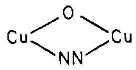
magnetic interactions (up to -100 cm^{-1})[21] than substituted-oxide bridges.[22-24] With the assumption that the exchange via the oxygen atom is the most important, the actual J value is relatively small in view of what can be expected from a correlation between the J value and the Cu–O–Cu angle, as reported by Hatfield et al.[25] Although the observed bridge angle (Cu(1)–O(31)–Cu(2)* = 119.0°) is far beyond the region in which the linear relationship has been observed, a $2J$ value of -1600 cm^{-1} would be expected.[25] Even compared with the pyridine N-oxide bridged systems[23] ($2J \approx -900$), the observed J value is very small. The distortion of the geometry of the Cu(1) atom from square planar toward tetrahedral, as additionally seen from the angles between the O(31)–Cu(1)–O(41) and N(11)–Cu(1)–N(22) planes (that amounts to 27.7°), may be the main reason for the small J value. In this case the magnetic orbital for Cu(1) may not be entirely $d_{x^2-y^2}$, bringing the direction of the molecular orbital containing the unpaired spin density out of the Cu_4 plane[22,26-29] and reducing the exchange interaction.

So that further information about the electronic structure of the tetranuclear compound could be obtained, EPR spectra were recorded. When the approximation of magnetic dimers would be valid, one might expect triplet EPR spectra.[30] However, spectra recorded both at X-band and at Q-band frequencies (77 and 300 K) did only show broad, structureless bands, indicating that either the coupling between the dimers is too strong to observe triplet spectra or the zero-field splittings in the triplet states are too large (larger than the Q-band frequency) to be observed.

Concluding Remarks

The present study has made clear that interesting, new coordination compounds of Cu^{II} may be obtained by oxidation of Cu^{I} coordination compounds. One should however be aware of the occurrence of side reactions, as met in the present preparation. As is shown, the solvent was oxidized and a reaction of the oxidized product with the ligand 3(5)-methylpyrazole followed, giving an interesting new type of ligand. Although the mechanism of formation is not clear, it is evident that both the moist air and the ethanol play a key role in the formation of the title compound. The observed, relatively weak magnetic exchange within the tetranuclear cluster might be due to the fact that half of the copper ions has a magnetic orbital which is not coplanar with the unit



Further studies in which different pyrazole ligands and counterions are used are in progress.

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Registry No. $Cu_4(MPZ)_4(AcMPZ)_2(NO_3)_2$, 80997-18-8; $Cu^I(MPZH)_2(NO_3)$, 81011-46-3; ethanol, 64-17-5; $Cu(MPZH)_4(NO_3)_2$, 41667-46-3.

Supplementary Material Available: A listing of structure factor amplitudes, tables of thermal parameters of all atoms, and additional information about bond angles and bond distances for the ring systems and hydrogen to carbon and nitrogen bonds (12 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactivity of Bis(1,4-diaryltetraazabutadiene)nickel Complexes. Crystal and Molecular Structure of Bis[1,4-bis(3,5-dimethylphenyl)tetraazabutadiene]nickel

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Bis(tetraazabutadiene)nickel complexes, $[Ni(Ar_2N_4)_2]$, have been prepared by reactions of bis(1,5-cyclooctadiene)nickel or bis(cyclopentadienyl)nickel with aryl azides (Ar = 4-MeC_6H_4, 4-MeOC_6H_4, 4-ClC_6H_4, and $3,5\text{-Me}_2C_6H_3$). The reaction with bis(cyclopentadienyl)nickel proceeds via $[Ni(Ar_2N_4)(\eta^5\text{-}C_5H_5)]$. The crystal and molecular structure of bis[1,4-bis(3,5-dimethylphenyl)tetraazabutadiene]nickel, which is the first example of a bis(tetraazabutadiene)metal complex, have been determined by a single-crystal X-ray diffraction study. Crystals are tetragonal, space group $P4_2/n$, with $Z = 2$ in a unit cell of dimensions $a = b = 9.677$ (1) and c = 16.601 (1) Å. The final R value is 0.034 for 1307 reflections. The nickel atom has a pseudotetrahedral geometry with two planar Ar_2N_4 ligands orientated perpendicular to each other. Furthermore the three N–N bond distances are nearly equal with a mean value of 1.322 Å. On the basis of these structural features the compounds are formulated as 18e Ni^0 species. Bis[1,4-bis(4-tolyl)tetraazabutadiene]nickel reacts with *tert*-butyl isocyanide to give $[Ni[1,4\text{-}(4\text{-MeC}_6H_4)_2N_4](t\text{-BuNC})_2]$. The latter product could also be prepared via the 1/1 reaction of $[Ni[1,4\text{-}(4\text{-MeC}_6H_4)_2N_4]_2]$ with $[Ni(t\text{-BuNC})_4]$ in the presence of excess t-BuNC.

