

Figure 3. Correlation between substituent effects on $\text{Ni}(\text{R-SacR}')_2$ (approximated by $\Sigma\sigma_m$) and the reduction potentials of the complexes.

exhibits a reasonable correlation although the nonavailability of some parameters and the inadequacy of σ_m values in the present context detracts from the correlation (Figure 3). The observed trend is obviously related to the electron density at the ligating sulfur groups which is at a maximum with $-\text{NR}_2$ groups and a minimum with the electron-withdrawing $-\text{CF}_3$ substituent. The electron-rich sulfur ligands stabilize the $\text{Ni}(\text{II})$ complex with respect to the reduced form, while the opposite pertains for the electron-withdrawing substituents. These phenomena are discussed more fully in a forthcoming review article.¹⁸

Registry No. $\text{Ni}(\text{OEt-SacSac})_2$, 41523-92-6; $\text{Ni}(\text{OMe-SacSac})_2$, 19998-79-9; $\text{Ni}(\text{O-}n\text{-Pr-SacSac})_2$, 58298-11-6; $\text{Ni}(\text{O-}n\text{-Bu-SacSac})_2$, 58298-12-7; $\text{Ni}(\text{Et}_2\text{N-SacSac})_2$, 58298-13-8; $\text{Ni}(\text{pyrr-SacSac})_2$, 58298-14-9; $\text{Ni}(\text{pip-SacSac})_2$, 58298-15-0; $\text{Ni}(\text{4-Me(pip)-SacSac})_2$, 58298-16-1; $\text{Ni}(\text{OEt-SacSac})(\text{NEt}_2\text{-SacSac})$, 58298-17-2; $\text{Ni}(\text{OEt-SacSac})(\text{pyrr-SacSac})$, 58298-18-3; $\text{Ni}(\text{OEt-SacSac})(\text{Ph-SacPh-Sac})$, 58312-82-6; $[(n\text{-Bu})_4\text{N}][\text{Ni}(\text{SacSac})(\text{MNT})]$, 58312-81-5; $\text{Ni}(\text{SacSac})_2$, 10170-79-3; $[(n\text{-Bu})_4\text{N}]_2[\text{Ni}(\text{MNT})_2]$, 18958-57-1; $\text{Ni}(\text{Ph-SacPh-Sac})_2$, 21609-14-3; MeOH , 67-56-1; $n\text{-PrOH}$, 71-23-8; $n\text{-BuOH}$, 71-36-3; Et_2NH , 109-89-7; pyrrolidine, 123-75-1; piperidine, 110-89-4; 4-methylpiperidine, 626-58-4.

References and Notes

- (1) A. R. Hendrickson and R. L. Martin, *Inorg. Chem.*, **12**, 2582 (1973).
- (2) C. G. Barraclough, R. L. Martin, and I. M. Stewart, *Aust. J. Chem.*, **22**, 891 (1969).
- (3) A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, **13**, 1933 (1974).
- (4) J. P. Fackler, D. Coucouvanis, W. C. Seidel, R. C. Masek, and W. Holloway, *Chem. Commun.*, 924 (1967).
- (5) J. P. Fackler and W. C. Seidel, *Inorg. Chem.*, **8**, 1631 (1969).
- (6) D. Coucouvanis and J. P. Fackler, *Inorg. Chem.*, **6**, 2047 (1967).
- (7) A. R. Hendrickson and R. L. Martin, *Inorg. Chim. Acta*, **13**, 29 (1975).
- (8) R. L. Martin and I. M. Stewart, *Nature (London)*, **210**, 522 (1966).
- (9) A. R. Hendrickson and R. L. Martin, *Aust. J. Chem.*, **25**, 257 (1972).
- (10) K. Nakamoto, J. Fujita, R. A. Condrate, and Y. Morimoto, *J. Chem. Phys.*, **39**, 423 (1963).
- (11) G. Durgaprasad, D. N. Sathyanarayana, and C. C. Patel, *Can. J. Chem.*, **47**, 631 (1969).
- (12) A. M. Bond, G. A. Heath, and R. L. Martin, *Inorg. Chem.*, **10**, 2026 (1971).
- (13) A. M. Bond, A. R. Hendrickson, and R. L. Martin, *J. Am. Chem. Soc.*, **95**, 1449 (1973).
- (14) G. A. Heath, R. L. Martin, and I. M. Stewart, *Aust. J. Chem.*, **22**, 83 (1968).
- (15) J. A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).
- (16) A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, **14**, 2980 (1975).
- (17) T. E. Mines and W. E. Geiger, *Inorg. Chem.*, **12**, 1189 (1973).
- (18) A. M. Bond, A. R. Hendrickson, and R. L. Martin, to be submitted for publication in *Coord. Chem. Rev.*

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Electron Distribution in μ -Acetylene-bis(cyclopentadienylnickel) by Low-Temperature X-Ray Diffraction

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The crystal and molecular structure of μ -acetylene-bis(cyclopentadienylnickel), $(\eta^5\text{-C}_5\text{H}_5\text{Ni})_2\text{CH}\equiv\text{CH}$, has been determined by single-crystal x-ray diffraction at room and liquid nitrogen temperature. The compound crystallizes in an orthorhombic space group $Fm2m$, with four molecules in the unit cell. Cell dimensions are $a = 17.209$ (8), $b = 6.606$ (3), and $c = 9.311$ (5) Å, at room temperature and $a = 17.195$ (14), $b = 6.489$ (14), and $c = 9.162$ (8) Å at 77 K. The dinuclear molecule has mm symmetry. A short Ni-Ni distance of 2.345 (3) Å is found. The cyclopentadienyl ring shows a static disorder around the axis that passes through the nickel and the center of the ring. The acetylene ligand is cis bent with a CC distance of 1.341 (6) Å. The electron density maps support a straight metal-metal bond with a double maximum along its axis and a predominance of bonding between the nickel atoms and a slightly antibonding acetylene b_1 orbital in the metal-acetylene interaction.

