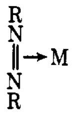
A π-Bonded Azo–Transition Metal Complex. The Structure of Bis(*tert*-butyl isocyanide)(azobenzene)nickel(0)

Ron S. Dickson and James A. Ibers*

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received August 16, 1971*

Abstract: The structure of bis(*tert*-butyl isocyanide)(azobenzene)nickel(0), $Ni(C_6H_5N{=}NC_6H_5)((CH_3)_3C{-}N{\equiv}C)_2$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in space group C_{2h}^5-$P2_1/c$ of the monoclinic system, with four molecules in a cell of dimensions a = 12.404 (8), b = 17.154 (8), c = 12.487 (6) Å, β = 117.46 (6)°. The structure has been refined by least-squares techniques to a final R factor on F of 7.0% based on 2694 observations above background. The coordination about the Ni atom is trigonal if the azobenzene is regarded as a monodentate ligand. The molecule possesses essentially C_2 symmetry. The dihedral angle between the Ni-NN (of azobenzene) and Ni–CC (of *tert*-butyl isocyanide) planes is 1.2 (3)° and the inner coordination sphere is essentially planar. The *tert*-butyl isocyanide ligands are very nearly linear, and the average Ni-C distance is 1.841 (5) Å. The azobenzene nitogen atoms are equidistant from the metal, with an average Ni–N bond length of 1.898 (4) Å. The N–N distance of 1.385 (5) Å is very close to an N–N single bond distance. The phenyl rings of the coordinated azobenzene are twisted 14° from ideal planarity, and there is a dihedral angle of 26.8 (4)° between the two N–N–C (phenyl) planes. The bond lengthening and the geometry within the coordinated azobenzene are both consistent with the usual description of π bonding of olefinic-type ligands to transition metals. The complex is suggested as a suitable model for consideration of the possible role of π-bonded diimide in the biological fixation of nitrogen.

There is an abundance of complexes in which an olefin or an acetylene is π bonded to a transition metal. In contrast, there are no confirmed reports of similar complexes in which an azo molecule is π bonded from the N═N linkage to a single transition metal (**1**). The possibility of this form of bonding seems to have been discussed first in 1936[1] and again in 1947.[2] In the succeeding 30 years or so, numerous azo–transition metal complexes have been synthesized, but these have been shown to incorporate N-to-M σ interactions of type **2**[3] or **3**.[4] The structure of a polymeric cuprous chloride azomethane complex[5] also incorporates N-M interactions of type **2**. In two structures where an azo function bridges two iron atoms,[6,7] the bonding is thought to be more consistent with a metal-to-nitrogen σ interaction than with the π-bonded model.



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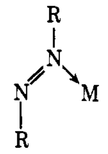

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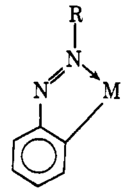

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In 1971, Otsuka and coworkers reported[8] the formation of an azobenzene complex of nickel(0), $Ni(C_6H_5{-}N{=}NC_6H_5)((CH_3)_3C{-}N{\equiv}C)_2$. On the basis of displacement reactions and spectroscopic data, they predicted a π-type azo-to-transition metal linkage for this compound. Simultaneously, Klein and Nixon reported[9] the preparation and some reactions of the rather similar complex $Ni(C_6H_5N{=}NC_6H_5)(P(C_6H_5)_3)_2$.

Considerable recent interest in the chemistry of unsaturated organic compounds coordinated to transition metals has prompted us to investigate the solid-state structure of one of these azo complexes. We have chosen $Ni(C_6H_5N{=}NC_6H_5)((CH_3)_3C{-}N{\equiv}C)_2$ since it is closely related to other complexes $Ni(L)((CH_3)_3{-}C{-}N{\equiv}C)_2$, where L = tetracyanoethylene[10] or diphenylacetylene,[11] which have been examined in this laboratory. The possible role of the coordinated azo compound diimide (HN═NH) in the biological N_2-fixation process[12] provides further stimulus for the study. It is of particular interest to determine if the nitrogen lone pairs complicate the N═N to transition metal bonding interaction in any way. A brief account of earlier work on this compound has appeared.[13]

Experimental Section

Unit Cell and Space Group. The crystals of $Ni(C_6H_5N{=}NC_6H_5)$-$((CH_3)_3C{-}N{\equiv}C)_2$ used in this study were kindly supplied by Professor S. Otsuka. The compound had been crystallized from diethyl ether as very air-sensitive, red, needle-like plates. A crystal of approximate dimensions 0.030 × 0.062 × 0.095 cm was mounted in a predried, nitrogen-filled, quartz capillary and sealed with the longest crystal edge roughly parallel to the capillary walls. Precession photographs taken with Cu Kα radiation of zero- and first-level zones showed systematic absences $0k0$ for k odd and $h0l$ for l odd that are characteristic of the monoclinic space group C_{2h}^5-$P2_1/c$. The lattice parameters, obtained with Cu $K\alpha_1$ radiation (λ 1.54056 Å) at 26° from least-squares refinement of the setting angles of 12 reflections centered on a Picker four-circle diffractometer,[14] are a = 12.404 (8), b = 17.154 (8), c = 12.487 (6) Å, β = 117.46 (6)°. The standard deviations in parentheses are those from the least-squares refinement of the setting angles. The

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[2] A. E. A. Werner, *Nature (London)*, 160, 644 (1947).

