served diamagnetism resulted from material that had dimerized, possibly upon recrystallization of an authentic sample of $Fe(S_2CSC_2H_5)_3$. This suggestion is further supported by the fact that solution electronic spectra (especially the visible and near-ir bands) reported in ref 6 for the iron thioxanthate complexes correspond more closely to the results for the dimers[3] than for the monomeric $Fe(S_2CSR)_3$ compounds.[2,3] The results of the crystal structure analysis of $(n\text{-}C_3H_7SCS_2)_3Fe$, reportedly in progress,[6] will be of interest.

Acknowledgments.—We are grateful to the National Institutes of Health for support of this research under Grant No. GM 16449. S. J. L. also thanks the Alfred P. Sloan Foundation for a research fellowship (1968–1970).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND 02912

The Crystal and Molecular Structure of Diiodocarbonylferrocene-1,1′-bis(dimethylarsine)nickel(II). A Nickel(II) Carbonyl Complex

BY CORTLANDT G. PIERPONT[1] AND RICHARD EISENBERG*

Received July 6, 1971

The crystal and molecular structure of the five-coordinate complex diiodocarbonylferrocene-1,1′-bis(dimethylarsine)-nickel(II), $NiI_2(CO)$(fdma), has been determined from three-dimensional X-ray data collected by the θ–2θ scan technique. The structure was solved by standard heavy-atom methods and has been refined by least-squares procedures to a conventional R factor of 0.038 for 1733 nonzero reflections. The complex crystallizes in space group $P2_12_12_1$ of the orthorhombic system in a cell of dimensions a = 15.16 (1), b = 11.51 (1), c = 12.01 (1) Å, and V = 2096 Å^3. There are four molecules per unit cell (ρ_{exptl} = 2.32 (2) g/cm^3; ρ_{calcd} = 2.326 g/cm^3). The coordination geometry about the Ni(II) ion is a nearly regular trigonal bipyramid with the fdma ligand occupying both an axial and an equatorial position. The Ni–As$_{\text{ax}}$ and Ni–As$_{\text{eq}}$ bond lengths are 2.310 (3) and 2.331 (3) Å, respectively. The carbonyl ligand is located in the other axial position with an Ni–C bond length of 1.82 (2) Å. The fdma ligand chelates with a stepped configuration in which the Ni, Fe, and two As atoms are not coplanar. The dihedral angle between the $NiAs_2$ and $FeAs_2$ planes is 46.6 (1)°. The cyclopentadienyl rings exhibit a twist angle (ω) of 8.8° from the completely eclipsed configuration.

Introduction

Many five-coordinate low-spin Ni(II) complexes have been reported within the past decade,[2] and a number of them have been structurally characterized by single-crystal X-ray methods.[3-10] In none of these systems, however, has carbonyl been found to exist within the coordination sphere. This apparent reluctance of Ni(II) to coordinate CO is well known and has been ascribed to the relatively stable and contracted 3d orbitals of the Ni(II) ion which render back-donation into the carbonyl π^* functions much less effective.[11,12] It was therefore of some structural interest when Bishop and Davison[13] reported the complexes $NiI_2(CO)$(fdma) and $NiI_2(CO)$(fdpa) (fdma = ferrocene-1,1′-bis(dimethylarsine) and fdpa = ferrocene-1,1′-bis(diphenylarsine)) as authentic five-coordinate carbonyl complexes of Ni(II). We report herein the structure determination of the $NiI_2(CO)$(fdma) complex which was undertaken in part to establish the coordination geometry about the Ni(II) ion in these systems.

A second important reason for examining the structure of $NiI_2(CO)$(fdma) lies in establishing the chelating properties of the fdma ligand, which at least generically is similar to the well-studied chelating agent *o*-phenylenebis(dimethylarsine) or diars.[14] The most significant difference between these two ligand systems is that whereas the C–C distance within the five-membered chelate ring in diars complexes is approximately 1.40 Å, the corresponding C···C separation in fdma complexes is at least the ferrocene inter-ring distance of *ca.* 3.30 Å. In order to take this increased separation and its consequent steric effects into account, Bishop and Davison[15] have proposed two different chelate conformations for the fdma (and fdpa) ligands. In the first case (structure I), the cyclopentadienyl rings are in a staggered configuration and the metal–fdma moiety possesses C_2 symmetry, whereas in the second case (structure II), the rings are in an eclipsed configuration and the metal, the two As donor atoms, and the ferrocene Fe are no longer coplanar. This latter conformation has been called "stepped"

---

(1) National Institutes of Health Predoctoral Fellow, 1969–1971.