Introduction

Metal clusters have been of major interest for the recent quarter of the century. Because of the normally found short metal-metal distance and diamagnetic behavior, a metal-metal interaction is firmly established. However, the nature of this bond is still controversial. $\text{Co}_2(\text{CO})_8$ is an example. The structure¹ was found to be surprisingly close to that of $\text{Fe}_2(\text{CO})_9$ ² with one bridge carbonyl missing. In both cases, there are 17 valence electrons around Co and Fe atoms. By introducing a metal-metal bond between the two metal atoms, the 18-electron rule would be satisfied and the short inter-metallic distance could be explained. Early studies on di-

nuclear Rh ,³ Co ,^{4a} Fe ,^{4b} and Ni ^{4a} complexes led to a proposal of a "bent" metal-metal bond shared by one electron of d^2sp^3 hybridization from each metal atom and a completely filled t_{2g} orbital (t_{2g}^6). The molecular orbital scheme described by Sumner et al. corresponds to a "straight" metal-metal bond, with the sixth octahedral vertex occupied by a lone pair of electrons and five electrons in the t_{2g} orbital around each atom (t_{2g}^5), which forms an a_1 σ type "straight" metal-metal bond and e π , π^* molecular orbitals. The purpose of the present work is to investigate the nature of this metal-metal bond with density maps based on accurate x-ray diffraction data. This technique has been applied successfully on a number of

Table I. Crystallographic Information

	298 K	77 K
<i>a</i> , Å	17.209 (8)	17.195 (14)
<i>b</i> , Å	6.606 (3)	6.489 (14)
<i>c</i> , Å	9.311 (5)	9.162 (8)
<i>V</i> , Å ³	1058.6	1022.3
[(<i>sin</i> θ)/ λ] _{max} , Å ⁻¹	0.86	1.0
No. of observs	800	914 ^a
Space group	<i>Fm</i> 2 <i>m</i>	
<i>Z</i>	4	
μ (Mo <i>K</i> α), cm ⁻¹	20.96	
Abs coeff <i>A</i>	0.686–0.878	

^a Of which 361 are at (*sin* θ)/ λ > 0.75 Å⁻¹.

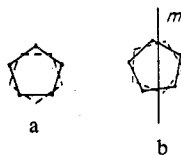
molecules containing first-row elements.⁵ Recent results on benzenechromium tricarbonyl,⁶ chromium hexacarbonyl,⁷ (NH₃)₆Co³⁺Co(CN)₆³⁻,⁸ and γ -Ni₂SiO₄⁹ show the feasibility of similar studies of first-row transition metal complexes. The molecule of μ -acetylene-bis(cyclopentadienylnickel) was selected because of its relatively simple composition, stability, the chemical interest of the coordinated acetylene molecule, and the possibility of resolving the ambiguity between "straight" and "bent" metal-metal bonds. A definite disadvantage is its acentric crystal structure which leads to complications in the calculation of difference densities.¹⁰ This difficulty was accepted as no good single crystals of other compounds with similar properties were available.

Experimental Section

Single-crystal x-ray diffraction data at both room and liquid nitrogen temperatures were collected on an automatic Picker four-circle diffractometer controlled by a PDP-8/I computer with Mo *K* α radiation. The low-temperature cryostat was described previously.¹¹ Two symmetry-related sets of intensity data were measured on a greenish plate-shaped crystal with dimensions of 0.22 \times 0.24 \times 0.05 mm mounted along the *b* axis. The internal consistency factors between the symmetry-related reflections (analogous to the agreement factor between observed and calculated structure factors) are, for the low-temperature data, $R(F^2) = 1.9\%$ (1.6% for 512 strongest reflections where $F^2/\sigma(F^2) > 50$) and, for the room temperature data, 2.2% (1.5% for 303 reflections with $F^2/\sigma(F^2) > 50$). Each reflection was recorded with the θ -2 θ step scan technique and was then subjected to a full profile analysis.¹² Two symmetry-related sets were averaged after the application of Lorentz, polarization, and absorption corrections. Crystallographic information is given in Table I.

Refinement of Structure

The structure was solved by the standard heavy-atom method. The nickel atom was located from the Patterson map, while the rest of the molecule (except the hydrogen atoms) showed up in the Fourier synthesis based on the phases calculated from the nickel parameters. A disorder of the five-membered ring was discovered in the later stage of the refinement. Two possible types of disorder were tested: (a)



a 180° rotation around the axis passing through the nickel atom and the center of the ring, (b) a disorder across the mirror plane required by the symmetry of the space group. A TLS rigid-body-constrained least-squares refinement¹³ was performed with each of the models as the starting point. The result showed a better agreement on the 180° rotational disorder, which is further confirmed by an *h*0*l* projection of the Fourier summation. This projection is centrosymmetric and the Fourier summation is therefore less dependent on details of the model employed in calculating the phases of the observations. The agreement factors of various refinements on this type of disorder are shown in Table II. Since the results from various refinements are similar at both temperatures, only the more accurate low-temperature results are discussed here. The final result of the