Introduction

The reactions of organic azides with transition-metal complexes have attracted considerable attention in recent years. Among the products are isocyanate (RNCO), imido (RN), ureylene (RNCONR), imino (RHN), and tetraazabutadiene (RN_4R) derivatives.[1]

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[1] See: Cenini, S.; La Monica, G. *Inorg. Chim. Acta Rev.* **1976**, *18*, 179.

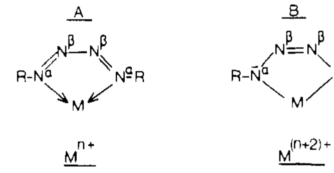


Figure 1. Two canonical forms for the formal valence structure of the coordinated tetraazabutadiene ligand.

Of the polyazo ligands such as triazenido(RN_3R),[2] triazabutadiene (HNC(R)NNH),[3,6] tetrazene ($R_2N_4R_2$),[4] and triarylformazans ($RN_2C(R)N_2R$),[5] the triazabutadiene (RNC(R)N_2R)[3,6] and the tetraazadiene(RN_4R) ligands are rather special as they have to be generated at a metal center and subsequently stabilized by coordination because they are unstable as free molecules.

Since 1967 several tetraazabutadiene complexes have been reported, including derivatives of Ni, Pt, Co, Ir, Rh, and Fe.[7] These complexes contain only one tetraazabutadiene ligand, which is proposed to be chelate bonded. They are stable in air and show no reactivity of the R_2N_4 unit.[8]

In three cases crystal structure determinations were carried out in order to obtain more information about the bonding in these complexes.[7a–c] For the metal–N_4 chelate ring a number of canonical forms have been proposed,[7a–c,g,i,o,r] and several calculations have been performed on the MN_4 moiety.[7c,r–u] The results of these calculations seem to vary with the method adopted, and no model presented seems to be able to account for all known structures and observations in the chemistry of the tetraazabutadiene–metal complexes. However, the simple valence-bond representations depicted in Figure 1, in which the Ar_2N_4 ligand acts either as a 4e (A) or a 2e (B) donor ligand, seem to be relevant in considering these complexes.

Table I

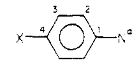
^{1}H NMR of $[Ni(Ar_2N_4)_2]$

Ar	CH_3	δ ortho	δ meta	J_{AB}, Hz	solvent
$4\text{-}MeC_6H_4$	1.50	8.40	6.50	8	toluene-d_8
$4\text{-}MeOC_6H_4$	3.40	9.10	6.80	8	C_6D_6
$4\text{-}ClC_6H_4$		8.10	6.80	9	C_6D_6
$3,5\text{-}Me_2C_6H_3$	2.35	8.50	7.05 (para)		C_6D_6

^{1}H NMR of $[Ni(t\text{-}BuNC)_2(Ar_2N_4)]$

Ar	*t*-Bu	CH_3(tolyl)	δ ortho	δ meta	J_{AB}, Hz	solvent
$4\text{-}MeC_6H_4$	1.35	2.30	7.40	7.05	8	acetone-d_6
$3,5\text{-}Me_2C_6H_3$	1.30	2.30	7.10	6.75 (para)	8	acetone-d_6

^{13}C NMR of $[Ni(Ar_2N_4)_2]$[a]



X	chem shift, ppm 1	2	3	4	CH_3
Me	152.2	123.9	131.8	138.2	21.3
Cl	153.2	127.8	132.9	135.7	
MeO	148.7	125.7	116.9	160.2	55.7
$3,5\text{-}Me_2$	141.1	124.6	129.6	130.6	21.4

[a] In THF-d_8 at room temperature.