(2) Recent pertinent reviews include (a) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **29**, 245 (1966); (b) L. Sacconi, *Transition Metal Chem.*, **4**, 199 (1968).

(3) D. L. Stevenson and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 3424 (1967).

(4) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 1362 (1968).

(5) L. P. Haugen and R. Eisenberg, *ibid.*, **8**, 1072 (1969).

(6) J. K. Stalick and J. A. Ibers, *ibid.*, **8**, 1084 (1969).

(7) J. K. Stalick and J. A. Ibers, *ibid.*, **8**, 1090 (1969).

(8) D. W. Meek and J. A. Ibers, *ibid.*, **8**, 1915 (1969).

(9) P. L. Orioli and L. Sacconi, *Chem. Commun.*, 1310 (1968); P. L. Orioli and C. A. Ghilardi, *J. Chem. Soc. A*, 1511 (1970).

(10) P. Dapporto and L. Sacconi, *ibid.*, *A*, 1804 (1970).

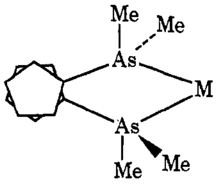
(11) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 743.

(12) M. Bressan, B. Corain, P. Rigo, and A. Turco, *Inorg. Chem.*, **9**, 1733 (1970).

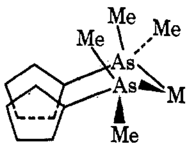
(13) J. J. Bishop and A. Davison, *ibid.*, **10**, 832 (1971).

(14) For a partial listing of diars complexes, see C. M. Harris and S. E. Livingstone in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, pp 129–132.

(15) J. J. Bishop and A. Davison, *Inorg. Chem.*, **10**, 826 (1971).



I



II

and it possesses C_s or *m* symmetry. The preferred conformational mode in any given system depends upon the size of the central metal aom and the As–M–As bond angle, with I being favored for large metal atoms and bond angles significantly greater than 90° while II is more preferable for smaller metal atoms and bond angles of *ca.* 90°. Bishop and Davison have also found that in some of the fdma complexes fluxional behavior exists with all of the methyl groups appearing equivalent on the nmr time scale.[13,15] Because of the interesting behavior of these systems and the range of possible As–Ni–As bond angles in five-coordinate geometries, it was deemed necessary to establish unequivocally the conformational mode of the fdma ligand in this complex in order to aid in explaining the fluxional behavior and other interesting properties in this and related systems.

Collection and Reduction of the X-Ray Data

Crystals of the complex $NiI_2(CO)(fdma)$ were kindly provided by Professor Alan Davison of Massachusetts Institute of Technology. One large crystal was ground into a sphere of approximate radius 0.27 mm. On the basis of Weissenberg and precession photographs of the *hk*0, *hk*1, *h*0*l*, *h*1*l*, 0*kl*, and 1*kl* zones, it was established that the complex crystallizes in the orthorhombic system. The observed extinctions of $h = 2n + 1$ for *h*00, $k = 2n + 1$ for 0*k*0, and $l = 2n + 1$ for 00*l* uniquely determine the space group as $P2_12_12_1$ (D_2^4, no. 19).[16] The lattice constants were determined at ambient room temperature from a least-squares refinement of the angular settings of 17 strong reflections centered on a Picker four-circle automated diffractometer using Mo Kα radiation (λ 0.7107 Å) and are $a = 15.16$ (1), $b = 11.51$ (1), $c = 12.01$ (1) Å, and $V = 2096$ Å^3. This refinement was performed using our local PICKLST program.[17] An experimental density of 2.32 (2) g/cm^3 obtained by the flotation method agrees with a calculated value of 2.326 g/cm^3 for four $NiI_2(CO)(fdma)$ molecules per unit cell.

The spherical crystal was positioned so that it was mounted along the c^* axis. The mosaic spread of the crystal was determined using the narrow-source, open-counter, ω-scan technique.[18] The average width at half-height was found to be 0.08°. An independent set of intensity data was collected by the θ–2θ scan technique using Zr-filtered Mo Kα radiation at a takeoff angle of 1.5°. A receiving aperture of dimensions 3 × 4.5 mm was positioned 21 cm from the crystal. An unsymmetrical scan range in 2θ was used from −0.6 to +0.7° of the Mo Kα peak with allowances made for the $K\alpha_1$–$K\alpha_2$ separation at higher 2θ values. The data set was collected within the angular range $5° \leqslant 2\theta \leqslant 60°$. Attenuators were inserted automatically if the count rate of the diffracted beam exceeded about 9000 counts/sec during the scan. The attenuators used were brass foil of thickness chosen to give an approximate attenuation factor of 3.0. During data collection the intensities of four standard reflections in different regions of reciprocal space were monitored after every 100 reflections measured. None of these standards deviated from its mean value by more than 2% during the time required to collect data. The data were processed in the usual way and the values of *I* and σ(*I*) were corrected for Lorentz and polarization effects. The intensities of a total of 3437 reflections were measured, of which 1733 were observed to be greater than 2σ. Since the crystal was spherical, no correction was made for absorption effects.

