introduction of the last hydrogen atom gave $wR = 6.05\%$. At this point the calculation had

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(8) "International Tables for X-Ray Crystallography," Vol. 1, No. 14, The Kynoch Press, Birmingham, England, 1952, p 99.

(9) The intensity data were collected using a Philips automated diffractometer, PAILRED. The conditions of data collection were identical with those reported[1] for $Co(AA)_2(py)_2$.

(10) Owing to the errors in the data set caused by decomposition, no corrections were made for absorption.

(11) The R_{sym} factor, a measure of the agreement between the nonzero data sets, is computed from $\Sigma|F_1 - F_2|/\Sigma F_{mean}$. In the case for $Co(AA)_2(py)_2$,[1] where no decomposition was evident, the value found was 2.5%.

(12) Fourier syntheses were calculated using "ERFR-2, a Fourier Summation Program," by W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, Esso Research, CBRL-22M-52, 1962. Structure factor calculations and least-squares refinements were performed with "SORFLS, Son of ORFLS" by R. B. K. Dewar, University of Chicago, 1968. Calculations of molecular geometry were made with "SORFFE, Son of ORFFE" by R. B. K. Dewar, University of Chicago, 1968.

(13) "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1952, Table 3.3.1A.

(14) The R factor is the usual discrepancy index $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{1/2}$. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized.

(15) "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1952, Table 3.3.2C.

(16) This correction is that suggested by W. H. Zachariasen, *Acta Cryst.*, **23**, 558 (1967). The formulas used in the least-squares program SORFLS are $F_{cor} = KF_c/[1 + 2x]^{1/4}$ and $x = [(1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)]F_c^2Cr'/\sin 2\theta$; the quantity $200Cr'$ is varied as a least-squares parameter. A value of zero corresponds to no correction. The final value obtained was 0.00025 ± 0.00004. The value found for $Co(AA)_2(py)_2$ was 0.00036.

converged with the exception of the disturbance introduced by the last hydrogen atom. If we assume that this wR is not too different from that for convergence with fixed hydrogen atoms, the weighted R factor ratio for Hamilton's test[17] is 1.086 whereas that calculated to show significant improvement at the 0.005 confidence level ($R_{36,1480,0.005}$) is 1.021. Thus, it seems likely that the refinement of the hydrogen atom positions results in significant improvement. Refinement was terminated at this point.[18]

Results and Discussion

Structure Description.—The final atomic positional parameters and their estimated standard deviations are listed in Table I. The anisotropic temperature parameters are given in Table II and their effects are shown in Figure 1, which is a parallel projection of the molecule composed with ORTEP.[19] The unlabeled small spheres, which are made artificially small for clarity, represent the hydrogen atoms as found. The root-mean-square amplitudes of vibration for nonhydrogen atoms are given in Table III; the directions of the motions are indicated in the drawing. Structure factor calculations after the final cycle of refinement are shown in Table IV. The last 907 reflections are in the zero class. Table V contains the bond distances and Table VI the bond angles found in the molecule. The analagous values found for the $Co(AA)_2(py)_2$ molecule are also shown.

Table I

Fractional Atomic Positional Parameters[a]

Atom	x	y	z
Ni	0.0 (–)	0.0 (–)	0.0 (–)
O_1	0.2180 (4)	−0.0267 (4)	0.1377 (2)
O_2	0.1412 (5)	0.1177 (4)	−0.0518 (3)
N	0.0702 (6)	−0.1792 (5)	−0.0563 (3)
C_1	0.5164 (10)	−0.0153 (12)	0.2664 (5)
C_2	0.3714 (7)	0.0189 (8)	0.1600 (4)
C_3	0.4185 (8)	0.0996 (7)	0.0976 (5)
C_4	0.3056 (8)	0.1438 (6)	−0.0022 (5)
C_5	0.3871 (12)	0.2294 (9)	−0.0567 (7)
C_6	0.0677 (9)	−0.1792 (8)	−0.1474 (5)
C_7	0.1038 (10)	−0.2951 (10)	−0.1905 (5)
C_8	0.1479 (10)	−0.4143 (9)	−0.1359 (6)
C_9	0.1542 (10)	−0.4173 (8)	−0.0406 (6)
C_{10}	0.1156 (8)	−0.2975 (8)	−0.0206 (5)
H_1C_1	0.488 (9)	−0.103 (8)	0.288 (5)
H_2C_1	0.544 (9)	0.059 (7)	0.313 (5)
H_3C_1	0.627 (8)	0.014 (9)	0.274 (4)
HC_3	0.550 (9)	0.134 (7)	0.130 (4)
H_1C_5	0.474 (9)	0.187 (8)	−0.062 (5)
H_2C_5	0.419 (9)	0.305 (8)	−0.026 (5)
H_3C_5	0.307 (9)	0.261 (7)	−0.129 (5)
HC_6	0.032 (9)	−0.096 (8)	−0.188 (5)
HC_7	0.106 (8)	−0.280 (7)	−0.252 (5)
HC_8	0.168 (8)	−0.503 (8)	−0.167 (5)
HC_9	0.173 (8)	−0.491 (8)	−0.006 (5)
HC_{10}	0.114 (9)	−0.292 (8)	0.056 (5)

[a] The estimated errors in the last digit reported are given in parentheses. (–) means that this coordinate was symmetry fixed and there is no error. The notation H_nC_m refers to the nth hydrogen atom bound to the mth carbon atom; where n is not given, its value is 1.

