Janssen, T. (1979). Private communication.
Janssen, T. & Janner, A. (1979). Proceedings of the 4th European Meeting on Ferroelectricity, Portoroz.
Kind, R. & Roos, J. (1976). *Phys. Rev. B*, **13**, 45–54.
Korekawa, M. (1967). Habilitationsschrift, Univ. München.
Peterson, E. R. & Willet, R. D. (1972). *J. Chem. Phys.* **56**, 1879–1882.
Seliger, J., Blinc, R., Kind, R. & Arend, H. (1976). *Z. Phys. B*, **25**, 189–195.
Wolff, P. M. de (1974). *Acta Cryst.* A**30**, 777–785.
Wolff, P. M. de (1977). *Acta Cryst.* A**33**, 493–497.
Wolff, P. M. de (1980). Private communication.
XRAY system (1976). Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1981). B**37**, 339–344

Organometallic Structures. IV.* 1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3-μ-dimethyliminiocarbene-2,3-μ-hydrido-*triangulo*-triiron

By F. H. Herbstein

Department of Chemistry, Technion–Israel Institute of Technology, Haifa, Israel

(*Received* 23 *July* 1980; *accepted* 1 *September* 1980)

Abstract

(μ-H) [μ-C=N(CH$_3$)$_2$]Fe$_3$(CO)$_{10}$, M_r = 504·74, m.p. 435–437 K (dec.), crystallizes (red prisms or needles elongated along [001]) in space group $P2_12_12_1$, with $Z = 4$, a = 16·255 (6), b = 12·148 (4), c = 9·428 (3) Å, V = 1861·7 (11) Å^3, D_c = 1·801 Mg m^{-3}, $F(000)$ = 1000. The structure was refined to R = 4·84% for the correct enantiomorph (1423 diffractometer intensities, Mo $K\alpha$ radiation, μ = 2·253 mm^{-1}). The molecular structure is similar to that of the Ru analogue, thus confirming conclusions drawn from mass spectrometric and Mössbauer measurements. The shortening of the doubly bridged Fe–Fe bond compared to the unbridged Fe—Fe bonds is accounted for in terms of the different coordination numbers of the Fe atoms involved. The molecules in their crystal environment show appreciable deviations from the mirror symmetry anticipated from the chemical formula, and this is in accordance with the chiral space group of the crystals.

1. Introduction

The title compound was first prepared by Rhee, Ryang & Tsutsumi (1968); the correct formula and structure, inferred from a combination of mass spectrometric and Mössbauer measurements, were proposed by Greatrex, Greenwood, Rhee, Ryang & Tsutsumi (1970). The present analysis confirms their conclusions and provides geometrical information for comparison with analogous molecules; in particular, there is considerable current interest in transition-metal complexes with bridging hydride ligands (Bau & Koetzle, 1978; Churchill, 1978; Bau, Teller, Kirtley & Koetzle, 1979). The structure of the Ru analogue has been reported (Churchill, DeBoer, Rotella, Abel & Rowley, 1975) as well as those of many related Fe, Ru and Os compounds.

2. Experimental

The compound was prepared by Altman & Welcman (1979) from the reaction of Fe$_3$(CO)$_{12}$ and chlorodimethylformiminium chloride. A cubic crystal (edge ~0·2 mm) was sealed in a capillary (the crystals appear to decompose slowly in air). Crystal data (Philips PW 1100 four-circle diffractometer) are given in the *Abstract*. The intensities of 1659 reflections were measured [Mo $K\alpha$ radiation; $\omega/2\theta$ technique, scan width 1·4° in ω, scan speed 0·05° (ω) s^{-1}, background measured for 28s at each of the scan extremities]; 219 reflections had $I < 3\sigma(I)$ and were omitted. In the final stage of the refinement another 17 reflections were found to have been affected by spurious counts and were also omitted. Thus 244 parameters were determined with 1423 measured intensities. Intensities were not corrected for absorption ($\mu R \sim 0·2$).

The positions of the three Fe and fourteen other

---

* Part III: Cais, Dani, Herbstein & Kapon (1978).