Table II

Agreement Factors from Various Refinements at 77 K (Rigid-Body Constraint Refinement) ^a				
Mol symmetry	<i>R</i> (<i>F</i>)	<i>R</i> _w (<i>F</i>)	<i>S</i>	NV
TLX + 5/ <i>m</i>	0.055	0.074	3.26	33
TLX + <i>m</i>	0.052	0.065	2.86	37
TLS + 5/ <i>m</i>	0.050	0.068	3.01	37
TLS + <i>m</i>	0.051	0.062	2.77	41
Unconstrained ^b	0.026	0.032	1.50	60
Agreement Factors from Final Least-Squares Refinement				
Parameter	298 K	77 K		
$R(F) = \sum F_o - F_c / \sum F_o$	0.032	0.025		
$R_w(F) = (\sum w F_o - F_c ^2 / \sum w F_o^2)^{1/2}$	0.028	0.028		
$R(F^2) = \sum F_o^2 - F_c ^2 / \sum F_o^2$	0.032	0.032		
$R_w(F^2) = [\sum w (F_o^2 - F_c ^2)^2 / \sum w F_o^4]^{1/2}$	0.054	0.054		
$S = [\sum w (F_o^2 - F_c ^2)^2 / \text{NO} - \text{NV}]^{1/2}$	1.11	1.34		
NO	638	857		
NV	69	69		

^a $R_{4,826,0.005} = 1.0091$; ¹⁵ $R_{23,820,0.005} = 1.0279$. ^b Not varying H atom parameters.

Table III. Results from Rigid-Body Refinement of Cyclopentadienyl Group with TLS Model and 5/*m* Molecular Symmetry

Rotation Angle and Center of Mass of Major Component^a

$$\psi = 54.34 (1)^\circ; X_0 = 2.570 (5) \text{ \AA}, 1.038 \text{ \AA}, 0$$

Translational Tensor *T* (Å²)

$$\begin{matrix} 0.070 (8) & 0.020 (11) & 0.004 (2) \\ & 0.054 (5) & -0.007 (2) \\ & & 0.015 (2) \end{matrix}$$

Librational Tensor *L* (radian²) and Its Origin

$$\begin{matrix} -0.014 (4) & 0.035 (7) & 0.004 (3) \\ & -0.024 (6) & -0.013 (2) \\ & & -0.046 (9) \end{matrix}$$

$$\xi = 2.605 (0) \text{ \AA}, 1.047 (0) \text{ \AA}, 0.005 (0) \text{ \AA}$$

Screw Rotation Tensor *S*

$$\begin{matrix} 0 & 0 & -0.008 \\ 0 & 0 & -0.006 \\ -0.006 & 0.004 & 0 \end{matrix}$$

Distance from center of ring to the ring carbon atom: 1.193 (8) Å

^a ψ is the angle between the ring and *bc* planes; other rotation angles are fixed by symmetry. Center of mass coordinates refer to crystal coordinate system.

constrained refinement gave an occupancy ratio of 0.62/0.38 for the two disorder positions. *T*, *L*, and *S* are the tensors defined elsewhere;¹⁴ the tensors and vectors given in Table III are obtained under the constraint of 5/*m* symmetry of the cyclopentadienyl rings. According to the Hamilton ratio test,¹⁵ the lifting of all constraints (including rigid-body motion) is significant because of the substantial drop in the *R* factor. Nevertheless, the constraint did help the convergence of the refinement as well as the determination of the occupancy number which was kept constant in the unconstrained refinement. The acetylene hydrogen atom was found in the difference Fourier map. All of the cyclopentadienyl hydrogen atoms were assumed in the five-membered ring plane at a distance of 0.95 Å from the carbon atoms. An additional high-order [(*sin* θ)/ λ > 0.75 Å⁻¹] data refinement was performed on nickel and the acetylene carbon atoms in order to obtain atomic parameters less affected by the spherical-atom assumption. The function minimized in the refinement is $\sum w (F_o - k|F_c|)^2$ where the weight *w* is defined as 1/ σ^2 and $\sigma^2 = [\sigma^2(\text{counting}) + (0.03F_o^2)^2]/4F^2$. The scattering factors for Ni and C were taken from ref 28a. The scattering factor for H is as derived by Stewart, Davidson, and Simpson.¹⁶ Anomalous dispersion corrections were applied for nickel according to the values given in ref 28b.

Results and Description of Molecular Structure

The positional and thermal parameters at both temperatures from the unconstrained least-squares refinement, as well as the results of the high-order refinement, are given in Table IV. The thermal ellipsoids are considerably smaller at liquid

Table IV. Fractional Atomic Coordinates and Thermal Ellipsoids ($U_{ij} \times 10^3, \text{\AA}^2$)