[3] A. L. Balch and D. Petridis, *Inorg. Chem.*, 8, 2247 (1969), and references therein.

[4] G. Parshall, *Accounts Chem. Res.*, 3, 139 (1970), and references therein.

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[6] R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 8, 2709 (1969).

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[13] R. S. Dickson, J. A. Ibers, S. Otsuka, and Y. Tatsuno, *J. Amer. Chem. Soc.*, **93**, 4636 (1971).

[14] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

extreme air sensitivity of the compound precluded an experimental density determination; a reasonable density of 1.16 g/cm^3 was calculated for four formula units in the cell.

Collection and Reduction of Intensity Data. Intensity data were collected with Cu Kα radiation using the Picker FACS-1 system with magnetic tape output. The methods used for collection of the diffractometer data were essentially those previously described.[14,15] A unique data set was first collected out to 2θ(Cu Kα_1) = 85°. Additional data were subsequently collected out to 117° in 2θ. Data collection was then terminated, since there were relatively few intensities above background. The intensities of 3408 independent reflections were measured; of these, 2694 obeyed the condition $F_o^2 > 3\sigma(F_o^2)$, and only these were used in subsequent calculations. Four standard reflections, monitored at regular intervals throughout the data collection, showed no significant variations in intensity.

These data were collected by the θ–2θ scan technique with a symmetric scan range of ±0.9° in 2θ from the calculated scattering angle. The X-ray beam was prefiltered through 0.5-mil Ni foil. The scan rate was 1.0°/min out to $2\theta = 85°$, and 0.5°/min from 85 to 117°. Background counts of 10 sec were taken at each end of the scan out to $2\theta = 72°$; these were increased to 20 sec between 72 and 85°, and subsequently to 40 sec between 85 and 117°. The counter aperture, 7 mm high by 7 mm wide, was positioned 31 cm from the crystal. The pulse-height analyzer was set to admit 90% of the Cu Kα peak. The takeoff angle was 3.5°. Whenever the counting rate exceeded about 7000 counts/sec, the diffracted beams were attenuated by Cu foil to prevent coincidence losses; the most intense reflection (11$\bar{1}$) required five attenuators.

The intensities were corrected for Lorentz–polarization effects. Processing of the data was carried out in the manner previously described[14,15] to yield values of F_o^2 and $\sigma(F_o^2)$. A value of 0.03 was used for p in the estimation of $\sigma(F_o^2)$.

Solution and Refinement of the Structure

Initial solution of the structure was achieved using standard heavy-atom methods.[16] In the ensuing least-squares calculations, the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and where the weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for Ni, C, and N tabulated by Ibers,[17] and those for H of Stewart, *et al.*,[18] were used in all structure factor calculations. The values of the anomalous terms $\Delta f'$ and $\Delta f''$ for Ni were taken from the calculations of Cromer[19] and were applied to the correction of the calculated structure factors.[20]