Table II. FD Mass Spectra[a] Data of $Ni(Ar_2N_4)_2$ Complexes

Ar	*M*	*m/z*[b] obsd peaks (rel intens)
$4\text{-}MeC_6H_4$	534	*534* (*100*), 535 (30), 536 (32), 537 (13), 538 (9), 539 (5), 540 (4), 541 (2)
$4\text{-}MeOC_6H_4$	598	*598* (*100*), 599 (48), 600 (55), 601 (27), 602 (22)
$3,5\text{-}Me_2C_6H_3$	590	*590* (*100*), 591 (50), 592 (64), 593 (27), 594 (14), 595 (8), 596 (5)
$4\text{-}ClC_6H_4$	614	614 (62), 615 (24), *616* (*100*), 617 (42), 618 (86), 619 (27), 620 (39), 621 (16), 622 (16), 623 (17)

[a] Emitter current = 10 mA. [b] The italicized ions represent the highest intensity peak in the parent ion pattern. *M* is the mass of the parent ion calculated for Ni = 58, C = 12, H = 1, N = 14, O = 16, and Cl = 35.

Two main synthetic methods leading to tetraazabutadiene–metal complexes have been described: namely, reaction of a metal complex with either a diazonium salt[7b] or an azide. The mechanism for both types of reactions have been discussed.[7g,j,k] Azides, activated by strongly electron-withdrawing substituents, were used in some cases. Examples are $[Ni[1,4\text{-}(C_6F_5)_2N_4](COD)]$[7j] and $[Pt[1,4\text{-}(4\text{-}MeC_6H_4SO_2)_2N_4](PPh_3)_2]$.[7n]

In order to obtain more insight into the properties of tetraazabutadiene–metal complexes and the mechanisms of formation, we have studied reactions of zerovalent nickel and platinum complexes with aryl azides containing substituents with moderate inductive and mesomeric effects. In this paper we report the synthesis of the first bis(tetraazabutadiene)metal complexes: $[Ni(Ar_2N_4)_2]$ (Ar = $4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$, $4\text{-}ClC_6H_4$, $3,5\text{-}Me_2C_6H_3$) via reactions of either $[Ni(COD)_2]$ or $[Ni(Cp)_2]$ with the corresponding azides. The latter reactions proceed via $[Ni(Ar_2N_4)(Cp)]$.

The bonding in these $[Ni(Ar_2N_4)_2]$ complexes will be discussed on the basis of the X-ray crystal structure determination of $[Ni[1,4\text{-}(3,5\text{-}Me_2C_6H_3)_2N_4]_2]$ and data obtained from NMR and IR measurements.

A comparison is made between $[Ni(Ar_2N_4)_2]$ complexes and isoelectronic $[Ni(R\text{-}DAB)_2]$ complexes.[9]

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(8) Recently we reported the first examples of reactions involving transfer of complete tetraazabutadiene ligands between either two Ni centers or one Ni and one Pt center.[7p] These reactions proceed via an isolable intermediate in which two metals are bonded to one tetraazabutadiene ligand. This indicates that in addition to the proven σ,σ-N,N′-bonding mode for the R_2N_4 moiety other coordination modes, possibly like those of the isoelectronic RN═CHCH═NR (R-DAB) ligand are feasible.[24]

It will be shown that one of the coordinated tetraazabutadiene ligands is displaced upon reactions of these complexes with *tert*-butyl isocyanide. Part of this work has been reported in a preliminary communication.[7c]

Experimental Section

All preparations were carried out in a dry deoxygenated N_2 atmosphere, unless otherwise stated. All solvents were dried and distilled prior to use. Bis(1,5-cyclooctadiene)nickel ([Ni(COD)$_2$]),[10] *tert*-butyl isocyanide (*t*-BuNC),[11] 4-MeC$_6$H$_4$N$_3$, 4-MeOC$_6$H$_4$N$_3$, 3,5-Me$_2$C$_6$H$_3$N$_3$, 4-NO$_2$C$_6$H$_4$N$_3$, 4-ClC$_6$H$_4$N$_3$, 3,5-Cl$_2$C$_6$H$_3$N$_3$,[12] and bis(cyclopentadienyl)nickel ([Ni(Cp)$_2$])[13] were prepared according to the literature. ^{1}H NMR spectra were recorded on Varian HA-100, XL-100, and T-60 spectrometers at various temperatures in C$_6$D$_6$ and toluene-d_8. ^{13}C NMR spectra were recorded on a Bruker WP 80 spectrometer in THF-d_8 at ambient temperature. For NMR data see Table I.

