LOW-VALENT METAL ISONITRILE COMPLEXES. I. THE STRUCTURE OF DI-(μ-METHYLISONITRILE)DI-(h^5-CYCLOPENTADIENYL)DINICKEL

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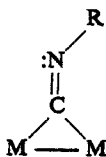
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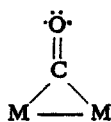
The crystal and molecular structures of a compound with the formula [(C_5H_5)(CH_3NC)Ni]$_2$ have been determined by X-ray crystallography. The dinuclear molecule has virtual C_2 symmetry; its important structural features are: (1) bridging CH_3NC groups; (2) *pentahapto*cyclopentadienylnickel groups; (3) a short Ni–Ni bond, 2.322(1) A. Each Ni_2CNC group is planar; the dihedral angle between the two Ni_2CN planes, which meet along the Ni–Ni line is 121.1°. The Ni–C–Ni groups are slightly unsymmetrical. The crystals belong to space group P2$_1$/c (No. 14) and the unit cell dimensions are: $a = 6.999(2)$ A, $b = 22.07(1)$ A, $c = 9.130(3)$ A and $\beta = 93.433(5)°$.

INTRODUCTION

Despite the fact that isonitrile complexes of transition metals have been known and studied for many years,[1] many facets of this chemistry remain poorly understood. One of these has to do with the ability of an isonitrile to serve as a bridging group, I, isoelectronic with the bridging ("ketonic") carbonyl group, II.

Previous literature on this matter is both limited and confused. The compound [(h^5-C_5H_5)NiCNPh]$_2$ has been reported and, after some difficulties owing to decomposition of solutions, formulated as a doubly-bridged molecule on the basis of $\nu_{CN} = 1785$ cm^{-1} for the solid.[2,3] A little later, [h^5-C_5H_5NiCNC$_6$H$_{11}$]$_2$ was reported[4] and from the infrared spectra observed in several solvents, an interconversion of bridged and nonbridged isomers was postulated. This seemed surprising to us, since we believed, for reasons given elsewhere,[5] that the nonbridged structure would be vastly less stable than the bridged one. In order to examine this problem more closely, the methylisonitrile compound, [(h^5-C_5H_5)Ni(CNCH$_3$)]$_2$, was prepared and studied.[5] As part of the complete study, we have examined the molecular structure of this compound

in the crystal. That part of the work is reported here.

Only one previous crystallographic study[3] of a molecule with a bridging isonitrile has been reported, and then only in preliminary form. The molecule in question is

$(h^5$-$C_5H_5)(CO)Fe(\mu$-CO)

(μ-CNPh)Fe(CO)(h^5-C_5H_5).

The C–N–Ph angle was found to be 131°, but other structure parameters of interest are not given. Thus, the work reported here seemed to be worthwhile not only in relation to our other investigations of the [(h^5-C_5H_5)Ni(CNCH$_3$)]$_2$ molecule itself, but with regard to the general question of the structural features characteristic of bridging isonitrile groups as a class.

EXPERIMENTAL

Collection and Reduction of Data   The
(C$_5$H$_5$NiCNCH$_3$)$_2$ was prepared in a manner to be described elsewhere.[5] A crystal of pyramidal habit and maximum dimensions 0.11 × 0.29 × 0.30 mm along its *a*, *b* and *c* axes, respectively, was mounted in a thin-walled glass capillary tube. Film techniques indicated a reciprocal lattice symmetry of C$_{2h}$, consistent with the monoclinic system. The systematic absences, h0*l*, *l* = 2n + 1, and 0k0, *k* = 2n + 1, uniquely defined the space group as P2$_1$/c (No. 14[6]). The unit cell dimensions, *a* = 6.999(2) A, *b* = 22.07(1) A, *c* = 9.130(3) A and β = 93.433(5)°, were obtained from a least squares treatment of the angular settings for 31 high angle reflections, measured on a General Electric four-circle diffractometer using Mo Kα radiation.

The calculated density, assuming four molecules per unit cell of di(μ-methylisonitrile)di(h^5–cyclopentadienyl)dinickel (molecular weight $= 329.7$), is 1.56 g cm^{-3}. The experimental density was not measured because of the instability or solubility of the compound in the liquid mixtures normally employed for this purpose.