Interpretation of a sharpened three-dimensional Patterson function led to the position of the nickel atom at 0.25, 0.12, 0.25. Two cycles of least-squares refinement, each followed by a difference Fourier synthesis, led to positions for all carbon and nitrogen atoms. Vectors from Ni to all the nonhydrogen atoms in the molecule were located in the Patterson function, thus confirming the reasonableness of the model. An additional cycle of refinement of all positional and isotropic thermal parameters, with the phenyl groups constrained to D_{6h} symmetry with a C–C distance of 1.39 Å, led to values of R_1 and R_2 of only 0.324 and 0.440, respectively, where $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$. An analysis of the agreement factors as a function of Miller indices revealed that this agreement for reflections with $h + k$ odd was extremely poor. Clearly there was something wrong with the model. It can be shown that if the Ni atom is exactly at $^1/_4$, y, $^1/_4$ and if the molecule possesses a twofold axis coincident with the y axis, then false symmetry is introduced and all reflections with $h + k$ odd will have zero structure factors. In essence, then, the observed structure factors for reflections with $h + k$ odd arise because the Ni is slightly off the $^1/_4$, y, $^1/_4$ position and because the molecule need not possess exact C_2 symmetry. If one takes a molecule with C_2 symmetry and moves it off the $^1/_4$, y, $^1/_4$ position to $^1/_4 + \epsilon_1$, y, $^1/_4 + \epsilon_2$, then one can show that those reflections with $h + k$ even are affected but little and more importantly the effect is independent of the signs of ϵ_1 and ϵ_2. On the other hand, the reflections for $h + k$ odd are severely affected and are sensitive to the signs of ϵ_1 and ϵ_2. A series of structure factor calculations for the four possible combinations of $\pm\epsilon_1$, $\pm\epsilon_2$, based on the values of ϵ_1 and ϵ_2 at the present stage of refinement, indicated that the wrong model had been chosen. In the initial refinement with Ni, only the Ni atom shifted slightly off axis, apparently in the wrong direction. Subsequent additions to the model, based upon this incorrect shift, failed to bring about convergence to the correct Ni position. When the Ni atom was correctly placed and the structure refined, the values of R_1 and R_2 were reduced to 0.149 and 0.207, respectively, and there was no disparity in the agreement between $h + k$ odd and $h + k$ even reflections. The observed intensities were then corrected for absorption; the calculated transmission factors, based on $\mu = 13.0$ cm^{-1}, varied from 0.459 to 0.686. A cycle of isotropic refinement, followed by cycles in which all nongroup atoms were refined anisotropically while the phenyl groups were refined isotropically, reduced R_1 and R_2 to 0.083 and 0.118, respectively. Difference Fourier syntheses in the separate planes where the hydrogen atoms of the methyl groups were expected led to reasonable positions for all 18 methyl hydrogen atoms, despite the very large thermal motion exhibited by the methyl carbon atoms. These positions were idealized using C–H = 1.00 Å and ∠C–C–H = 109.5°. The contributions from these idealized hydrogen atoms and the phenyl groups hydrogen atoms in ideal positions were added to all subsequent structure factor calculations. Thermal parameters of 15 and 12 Å^2 were assigned to the hydrogen atoms of the two groups of methyl carbon atoms C_5, C_6, and C_7 and C_8, C_9, and C_{10}, respectively. These values correspond approximately to the average isotropic equivalent of the thermal parameters for the appropriate methyl carbon atoms. The phenyl hydrogen atoms were given the isotropic thermal parameters of the ring carbon atoms to which they were attached. Two further cycles of refinement for 161 variables and 2694 observations led to $R_1 = 0.072$ and $R_2 = 0.101$. In a final cycle of refinement, the phenyl carbon atoms were freed from their group constraints and the final values of R_1 and R_2 were 0.070 and 0.099. The final atomic positional and thermal parameters together with their standard deviations as

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(15) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 6, 204 (1967).

(16) In addition to various local programs for the CDC 6400, computer programs used in this work include local versions in Dewar's FAME program, Zalkin's FORDAP Fourier program, Coppens, Leiserowitz, and Rabinovich's absorption program, Busing and Levy's ORFFE function and error program, Johnson's ORTEP thermal ellipsoid plotting program, and Watkins' RBANG group orientation program. Our least-squares program NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program.

(17) J. A. Ibers in "International Tables for X-ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962.

(18) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(19) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

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Table I. Positional and Anisotropic Thermal Parameters for Individual Atoms, $Ni(C_6H_5N{=}NC_6H_5)((CH_3)_3C{-}N{\equiv}C)_2$[a]

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.24547 (7)	0.11546 (4)	0.25788 (7)	86.4 (8)	28.4 (3)	107.7 (9)	1.1 (4)	55.0 (6)	2.3 (4)
N(1)	0.2017 (3)	0.0099 (2)	0.2619 (3)	79 (4)	32 (1)	92 (4)	0 (2)	48 (3)	2 (2)
N(2)	0.3003 (3)	0.0156 (2)	0.2386 (3)	74 (4)	30 (1)	94 (4)	1 (2)	43 (3)	2 (2)
N(3)	0.0766 (4)	0.2168 (2)	0.3072 (4)	113 (5)	34 (2)	160 (6)	8 (2)	72 (4)	−3 (2)
N(4)	0.4014 (4)	0.2346 (3)	0.2204 (4)	120 (5)	37 (2)	165 (6)	−10 (2)	70 (5)	12 (2)
C(1)	0.1417 (5)	0.1771 (3)	0.2892 (5)	108 (5)	32 (2)	138 (6)	1 (3)	65 (5)	−1 (3)
C(2)	0.3417 (5)	0.1888 (3)	0.2359 (5)	107 (5)	34 (2)	129 (6)	1 (3)	63 (5)	3 (3)
C(3)	0.0024 (6)	0.2714 (4)	0.3309 (7)	130 (7)	49 (3)	209 (9)	14 (3)	100 (7)	−19 (4)
C(4)	0.4713 (7)	0.2931 (4)	0.1971 (8)	155 (8)	49 (3)	240 (11)	−15 (4)	111 (8)	24 (4)
C(5)	−0.0199 (20)	0.2458 (10)	0.4228 (18)	817 (46)	201 (12)	716 (41)	294 (20)	684 (41)	235 (19)
C(6)	0.0541 (14)	0.3454 (7)	0.3454 (20)	382 (23)	78 (5)	1079 (52)	−40 (9)	485 (32)	−170 (14)
C(7)	−0.1150 (11)	0.2788 (8)	0.2201 (14)	209 (14)	153 (9)	435 (27)	84 (9)	95 (16)	−40 (12)
C(8)	0.5051 (16)	0.2636 (7)	0.1108 (15)	568 (31)	118 (7)	527 (30)	−129 (13)	455 (28)	−65 (12)
C(9)	0.4072 (11)	0.3665 (6)	0.1709 (15)	295 (17)	66 (4)	733 (35)	42 (7)	307 (22)	140 (10)
C(10)	0.5892 (10)	0.3022 (6)	0.3140 (13)	210 (13)	82 (5)	428 (23)	−63 (7)	68 (15)	14 (8)

