Acta Cryst. (1981). **B37**, 1194–1198

Structural Variations in Macrocyclic Complexes: The Structure of {Difluoro[3,3′-(trimethylenediimino)bis(2-butanone oximato)]borato}iodonickel(II),* [Ni(cyclops)I]

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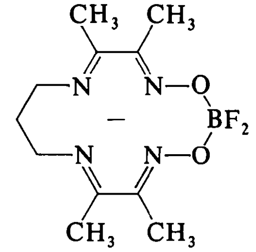
(*Received* 27 *May* 1980; *accepted* 20 *January* 1981)

Abstract

[$Ni(C_{11}H_{18}BF_2N_4O_2)I$], $M_r = 472{\cdot}67$, crystallizes in the monoclinic space group $P2_1/n$, with $a = 15{\cdot}56\,(1)$, $b = 7{\cdot}513\,(8)$, $c = 14{\cdot}24\,(1)$ Å, $\beta = 98{\cdot}25\,(2)°$, $V = 1647{\cdot}5$ Å^3, $\rho_c = 1{\cdot}91$ Mg m^{-3} (for $Z = 4$), $F(000) = 928$, Mo $K\alpha$ radiation ($\lambda_1 = 0{\cdot}70930$, $\lambda_2 = 0{\cdot}71359$ Å), μ(Mo $K\alpha$) = 3·10 mm^{-1}. Final $R = 0{\cdot}036$ for 2096 reflections. The neutral, monomeric, low-spin complex exhibits square-pyramidal coordination about the Ni^{II} ion. The four basal coordination positions are occupied by the N atoms of the macrocyclic cyclops ligand, [Ni—N(imine, av.) = 1·886 (5), Ni—N(oxime, av.) = 1·863 (5) Å] while the apical position is occupied by iodide [Ni—I = 2·834 (3) Å]. With respect to the structure of the corresponding Cu^{II} complex, [Cu(cyclops)I], the Ni—N distances are ~0·1 Å shorter, the Ni—I distance is ~0·1 Å longer, and the Ni^{II} ion is ~0·15 Å closer to the plane of the coordinating N atoms. These structural changes relative to the Cu^{II} complex arise from the lack of electron density in the $d_{x^2-y^2}$ orbital of the metal in the d^8 Ni complex.

Introduction

Recent determinations in this laboratory of the structures of the five-coordinate macrocyclic complexes [Cu(cyclops)L]$^+$ and [Cu(cyclops)X] [$X^- = NCO^-, CN^-, I^-$; $L = H_2O$, pyridine; cyclops = difluoro-3,3′-(trimethylenediimino)bis(2-butanone oximato)borate (1)] have demonstrated more highly variable structures for these Cu^{II} complexes than had previously been thought possible (Anderson & Marshall, 1978; Anderson & Packard, 1979*a*,*b*, 1980*a*,*b*). In particular, in this series of complexes the Cu^{II} ion was found to form bonds of unusual strength to the anionic apical ligands investigated, and the positioning of the Cu^{II} ion relative to the basal plane of coordinating N atoms was found to vary from a displacement (in the direction of the apical ligand) of only 0·32 Å in the aqua complex ion to a maximum of 0·58 Å in the cyanato-*N* complex. In investigating the origins of these surprising structural effects, our previous studies have considered the influence of apical ligand type and of structural restrictions associated with closure of the macrocyclic ring. To investigate the degree to which the unpaired $d_{x^2-y^2}$ electron of the d^9 Cu^{II} electronic distribution was responsible for the metal apical displacement observed in the above series of complexes, it was necessary to investigate the structure of a low-spin five-coordinate Ni^{II} cyclops complex in which the apical ligand was identical to that in one of the previously investigated Cu^{II} complexes. In consequence, the crystal and molecular structure of the complex [Ni(cyclops)I] has been determined, and is the subject of this report.



(1)

Experimental section

Crystals of [Ni(cyclops)I] were kindly provided by Professor M. Wicholas.