The crystal was aligned on a General Electric XRD-5 manual diffractometer so that the reciprocal lattice vector $\bar{1}50$ was coincident with the ϕ axis of the diffractometer, thereby reducing the possibility of multiple reflection. Mo Kα radiation filtered by 0.04 mm niobium foil was used to measure 4104 independent reflections within the sphere $2\theta < 60°$. Intensities were measured by a scintillation counter with the pulse height discriminator set to accept 95% of the Mo Kα peak with the window centred on the Mo Kα peak. A $\theta/2\theta$ moving crystal-moving counter technique was employed with a scan range of $1.33°$ conforming with the mosaic spread of the crystal, the $\alpha_1 \alpha_2$ splitting and the take-off angle of $2°$. The scan rate was $4°$/min while the background radiation was measured at each extreme of the $\theta/2\theta$ scan for 10 seconds with both the counter and the crystal stationary. Three intense reflections which were frequently monitored during data collection exhibited only random statistical variation with time. Thus there was no evidence of crystal decomposition.

The recorded data were used to calculate structure factor amplitudes on a relative scale using the equations $|F_{obs}| = (I/Lp)^{1/2}$, where $Lp =$ Lorentz-polarization factor, and the net intensity, I, is given by $I = P - [(B_1 + B_2)T_P/2T_B]$, P represents the scanned count, B_1 and B_2 the stationary background counts, and T_P and T_B the counting times of the scan and each background, respectively. Their estimated standard deviations, $\sigma_F = [\sigma_I^2 + (0.02I)^2]^{1/2}$ $(4ILp)^{-1/2}$, were also computed; $\sigma_I = [P + (T_P/2T_B)^2(B_1 + B_2)]^{1/2}$. The eight crystal faces were identified and carefully measured. These data were used to correct the observed intensities for absorption effects; using an absorption coefficient of 2.66 mm^{-1}, the calculated maximum and minimum transmission coefficients were 0.77 and 0.53, respectively. The systematic variation of intensity with ϕ for the $\bar{1}50$ reflection at $\chi = 90°$ was eliminated by the absorption corrections. The amount of data was reduced to 2416 reflections by omitting from further considerations those reflections for which $F^2(\text{obs})/\sigma[F^2(\text{obs})] < 3.0$.

Solution and Refinement   A three-dimensional Patterson synthesis was calculated from which the coordinates of the nickel atoms were derived. Two cycles of least squares refinement of the metal parameters gave discrepancy indices of $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.242$ and $R_2 = \Sigma w_F ||F_o| - |F_c||^2/\Sigma w_F |F_o|^2 = 0.326$, where the weight, w_F, is equal to $\sigma^{-2}(F_o)$. All remaining (16) non-hydrogen atoms were located from a difference Fourier synthesis and were included in further least squares refinement. Three cycles reduced R_1 to 0.110 and R_2 to 0.121. Anisotropic temperature factors were then assigned to all atoms, which reduced R_1 to 0.044 and R_2 to 0.050 after a further four cycles. A difference Fourier synthesis was then computed, and from it the coordinates of all the hydrogen atoms were derived in stereochemically credible positions. The hydrogen parameters, with isotropic temperature factors, were then included in the least squares refinement, thereby reducing both R_1 and R_2 after three more cycles to 0.037. All shifts for the non-hydrogen atom parameters were less than 0.1 σ. For each hydrogen atom the shifts were less than 1 σ with the exception of those for the cyclopentadienyl hydrogen atom labelled H24 for which the parameters did not refine to give a chemically sensible position. The parameters for H24 were therefore calculated assuming coplanarity with the cyclopentadienyl ring.

After the final cycle of refinement the e.s.d. of an observation of unit weight was 1.34, and the quantity $w_F |F_o - F_c|^2$ was independent of both the magnitude of F_o and $\lambda^{-1} \sin \theta$. The final difference Fourier synthesis had no peak greater than 0.25 eA^{-3}, (the e.s.d.[7] in the electron density being 0.09 eA^{-3}) except one, 0.28 eA^{-3}, close to a metal atom. A final structure factor calculation for all recorded reflections showed that the calculated structure factors for the rejected reflections were acceptably low.

All cycles of least squares refinement were of the full matrix type. Atomic scattering factors[8] were corrected for the real and imaginary parts of anomalous dispersion.[9]

Computer programs employed were: PICK2 (J. A. Ibers) for refining cell constants and generating angular settings for data collection; DRAB (B. G. DeBoer) for data reduction and absorption correction; FORDAP (A. Zalkin), for Patterson and Fourier sytheses; SFIX (local version of C. T. Prewitt's SFLS-5), for least squares refinement, based on the minimization of the quantities $w_F (|F_o| - |F_c|)^2$; STAN1 (B. G. DeBoer), for molecular geometry; and ORTEP (C. K. Johnson) for illustrations.