[a] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. [b] The form of the anisotropic thermal ellipsoid is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. The values of β have been multiplied by 10^4.

Table II. Positional and Isotropic Thermal Parameters for Phenyl Carbon Atoms

Atom	x	y	z	B, A^2
C(11)	0.2372 (4)	−0.0125 (2)	0.3831 (4)	3.7 (1)
C(12)	0.3485 (4)	−0.0451 (3)	0.4591 (4)	4.4 (1)
C(13)	0.3743 (5)	−0.0703 (3)	0.5732 (5)	5.8 (1)
C(14)	0.2873 (6)	−0.0648 (4)	0.6130 (6)	6.3 (1)
C(15)	0.1761 (6)	−0.0321 (3)	0.5369 (5)	6.1 (1)
C(16)	0.1506 (4)	−0.0069 (3)	0.4238 (4)	4.8 (1)
C(17)	0.2661 (4)	0.0025 (2)	0.1145 (4)	3.9 (1)
C(18)	0.1574 (5)	−0.0315 (3)	0.0348 (5)	5.0 (1)
C(19)	0.1318 (6)	−0.0472 (4)	−0.0837 (6)	7.0 (1)
C(20)	0.2164 (7)	−0.0284 (4)	−0.1223 (7)	7.8 (2)
C(21)	0.3240 (6)	0.0056 (4)	−0.0433 (6)	7.2 (1)
C(22)	0.3511 (5)	0.0213 (3)	0.0758 (5)	5.4 (1)

Table III. Idealized Positional Coordinates for Hydrogen Atoms[a]

Atom	x	y	z
C(5)H(1)	−0.057	0.190	0.404
C(5)H(2)	0.057	0.241	0.503
C(5)H(3)	−0.080	0.279	0.436
C(6)H(1)	0.127	0.358	0.426
C(6)H(2)	0.094	0.355	0.283
C(6)H(3)	−0.003	0.392	0.324
C(7)H(1)	−0.170	0.319	0.231
C(7)H(2)	−0.108	0.291	0.147
C(7)H(3)	−0.164	0.226	0.205
C(8)H(1)	0.547	0.203	0.139
C(8)H(2)	0.444	0.253	0.027
C(8)H(3)	0.579	0.290	0.108
C(9)H(1)	0.349	0.374	0.079
C(9)H(2)	0.351	0.371	0.212
C(9)H(3)	0.462	0.414	0.197
C(10)H(1)	0.629	0.249	0.338
C(10)H(2)	0.647	0.335	0.291
C(10)H(3)	0.577	0.327	0.374
C(17)H	0.413	−0.050	0.430
C(18)H	0.456	−0.094	0.627
C(19)H	0.305	−0.083	0.695
C(20)H	0.111	−0.027	0.556
C(21)H	0.068	0.017	0.368
C(23)H	0.096	−0.045	0.063
C(24)H	0.053	−0.071	−0.141
C(25)H	0.199	−0.038	−0.208
C(26)H	0.388	0.021	−0.072
C(27)H	0.430	0.047	0.132

[a] A C–H distance of 1.00 Å and tetrahedral geometry were assumed. This C–H distance is about 0.1 Å shorter than the spectroscopic value and is typical of values found in direct X-ray determinations.

estimated from the inverse matrix are given in Tables I and II and the idealized positions for the hydrogen atoms in Table III. An analysis of $|F_o|$ and $|F_c|$ as a function of scattering angle, magnitude of $|F_o|$, and Miller indices clearly revealed that agreement was worst at low scattering angles. Data collected in a similar manner on similar structures[10] have generally led to values of R_1 well below the present 7% level. In the present instance 168 pairs of $0kl$ and $0k\bar{l}$ reflections were collected. After correction for absorption, the average agreement between pairs was 2.6%. Presumably then, the poor agreement in the present study is the fault of the model, rather than of the data. The *tert*-butyl groups display extreme anisotropic thermal motion that is suggestive of considerable torsional motion about the threefold axes of the groups. The anisotropic thermal model is simply inadequate to account for the actual scattering process. Whereas the anisotropic thermal parameters are effective in bringing about agreement between observation and model at high scattering angles, they are not effective at low scattering angles. Consequently, the poorer agreement there is not surprising. Difference Fourier syntheses in the planes of the *tert*-butyl carbon atoms did not suggest a more adequate scattering model. The analysis of $|F_o|$ *vs.* $|F_c|$ did not suggest that extinction was important. The error in an observation of unit weight is 4.93. The maximum density on a final difference Fourier synthesis is 0.70 e/Å^3; this can be compared with the range of 2.03–4.74 e/Å^3 for the electron densities of methyl carbon atoms in the previous difference Fourier synthesis. A comparison of $|F_o|$ and $|F_c|$ for 714 reflections with $F_o^2 \leq 3\sigma(F_o)^2$ revealed two reflections for which $|F_o - F_c|$ lay near $8\sigma(F_o)$ and 20 for which $|F_o - F_c|$ was between 4 and $6\sigma(F_o)$. All others have $|F_o - F_c| < 4\sigma(F_o)$. Thus, these data are omitted from the tabulation of structure amplitudes (Table IV),[21] where we present the final values of 10 $|F_o|$ and 10 $|F_c|$ (in electrons) for those reflections used in the refinement.