0567-7408/81/020339-06$01.00

atoms were found with *MULTAN* (Germain, Main & Woolfson, 1971) and the remaining atoms, including six H atoms of the two methyl groups and one hydride H, from difference syntheses and least-squares refinement with *SHELX* (Sheldrick, 1976). *F* values were weighted according to counting statistics, with an additional correction of $0{\cdot}04I$; the empirical weighting factor found in the final refinement stages was $w(F) = 0{\cdot}8664/[\sigma^2(F) + 0{\cdot}000642F^2]$. H atom positions and temperature factors (isotropic) were refined; the large temperature factors of H(5) and H(6) suggest that their positions may be in error but this has not been investigated further. Complex neutral-atom scattering factors were used together with appropriate dispersion corrections (*International Tables for X-ray Crystallography*, 1974; Tables 2.2A and 2.3.1). A final difference synthesis was featureless (largest peak height $\sim 0{\cdot}2$ e Å^{-3}). The original coordinates refined to $R = 5{\cdot}09\%$ ($R_G = 5{\cdot}28\%$) while inversion of these coordinates gave $R = 4{\cdot}84\%$ ($R_G = 4{\cdot}83\%$). Use of the $\mathscr{R}$ test on the R_G values [Hamilton (1965); see also *International Tables* (1974, Table 4.2)] indicated that the difference is highly significant. The atomic coordinates of Table 1 (numbering of the atoms is shown in Fig. 1) have the chirality of the crystal from which the intensities were measured.*

Table 1. *Atomic coordinates* (*for heavy atoms* $\times 10^4$, *for* H *atoms* $\times 10^3$; *e.s.d.'s in parentheses are in units of the least significant digit*)

	x	*y*	*z*	U_{eq}/U (Å$^2 \times 10^4$)*
Fe(1)	−1237 (1)	−891 (1)	653 (2)	418
C(1)	−1487 (7)	473 (12)	96 (15)	623
O(1)	−1681 (6)	1350 (8)	−222 (12)	848
C(2)	−1469 (7)	−769 (12)	2497 (14)	626
O(2)	−1596 (6)	−682 (12)	3668 (10)	1036
C(3)	−169 (6)	−561 (10)	938 (14)	426
O(3)	474 (5)	−273 (7)	1229 (9)	665
C(4)	−2267 (8)	−1406 (9)	212 (13)	573
O(4)	−2924 (5)	−1683 (8)	7 (11)	807
Fe(2)	−651 (1)	−2965 (1)	647 (2)	440
C(5)	−388 (8)	−4376 (12)	338 (15)	601
O(5)	−227 (8)	−5270 (9)	177 (12)	1014
C(6)	−1442 (8)	−3186 (11)	1908 (14)	572
O(6)	−1909 (7)	−3372 (9)	2771 (12)	1002
C(7)	157 (8)	−2705 (12)	1923 (13)	625
O(7)	682 (7)	−2636 (10)	2720 (11)	1060
Fe(3)	−525 (1)	−1837 (1)	−1633 (1)	378
C(8)	399 (8)	−983 (10)	−1787 (12)	554
O(8)	1002 (6)	−535 (8)	−1934 (11)	899
C(9)	−1207 (8)	−909 (11)	−2505 (11)	575
O(9)	−1625 (6)	−214 (9)	−3082 (10)	938
C(10)	−277 (8)	−2635 (10)	−3130 (13)	581
O(10)	−145 (6)	−3162 (9)	−4107 (11)	989
C(11)	−1309 (6)	−2895 (10)	−1007 (10)	419
N	−1933 (5)	−3403 (8)	−1559 (12)	556
C(12)	−2374 (9)	−4281 (12)	−789 (19)	929
C(13)	−2238 (7)	−3201 (14)	−3011 (16)	790
H(1)	−239 (9)	−479 (8)	−119 (10)	880
H(2)	−222 (6)	−437 (7)	19 (9)	730
H(3)	−293 (5)	−408 (7)	−53 (10)	820
H(4)	−272 (4)	−328 (5)	−287 (7)	450
H(5)	−211 (7)	−239 (9)	−332 (12)	1590
H(6)	−196 (8)	−355 (12)	−391 (14)	2060
H(7)	0 (6)	−249 (8)	−45 (10)	1240

* $U_{eq} = \frac{1}{3}\mathrm{tr}\,\tilde{\mathbf{U}}$.

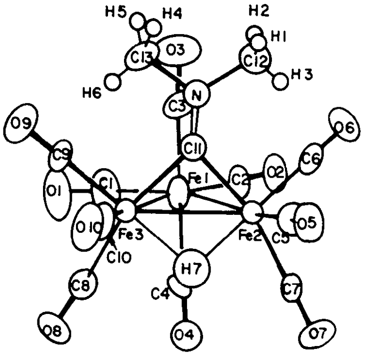

Fig. 1. The numbering scheme of the title compound.