Data collection and structure determination

Preliminary precession and Weissenberg photographs revealed monoclinic symmetry, together with systematic absences ($0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$) requiring the assignment of $P2_1/n$ as the space group.

Data collection, data reduction, structure determination, and structure refinement were carried out in a manner similar to other studies in this laboratory (Anderson, Packard & Wicholas, 1976). Periodic

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* Alternative name: (2,2-difluoro-5,6,12,13-tetramethyl-1,3-dioxa-4,7,11,14-tetraaza-2-boracyclotetradeca-4,6,11,13-tetraenido-*N*,*N*′,*N*″,*N*‴)iodonickel(II).

0567-7408/81/061194-05$01.00

measurement of the intensities of three reflections ($22\bar{6}$, $\bar{5}0\bar{5}$, and 040) showed no significant changes occurring during data collection. The data were corrected for absorption by a numerical Gaussian integration technique (6 × 4 × 4 grid). The dimensions of the data collection crystal were 0·45 mm ($\{010\} \rightarrow \{0\bar{1}0\}$) × 0·10 mm ($\{\bar{1}01\} \rightarrow \{10\bar{1}\}$) × 0·20 mm ($\{101\} \rightarrow \{\bar{1}0\bar{1}\}$). Extrema in the calculated transmission coefficients were 0·562 and 0·740. The uncertainty parameter, g, used in the calculation of $\sigma(F_o^2)$ was taken as 0·04. The 2096 unique reflections (of 2987 measured) with $F^2 > 3\sigma(F^2)$ were used in the solution and refinement of the structure.

The positions of the I^- and Ni^{II} ions were assigned from the Patterson map, and initial positions for all non-hydrogen atoms were subsequently obtained from Fourier syntheses. Atomic scattering factors, together with anomalous-dispersion correction terms for Ni and I, were taken from *International Tables for X-ray Crystallography* (1974). Observed disorder at the position corresponding to the central methylene carbon, C(4), of the propylene portion of the macrocycle was modeled by two partial atoms [C(4) and C(4′)], each with fixed population parameters of 0·5. No attempt was made to locate H atoms, because of the presence of this disorder.

All atoms were given anisotropic thermal parameters during refinement. The final R value was 0·036, R_w was 0·053, and the error in an observation of unit weight was 1·85. A final difference electron density map showed two residual peaks (0·8 and 1·0 e Å^{-3}) in the immediate vicinity of the iodide ligand. All other peaks were below 0·6 e Å^{-3}.

Final atomic positional parameters are listed in Table 1.*

Table 1. *Atomic coordinates for* [Ni(cyclops)I]

Fractional coordinates have been multiplied by 10^4. Estimated standard deviations in the least significant digit(s) are in parentheses.

	x	y	z	U_{eq}* (Å^2)
I	315·7 (3)	1805·0 (6)	−2257·5 (3)	53
Ni	344·5 (5)	1672·6 (10)	2653·9 (5)	34
N(1)	202 (3)	1949 (7)	3920 (3)	34
N(2)	−747 (3)	2774 (7)	2472 (4)	40
N(3)	629 (3)	2020 (7)	1415 (3)	39
N(4)	1525 (3)	1116 (7)	2901 (3)	35
C(1)	−483 (4)	2700 (8)	4110 (4)	35
C(2)	−1047 (4)	3196 (9)	3244 (5)	43
C(3)	−1267 (5)	3139 (13)	1539 (5)	66
C(4)	−690 (11)	3639 (21)	812 (11)	46
C(4′)	−895 (13)	2415 (37)	772 (14)	86
C(5)	−26 (5)	2400 (16)	598 (5)	86
C(6)	1426 (4)	1737 (8)	1325 (4)	38
C(7)	1969 (4)	1228 (8)	2201 (4)	35
C(8)	−684 (4)	3070 (9)	5091 (5)	47
C(9)	−1926 (5)	4049 (13)	3287 (6)	72
C(10)	1819 (5)	1864 (11)	421 (5)	57
C(11)	2942 (4)	892 (11)	2301 (5)	52
O(1)	762 (3)	1293 (6)	4676 (3)	41
O(2)	1932 (3)	490 (6)	3755 (3)	43
B	1693 (5)	1401 (10)	4593 (4)	41
F(1)	2107 (2)	458 (6)	5356 (2)	55
F(2)	1948 (3)	3137 (5)	4591 (3)	61

* Calculated by the formula $U_{eq} = (1/6\pi^2) \sum_i \sum_j \beta_{ij} \mathbf{a}_i . \mathbf{a}_j$, and multiplied by 10^3.