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(21) A listing of structure amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-2988. Remit check or money order for $3.00 for photocopy of $2.00 for microfiche.

Table V. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Minimum	Intermediate	Maximum
Ni	0.205 (1)	0.212 (1)	0.260 (1)
N(1)	0.202 (4)	0.219 (5)	0.242 (5)
N(2)	0.206 (4)	0.212 (5)	0.243 (5)
N(3)	0.212 (6)	0.261 (5)	0.316 (6)
N(4)	0.209 (6)	0.279 (5)	0.328 (6)
C(1)	0.217 (6)	0.246 (6)	0.293 (6)
C(2)	0.225 (6)	0.245 (6)	0.284 (6)
C(3)	0.205 (7)	0.300 (7)	0.369 (7)
C(4)	0.211 (8)	0.318 (8)	0.395 (9)
C(5)	0.268 (11)	0.371 (13)	0.892 (24)
C(6)	0.228 (11)	0.382 (13)	0.846 (20)
C(7)	0.274 (11)	0.468 (14)	0.610 (18)
C(8)	0.257 (11)	0.414 (13)	0.684 (18)
C(9)	0.223 (10)	0.363 (11)	0.710 (17)
C(10)	0.254 (10)	0.415 (13)	0.582 (15)

Table VI. Selected Distances (Å) in $Ni(C_6H_5N{=}NC_6H_5)((CH_3)_3C{-}N{\equiv}C)_2$

	Bond Distances	
Ni-C(1)	1.842 (5)	1.841 (5)[a]
Ni-C(2)	1.839 (5)	
Ni-N(1)	1.897 (4)	1.898 (4)
Ni-N(2)	1.899 (5)	
C(1)-N(3)	1.155 (6)	1.156 (6)
C(2)-N(4)	1.156 (6)	
N(3)-C(3)	1.437 (6)	1.440 (7)
N(4)-C(4)	1.442 (7)	
C(3)-C(5)	1.370 (13)	1.44 (6)
C(3)-C(6)	1.395 (12)	
C(3)-C(7)	1.481 (13)	
C(4)-C(8)	1.418 (13)	
C(4)-C(9)	1.443 (11)	
C(4)-C(10)	1.525 (13)	
N(1)-N(2)	1.385 (5)	
N(1)-C(11)	1.421 (5)	1.423 (5)
N(2)-C(17)	1.424 (5)	
C(11)-C(12)	1.383 (6)	1.381 (8)
C(12)-C(13)	1.378 (7)	
C(13)-C(14)	1.385 (8)	
C(14)-C(15)	1.382 (8)	
C(15)-C(16)	1.368 (7)	
C(16)-C(11)	1.387 (6)	
C(17)-C(18)	1.382 (7)	1.383 (9)
C(18)-C(19)	1.389 (8)	
C(19)-C(20)	1.380 (9)	
C(20)-C(21)	1.372 (9)	
C(21)-C(22)	1.391 (8)	
C(22)-C(17)	1.385 (7)	
	Nonbonded Distances	
C(1)-C(2)	2.856 (7)	
N(1)-C(1)	3.021 (6)	3.020 (6)
N(2)-C(2)	3.017 (6)	
N(1)-C(12)	2.477 (6)	2.475 (6)
N(2)-C(18)	2.472 (6)	
N(1)-C(16)	2.399 (6)	2.395 (6)
N(2)-C(22)	2.392 (6)	
N(1)-C(18)	2.723 (6)	2.732 (13)
N(2)-C(12)	2.740 (6)	
N(1)-C(22)	3.584 (6)	3.589 (7)
N(2)-C(16)	3.593 (6)	
N(1)-C(17)	2.324 (5)	2.325 (5)
N(2)-C(11)	2.325 (5)	

[a] These are average quantities. The estimated standard deviation in parentheses is the larger of an individual standard deviation or of the standard deviation of a single observation as calculated from the mean on the assumption that the quantities involved are equivalent. The excellent agreement between the two ways of estimating standard deviations is a test of the reasonableness of the values derived from the inverse matrix and of equivalence of the distances involved.