Nyburg's (1974) *BMFIT* program was used to test how well the final coordinates conform to the mirror symmetry indicated by the chemical formula; appreciable deviations were found. The enantiomorph of the molecule represented by the coordinates of Table 1 was generated by reversing the signs of the *x* coordinates; positions of corresponding atoms [*e.g.* Fe(2) and Fe(3); C(1) and C(2)] were then matched and the distances between them calculated. When the best match was made for all the atoms except the methyl H atoms, the r.m.s. distance between corresponding atoms was 0·20 Å, with smallest distances between Fe atoms (~0·05 Å) and largest between O(1) and O(2) (0·40 Å); the corresponding values for a match restricted to the three Fe atoms were 0·24, 0·003, and 0·53 Å respectively.

3. Results and discussion

3.1. *The overall molecular structure*

The molecular structure (Fig. 2 and Table 2) is very similar to that of the Ru analogue; structures are also known for a number of similar *triangulo* Fe_3 and Ru_3 molecules (Table 3, where only compounds with σ-bonded ligands have been included). In the present molecule the unique Fe atom has distorted octahedral coordination (ligands: 4CO, 2Fe) while the two equivalent Fe atoms are seven-coordinate [ligands:

---

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35690 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Molecular dimensions* (Å *and* deg)

Fe$_3$ triangle			
Fe(1)–Fe(2)	2·694 (2)	Fe(1)–Fe(2)–Fe(3)	61·7 (1)
Fe(1)–Fe(3)	2·698 (2)	Fe(1)–Fe(3)–Fe(2)	61·5 (1)
Fe(2)–Fe(3)	2·565 (2)	Fe(2)–Fe(1)–Fe(3)	56·8 (1)
Carbonyl groups			
Fe(1)–(CO)$_4$			
Fe(1)–C(1)	1·786 (15)	C(1)–Fe(1)–C(2)	99·3 (6)
–C(2)	1·785 (13)	C(1)–Fe(1)–Fe(3)	104·7 (4)
–C(3)	1·802 (11)	C(2)–Fe(1)–Fe(2)	98·9 (5)
–C(4)	1·835 (12)	C(1)–Fe(1)–C(3)	93·3 (6)
C(1)–O(1)	1·151 (18)	C(2)–Fe(1)–C(3)	92·3 (6)
C(2)–O(2)	1·128 (16)	C(3)–Fe(1)–C(4)	171·4 (6)
C(3)–O(3)	1·136 (13)	Fe(1)–C(1)–O(1)	176·8 (1·1)
C(4)–O(4)	1·136 (15)	Fe(1)–C(2)–O(2)	178·3 (1·1)
		Fe(1)–C(3)–O(3)	172·3 (1·1)
		Fe(1)–C(4)–O(4)	175·6 (1·1)
Fe(2)–(CO)$_3$			
Fe(2)–C(5)	1·789 (15)	C(5)–Fe(2)–C(6)	97·9 (6)
–C(6)	1·773 (13)	C(5)–Fe(2)–C(7)	95·9 (6)
–C(7)	1·808 (13)	C(6)–Fe(2)–C(7)	96·2 (6)
C(5)–O(5)	1·127 (18)	Fe(2)–C(5)–O(5)	178·3 (1·1)
C(6)–O(6)	1·135 (17)	Fe(2)–C(6)–O(6)	175·0 (1·2)
C(7)–O(7)	1·141 (17)	Fe(2)–C(7)–O(7)	174·1 (1·3)
		Fe(3)–Fe(2)–C(5)	111·2 (4)
		Fe(3)–Fe(2)–C(6)	134·6 (4)
		Fe(3)–Fe(2)–C(7)	113·9 (4)
Fe(3)–(CO)$_3$			
Fe(3)–C(8)	1·824 (13)	C(8)–Fe(3)–C(9)	97·2 (6)
–C(9)	1·774 (13)	C(8)–Fe(3)–C(10)	93·5 (6)
–C(10)	1·766 (12)	C(9)–Fe(3)–C(10)	97·0 (5)
C(8)–O(8)	1·129 (16)	Fe(3)–C(8)–O(8)	174·2 (1·1)
C(9)–O(9)	1·131 (16)	Fe(3)–C(9)–O(9)	178·1 (1·2)
C(10)–O(10)	1·142 (16)	Fe(3)–C(10)–O(10)	177·6 (1·2)
		Fe(2)–Fe(3)–C(8)	115·8 (4)
		Fe(2)–Fe(3)–C(9)	132·6 (4)
		Fe(2)–Fe(3)–C(10)	112·8 (4)
Carbene group			
C(11)–N	1·297 (14)	C(11)–N–C(12)	121·8 (1·1)
N–C(12)	1·476 (18)	C(11)–N–C(13)	123·7 (1·0)
–C(13)	1·477 (18)	C(12)–N–C(13)	114·4 (1·1)
C–H distances in range 0·72 (12) to 1·05 (14)			
Dimensions involving bridging groups			
C(11)–Fe(2)	1·893 (11)	Fe(2)–H(7)–Fe(3)	106 (5)
–Fe(3)	1·912 (11)	Fe(2)–C(11)–Fe(3)	84·8 (4)
H(7)–Fe(2)	1·59 (9)	H(7)–Fe(3)–C(9)	164 (3)
–Fe(3)	1·63 (9)	H(7)–Fe(2)–C(6)	168 (3)
		C(11)–Fe(2)–C(7)	161·8 (5)
		C(11)–Fe(3)–C(8)	162·7 (5)