Solution and Refinement of the Structure

The positions of the two iodine atoms were determined from a three-dimensional Patterson function. After a cycle of least-squares refinement of the positional and isotropic thermal parameters of these two atoms and a single scale factor, the discrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ were 0.413 and 0.485, respectively. From a difference Fourier map based on phases obtained from the iodine atom contributions, the nickel, iron, and two aresenic atom positions were readily determined. Two cycles of least-squares refinement of the scale factor and the positional and isotropic thermal parameters of these six atoms reduced the discrepancy factors to $R_1 = 0.123$ and $R_2 = 0.170$. A difference Fourier map based on this refinement revealed the positions of all other nonhydrogen atoms in the structure.

The complete trial structure was refined by a least-squares procedure in which the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weights *w* were assigned as $4F^2/\sigma^2(F^2)$ where the standard deviations $\sigma(F^2)$ were estimated from counting statistics according to the formula given by Corfield, *et al.*,[19] with a value of 0.03 for the uncertainty parameter *p*. In all refinements, only the 1733 reflections for which $F_o^2 \geqslant 2\sigma(F_o^2)$ were used. The atomic scattering factors of the nonhydrogen atoms were taken from Cromer and Waber's report[20] while that of hydrogen was taken from the report by Stewart, *et al.*[21] The effects of anomalous dispersion were included in the calculated structure factors with the values of $\Delta f'$ and $\Delta f''$ for I, As, Fe, and Ni taken from Cromer's tabulation.[22] One cycle of refinement including all nonhydrogen atoms with individual isotropic temperature factors reduced the discrepancy factors R_1 and R_2 to values of 0.075 and 0.079, respectively.

Least-squares refinement was continued with anisotropic thermal models assumed for all of the atoms, and two cycles of least squares converged to $R_1 = 0.043$ and $R_2 = 0.041$. An additional cycle of refinement was then performed setting the *hkl* indices to $\overline{hkl}$ in order to determine the correct enantiomorph. This refinement led to a highly significant improvement in the agreement factors with $R_1 = 0.038$ and $R_2 = 0.036$ and this configuration was therefore chosen as the correct one. A difference Fourier map based on this cycle of refinement failed to yield unambiguous and chemically reasonable positions for the hydrogen atoms in the structure. However the positions of the cyclopentadienyl ring hydrogen atoms were idealized (d(C–H) = 1.08 Å) and included as fixed contributions with unrefined isotropic temperature factors of 5.0 Å^2 in the final cycle of refinement. This refinement showed no change in the discrepancy factors with final values for R_1 and R_2 of 0.038 and 0.036, respectively. No parameter changed by more than 40% of its standard deviation on the final cycle of refinement with the largest changes occurring for the methyl group carbon atoms. The estimated standard deviation of an observation of unit weight is 0.87 indicating that the standard deviations σ were slightly overestimated. A final difference Fourier map showed residual electron density equivalent to about 30% the height of a carbon atom in the region of I(2). The final positional and anisotropic thermal parameters of the atoms in this structure are given in Table I. The final F_o and $|F_c|$ values (in electrons × 10) for the 1733 reflections used in the refinements have been tabulated.[23] In Table II, the root-mean square amplitudes of

---

(16) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1960, p 105.

(17) In addition to the PICKLST setting program, the main programs used in this work were local versions of the Busing–Levy ORFLS least-squares program, the Zalkin FORDAPER Fourier summation program, the Busing–Martin–Levy ORFFE function and error program, and the Johnson ORTEP plotting program. Various other local programs were also used. All computing was performed on Brown's IBM 360/67 computer.

(18) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957, Chapter 10.