Temp	<i>k</i>	NO	Occupancy (77 K)						
			Atoms			Value			
298 K	1.012 (2)	638	C(1), C(2), C(3)			0.62			
77 K	1.246 (3)	857	C(1'), C(2'), C(3')			0.38			
77 K high order (HO)	1.219 (13)	361							
Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	298 K 0.067 97 (2)	0	0	21.7 (1)	34.1 (2)	40.0 (2)	-1.3 (4)	0	0
	77 K 0.068 19 (1)	0	0	7.0 (1)	13.3 (1)	12.3 (1)	-0.3 (2)	0	0
	HO 0.068 18 (2)	0	0	6.6 (2)	12.6 (4)	12.0 (2)	-1.0 (5)	0	0
C(acetylene)	298 K 0	-0.2044 (7)	0.0706 (6)	27 (1)	40 (2)	62 (2)	0	0	14 (2)
	77 K 0	-0.2025 (5)	0.0732 (3)	13 (1)	15 (1)	19 (1)	0	0	6 (1)
	HO 0	-0.1997 (13)	0.0739 (5)	14 (1)	16 (5)	17 (1)	0	0	6 (2)
C(1)(Cp)	298 K 0.189 0 (4)	0.0239 (24)	0	19 (2)	33 (11)	164 (16)	4 (3)	0	0
	77 K 0.190 9 (3)	0.0246 (16)	0	9 (1)	28 (6)	81 (6)	-2 (2)	0	0
C(2)(Cp)	298 K 0.161 2 (7)	0.1232 (23)	-0.1248 (16)	45 (5)	68 (7)	78 (8)	-21 (5)	34 (6)	28 (6)
	77 K 0.162 3 (4)	0.1315 (14)	-0.1222 (7)	30 (3)	31 (3)	31 (3)	-22 (3)	22 (2)	-20 (3)
C(3)(Cp)	298 K 0.115 5 (3)	0.2782 (9)	-0.0760 (8)	42 (3)	42 (3)	30 (3)	15 (2)	-5 (2)	8 (2)
	77 K 0.114 6 (2)	0.2935 (6)	-0.0790 (3)	19 (1)	18 (2)	13 (1)	-8 (1)	-5 (1)	7 (1)
C(1')(Cp)	298 K 0.184 0 (6)	0.0120 (45)	0.0757 (13)	35 (5)	69 (12)	64 (9)	-14 (8)	-23 (5)	29 (14)
	77 K 0.185 3 (3)	0.0174 (24)	0.0744 (9)	16 (2)	20 (5)	40 (4)	-15 (4)	-11 (2)	19 (6)
C(2')(Cp)	298 K 0.142 8 (10)	0.1795 (31)	0.1200 (14)	49 (9)	81 (15)	43 (7)	-21 (8)	5 (6)	-34 (9)
	77 K 0.147 5 (6)	0.1756 (23)	0.1319 (11)	26 (4)	53 (8)	28 (4)	-19 (4)	19 (3)	-35 (5)
C(3')(Cp)	298 K 0.116 0 (5)	0.2861 (22)	0	35 (4)	39 (9)	52 (4)	15 (5)	0	0
	77 K 0.117 6 (5)	0.2885 (18)	0	10 (3)	8 (5)	130 (16)	-4 (3)	0	0
Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U, \text{\AA}^2$					
H(acetylene)	298 K 0	-0.274 (10)	0.145 (6)	0.05 (2)					
	77 K 0	-0.283 (8)	0.164 (5)	0.02 (1)					
H(1)(Cp) ^a	298 K 0.2233	-0.1123	0	0.6 (2)					
	77 K			0.16 (5)					
H(2)(Cp)	298 K 0.1730	0.0738	-0.2232	0.09 (2)					
	77 K			0.07 (2)					
H(3)(Cp)	298 K 0.0915	0.3746	-0.1380	0.08 (2)					
	77 K			0.04 (2)					
H(1')(Cp)	298 K 0.2094	-0.0609	0.1380	0.003 (5)					
	77 K			0.08 (4)					
H(2')(Cp)	298 K 0.1279	0.2399	0.2322	0.12 (5)					
	77 K			0.10 (3)					
H(3')(Cp)	298 K 0.0766	0.4261	0	1.7 (11)					
	77 K			0.2 (1)					

^a All cyclopentadienyl hydrogen atoms were assumed at a distance of 0.95 Å from the carbon atoms in the plane of the five-membered ring.

nitrogen temperature than at room temperature (see Figure 1). Selected bond distances and angles calculated from the low-temperature results are given in Table V.

Molecules of ($\eta^5\text{-C}_5\text{H}_5\text{Ni}$)₂C₂H₂ are discrete in the solid; there are no short intermolecular distances. The molecule has *mm* symmetry with one mirror plane along the Ni-Ni line bisecting the acetylene bond and cyclopentadienyl rings, while the second mirror plane contains the acetylene molecule and bisects the Ni-Ni vector. The bond distances and angles (at 77 K) are comparable with other bridged nickel complexes.¹⁷ The average distance from nickel to the cyclopentadienyl ring carbon atoms is 2.15 Å, comparable with 2.13 and 2.12 Å for Cp₂NiC₂(CO₂CH₃)₂²⁷ and (CpNi)₃(CO)₂,¹⁷ respectively. The metal-C (acetylene) distance, 1.884 (2) Å, is similar to those found in (CO)₆Co₂C₂Ph₂ (1.89–2.02 Å)¹⁸ and (CpNi)₂C₂Ph₂ (1.89 (2) Å^{17b}). The C-C (acetylene) distance, 1.341 (6) Å, is much longer than the triple-bond length and close to the CC double-bond distance. This distance is the same in the diphenylacetylene Ni complex^{17b} (1.35 (3) Å) but even longer in (CO)₆Co₂C₂Ph₂ (1.46 Å) (no errors were given in the latter publication). The nickel atoms are separated by 2.345 (2) Å which is slightly longer than in the nitrile-bridged complex^{17a} (2.322 (1) Å) and the diphenyl-substituted acetylene-bridged complex (2.329 (4) Å) but shorter than the corresponding distances in (CpNi)₃(CO)₂ (2.39 Å) and (CpNi)₂(CO)₂ (2.36 Å).^{17c} The dihedral angle between the NiCNi planes is 96.5° compared with 105° in [(C₆H₅)₂PCoC₅H₅]₂, 180° in the corresponding Ni complex,^{4a} and 95.2° in [C₂H₅SFe(CO)₃]₂.^{4b}