RESULTS

A table of the final values of $|F_c|$ and $|F_o|$ scaled to $|F_c|$ is available.[10]

The molecular structure and numbering system are shown in Figs. 1 and 2. Final atomic positional and thermal parameters are given in Tables I and II, respectively. The standard deviations, which are given in parentheses for the last figure quoted, were derived from the inverse matrix of the final least-squares refinement cycle. Bond lengths and angles are given in Tables III and IV, while Table V gives the equations of various molecular planes, their associated dihedral angles, and the distances of pertinent atoms from these mean planes.

TABLE I

Atomic positional parameters and isotropic temperature factors[a]

Atom	x	y	z	B, A^2
Ni1	0.97428(6)	0.15103(2)	0.18054(5)	2.4
Ni2	0.79118(7)	0.11348(2)	−0.01968(5)	2.9
C11	1.1078(7)	0.1607(3)	0.3919(4)	5.2
C12	1.1170(7)	0.2147(2)	0.3160(5)	5.0
C13	1.2263(7)	0.2050(3)	0.1937(5)	5.6
C14	1.2887(6)	0.1453(3)	0.1959(6)	6.1
C15	1.2115(8)	0.1165(3)	0.3146(6)	5.8
C1	0.7963(5)	0.0856(2)	0.1738(4)	3.5
N1	0.7230(5)	0.0490(2)	0.2485(4)	4.7
C3	0.733(1)	0.0340(3)	0.4025(6)	6.8
C21	0.797(1)	0.1300(3)	−0.2485(4)	6.8
C22	0.614(1)	0.1103(3)	−0.2145(6)	7.4
C23	0.639(1)	0.0514(4)	−0.1553(6)	8.1
C24	0.835(2)	0.0364(3)	−0.1577(7)	8.0
C25	0.927(1)	0.0844(4)	−0.2164(6)	7.9
C2	0.8020(5)	0.1933(2)	0.0561(4)	3.1
N2	0.7378(5)	0.2431(2)	0.0375(3)	4.1
C4	0.6031(8)	0.2722(3)	−0.0674(5)	5.3
H11	1.032(8)	0.155(3)	0.491(6)	10(2)
H12	1.057(7)	0.258(3)	0.338(5)	8(1)
H13	1.241(8)	0.244(2)	0.112(6)	9(1)
H14	1.382(8)	0.127(2)	0.123(5)	9(1)
H15	1.225(8)	0.065(3)	0.341(6)	10(2)
H31	0.747(8)	−0.008(3)	0.425(6)	9(2)
H32	0.84(1)	0.046(3)	0.458(8)	12(2)
H33	0.61(1)	0.050(4)	0.464(9)	18(3)
H41	0.69(1)	0.287(3)	−0.152(7)	13(2)
H42	0.52(1)	0.240(3)	−0.124(7)	11(2)
H43	0.50(1)	0.304(3)	−0.005(7)	14(2)
H21	0.825(8)	0.178(3)	−0.294(6)	10(2)
H22	0.49(1)	0.138(3)	−0.241(8)	14(2)
H23	0.53(1)	0.027(4)	−0.123(7)	15(3)
H24	0.900	−0.004	−0.122	13
H25	1.08(1)	0.085(3)	0.210(7)	14(2)

Effective isotropic B's are given for the anisotropically refined atoms.

DISCUSSION

The structure of the crystalline form of $[(h^5\text{-}C_5H_5)Ni(CNCH_3)]_2$ consists of discrete molecules with no abnormally short intermolecular contacts. It does not appear that packing forces exert any significant influence upon the shape of the molecules. The qualitative form of the molecule presents no surprises. The molecule has nearly perfect C_2 symmetry, though no C_2 axis is imposed crystallographically. The two Ni–C$_5$H$_5$ groups have approximately C_{5v} local symmetry, although there are small but distinct distortions. The mean Ni–C and Ni–(ring plane) distances, 2.13 A and 1.77 A, are similar to those found in other M–C$_5$H$_5$ groups.[11-16] Each cyclopentadienyl ring is essentially planar; no carbon atom deviates from the mean plane of its ring by more than 0.02 A. The rings adopt a partially staggered relationship to each other, and there is no unusually close contact between them.