Table II

Anisotropic[a] Thermal Parameters ($\times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	136 (2)	131 (1)	36 (1)	−15 (2)	30 (1)	2 (1)
O_1	159 (8)	157 (7)	39 (2)	8 (6)	28 (3)	9 (3)
O_2	152 (8)	167 (7)	48 (3)	−17 (6)	39 (4)	14 (3)
N	170 (10)	128 (7)	47 (3)	6 (7)	40 (5)	−2 (4)
C_1	197 (14)	256 (16)	62 (5)	−67 (16)	5 (7)	8 (8)
C_2	138 (11)	146 (10)	48 (3)	24 (10)	20 (5)	−19 (5)
C_3	132 (11)	146 (9)	75 (5)	−44 (9)	36 (6)	2 (5)
C_4	205 (14)	75 (7)	76 (5)	13 (8)	78 (7)	1 (5)
C_5	257 (18)	141 (12)	110 (7)	−5 (12)	106 (10)	24 (7)
C_6	270 (17)	186 (12)	45 (4)	52 (12)	55 (7)	14 (6)
C_7	282 (17)	243 (15)	39 (4)	38 (13)	51 (7)	−12 (7)
C_8	289 (18)	171 (12)	72 (6)	2 (13)	43 (8)	−33 (7)
C_9	266 (18)	132 (11)	94 (7)	1 (12)	68 (9)	5 (6)
C_{10}	206 (14)	148 (10)	56 (4)	−10 (10)	50 (6)	0 (6)

[a] The thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

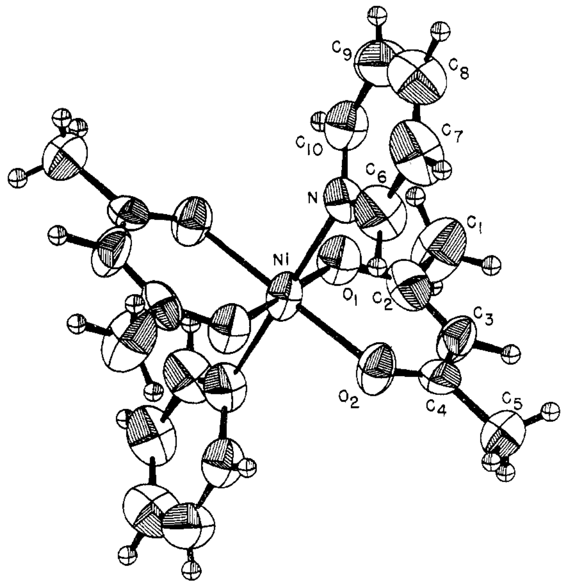

Figure 1.—A parallel projection of the $Ni(AA)_2(py)_2$ molecule composed using ORTEP. The nickel atom lies on a crystallographic center of symmetry. The idealized molecule has D_{2h} symmetry. Both the acetylacetone and the pyridine ligands are planar within experimental error.

Table III

Root-Mean-Square Amplitudes[a] of Vibration (Å $\times$ 10^3)

Atom	1	2	3	Atom	1	2	3
Ni	175	193	252	C_4	182	211	264
O_1	181	217	276	C_5	209	266	321
O_2	189	206	289	C_6	190	252	319
N	202	218	246	C_7	174	274	352
C_1	193	279	374	C_8	220	282	330
C_2	185	203	289	C_9	248	272	291
C_3	171	254	287	C_{10}	218	238	266

[a] The directions of vibration are indicated in the figure. In general, the vibrations of the ligand atoms increase with distance from the metal atom and are largest perpendicular to the ligand plane.

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(17) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

(18) The shifts of all nonhydrogen atom parameters were less than half of their estimated standard deviations with the exception of C_1; its y positional parameter and its β_{11} shifted 1.1 esd. Of the 36 hydrogen atom positional parameters, six shifted between 0.5 and 1.5 esd's. The standard error of an observation of unit weight was 1.06. A final difference map showed no peaks greater than 0.5 e$^-$ Å^{-3}.

(19) C. K. Johnson, "ORTEP, Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations," Oak Ridge National Laborarory, ORNL-3794 UC-4-Chemistry, 1965

TABLE IV

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (ELECTRONS × 131.3) FOR $Ni(AA)_2(py)_2$