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

(20) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(21) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(22) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965)

(23) The table of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE I

FINAL POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS FOR $NiI_2(CO)$ (fmda)

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.1978(1)	0.2657(2)	-0.1750(2)	0.0028(1)	0.0082(2)	0.0066(2)	-0.0003(1)	0.0005(1)	-0.0010(2)
Fe	0.4004(1)	0.2577(2)	-0.4310(2)	0.0033(1)	0.0069(2)	0.0060(2)	-0.0008(1)	0.0007(1)	-0.0004(2)
I(1)	0.1820(1)	0.2587(1)	0.0425(1)	0.0050(1)	0.0090(1)	0.0064(1)	0.0001(1)	0.0013(1)	0.0003(1)
I(2)	0.1438(1)	0.4575(1)	-0.2685(1)	0.0063(1)	0.0111(1)	0.0092(1)	0.0030(1)	-0.0005(1)	0.0015(1)
As(1)	0.2416(1)	0.1043(1)	-0.2782(1)	0.0028(1)	0.0058(1)	0.0057(1)	-0.0003(1)	-0.0002(1)	0.0004(1)
As(2)	0.3402(1)	0.3339(1)	-0.1544(1)	0.0030(1)	0.0094(1)	0.0055(1)	-0.0009(1)	-0.0002(1)	-0.0012(1)
C	0.0821(10)	0.2265(18)	-0.1873(15)	0.0035(8)	0.0163(26)	0.0118(19)	0.0001(13)	-0.0008(11)	-0.0023(19)
O	0.0126(7)	0.1990(13)	-0.1938(12)	0.0027(6)	0.0249(24)	0.0190(18)	-0.0031(10)	0.0007(9)	-0.0088(16)
R(1)	0.3036(9)	0.1355(11)	-0.4133(11)	0.0030(7)	0.0059(12)	0.0062(12)	-0.0008(8)	0.0010(8)	-0.0016(10)
R(2)	0.3802(9)	0.0826(13)	-0.4573(14)	0.0034(8)	0.0074(14)	0.0101(16)	0.0004(8)	-0.0002(10)	-0.0032(14)
R(3)	0.4053(12)	0.1378(17)	-0.5574(16)	0.0070(11)	0.0115(20)	0.0074(16)	0.0004(13)	0.0019(12)	0.0001(16)
R(4)	0.3433(12)	0.2239(17)	-0.5820(12)	0.0065(10)	0.0146(22)	0.0045(12)	-0.0063(14)	-0.0001(9)	0.0014(14)
R(5)	0.2765(10)	0.2286(13)	-0.4947(13)	0.0046(8)	0.0068(15)	0.0079(13)	-0.0011(9)	-0.0011(9)	0.0000(12)
R(6)	0.4155(9)	0.3460(12)	-0.2821(12)	0.0036(7)	0.0056(12)	0.0071(13)	-0.0011(8)	0.0000(9)	-0.0010(12)
R(7)	0.4931(9)	0.2822(14)	-0.3057(14)	0.0026(7)	0.0087(16)	0.0112(17)	0.0003(9)	0.0004(9)	-0.0033(14)
R(8)	0.5293(10)	0.3212(16)	-0.4147(14)	0.0026(7)	0.0121(19)	0.0083(16)	-0.0022(10)	-0.0017(9)	-0.0006(15)
R(9)	0.4684(11)	0.4091(16)	-0.4543(16)	0.0052(9)	0.0132(20)	0.0111(17)	-0.0058(11)	0.0037(11)	-0.0009(17)
R(10)	0.4003(10)	0.4237(13)	-0.3754(13)	0.0045(8)	0.0057(13)	0.0082(14)	-0.0024(8)	0.0013(9)	-0.0018(11)
Me(1)	0.3215(11)	-0.0081(12)	-0.2059(13)	0.0070(10)	0.0064(13)	0.0078(15)	0.0031(10)	-0.0008(11)	0.0012(12)
Me(2)	0.1453(8)	0.0006(13)	-0.3344(12)	0.0028(7)	0.0078(14)	0.0079(14)	-0.0025(8)	-0.0002(9)	-0.0008(11)
Me(3)	0.3490(11)	0.4949(15)	-0.0960(14)	0.0073(12)	0.0115(18)	0.0112(18)	-0.0031(12)	0.0049(13)	-0.0048(15)
Me(4)	0.4172(9)	0.2508(19)	-0.0493(13)	0.0030(7)	0.0220(23)	0.0075(14)	0.0004(13)	-0.0022(9)	0.0046(21)

[a] Standard deviations of the least significant figures are given in parentheses here and in subsequent tables. [b] Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