3CO, 2Fe, 1H, 1C (of the carbene)], the arrangement being a distorted version of capped octahedral (Drew, 1977), rather similar to that found for seven-coordinate Fe in tricarbonyl (tricarbonylferracyclopentadiene)-triiron(*Fe–Fe*) fragments [see, for example, Fig. 9 of Herbstein & Reisner (1977), or Fig. 2 of Chin & Bau (1973)]. We shall refer to the difference between the lengths of bridged and unbridged sides of the metal-atom triangles in these molecules as a length difference, defined as negative if l(bridged) < l(unbridged).

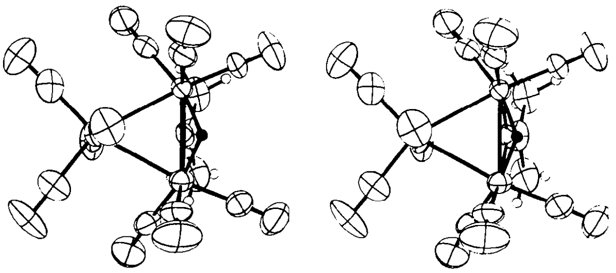

Fig. 2. *ORTEP* stereoview (Johnson, 1965) of (μ-H)[μ-C=N(CH$_3$)$_2$]Fe$_3$(CO)$_{10}$ viewed approximately normal to the triangle of Fe atoms and showing 50% probability contours for thermal ellipsoids of all non-hydrogen atoms.

A single bridging hydride ligand normally causes a lengthening of the distance between metal atoms (Churchill *et al.*, 1975; Churchill, DeBoer, Shapley & Keister, 1976) but a single CO bridge produces little change, *e.g.* in (μ-1,2-diazine)(μ-CO)$_2$Ru$_3$(CO)$_{10}$ the two pairs of Ru atoms singly bridged by CO are 2·858 Å apart (Cotton & Jamerson, 1976), compared to 2·848 Å in unbridged Ru$_3$(CO)$_{12}$. Double bridging of bonds can have quite different results. For example, in (μ-1,2-diazine)(μ-CO)$_2$Ru$_3$(CO)$_{10}$ the distance between Ru doubly bridged by CO and 1,2-diazine is 2·743 Å, while in (μ-H)$_2$(μ-CH$_2$)Os$_3$(CO)$_{10}$ (Schultz, Williams, Calvert, Shapley & Stucky, 1979), the Os–Os bond singly bridged by H is 3·053 Å, that doubly bridged by H and CH$_2$ is 2·824 Å, while the unbridged bond is 2·855 Å. Such results are not unreasonable as the positions of the bridging ligands relative to the metal atoms and other ligands are quite different in singly and doubly bridged species and hence the effect of two ligands in a double bridge is unlikely to be the sum of their effects as singly bridging ligands.

Although the Fe–Fe bonds in the compounds listed in Table 3 are all single on the basis of the 18-electron rule, it is clear that there is a consistent length difference of ~–0·13 Å, irrespective of the nature of the bridging ligands (the range for both bridged and unbridged Fe–Fe distances is ~0·026 Å). There are indications of similar but less marked behaviour in Ru compounds. Analogous Os compounds have not been included in Table 3 because a comprehensive list has been given by Churchill & Lashewycz (1979). The Os compounds differ from the Fe compounds in that a much wider range (in the chemical sense) of bridging moieties has been used, and the length difference for Os–Os bonds varies from –0·132 Å [in (μ-H)$_2$Os$_3$(CO)$_{10}$] to +0·040 Å [in (μ-H)(μ-Br)Os$_3$(CO)$_{10}$]; furthermore, the unbridged distances have a range of 0·063 Å, much larger than for the Fe compounds (this difference between Fe and Os compounds may well arise from the more restricted group of ligands appearing in the Fe compounds).

