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THE STRUCTURE OF μ-CARBONYL-μ-DICYANOVINYLIDENE-BIS-(CARBONYLCYCLOPENTADIENYLIRON(0)), *cis*-$Fe_2(CO)_2(\pi\text{-}C_5H_5)_2$-($\mu$-CO) [$\mu$-C=C(CN)$_2$]

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Summary

The structure of *cis*-$Fe_2(CO)_2(\pi\text{-}C_5H_5)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$ has been determined from three-dimensional X-ray data collected by counter methods. The dark-red compound crystallizes in space group C_{2h}^5 ($P2_1/c$) of the monoclinic system with two independent dimeric molecules in the asymmetric portion of a unit cell of dimensions a = 7.218(1), b = 33.275(6), c = 13.364(2) Å, and β = 99.71(1)°. The observed and calculated densities are 1.64(2) g cm^{-3} and 1.69 g cm^{-3}, respectively. Least-squares refinement led to a final value of the conventional R index (on F) of 0.135 for the 2577 reflections having $F_0 > 0.0$. The value of R is 0.084 for those reflections having $F_0^2 > 3\sigma(F_0^2)$. The structure consists of discrete dimeric molecules with bridging dicyanovinylidene and bridging carbonyl ligands, and *cis*-cyclopentadienyl rings. The average value for the Fe—Fe distance is 2.511(4) Å. The dicyanovinylidene ligand is planar and symmetrically bridges the two iron atoms. The average Fe—C (of dicyanovinylidene) distance is 1.87(4) Å. The average Fe—C (of bridging CO) distance is 1.94(3) Å.

Introduction

Recently King and Saran [1,2] have prepared and isolated both *cis* and *trans* isomers of the dimeric complex $Fe_2(CO)_2(\pi\text{-}C_5H_5)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$, which contain a bridging dicyanovinylidene ligand. These complexes are dicyanomethylene analogues of the well-characterized dimeric complexes $[Fe(C_5H_5)(CO)_2]_2$ [3-6]. The chemical properties of the dicyanovinylidene complexes indicate that the dicyanovinylidene ligand is a stronger π-acceptor than carbonyl

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[1,7], making it currently one of the strongest π-acceptor ligands in transition metal chemistry.

Complexes that contain a terminal instead of a bridging dicyanovinylidene ligand have also been prepared and characterized [8]. The X-ray structure of one of these complexes, $MoCl(\pi\text{-}C_5H_5)[C{=}C(CN)_2][P(OCH_3)_3]_2$, revealed some unusual features [9,10]. The dicyanovinylidene ligand-to-metal linkage is bent (Mo—C—C angle of 166.6(4)°) in the direction toward the cyclopentadienyl ring, which in turn is tipped toward the dicyanovinylidene ligand. This suggests the possibility of a through-space ligand-ligand attractive interaction. In order to characterize further the properties of the dicyanovinylidene ligand we undertook and present here the X-ray structure determination of *cis*-$Fe_2(CO)_2(\pi\text{-}C_5H_5)_2(\mu\text{-}CO)[(\mu\text{-}C{=}C(CN)_2]$.

Experimental

King and Saran generously supplied a microcrystalline sample of $Fe_2(CO)_2(\pi\text{-}C_5H_5)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$ [1]. A variety of recrystallization techniques under dry and oxygen-free conditions were employed with limited sucess. Very small crystals were obtained at —10°, employing a slow diffusion of hexane into a dichloromethane solution saturated with the compound. The largest of the deep-red crystals that had an identifiable crystal habit was chosen for subsequent work. The crystal was approximately 0.06 mm thick with a cross section of 0.11 × 0.13 mm with a calculated volume of 2.06×10^{-3} mm^3 and calculated weight of 3.5 μg. Preliminary Weissenberg and precession photography of the $0kl$, hkl, $h0l$, and $hk0$ nets showed that the crystal belonged to the monoclinic system. The systematic absences observed for the reflections $h0l$ with l odd and $0k0$ with k odd are consistent with space group $C_{2h}^5(P2_1/c)$. Six of the faces of the crystal were identified from optical goniometry as belonging to the forms {111} and {011}. The seventh face was (010). Cell parameters were determined at 22° from a least-squares refinement [11,12] of the setting angles of 14 intense high-order reflections centered on a Picker four-circle automated diffractometer. Cu-K_{α_1} radiation (λ 1.540562 Å) was used. The cell parameters are a = 7.218(1), b = 33.275(6), c = 13.364(2) Å, and β = 99.71(1)°. The density calculated for eight formula weights per unit cell is 1.69 g cm^{-3} and is in fair agreement with that of 1.64(2) g cm^{-3} measured by flotation in aqueous $ZnCl_2$. With eight formula weights in space group $P2_1/c$ there are two independent dimeric molecules in the asymmetric unit.