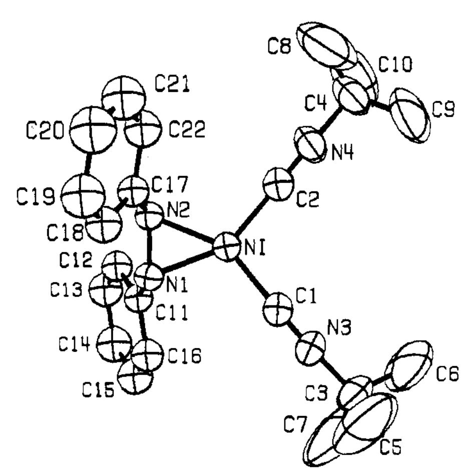

Figure 1. The $Ni(C_6H_5N{=}NC_6H_5)((CH_3)_3CN{\equiv}C)_2$ molecule, with H atoms omitted for the sake of clarity. The 50% probability ellipsoids of thermal vibration are shown.

Description and Discussion of Structure

The crystal structure consists of the packing of monomeric molecules. There are no unusual intermolecular contacts.

A drawing of the molecule is presented in Figure 1, which also indicates the atom numbering scheme. Figure 1 displays the vibrational thermal ellipsoids and Table V presents the root-mean-square amplitudes of vibration. The methyl carbon atoms exhibit high thermal motion, but otherwise the vibrational data are qualitatively reasonable. No attempt was made to correct the interatomic distances for thermal motion. Tables VI, VII, and VIII present relevant bond distances and angles.

Although there are no crystallographic requirements, the molecule possesses essentially C_2 symmetry. This is evident from Figure 1. Note in Table I that a given atom at x, y, z has its pseudosymmetry equivalent at approximately $^1/_2 - x, y, ^1/_2 - z$.

The gross features of the structure are similar to those of the related tetracyanoethylene complex,[10] $Ni((CN)_2C{=}C(CN)_2)((CH_3)_3C{-}N{\equiv}C)_2$, and it is instructive to compare parameters for the two structures. With azobenzene regarded as a single ligand, the Ni atom has its expected trigonal coordination. The dihedral angle between the Ni-N(1)-N(2) and Ni-C(1)-C(2) planes is only 1.2 (3)°, and the N(1)-N(2) vector makes an angle of 88.8 (3)° with the normal to the Ni-C(1)-C(2) plane. Hence the inner coordination sphere is essentially planar. Indeed, the maximum displacement of any of the atoms Ni, N(1), N(2), N(3), N(4), C(1), C(2), C(3), and C(4) from the least-squares plane through these atoms (Table IX) is 0.070 (9) Å. The planarity observed here contrasts with the rather large dihedral angle of 23.9° between the Ni-C-C (of tetracyanoethylene) and Ni-C-C (of *tert*-butyl isocyanide) planes in $Ni((CN)_2C{=}C(CN)_2)\ ((CH_3)_3C{-}N{\equiv}C)_2$. The reasons for this difference are not obvious,[22] but one set of recent calculations[23] does indicate that a

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Table VII. Selected Intramolecular Bond Angles (deg) in $\mathrm{Ni(C_6H_5N{=}NC_6H_5)((CH_3)_3C{-}N{\equiv}C)_2}$

C(1)-Ni-C(2)	101.8 (2)	
N(1)-Ni-N(2)	42.8 (2)	
C(1)-Ni-N(1)	107.8 (2)	107.7 (2)
C(2)-Ni-N(2)	107.6 (2)	
Ni-C(1)-N(3)	178.7 (5)	178.9 (5)
Ni-C(2)-N(4)	179.1 (5)	
C(1)-N(3)-C(3)	175.3 (5)	176.4 (1.6)
C(2)-N(4)-C(4)	177.5 (6)	
N(3)-C(3)-C(5)	111.1 (7)	108.7 (1.7)
N(3)-C(3)-C(6)	108.6 (7)	
N(3)-C(3)-C(7)	108.1 (7)	
N(4)-C(4)-C(8)	108.7 (7)	
N(4)-C(4)-C(9)	109.6 (6)	
N(4)-C(4)-C(10)	106.1 (7)	
C(5)-C(3)-C(6)	116.2 (1.3)	110.0 (5.5)
C(5)-C(3)-C(7)	108.6 (1.2)	
C(6)-C(3)-C(7)	103.7 (1.1)	
C(8)-C(4)-C(9)	117.6 (1.1)	
C(8)-C(4)-C(10)	105.9 (1.1)	
C(9)-C(4)-C(10)	108.3 (1.0)	
Ni-N(1)-N(2)	68.7 (2)	68.6 (2)
Ni-N(2)-N(1)	68.5 (2)	
Ni-N(1)-C(11)	109.6 (3)	109.6 (3)
Ni-N(2)-C(17)	109.6 (3)	
N(1)-C(11)-C(12)	124.2 (4)	123.9 (5)
N(2)-C(17)-C(18)	123.6 (4)	
N(1)-C(11)-C(16)	117.4 (4)	117.1 (5)
N(2)-C(17)-C(22)	116.8 (4)	
N(1)-N(2)-C(17)	111.6 (3)	111.8 (3)
N(2)-N(1)-C(11)	111.9 (3)	
C(12)-C(11)-C(16)	118.3 (4)	120.0 (1.4)
C(11)-C(12)-C(13)	121.3 (5)	
C(12)-C(13)-C(14)	120.1 (5)	
C(13)-C(14)-C(15)	118.5 (6)	
C(14)-C(15)-C(16)	121.4 (6)	
C(15)-C(16)-C(11)	120.5 (5)	
C(18)-C(17)-C(22)	119.6 (4)	120.0 (1.2)
C(17)-C(18)-C(19)	121.1 (5)	
C(18)-C(19)-C(20)	119.3 (6)	
C(19)-C(20)-C(21)	119.5 (7)	
C(20)-C(21)-C(22)	121.8 (6)	
C(21)-C(22)-C(17)	118.7 (5)	