Each cyclopentadienyl ring is slightly tilted away from the bridging methylisonitrile groups so that the distances from the nickel atoms to individual carbon atoms increase in the order C11, C12 > C15, C13 > C14, for ring 1 and C22, C23 > C24, C21 > C25 for ring 2. The maximum variation for ring 1 is 2.086(5) to 2.201(5)A while for ring 2 it is 2.094(6) to 2.179(6)A. Such a distortion is probably due to intramolecular packing around the metal atoms rather than to any genuine asymmetrical bonding as found in Cp$_2$MoNOX molecules.[17, 18] Several carbon atoms, C11, C12, C22 and C23, exhibit short non-bonded contacts of ∼ 3.3 A to the bridging carbon atoms and ∼ 3.8 A to the nitrogen atoms.

The dihedral angle between the two ring planes is 43.7°, which is less than the value 65° found[19] for $[h^5\text{-}C_5H_5)Ni]_2[PhC \equiv CPh)$.

The mean C-C distances, 1.399 A and 1.395A, for rings 1 and 2, respectively, are equal within their anticipated error. These mean values, together with the range of C-C distances from which they were derived are typical of $(h^5\text{-}C_5H_5)M$ systems.[11-16]

The C-H bond distances (excluding C24–H24, discussed in the Experimental section) for the cyclopentadienyl and methyl groups are numerically longer, although not significantly, than those derived from other least squares refinements.[15]

TABLE II

Anisotropic temperature factors[a]

Atom	B11	B22	B33	B12	B13	B23
Ni1	2.17(2)	3.00(2)	2.13(2)	−0.09(2)	−0.28(1)	−0.10(2)
Ni2	3.43(2)	2.99(2)	2.11(2)	−0.46(2)	−0.47(1)	−0.15(2)
C11	4.4(2)	8.1(3)	3.0(2)	−1.3(2)	−1.1(1)	−0.4(2)
C12	3.9(2)	4.6(2)	6.1(2)	0.1(2)	−1.5(2)	−1.8(2)
C13	3.8(2)	7.8(3)	5.0(2)	−2.4(2)	−1.1(2)	1.1(2)
C14	2.6(2)	9.8(4)	5.8(3)	0.3(2)	−0.3(2)	−3.1(3)
C15	5.4(3)	5.2(3)	6.3(3)	0.2(2)	−2.8(2)	0.1(2)
C1	3.5(2)	3.7(2)	3.2(1)	0.1(1)	−0.2(1)	0.1(1)
N1	4.7(2)	5.3(2)	4.2(2)	−1.1(1)	0.1(1)	0.8(1)
C3	9.0(4)	7.5(4)	3.8(2)	−1.5(3)	0.5(2)	1.9(2)
C21	12.0(5)	5.6(3)	2.7(2)	−1.0(3)	−0.7(2)	−0.3(2)
C22	8.4(4)	8.6(4)	4.6(2)	0.5(4)	−3.4(3)	−2.1(3)
C23	11.8(6)	7.8(4)	4.4(3)	−5.6(4)	−1.4(3)	−1.3(2)
C24	12.9(6)	5.7(3)	5.1(3)	0.8(4)	−2.6(3)	−2.1(3)
C25	8.6(4)	10.9(6)	4.3(2)	−0.2(4)	1.0(3)	−3.4(3)
C2	2.9(2)	3.7(2)	2.7(1)	−0.5(1)	0.0(1)	−0.1(1)
N2	4.2(2)	3.9(2)	4.2(1)	0.5(1)	−0.2(1)	0.2(1)
C4	4.6(2)	6.4(3)	4.8(2)	1.5(2)	−0.4(2)	1.3(2)

[a] The form of the temperature factor expression is:

$$\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)].$$

TABLE III

Bond distances, Å

Bonds to Nickel Atoms:

Ni1–Ni2	2.3217(8)		
Ni1–C11	2.104(4)	Ni2–C21	2.125(5)
Ni1–C12	2.086(5)	Ni2–C22	2.109(6)
Ni1–C13	2.126(4)	Ni2–C23	2.094(6)
Ni1–C14	2.201(5)	Ni2–C24	2.149(6)
Ni1–C15	2.143(5)	Ni2–C25	2.179(6)
Ni1–C1	1.905(4)	Ni2–C1	1.869(4)
Ni1–C2	1.858(4)	Ni2–C2	1.893(4)

Bridging Methylisonitrile Groups:

C1–N1	1.193(5)	C2–N2	1.195(5)
N1–C3	1.443(6)	N2–C4	1.452(6)
C3–H31	0.96(6)	C4–H41	1.06(7)
C3–H32	0.91(7)	C4–H42	1.03(6)
C3–H33	1.08(8)	C4–H43	1.19(7)