TABLE II

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Atom	Min	Intermed	Max
Ni	0.176 (3)	0.212 (3)	0.245 (3)
Fe	0.179 (4)	0.206 (3)	0.233 (3)
I(1)	0.198 (2)	0.245 (2)	0.257 (2)
I(2)	0.207 (2)	0.267 (2)	0.317 (2)
As(1)	0.176 (2)	0.193 (2)	0.210 (2)
As(2)	0.175 (3)	0.200 (2)	0.259 (2)
C	0.20 (3)	0.28 (3)	0.34 (3)
O	0.16 (2)	0.30 (2)	0.47 (2)
R(1)	0.17 (2)	0.18 (3)	0.24 (2)
R(2)	0.19 (3)	0.20 (2)	0.30 (2)
R(3)	0.21 (3)	0.28 (2)	0.30 (2)
R(4)	0.16 (3)	0.19 (3)	0.38 (3)
R(5)	0.19 (2)	0.23 (2)	0.26 (2)
R(6)	0.17 (2)	0.22 (2)	0.24 (2)
R(7)	0.17 (2)	0.21 (2)	0.31 (2)
R(8)	0.13 (3)	0.26 (2)	0.30 (2)
R(9)	0.11 (2)	0.28 (2)	0.37 (2)
R(10)	0.15 (2)	0.22 (2)	0.29 (2)
Me(1)	0.16 (3)	0.25 (2)	0.31 (2)
Me(2)	0.13 (3)	0.24 (2)	0.26 (2)
Me(3)	0.19 (3)	0.23 (2)	0.39 (2)
Me(4)	0.14 (3)	0.25 (2)	0.40 (2)

TABLE III

FIXED POSITIONAL PARAMETERS OF CYCLOPENTADIENYL RING HYDROGEN ATOMS

Atom[a]	*x*	*y*	*z*
H(2)	0.4246	0.0046	−0.4087
H(3)	0.4689	0.1138	−0.6193
H(4)	0.3364	0.2895	−0.6657
H(5)	0.2103	0.2889	−0.4838
H(7)	0.5283	0.2039	−0.3391
H(8)	0.5948	0.2869	−0.5513
H(9)	0.4756	0.4657	−0.6316
H(10)	0.3355	0.4932	−0.4690

[a] Hydrogen atom H (*i*) bonded to ring carbon R (*i*). Each H atom was assigned a fixed isotropic thermal parameter of 5.0 Å².

vibration of the anisotropically refined atoms are presented. The fixed H atom positional parameters are given in Table III.

Description of the Structure

The crystal structure of the complex consists of the packing of discrete enantiomeric molecules according to the symmetry of space group $P2_12_12_1$. All intermolecular contacts are normal and are therefore not tabulated. Within the molecule, the Ni atom possesses a nearly regular trigonal-bipyramidal coordination geometry with the fdma ligand occupying both an axial and an equatorial position. A perspective drawing of the complex which clearly shows the coordination geometry is presented in Figure 1, and all important intramolecular distances and angles are tabulated in Table IV. The two independent Ni–As distances average 2.320 (3) Å which agrees well with the average value of 2.322 (3) Å found by Stevenson and Dahl in the structure of $[Ni(TAP)CN]^+$ (TAP = tris(3-dimethylarsinopropyl)phosphine).[3] However, the difference between the two Ni–As bond lengths in the present structure is statistically significant (the difference equals 0.020 (4) Å) with the axial bond length being the shorter one in accordance with the observations of Raymond, *et al.*, in their study of d^8 and d^9 trigonal-bipyramidal structures.[24] The presence of the carbonyl ligand trans to the axial As atom may serve to reduce the difference between the two Ni–As bond lengths in the present study.

---

(24) K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **7**, 1111 (1968), and references therein.

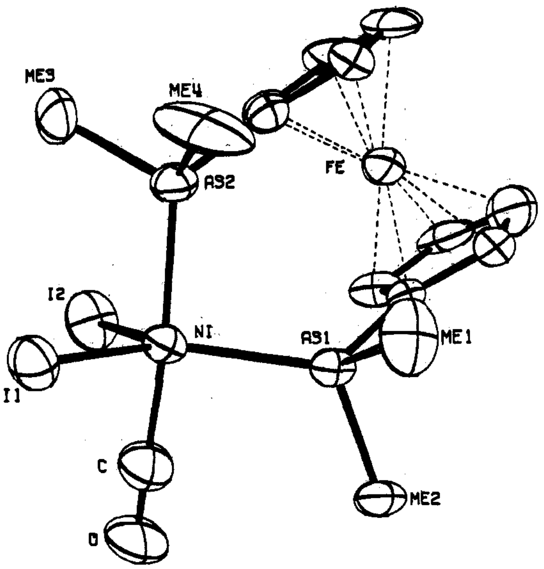


Figure 1.—A perspective view of $NiI_2(CO)(fdma)$ showing the coordination geometry about the nickel(II) ion.