Infrared spectra of the compounds in KBr disks were recorded on Beckman IR 4250 and Perkin-Elmer 283 spectrophotometers. Ultraviolet and visible spectra were measured with a Cary 14 spectrophotometer.

Field desorption mass spectra were obtained with a Varian MAT 711 spectrometer. The samples were loaded onto the emitter with the dipping technique. For FD-mass spectral data see Table II.

Preparation of Bis[1,4-bis(4-tolyl)tetraazabutadiene]nickel, [Ni[1,4-(4-MeC$_6$H$_4$)$_2$N$_4$]$_2$] (I). Via [Ni(COD)$_2$]. I was prepared by the addition of 4-MeC$_6$H$_4$N$_3$ (4 g, 30 mmol) to bis(1,5-cyclooctadiene)nickel ([Ni(COD)$_2$]) (2 g, 7.3 mmol) in toluene (30 mL) at −10 °C. The reaction was exothermic, and the mixture turned black immediately. After the evolution of N_2 had ceased, the reaction mixture was brought into the air and extracted with toluene in a Soxhlet apparatus. The extract was concentrated to 10 mL under reduced pressure and chromatographed with toluene on a silica-60 column (1 m × 2 cm). A deep purple fraction was collected separately, evaporated to dryness in vacuo, and washed with pentane (3 × 100 mL) to yield 0.82 g (21%) of microcrystalline [Ni[1,4-(4-MeC$_6$H$_4$)$_2$N$_4$]$_2$] (I), dec pt 180–185 °C. The bis(tetraazabutadiene)nickel complexes [Ni(Ar$_2$N$_4$)$_2$], in which Ar = 4-MeOC$_6$H$_4$ (II), 3,5-Me$_2$C$_6$H$_3$ (III), and 4-ClC$_6$H$_4$ (IV), were prepared in the same way. Yields varied from 20% to 25% for II and III to 1% for IV. Reactions of [Ni(COD)$_2$] with 3,5-Cl$_2$C$_6$H$_3$N$_3$ or 4-NO$_2$C$_6$H$_4$N$_3$ yielded as yet unidentifiable products.

Via [Ni(Cp)$_2$]. I was prepared by refluxing the azide (30 mmol) with [Ni(Cp)$_2$] (1.32 g, 7 mmol) in toluene until evolution of N_2 had ceased (ca. 2 h). Workup of the reaction mixture followed the same procedure as the previously described preparation. Yields in this preparation are lower (ca. 15%). During the reaction the color of the mixture changed form green via brown to black-purple. The brown color is indicative of the formation of [Ni(Ar$_2$N$_4$)(η^5-C$_5$H$_5$)], which has been isolated for Ar = 4-MeC$_6$H$_4$.[7c]

Analyses for Products I–IV Prepared via [Ni(COD)$_2$]. Anal. Calcd for I (C$_{28}$H$_{28}$N$_8$Ni): C, 62.92; H, 5.24; O, 0.00; N, 20.97; Ni, 10.86. Found: C, 63.1; H, 5.6; O, <0.2; N, 19.5; Ni, 10.7. Calcd for II (C$_{28}$H$_{28}$O$_4$N$_8$Ni): C, 56.12; H, 4.71: O, 10.68; N, 18.70; Ni, 9.80. Found: C, 56.4; H, 4.9; O, 10.4; N, 18.5; Ni, 9.7. Calcd for III (C$_{32}$H$_{36}$N$_8$Ni): C, 64.99; H, 6.14; O, 0.00; N, 18.95; Ni, 9.93. Found: C, 64.8; H, 6.2; O, <0.2; N, 18.8; Ni, 10.2. Calcd for IV (C$_{24}$H$_{16}$Cl$_4$N$_8$Ni): C, 46.72; H, 2.61; Cl, 22.98; N, 18.17; Ni, 9.51. Found: C, 46.4; H, 2.7; Cl, 22.3; N, 17.8; Ni, 9.2. IR spectra (in KBr) of I–IV have been deposited as supplementary material.