Results and discussion

As is shown in Fig. 1, the [Ni(cyclops)I] complex exhibits a square-pyramidal coordination geometry about the Ni^{II} ion, with the I^- ligand at the apex and the four N atoms of the macrocyclic ligand occupying the basal positions. Table 2 lists the bond lengths and angles characteristic of this species, while Table 3 summarizes the results of tests of the planarity of various parts of the macrocyclic complex. As the complex units pack in the lattice (Fig. 2), the Ni remains five-coordinate, as no intermolecular contacts

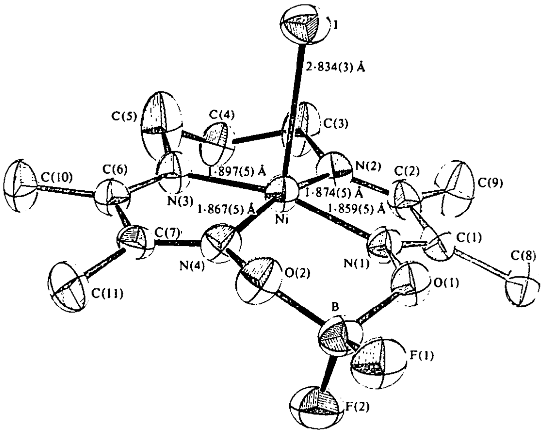

Fig. 1. A view of the complex [Ni(cyclops)I]. Thermal ellipsoids are drawn at the 50% probability level.

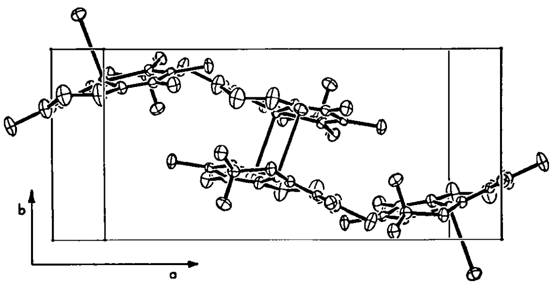

Fig. 2. A view of the contents of one unit cell of [Ni(cyclops)I].

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35691 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *for* [Ni(cyclops)I]

Ni—I	2·834 (3)	C(5)—C(4)	1·456 (20)
Ni—N(1)	1·859 (5)	C(5)—C(4′)	1·410 (23)
Ni—N(2)	1·874 (5)	N(3)—C(5)	1·461 (9)
Ni—N(3)	1·897 (5)	N(3)—C(6)	1·283 (8)
Ni—N(4)	1·867 (5)	C(6)—C(10)	1·505 (10)
N(1)—O(1)	1·376 (6)	C(6)—C(7)	1·454 (8)
N(1)—C(1)	1·269 (8)	C(7)—C(11)	1·522 (9)
C(1)—C(8)	1·501 (9)	N(4)—C(7)	1·294 (8)
C(1)—C(2)	1·456 (8)	N(4)—O(2)	1·371 (6)
C(2)—C(9)	1·519 (10)	B(1)—O(1)	1·472 (9)
N(2)—C(2)	1·294 (9)	B(1)—O(2)	1·470 (9)
N(2)—C(3)	1·478 (8)	B(1)—F(1)	1·377 (8)
C(3)—C(4)	1·511 (19)	B(1)—F(2)	1·363 (9)
C(3)—C(4′)	1·415 (24)		

