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

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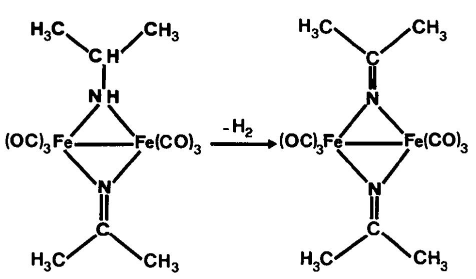
Abstract

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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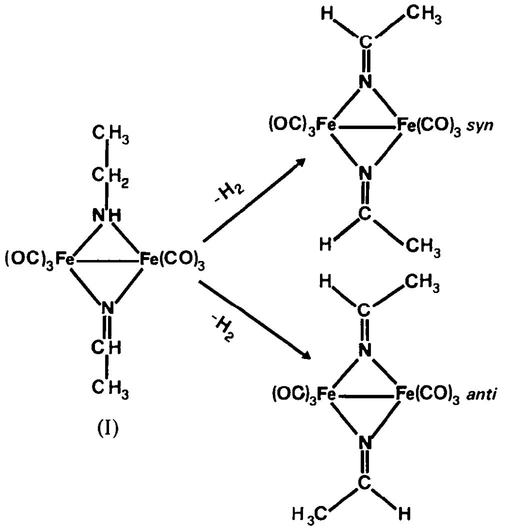
While the previous reaction can give rise to one isomeric form, from (I) two geometrical isomers are expected:



As we have isolated a complex of general formula $[Fe_2(CO)_6(N_2C_4H_8)]$, a product of the second reaction, we carried out an X-ray analysis to clarify its geometry and to collect other structural data on this class of complex.

Experimental

$[Fe_2(CO)_6(N{=}CHCH_3)_2]$, labelled as *X* in Aime, Gervasio, Milone, Rossetti & Stanghellini (1978), where full details on the preparation are reported, was obtained in low yield as yellow-orange crystals; the crystals are very soluble in organic solvents and melt at 362 K. The infrared spectrum shows absorptions (ν in cm^{-1}): in the ν_{CH} region at 2965(*m*), 2929(*m*), 2857(*m*) (CCl_4); in the ν_{CO} region at 2067(*s*), 2027(*vs*), 1990(*s*), 1978(*s*), *ca* 1970(*m*,*sh*) (*n*-heptane); at 1630(*m*,*br*), 1540(*m*) ($\nu_{C=N}$) (KBr). Proton NMR signals are a doublet, centered at 1·9 p.p.m. (CH_3) and a quadruplet centered at 7·9 p.p.m. (CH). In the mass spectrum the molecular ion at 364 *m*/*e* was present, together with the $[Fe_2(CO)_{5-n}(N_2C_4H_8)]^+$ (n = 0–5) peaks and other fragmentation ions at 194, 155, 153, 112, 78 *m*/*e*.

Weissenberg photographs of crystals, sealed in thin-walled glass capillaries under nitrogen, showed orthorhombic symmetry with a = 7·106 (3), b = 15·062 (4), c = 14·180 (4) Å, U = 1517·7 Å^3; M_r = 356·84, D_m = 1·59 (3), D_c = 1·57 Mg m^{-3}, Z = 4, μ = 2·16 mm^{-1}. The lattice parameters were determined by least squares from the θ values of 15 reflections centered on a Syntex automatic four-circle diffractometer. The reflection intensities were collected up to θ = 25° on the same diffractometer (graphite-monochromatized Mo $K\alpha$ radiation, scan width 1·0°, background measured 0·5° before and after the peak). Three standard reflections were checked at regular intervals but no significant change was detected.

The observed systematic absences $h00$ with $h = 2n + 1$, $0k0$ with $k = 2n + 1$, $00l$ with $l = 2n + 1$, $0kl$ with $k = 2n + 1$ and $h0l$ with $h + l = 2n + 1$, indicate the space groups $Pn2_1a$ (non-standard setting of $Pna2_1$) or *Pnma*. Our choice of the centrosymmetric space group from the concentration of peaks in the Patterson function was verified by the satisfactory refinement of the structure. The Patterson map was interpreted with the heavy atoms lying on the mirror plane. A sequence of difference maps followed by an isotropic least-squares refinement, including the 1323 measured reflections, with a local version of *ORFLS* (Busing, Martin & Levy, 1962) led to $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0{\cdot}128$ for the non-hydrogen atoms. Anisotropic refinement led to R = 0·054 for 846 *hkl* with $I > 3\sigma(I)$. A difference map showed residual electron density ranging from 0·4–0·6 e Å^{-3}. Some of these peaks corresponded to the four H atoms of the asymmetric unit. In the final cycles the H atoms were kept fixed with thermal parameters one unit greater than those of the corresponding C atoms. The final R = 0·044 and R_w = 0·051 with $w = 4F_o^2/\sigma(F_o)^2$.