TABLE IV
INTRAMOLECULAR DISTANCES AND ANGLES

Intramolecular Distances, Å		Intramolecular Angles, deg	
Ni–I(1)	2.624 (3)	I(1)–Ni–I(2)	115.24 (8)
Ni–I(2)	2.609 (3)	I(1)–Ni–As(1)	122.1 (1)
Ni–As(1)	2.331 (3)	I(2)–Ni–As(1)	122.3 (1)
Ni–As(2)	2.310 (3)	I(1)–Ni–As(2)	89.38 (8)
Ni–C	1.817 (16)	I(2)–Ni–As(2)	92.98 (9)
Ni···Fe	4.348 (3)	As(1)–Ni–As(2)	93.49 (8)
C–O	1.103 (17)	I(1)–Ni–C	89.2 (6)
As(1)–Me(1)	1.974 (14)	I(2)–Ni–C	82.7 (6)
As(1)–Me(2)	2.003 (13)	As(1)–Ni–C	91.9 (6)
As(2)–Me(3)	1.987 (16)	As(2)–Ni–C	174.3 (6)
As(2)–Me(4)	1.967 (15)	Ni–C–O	178 (2)
As(1)–R(1)[a]	1.909 (14)	Ni–As(1)–Me(1)	117.6 (5)
As(2)–R(6)	1.917 (14)	Ni–As(1)–Me(2)	116.5 (4)
R(1)–R(2)	1.413 (18)	Ni–As(1)–R(1)	116.3 (4)
R(2)–R(3)	1.412 (22)	Ni–As(2)–Me(3)	114.7 (5)
R(3)–R(4)	1.397 (23)	Ni–As(2)–Me(4)	117.3 (5)
R(4)–R(5)	1.459 (21)	Ni–As(2)–R(6)	119.7 (4)
R(5)–R(1)	1.507 (20)	Me(1)–As(1)–Me(2)	101.8 (7)
R(6)–R(7)	1.416 (18)	Me(1)–As(1)–R(1)	101.2 (6)
R(7)–R(8)	1.488 (22)	Me(2)–As(1)–R(1)	100.6 (6)
R(8)–R(9)	1.449 (23)	Me(3)–As(2)–Me(4)	100.8 (8)
R(9)–R(10)	1.411 (20)	Me(3)–As(2)–R(6)	100.0 (6)
R(10)–R(6)	1.452 (19)	Me(4)–As(2)–R(6)	101.3 (6)
Fe–R(1)	2.044 (14)	R(1)–R(2)–R(3)	110 (1)
Fe–R(2)	2.063 (15)	R(2)–R(3)–R(4)	109 (1)
Fe–R(3)	2.053 (18)	R(3)–R(4)–R(5)	110 (1)
Fe–R(4)	2.047 (15)	R(4)–R(5)–R(1)	104 (1)
Fe–R(5)	2.056 (15)	R(5)–R(1)–R(2)	107 (1)
Fe–R(6)	2.069 (14)	R(6)–R(7)–R(8)	109 (1)
Fe–R(7)	2.078 (15)	R(7)–R(8)–R(9)	105 (1)
Fe–R(8)	2.095 (14)	R(8)–R(9)–R(10)	109 (2)
Fe–R(9)	2.044 (15)	R(9)–R(10)–R(6)	109 (1)
Fe–R(10)	2.023 (14)	R(10)–R(6)–R(7)	107 (1)

Dihedral Angles between Planes, Deg	
[I(1),I(2),As(1)]–[R(1),R(3),R(4)]	140.8 (8)
[I(1),I(2),As(1)]–[R(6),R(8),R(9)]	140.8 (6)
[As(1),Me(1),Me(2)]–[As(1),Ni,R(1)]	90.1 (5)
[As(2),Me(3),Me(4)]–[As(2),Ni,R(6)]	89.9 (5)
[As(1),As(2),Ni]–[As(1),As(2),R(1)]	50.3 (4)
[As(1),As(2),Ni]–[As(1),As(2),R(6)]	41.0 (4)
[R(1),R(3),R(4)]–[R(6),R(8),R(9)]	3 (1)
[Ni,As(1),As(2)]–[Fe,As(1),As(2)]	46.6 (1)

[a] The cyclopentadienyl ring carbon atoms are labeled R(1)–R(10). R(1)–R(5) comprise one cyclopentadienyl ring which is bonded to As(1) through R(1), while R(6)–R(10) comprise the other ring which is bonded to As(2) through R(6). The order of labels in each ring is sequential and established in such a way that R(1) is closest to R(6) of the other C_5H_5 ring, R(2) to R(7), etc.