Table VIII. Intraplanar and Vector–Plane–Normal Angles (deg) in $\mathrm{Ni(C_6H_5N{=}NC_6H_5)((CH_3)_3C{-}N{\equiv}C)_2}$

Dihedral angles[a]		Vector–plane–normal angles[a]	
Ni-N(2)-N(1) Ni-C(1)-C(2)	1.2 (3)	N(1)-N(2) Ni-C(1)-C(2)	91.2 (3)
C(1)-Ni-N(1) C(2)-Ni-N(2)	179.3 (2)	N(1)-N(2) C(17)-C(19)-C(21)	78.3 (3)
C(11)-C(13)-C(15) C(17)-C(19)-C(21)	49.0 (3)	N(2)-N(1) C(11)-C(13)-C(15)	79.1 (3)
N(1)-N(2)-C(11) N(2)-N(1)-C(17)	26.8 (4)	N(1)-C(11) C(11)-C(13)-C(15)	93.9 (3)
N(2)-N(1)-C(17) C(17)-C(19)-C(21)	14.3 (4)	N(2)-C(17) C(17)-C(19)-C(21)	93.2 (4)
N(1)-N(2)-C(11) C(11)-C(13)-C(15)	13.9 (4)		
Ni-N(1)-N(2) N(1)-N(2)-C(11)	103.3 (3)		
Ni-N(2)-N(1) N(2)-N(1)-C(17)	103.4 (3)		

[a] The senses of these angles are defined in ref 10.

Table IX. Weighted Least-Squares Planes[a]

Atom	Deviations from the planes (Å) of atoms used to define the planes Plane 1	2	3
Ni	0.002 (1)		
N(1)	−0.027 (4)	−0.027 (4)	
N(2)	0.005 (4)		0.019 (3)
N(3)	−0.012 (5)		
N(4)	−0.002 (5)		
C(1)	0.003 (6)		
C(2)	0.010 (5)		
C(3)	−0.003 (8)		
C(4)	−0.070 (9)		
C(11)		0.038 (4)	
C(12)		0.013 (5)	
C(13)		−0.008 (6)	
C(14)		−0.033 (6)	
C(15)		−0.006 (6)	
C(16)		0.017 (5)	
C(17)			−0.030 (4)
C(18)			−0.015 (5)
C(19)			0.017 (7)
C(20)			0.031 (7)
C(21)			0.011 (7)
C(22)			−0.014 (5)

[a] Plane equation: $Ax + By + Cz - D = 0$ with x, y, z in monoclinic coordinates, A, B, C, and D in ångströms.

	A	B	C	D
Plane 1	2.623	−0.447	9.609	3.068
Plane 2	2.521	15.686	2.705	1.400
Plane 3	4.065	−15.610	0.924	1.179

planar configuration should be the most stable for an isolated zerovalent metal complexes.

The average Ni—C and C≡N distances are 1.841 (5) and 1.156 (6) Å, respectively. These differ somewhat from the corresponding bond lengths of 1.866 (5) and 1.143 (5) in the tetracyanoethylene complex,[10] possibly indicating that azobenzene is a poorer acceptor relative to tetracyanoethylene.[8] The average N—C distance is 1.440 (7) Å, and each C≡N—C fragment is essentially linear. There is some variation in the C–($\mathrm{CH_3}$) distances and the $\mathrm{CH_3}$-C-$\mathrm{CH_3}$ angles, but the overall averages of 1.44 (6) Å and 110.0 (5.5)° are reasonable. The variations are probably not significant.