H	L	FOBS	FCAL
****K = 0*******			
0	2	6910	7037
0	4	2858	2830
0	6	4247	4138
0	8	2124	2107
0	12	965	902
0	14	1439	1343
-1	0	5597	5705
1	2	6692	6650
-1	2	4200	4180
1	4	4864	4809
1	6	5850	5793
-1	6	1107	1188
1	8	1555	1544
-1	10	1046	1096
-1	14	1662	1717
2	0	4100	4081
2	2	5613	5617
-2	2	4074	4088
2	4	3469	3399
-2	4	3840	3910
2	6	1796	1818
-2	6	1010	846
2	8	1665	1604
2	10	956	938
-2	10	2033	2101
2	12	875	808
-2	12	1867	1825
-2	14	947	960
3	2	4350	4285
3	4	2187	2207
-3	4	1436	1369
3	6	2320	2431
-3	6	1893	1858
3	8	1706	1811
3	10	1137	1307
-3	10	2293	2293
-3	12	3063	3134
-3	14	1952	2049
4	0	858	710
4	2	1534	1545
-4	2	1714	1576
4	4	1307	1233
-4	4	2534	2591
-4	6	2541	2532
4	8	1480	1457
-4	8	3701	3663
4	10	906	823
-4	10	2105	2107
-4	12	1693	1665
-4	14	1130	1193
5	0	1213	1210
-5	2	2259	2334
-5	4	790	856
5	6	818	769
-5	6	1693	1735
-5	8	1659	1722
-5	10	1580	1442
-5	12	911	931
6	0	1091	1013
-6	2	2252	2263
6	4	1624	1511
-6	4	1936	1954
6	6	784	854
-6	6	1380	1343
-6	8	2444	2454
-6	10	1380	1462
-6	12	1112	998
7	2	1566	1528
-7	2	1643	1681
-7	4	1660	1729
-7	6	1415	1436
-7	10	1686	1654
-7	12	973	1004
8	0	945	879
-8	4	980	908
-8	6	935	855
-8	12	1265	1188
-8	14	944	725
-9	6	871	901
-9	8	1161	1191
-9	10	1058	1023
****K = 1******			
0	2	2675	2621
0	3	2008	2101
0	4	2033	2020
0	5	887	981
0	6	566	425
0	7	3161	3130
0	11	989	991
0	13	1044	1160
-1	0	769	831
1	2	3590	3567
-1	2	891	961
1	3	1951	2011
-1	3	4684	4593
-1	4	652	648
1	5	5260	5065
-1	6	2129	2041
1	7	1208	1294
-1	7	949	940
-1	8	1190	1148
-1	9	2462	2565
1	13	1036	931
-1	13	1107	1075
-1	15	1162	1087
2	0	6122	6227
2	1	2597	2596
-2	1	2854	2848
-2	2	3939	3870
2	3	4205	4154
-2	3	2706	2614
2	5	1970	1990
-2	5	1263	1252
2	6	634	716
-2	6	1329	1340
2	7	1655	1636
-2	7	934	1191
-2	9	1954	1926
-2	11	2507	2590
3	0	1602	1655
3	1	3714	3783
-3	1	3098	3192
3	3	2072	2108
-3	3	2053	2040
-3	4	1366	1338
3	5	2599	2660
-3	5	3871	3912
3	6	864	669
-3	6	2042	1942
3	7	1621	1584
-3	7	2799	2702
3	9	1555	1639
-3	9	1450	1475
-3	11	2185	2236
-3	13	2268	2367
4	0	1231	1337
4	1	2630	2685
-4	1	1193	1338
4	3	2503	2572
-4	3	610	740
-4	4	903	922
4	5	821	820
-4	5	3068	3028
4	7	1571	1514
-4	7	3419	3518
-4	8	1162	1105
4	9	1276	1242
-4	9	1838	1772
-4	10	838	819
-4	11	1395	1429
-4	12	788	669
-4	13	1261	1284
-4	15	1123	1117
5	0	681	644
5	1	2121	2190
-5	1	1708	1709
-5	3	896	867
-5	5	1822	1875
-5	6	860	859
5	7	1060	1076
-5	7	1695	1664
-5	8	1107	1127
-5	9	1392	1492
-5	10	837	775
-5	11	1245	1306
-5	13	926	987
-6	1	1485	1478
6	3	1177	1151
-6	3	2141	2114
6	5	1040	1159
-6	5	1574	1572
-6	7	1410	1553
-6	9	1710	1671
-6	11	1254	1218
-6	13	776	670
7	1	1018	1004
7	3	1062	1043
-7	3	1695	1791
-7	5	1420	1396
-7	6	967	999
-7	9	1424	1425
-7	11	1536	1484
-8	5	1001	1090
-9	7	893	957
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7	0	672	696
7	1	128	219
-7	1	231	20
7	3	184	137
-7	3	586	556
7	4	695	620
-7	5	694	630
-7	6	486	433
-7	8	315	223
-7	9	443	491
-7	11	687	485
-7	12	616	660
-7	13	234	462
-7	15	371	178
8	0	851	829
8	1	128	216
-8	2	328	214
-8	3	343	434
-8	5	128	10
-8	7	105	58
-8	8	655	635
-8	9	50	178
-8	10	79	254
-8	11	656	551
-8	13	129	311
-9	3	260	23
-9	4	609	132
-9	5	352	158
-9	6	590	462
-9	7	381	169
-9	8	128	584
-9	9	580	548
-9	10	128	256
-9	11	654	646
****K = 3*******			
0	6	290	476
0	8	360	217
0	10	84	216
0	12	74	75
0	14	328	309
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1	4	522	332
1	6	450	576
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1	8	392	275
1	10	321	551
-1	10	235	200
1	12	128	355
-1	12	128	275
-1	13	220	437
-1	14	258	145
2	0	114	300
-2	2	248	114
2	6	447	317
-2	6	254	38
2	10	232	72
-2	10	344	333
2	12	59	81
-2	12	188	43
-2	13	199	137
-2	14	227	34
-2	15	665	565
3	2	89	75
-3	2	477	434
3	4	154	233
3	6	132	184
3	7	515	221
3	8	231	88
-3	8	40	57
3	9	596	626
3	10	373	144
-3	10	244	480
3	11	810	845
-3	11	146	182
-3	12	128	147
-3	14	224	227
-3	15	449	245
-3	16	240	84
4	2	448	428
4	4	128	5
-4	4	530	403
4	5	128	173
-4	6	128	24
4	7	693	756
4	8	198	72
-4	8	452	574
4	9	519	555
-4	10	128	56
-4	11	128	124
-4	12	534	464
-4	14	123	343
-4	16	128	224
5	0	319	111
5	2	308	240
-5	2	128	578
5	3	669	658
5	4	128	91
5	6	128	33
5	8	108	51
-5	8	128	152
-5	10	219	251
-5	11	214	356
-5	12	286	273
-5	14	128	86
-5	16	157	114
6	0	427	621
6	1	164	419
6	2	595	331
-6	2	442	410
6	4	444	483
-6	4	154	75
-6	5	128	107
6	6	315	26
-6	6	128	45
-6	8	433	283
-6	10	142	375
-6	11	483	438
-6	12	145	14
-6	13	800	741
-6	14	261	91
7	0	243	181
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-7	1	299	567
7	2	128	172
-7	2	59	378
7	3	662	752
-7	4	128	50
-7	6	128	229
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-7	8	128	26
-7	10	449	587
-7	12	430	224
-7	13	805	930
-7	14	128	50
-7	15	616	567
8	0	149	41
-8	2	290	40
-8	3	453	486
-8	4	201	219
-8	6	230	166
-8	8	163	193
-8	9	580	557
-8	10	59	12
-8	12	362	179
-9	5	325	488
-9	6	128	15
-9	7	629	703
-9	8	239	39
-9	9	585	476
-9	10	128	274
****K = 4*******			
0	2	186	108
0	5	114	104
0	7	466	48
0	11	336	369
0	13	732	650
0	14	655	715
1	7	478	556
-1	7	241	219
-1	9	231	181
1	11	138	68
-1	12	639	562
1	13	146	289
-1	13	348	497
-1	14	675	635
-2	3	153	257
-2	5	341	267
2	7	128	426
-2	7	368	345
2	9	128	412
2	11	637	322
2	12	852	944
-2	13	128	13
-2	14	256	271
-2	15	164	38
-3	1	224	406
3	3	128	195
3	6	772	765
3	7	74	177
-3	7	181	357
3	8	181	164
3	9	128	9
3	10	521	437
-3	10	426	279
-3	12	128	410
-3	13	345	392
-3	14	415	605
-3	15	128	13
4	1	299	468
-4	1	182	316
4	3	534	119
4	5	142	30
4	6	551	498
4	7	128	9
-4	7	473	205
4	9	224	236
-4	10	455	345
-4	11	711	811
-4	13	286	299
-4	15	128	127
5	1	128	125
-5	1	232	14
5	3	206	393
-5	3	286	164
5	5	138	124
-5	5	309	411
5	7	128	153
-5	7	80	191
-5	9	128	52
-5	10	687	650
-5	11	528	700
-5	13	205	217
-5	15	340	34
6	0	816	849
6	1	156	21
-6	1	128	165
6	2	406	406
6	3	128	86
-6	3	324	150
-6	4	308	94
6	5	75	205
-6	6	133	121
-6	7	311	32
-6	9	128	219
-6	11	247	531
-6	13	490	421
-6	15	342	136
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7	1	128	245
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7	2	481	480
-7	2	547	699
7	3	203	188
-7	3	128	231