Scattering factors were those of Cromer & Waber (1965), and f' and f'' for the anomalous dispersion of Fe were from Cromer & Liberman (1970). No extinction or absorption corrections were applied.

Atomic coordinates are listed in Table 1.*

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3} \textstyle\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
Fe(1)	0·2480 (3)	0·25	0·0643 (1)	3·85 (2)
Fe(2)	0·0704 (2)	0·25	−0·0808 (1)	3·39 (2)
C(1)	0·4827 (24)	0·25	0·1102 (9)	5·9 (2)
C(2)	0·1444 (15)	0·1633 (7)	0·1361 (6)	6·0 (2)
C(3)	0·0810 (19)	0·25	−0·2083 (9)	3·7 (2)
C(4)	−0·1015 (15)	0·1650 (7)	−0·0656 (7)	5·1 (2)
C(5)	0·3137 (15)	0·0857 (6)	−0·0525 (7)	6·2 (2)
C(6)	0·3097 (16)	0·0420 (6)	−0·1459 (7)	6·0 (2)
O(1)	0·6331 (16)	0·25	0·1377 (8)	9·5 (2)
O(2)	0·0773 (14)	0·1098 (6)	0·1801 (5)	10·1 (2)
O(3)	0·0846 (15)	0·25	−0·2878 (6)	7·2 (2)
O(4)	−0·2122 (11)	0·1102 (6)	−0·0560 (6)	7·8 (2)
N(1)	0·2729 (10)	0·1708 (4)	−0·0427 (4)	4·2 (2)
H(1)	0·440	0·065	−0·014	
H(2)	0·445	0·045	−0·183	
H(3)	0·320	−0·020	−0·150	
H(4)	0·220	0·070	−0·197	

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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 35777 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Description and discussion

The molecular formula of the complex is $[Fe_2(CO)_6(N{=}CHCH_3)_2]$. It consists of two $Fe(CO)_3$ groups, joined by an Fe–Fe bond and bridged by two $N{=}CHCH_3$ ligands. Table 2 reports the bond distances and angles.

The unit OC(1)–Fe(1)–Fe(2)–CO(3) lies on the mirror plane and the remaining carbonyl groups and nitrogen ligands are related by it.

The $Fe_2(CO)_6N_2$ core is typical of a wide set of compounds (Baikie & Mills, 1967; Piron, Piret & Van Meerssche, 1967; Jarvis, Job, Kilbourn, Mais, Owston & Todd, 1967; Bright & Mills, 1967; Bagga, Baikie, Mills & Pauson, 1967; Doedens, 1968, 1970; Dahl, Costello & King, 1968; Doedens & Ibers, 1969; Little & Doedens, 1972; Madden, Carty & Birchall, 1972; Carty, 1972; Khare & Doedens, 1976; Tikhonova *et al.*, 1976) which can be collected into two classes: (1) with a N–N bond, and (2) without a N–N bond: our complex belongs to the second class, owing to the long N···N distance [2·388 (9) Å].

N(1)–C(5) corresponds to a double bond, according to the majority of class (2) complexes, which show a bridging N atom bonded to an organic residue, even if the length (1·31 Å) is a little longer than the average N=C distance (Table 3).

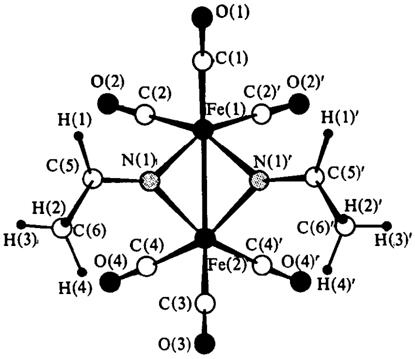

Fig. 1. Molecular configuration and numbering scheme.

The complex is the *syn* isomer and Fig. 1, which is an orthographic projection of one molecule on the plane (20$\bar{3}$), shows the crystallographic mirror plane passing through the Fe–Fe bond.