The mosaicity of the crystal was examined by means of the narrow-source, open-counter ω-scan technique. The peak width at half-height for a typical strong reflection was found to be less than 0.2°. The crystal was mounted on the diffractometer with the a axis slightly offset from the spindle axis. Intensity data were collected as previously described [11] using Cu-K_α radiation prefiltered through 0.5 mil nickel foil. Cu-K_α rather than Mo-K_α radiation was chosen to maximize the signal-to-noise ratio. The take-off angle was 1.8°. The scan range was ca. ±0.45° in 2θ from the calculated positions of the K_{α_1} and K_{α_2} peaks. The scan speed was 2°/min for reflections with $2\theta < 50°$, and 1° /min for all higher order reflections. Background counts were measured at each end of the scan for preset times of 10 sec for reflections with $2\theta < 40°$, and 20 sec for higher order reflections. A receiving aperture positioned 32 cm from the crystal directly in front of the counter had its windows set such that the opening was 4.3 mm high and 3.0 mm wide. The pulse height analyzer was set for approximately a 90% window centered on the Cu-K_{α_1} peak.

The intensities of six standard reflections were measured every 100 reflections. They showed an average deviation from their average intensity of less than $\pm 2.8\sigma$. Intensity data were collected for the unique *hkl* planes up to 2θ (Cu-K_{α_1}) = 96°. Past this value of 2θ there were very few reflections above background. The data were processed as previously described [11] using a value for p of 0.04. Of the 2577 unique reflections observed, only 1441 have $F^2 > 3\sigma(F^2)$ while 959 have $F^2 < \sigma(F^2)$. The linear absorption coefficient for the compound for Cu-K_α radiation is 149.4 cm^{-1} and the data were corrected for absorption*, with maximum and minimum transmission factors of 0.391 and 0.134, respectively.

Direct methods were used to solve the structure. Normalized structure factors (E's) were calculated and the 189 strongest reflections ($E > 1.85$) were used as input to the symbolic addition program LSAM. An E map was generated which revealed the positions of the four iron atoms of the asymmetric unit together with some associated ligand atoms. One cycle of isotropic least-squares refinement on only the positions of the four iron atoms (associated with the two crystallographically unique dimers per unit cell) gave the agreement indices R = 0.336 and R_w = 0.428, where

$$R = \sum \big| |F_0| - |F_c| \big| / \sum |F_0|$$

and

$$R_w = \left(\sum w(|F_0| - |F_c|)^2 / \sum wF_0^2 \right)^{\frac{1}{2}}$$

and weights, w, were taken as $4F_0^2/\sigma^2(F_0^2)$. In this and succeeding full-matrix least-squares, the function minimized was $\Sigma w(|F_0| - |F_c|)^2$. Atomic scattering factors for neutral iron, oxygen, nitrogen, and carbon atoms were taken from the new tabulation [13]. Hydrogen atom scattering factors were those of Stewart, Davidson, and Simpson [14]. Anomalous dispersion effects were included in the calculation of F_c [15] using the values of $\Delta f'$ and $\Delta f''$ for iron, oxygen, and nitrogen calculated by Cromer and Liberman [16].

Further three-dimensional difference Fourier syntheses revealed the positions of the remaining nonhydrogen atoms. The cyclopentadienyl atoms were treated as rigid groups [17-19] of D_{5h} symmetry (C—C = 1.42 Å) with an overall group thermal parameter. Using the 2141 unique reflections that had $F_0^2 > \sigma(F_0^2)$ the isotropic full-matrix least-squares refinement converged giving the agreement indices R = 0.130 and R_w = 0.120, with a goodness of fit, the stand-

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* In addition to various local programs, those used in this work include the absorption program AGNOST, and local modifications of Dewar's FAME statistics and normalized structure factor (E's) program, the York LSAM series of programs for direct methods, Johnson's ORTEP thermal ellipsoid program, and Zalkin's FORDAP Fourier program. Our local least-squares program, NUCLS, in its nongroup form, closely resembles the Busing—Levy ORFLS program.

