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Structural Studies of Organonitrogen Compounds of the Transition Elements. I. The Crystal and Molecular Structure of μ-Dimethylureylene-bis(tricarbonyliron), $[(CH_3N)_2CO]Fe_2(CO)_6$

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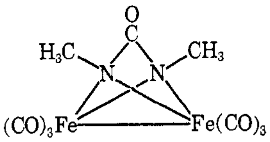
The crystal and molecular structure of μ-dimethylureylene-bis(tricarbonyliron), the principal product of the reaction of methyl azide with $Fe_2(CO)_9$, has been determined by means of a single-crystal X-ray structural analysis. Crystals of $[(CH_3N)_2CO]Fe_2(CO)_6$ are triclinic with reduced cell parameters a = 7.79 (2) Å, b = 7.87 (2) Å, c = 11.88 (2) Å, α = 92° 10′ (10′), β = 103° 45′ (10′), γ = 97° 38′ (10′). The probable space group is C_i^1-P$\bar{1}$. Observed and calculated densities for two formula units per primitive cell are 1.72 (2) and 1.74 g/cm³, respectively. A total of 468 independent visually estimated film data were employed in the structural analysis, and full-matrix least-squares refinement led to a final conventional R factor of 6.4%. The $[(CH_3N)_2CO]Fe_2(CO)_6$ molecule is made up of two $Fe(CO)_3$ groups symmetrically linked by two Fe–N–Fe bridges through the nitrogen atoms of the dimethylureylene ligand and also by an iron–iron bond of length 2.391 (7) Å. Each iron atom is thus coordinated to six other atoms in a distorted octahedral configuration and the molecular symmetry (excluding the methyl hydrogen atoms) is approximately C_{2v}-2mm.

Introduction

Considerable recent interest has centered on nitrogen-bridged bi- and trinuclear derivatives of the metal carbonyls, and several crystallographic studies of such compounds have been reported within the past 2 years.[1-9] These studies have revealed a number of new types of bridging systems and have provided some new insight into the factors which determine the stereochemistry of these bridged complexes. The existence of a variety of related compounds and of electronically equivalent compounds with different bridging groups affords a good opportunity to study structural trends in a series of similar compounds and the relation of these trends to the properties of the bridging ligands. The structures of a number of organonitrogen–iron carbonyl derivatives are currently under study in this laboratory. The present paper reports the structure of the principal product of the reaction of methyl azide with $Fe_2(CO)_9$,[10] μ-dimethylureylene-bis(tricarbonyliron),[11] $[(CH_3N)_2CO]Fe_2(CO)_6$.



The correct molecular formula of the sample studied became clear during the course of the structural analysis; initially it was believed to be di-μ-methylamido-bis(tricarbonyliron), a minor product of the same reaction.

Experimental Section

Crystals of $[(CH_3N)_2CO]Fe_2(CO)_6$ were supplied by Dr. G. R. Knox of the University of Strathclyde. Preliminary precession and Weissenberg photographs revealed no evidence of crystallographic symmetry and hence a tentative assignment to the triclinic crystal system was made. An A-centered triclinic cell was chosen for convenience in indexing, and unit cell constants were determined from *h*0*l* and *hk*0 precession photographs on which a zero-level NaCl exposure was superimposed for calibration (a(NaCl) = 5.640 Å, λ(Mo Kα) 0.7107 Å). Lattice constants at 22° obtained in this manner were: a = 7.79 (2) Å, b = 14.00 (3) Å, c = 14.50 (3) Å, α = 67° 3′ (10′), β = 97° 3′ (10′), and γ = 106° 3′ (10′). The standard deviations in parentheses are estimates based upon the reproducibility of the measurements. No evidence of higher symmetry resulted from a Delaunay reduction of this cell. The three shortest noncoplanar lattice translations define a reduced cell with a' = 7.79 (2) Å, b' = 7.87 (2) Å, c' = 11.88 (3) Å, α' = 92° 10′ (10′) β' = 103° 45′ (10′), and γ' = 97° 38′ (10′), which is related to the A-centered cell by the transformation: $a' = a$, $b' = {}^1/_2(b - c)$, $c' = {}^1/_2(b + c)$. The centered cell was used throughout the solution of the structure and all results are reported in terms of this nonprimitive cell. The centrosymmetric space group C_i^1-A$\bar{1}$ (equivalent general positions: (0, 0, 0), (0, $^1/_2$, $^1/_2$) ± (x, y, z)) was assumed; this assumption was supported by the successful interpretation of the Patterson function and the satisfactory solution of the structure. A value of 1.72 (2) g/cm³ was determined for the density by flotation in aqueous zinc bromide solution. This is in satisfactory agreement with the calculated density of 1.74 g/cm³ based on four formula units per A-centered cell. With Z = 4, no molecular symmetry is imposed and all atoms may occupy general positions of the centrosymmetric space group.