I—Ni—N(1)	101·9 (2)	O(1)—N(1)—C(1)	116·7 (5)
I—Ni—N(2)	94·8 (2)	O(2)—N(4)—C(7)	118·4 (5)
I—Ni—N(3)	93·9 (2)	N(1)—C(1)—C(8)	125·1 (5)
I—Ni—N(4)	98·6 (2)	N(4)—C(7)—C(11)	123·4 (5)
N(1)—Ni—N(2)	81·5 (2)	N(1)—C(1)—C(2)	110·8 (5)
N(1)—Ni—N(3)	164·2 (2)	N(4)—C(7)—C(6)	111·7 (5)
N(1)—Ni—N(4)	95·4 (2)	C(8)—C(1)—C(2)	124·1 (6)
N(2)—Ni—N(3)	98·0 (2)	C(11)—C(7)—C(6)	124·8 (6)
N(2)—Ni—N(4)	166·6 (2)	C(1)—C(2)—C(9)	120·7 (6)
N(3)—Ni—N(4)	81·4 (2)	C(7)—C(6)—C(10)	119·6 (6)
Ni—N(1)—O(1)	124·6 (4)	C(1)—C(2)—N(2)	114·2 (5)
Ni—N(1)—C(1)	118·5 (4)	C(7)—C(6)—N(3)	114·0 (5)
Ni—N(2)—C(2)	114·9 (4)	C(9)—C(2)—N(2)	125·0 (6)
Ni—N(2)—C(3)	125·0 (4)	C(10)—C(6)—N(3)	126·3 (5)
Ni—N(3)—C(5)	122·5 (5)	C(2)—N(2)—C(3)	120·1 (5)
Ni—N(3)—C(6)	115·4 (4)	C(6)—N(3)—C(5)	121·7 (6)
Ni—N(4)—C(7)	117·4 (4)	N(2)—C(3)—C(4)	111·1 (8)
Ni—N(4)—O(2)	124·1 (4)	N(2)—C(3)—C(4′)	113·0 (10)
N(1)—O(1)—B(1)	116·0 (5)	N(3)—C(5)—C(4)	113·2 (8)
N(4)—O(2)—B(1)	114·9 (5)	N(3)—C(5)—C(4′)	116·0 (9)
O(1)—B(1)—O(2)	113·9 (5)	C(3)—C(4)—C(5)	119·6 (12)
O(1)—B(1)—F(1)	105·2 (6)	C(3)—C(4′)—C(5)	130·4 (16)
O(1)—B(1)—F(2)	110·1 (6)		
O(2)—B(1)—F(1)	104·8 (5)		
O(2)—B(1)—F(2)	109·6 (6)		

Table 3. *Least-squares planes for* [Ni(cyclops)I]

(*a*) Deviations from the planes (Å) with e.s.d.'s in parentheses (the first *n* atoms in each case determine the given plane)

Plane (1) ($n = 4$): N(1) 0·049 (12), N(2) –0·003 (3), N(3) 0·000 (3), N(4) –0·025 (8), Ni –0·232 (1)

Plane (2) ($n = 6$): N(1) –0·040 (12), N(2) 0·004 (4), C(1) –0·013 (7), C(2) 0·018 (8), C(8) 0·013 (6), C(9) –0·004 (3), Ni –0·018 (1), O(1) –0·172 (23), C(3) –0·017 (8)

Plane (3) ($n = 6$): N(3) 0·000 (3), N(4) –0·060 (9), C(6) 0·002 (1), C(7) –0·012 (5), C(10) 0·000 (3), C(11) 0·046 (8), Ni –0·050 (1), O(2) –0·203 (2), C(5) –0·098 (1)