Table 3. *Comparison of metal–metal distances* (Å) *in doubly bridged triangulo-trimetal molecules* (*M* = Fe, Ru)

Molecule	*D*(*M*–*M*)		Remarks	Reference
	unique to bridged *M*	bridged *M*–*M*		
$(\mu\text{-CO})_2Fe_3(CO)_{10}$	2·677 (2) 2·683 (2)	2·558 (2)	Both CO bridges unsymmetrical	(*a*)
$(\mu\text{-CO})_2Fe_3(CO)_9PPh_3$, isomer *B* ($PPh_3$ bonded to unbridged Fe)	2·711 2·703	2·556	Both CO bridges unsymmetrical	(*b*)
$(\mu\text{-CO})_2Fe_3(CO)_7(PMe_2Ph)_3$, equatorial CO on each Fe replaced by PMe_2Ph	2·688 (7)	2·540 (7)	Both CO bridges symmetrical	(*c*)
$(\mu\text{-CO})_2Fe_3(CO)_9PPh_3$, isomer *A* ($PPh_3$ bonded to bridged Fe)	2·666	2·568	Both CO bridges unsymmetrical	(*b*)
$[Et_3NH]^+.[(\mu\text{-H})(\mu\text{-CO})Fe_3(CO)_{10}]^-$	2·685 (3) 2·696 (3)	2·577 (3)	Symmetrical CO bridge	(*d*)
$(\mu\text{-H})(\mu\text{-C}{=}NMe_2)Fe_3(CO)_{10}$	2·694 (2) 2·698 (2)	2·565 (2)	Both bridges symmetrical	(*e*)*
$Ru_3(CO)_{12}$	2·848 (6)		Not bridged	(*f*)
$(\mu\text{-H})(\mu\text{-C}{=}NMe_2)Ru_3(CO)_{10}$	2·8284 (4)	2·8007 (4)	Both bridges symmetrical	(*g*)*
$[N(PPh_3)_2]^+.[(\mu\text{-H})(\mu\text{-CO})Ru_3(CO)_{10}]^-$	2·843 (2) 2·845 (3)	2·915 (2)	Both bridges symmetrical	(*h*)*

References: (*a*) Cotton & Troup (1974*b*). (*b*) Dahm & Jacobson (1968). (*c*) Raper & McDonald (1971). (*d*) Dahl & Blount (1965). (*e*) Present paper. (*f*) Mason & Rae (1968). (*g*) Churchill *et al.* (1975). (*h*) Johnson *et al.* (1979).

* Hydride H found in diffraction experiment.

Broach & Williams (1979) have discussed the bonding in this group of compounds in terms of a qualitative molecular-orbital scheme. For $(\mu\text{-H})_2Os_3(CO)_{10}$ there are 46 valence electrons (eight from each Os, two from each CO, one from each H). With six electrons from each Os in non-bonding d_{xy}, d_{xz} and d_{yz} orbitals, the remaining metal orbitals form d^2sp^3 hybrids. Twenty electrons are involved in Os–(CO) bonding and four in the unbridged metal–metal bonds. Linear combinations of the four d^2sp^3 orbitals from the bridged metal atoms and 1*s* orbitals from the two H atoms produce six molecular orbitals depicted in their chart I. The remaining four electrons enter the a_1 and b_1 MO's which both have metal–metal bonding character; thus the doubly bridged Os–Os bond has order 2, in agreement with the measured length difference of −0·132 Å [*d*(unbridged) = 2·815 (1), *d*(bridged) = 2·683 (1) Å]. Broach & Williams extended their treatment to $(\mu\text{-H})[\mu\text{-C}{=}N(CH_3)_2]Ru_3(CO)_{10}$, which has 48 valence electrons. The extra two electrons are placed in a molecular orbital formed by overlap of the unfilled $p\pi$ orbital of the methylene C atom with the a_2 or b_2 MO of the Broach–Williams scheme. As these MO's are metal–metal antibonding, the bond order of the doubly bridged Ru–Ru bond decreases to 1. All the molecules listed in Table 3 have 48 bonding electrons and would therefore be expected to have zero length difference, in contradiction to the experimental results. However, the molecular-orbital treatment has not taken into account the fact that the doubly bridged Fe–Fe bond is between two seven-coordinate Fe atoms, while the unbridged Fe–Fe bonds are between a seven-coordinate and a six-coordinate Fe atom. We propose that the length difference of −0·13 Å in the 48-electron Fe_3 molecules results from this effect. In $Fe_2(CO)_9$, where a carbonyl group replaces the $Fe(CO)_4$ group of $(\mu\text{-CO})_2Fe_3(CO)_{10}$ the Fe–Fe bond is also between two seven-coordinate Fe atoms; its length is 2·523 (1) Å (Cotton & Troup, 1974*a*). In tricarbonyl(tricarbonylferracyclopentadiene)triiron(*Fe–Fe*) fragments the analogous Fe–Fe distance is ~2·50 Å [see Herbstein & Reisner (1977) for references]. In the two Ru_3 moieties of Table 3 the length difference is −0·028 Å; Churchill & Lashewycz (1979) (see their Table VII) give results for two 48-electron molecules $(\mu\text{-H})(\mu\text{-}L)Os_3(CO)_{10}$ where L = $^-CHCH{=}N^+Et_2$ and $^-CH_2CH_2P^+Me_2Ph$, the length differences being −0·083 and −0·071 Å respectively. The absence of a smooth dependence of length difference on atomic number is in accordance with the well known absence of a smooth progression in chemical properties from Fe through Ru to Os.