TABLE 1

POSITIONAL AND THERMAL PARAMETERS FOR $Fe_2(CO)_2(C_5H_5)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Molecule A									
Fe(1)	0.0073(4)[b]	0.4777(1)	0.2120(2)	0.0160(7)	0.00086(3)	0.0039(2)	−0.0004(1)	0.0015(3)	0.0001(1)
Fe(2)	−0.0431(4)	0.4047(1)	0.2468(2)	0.0179(8)	0.00086(4)	0.0044(2)	−0.0002(1)	0.0011(3)	−0.0001(1)
O(1)	−0.353(2)	0.4977(5)	0.090(1)	0.030(5)	0.0022(3)	0.007(1)	0.001(1)	−0.003(2)	0.0000(4)
O(2)	−0.433(2)	0.3940(5)	0.150(1)	0.026(5)	0.0024(3)	0.010(1)	−0.002(1)	0.000(2)	0.0004(5)
O(3)	0.066(2)	0.4224(5)	0.048(1)	0.044(5)	0.0018(2)	0.006(1)	0.003(1)	0.007(2)	−0.0003(4)
N(1)	−0.255(3)	0.5355(6)	0.431(1)	0.041(6)	0.0012(3)	0.007(2)	0.001(1)	0.000(2)	−0.0003(6)
N(2)	−0.353(3)	0.4094(6)	0.483(1)	0.033(8)	0.0018(3)	0.004(1)	−0.001(1)	0.004(2)	0.0006(5)
C(1)	−0.210(3)	0.4904(6)	0.139(1)	0.023(6)	0.0012(3)	0.004(1)	0.000(1)	0.005(3)	−0.0008(5)
C(2)	−0.286(3)	0.3983(6)	0.190(2)	0.029(8)	0.0011(3)	0.006(2)	0.000(1)	0.003(3)	0.0007(6)
C(3)	0.020(3)	0.4294(6)	0.128(2)	0.010(5)	0.0009(3)	0.012(2)	−0.001(1)	−0.004(3)	0.0010(7)
C(4)	−0.109(2)	0.4527(5)	0.306(1)	0.012(5)	0.0009(2)	0.005(1)	0.000(1)	−0.007(2)	−0.0004(5)
C(5)	−0.215(2)	0.4625(6)	0.381(1)	0.009(5)	0.0012(3)	0.002(1)	0.001(1)	0.002(2)	−0.0002(5)
C(6)	−0.241(3)	0.5030(8)	0.409(2)	0.026(7)	0.0011(3)	0.004(2)	0.001(1)	0.005(2)	0.0004(6)
C(7)	−0.287(3)	0.4322(7)	0.440(1)	0.017(6)	0.0017(3)	0.002(1)	−0.002(1)	0.005(2)	−0.0002(6)
Molecule B									
Fe(1)	0.4321(4)	0.3523(1)	0.8164(2)	0.0227(9)	0.00080(4)	0.0057(2)	−0.0006(1)	0.0033(4)	0.0001(1)
Fe(2)	0.3134(4)	0.2967(1)	0.6952(2)	0.0228(9)	0.00101(4)	0.0048(2)	0.0001(1)	0.0011(4)	0.0000(1)
O(1)	0.203(3)	0.3383(5)	0.974(1)	0.046(6)	0.0021(3)	0.012(2)	−0.002(1)	0.016(3)	−0.0015(5)
O(2)	0.026(2)	0.2612(5)	0.795(2)	0.028(5)	0.0019(3)	0.018(2)	−0.003(1)	0.011(3)	−0.0020(6)
O(3)	0.080(2)	0.3699(5)	0.677(1)	0.031(5)	0.0016(2)	0.014(2)	0.003(1)	−0.005(2)	0.0004(5)
N(1)	0.816(3)	0.2927(7)	1.037(1)	0.044(7)	0.0024(3)	0.005(2)	0.000(1)	−0.004(3)	0.0012(6)
N(2)	0.581(3)	0.1951(6)	0.837(2)	0.055(8)	0.0014(3)	0.009(2)	0.002(1)	0.008(3)	0.0012(7)
C(1)	0.293(3)	0.3441(6)	0.913(2)	0.018(6)	0.0007(2)	0.010(2)	0.002(1)	0.004(3)	−0.0006(6)
C(2)	0.138(3)	0.2758(6)	0.758(2)	0.008(5)	0.0014(3)	0.007(2)	0.000(1)	−0.001(2)	−0.0004(6)
C(3)	0.214(3)	0.3494(8)	0.707(2)	0.028(7)	0.0020(4)	0.007(2)	0.001(1)	0.000(3)	0.0009(7)
C(4)	0.483(3)	0.2980(6)	0.822(1)	0.016(5)	0.0015(3)	0.003(1)	−0.001(1)	0.006(2)	−0.0004(5)
C(5)	0.593(3)	0.2703(8)	0.878(2)	0.021(6)	0.0014(4)	0.005(2)	0.003(1)	0.006(3)	0.0007(7)
C(6)	0.719(3)	0.2829(7)	0.969(2)	0.022(7)	0.0016(4)	0.005(2)	0.001(1)	0.003(3)	0.0020(7)
C(7)	0.584(3)	0.2285(9)	0.856(2)	0.025(6)	0.0013(3)	0.007(2)	0.002(1)	0.005(3)	0.0011(8)

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{12}hl + 2\beta_{23}kl)]$. [b] The numbers given in parentheses here and in succeeding tables are estimated standard deviations in the least significant figures.

ard deviation of an observation of unit weight, of 2.15 *e*. At this point the hydrogen atoms of the cyclopentadienyl ring were idealized (D_{5h} symmetry with C—H = 0.97 Å) and each was assigned an isotropic thermal parameter equal to the isotropic value of the rigid group to which the hydrogen was attached. A fixed-atom structure factor calculation was performed for these hydrogen atoms and applied in subsequent refinements. In the final two cycles of least-squares refinement the carbon atoms of the rigid group were allowed individual isotropic thermal parameters while the remaining nonhydrogen atoms were allowed anisotropic thermal parameters. Since the number of variables was large (315) the final cycles of refinement were blocked, with one of the two dimeric molecules of the asymmetric unit and all iron atoms constituting a block. In the final cycle no parameter shifted by more than 1.1 standard deviations. In this refinement the thermal parameters of atoms C(7)A and C(4)B went non-positive definite and these were reset (by less than a standard deviation of their values) to be positive definite. The final agreement factors using all reflections are R = 0.135 and R_w = 0.105 with a goodness of fit of 1.71 e. The final agreement factors calculated using only those reflections for which $F_0{}^2 > 3\sigma(F_0{}^2)$ are R = 0.084 and R_w = 0.093.