Cyclopentadienyl Groups:

C11–C12	1.382(7)	C21–C22	1.406(9)
C11–C15	1.427(8)	C21–C25	1.38(1)
C12–C13	1.407(7)	C22–C23	1.41(1)
C13–C14	1.388(8)	C23–C24	1.41(1)
C14–C15	1.393(9)	C24–C25	1.37(1)
C11–H11	1.08(6)	C21–H21	1.16(6)
C12–H12	1.06(6)	C22–H22	1.05(7)
C13–H13	1.14(5)	C23–H23	0.99(8)
C14–H14	1.04(5)	C24–H24	1.05*
C15–H15	1.17(6)	C25–H25	1.07(8)

* H24 not refined; and see text.

The two nickel atoms and each of the two bridging CN groups form strictly planar arrays, no atom deviating by as much as 0.01 Å. The methyl carbon atoms, which were not included in calculating the mean planes deviate by 0.07 and 0.03 Å for C3 and C4 respectively. The dihedral angle between the two planes is 121.1°, which is in good agreement with the angle which can be inferred from the intensity ratio between the symmetric and antisymmetric C = N stretching frequencies.[5]

As a consequence of the Ni–Ni bond, to be discussed below, the planes defined by Ni1, C1, C2 and Ni2, C1, C2 make a dihedral angle of 117.9°. This value is larger than those values found in [EtSFe(CO)$_3$]$_2$[20] (95.4°), [Ph$_2$PCoCp]$_2$[11] (105°), and [(h^5–C$_5$H$_5$)Ni]$_2$(PhC $\equiv$ CPh)[19] (97.1°) but as all equivalent bond lengths and angles within the bridged fragments for the two nickel compounds are comparable, it can be seen that this dihedral angle is dependent to a large extent on the intramolecular distance between the bridging atoms. This distance in [h^5–C$_5$H$_5$Ni(CNCH$_3$)]$_2$ is 2.610(6) Å while only 1.35(3) Å in [(h^5–C$_5$H$_5$)Ni]$_2$PhC $\equiv$ CPh.