-7	5	247	64
-7	7	198	10
-7	8	581	599
-7	9	199	252
-7	11	240	22
-7	13	520	54
-7	14	424	414
-8	1	457	49
-8	2	180	357
-8	3	287	260
-8	5	128	100
-8	7	224	216
-8	9	77	84
-8	10	739	759
-8	11	214	110
****K = 5*******			
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0	4	128	22
0	8	251	57
0	9	361	223
0	10	128	32
0	11	117	108
0	12	40	253
1	4	39	132
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1	6	128	88
1	8	632	511
-1	8	584	533
1	10	46	67
-1	10	167	250
1	11	157	401
-1	11	96	359
1	12	128	347
-1	12	359	101
-1	14	228	20
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2	6	144	288
2	8	128	4
-2	8	275	292
-2	9	126	151
2	10	574	370
-2	10	420	224
2	11	428	440
-2	12	128	326
-2	14	298	42
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-3	2	542	428
-3	4	66	312
3	6	128	238
3	7	83	284
3	8	128	175
-3	8	181	135
-3	9	579	481
3	10	495	285
-3	10	494	487
-3	12	16	59
-3	14	45	54
4	0	271	244
4	2	411	465
-4	2	25	277
4	4	447	423
4	6	123	40
-4	6	568	491
4	8	173	342
-4	8	260	21
-4	10	501	535
-4	12	436	581
-4	14	128	151
5	0	241	356
5	2	284	70
-5	2	364	370
-5	3	716	775
5	4	128	70
-5	4	360	385
5	6	128	186
-5	6	205	239
-5	8	461	270
-5	10	183	6
-5	12	258	216
-5	14	367	273
6	0	118	273
6	1	360	634
6	2	375	545
-6	2	75	7
6	3	187	653
-6	3	559	615
6	4	65	223
-6	4	146	34
-6	5	459	301
-6	6	128	17
-6	8	539	701
-6	10	400	303
-6	12	128	228
-6	13	346	621
-6	14	128	154
7	0	116	152
7	1	200	219
-7	1	133	74
7	2	290	88
-7	4	424	458
-7	6	205	453
-7	7	552	511
-7	8	364	310
-7	10	56	193
-7	12	164	37
-7	13	352	350
-8	3	200	203
-8	4	128	185
-8	5	691	688
-8	6	43	52
-8	7	721	731
-8	8	159	214
-8	9	528	575
-8	10	392	62
-8	11	573	602
****K = 6*******			
0	3	78	237
0	5	322	397
0	7	541	618
0	9	128	147
0	11	314	318
0	12	579	863
1	1	245	559
1	3	491	571
1	7	412	192
-1	7	271	275
1	8	399	346
1	9	246	88
-1	9	128	77
1	10	142	567
1	11	244	115
-1	12	385	408
-1	13	279	113
2	1	52	159
2	3	431	477
-2	3	128	26
2	5	237	20
2	7	128	150
-2	7	154	252
-2	8	511	525
2	9	769	781
2	10	91	170
-2	13	372	137
3	1	588	532
-3	1	29	20
3	3	351	423
-3	3	128	10
3	5	171	125
3	7	128	267
3	8	613	530
3	9	443	240
-3	9	281	34
-3	11	148	97
-3	12	677	840
-3	13	70	25
-3	14	580	647
4	1	578	282
-4	1	199	105
4	3	610	481
-4	3	173	290
4	5	347	92
-4	5	355	391
4	6	439	545
-4	6	517	413
4	7	263	138
-4	7	185	31
-4	8	367	463
-4	9	269	450
-4	10	224	462
-4	11	352	486
-4	13	414	472
-4	14	683	837
5	0	462	370
5	1	411	280
-5	1	312	138
-5	2	271	198
5	3	411	190
-5	4	444	194
5	5	150	113
-5	5	106	77
-5	7	392	511
-5	9	39	118
-5	11	309	170
-5	13	247	528
6	0	352	540
6	1	583	104
-6	1	132	174
6	2	579	362
6	3	247	202
-6	3	539	36
-6	5	154	7
-6	6	606	575
-6	7	50	372
-6	9	169	290
-6	11	195	228
-6	13	128	31
7	0	171	114
-7	1	128	306
-7	2	492	556
-7	3	128	239
-7	5	401	518
-7	6	508	684
-7	7	204	335
-7	9	463	248
-7	11	351	203
-8	5	128	88
-8	6	568	633
-8	7	128	46
****K = 7*******			
0	2	20	164
0	4	210	392
0	8	513	330
0	10	216	245
0	11	634	602
1	2	188	42
-1	4	201	320
1	6	223	327
-1	6	75	101
1	7	585	646
1	8	235	22
-1	8	193	88
1	10	155	11
-1	10	308	260
-1	11	131	207
-1	12	66	159
-2	1	258	126
2	2	128	234
2	4	49	159
-2	4	97	20
2	5	689	852
2	6	128	327
-2	6	75	230
-2	7	136	217
2	8	281	319
-2	8	212	245
2	9	268	536
-2	9	544	544
-2	10	128	183
-2	12	138	236
3	0	574	545
3	2	128	199
3	4	383	321
-3	4	189	43
3	6	260	25
-3	6	328	578
3	7	265	553
3	8	128	420
-3	8	139	94
-3	10	128	146
-3	12	128	94
4	0	185	176
4	1	248	397
-4	1	539	502
4	2	323	352
-4	2	128	340
4	3	551	621
4	4	453	234
-4	4	233	172
4	5	377	321
4	6	226	137
-4	6	189	12
-4	8	482	488
-4	10	221	108
-4	11	649	627
-4	12	419	326
-4	13	447	580
5	0	316	384
5	1	244	264
-5	1	282	301
5	2	634	329
-5	2	54	339
5	3	414	186
-5	3	219	405
5	4	128	140
-5	4	279	470
-5	6	477	444
-5	8	234	265
-5	10	128	165
-5	11	471	384
-5	12	248	133
6	0	284	188
6	1	519	390
-6	2	20	20
-6	4	193	11
-6	5	562	576
-6	6	268	199
-6	8	138	57
-6	10	169	48
-6	11	317	389
-7	2	344	173
-7	4	161	51
-7	5	644	593
-7	6	128	138
-7	7	521	510
-7	8	128	45
-7	9	429	551
****K = 8*******			
0	3	159	243
0	5	361	271
0	7	413	498
0	8	572	615
0	9	173	53
0	10	478	457
1	0	49	148
1	1	151	325
1	3	434	386
-1	3	128	44
1	5	438	455
-1	5	128	106
-1	6	366	434
1	7	199	10
-1	7	201	119
1	8	540	448
-1	8	608	642
1	9	97	93
-1	9	128	106
-1	10	505	559
-1	11	42	184
2	0	440	401
2	2	285	398
2	3	52	78
-2	3	128	114
2	4	468	623
2	5	308	497
-2	5	182	235
2	6	307	383
-2	6	432	520
2	7	413	327
-2	7	536	610
2	8	404	452
-2	9	217	114
-2	11	151	95
-3	1	353	580
3	2	461	572
3	3	54	391
-3	3	470	383
3	4	670	622
3	5	60	169
-3	5	182	47
3	6	148	634
-3	7	251	350
-3	9	160	142
-3	11	126	94
4	0	562	600
4	1	121	65
4	2	324	377
4	3	281	208
-4	3	394	231
4	4	533	551
4	5	96	11
-4	5	128	141
-4	7	250	369
-4	9	244	375
-4	10	568	591
-4	11	458	241
5	0	589	661
5	1	128	174
-5	1	286	47
5	2	614	402
-5	3	230	220
-5	4	372	609
-5	5	108	171
-5	7	449	334
-5	8	487	483
-5	9	242	193
-5	10	198	318
-6	1	245	149
-6	3	128	359
-6	5	128	18
-6	6	297	562
-6	7	151	43
-6	8	372	473
-6	9	128	166
****K = 9*******			
0	4	128	283
0	5	181	318
0	6	201	78
0	7	393	290
0	8	20	206
1	1	70	229
-1	1	128	464
1	2	235	91
1	4	514	398
-1	4	232	346
-1	5	335	402
1	6	195	171
-1	6	178	366
1	7	550	427
-1	7	535	497
-1	8	99	258
2	0	148	226
2	1	455	498
2	2	132	224
-2	2	144	88
2	4	209	49
-2	4	37	52
2	5	184	442
2	6	128	191
-2	6	204	58
-2	8	263	261
3	0	389	379
3	1	204	307
-3	1	549	621
3	2	453	187
-3	2	128	314
3	3	289	248
-3	3	324	438
3	4	309	112
-3	4	113	171
-3	6	128	193
-3	7	389	465
-3	8	203	313
4	0	68	321
4	1	167	247
-4	1	314	372
4	2	351	103
-4	2	128	160
-4	4	403	291
-4	6	46	153
-4	8	60	41
-4	9	463	611
-5	1	669	712
-5	2	128	193
-5	3	598	647
-5	4	200	39
-5	6	91	310
-5	7	301	413
****K = 10******			
0	2	128	387
0	3	57	189
0	4	336	276
0	5	107	188
0	6	333	304
1	1	28	26
1	3	128	62
-1	3	248	228
1	4	501	567
1	5	331	156
-1	5	39	23
-1	7	128	19
2	1	350	141
-2	1	128	92
-2	2	322	291
2	3	128	32
-2	3	202	99
2	4	572	496
-2	4	280	432
-2	5	128	129
-2	6	400	354
-2	7	284	147
3	0	176	100
3	1	284	291
-3	1	128	152
3	2	120	108
-3	2	133	171
-3	3	128	71
-3	4	261	201
-3	5	128	10
-3	6	128	135
-4	2	240	194
-4	3	223	82
-4	4	309	319