The two $Fe(CO)_3$ groups are not symmetry related, and show slight but significant differences. For example, the C(1)–Fe(1)–N(1) angle (101·6°) differs from the related C(3)–Fe(2)–N(1) (104·3°) (2·7° > 10σ). As the methyl groups are on the same side as the CO(3) (Fig. 1), this difference can be attributed to the steric hindrance of the CH_3 groups which push the CO(3) towards the other two carbonyls. Accordingly, the angles C(3)–Fe(2)–C(4) and C(1)–Fe(1)–C(2) are different (98·6 *vs* 100·0°). This distortion, however, does not produce a rotation of all the $(CO)_3$ groups but only a closing of the angles within the group, as revealed by the values of the angles formed by C(4) and

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

The prime refers to atoms of the same molecule related by the mirror plane.

Fe(1)–Fe(2)	2·415 (2)	C(1)–O(1)	1·138 (20)
Fe(1)–C(1)	1·789 (16)	C(2)–O(2)	1·126 (13)
Fe(1)–C(2)	1·813 (10)	C(3)–O(3)	1·128 (16)
Fe(1)–N(1)	1·939 (6)	C(4)–O(4)	1·147 (13)
Fe(2)–C(3)	1·809 (13)	C(5)–C(6)	1·480 (14)
Fe(2)–C(4)	1·783 (10)	C(5)–N(1)	1·321 (11)
Fe(2)–N(1)	1·946 (7)	N(1)···N(1)'	2·388 (9)

Fe(2)–Fe(1)–C(1)	142·9 (4)	C(3)–Fe(2)–N(1)	104·3 (2)
Fe(2)–Fe(1)–C(2)	105·5 (3)	C(4)–Fe(2)–N(1)	91·8 (4)
Fe(2)–Fe(1)–N(1)	51·7 (2)	C(4)–Fe(2)–N(1)'	156·0 (4)
C(1)–Fe(1)–C(2)	100·0 (3)	N(1)–Fe(2)–N(1)'	75·7 (3)
C(1)–Fe(1)–N(1)	101·6 (2)	Fe(1)–C(1)–O(1)	178·7 (0)
C(2)–Fe(1)–C(2)'	92·2 (5)	Fe(1)–C(2)–O(2)	178·9 (0)
C(2)–Fe(1)–N(1)	91·9 (4)	Fe(2)–C(3)–O(3)	178·9 (0)
C(2)–Fe(1)–N(1)'	157·0 (4)	Fe(2)–C(4)–O(4)	179·9 (0)
N(1)–Fe(1)–N(1)'	76·0 (3)	N(1)–C(5)–C(6)	121·5 (8)
Fe(1)–Fe(2)–C(3)	146·1 (4)	Fe(1)–N(1)–Fe(2)	76·9 (2)
Fe(1)–Fe(2)–C(4)	104·8 (3)	Fe(1)–N(1)···N(1)'	52·0 (2)
Fe(1)–Fe(2)–N(1)	51·4 (2)	Fe(1)–N(1)–C(5)	134·4 (6)
C(3)–Fe(2)–C(4)	98·6 (3)	Fe(2)–N(1)···N(1)'	52·2 (2)
C(4)–Fe(2)–C(4)'	91·9 (5)	Fe(2)–N(1)–C(5)	136·7 (6)

Table 3. *Some relevant parameters in complexes containing the* Fe_2N_2 *core with* N *double bonded to a* C *atom*

	Fe–Fe	Fe–N	N···N	N=C	Sum of angles around N
$[Fe_2(CO)_6(N{=}C_6H_{10})_2]^a$	2·437 Å	1·92 Å	2·42 Å	1·27 Å	–
$[Fe_2(CO)_6(N{=}CPh_2)_2]^b$	2·403 (6)	1·94	–	1·26 (2)	–
$[Fe_2(CO)_6(N_2C_{23}H_{18})]^c$	2·392	1·920 1·965	2·248	1·258	–
$[Fe_2(CO)_6(N{=}CHCH_3)_2]^d$	2·415 (2)	1·942 (7)	2·388 (9)	1·32 (1)	348·0°
$[Fe_2(CO)_6\{ON{=}C(CH_3)_2\}\{N{=}C(CH_3)_2\}]^e$	2·484 (2)	1·911 (4)	2·652	1·254 (7)	360·0

References: (*a*) Tikhonova *et al.* (1976). (*b*) Bright & Mills (1967). (*c*) Madden, Carty & Birchall (1972). (*d*) Present paper. (*e*) Khare & Doedens (1976); the reported values refer to the second nitrogenated ligand.

C(2) with the Fe—Fe line (104·8 and 105·5° respectively). This distortion is reflected by the difference between the Fe(2)—Fe(1)—C(1) and Fe(1)—Fe(2)—C(3) angles (142·9 and 146·1°). The bond distances in the Fe_2N_2 core of the series $[Fe_2(CO)_6N_2R_1R_2]$ show a typical behavior, which appears to be dependent on the presence of an N—N bond.