The chemically equivalent C-N, 1.195(5) and 1.195(5) Å, and C-CH$_3$, 1.443(6) and 1.452(6) Å,
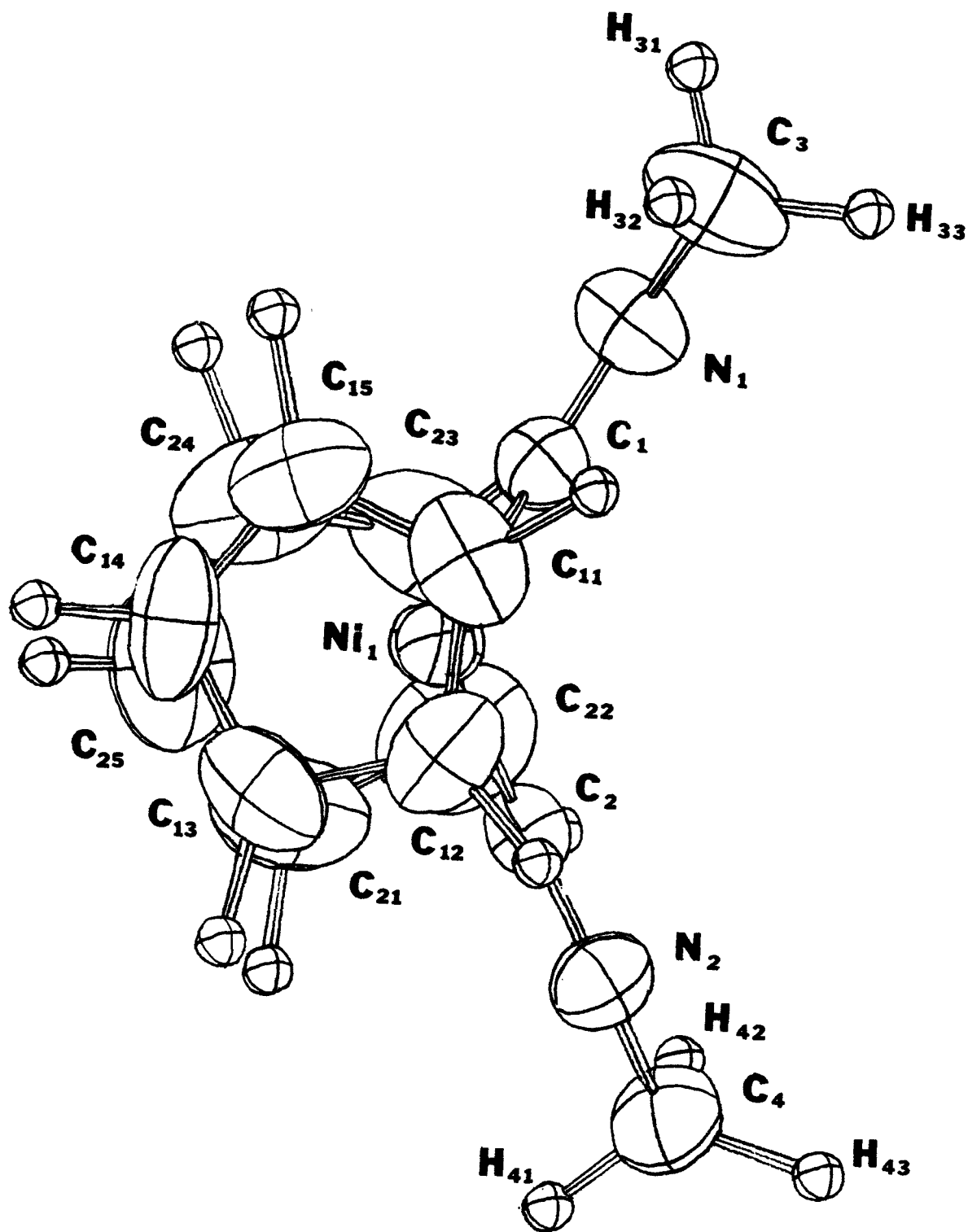
FIGURE 1 A projection of the molecule in the direction of Ni–Ni axis. This view shows clearly the partial staggering of the C_5H_5 rings and the planarity of the bridging groups. All atoms except hydrogen atoms are represented by thermal ellipsoids enclosing 50% of the electron density. Hydrogen atoms are represented by spheres of arbitrary size.
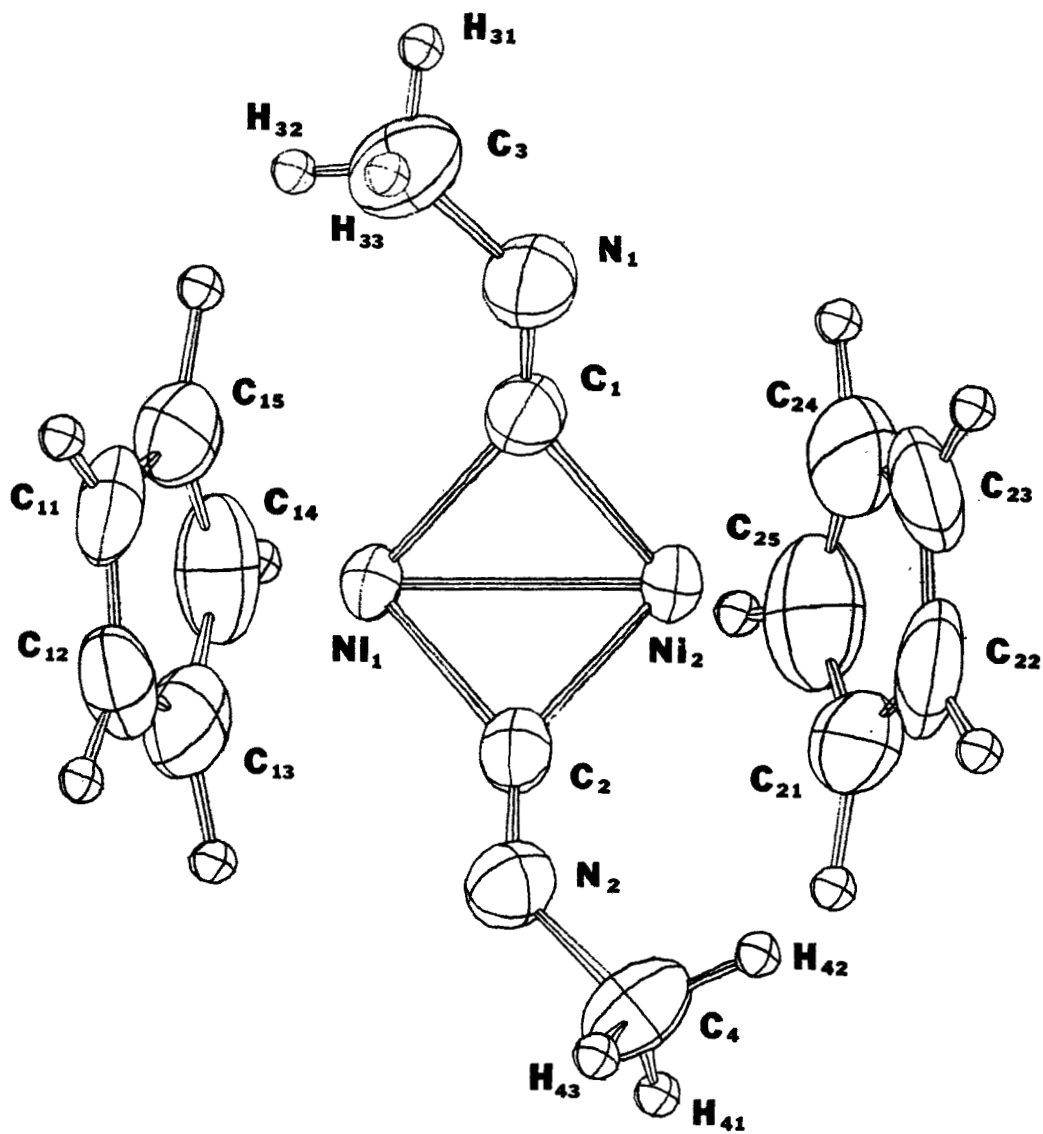
FIGURE 2   A view of the molecule along its virtual two-fold axis, showing clearly the opposed orientations of the methyl groups