The molecule $Ni(AA)_2(py)_2$ is the *trans*-dipyridine adduct to nickel acetylacetonate with crystallographic symmetry $\bar{1}$. The actual symmetry is only slightly different from that of the point group D_{2h}. The two pyridine rings are in an eclipsed configuration and in the idealized molecule they lie in the mirror plane passing between the two acetylacetone ligands. $Co(AA)_2(py)_2$ belongs to the point group C_{2v} and its conformation may be obtained from that of the nickel structure by rotating one of the pyridine rings by 90° around the NMN axis. The differences in these structures are discussed below.

Neither the acetylacetone nor the pyridine ligand of $Ni(AA)_2(py)_2$ is required to be planar by crystallographic symmetry; however, both are found to be planar within experimental error. The least-squares planes

TABLE V

$Ni(AA)_2(py)_2$ BOND LENGTHS (Å)

$Ni-O_1$	2.031 (3)	$Ni-N$	2.112 (5)
$Ni-O_2$	2.017 (4)	$N-C_6$	1.332 (7)
O_1-C_2	1.245 (6)	$N-C_{10}$	1.334 (8)
O_2-C_4	1.249 (6)	C_6-C_7	1.385 (10)
C_1-C_2	1.517 (8)	$C_{10}-C_9$	1.376 (10)
C_5-C_4	1.510 (9)	C_7-C_8	1.355 (10)
C_2-C_3	1.390 (8)	C_9-C_8	1.381 (10)
C_4-C_3	1.402 (8)		