3.2. *The* Fe(CO)$_4$ *group*

Axial and equatorial Fe–C(carbonyl) distances are not significantly different in a series of octahedral $LL'Fe(CO)_4$ molecules (Herbstein & Kaftory, 1977). However, in the present compound axial Fe–C is longer than equatorial Fe–C [1·818 (11) compared to 1·786 (10) Å]. Although this difference is only significant at the 3% level, it is in agreement with the similar effects found in $(\mu\text{-H})_2Os_3(CO)_{10}$ [1·950 (1) compared to 1·923 (3) Å] and in the anion of $[N(PPh_3)_2]^+.[(\mu\text{-H})(\mu\text{-CO})Ru_3(CO)_{10}]^-$ (1·933 compared to 1·897 Å) (Johnson, Lewis, Raithby & Süss, 1979). Johnson *et al.*

note that these differences are in accord with the accepted model for metal–carbonyl bonding, the longer axial lengths being due to competition for $d\pi$ electron density between mutually *trans* carbonyl groups.

3.3. *The* Fe(CO)$_3$ *groups*

The three CO groups are arranged with a closer approximation to C_{3v} symmetry than those in (*cis*-butadiene)tricarbonyliron moieties (Herbstein & Reisner, 1977). The Fe–C distances *trans* to the bridging H atom [*i.e.* to C(6) and C(9)] are slightly shortened [mean 1·773 (9) Å] while those *trans* to C(11) are slightly lengthened [mean 1·816 (9) Å]. Similar differences have been found in $(\mu\text{-H})_2Os_3(CO)_{10}$ and $[(\mu\text{-H})(\mu\text{-CO})Ru_3(CO)_{10}]^-$ and the generalization that bridging H has a *trans*-shortening influence and bridging C a *trans*-lengthening influence in doubly bridged systems seems well founded.

3.4. *The* [C=N(CH$_3$)$_2$] *moiety*

The dimensions of this moiety are very similar in the present compound, in its Ru analogue (Churchill *et al.*, 1975) and in hexacarbonylbis(μ-diethyliminiocarbene)-diiron(–I) (Pettersen & Cash, 1977). There are no significant deviations of the non-hydrogen atoms from the mean moiety plane.

3.5. *The bridging groups*

The angles between the Fe(2)–C(11)–Fe(3) and Fe(2)–H(7)–Fe(3) planes, on the one hand, and that of the three Fe atoms, on the other, are 96·8 and 121·1° respectively; the angle between the planes of the two bridging groups is 142°; these values are similar to those reported for the Ru analogue, while in $(\mu\text{-H})_2Os_3(CO)_{10}$ the angle between the two Os–H–Os planes is 137·6°. The C=N(CH$_3$)$_2$ moiety is bent out of the Fe(2)–C(11)–Fe(3) plane by 5·8° towards H(7); presumably this is a crystal packing effect for the corresponding Ru atoms are coplanar with the carbene moiety in the Ru analogue. d(Fe–H) is 1·61 (6) Å in the present compound and 1·80 (9) Å in $HFe_3(CO)_9S(i\text{-}C_3H_7)$ (Bau, Don, Greatrex, Haines, Love & Wilson, 1975). Although the difference is significant only at the 8% level, one would not expect the distances to be equal as the hydride H is almost perpendicular to the plane of the Fe$_3$ triangle in the present compound but is in this plane in $HFe_3(CO)_9S(i\text{-}C_3H_7)$.