Two crystals, both fragments cut from orange needles, were utilized in the collection of intensity data by multiple-film equi-inclination Weissenberg techniques with a Supper Model WI-24 camera operated in the nonintegrating mode. Data for levels *h*0*l*–*h*5*l* were obtained from a rhombic fragment of length 0.14 mm along the rotation axis and 0.13 × 0.10 mm in cross section (crystal 1) mounted in a sealed thin-walled glass capillary. Signs of extensive decomposition of this crystal became evident after the collection of the *h*5*l* intensity data and further data were obtained from a second crystal. This crystal (crystal 2) measured 0.20 × 0.18 × 0.10 mm and was mounted parallel to its longest dimension, which coincided with the [110] direction. A

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[2] D. Bright and O. S. Mills, *Chem. Commun.*, 245 (1967).

[3] M. M. Bagga, P. E. Baikie, O. S. Mills, and P. L. Pauson, *ibid.*, 1106 (1967).

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[8] P. E. Baikie and O. S. Mills, *Chem. Commun.*, 1228 (1967).

[9] L. F. Dahl, W. R. Costello, and R. B. King, *J. Amer. Chem. Soc.*, **90**, 5422 (1968).

[10] M. Dekker and G. R. Knox, *Chem. Commun.*, 1243 (1967).

[11] This name was chosen to conform with the more descriptive of the two names[4,5] which have been given to the analogous phenyl compound.

total of ten levels of data was collected from crystal 2. Zirconium-filtered Mo Kα radiation was employed throughout the data collection. Intensities were estimated visually by comparison with timed exposures of a selected reflection. A full 360° of data (two sets of exposures per layer) was collected from crystal 2 and intensities were measured only on the top half of the film; for crystal 1, 180° of data was collected and intensities were measured on both halves of the film. Separate scale factors were maintained for the top and bottom halves of the film for each level from crystal 1 and for each of the two 180° sets of exposures making up a level for crystal 2. A total of 732 data was obtained within the sphere limited by $\theta = 17.5°$; beyond this value of the Bragg angle very few reflections were above the background. Since 264 reflections were observed for both crystals, the total number of nonzero independent data measured was 468. This represents 54% of the possible reflections with $\theta \leqslant 17.5°$.

The usual Lorentz-polarization corrections were made to the raw intensities and spot extension corrections were applied to the intensities of upper-level reflections which were observed on the top halves of the films. The appropriateness of the spot extension correction[12] was empirically confirmed by comparison of the predictions of Phillips' formula with actual measured extensions of selected upper-level spots. From the calculated value of 21.6 cm^{-1} for the linear absorption coefficient for Mo Kα radiation and from the variation in thickness of the larger of the two crystals used for data collection it was estimated that the maximum effect of absorption within a given layer was less than 10%, and hence correction for absorption was neglected. In view of the different shapes and consequent different absorption characteristics of the two crystals, no attempt was made to merge the data from the two crystals; rather all data, including duplicate data, were used in the refinement of the structure and a separate scale factor was maintained for each half-layer (see above) of data. The observed structure factors were ultimately brought onto a common scale by comparison with the calculated structure factors. For the final refinement, standard deviations were assigned to the observed structure amplitudes as follows: if $I \leqslant 8.75I_{\min}$, $\sigma(F) = 1.0$; if $I > 8.75I_{\min}$, $\sigma(F) = (I/8.75I_{\min})^{1/2}$. I is the uncorrected intensity on an arbitrary scale and $I_{\min}$ is the minimum observed intensity for the entire data set.