	Mean distances	Differences	Co analog[a]
$Ni-O_{1,2}$	2.024 (2)	0.015 (5)	2.034 (5)
$Ni-N$	2.112 (5)	. . .	2.187 (5)
$O_{1,2}-C_{2,4}$	1.247 (4)	0.006 (8)	1.241 (6)
$C_{1,5}-C_{2,4}$	1.513 (6)	0.003 (12)	1.535 (8)
$C_{2,4}-C_3$	1.397 (5)	0.012 (13)	1.393 (6)
$N-C_{6,10}$	1.332 (5)	0.004 (11)	1.317 (5)
$C_{6,10}-C_{7,9}$	1.380 (7)	0.003 (14)	1.372 (7)
$C_{7,9}-C_8$	1.368 (6)	0.023 (16)	1.343 (6)

Carbon–hydrogen distances[b]

$H_1C_1-C_1$	0.97 (7)	$H_2C_5-C_5$	0.84 (7)	HC_7-C_7	0.92 (6)
$H_2C_1-C_1$	0.94 (7)	$H_3C_5-C_5$	1.01 (7)	HC_8-C_8	1.02 (7)
$H_3C_1-C_1$	0.92 (6)	HC_3-C_3	1.03 (6)	HC_9-C_9	0.85 (7)
$H_1C_5-C_5$	0.87 (7)	HC_6-C_6	0.97 (7)	$HC_{10}-C_{10}$	0.88 (6)

[a] The corresponding distances found in $CoAA_2(py)_2$ are quoted in this column. [b] Average of all carbon hydrogen distances is 0.94 Å.

TABLE VI

BOND ANGLES IN $Ni(AA)_2(py)_2$ (DEG) WHERE THE CENTRAL ATOM IS AT THE VERTEX

Metal Coordination Angles

O_1-Ni-O_2	92.3 (1)	O_1-Ni-N	89.6 (2)
O_2-Ni-N	90.0 (2)		

Pyridine Ring Angles[a]

$Ni-N-C_6$	121.0 (5)	$C_6-C_7-C_8$	118.0 (6)
$Ni-N-C_{10}$	121.9 (4) [121.6]	$C_{10}-C_9-C_8$	118.4 (7) [119.3]
$N-C_6-C_7$	123.6 (7)	$C_7-C_8-C_9$	119.8 (7) [118.7]
$N-C_{10}-C_9$	123.0 (6) [123.0]		

Acetylacetone Angles

$Ni-O_1-C_2$	124.2 (3)	$O_1-C_2-C_3$	126.0 (5)
$Ni-O_2-C_4$	124.3 (4) [125.8]	$O_2-C_4-C_3$	125.8 (5) [126.1]
$O_1-C_2-C_1$	115.7 (5)	$C_2-C_3-C_4$	127.4 (5) [125.9]
$O_2-C_4-C_5$	115.9 (6) [114.5]		

Hydrogen Atom Angles

$H_1C_1-C_1-C_2$	109 (4)	HC_6-C_6-N	119 (4)
$H_2C_1-C_1-C_2$	114 (4)	$HC_{10}-C_{10}-N$	113 (5)
$H_3C_1-C_1-C_2$	110 (4)	$HC_6-C_6-C_7$	117 (4)
$H_1C_1-C_1-H_2C_1$	116 (6)	$HC_{10}-C_{10}-C_9$	124 (5)
$H_1C_1-C_1-H_3C_1$	127 (7)	$HC_7-C_7-C_6$	115 (4)
$H_2C_1-C_1-H_3C_1$	77 (6)	$HC_9-C_9-C_{10}$	119 (5)
$H_1C_5-C_5-C_4$	113 (5)	$HC_7-C_7-C_8$	127 (4)
$H_2C_5-C_5-C_4$	107 (5)	$HC_9-C_9-C_8$	122 (5)
$H_3C_5-C_5-C_4$	119 (4)	$HC_8-C_8-C_7$	120 (4)
$H_1C_5-C_5-H_2C_5$	113 (7)	$HC_8-C_8-C_9$	120 (4)
$H_1C_5-C_5-H_3C_5$	103 (6)	$HC_3-C_3-C_2$	116 (3)
$H_2C_5-C_5-H_3C_5$	101 (7)	$HC_3-C_3-C_4$	117 (3)

[a] Numbers given in brackets are the corresponding values from $CoAA_2(py)_2$.

through these ligands were determined using SORFFE, where the errors are determined using the variance–covariance matrix. The distances and estimated errors (Å) of each atom from this plane for the acetylacetone ligand are: O_1, −0.001 (4); O_2, 0.003 (4); C_1, 0.005 (5); C_2, −0.009 (6); C_3, 0.003 (7); C_4, 0.006 (5); C_5, −0.005 (5); HC_3, 0.06 (6); and for the pyridine ligand: N, 0.009 (4); C_6, −0.008 (5); C_7, 0.003 (5); C_8, 0.001 (5); C_9, −0.000 (5); C_{10}, −0.005 (5); HC_6, 0.03 (7); HC_7, −0.07 (5); HC_8, 0.06 (6); HC_9, 0.06 (7); HC_{10}, 0.01 (7). In D_{2h} symmetry not only must these ligands be planar but the nickel atom must also lie on the intersection of these planes. This is nearly but not completely so. The nickel atom lies 0.092 (9) Å out of the pyridine plane; thus, the nickel–nitrogen vector makes an angle of 2.5° with its projection onto the pyridine plane. The nickel atom lies 0.049 (9) Å out of the acetylacetonate plane; the vector between the nickel atom and the midpoint of the O_1-O_2 line makes an angle of 2.0° with its projection onto this ligand plane. Finally the common plane of the pyridine rings in the idealized structure should coincide with the mirror plane relating the two acetylacetone ligands; here, the plane parallel to those of the two pyridine rings which passes through the nickel atom is rotated 2.5° about the NMN axis from that position toward O_2.

The geometries of the ligands themselves agree closely with the analogous cobalt compound, as can be seen in Tables V and VI. The structure of the acetylacetone ligand has been determined many times and these bond distances and angles are as expected. The vibration of the ligand is seen to be largest perpendicular to the ligand plane. The only other determination of the structure of pyridine coordinated to a metal, which claims relatively high accuracy, is in the structure of $Co(AA)_2(py)_2$. All of the pyridine distances found here are somewhat longer than those found previously (Table V) and the agreement is only fair. These distances are still somewhat shorter than those determined spectroscopically[20] for the pyridine molecule; however, it seems unlikely that the disagreement is significant. The thermal motion of the pyridine ligand can be seen to increase as the distance from the metal atom increases and is generally largest perpendicular to the plane of the ligand. No corrections have been made in the bond lengths to account for this motion.