(*b*) Equations of the planes in the form $Ax + By + Cz = D$

Plane	*A*	*B*	*C*	*D*
(1)	4·833	7·073	1·221	1·905
(2)	6·771	6·765	–0·893	1·145
(3)	2·856	7·249	2·283	1·967

less than 4·0 Å involving the metal atom were found. Since the primary purpose of the present study was to ascertain the degree to which the presence of the unpaired electron in the $d_{x^2-y^2}$ orbital of the d^9 $\mathrm{Cu^{II}}$–cyclops complexes previously studied (Anderson & Marshall, 1978; Anderson & Packard, 1979*a*,*b*, 1980*a*,*b*) was associated with the unusual structural parameters characteristic of those $\mathrm{Cu^{II}}$ species, comparison of the structure of the present low-spin (Wicholas, 1979) d^8 $\mathrm{Ni^{II}}$ complex (in which $d_{x^2-y^2}$ is empty) will be mainly to those previously determined $\mathrm{Cu^{II}}$–cyclops structures.

The four N atoms of the coordinating cyclops macrocycle make up a highly planar (see Table 3) base for the square-pyramidal coordination array about the $\mathrm{Ni^{II}}$ ion. Despite the fact that the Ni atom is displaced 0·23 Å out of this N atom plane in the direction of the apical $\mathrm{I^-}$ ligand, the bonds between the metal atom and the N atoms are strong, with Ni—N(imine, av.) = 1·886 (5) Å and Ni—N(oxime, av.) = 1·863 (5) Å. These bond distances are similar to those reported in a series of structures of complexes involving tetradentate ligands which incorporate both amine and oxime N ligand atoms (Schlemper, Hamilton & LaPlaca, 1971; Fair & Schlemper, 1978; Hussain & Schlemper, 1979). In those earlier cases, observed Ni—N(oxime) distances ranged from 1·839 to 1·886 Å, while Ni—N(amine) distances were generally approximately 0·04 Å longer than the Ni—N(oxime) distances. Although the structures of the $\mathrm{Cu^{II}}$–cyclops complexes have not generally shown a significant difference between the Cu—N(imine) and Cu—N(oxime) bond lengths, this difference has been seen in related systems (Liss & Schlemper, 1975; Gagné, Allison, Gall & Koval, 1977; Bertrand, Smith & Van Derveer, 1977; Collman, Rothrock, Sen, Tullius & Hodgson, 1976; Calligaris, 1974) in which the metal—N(oxime) bond lengths are usually slightly, but significantly, shorter than the metal—N(imine or amine) bond lengths. Thus, the Ni—N bond lengths seen here for [Ni(cyclops)I] must be considered to be quite normal in their magnitude and in the difference between the two types of N ligand atoms.

These observed Ni—N distances in [Ni(cyclops)I] are considerably shorter than the corresponding Cu—N bond lengths in [Cu(cyclops)I] (Anderson & Packard, 1979*b*). In this latter case, where all four Cu—N distances were best regarded as equal within the experimental errors, Cu—N(av.) equalled 1·956 (7) Å. These Cu—N bond lengths were intermediate between the two extremes of the aqua cyclops complex (Anderson & Packard, 1979*a*) where Cu—N(av.) = 1·940 (8) Å, and the (cyanato-*N*)cyclops complex (Anderson & Marshall, 1978), where Cu—N(av.) = 2·001 (4) Å. Since the ionic radii of $\mathrm{Ni^{II}}$ and $\mathrm{Cu^{II}}$ are very similar for all coordination numbers (Shannon, 1976), this large difference in metal–nitrogen bond lengths is a direct consequence of the removal of the unpaired electron from the $d_{x^2-y^2}$ orbital of the d^9 configuration of Cu^{II} on going to the low-spin d^8 Ni^{II} complex.