Solution and Refinement of the Structure

Since all atoms occupy general positions of space group $A\bar{1}$ with four molecules per unit cell, determination of the structure required location of a total of 20 nonhydrogen atoms. The coordinates of the iron atoms were determined from a three-dimensional Patterson function, in the computation of which only the data from crystal 2 were used. Two cycles of least-squares refinement of the iron atom positional parameters and the scale factors yielded discrepancy factors $R_1 = 100 \times \Sigma||F_o| - |F_c||/\Sigma|F_o| = 31.0\%$ and $R_2 = 100 \times [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 38.6\%$. In all least-squares calculations the full matrix of the normal equations was used and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Unit weights were employed in partial least-squares refinements, and in the final refinement the weights were taken as $1/\sigma^2(F_o)$ for each reflection. The positions of the 16 remaining nonhydrogen atoms present in the original formulation were found from two successive difference Fourier maps. Data from both crystals were utilized in refinement of positional and isotropic thermal parameters for these 18 atoms together with individual scale factors. This refinement converged to the unsatisfying discrepancy factors $R_1 = 13.0\%$ and $R_2 = 16.8\%$. Introduction of anisotropic thermal parameters for the two iron atoms reduced the R factors only slightly to 12.7 and 16.2%. At this point a difference Fourier synthesis clearly revealed the presence of the initially unsuspected seventh carbonyl group. Two further cycles of refinement in which this group was included resulted in final discrepancy factors of $R_1 = 6.4\%$ and $R_2 = 8.0\%$. During the last cycle of refinement, no positional parameter shifted by more than one standard deviation. The largest positive peak on a final difference Fourier map was one of electron density 0.7 e$^-$/Å^3, which may be compared to the value of 1.9 e$^-$/Å^3 observed for the bridging carbon atom on the preceding difference map.

In Table I, the final observed and calculated structure factors (in electrons) are listed. Unobserved data were not included in the refinement and are not tabulated. Calculation of structure factors for unobserved data within the limiting value of θ was carried out, and of these only five experimentally accessible data had calculated structure factors greater than 1.5 times the minimum observed value on the corresponding reciprocal lattice level. The final standard deviation of an observation of unit weight was 0.63. The relative values of the standard deviations for the reflection data were chosen to make the average value of $\Delta F/\sigma$ as nearly independent of intensity as possible; this condition is well fulfilled for the weighting scheme used. Inspection of the final structure factors did not suggest that a correction for secondary extinction should be attempted. Final positional and thermal parameters are given in Table II, and intramolecular distances and angles are listed in Tables III and IV, respectively. Standard deviations include the effects of correlation between parameters, and in the case of bond lengths and angles the effects of lattice parameter errors are also included.

In the structure factor calculations the scattering factors tabulated by Ibers[13] were employed for all atoms. The $\Delta f'$ and $\Delta f''$ values for iron of Cromer[14] were used in the correction of the calculated structure factors for the anomalous dispersion of the iron atoms. All computations were carried out on the IBM 360/50 computer. Programs employed included modified versions of Zalkin's FORDAP Fourier summation program, the Busing–Martin–Levy ORFLS and ORFFE least-squares and function and error programs, the Brookhaven–Northwestern data processing programs, and various locally written programs.