The Ni–C distance is 1.82 (2) Å and the Ni–C–O moiety is essentially linear. This bond length cannot be compared directly with other Ni(II)–CO distances but it does agree with the 1.84 (1) Å value found for the Ni–axial C distance in the trigonal-bipyramidal form of $Ni(CN)_5{}^{3-}$.[4] This distance is also in agreement with the Ni–C distances of 1.82 (3), 1.80 (1), and 1.79 (1) Å found in the carbonyl complexes $Ni(CO)_4$,[25] $Ni_2(CO)_6(P_2(C_6H_5)_4)$,[26] and $Ni_2(P(C_6H_5)_2)_2(CO)_4$[27] where the nickel atom is formally in the 0 or 1+ oxidation state. The C–O distance of 1.102 (17) Å is slightly (and possibly not significantly) shorter than is usually found in carbonyl complexes (*ca.* 1.15 Å), but it is commensurate with the high stretching frequency of 2054 cm^{-1} reported by Bishop and Davison.[13] The two Ni–I distances in the equatorial plane of the complex average 2.616 (2) Å. The difference of 0.015 (4) Å in these two Ni–I distances is possibly significant in a statistical sense, but the magnitude of the difference is quite small. If significant, such a difference in equatorial bond lengths can be attributed to minor bonding effects resulting from the unsymmetrical nature of the chelating fdma ligand as seen by the two iodides (*vide infra*) or from minor crystal-packing effects. In any case, the two Ni–I distances can be averaged for comparison with corresponding distances in other structures. The value of 2.616 (2) Å is very significantly shorter than the axial Ni–I distance of 2.71 (1) Å reported for the tripod-type complex $Ni(tda)I^+$ (tda = tris(2-diphenylphosphinoethyl)amine)[10] in which important nonbonded repulsions exist between the iodine and the equatorial phosphine ligands. The Ni–I distance may also be compared with the values of 2.514 (5) and 2.567(5) Å found in the low-spin square-pyramidal complex $Ni(DSP)I_2$ (DSP = bis(*o*-methylthiophenyl)phenylphosphine).[8] These shorter distances are approximately consistent with the value of 2.616 Å if one assumes that the bonding radius of low-spin Ni(II) in the equatorial plane of a trigonal bipyramid is *ca.* 0.08 Å longer than in the basal plane of a square pyramid as has been suggested previously.[4] It should be noted that the bond angles about the Ni atom given in Table IV indicate a very nearly regular trigonal-bipyramidal geometry despite the unsymmetrical nature of the coordination sphere.

One of the aims of the present study and an important feature of the structure is the conformation of the chelating fdma ligand. We find the chelate conformation to be of the "stepped" type (structure II) and a perspective drawing of the complex which illustrates this feature is given in Figure 2. The two cyclopentadienyl rings exhibit an average twist angle of 8.8° from the completely eclipsed configuration. The twist angle is defined by Palenik[28] as the dihedral angle between a ring carbon atom, the two ring centers, and the corresponding carbon on the opposite ring. The average value of 8.8° is clearly closer to the eclipsed configuration than to the staggered and it agrees well with a number of other ferrocene derivative structures which have been tabulated by Churchill and Wormald.[29]

(25) L. O. Brockway and P. C. Cross, *J. Chem. Phys.*, **3**, 828 (1935).

(26) R. H. B. Mais, P. G. Owston, D. T. Thompson, and A. M. Wood, *J. Chem. Soc. A*, 1744 (1967).

(27) J. A. J. Jarvis, R. H. B. Mais, P. G. Owston, and D. T. Thompson, *ibid.*, *A*, 1867 (1970).

(28) G. J. Palenik, *Inorg. Chem.*, **9**, 2424 (1970).

(29) M. R. Churchill and J. Wormald, *ibid.*, **8**, 716 (1969).