The refinement of hydrogen atom positional parameters seems to give, generally, reasonable bond distances and angles, although the angles associated with H_3C_1 are an exception. The average of 0.94 Å found for carbon–hydrogen atom distances is presumably shorter than the value of 1.08 Å, found in neutron diffraction, owing to the concentration of electron density in a bonding orbital between the nuclei.[21]

Stereochemical Effects of Packing Energy.—The staggered configuration of $Co(AA)_2(py)_2$ was previously assumed to occur owing to the availability of two metal orbitals for back-donation of electrons into pyridine π^* orbitals (one metal orbital for each pyridine ligand), and, indeed, the conformation was taken as evidence of π bonding. However, the structure of $Ni(AA)_2(py)_2$ is eclipsed and thus only one metal orbital is of the proper symmetry to donate electrons to the two pyridine ligands. In an attempt to determine whether the changes from staggered to eclipsed configurations and from a highly symmetrical crystal habitat (Co, ortho-

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(20) B. Bak, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectry.*, **2**, 361 (1958).

(21) B. Dawson, *Australian J. Chem.*, **18**, 595 (1965).

rhombic Cmcm) to a less symmetric one (Ni, monoclinic $P2_1/c$) were related to bonding or were merely a packing artifact, a series of calculations of packing energies was undertaken.

A modified version of the program PACK2[22] was used for the calculations; also used were several auxiliary programs written here. The calculations were based on four different models. These were as follows: the structure of $Co(AA)_2(py)_2$ in space group Cmcm (hereafter referred to as Co in Co stereo); the hypothetical structure with the stereochemistry of $Co(AA)_2(py)_2$ in space group Cmcm but with the pyridine ligands moved 0.075 Å closer to the metal atom and the acetylacetone ligands moved 0.01 Å closer to the metal atom to agree with the nickel–nitrogen and nickel–oxygen atom bond lengths (Ni in Co stereo); the structure of $Ni(AA)_2(py)_2$ in space group $P2_1/c$ (Ni in Ni stereo); and the hypothetical cobalt compound in space group $P2_1/c$ of nickel stereochemistry, but with the pyridine and acetylacetone ligands moved away from the metal atom by 0.075 and 0.01 Å, respectively (Co in Ni stereo).

The packing energy of the crystal is defined in terms of inter- and intramolecular parts. The intermolecular part is the sum of all potential energies of nonbonded atomic interactions between atoms in different molecules. Thus $E_{\text{inter}} = \Sigma_j \Sigma_k E_{jk}$, where E_{jk} is the pair potential between atom j of the reference molecule and atom k of any other molecule, separated by the distance d_{jk}, and where the sum in j is over all atoms in the reference molecule and the sum in k is over all other atoms in the structure with d_{jk} less than some maximum distance. The potential energy E_{jk} is evaluated using a modified Buckingham potential function $E_{jk} = -Ad_{jk}^{-6} + B\exp(-d_{jk}/\rho)$, which is rewritten as $E_{jk} = [E^0_{jk}/(1 - (6\rho/d^0_{jk}))][(d^0_{jk}/d_{jk})^6 - (6\rho/d^0_{jk})\exp(d^0_{jk} - d_{jk})/\rho)]$, where E^0_{jk} is the potential energy at the minimum and d^0_{jk} is the interatomic distance at the minimum potential. The intramolecular potential energy was calculated as $E_{\text{intra}} = \Sigma_j \Sigma_h E_{jh}$ where j ranged over all ligand atoms of the reference molecule and h ranged over the same atoms excluding any atom in the same ligand as atom j. Thus the intramolecular energy takes into account ligand–ligand interaction.

The potential parameters used in the calculation are listed in Table VII. Several different forms of potential functions have been used for similar calculations. There have been several different approaches to the nature of nonbonded interactions in molecular crystals.[23] These result in differences in both the form of the functions and the values of the parameters to be used. Those chosen here were used by Williams[22] in calculations on naphthalene. A further gross simplification in the calculations was made by considering the nitrogen and oxygen atoms to have the same interactions as carbon atoms. Although this may introduce errors on the order 30% into the terms involving the interaction of a nitrogen or oxygen atom with a carbon or hydrogen atom, such an approximation is not likely to influence greatly the final results. Since the oxygen and nitrogen atoms are effectively buried inside the molecule, they will contribute very little to the intermolecular energy terms. Also, since the main comparisons are to be made between models of the same bond lengths but different conformations and since the nitrogen–oxygen framework is practically unchanged by changes in conformation, the intramolecular energies will be only slightly affected by the choice of potential parameters for oxygen and nitrogen atoms.

TABLE VII

POTENTIAL PARAMETERS[a] USED IN PACKING CALCULATIONS

Interaction type	$^1/_2E^0_{jk}$	d^0_{jk}	ρ
H–H	−0.012	3.1	0.283
C–H	−0.018	3.5	0.281
C–C	−0.031	3.8	0.279

[a] E^0_{jk} is in kilocalories per mole and d^0_{jk} and ρ are in ångströms.

To obtain the total energy of each model, a deformation term was added to the inter- and intramolecular energy terms. This term is used to account for the energy necessary to distort the molecules from their idealized symmetry. In all of the models the acetylacetone ligand is planar but its plane does not contain the metal atom. In Co stereo the bending angle for each ligand is 5.8°; in Ni stereo it is 2.0°. An estimate of the energy of this distortion can be made using force constants which are available for out-of-plane bending in various metal acetylacetonate complexes.[24] The energy of the deformation is given by $E_{\text{def}} = {}^1/_2K_{\text{def}}(\Delta\pi)^2$, where K_{def} is the force constant expressed in kilocalories per mole and $\Delta\pi$ is the deformation in radians for a small change. A value of 50 kcal/mol is probably a reasonable upper limit[25] for K_{def} for these compounds.