Description and Discussion of the Structure

In the crystalline state, μ-dimethylureylene-bis(tricarbonyliron) exists as monomeric molecular units comprised of two Fe(CO)$_3$ groups symmetrically linked by two Fe–N–Fe bridges through the nitrogen atoms of the dimethylureylene ligand. A further link *via* an iron–iron bond is proposed to account for the dia-

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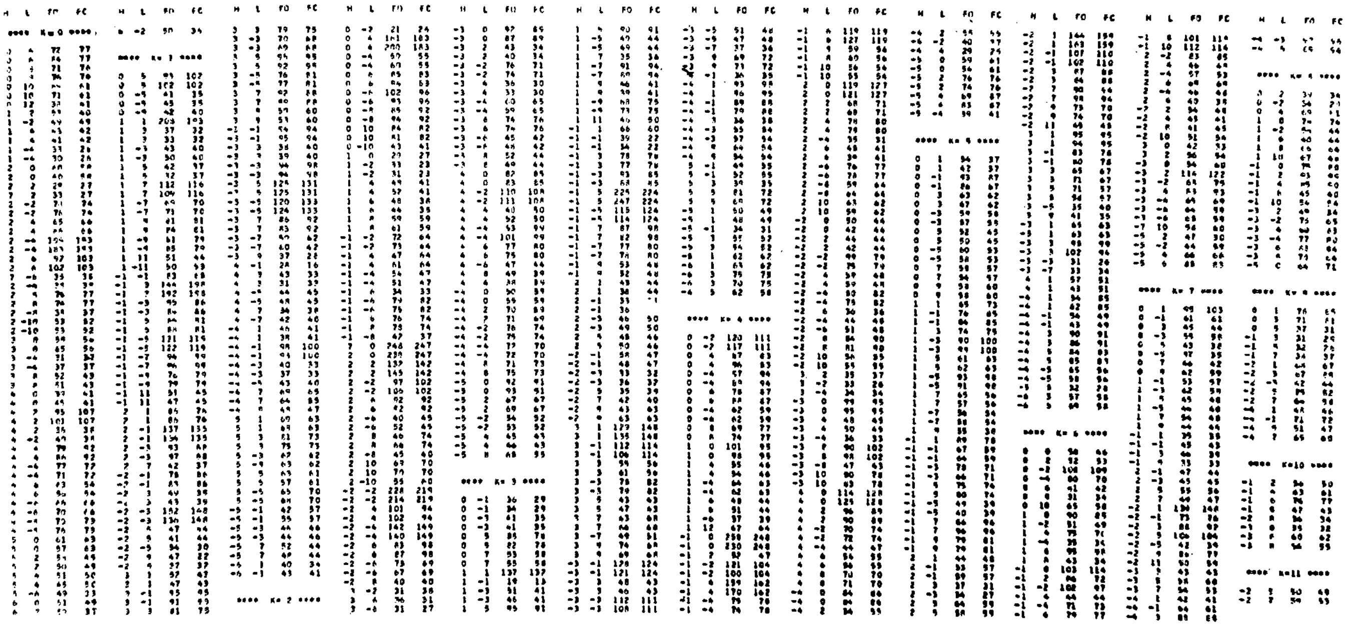
[12] D. C. Phillips, *Acta Crystallogr.*, **7**, 746 (1954); **9**, 819 (1956).

[13] J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962.

[14] D. T. Cromer, *Acta Crystallogr*, **18**, 17 (1965).

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES[a] (IN ELECTRONS) FOR $[(CH_3N)_2CO]Fe_2(CO)_6$



[a] Duplicate data (see text) are included in this table as double entries.