Preparation of Bis(*tert*-butyl isocyanide)[1,4-bis(4-tolyl)tetraazabutadiene]nickel, [Ni[1,4-(4-MeC$_6$H$_4$)$_2$N$_4$](*t*-BuNC)$_2$] (V). Via Direct Reaction with I. V was prepared by the dropwise addition of *t*-BuNC (2 mL, 19 mmol) to I (0.3 g, 1.1 mmol) in refluxing toluene (20 mL). During the addition the color of the reaction mixture changed from deep purple to green. After the mixture was cooled to room temperature, pentane was added (50 mL) and the mixture was left to crystallize for 18 h at −20 °C. Green microcrystalline [Ni[1,4-(4-MeC$_6$H$_4$)$_2$N$_4$](*t*-BuNC)$_2$] was obtained in 17% yield (85 mg) after the crystals were washed with pentane (3 × 3 mL).

Table III. Fractional Coordinates × 10^4 and Equivalent Thermal Parameters (Å^2) with Estimated Thermal Parameters in Parentheses

	x	y	z	B_{eq}
Ni	2500	2500	2500	3.2
N(1)	3637 (2)	2950 (1)	1643 (1)	3.6
N(2)	3131 (2)	2744 (2)	909 (1)	4.7
C(1)	5007 (2)	3493 (2)	1667 (1)	3.7
C(2)	5577 (2)	3720 (2)	2423 (1)	4.2
C(3)	6912 (3)	4245 (3)	2499 (1)	4.7
C(4)	7649 (2)	4518 (2)	1796 (2)	5.2
C(5)	7098 (2)	4300 (2)	1042 (1)	5.0
C(6)	5753 (2)	3790 (2)	975 (1)	4.5
C(7)	7533 (3)	4505 (4)	3314 (2)	6.7
C(8)	7946 (3)	4561 (3)	289 (2)	7.1

Alternative Preparations for [Ni(Ar$_2$N$_4$)(*t*-BuNC)$_2$]. (1) A solution of I (225 mg, 0.42 mmol) in 30 mL of toluene was added to [Ni(*t*-BuNC)$_4$] (165 mg, 0.42 mmol) in 10 mL of toluene in the presence of excess *t*-BuNC. The mixture was heated at 60 °C for 16 h. After the mixture was cooled to room temperature, 50 mL of pentane was added to the green reaction mixture, which was subsequently stored for 8 h at −20 °C. The resulting microcrystalline precipitate was isolated by decanting the solution and was washed with pentane (3 × 5 mL), yielding 180 mg (40%) of V.

(2) A solution of III (70 mg, 0.12 mmol) in 20 mL of toluene was added to a slurry of [Ni(COD)$_2$] (32 mg, 0.12 mmol) in 10 mL of toluene. The color of the mixture turned immediately brown. Addition of an excess of *t*-BuNC (1 mL, 9.6 mmol) changed the color to red-brown. With the same reaction conditions and methods as used in the preparation 1, [Ni[1,4-(3,5-Me$_2$C$_6$H$_3$)$_2$N$_4$](*t*-BuNC)$_2$] (VI) was isolated in 80% yield (95 mg). (Yields for methods 1 and 2 have been calculated on the total amount of Ni present.)

Anal. Calcd for V (C$_{24}$H$_{32}$N$_6$Ni): C, 62.22; H, 6.96; O, 0.00; N, 18.15; Ni, 12.67. Found: C, 62.0; H, 6.9; O, <0.2; N, 18.0; Ni, 12.7. Calcd for VI (C$_{26}$H$_{36}$N$_6$Ni): C, 63.56; H, 7.39; O, 0.00; N, 17.11. Found: C, 63.1; H, 7.3; O, <0.2; N, 16.7. IR spectra of V and VI have been deposited as supplementary material.