A comparison of $\Sigma w(|F_0| - |F_c|)^2$ for various classes of reflections based upon $|F_0|$, Miller indices, and the scattering angle shows no unusual trends. A final difference Fourier synthesis revealed peaks as large as 0.8(3) e Å^{-3}, which is approximately 1/3 the height of a typical carbon atom in a previous difference Fourier map. All of these residual peaks are associated with the cyclopentadienyl ring regions or the iron atoms.

The positional and thermal parameters of the nongroup atoms obtained from the last cycle of least-squares refinement are given in Table 1 along with the associated standard deviations as estimated from the inverse matrix. The group positional and thermal parameters with their estimated standard deviations are given in Table 2, together with the rigid body atom positions which are derived from the group parameters.

Values of 10 $|F_0|$ and 10$|F_c|$ in electrons have been deposited*.

Description of the Structure

The crystal structure consists of the packing of discrete dimeric molecules of formula *cis*-$Fe_2(CO)_2(\pi\text{-}C_5H_5)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$. The closest intermolecular contacts are between the nitrogen atoms of the dicyanovinylidene ligand and neighboring cyclopentadienyl hydrogen atoms, as can be seen in the stereoscopic packing diagram given in Fig. 1. These calculated contact distances range from 2.56 to 2.68 Å. There are no other short intermolecular contacts.

The unit cell contains eight dimeric molecules of $Fe_2(CO)_2(\pi\text{-}C_5H_5)_2(\mu\text{-}CO)$-$[\mu\text{-}C{=}C(CN)_2]$, with two of these constituting the asymmetric unit. The two independent molecules, labelled A and B, are shown in Fig. 2 and Fig. 3, re-

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TABLE 2
GROUP AND DERIVED PARAMETERS

Group	x_c[a]	y_c	z_c	δ	ε	η
Cp(1)A	0.194(1)	0.5107(3)	0.238(1)	0.71(1)	−3.09(1)	−1.51(1)
Cp(2)A	0.090(1)	0.3664(3)	0.310(1)	−0.88(1)	3.32(1)	−1.14(1)
Cp(1)B	0.594(1)	0.3908(3)	0.821(1)	0.81(1)	−2.58(1)	1.49(1)
Cp(2)B	0.364(2)	0.2802(4)	0.579(1)	−1 66(1)	−2.91(1)	−2.83(1)

Derived C_5H_5-group carbon atoms					Derived C_5H_5-group hydrogen atoms[b]			
Atom	x	y	z	B, Å²	Atom	x	y	z
C(11)A	0.089(2)	0.5378(4)	0.206(1)	5.8(6)	H(11)A	0.006	0.5595	0.180
C(12)A	0.196(2)	0.5137(5)	0.148(1)	6.7(5)	H(12)A	0.196	0.5164	0.076
C(13)A	0.230(2)	0.4855(4)	0.215(1)	6.1(5)	H(13)A	0.385	0.4654	0.196
C(14)A	0.257(2)	0.4922(4)	0.314(1)	5.3(5)	H(14)A	0.310	0.4770	0.374
C(15)A	0.127(2)	0.5245(5)	0.308(1)	7.0(6)	H(15)A	0.076	0.5352	0.365
C(21)A	−0.013(2)	0.3424(4)	0.261(1)	4.2(4)	H(21)A	−0.097	0.3234	0.222
C(22)A	0.155(2)	0.3584(5)	0.235(1)	6.5(6)	H(22)A	0.207	0.3521	0.175
C(23)A	0.233(2)	0.3855(4)	0.313(1)	5.6(5)	H(23)A	0.349	0.4006	0.316
C(24)A	0.113(2)	0.3861(4)	0.387(1)	5.1(5)	H(24)A	0.133	0.4020	0.450
C(25)A	−0.039(2)	0.3595(4)	0.355(1)	5.2(5)	H(25)A	−0.143	0.3543	0.391
C(11)B	0.518(2)	0.4074(5)	0.883(1)	6.5(6)	H(11)B	0.457	0.4210	0.934
C(12)B	0.472(2)	0.4123(3)	0.777(1)	7.5(6)	H(12)B	0.375	0.4291	0.741
C(13)B	0.594(2)	0.3875(5)	0.731(1)	7.7(7)	H(13)B	0.596	0.3841	0.660
C(14)B	0.716(2)	0.3673(4)	0.810(1)	6.2(6)	H(14)B	0.815	0.3482	0.802
C(15)B	0.669(2)	0.3797(5)	0.904(1)	6 0(6)	H(15)B	0.729	0.3710	0.972
C(21)B	0.246(2)	0.2545(5)	0.577(1)	7.6(7)	H(21)B	0.153	0.2338	0.577
C(22)B	0.216(2)	0 2939(6)	0.537(1)	7.1(6)	H(22)B	0.097	0.3049	0.505
C(23)B	0.391(3)	0.3144(4)	0.554(1)	7.3(7)	H(23)B	0.412	0.3420	0.534
C(24)B	0.529(2)	0.2877(6)	0.605(1)	7.2(6)	H(24)B	0.662	0.2940	0.625
C(25)B	0.439(3)	0.2506(4)	0.619(1)	7.9(7)	H(25)B	0.502	0.2271	0.652

[a] x_c, y_c, and z_c are the fractional coordinates of the group center (Cp c.g.); δ, ε, and η (in radians) have been defined previously [8]. [b] Hydrogen atoms were assigned thermal parameters equal to those of the carbon atom to which each hydrogen atom is attached.