TABLE II

ATOMIC POSITIONAL AND THERMAL PARAMETERS FOR $[(CH_3N)_2CO]Fe_2(CO)_6$

	x	y	z	B, Å^2
Fe(1)	0.1907 (4)[a]	0.0438 (3)	0.1979 (2)	[b]
Fe(2)	0.3436 (4)	−0.0891 (3)	0.2997 (2)	[b]
C(1–1)	0.1409 (37)	0.1752 (27)	0.1510 (20)	6.3 (8)
O(1–1)	0.0870 (24)	0.2480 (18)	0.1378 (13)	7.5 (5)
C(1–2)	0.2051 (33)	[illegible] 0.0414 (22)	0.0798 (22)	5.7 (7)
O(1–2)	0.2232 (21)	[illegible] 0.0348 (14)	0.0063 (14)	6.3 (4)
C(1–3)	−0.0290 (37)	−0.0329 (21)	0.2158 (16)	4.0 (6)
O(1–3)	−0.1755 (23)	−0.0869 (14)	0.2269 (11)	5.3 (4)
C(2–1)	0.5156 (35)	−0.1324 (21)	0.3867 (19)	4.9 (6)
O(2–1)	0.6282 (23)	−0.1623 (14)	0.4408 (13)	6.1 (4)
C(2–2)	0.3942 (27)	−0.1301 (20)	0.2073 (18)	4.1 (6)
O(2–2)	0.4246 (19)	−0.1634 (14)	0.1491 (12)	5.6 (4)
C(2–3)	0.1728 (34)	−0.2000 (23)	0.3483 (18)	4.5 (6)
O(2–3)	0.0478 (23)	−0.2722 (16)	0.3831 (12)	6.3 (5)
N(1)	0.4472 (22)	0.0635 (16)	0.2310 (13)	3.9 (5)
N(2)	0.2531 (23)	0.0056 (15)	0.3418 (13)	3.6 (4)
C(4)	0.4211 (37)	0.0813 (25)	0.3131 (19)	4.3 (7)
O(4)	0.5060 (23)	0.1363 (15)	0.3578 (13)	5.8 (5)
C(5)	0.6237 (30)	0.1292 (20)	0.1749 (17)	4.8 (6)
C(6)	0.1539 (28)	−0.0051 (18)	0.4284 (16)	4.4 (6)

Anisotropic Thermal Parameters[c] for $[(CH_3N)_2CO]Fe_2(CO)_6$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	0.0122 (11)	0.0058 (6)	0.0036 (3)	0.0025 (6)	0.0012 (4)	−0.0011 (3)
Fe(2)	0.0128 (11)	0.0039 (6)	0.0036 (3)	0.0011 (6)	−0.0004 (4)	−0.0013 (3)

[a] Numbers in parentheses in all tables and in the text are estimated standard deviations in the least significant digits. [b] See anisotropic thermal parameters below. [c] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

magnetism of the compound, the iron–iron distance of 2.391 (7) Å, and the configuration of the bridging system. A perspective view of the molecular structure is shown in Figure 1. Though no crystallographic symmetry is required for the $[(CH_3N)_2CO]Fe_2(CO)_6$ molecule, its structure is very nearly one of C_{2v}-2mm symmetry. Each iron atom is bonded to three terminal carbonyl groups, two bridging nitrogen atoms, and the other iron atom in a distorted octahedral configuration. This compound is thus similar in structure to other nitrogen-, sulfur-, and phosphorus-bridged binuclear iron and cobalt compounds whose structures have been reported;[15] in particular its structure is closely related to that of its phenyl analog which has been the subject of two recent independent structural determinations.[4,5]

The presence of methyl rather than phenyl groups

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[15] See ref 9 for a summary of pertinent structural data for several of these compounds.

Table III

Bond Lengths and Selected Intramolecular Nonbonded Contacts (Å)

Fe(1)–Fe(2)	2.391 (7)	N(1)–C(4)	1.36 (3)
Fe(1)–C(1–1)	1.83 (4)	N(2)–C(4)	1.43 (3)
Fe(1)–C(1–2)	1.74 (3)	Mean N–C(bridging)	1.395 (20)
Fe(1)–C(1–3)	1.74 (3)	N(1)–C(5)	1.55 (3)
Fe(2)–C(2–1)	1.79 (3)	N(2)–C(6)	1.49 (3)
Fe(2)–C(2–2)	1.77 (3)	Mean N–C(methyl)	1.520 (19)
Fe(2)–C(2–3)	1.71 (3)	C(4)–O(4)	1.21 (3)
Mean Fe–C	1.763 (13)	N(2)···N(1)	2.10 (2)
Fe(1)–N(1)	1.97 (2)	N(1)···C(1–1)	3.07 (4)
Fe(1)–N(2)	1.98 (2)	N(1)···C(1–2)	2.77 (3)
Fe(2)–N(1)	1.95 (2)	N(1)···C(2–1)	2.93 (3)
Fe(2)–N(2)	1.97 (2)	N(1)···C(2–2)	2.78 (4)
Mean Fe–N	1.965 (10)	N(2)···C(1–1)	3.08 (4)
C(1–1)–O(1–1)	1.15 (3)	N(2)···C(1–3)	2.75 (3)
C(1–2)–O(1–2)	1.13 (3)	N(2)···C(2–1)	3.04 (3)
C(1–3)–O(1–3)	1.17 (2)	N(2)···C(2–3)	2.74 (4)
C(2–1)–O(2–1)	1.16 (2)		
C(2–2)–O(2–2)	1.18 (2)		
C(2–3)–O(2–3)	1.18 (2)		
Mean terminal C–O	1.162 (11)		