Table V. Selected Bond Distances (Å) and Bond Angles (deg) at 77 K^a

(a) Ni Distances			
Ni-Ni	2.345 (3)	Ni-C(2)	2.145 (7)
Ni-C(acetylene)	1.884 (4)	Ni-C(3)	2.188 (4)
Ni-C(1)	2.116 (6)	Ni-(center of Cp)	1.74
(b) Cyclopentadienyl Distances			
C(1)-C(2)	1.406 (11)	C(1')-C(2')	1.325 (16)
C(2)-C(3)	1.391 (8)	C(2')-C(3')	1.504 (16)
C(3)-C(3')	1.447 (6)	C(3')-C(3'')	1.364 (17)
(c) Acetylene Distances			
C-C	1.341 (6)	H-C	0.98 (5)
(d) Acetylene Angles			
Ni-C-C'	69.2 (1)	H-C-C	148.1 (5)
C'-Ni-C	41.7 (2)		
(e) Cyclopentadienyl Angles			
C(1)-C(2)-C(3)	110.6 (5)	C(2)-C(3)-C(3')	106.5 (3)
C(2)-C(1)-C(2')	105.6 (8)		
(f) Dihedral Angles			
(Ni-C-C')-(Ni'-C-C') (acetylene)	96.5 (1)	Between two Cp rings in one dimer	73.9 (4)
(Ni-C-C')-Cp ring	78.7 (2)		

^a C(*n'*) indicates a carbon atom in the disordered second cyclopentadienyl ring; C(*n*)' indicates a symmetry-related atom.

Deformation Density Map

The deformation density is defined as the difference between the observed electron density and the electron density calculated for a superposition of spherical atoms, i.e., $\rho_{\text{def}} = \rho_{\text{obsd}}$

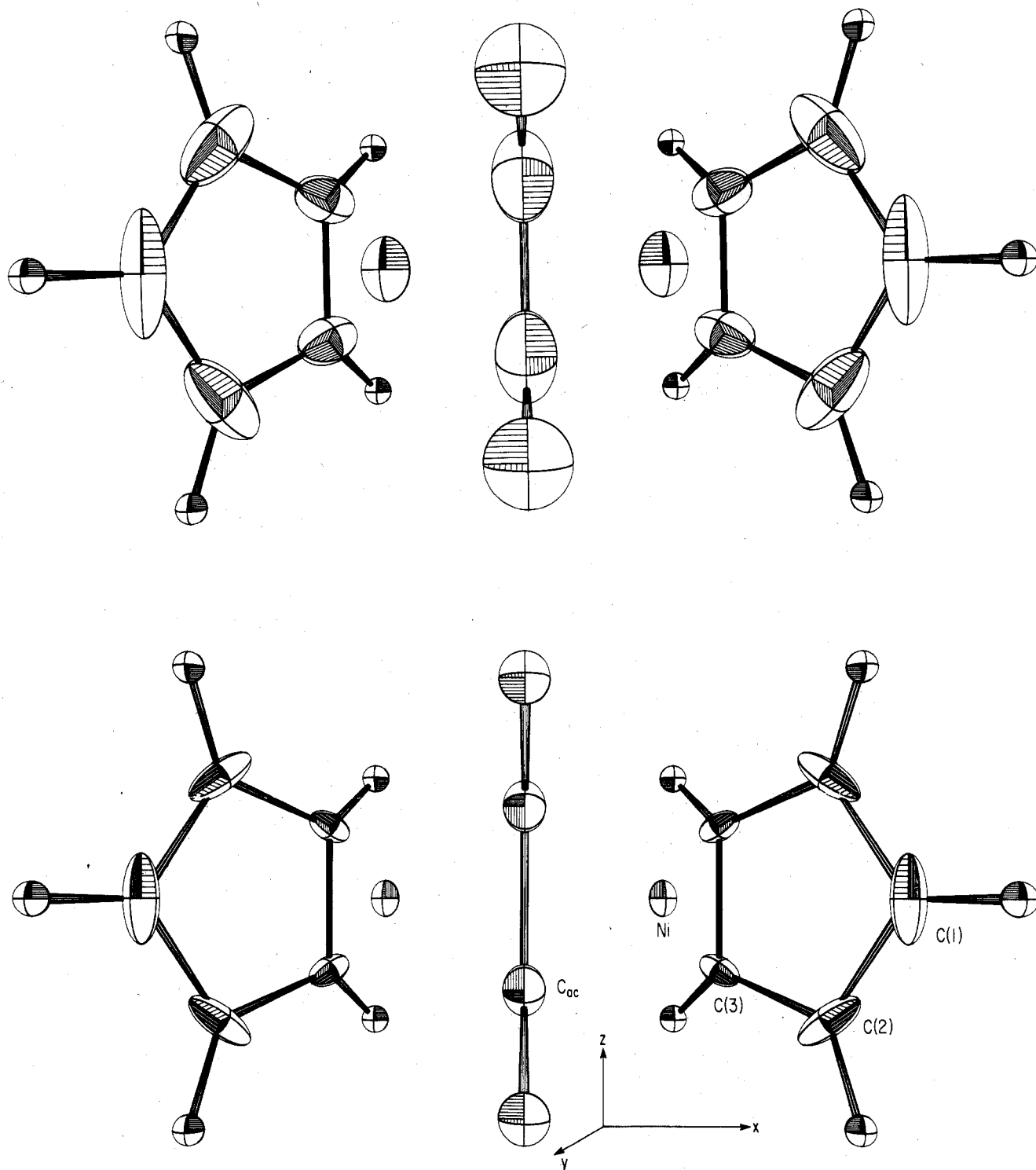


Figure 1. Molecular structure and thermal ellipsoids at 300 K (top) and 77 K (bottom).