The angle subtended by the two Fe atoms at the bridge C atom is 84·8° and at the bridge H atom 106°. We consider that these angles are determined by the interatomic distances [d(Fe–Fe) ~ 2·5, d(Fe–C) ~ 1·9, d(Fe–H) ~ 1·6 Å] and not by hybridization at the bridge atoms; similar views have been expressed regarding the geometry of the Os$_2$H$_2$ moiety in $(\mu\text{-H})_2Os_3(CO)_{10}$ (Broach & Williams, 1979). The angles (carbonyl)C–Fe–bridge atom are all ~165° (see Table 2 for details) and we ascribe the deviations from 180° to the geometrical constraints imposed by the bridging groups.

4. Molecular packing

There are only van der Waals interactions between neighbouring molecules. The packing is unusual in the sense that the space group is chiral although the individual molecules have mirror symmetry. However, as noted previously, the molecule in the crystal deviates appreciably from this symmetry. We infer that the chiral arrangement in space group $P2_12_12_1$ has a lower free energy than alternative packing arrangements and that the distortions from mirror symmetry, which primarily affect the somewhat flexible CO groups, arise from lattice forces. The free-energy difference between alternative arrangements must be very small as the Ru analogue crystallizes in a centrosymmetric space group ($P2_1/n$) with two molecules in the asymmetric unit; the detailed geometry of the Ru analogue is not available as atomic coordinates have not been published.

I thank Professor N. Welcman and Dr J. Altman for the crystals and Professor H. B. Gray (Pasadena) and M. Cais, Z. Dori and E. A. Halevi (Haifa) for helpful discussions.

References

Altman, J. & Welcman, N. (1979). *J. Organomet. Chem.* **165**, 353–355.

Bau, R., Don, B., Greatrex, R., Haines, R. J., Love, R. A. & Wilson, R. D. (1975). *Inorg. Chem.* **14**, 3021–3025.

Bau, R. & Koetzle, T. F. (1978). *Pure Appl. Chem.* **50**, 55–64.

Bau, R., Teller, R. G., Kirtley, S. W. & Koetzle, T. F. (1979). *Acc. Chem. Res.* **12**, 176–183.

Broach, R. W. & Williams, J. M. (1979). *Inorg. Chem.* **18**, 314–319.

Cais, M., Dani, S., Herbstein, F. H. & Kapon, M. (1978). *J. Am. Chem. Soc.* **100**, 5554–5558.

Chin, H. B. & Bau, R. (1973). *J. Am. Chem. Soc.* **95**, 5068–5070.

Churchill, M. R. (1978). *Transition Metal Hydrides* (*Advances in Chemistry Series* 167), edited by R. Bau, pp. 36–60. Washington: American Chemical Society.

Churchill, M. R., DeBoer, B. G., Rotella, F. J., Abel, E. W. & Rowley, R. J. (1975). *J. Am. Chem. Soc.* **97**, 7158–7159.

Churchill, M. R., DeBoer, B. G., Shapley, J. R. & Keister, J. B. (1976). *J. Am. Chem. Soc.* **98**, 2357–2358.

Churchill, M. R. & Lashewycz, R. A. (1979). *Inorg. Chem.* **18**, 3261–3267.

Cotton, F. A. & Jamerson, J. D. (1976). *J. Am. Chem. Soc.* **98**, 5396–5397.

COTTON, F. A. & TROUP, J. M. (1974*a*). *J. Chem. Soc. Dalton Trans.* pp. 800–802.

COTTON, F. A. & TROUP, J. M. (1974*b*). *J. Am. Chem. Soc.* **96**, 4155–4159.

DAHL, L. F. & BLOUNT, J. F. (1965). *Inorg. Chem.* **4**, 1373–1375.

DAHM, D. J. & JACOBSON, R. A. (1968). *J. Am. Chem. Soc.* **90**, 5106–5112.

DREW, M. G. B. (1977). *Prog. Inorg. Chem.* **23**, 67–210.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

GREATREX, R., GREENWOOD, N. N., RHEE, I., RYANG, M. & TSUTSUMI, S. (1970). *Chem. Commun.* pp. 1193–1194.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

HERBSTEIN, F. H. & KAFTORY, M. (1977). *Acta Cryst.* B**33**, 3318–3321.