In class (1) complexes with an N—N bond, the Fe—Fe bond is longer (2·49–2·53 Å) and the Fe—N bond shorter (1·88–1·92 Å) than the corresponding bonds of class (2) complexes without an N—N bond, which lie in the ranges 2·37–2·42 Å and 1·97–2·02 Å, respectively. This behavior was tentatively rationalized (Teo, Hall, Fenske & Dahl, 1975) on the basis of a semi-empirical MO model.

Our complex shows an Fe—Fe distance [2·415 (2) Å] lying in the expected range (Table 3), whereas the Fe—N distances [1·942 (7) Å] approach those of class (1) complexes. The closing of the Fe_2N_2 core is particularly evident if compared with that of $[Fe_2(CO)_6(NH_2)_2]$ (Dahl, Costello & King, 1968): the Fe—N bonds are shorter (1·94 *vs* 1·98 Å), NFeN angles narrower (75·8 *vs* 77·8°) and FeNFe angles wider (76·9 *vs* 74·4°). The main feature is the shortening of the N···N distance (2·39 *vs* 2·50 Å), which suggests an incipient interaction between the two N atoms: the same observation probably holds for each class (2) compound with the bridging N double bonded to the organic residue (Table 3). The great distortion of the $N{=}CH{-}CH_3$ ligand from planarity, shown by the projection of the molecule down the Fe—Fe bond (Fig. 2), is probably related to this feature.

The clear step at N(1) makes the calculation of the mean plane passing through Fe(1), Fe(2), N(1), C(5) and C(6) (Table 4) meaningless. On the other hand, a rough plane is defined by C(2)O(2)C(4)O(4)Fe(1)Fe(2)-N(1), with C(5) and C(6) lying ~0·63 Å from it.

The step at N(1) is also reflected in the values of the angles around it: the sum of the three angles [Fe(1)—N(1)—Fe(2), Fe(1)—N(1)—C(5) and Fe(2)—N(1)—C(5)] is significantly different from 360° (Table 3). In agreement with this, the length of the C=N bond is longer than the usual value for a double bond.

Other similar complexes with a short N···N non-bonding distance should show a similar distortion from planarity around C=N, but the lack of data for $[Fe_2(CO)_6(N{=}C_6H_{10})_2]$, $[Fe_2(CO)_6(N{=}CPh_2)_2]$ and $[Fe_2(CO)_6(N_2C_{23}H_{18})]$ does not allow a direct comparison. On the other hand, indirect support for the last conclusion is offered by $[Fe_2(CO)_6\{ON{=}C(CH_3)_2\}\{N{-}C(CH_3)_2\}]$ (Khare & Doedens, 1976) and $[Mn_2(CO)_7\{N{=}C(CF_3)_2\}_2]$ (Churchill & Lin, 1975) which have a greater N···N distance and do not show any particular distortion at the N atom of the bridging ligand. Another reason for the ligand distortion can be offered by the value of the H(1)···H(1) intermolecular contact (Table 5) which is shorter than twice the van der Waals radius (1·2 Å). Fig. 3 shows the packing in the crystal.

In principle, two isomeric forms of the complex are possible, *syn* or *anti*. Only a few examples of similar structures have been reported: $[Al_2Ph_4\{N{=}CPh(C_6H_4Br)_2\}].2C_6H_6$ (McDonald, 1969), $[B_2Me_4(N{=}CHMe)_2]$ and $[Al_2Me_4(N{=}CMeBu^t)_2]$ (Coates, Green

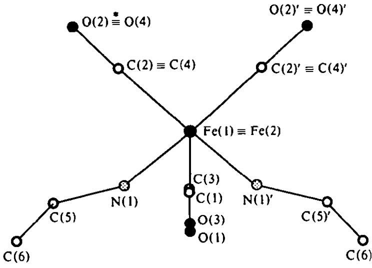

Fig. 2. Projection of one molecule down the Fe—Fe bond.

Table 4. *Some relevant planes for* $[Fe_2(CO)_6(N{=}CHCH_3)_2]$

The equations of weighted planes are in the form $AX + BY + CZ = D$, in fractional coordinates, referred to the cell axes. Distances ($Å \times 10^2$) of relevant atoms from the planes are given, with e.s.d.'s in parentheses (asterisks indicate atoms not used to calculate the planes); $\chi^2 = \sum(d/\sigma)^2$ gives the statistical significance of the planarity.