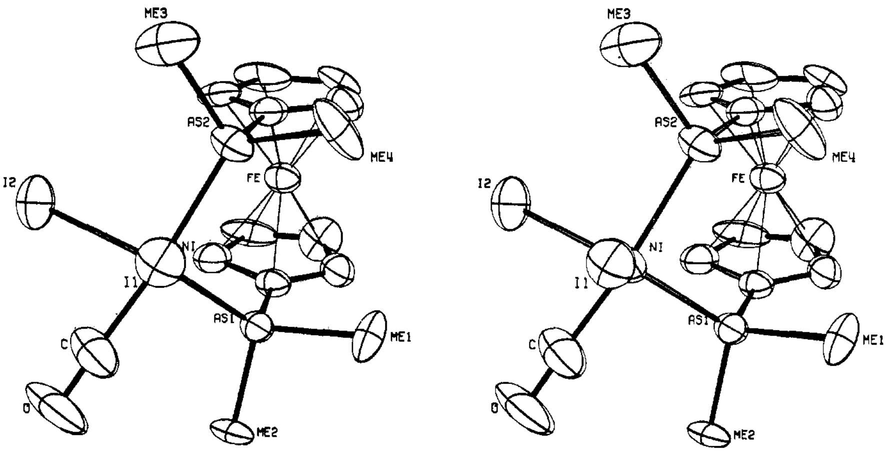


Figure 2.—A view of the $NiI_2(CO)(fdma)$ complex which illustrates the stepped conformation of the fdma ligand in this structure. These drawings constitute a stereo pair and should be viewed with a hand viewer

In the stepped conformation of the chelating fdma ligand, the Ni, Fe, and two As atoms are no longer coplanar with a dihedral angle of 46.6 (1)° between the $NiAs_2$ and $FeAs_2$ planes.

The cyclopentadienyl rings are rigorously planar in the present structure. Least-squares planes through the two rings and the deviations of atoms from these planes are given in Table V. The intra-ring C–C distances range from 1.40 (2) to 1.51 (2) Å with an average value of 1.44 Å. This average distance is in agreement with the values of 1.431, 1.430, and 1.426 Å found in the structures of ferrocene (by electron diffraction),[30] bis(π-azulene)iron,[29] and diacetylferrocene,[28] respectively. The Fe–ring C distances vary from 2.023 to 2.095 Å with estimated standard deviations of 0.015 Å. The average Fe–ring C distance of 2.058 Å is in essential agreement with the corresponding values found in other ferrocene structures.[29] Finally, it should be noted that the two cyclopentadienyl rings are very slightly canted with respect to each other, the dihedral angle (ϕ) being 3 (1)°.

TABLE V

EQUATIONS OF WEIGHTED LEAST-SQUARES PLANES[a] AND DEVIATIONS OF THE ATOMS FROM THE PLANES

Atom	Distance, Å	Atom	Distance, Å
Plane through Cyclopentadienyl Ring R(1)–R(5) $8.45x + 7.60y + 6.04z = 1.09$			
R(1)	0.01 (1)	R(5)	−0.01 (1)
R(2)	−0.01 (1)	Fe	1.65[b]
R(3)	0.02 (2)	As(1)	0.06[b]
R(4)	−0.00 (2)		
Plane through Cyclopentadienyl Ring R(6)–R(10) $8.19x + 8.11y + 5.52z = 4.65$			
R(6)	0.01 (1)	R(10)	0.00 (1)
R(7)	−0.01 (1)	Fe	−1.66[b]
R(8)	0.00 (2)	As(2)	0.00[b]
R(9)	0.00 (2)		
Plane through As(1), As(2), Fe, R(1), and R(6) $-10.81x + 6.96y - 4.26z = -0.70$			
As(1)	−0.002 (1)	R(1)	0.121 (14)
As(2)	0.003 (2)	R(2)	−0.182 (14)
Fe	0.001 (2)	Ni	1.16[b]

[a] Least-squares planes calculated according to W. C. Hamilton, *Acta Crystallogr.*, **14**, 185 (1961). Equations are given in orthorhombic coordinates. [b] Not included in the calculation of the plane.

An examination of Figure 2 clearly shows that the two methyl groups bonded to each arsenic are nonequivalent. In the present case, Me(1) and Me(4) comprise a pseudoaxial set while Me(2) and Me(3) occupy the corresponding equatorial positions with regard to the chelate ring. By virtue of the chelate conformation and the nonequivalence of the methyl groups, the four protons of each cyclopentadienyl ring are also nonequivalent. However, Bishop and Davison[13,15] have found that the nmr spectra of a number of fdma complexes exhibit cyclopentadienyl ring proton resonances in an AA′BB′ pattern and are much simpler than those expected for the purely static systems. In complexes which possess the "stepped" configuration as found in the present study, interconversion of the pseudoaxial and equatorial methyl groups may occur on the nmr time scale by a "flipping" of the chelated metal atom and its associated ligands from one side of the $FeAs_2$ plane to the other.

Acknowledgments.—We wish to thank Professor Alan Davison for crystals of the complex and his very helpful comments. We also thank the National Science Foundation (Grant GP-23139) and the Advanced Research Projects Agency for support of this research.

---

(30) R. K. Bohn and A. Haaland, *J. Organometal. Chem.*, **5**, 470 (1966).