Table IV

Selected Bond Angles (deg)

Fe(2)–Fe(1)–N(1)	52.0 (6)	Fe(1)–Fe(2)–N(1)	52.7 (5)
Fe(2)–Fe(1)–N(2)	52.6 (6)	Fe(1)–Fe(2)–N(2)	52.8 (5)
Fe(2)–Fe(1)–C(1–1)	155.2 (9)	Fe(1)–Fe(2)–C(2–1)	152.4 (9)
Fe(2)–Fe(1)–C(1–2)	101.2 (9)	Fe(1)–Fe(2)–C(2–2)	99.7 (8)
Fe(2)–Fe(1)–C(1–3)	100.0 (8)	Fe(1)–Fe(2)–C(2–3)	102.8 (8)
N(1)–Fe(1)–N(2)	64.5 (7)	N(1)–Fe(2)–N(2)	65.0 (8)
N(1)–Fe(1)–C(1–1)	108.1 (11)	N(1)–Fe(2)–C(2–1)	103.3 (10)
N(1)–Fe(1)–C(1–2)	96.3 (10)	N(1)–Fe(2)–C(2–2)	96.5 (10)
N(1)–Fe(1)–C(1–3)	151.5 (9)	N(1)–Fe(2)–C(2–3)	154.6 (10)
N(2)–Fe(1)–C(1–1)	108.0 (11)	N(2)–Fe(2)–C(2–1)	107.7 (10)
N(2)–Fe(1)–C(1–2)	153.3 (11)	N(2)–Fe(2)–C(2–2)	152.3 (9)
N(2)–Fe(1)–C(1–3)	95.5 (9)	N(2)–Fe(2)–C(2–3)	96.0 (11)
C(1–1)–Fe(1)–C(1–2)	95.3 (13)	C(2–1)–Fe(2)–C(2–2)	96.3 (11)
C(1–1)–Fe(1)–C(1–3)	97.1 (12)	C(2–1)–Fe(2)–C(2–3)	98.3 (11)
C(1–2)–Fe(1)–C(1–3)	94.4 (12)	C(2–2)–Fe(2)–C(2–3)	94.2 (12)
Fe(1)–N(1)–Fe(2)	75.3 (7)	Fe(1)–N(2)–Fe(2)	74.6 (7)
Fe(1)–N(1)–C(4)	90.2 (16)	Fe(1)–N(2)–C(4)	87.8 (14)
Fe(1)–N(1)–C(5)	136.4 (14)	Fe(1)–N(2)–C(6)	132.0 (14)
Fe(2)–N(1)–C(4)	90.0 (16)	Fe(2)–N(2)–C(4)	87.1 (17)
Fe(2)–N(1)–C(5)	133.7 (15)	Fe(2)–N(2)–C(6)	136.9 (14)
C(4)–N(1)–C(5)	116.5 (21)	C(4)–N(2)–C(6)	121.5 (21)
N(1)–C(4)–O(4)	135.6 (26)	N(2)–C(4)–O(4)	126.1 (26)
N(1)–C(4)–N(2)	98.3 (25)	Fe(2)–C(2–1)–O(2–1)	177.4 (26)
Fe(1)–C(i–1)–O(1–1)	166.2 (24)	Fe(2)–C(2–2)–O(2–2)	176.3 (22)
Fe(1)–C(1–2)–O(1–2)	174.7 (25)	Fe(2)–C(2–3)–O(2–3)	175.1 (25)
Fe(1)–C(1–3)–O(1–3)	177.8 (27)		