Plane I: $A = 5{\cdot}20, B = 7{\cdot}75, C = -6{\cdot}33, D = 2{\cdot}83, \chi^2 = 448$

Fe(1) −0·6 (2), Fe(2) −1·0 (2), N(1) 18·6 (1·1), C(5) −19·8 (1·7), C(6) 3·4 (1·8)

Plane II: $A = 4{\cdot}55, B = -9{\cdot}93, C = -5{\cdot}58, D = -1{\cdot}72, \chi^2 = 87$

Fe(1) 1·0 (2), Fe(2) 1·2 (2), N(1)′ −6·7 (1·1), C(2) 0·0 (1·8), O(2) −1·9 (1·5), C(4) −1·0 (1·7), O(4) −2·2 (1·5), C′(5)* −67 (2), C′(6)* −60 (2)

Table 5. *The shortest intermolecular contacts* (Å) *relative to the molecule at x,y,z*

$C(4)\cdots O(3)^{I}$	3·31 (1)	$O(4)\cdots H(1)^{VII}$	2·63 (1)
$C(5)\cdots O(4)^{II}$	3·39 (1)	$O(4)\cdots H(2)^{VII}$	3·18 (1)
$C(5)\cdots H(1)^{III}$	3·02 (1)	$O(4)\cdots H(1)^{VIII}$	3·25 (1)
$C(6)\cdots H(1)^{III}$	3·30 (1)	$O(4)\cdots H(3)^{VIII}$	3·31 (1)
$O(1)\cdots O(2)^{IV}$	3·36 (1)	$H(1)\cdots H(1)^{III}$	2·17
$O(2)\cdots H(2)^{V}$	3·04 (1)	$H(1)\cdots H(2)^{III}$	3·35
$O(2)\cdots H(3)^{V}$	2·86 (1)	$H(1)\cdots H(3)^{III}$	2·96
$O(3)\cdots O(4)^{VI}$	3·38 (1)	$H(2)\cdots H(4)^{IX}$	2·62
$O(3)\cdots H(2)^{I}$	3·27 (1)		

Superscripts refer to the following positions:

(I)	$x-\frac{1}{2}, \frac{1}{2}-y, -z-\frac{1}{2}$	(II)	$1+x, y, z$
(III)	$1-x, \bar{y}, \bar{z}$	(IV)	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$
(V)	$\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$	(VI)	$\frac{1}{2}+x, \frac{1}{2}-y, -z-\frac{1}{2}$
(VII)	$x-1, y, z$	(VIII)	$-x, -y, -z.$
(IX)	$\frac{1}{2}+x, y, -z-\frac{1}{2}$		

& Wade, 1967), which show the *anti* form, but their structures are substantially different as the central M_2N_2 core is planar, without a N—N or M—M bond.

The *anti* form (which results from the steric hindrance of the *tert*-butyl groups) has been proposed for $[Fe_2(CO)_6(N{=}CPhBu^t)_2]$ to explain the ν_{CO} IR pattern, but no structural data are available (Kilner & Midcalf, 1974). In our case steric reasons can hardly be advanced because of the small size of the methyl group. Both forms would be expected to be present in solution, but, if that was the case, they could not be detected or separated, as they would have nearly identical chemical properties and IR or H NMR spectroscopic behavior. On the other hand, a co-crystallization of the two isomers to give mixed crystals is clearly excluded by the results of the present analysis.

So, in the solid state, and probably in solution, only the *syn* form is present and the reason why it is more stable than the hypothetical *anti* form is not straightforward. We tentatively suggest that the intermolecular interaction among CH groups [not negligible, considering the H(1)···H(1) distance] would require a *syn* arrangement of the two bridging groups for a better packing of the molecules.

Another possibility is that the *syn* disposition can favor the N···N intramolecular interaction by means of a slight deformation of the $N{=}CHCH_3$ units, symmetrical with respect to the mirror plane.

The *syn* and *anti* isomers are probably present in equilibrium in solution with similar stabilities: previous considerations suggest that the *syn* form gains a small stability with respect to the *anti* form particularly in the solid state.

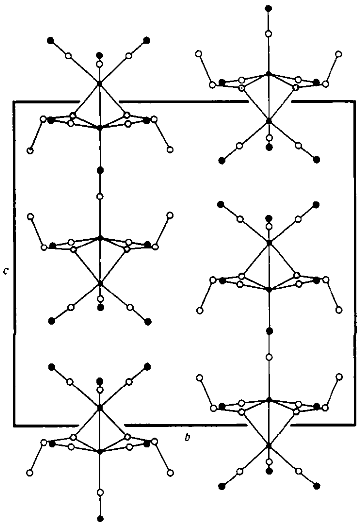

Fig. 3. Projection of the unit cell along *a*. H atoms are not shown.

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