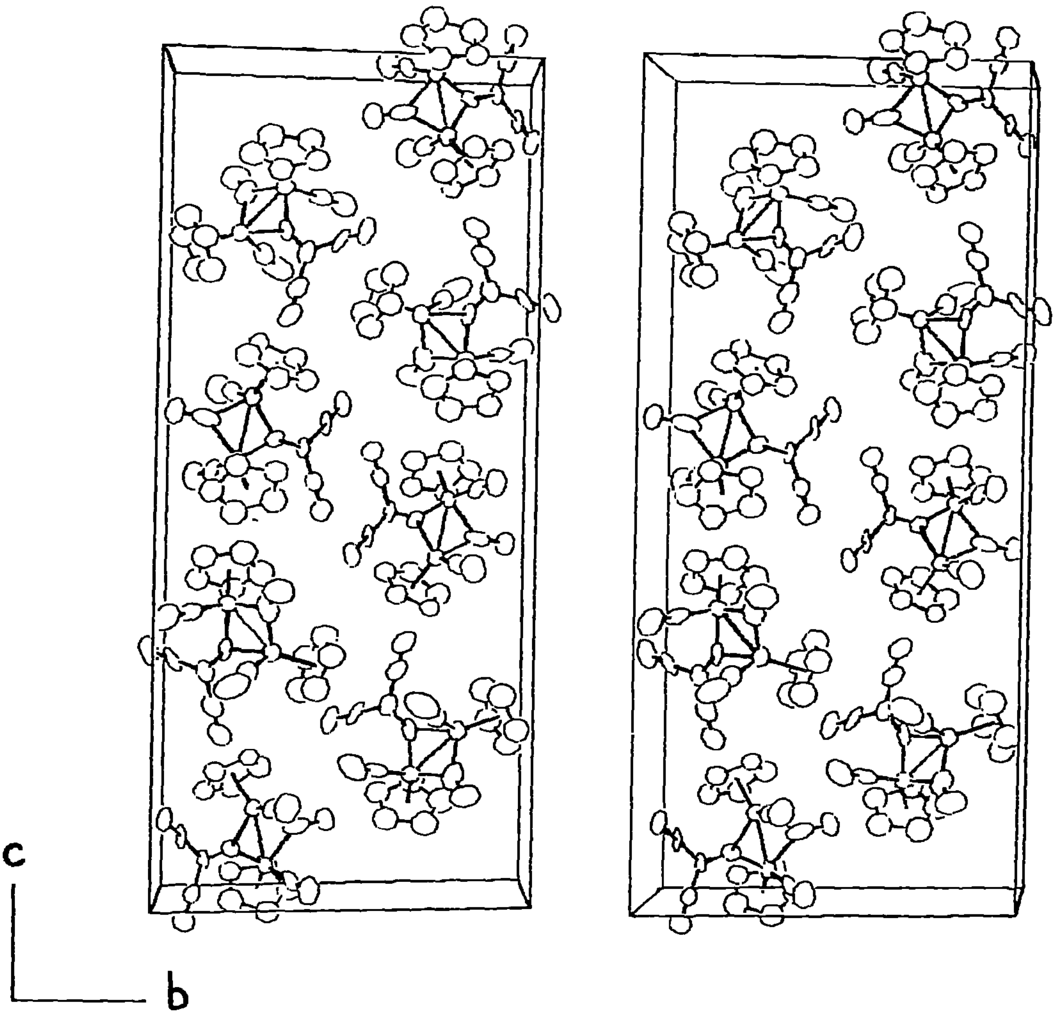

Fig. 1. Stereoscopic packing diagram for $Fe_2(CO)_2(\pi\text{-}C_5H_5)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$. The 50% probability vibrational ellipsoids are shown. Cyclopentadienyl hydrogen atoms have been omitted.

spectively. They are chemically (but not crystallographically) equivalent, differing only in small conformational distortions that presumably result from packing forces. The differences in intramolecular contact distances, bond distances (Table 3), bond angles (Table 4), and least-squares planes (Table 5) between molecule A and B are not significant. We will therefore discuss the structural properties in terms of averaged values from molecules A and B. The atom-labeling scheme is given in Fig. 2, while some of the important average bond angles and bond distances are given in Fig. 3.

The molecular geometry of $Fe_2(CO)_2(\pi\text{-}C_5H_5)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$ consists of a dimeric unit containing a presumed iron—iron single bond bridged by a carbonyl and a dicyanovinylidene ligand. In addition, about each iron atom there is a cyclopentadienyl ring and a terminal carbonyl ligand which give the dimeric molecule a *cis* configuration.