While removal of this electron allows considerable shortening of the metal–nitrogen bonds, it does not allow the metal atom to occupy a position coplanar with the four N atoms. The displacement of the Ni atom of 0·23 Å in the direction of the apical I$^-$ ligand is similar to displacements seen in so-called 'square-planar' Ni^{II} complexes (Hussain & Schlemper, 1979). The Ni–I bond length of 2·834 (3) Å cannot be characterized as a strong bond, since Ni–I bond lengths of ~2·54 Å have been observed (Butcher, O'Connor & Sinn, 1979). The apical displacement for Ni^{II} in [Ni(cyclops)I] is distinctly less than that observed for Cu^{II} in [Cu(cyclops)I], where the corresponding distance was 0·38 Å. This difference in apical displacement is also due to the lack of any significant electron density in the $d_{x^2-y^2}$ orbital of the low-spin Ni^{II} complex. In addition, the Ni–I bond length is significantly longer than the corresponding Cu–I bond length [2·742 (2) Å] in the [Cu(cyclops)I] complex. Thus, removal of the unpaired electron from the $d_{x^2-y^2}$ orbital of the metal ion on going from [Cu(cyclops)I] to the low-spin [Ni(cyclops)I] is seen to produce the following observed differences: (*a*) shorter metal–nitrogen basal bond lengths in the d^8 case as compared with the d^9 case, (*b*) a smaller degree of apical displacement of the metal atom out of the basal plane in the d^8 case, and (*c*) weakening of the bond to the apical ligand in the d^8 case relative to the d^9 case. The structures of the Cu^{II}–cyclops complexes showed a clear inverse connection between the strength of the bonding of the atoms of the basal plane and the bonding to the apical ligand, and the comparison of the Ni–I and Cu–I bond lengths above makes it clear that this correlation extends to the Ni^{II} case as well.

Within the cyclops macrocycle itself, the observed bond distances are all quite similar to those seen in our earlier studies of the Cu^{II} complexes. The overall conformation of the macrocycle again underscores the flexibility of this ligand. If 'chair' or 'boat' designations are assigned based on the relative positions of the six atoms B, N(1)–N(4), and the central atom of the propylene linkage, crystals of [Ni(cyclops)I] are seen to contain both chair and boat forms, due to the disorder present at the C(4) position. This clearly implies a small energy barrier between these two conformations, as does the observation of a chair conformation for [Cu(cyclops)I] (Anderson & Packard, 1979*b*) and [Cu(cyclops)py]$^+$ (Anderson & Packard, 1980*a*), a chair/boat disordered mixture for [Cu(cyclops)H$_2$O]$^+$ (Anderson & Packard, 1979*a*), and a boat conformation for [Cu(cyclops)NCO] (Anderson & Marshall, 1978). Unfortunately, it is difficult to discern any pattern in these conformational changes which correlates well with the observed variations in metal–ligand bonding parameters.

One conformational parameter which does correlate well with the magnitude of the metal-ion apical displacement and with the strength of the metal–ligand bonding is the flexion angle of the macrocycle [defined as the dihedral angle between either of the planes N(1)–C(1)–C(2)–N(2) or N(3)–C(6)–C(7)–N(4) and the reference plane of four coordinating N atoms]. The flexion angles of 11° and 8° seen in the present study are similar in magnitude to the angles of 10° and 9° seen in the case of [Cu(cyclops)I], and are large enough so that the Ni^{II} atom is essentially coplanar with the unsaturated portions of the macrocycle (see Table 3). The angles in these two iodo complexes are very different from the flexion angle of 28° seen in the [Cu(cyclops)NCO] complex, where the metal-atom apical displacement of 0·58 Å was much larger.

A final conformational detail of the [Ni(cyclops)I] structure which underscores the flexibility of the cyclops macrocycle concerns the positioning of the BF$_2$ moiety relative to the reference four-nitrogen plane and the metal atom. In all of the Cu complexes investigated previously, the B atom of the BF$_2$ group was positioned on the same side of the four-nitrogen reference plane as the metal atom, and one of the F atoms was directed back toward the Cu^{II} atom and the apical ligand. This led to clear steric interaction between this F atom and the apical ligand {angle I–Cu–N(oxime) ~108° *vs* I–Cu–N(imine) ~95° in [Cu(cyclops)I], for example} and a surprisingly close Cu–F contact {Cu–F = 3·192 (5) Å in [Cu(cyclops)(NCO)]}. In the [Ni(cyclops)I] case, however, this B atom is found on the side of the four-nitrogen reference plane *opposite* to the apical iodide ligand, and the closest contact between the Ni^{II} atom and a F atom is on this opposite side at a distance of 3·615 (5) Å. The magnitude of this Ni–F distance makes any appreciable interaction between these two atoms appear extremely unlikely. Surprisingly, the I–Ni–N angles remain significantly different in [Ni(cyclops)I] despite the absence of any fluorine–apical ligand interaction, with I–Ni–N(oxime) ~100° and I–Ni–N(imine) ~94°.