$-\rho_{\text{calcd}}(\text{sph})$. As the chemical bonding between the atoms perturbs the spherical distribution, the deformation density is a detailed indicator of bonding effects. In order to obtain a meaningful deformation density map, a set of accurate atomic parameters unbiased by the least-squares model for the electronic distribution is needed. When the large single crystals required for neutron diffraction are not available, parameters may be obtained from a refinement of the high-order data for which the spherical atom assumption is valid to a much better approximation. A data cutoff of $[(\sin \theta)/\lambda]_{\text{min}} = 0.75 \text{ \AA}^{-1}$ was used and only the nickel and acetylene carbon atomic parameters were varied, as the disorder in the

cyclopentadienyl ring interferes with a density determination in this region of the crystal. The results are used in all of the deformation density calculations with a scale factor $k = 1.231$ (obtained in one cycle of least-squares refinement varying only the scale factor with the parameters obtained from high-order refinement). The expression used in calculating $\Delta\rho$ is

$$\Delta\rho = \frac{2}{V} \sum_{h=0}^{\infty} \sum_k \sum_l [(A_{\text{obsd}}/k - A_{\text{calcd}}) \cos 2\pi(hx + ky + lz) + (B_{\text{obsd}}/k - B_{\text{calcd}}) \sin 2\pi(hx + ky + lz)]$$

where the calculated values are obtained with high-order

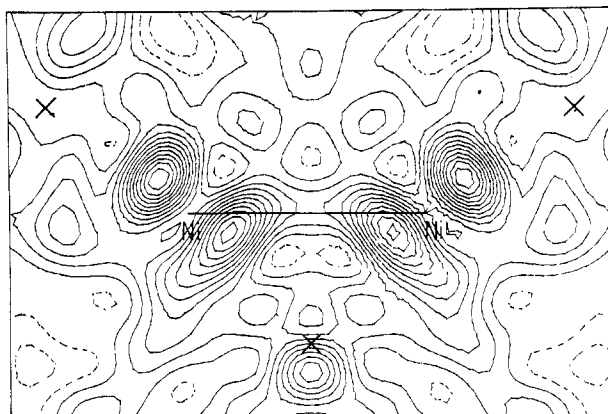


Figure 2. Deformation density in the plane containing two nickel atoms and the midpoint of the acetylene CC bond; contours at $0.1 \text{ e } \text{Å}^{-3}$; negative contours dotted; crosses at the upper left and upper right of the figure indicate the centers of the cyclopentadienyl rings.

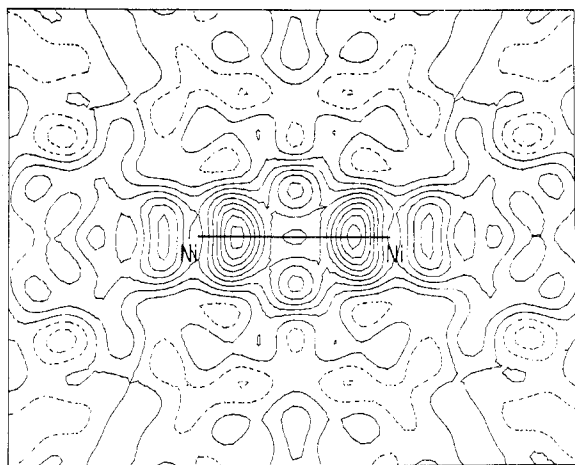


Figure 3. Diagram as in Figure 2 containing two nickel atoms and parallel to the acetylenic CC bond.

parameters and phases, and the phases from the full data refinement are used to obtain A_{obsd} and B_{obsd} from the observed structure factors.¹⁰ The root-mean-square phase angle difference between the high-order refinement and the full data refinement was found to be about 1.7° . All the maps are plotted with contour interval $0.1 \text{ e } \text{Å}^{-3}$ and have an estimated average standard deviation of $0.06 \text{ e } \text{Å}^{-3}$ which is underestimated by perhaps 50% because of the phase angle uncertainty. Figures 2 and 3 show substantial electron density between the two nickel nuclei with two maxima along the bond, at about 0.5 Å from the adjacent nucleus. A similar but less pronounced double maximum was found in the sulfur-sulfur bond in orthorhombic sulfur.¹⁹ Figure 2 further indicates accumulation of charge along the Ni-(center of ring) axis on both sides of the Ni atom. In addition, there is density near the Ni-Ni midpoint on each side of the bond axis (Figure 4). No peaks are observed at or near the C-Ni midpoints in either Ni-C-C or Ni-C-Ni triangular planes, though some density is concentrated within these triangles (Figures 5 and 6). The electron distribution along the CC bond appears to be of approximately cylindrical shape but its center no longer coincides exactly with the bond axis.