Crystal and Intensity Data. Crystals of III are tetragonal with space group $P4_2/n$, $Z = 2$, in a unit cell with dimensions $a = b = 9.677$ (1) and $c = 16.601$ (1) Å ($d_{calcd} = 1.26$ g cm^{-3}). A crystal in the shape of a tetragonal pyramid with both base edges and height 0.5 mm was used to collect 1478 independent reflections, of which 171 had intensities below the 2.5σ level and were considered as not significant. No absorption correction was applied ($\mu = 11.4$ cm^{-1}). The diffractometer used was a Nonius CAD 4 employing graphite-monochromatized Cu Kα radiation.

Structure Determination and Refinement. The space group symmetry requires nickel to be situated at the center of the $\bar{4}$ axes. The remaining nonhydrogen atoms could be located directly in an E^2–Patterson synthesis. Refinement proceeded by means of anisotropic block-diagonal least-squares calculations. The H atoms were indicated in a ΔF synthesis and were introduced with isotropic thermal parameters in the final cycles of refinement. A weighting scheme $w = (0.54 + F_o + 0.024F_o^2)^{-1}$ was used. An extinction correction

$$F_c^{cor} = F_c\left[1 + g|F_c|^2\frac{1 + \cos^4 2\theta}{(1 + \cos^2 2\theta)\sin 2\theta}\right]^{-1/4}$$

was included in the refinement; the final g value was 1.1×10^{-6}. The anomalous scattering of Ni was taken into account. The refinement converged to $R = 0.034$ for 1307 observed reflections.

The final coordinates are listed in Table III; they are referred to an origin at $\bar{1}$, which is $^1/_4$, $^1/_4$, $^1/_4$ from $\bar{4}$. Bond distances and angles are given in Table IV. Least-square planes (Table V), fractional coordinates and isotropic thermal parameters for H atoms (Table VI), and anisotropic thermal parameters (Table VII) have been deposited as supplementary material.

Results

Bis(tetraazabutadiene)nickel complexes were prepared by reacting [Ni(COD)$_2$] with the aryl azides 4-MeC$_6$H$_4$N$_3$, 4-

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(9) (a) tom Dieck, H.; Svoboda, M.; Greiser, Th. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36b* (7), 823. (b) Walther, D. *Z. Chem.* **1975**, *15*, 72. (c) Svoboda, M.; tom Dieck, H.; Krüger, C.; Tsay, Y-H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B* (7), 814. (d) tom Dieck, H.; Svoboda, M.; Kopf, J. *Ibid.* **1978**, *33B*, 1381.

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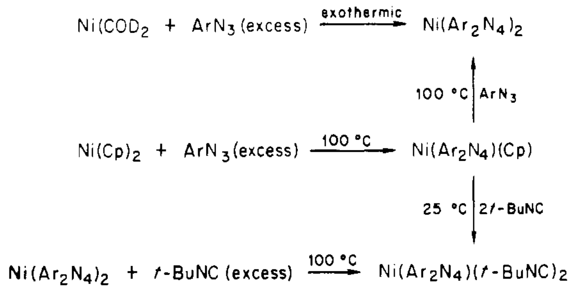
Table IV. Bond Lengths (Å) and Bond Angles (Deg) with Estimated Standard Deviations in Parentheses

Ni-N(1)	1.851 (2)	C(2)-C(3)	1.394 (4)
N(1)-N(2)	1.328 (3)	C(3)-C(4)	1.393 (4)
N(2)-N(2′)	1.309 (3)	C(3)-C(7)	1.502 (4)
N(1)-C(1)	1.427 (3)	C(4)-C(5)	1.377 (5)
C(1)-C(2)	1.388 (3)	C(5)-C(6)	1.396 (3)
C(1)-C(6)	1.387 (4)	C(5)-C(8)	1.517 (5)
N(1)-Ni-N(1′)	79.5 (1)	C(1)-C(2)-C(3)	120.5 (2)
N(1)-Ni-N(1″)	126.2 (1)	C(2)-C(3)-C(4)	117.9 (2)
Ni-N(1)-N(2)	116.8 (2)	C(2)-C(3)-C(7)	120.9 (2)
Ni-N(1)-C(1)	128.2 (2)	C(4)-C(3)-C(7)	121.2 (3)
N(2)-N(1)-C(1)	115.1 (2)	C(3)-C(4)-C(5)	122.3 (2)
N(1)-N(2)-N(2′)	113.5 (2)	C(4)-C(5)-C(6)	119.2 (3)
N(1)-C(1)-C(2)	116.9 (2)	C(4)-C(5)-C(8)	121.0 (2)
N(1)-C(1)-C(6)	122.5 (2)	C(6)-C(5)-C(8)	119.8 (2)
C(2)-C(1)-C(6)	120.6 (2)	C(1)-C(6)-C(5)	119.5 (3)