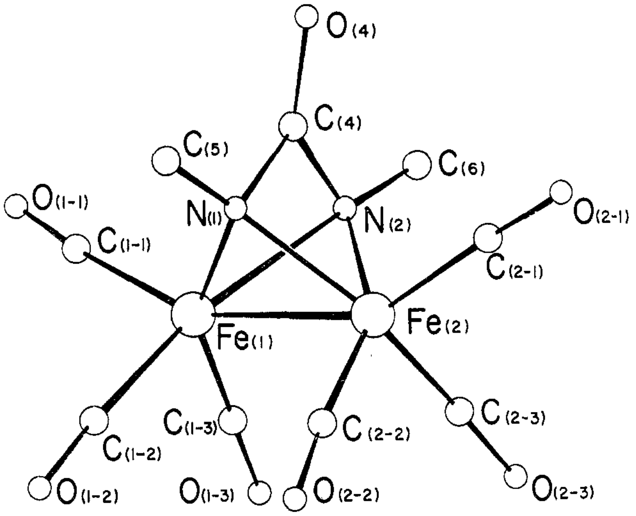

Figure 1.—The molecular structure of $[(CH_3N)_2CO]Fe_2(CO)_6$.

has the following effects on the molecular configuration: (1) an apparently significant lengthening of the average N–C(methyl) distance to 1.520 (19) Å compared with the mean N–C(phenyl) bond distance of 1.438 (10) Å[16] and (2) a marginally significant shortening of the mean Fe–N distance from 1.996 (6) to 1.965 (10) Å. Though the evidence for these two effects cannot be said to be conclusive solely on the basis of differences of 4.3 and 3.1 standard deviations in average bond lengths, the trends observed are reasonable ones. The average C–N bond length in the phenyl compound is a typical value for a bond between a trigonal carbon atom and a nitrogen atom; thus, for example, N–C(phenyl) bond lengths of 1.413 (3) and 1.42 (4) Å are observed in acetanilide[17] and triphenylamine,[18] respectively. In $[(t\text{-}C_4H_9N)_2CO](CoC_5H_5)_2$,[6,7] the only other similar compound containing a $(RN)_2CO$ bridging group for which structural data are available, the N–C(*t*-butyl) distance of 1.49 Å (no esd given) is again longer than the N–C(phenyl) distance in the diphenylureylene-bridged iron compound but somewhat shorter than the corresponding distance in the methyl compound. Though the Fe–N distance in the phenyl compound is longer than the Co–N distance in the cobalt dimer, the fact that the cobalt atom has a chemical environment different from that of the iron atom and the uncertainty in the relative single-bond radii of cobalt and iron in these compounds make any evaluation of the significance of this difference impossible.

The N(1)···N(2) intramolecular nonbonded distance of 2.10 (2) Å and the (Fe(1)–N(1)–Fe(2))–(Fe(1)–N(2)–Fe(2)) dihedral angle of 84.9 (10)° agree within experimental error with the values of 2.14 Å and 84.8° for the corresponding parameters in the phenyl compound. These may be compared with the values of 2.50 (3) Å and 104.0 (10)° for $[H_2NFe(CO)_3]_2$,[9] in which the constraint of a bridging carbonyl group is absent. The nonhydrogen atoms of the *μ*-dimethylureylene ligand are nearly coplanar; the maximum deviation from the "best" least-squares plane through these five atoms is 0.03 Å. Within the bridging ligand, the average N–C(carbonyl) bond distance of 1.395 (20) Å, the C–O distance of 1.21 (3) Å, the mean N–C–O angle of 130.8 (16)°, and the N–C–N angle of 98.3 (25)° all agree well with the corresponding values for the phenyl compound.[5] In free urea these parameters have the values:[19] C–N = 1.356 (7) Å, C–O = 1.276 (8) Å, N–C–N = 119.0 (6)°, and N–C–O = 120.5 (3)°. The individual N–C–O angles of 135.6 (26) and 126.1 (26)° in the bridged complex differ significantly from each other, a difference which may be rationalized as resulting from a 3.14-Å contact of O(4) with O(1–1) of a molecule displaced by one unit cell in the +*a* direction.