Discussion of the Density Maps

As in the Co atom in $\text{Co}_2(\text{CO})_8$, there are only 17 valence electrons around each nickel atom in $(\eta^5\text{-C}_5\text{H}_5\text{Ni})_2\text{CH}\equiv\text{CH}$ and a metal-metal bond is to be postulated to account for the observed diamagnetism and to satisfy the 18-electron rule. The

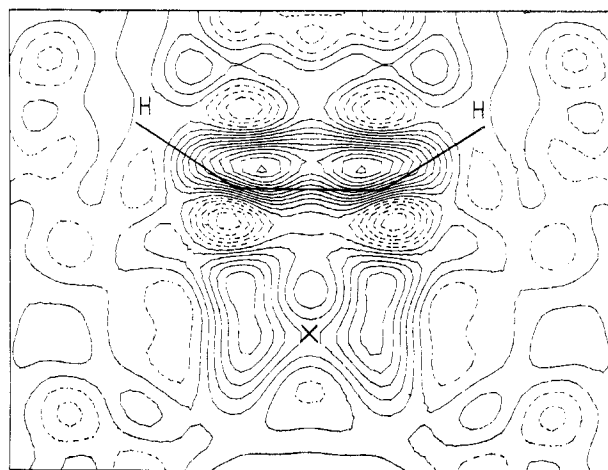


Figure 4. Diagram as in Figure 2 containing two acetylene carbon atoms and the midpoint of Ni-Ni line.

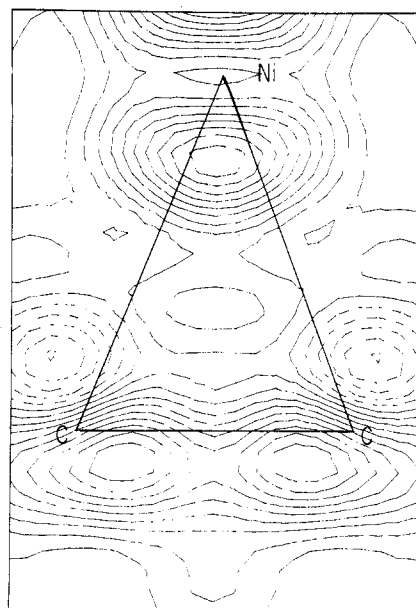


Figure 5. Diagram as in Figure 2 containing one nickel and two acetylenic carbon atoms.

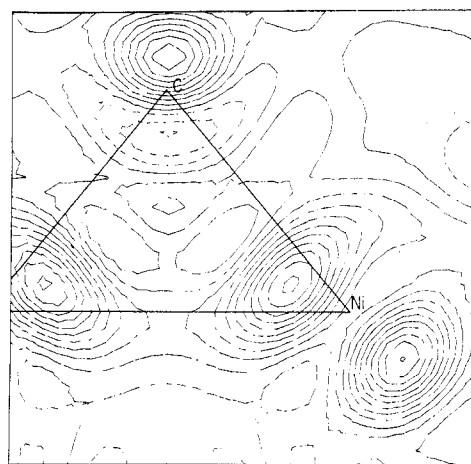
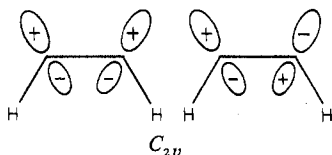


Figure 6. Diagram as in Figure 2 containing one acetylenic carbon and two nickel atoms.

short Ni-Ni distance found in the crystal supports its existence, while the electron density map gives further information on its nature. In the "bent"-bond model, density would be

concentrated on one side of (opposite to acetylene molecule) rather than on the Ni-Ni line. On the other hand, the "straight"-bond model would give electron density along the line connecting the two atoms. According to this criterion Figures 2 and 3 favor the "straight"-bond model. The two maxima in the σ bond may be typical for a bond between two d orbitals, but no definite conclusion can be drawn until other nuclear clusters have been studied. The peaks around the nickel are toward the center of cyclopentadienyl ligands and toward the other nickel and the acetylene carbon atoms. There is neither density in the direction in which the "bent"-bond model predicts a bond nor an indication of approximate spherical symmetry due to almost filled t_{2g} and e_g orbitals. However the symmetry around the nickel atom is far from octahedral so both bonding descriptions must be oversimplified. To a better approximation the symmetry may be described as trigonal with the symmetry axis along the line connecting the nickel atom and the center of the cyclopentadienyl ring. The density accumulation along this axis then corresponds to density in the d_{z^2} orbital. But it is clear that the best theoretical interpretation will be from comparison with more sophisticated MO calculations on this complex in which no assumptions on local symmetry are required.

Ir and NMR studies on the coordinated acetylene complexes²⁰⁻²² indicate the electron hybridization of the carbon atom to be close to sp^2 rather than sp ; i.e., the acetylene molecule actually exists in a configuration which has been compared to its electronic excited-state²³ configuration in which the molecule changes its geometry to an ethylene-like configuration in which trans (C_{2h}) or cis (C_{2v}) hydrogen atoms



are substituted by an unshared electron pair. Although the trans form is the first electronic excited state for the free acetylene molecule, the coordinated acetylene in several compounds is known to be in the cis configuration, a result interpreted theoretically by Blizzard and Santry,²⁴ who have emphasized a number of fundamental differences between the electronic states of the excited and the coordinated acetylene molecule. In the C_{2v} point group, the pair of sp^2 orbitals will combine to give a_1 and b_1 states with a_1 having slightly lower energy than the b_1 level, both being classified as nonbonding orbitals. A commonly adopted MO scheme for olefinic and acetylene complexes due to Dewar and Chatt²⁵ combines a σ donation from a filled olefinic $p\pi$ orbital to the metal atom with a back-donation from metal d orbitals to the empty ligand $p\pi^*$ orbital. A similar description of carbonyl-bridged dinuclear species by Braterman²⁶ involves σ donation from the lone pair of CO to two in-phase σ hybrid orbitals of the two metal atoms and a back-donation from two out-of-phase σ orbitals to the empty π^* orbital of the carbonyl.