TABLE IV

Bond angles, Deg.

Angles at Nickel Atoms:

Ni2-Ni1-C1	51.3(1)	Ni1-Ni2-C1	52.8(1)
Ni2-Ni1-C2	52.5(1)	Ni1-Ni2-C2	51.1(1)
C1-Ni1-C2	87.8(2)	C1-Ni2-C2	87.8(2)

Bridging Methylisonitrile Groups:

Ni1-C1-Ni2	75.9(1)	Ni1-C2-Ni2	76.5(2)
Ni1-C1-N1	142.8(3)	Ni2-C1-N1	141.2(3)
Ni1-C2-N2	140.7(3)	Ni2-C2-N2	142.9(3)
C1-N1-C3	135.7(5)	C2-N2-C4	136.3(4)
N1-C3-H31	115(4)	N2-C4-H41	105(4)
N1-C3-H32	118(5)	N2-C4-H42	111(4)
N1-C3-H33	116(5)	N2-C4-H43	110(3)
H31-C3-H32	95(6)	H41-C4-H42	100(5)
H31-C3-H33	106(6)	H41-C4-H43	124(5)
H32-C3-H33	104(6)	H42-C4-H43	107(5)

Cyclopentadienyl Groups:

C15-C11-C12	107.5(4)	C25-C21-C22	109.1(7)
C11-C12-C13	108.1(5)	C21-C22-C23	105.8(7)
C12-C13-C14	108.6(5)	C22-C23-C24	108.1(6)
C13-C14-C15	107.9(4)	C23-C24-C25	107.9(7)
C14-C15-C11	107.8(5)	C24-C25-C21	109.1(8)
C12-C11-H11	124(3)	C22-C21-H21	123(3)
C15-C11-H11	128(3)	C25-C21-H21	128(3)
C11-C12-H12	130(3)	C21-C22-H22	120(4)
C13-C12-H13	122(3)	C23-C22-H22	134(5)
C12-C13-H13	119(3)	C22-C23-H23	122(5)
C14-C13-H13	132(3)	C24-C23-H23	130(5)
C13-C14-H14	124(3)	C23-C24-H24	127*
C15-C14-H14	128(3)	C25-C24-H24	125*
C14-C15-H15	125(3)	C24-C25-H25	119(4)
C11-C15-H15	127(3)	C21-C25-H25	131(4)

* H24 position not refined; see text.