Other structural features are in close accord with those previously found for related compounds. The Fe–Fe distance of 2.391 (7) Å is within the range of

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(16) Bond lengths and angles quoted for the phenyl compound are averages of those reported in the two independent determinations of its structure if corresponding values from these two determinations are available. Since the results of one of these determinations have been published only as a preliminary note,[4] all standard deviations quoted are taken from ref 5. Likewise, calculations of the N(1)···N(2) distance and the (Fe(1)–N(1)–Fe(2))–(Fe(1)–N(2)–Fe(2)) dihedral angle were based on the parameters of ref 5.

(17) C. J. Brown, *Acta Crystallogr.*, **21**, 442 (1966).

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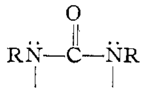
2.37–2.46 Å found for the lengths of other nitrogen-bridged Fe–Fe bonds.[20] Agreement is particularly good with the Fe–Fe distances in the compounds most closely resembling $[(CH_3N)_2CO]Fe_2(CO)_6$: 2.409 (3) Å in $[(C_6H_5N)_2CO]Fe_2(CO)_6$,[4,5] 2.402 (6) Å in $[H_2NFe(CO)_3]_2$,[9] and 2.40 Å (no esd given) in $[(p\text{-}CH_3C_6H_4)_2CNHNFe(CO)_3]_2$.[3] Nitrogen-bridged bonds are consistently among the shortest of iron–iron single bonds. The average Fe–N–Fe bridging angle of 75.0 (5)° is identical within experimental error with the corresponding angle in similar compounds (*e.g.*, 74.6 (2)° in $[(C_6H_5N)_2CO]Fe_2(CO)_6$,[4,5] 74.4 (5)° in $[H_2NFe(CO)_3]_2$,[9] and 74.6° (no esd given) in $[(t\text{-}C_4H_9N)_2CO](CoC_5H_5)_2)$.[7] The mean Fe–C and C–O distances for the terminal carbonyl groups are 1.763 (13) and 1.162 (11) Å, respectively; both of these values are normal. Only carbonyl group (1–1) is significantly nonlinear (Fe–C–O = 166.2 (24)°), though there seems to be no obvious reason for this nonlinearity.

The atomic thermal parameters show no anomalies, and the anisotropic temperature factor coefficients of the iron atoms suggest only a modest degree of anisotropy. The rms amplitudes of vibration along the principal axes of the thermal ellipsoid for Fe(1) are 0.225 (11), 0.191 (7), and 0.165 (8) Å, and for Fe(2) are 0.206 (9), 0.178 (8), and 0.173 (14) Å. The intermolecular contacts are all of normal lengths for molecular crystals, with the three shortest (all involving carbonyl oxygen atoms) being 3.10 (3), 3.14 (3), and 3.17 (2) Å.

Though unknown until quite recently, binuclear metal complexes of substituted ureylene ligands



$$R\ddot{N}-\overset{\overset{\displaystyle O}{\|}}{C}-\ddot{N}R$$

have now been formed from a variety of nitrogen-containing starting materials, including azides,[10] isocyanates,[4,21,22] nitromethane,[10] and di-*t*-butylsulfur diimide.[7] In at least one case,[7] the substituted urea itself was detected in the reaction mixture along with the binuclear metal complex. The formation of the bridged dimers from a variety of starting materials supports the suggestion[10] that all of these reactions proceed through nitrene intermediates. Furthermore, it is likely that one or more of the compounds $[RNFe(CO)_3]_2$, $[RNHFe(CO)_3]_2$, or $R_2N_4Fe(CO)_3$, all isolated from reactions in which the ureylene-bridged dimer was also formed,[10] may be its precursors under appropriate conditions.

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[20] A summary of N-bridged iron–iron bond lengths is given in ref 9. A compilation of other iron–iron bond distances may be found in: M. R. Churchill, *Inorg. Chem.*, **6**, 190 (1967).

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