Scheme I



$MeOC_6H_4N_3$, 4-$ClC_6H_4N_3$, and 3,5-$Me_2C_6H_3N_3$. The reactions are exothermic and start directly when the reagents are mixed above −10 °C. No evidence for the presence of complexes containing only one Ar_2N_4 ligand, e.g., [Ni(Ar_2N_4)(COD)], was obtained. From the reactions of [Ni$(COD)_2$] with 3,5-$Cl_2C_6H_3N_3$ and 4-$NO_2C_6H_4N_3$, though equally exothermic, neither [Ni$(Ar_2N_4)_2$] nor [Ni(Ar_2N_4)(COD)] could be isolated.

Attempts to prepare the bis(tetraazabutadiene)nickel complexes on a larger scale generally led to lower yields. On a 2-g scale the yields of the [Ni$(Ar_2N_4)_2$] compounds varied between 21% for Ar = 4-MeC_6H_4 and 1% for Ar = 4-ClC_6H_4.

An alternative route for the preparation of the [Ni$(Ar_2N_4)_2$] compounds involves reaction of [Ni$(Cp)_2$] with aryl azide in toluene, a method requiring initial heating of the reaction mixture to 110 °C. In the case of Ar = 4-MeC_6H_4, a low yield of [Ni(Ar_2N_4)(η^5-C_5H_5)] could be isolated. This paramagnetic compound, which is a stable intermediate between [Ni$(Cp)_2$] and [Ni$(Ar_2N_4)_2$], has been characterized by X-ray structure determination[14] (see Scheme I).

The [Ni$(Ar_2N_4)_2$] complexes I–IV are intensely colored red- to blue-purple compounds (I, λ_{max} = 480 nm; II, λ_{max} = 560 nm), with an ϵ of 1.5×10^4 M^{-1} cm^{-1}. The compounds are thermally stable and decompose in air only upon heating to 180 °C. The complexes decompose slowly in acetone but very rapidly in CCl_4, $CHCl_3$, CH_2Cl_2, and acids.

IR spectra of I–IV did not provide evidence for the structure of these compounds. Bands attributable to vibrations arising from the N_4 moiety could not be assigned. ^1H NMR spectra of I–IV showed isochronous resonances for the four aryl groups, which remained equivalent on the NMR time scale from −80 to +25 °C.

Attempts to prepare [Ni(Ar_2N_4)L_2] compounds by substitution of one of the Ar_2N_4 ligands by CO, PPh_3, or 2,2′-bipyridine failed, the starting materials being recovered even after refluxing the reaction mixtures in toluene for 5 h.

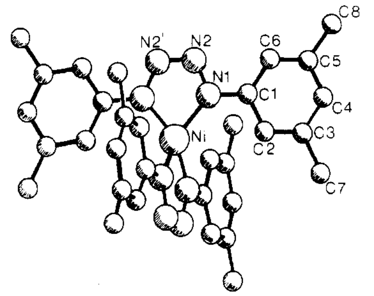


Figure 2. Structure of [Ni[1,4-(3,5-$Me_2C_6H_3)_2N_4]_2$] and the adopted numbering scheme.

Likewise both C_6H_5Br and MeI did not react with I.