The nitrogen–nitrogen distance in the coordinated azobenzene molecule is 1.385 (5) Å, and this is significantly longer than the corresponding distance in free azobenzene. The two different molecules in the asymmetric unit of *trans*-azobenzene have N—N distances[24] of 1.243 (3) and 1.172 (3) Å, while the corresponding bond distance in *cis*-azobenzene is 1.23 Å.[25] Structural data on other azo compounds[26–28] give N=N distances in the range 1.24–1.26 Å, so that 1.24 Å seems to be an acceptable N=N double-bond length. As has been pointed out by Doedens and Ibers,[6] there is a scarcity of data on N-N single bond lengths, but a distance of 1.40 Å seems to be reasonable. We conclude then that one effect of coordination of azobenzene to the $\mathrm{Ni((CH_3)_3C{-}N{\equiv}C)_2}$ moiety is to lengthen the N—N distance to that of an N—N single bond.

The nitrogen atoms of azobenzene are equidistant from the metal, with an average Ni–N bond length of 1.898 (4) Å. If Ni and N covalent radii of 1.35[29] and 0.70 Å, respectively, are accepted, then the observed Ni–N distance is somewhat shorter than the single-bond distance predicted by summing the covalent radii.

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Similar observations of short metal–nitrogen distances in the complexes $(CH_3N_2CH_3)Fe_2(CO)_6$ and $C_{12}H_8N_2Fe_2(CO)_6$ have been discussed by Doedens.[7] The N(1)–Ni–N(2) angle of 42.8 (2)° is very similar to the N–Fe–N angles in the μ-methazo-iron complex.[6]

The average N–C(phenyl) distance is 1.423 (5) Å and the average N–N–C(phenyl) angle is 111.8 (3)° in the coordinated azobenzene molecule. These are little different from those for free *trans*-azobenzene, where corresponding bond distances of 1.433 and 1.472 Å and bond angles of 113.6 and 111.1° have been reported[24] for the two molecules in the asymmetric unit. In the Ni complex, there is some indication of steric strain resulting from nonbonded interactions of the azobenzene nitrogen atoms with *o*-carbon atoms of the phenyl rings. This effect, which was also noted in the structural study on free *trans*-azobenzene, is revealed by differences in the angles N(1)–C(11)–C(12) = 124.2 (4)° (or N(2)–C(17)–C(18) = 123.6 (4)°) and N(1)–C(11)–C(16) = 117.4 (4)° (or N(2)–C(17)–C(22) = 116.8 (4)°) and by the rather short nonbonded distances of 2.740 (6) and 2.723 (6) Å for N(2)···C(12) and N(1)···C(18), respectively.

There is a large dihedral angle of 49.0 (3)° between the planes of the two phenyl rings, and it is useful to consider two separate components of this angle. First, there is a rotation of 14.1 (4)° of the phenyl rings about the N–C(phenyl) bond axis. This angle would be 0° if the molecule were strictly planar, but is 6.0 and 17.1° in the two molecules of free *trans*-azobenzene. Presumably, these rotation angles are the result of an attempt to relieve the steric strain mentioned earlier. There is then a skew angle of 26.8 (4)° between the two N–N–C-(phenyl) planes in the present complex. If the C–N–N–C part of the azobenzene molecule were planar, as it is in free azobenzene, then this angle would be 0°. The skew angle in coordinated azobenzene is analogous in a sense to the angles resulting from the bending back of substituents on olefins that are coordinated to transition metals.[22] Thus the N–N bond lengthening and the geometry within the coordinated azobenzene are consistent with the usual description[30] of the π bonding of olefins to transition metals.

On the basis of this type of description, we would suggest forward donation from a filled N=N π_{xy} orbital to a vacant dp^2 hybrid orbital ($d_{xy} + p_x + p_y$) on nickel plus back-donation from a filled $d_{x^2-y^2}$ orbital on the metal to an unoccupied $\pi_{xy}{}^*$ antibonding orbital of the azo function. There is no indication that the nitrogen lone pairs participate in the bonding scheme. Indeed, the approximately tetrahedral geometry assumed by the bonded nitrogen atoms suggests to us that the lone-pair electrons occupy orbitals that are directed away from the metal.

A current view is that the biological nitrogen fixation process involves some form of diimide (HN=NH), and a suggested pathway[12] involves several reduction steps.

$$N_2 \longrightarrow [\text{diimide}] \longrightarrow [\text{hydrazine}] \longrightarrow NH_3$$

It has been established[12] that the reduction intermediates must remain bonded to the metal if this pathway is used by nitrogen-fixing organisms, but the nature of the diimide–metal intermediates remains obscure.[12,31–33] Confirmation of the π-bonded nature of the azobenzene to Ni(0) interaction provides a useful model for consideration of the possible role of this type of linkage in nitrogen fixation. It may be particularly significant that the apparent requirements for the formation of π-bonded azobenzene–metal complexes are a very basic metal system and mild conditions for formation. High metal basicity[34] is achieved in the present system through the use of a zerovalent d^{10} metal system combined with relatively poor $d\pi$-acceptor ligands. These requirements are remarkably similar to those that must apply in the biological process where a porphyrin–metal system provides a basic metal site and ambient conditions prevail.

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