TABLE V

Least squares planes[a]

Plane	Atoms	Equation	Dihedral angle
1	C11-C15	−0.7925x − 0.2476y − 0.5573z = −8.8349 ⎫	
2	C21-C25	−0.1070x − 0.3834y − 0.9174z = 0.3791 ⎭	43.7°
3	Ni1, Ni2, C1, N1	0.7435x − 0.6425y − 0.1858z = 2.5519 ⎫	
4	Ni1, Ni2, C2, N2	0.7731x + 0.2181y − 0.5956z = 4.9422 ⎭	121.1°
5	Ni1, C1, C2	0.4790x − 0.3785y − 0.7921z = −0.6542 ⎫	
6	Ni2, C1, C2	−0.9991x − 0.0309y − 0.0289z = 5.4607 ⎭	117.9°

Distances (Å) of Atoms from Least Squares Planes

Plane 1		Plane 2		Plane 3		Plane 4	
C11	0.01	C21	0.01	Ni1	0.00	Ni1	0.00
C12	0.00	C22	−0.01	Ni2	0.00	Ni2	0.00
C13	−0.01	C23	0.00	C1	−0.01	C2	0.00
C14	0.02	C24	0.00	N1	0.00	N2	0.00
C15	−0.02	C25	−0.01	C3	0.07	C4	−0.03
Ni1	−1.77	Ni1	3.89				
Ni2	−3.92	Ni2	1.76				
H11	0.02	H21	0.06				
H12	0.01	H22	−0.08				
H13	−0.10	H23	−0.02				
H14	0.10	H24	−0.04				
H15	−0.10	H25	0.16				

[a] The equations of the planes are of the form $Lx + Mx + Nz = D$, where L, M and N are directional cosines referred to the orthogonal axis system a, b, c^*.

bond distances of the bridging groups differ by less than the sum of their e.s.d.'s, and are thus to be considered equal. The C-N bond lengths (mean 1.194 A), are perhaps increased relative to that in $CH_3N \equiv C$ itself[21] (1.66 A) or in the non-bridging form of coordination, as in $[Co(CNCH_3)_5]ClO_4$ (1.14(2) A) and $[Co(CNCH_3)_5]_2(ClO_4)_4$ (1.15(4) A),[22] but the e.s.d.'s of the earlier determinations are too large to permit conclusions to be drawn.

In the bridged form the methylisonitrile group is bent, and the lone pair on the nitrogen presumably exerts a stereochemical influence. The two independent C-N-CH_3 angles are 135.7(5)° and 136.3(4)° which are greater than the one reported[3] value (131°) for a bridging isonitrile ligand.

One feature of the bridging system deserves comment. The Ni-C distances *syn* to the methyl groups (1.905(4) A and 1.893(4) A) are longer than those *anti* to the methyl groups (1.858(4) A and 1.869(4) A). The difference between the mean values, 0.037 A is not great but it is very likely to be real ($> 4\sigma$). Whether this is a characteristic feature of bridging isonitrile groups will only be known when other structures of sufficient accuracy are reported.

The Ni-Ni distance in this compound is 2.322(1) A. In Table VI this is compared with Ni-Ni

TABLE VI

Nickel-Nickel distances in various molecules

	Molecule	Ni-Ni, A	Reference
1.	$[(h^5\text{-}C_5H_5)Ni(CNCH_3)]_2$	2.322(1)	This work
2.	$[(h^5\text{-}C_5H_5)Ni]_2PhC\equiv CPh$	2.329(4)	19
3.	$[(h^5\text{-}C_5H_5)Ni(CO)]_2$	2.36[a]	27
4.	$Ni_4(CO)_6[P(C_2H_6CN)_3]_6$	2.508(4)	28
5.	$[(h^5\text{-}C_5H_5)Ni]_3(CO)_2$	2.39[a]	27
6.	$[Ni(N_3Ph_2)_2]_2$	2.38[a]	23
7.	$[Ni(S_2CCH_2Ph)_2]_2$	2.56(1)	24
8.	$[Ni(OSCPh)_2]_2$	2.503(4)	25, 26

[a] No e.s.d. given.

distances[23-28] in some other molecules. Compounds 1-4 in this table may all be expected to contain Ni-Ni single bonds. The first three compounds are rather similar in general form and formal oxidation number of the metal, and their Ni-Ni distances differ very little. A value in the range 2.32-2.36 thus seems typical of a single bond under circumstances where the bridging groups allow a good deal of freedom for formally Ni^+ atoms to approach one another as closely as they prefer. In compounds

4 and 5, there are increasingly more severe constraints since the metal atoms are in Ni_4 and Ni_3 clusters, respectively, and the Ni-Ni distances become appreciably longer. Compounds 6, 7 and and 8 all have a pair of nickel atoms held with a set of four 3-atom bridging groups. The distances vary over a considerable range and it is difficult to say, *a priori*, what Ni-Ni bond order should be assigned in these cases.

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