The deformation energy therefore is estimated as 1.0 kcal/mol for Co stereo and 0.2 kcal/mol for Ni stereo.

Results of Packing Calculations.—Two types of calculation were performed which allowed comparison with experimental results. The first involved refinement of unit cell constants, and the second, calculations of the folding angles of the acetylacetone ligands.

Since two of the models, Co in Ni stereo and Ni in Co stereo, are hypothetical, no cell constants were available experimentally. The cell constants were obtained by the method of steepest descent using PACK2 to minimize the energy. Of course, these results depend on the potential functions chosen, particularly the position of the minima and shape of the curve near that point. The calculated results obtained for Ni in Ni stereo and Co in Co stereo can be compared with experimental values (see Table VIII) and the closeness of the agree-

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[22] D. E. Williams, "PACK2, A FORTRAN Crystallographic Molecular Packing Program," IS-1042 UC-4-Chemistry, Ames Laboratory, 1964.

[23] For an extensive review of calculations of this type see G. N. Ramachandran and V. Sasisekharan, *Advan. Protein Chem.*, in press. Other relevant papers are: D. E. Williams, *J. Chem. Phys.*, **45**, 3770 (1966); A. I. Kitaygorodsky, *Tetrahedron*, **14**, 230 (1961); D. P. Craig, R. Mason, P. Pauling, and D. P. Santry, *Proc. Roy. Soc.* (London), **A286**, 98 (1965).

[24] M. Mikami, U. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, **23A**, 1037 (1967).

[25] The value of K_{def} for the out-of-plane bending of the oxygen atom from the carbon atom framework is 55 kcal/mol. The value of K_{def} for bending the metal out of the ligand plane should be less than this.

TABLE VIII

CALCULATED AND EXPERIMENTAL CELL CONSTANTS[a]

	Exptl	Calcd	
	$Co(AA)_2(py)_2$	Co in Co stereo	Ni in Co stereo
a	11.13	10.63	10.61
b	16.18	16.19	16.06
c	11.91	11.82	11.83
	$Ni(AA)_2(py)_2$	Co in Ni stereo	Ni in Co stereo
a	8.32	8.29	8.29
b	9.65	9.65	9.64
c	14.72	14.73	14.73
β	117.1°	116.4°	116.5°

[a] Distances are in ångströms.

ment is, in some sense, a measure of the validity of the functions for these calculations.

In the latter two cases the agreement is rather good with the exception of the calculated *a* value for Co in Co stereo. The close intermolecular contacts along *a* are between the hydrogen atoms of adjacent acetylacetone ligands. These contacts were calculated using the hydrogen atom positions found in the previous X-ray study. The average carbon–hydrogen atom bond length was 0.88 Å instead of the 1.08 Å distance for which the potential functions were developed. It seems likely that the shortening of the *a* cell constant in the calculation relative to the experiment may be ascribed principally to these known errors in locating the centers of attraction and repulsion for the hydrogen atoms. Since the *a* cell constant of Co stereo is the only constant determined largely by hydrogen atom–hydrogen atom contacts, this shortening is only observed here.

Also the shortening of the *b* constant in Co stereo on going from Co to Ni is easily explained, since this is the direction of the nitrogen–metal–nitrogen atom vector, which was shortened by 0.15 Å on going from Co to Ni. Changes in the metal–nitrogen atom distances in the Ni stereo models do not result in shortening of head-on contacts of ligands but rather in slipping one pyridine ring past another. Thus this type of change does not seem to influence greatly the cell constants. The refined cell constants have been used in all subsequent calculations.

Further calculations were made on Co in Co stereo to see if the bending of the acetylacetone rings could be accounted for by packing forces. The starting model for this calculation was changed so that the two acetylacetone ligands were coplanar and normal to the nitrogen–metal–nitrogen vector. The acetylacetone ligands were then each allowed to rotate about a line through the two oxygen atoms of the ligand and the cell constants were refined. The ligands folded in the direction observed experimentally. The angle between the two ligands which gave the minimum energy was 161°. Thus each ligand was bent 9.5° from the common plane. No restoring force was included in this calculation, that is, the ligands were positioned to give the minimum packing energy with no account of the distortion energy.

The values of the energies calculated for the four models are shown in Table IX. The gross features of the results seem generally reasonable. Thus the increase in intramolecular energy of about 2.5 kcal/mol on decreasing the metal–nitrogen atom bond lengths reflects the increased repulsion between ligands. That the nickel compounds pack somewhat more efficiently than the cobalt compounds in both stereochemistries seems to reflect the smaller volume needed for the nickel compounds. Also the more favorable intermolecular packing in Co stereo is only achieved at the expense of bending the acetylacetone ligands from their expected positions.

TABLE IX

ENERGIES CALCULATED FOR VARIOUS MODELS (KCAL/MOL)

	Co stereo		Ni stereo	
	Co	Ni	Co	Ni
Intramolecular	0.19	2.71	0.25	2.45
Intermolecular	−26.83	−26.97	−25.71	−25.77
Distortion	1.00	1.00	0.20	0.20
Total	−25.64	−23.26	−25.26	−23.12

No account has been taken in these calculations of π-bonding energy. If the Ni stereo were found to be the more stable configuration for both compounds, then the argument could be made that the cobalt compound assumes the staggered configuration because of the additional π bond which can be formed and that the added π-bond energy must be enough to overcome the configurational instability. However, such arguments do not appear necessary. The staggered configuration is predicted to be the more stable on the basis of packing energy alone. That these calculations predict a staggered configuration for $Ni(AA)_2(py)_2$ is an indication of their limited applicability; however, an energy difference of approximately 0.1 kcal/mol is probably insignificant. Thus it appears that although packing calculations may support intuition concerning the folding of the acetylacetone ligands,[26] they discredit the idea that the staggered configuration of $Co(AA)_2(py)_2$ is a result of π bonding.

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(26) This folding of acetylacetone ligands has been observed many times and often attributed to packing forces although this is the first semiquantitative treatment of the problem. For an article discussing this problem see F. A. Cotton and J. S. Wood, *Inorg. Chem.*, **3**, 245 (1964).