A

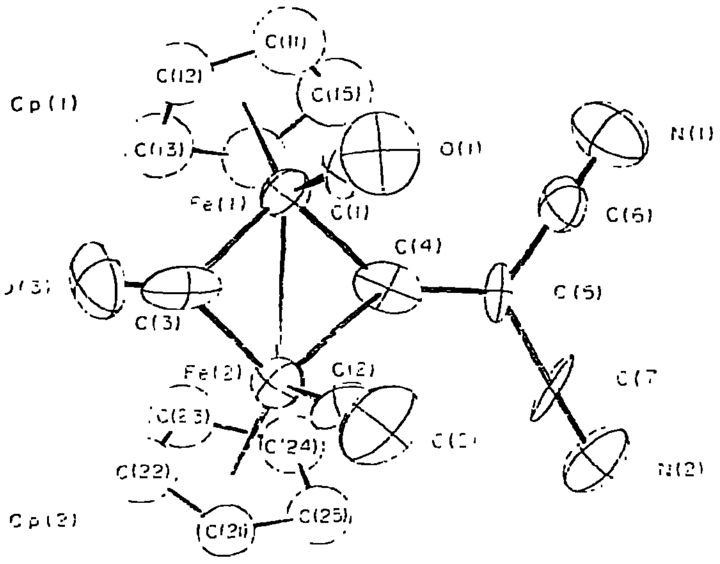

Fig. 2. A perspective view of molecule A of the asymmetric unit. The 50% probability vibrational ellipsoids are shown. Cyclopentadienyl hydrogen atoms have been omitted. This figure also presents the general atom labeling scheme.

The bridging linkage, made up of atoms Fe(1), Fe(2), C(3), and C(4), is not planar (Table 5). Considering this bridge to consist of two three-membered rings, C(3)—Fe(1)—C(4) and C(3)—Fe(2)—C(4), there is a folding of the bridg-

B

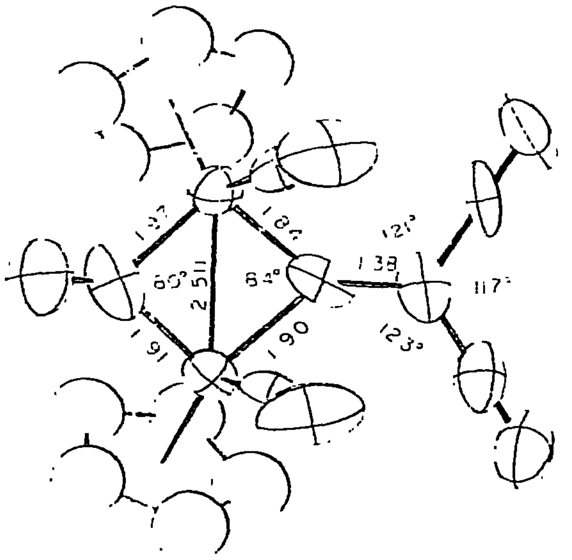

Fig. 3. A perspective view of molecule B of the asymmetric unit. The 50% probability vibrational ellipsoids are shown. Cyclopentadienyl hydrogen atoms have been omitted. Also presented in this figure are average values (from molecules A and B) of some important bond angles and distances for $Fe_2(CO)_2(\pi\text{-}C_5H_5)_2(\mu\text{-}CO)[(\mu\text{-}C{=}C(CN)_2]$.

TABLE 3

BOND DISTANCE (Å)

	Molecule A	Molecule B	Mean	
Fe(1)—Fe(2)	2.509(4)	2.512(4)	2.511(4)	
Fe(1)—C(1)	1.76(2)	1.79(2)	1.78(2)	1.78(2)
Fe(2)—C(2)	1.80(2)	1.78(2)	1.79(2)	
Fe(1)—C(3)	1.97(3)	1.96(2)	1.97(3)	1.94(3)
Fe(2)—C(3)	1.91(3)	1.91(3)	1.91(3)	
Fe(1)—C(4)	1.83(2)	1.84(2)	1.84(2)	1.87(4)
Fe(2)—C(4)	1.88(2)	1.92(2)	1.90(2)	
Fe(1)—C(11)	2.09(1)	2.09(2)	2.09(2)	2.11(2)
Fe(1)—C(12)	2.10(2)	2.10(2)	2.10(2)	
Fe(1)—C(13)	2.12(1)	2.12(2)	2.12(2)	
Fe(1)—C(14)	2.12(1)	2.13(1)	2.13(1)	
Fe(1)—C(15)	2.11(2)	2.11(1)	2.11(1)	
Fe(1)—Cp(1)c.g. [a]	1.73(1)	1.73(2)	1.73(2)	
Fe(2)—C(21)	2.09(1)	2.11(2)	2.10(2)	2.12(2)
Fe(2)—C(22)	2.13(2)	2.12(2)	2.13(2)	
Fe(2)—C(23)	2.14(1)	2.14(2)	2.14(2)	
Fe(2)—C(24)	2.11(1)	2.14(2)	2.13(2)	
Fe(2)—C(25)	2.08(1)	2.13(2)	2.11(2)	
Fe(2)—Cp(2) c.g.	1.73(1)	1.75(2)	1.74(2)	
C(1)—O(1)	1.15(2)	1.14(2)	1.13(2)	
C(2)—O(2)	1.12(2)	1.12(2)		
C(3)—O(3)	1.19(3)	1.20(2)	1.20(2)	
C(4)—C(5)	1.39(2)	1.36(3)	1.38(3)	
C(5)—C(6)	1.42(3)	1.45(3)	1.44(3)	
C(5)—C(7)	1.44(3)	1.42(3)	1.43(3)	
C(6)—N(1)	1.13(2)	1.10(3)	1.12(3)	
C(7)—N(2)	1.11(2)	1.14(3)	1.13(3)	

[a] Cp(1)c.g. denotes the center of gravity of the cyclopentadienyl ring.

ing linkage with a dihedral angle of 168° between the three-membered rings. This conformational feature is typical for complexes of this type [23]. A view of the nonplanarity of the bridging linkage and the partial staggering of the *cis*-cyclopentadienyl rings is given in Fig. 4. Table 6 gives a comparison between the present structure and other similar dimeric complexes, and shows that despite a variety of bridging ligands there are only small differences in the conformations of these dimeric molecules.