HERBSTEIN, F. H. & REISNER, M. G. (1977). *Acta Cryst.* B**33**, 3304–3317.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, B. F. G., LEWIS, J., RAITHBY, P. R. & SÜSS, G. (1979). *J. Chem. Soc. Dalton Trans.* pp. 1356–1361.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MASON, R. & RAE, I. M. (1968). *J. Chem. Soc. A*, pp. 778–779.

NYBURG, S. C. (1974). *Acta Cryst.* B**30**, 251–253.

PETTERSEN, R. C. & CASH, G. G. (1977). *Acta Cryst.* B**33**, 2331–2334.

RAPER, G. & MCDONALD, W. S. (1971). *J. Chem. Soc. A*, pp. 3430–3432.

RHEE, I., RYANG, M. & TSUTSUMI, S. (1968). *Chem. Commun.* pp. 455–456.

SCHULTZ, A. J., WILLIAMS, J. M., CALVERT, R. B., SHAPLEY, J. R. & STUCKY, G. D. (1979). *Inorg. Chem.* **18**, 319–323.

SHELDRICK, G. M. (1976). *SHELX*. A program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1981). B**37**, 344–346

The Ammonium and Potassium Salts of Nitromalonamide

BY OLE SIMONSEN

*Department of Chemistry, University of Odense, DK-*5230 *Odense, Denmark*

(*Received* 20 *March* 1980; *accepted* 24 *October* 1980)

Abstract

The ammonium and potassium salts of nitromalonamide are isomorphous. They are monoclinic, $P2_1/c$, with $Z = 4$. The ammonium salt, $C_3H_4N_3O_4^-.NH_4^+$, has $a = 7{\cdot}3522\,(9)$, $b = 12{\cdot}4391\,(9)$, $c = 7{\cdot}5608\,(9)$ Å, $\beta = 100{\cdot}376\,(9)°$, $D_m = 1{\cdot}61$, $D_x = 1{\cdot}603$ Mg m^{-3}. The potassium salt, $C_3H_4N_3O_4^-.K^+$, has $a = 7{\cdot}2228\,(8)$, $b = 12{\cdot}133\,(1)$, $c = 7{\cdot}4402\,(8)$ Å, $\beta = 99{\cdot}00\,(1)°$, $D_m = 1{\cdot}92$, $D_x = 1{\cdot}909$ Mg m^{-3}. The final residuals are 0·068 for the NH_4^+ salt and 0·052 for the K^+. The anion has a non-planar configuration.

Introduction

This structure determination is part of a study of aliphatic nitro compounds, nitronate salts and tautomeric forms of these compounds. The structure of nitromalonamide has been reported previously (Simonsen & Thorup, 1979). This structure determination has been carried out to study structural changes connected with nitromalonamide salt formation.

Nitromalonamide was prepared from malonamide by nitration as described by Ratz (1904). Evaporation of a solution made from nitromalonamide and aqueous ammonia gave suitable crystals of the ammonium salt. The potassium salt was prepared by an analogous procedure.

Values and statements which apply to the potassium salt structure are in the following text indicated by K^+; NH_4^+ is used for the ammonium salt.

Unit-cell dimensions were determined by a least-squares refinement of data from Guinier powder photographs taken with Cu $K\alpha_1$ radiation ($\lambda = 1{\cdot}54059$ Å) and calibrated with an internal standard (K^+: quartz; NH_4^+: silicon).

Single crystals with dimensions 0·50 × 0·68 × 0·75 mm (K^+) and 0·44 × 0·31 × 0·80 mm (NH_4^+) were used for data collection on an Enraf–Nonius CAD-3 diffractometer employing Mo $K\alpha$ radiation and different monochromators (K^+: Zr filter; NH_4^+: graphite crystal). All reflections (K^+: hkl and $hk\bar{l}$; NH_4^+: hkl and $\bar{h}kl$) in the range $2{\cdot}5° < \theta < 30°$ were measured applying the ω-scan technique. A reflection was designated unobserved for K^+ if $I < 2{\cdot}5\,\sigma(I)$, and for NH_4^+ if $I < 2{\cdot}2\,\sigma(I)$. With these criteria for K^+ 1556 out of 1834 and for NH_4^+ 1623 out of 1981 measured reflections were regarded as observed. One of the two reflections 080 and 400 was monitored every ten reflections. Lorentz and polarization corrections were

0567-7408/81/020344-03\$01.00