The location of the density in the CC bond suggests a bending of the carbon-bonding hybrids forming this bond away from the internuclear axis in a direction away from the nickel atoms which is further illustrated by the larger than 120° H-C-C angle. Such a bending would allow both a_1 and b_1 acetylene orbitals to point more closely toward the Ni-Ni region of the complex. The section shown in Figure 4 shows a nodal density plane bisecting the carbon-carbon bond and therefore implies that the bonding between the nickel atoms and acetylene is dominated by the overlap of the b_1 acetylene orbital with an in-phase combination of d orbitals or dsp hybrids on the two nickel atoms.

Conclusion

The compound studied here is far from an ideal case for an electron density study as it is partially disordered and not centrosymmetric. Especially the latter will lead to an increase in the noise level of the deformation maps. Nevertheless, a low-temperature study such as presented here can provide meaningful qualitative information. Specifically, the study indicates the metal-metal bond to be straight and the metal-acetylene interaction to be concentrated in the π^* antibonding region of the acetylene. In addition, the acetylene σ bond appears to be affected, as its center (as judged from the deformation density) no longer coincides with the geometric midpoint. Rather the bond appears bent with the sp^2 σ hybrids pointing at an angle with the bond axis, as observed in a number of strained three-membered rings.

More studies of related metalloorganic compounds are required to verify these conclusions and complement our knowledge of metal-metal bonding in cluster compounds. Electron density studies by low-temperature diffraction methods are the most informative and direct way to achieve this purpose.

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Registry No. (η^5 - C_5H_5Ni)₂CH₂CH, 52445-55-3.

Supplementary Material Available: Listings of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

References and Notes

- G. G. Sumner, H. P. Klug, and L. Alexander, *Acta Crystallogr.*, **17**, 732 (1964).
- (a) H. M. Powell and R. V. G. Evens, *J. Chem. Soc.*, 286 (1939); (b) F. A. Cotton and J. M. Troup, *J. Chem. Soc., Dalton Trans.*, 800 (1974).
- L. F. Dahl, C. Martell, and D. C. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961).
- (a) J. M. Coleman and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 542 (1967); (b) L. F. Dahl and G. Wei, *Inorg. Chem.*, **2**, 328 (1963).
- P. Coppens and A. Vos, *Acta Crystallogr., Sect. B*, **27**, 146 (1971); P. Coppens, T. M. Sabine, R. G. Delaplane, and J. A. Ibers, *ibid.*, **25**, 245 (1969); R. Brill, H. Dietrich, and H. Dierks, *ibid.*, **27**, 2003 (1971); J. C. Hanson, L. C. Sieker, and L. H. Jensen, *ibid.*, **29**, 797 (1973).
- B. Rees and P. Coppens, *Acta Crystallogr., Sect. B*, **29**, 2516 (1973).
- B. Rees and A. Mitschler, *Acta Crystallogr., Sect. B*, **31**, S221 (1975).
- M. Iwata and Y. Saito, *Acta Crystallogr., Sect. B*, **29**, 822 (1973).
- F. Marumo, M. Isobe, Y. Saito, T. Yagi, and S. Akimoto, *Acta Crystallogr., Sect. B*, **30**, 1904 (1974).
- P. Coppens, *Acta Crystallogr., Sect. B*, **30**, 255 (1974).
- P. Coppens, F. K. Ross, R. H. Blessing, W. F. Cooper, F. K. Larsen, J. G. Leipoldt, and B. Rees, *J. Appl. Crystallogr.*, **7**, 315 (1974).
- R. H. Blessing, P. Coppens and P. Becker, *J. Appl. Crystallogr.*, **7**, 488 (1974).
- G. S. Pawley, *Adv. Struct. Res. Diffr. Methods*, **4** (1972).
- V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **24**, 63 (1968).
- W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).
- R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- (a) R. D. Adams, F. A. Cotton, and G. A. Rushline, *J. Coord. Chem.*, **1**, 275 (1971); (b) O. S. Mills and B. W. Shaw, *J. Organomet. Chem.*, **11**, 595 (1968); (c) A. A. Hock and O. S. Mills, "Advances in the Chemistry of Coordination Compounds", S. Kirschner, Ed., Macmillan, New York, N.Y. 1961, p 647.
- W. G. Sly, *J. Am. Chem. Soc.*, **81**, 18 (1959).
- R. H. Blessing, W. F. Cooper, Y. W. Yang, and P. Coppens, American Crystallographic Association Abstracts, Series 2, Vol. 1, 1973, p 200; E. D. Stevens and P. Coppens, *Acta Crystallogr., Sect. A*, **31**, S222 (1975).
- Y. Iwashita, F. Tamura, and A. Nakamura, *Inorg. Chem.*, **8**, 1179 (1969).
- Y. Iwashita, *Inorg. Chem.*, **9**, 1178 (1970).
- Y. Iwashita, A. Iwashita, and M. Kainosko, *Spectrochim. Acta, Part A*, **27**, 271 (1971).
- C. K. Ingold and G. W. King, *J. Chem. Soc.*, 2702, 2704, 2706 (1953).
- A. C. Blizzard, and D. P. Santry, *J. Am. Chem. Soc.*, **90**, 5749 (1968).
- M. J. C. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C71 (1951); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).
- P. S. Braterman, *Adv. Organomet. Chem.*, **10**, 57 (1972).
- L. Dahl and C. Wei, *Inorg. Chem.*, **2**, 713 (1963).
- "International Tables for X-Ray Crystallography", Kynoch Press, Birmingham, England: (a) Vol. II; (b) Vol. III.