In summary, the present study of the structure of [Ni(cyclops)I] has provided new evidence concerning the high degree of flexibility characteristic of the cyclops macrocycle. In addition, the contribution of the unpaired *d* electron in the $d_{x^2-y^2}$ orbital toward producing the large metal-atom apical displacements and strong apical ligand bonding characteristic of the Cu^{II} cyclops complexes is clearly substantial, based on the variations reported here for the d^8 low-spin [Ni(cyclops)I] complex.

Computing funds for this research were supplied by Colorado State University and the Colorado State University Computer Center.

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Structure of Bis(μ-ethylideneamido)-bis(tricarbonyliron)(*Fe—Fe*)

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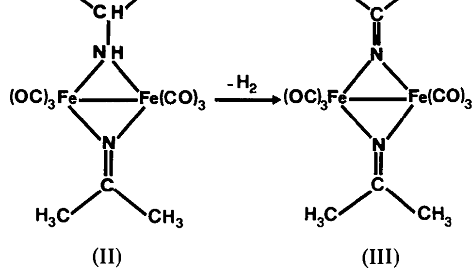
(*Received* 22 *July* 1980; *accepted* 21 *January* 1981)

Abstract

The structure of bis(μ-ethylideneamido)-bis(tricarbonyliron), $[Fe_2(CO)_6(N{=}CHCH_3)_2]$, has been determined by a single-crystal X-ray study. The compound is orthorhombic, space group *Pnma*, with $a = 7{\cdot}106$ (3), $b = 15{\cdot}062$ (4), $c = 14{\cdot}180$ (4) Å, $Z = 4$. Final $R = 0{\cdot}044$ for 846 reflections. The molecule contains two $Fe(CO)_3$ groups and the Fe—Fe bond, on the crystallographic mirror plane, is bridged by two $N{=}CHCH_3$ ligands. The complex is the *syn* isomer. A distortion involving the N atom is discussed and a comparison is made with the other complexes containing an Fe_2N_2 core.

Introduction

In the reaction between $[Fe_3(CO)_{12}]$ and RNO_2 (R = Et, *i*-Pr) several tetra-, tri- and binuclear derivatives were obtained (Aime, Gervasio, Milone, Rossetti & Stanghellini, 1978). Nitroethane gives rise to polynuclear complexes, such as $[Fe_4(CO)_{11}(\mu_4\text{-}NC_2H_5)(\mu_4\text{-}ONC_2H_5)]$ (Gervasio, Rossetti & Stanghellini, 1979), $[Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NC_2H_5)]$ and $[Fe_3(CO)_9(\mu_3\text{-}NC_2H_5)_2]$, while many binuclear compounds of general formula $[Fe_2(CO)_6(\mu\text{-}L)_2]$ were recovered with the ethyl and isopropyl reactants. The bridging ligands can be R_1R_2N, R_1NCONR_2, $ON{=}CR_1R_2$, $N{=}CR_1R_2$ where R_1 and R_2 are H, Me, Et, *i*-Pr variously combined. Among them, the similar compounds $[Fe_2(CO)_6(NHC_2H_5)(N{=}CHCH_3)]$ (I) and $[Fe_2(CO)_6\{NHCH(CH_3)_2\}\{N{=}C(CH_3)_2\}]$ (II) have been reported, together with $[Fe_2(CO)_6\{N{=}C(CH_3)_2\}_2]$ (III), which can be thought of as being derived from (II) by the loss of two H atoms:



(II) (III)

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