Discussion

The chemical and spectroscopic properties of dicyanovinylidene complexes [1,2,8] have been interpreted [7,24] on the basis that the dicyanovinylidene ligand is one of the strongest π-acceptors in transition metal chemistry. From an analysis of the ligand orbitals used in bonding, King suggested [24] that a terminal dicyanovinylidene ligand (bound to only one metal atom) will be a much stronger π-acceptor than a terminal carbonyl group, whereas a bridging dicyanovinylidene ligand (bound to two metal atoms) will be only a slightly stronger π-acceptor than a bridging carbonyl group. X-ray structural results on a complex containing a terminal dicyanovinylidene ligand [9], $MoCl(C_5H_5)[C{=}C(CN)_2]$-$[P(OCH_3)_3]_2$, and on a complex containing a bridging dicyanovinylidene ligand,

TABLE 4

SELECTED BOND ANGLES (°)

	Molecule A	Molecule B	Mean
Fe(1)—C(3)—Fe(2)	80(1)	80.9(9)	80(1)
Fe(1)—C(4)—Fe(2)	85(1)	83.9(9)	84(1)
Fe (1)—C(1)—O(1)	178(2)	179(2)	179(2)
Fe(1)—C(3)—O(3)	136(2)	137(2)	137(2)
Fe(1)—C(4)—C(5)	139(1)	141(2)	140(2)
Fe(2)—C(2)—O(2)	176(2)	177(2)	177(2)
Fe(2)—C(3)—O(3)	143(2)	142(2)	143(2)
Fe(2)—C(4)—C(5)	135(1)	135(2)	135(2)
Fe(1)—Fe(2)—Cp(2)c.g.	135.9(4)	134.8(6)	135.4(6)
Fe(2)—Fe(1)—Cp(1)c.g.	135.3(5)	136.4(5)	135.8(6)
C(1)—Fe(1)—C(3)	90.2(8)	93.0(10)	90.6(10)
C(1)—Fe(1)—C(4)	91.1(8)	87.4(8)	89.3(19)
C(1)—Fe(1)—Cp(1)c.g.	123.5(8)	123.1(8)	123.3(8)
C(2)—Fe(2)—C(3)	93.2(8)	90.7(10)	92.0(13)
C(2)—Fe(2)—C(4)	88.8(9)	89.6(8)	89.2(8)
C(2)—Fe(2)—Cp(2)c.g.	122.6(8)	124.9(9)	123.8(12)
C(3)—Fe(1)—C(4)	95.5(9)	96.4(9)	96.0(9)
C(3)—Fe(2)—C(4)	95.8(10)	95.7(9)	96.0(9)
C(3)—Fe(1)—Cp(1)c.g.	121.5(8)	121.0(9)	121.3(9)
C(3)—Fe(2)—Cp(2)c.g.	122.3(7)	120.0(9)	121.2(12)
C(4)—Fe(1)—Cp(1)c g.	125.7(7)	126.7(8)	126.2(8)
C(4)—Fe(2)—Cp(2)c.g.	125.2(7)	126.5(8)	125.9(8)
C(4)—C(5)—C(6)	122(2)	120(2)	121(2)
C(4)—C(5)—C(7)	122(2)	123(2)	123(2)
C(5)—C(6)—N(1)	177(3)	179(3)	178(3)
C(5)—C(7)—N(2)	176(2)	178(3)	177(3)
C(6)—C(5)—C(7)	116(2)	117(2)	117(2)

the present work, confirm the above prediction. In $MoCl(C_5H_5)[C{=}C(CN)_2][P(OCH_3)_3]_2$ the extremely strong π-acceptor nature of the terminal dicyanovinylidene ligand results in a very short metal—ligand bond, a bending of the metal—ligand linkage away from an expected linear configuration, and a concomitant tipping of the cyclopentadienyl ring toward the dicyanovinylidene ligand. Table 6 contains a comparison of similar dimeric complexes and shows that the bridging dicyanovinylidene ligand is only a slightly stronger π-acceptor than the carbonyl ligand. As the π-acceptor strength of the bridging ligand increases, the Fe—C (bridging ligand) and the Fe—Fe distances tend to decrease. However the effect obtained by replacing a bridging carbonyl ligand with a bridging dicyanovinylidene ligand is not large. Shorter Fe—C (bridging ligand) and Fe—Fe distances are obtained in the complex [Cp—R—Cp] $Fe_2(CO)_4$[21] as a result of the steric constraints imposed upon the molecule by the joined cyclopentadienyl rings. An even larger shortening of Fe—C and Fe—Fe bonds is observed when the bridging carbonyl ligand is coordinated to triethylaluminum [20], presumably because the bridging ligand becomes an extremely strong π-acceptor.

Within the estimated standard deviations, the bridging dicyanovinylidene ligand does not differ in metrical details from its terminal counterpart in $MoCl(C_5H_5)[C{=}C(CN)_2][P(OCH_3)_3]_2$.

TABLE 5

WEIGHTED LEAST-SQUARES PLANES

Atoms defining plane		Distances (Å) from plane	
		Molecule A	Molecule B
1	Fe(1)	0.003(3)	0.005(3)
	Fe(2)	0.009(3)	0.006(3)
	C(3)	−0.238(17)	−0.297(24)
	C(4)	−0.198(15)	−0.143(16)
2	C(4)	0.01(1)	−0.01(2)
	C(5)	−0.04(2)	0.02(2)
	C(6)	−0.02(2)	0.00(2)
	C(7)	0.02(2)	−0.01(2)
	N(1)	0.03(2)	−0.01(2)
	N(2)	0.00(2)	0.00(2)
3	Fe(1)	0.019(3)	0.012(3)
	Fe(2)	0.034(3)	0.036(3)
	C(3)	−0.40(2)	−0.33(2)
	O(3)	−0.66(2)	−0.73(2)
	C(4)	0.00(1)	−0.07(2)
	C(5)	−0.13(2)	−0.09(2)
	C(6)	−0.13(2)	−0.07(2)
	C(7)	−0.12(2)	−0.21(2)
	N(1)	−0.10(2)	−0.04(2)
	N(2)	−0.19(2)	−0.26(2)

Equations of the planes are in the form $Ax + By + Cz = D$ (in crystal coordinates)

		A	B	C	D
1	A	6.147	−1.970	4.941	0.148
	B	5.820	7.279	−9.057	−2.320
2	A	5.389	−1.051	7.073	1.086
	B	5.964	4.247	−9.089	−3.315
3	A	5.630	−1.008	6.475	0.914
	B	5.952	6.223	−8.892	−2.507

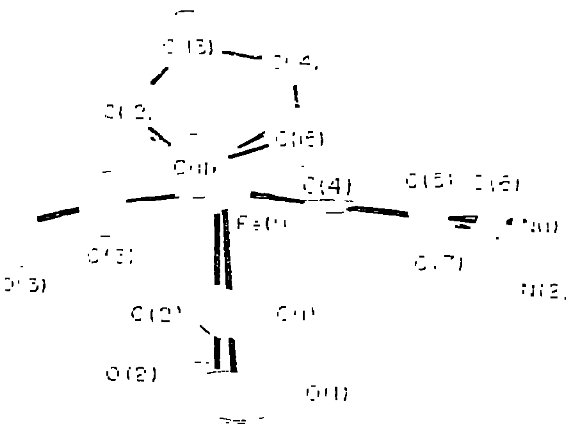

Fig. 4. A perspective view of a molecule of Fe$_2$(CO)$_2$(π-C$_5$H$_5$)$_2$(μ-CO)[μ-C=C(CN)$_2$] projected down the Fe—Fe axis. This view shows the partial staggering of the cyclopentadienyl rings and the planarity of the dicyanovinylidene ligand. Cyclopentadienyl hydrogen atoms have been omitted for the sake of clarity. The 50% vibrational ellipsoids are shown.

TABLE 6

COMPARISON OF MEAN GEOMETRIC PARAMETERS IN SIMILAR LIGAND–BRIDGED DIMERS THAT HAVE AN Fe—Fe SINGLE BOND[a].

Molecule	B	Ref.	Distances (Å)				Angles (deg.)		
			Fe—Fe	Fe—B	Fe—CO terminal	Fe—C(Cp)	Fe—B—Fe′	B—Fe—B′	Dihedral[b] angle
cis-$[CpFe(CO)_2]_2$ $2Al(C_2H_5)_3$	2(CO···· AlR_3)	20	2.491(8)	1.88(2)	1.70(2)	2.08(3)	n.a.[d]	n.a.[d]	167
[Cp—R—Cp] $Fe_2(CO)_4$[c]	2(CO)	21	2.510(2)	1.92(1)	1.70(1)	n.a.[d]	81.8(4)	96.1(4)	160
cis-$Fe_2(CO)_3Cp_2(C{=}C(CN)_2)$	(CO), $[CC(CN)_2]$	pres. work	2.511(4)	1.94(3) 1.87(2)	1.79(2)	2.13(2)	82(2)	96(1)	162
cis-$[CpFe(CO)_2]_2$	2(CO)	5	2.531(2)	1.92(1)	1.75(2)	2.11(2)	82.6(2)	96.0(3)	164
cis-$[CpFe(CO)(CNCH_3)]_2$	$2(CNCH_3)$	22	2.538(1)	1.94[e]	1.714(8)	2.12(1)	81.9(4)	95.8(5)	158

[a] B = Bridging ligand, Cp = (π-C_5H_5). [b] Dihedral angle between normals of Fe—B—Fe′ and Fe—B—Fe′ planes, in degrees. [c] Cp—R—Cp is (π-C_5H_4)$CH[N(CH_3)_2]$-$CH[N(CH_3)_2]$(π-C_5H_4), which forces a *cis* configuration. [d] Not reported. [e] The e.s.d. is not defined because non-equivalent bonds are averaged.

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