Displacement of one Ar_2N_4 ligand was observed, however, on reacting I with *t*-BuNC in boiling toluene to give green [Ni(Ar_2N_4)(*t*-BuNC)$_2$] (IV) in 17% yield. The symmetric and asymmetric isocyanide stretching frequencies of IV appeared at 2168 and 2146 cm^{-1}, respectively, which pointed to terminally bonded *t*-BuNC ligands while the ^1H NMR spectra revealed the presence of two equivalent Ar groups. These observations are in accord with a four-coordinate tetrahedral Ni complex containing a σ,σ-N,N′ chelate-bonded Ar_2N_4 ligand.

Reaction of I (Ar = 4-MeC_6H_4) with [Ni(*t*-BuNC)$_4$] in the presence of excess *t*-BuNC in toluene resulted under mild conditions in the formation of [Ni(Ar_2N_4)(*t*-BuNC)$_2$] (V) which was isolated in 40% yield. The reactions of [Ni$(COD)_2$] with I or III led to as yet unidentified brown complexes. Reaction of these complexes with excess *t*-BuNC and heating to 60 °C for 8 h afforded [Ni(Ar_2N_4)(*t*-BuNC)$_2$], which was isolated in 40 and 80% yields for Ar = 4-MeC_6H_4 and 3,5-$Me_2C_6H_3$, respectively.

Molecular Geometry of [Ni[1,4-(3,5-$Me_2C_6H_3)_2N_4]_2$]. The molecular structure along with the adopted numbering scheme is shown in a PLUTO drawing (Figure 2). Bond distances and angles are given in Table IV. The crystal structure consists of discrete monomeric bis[1,4-bis(3,5-dimethylphenyl)tetraazabutadiene]nickel units. Each tetraazabutadiene ligand has its NiN_4 ring and aryl rings coplanar. (Root-mean-square deviation of the C and N ring atoms from the least-squares plane through Ni(Ar_2N_4) is 0.008 Å, with a maximum of 0.011 Å.) The ligands are perpendicular to each other, thus forming a pseudotetrahedral conformation around the nickel, with a N(1)-Ni-N(1′) angle of 79.5 (1)°. The N(1)-N(2) [N(1′)-N(2′)] and N(2)-N(2′) bond distances are nearly equal (1.328 (3) and 1.309 (3) Å, respectively).

Discussion

Molecular Geometry and Bonding in [Ni$(Ar_2N_4)_2$]. [Ni[1,4-(3,5-$Me_2C_6H_3)_2N_4]_2$ is the first example of a bis(tetraazabutadiene)metal complex, and the structural features of this compound provide an insight into the bonding of the tetraazabutadiene ligand to a metal center. Earlier X-ray crystal structure determinations[7a,b] of tetraazabutadiene–metal complexes have led to the proposal of canonical forms A and B (Figure 1) for the formal valence structure of the tetraazabutadiene ligand. Form A represents a formally neutral ligand with a conjugated arrangement of the double bonds. Bonding to the metal occurs via donative bonds of the sp^2-hybridized N^α atoms to the metal center. Form B represents a formally doubly negative charged ligand, which is σ bonded to the metal via the N^α atoms. In the latter case the N^α atoms have either a tetrahedral configuration (sp^3 hybridization) or a configuration in which the N^α–N^β, N^α–M, and N^α–R bonds are in one plane (sp^2 hybridization). In the planar situation the N^α lone pair resides in an orbital perpendicular to this plane.[15] The actual geometry around an N^α atom in a given

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[14] Overbosch, P.; van Koten, G.; Brieze, K.; Spek, A. L.; Roelofsen, G.; Duisenberg, J., submitted for publication in *Inorg. Chem.*

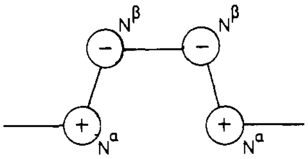

Figure 3. Nodal pattern of the LUMO of canonical form A (see Figure 1).

$M(R_2N_4)$ system of type B will be determined by the nature of R.

The difference between these two extreme bonding situations is that going from canonical structure A to B formally two electrons move from metal d orbitals into the LUMO of structure A (see Figure 3). This orbital is bonding between the N^{β} atoms and antibonding between the N^{α}–N^{β} pairs. Accordingly, distinctly different sets of N–N distances are expected for tetraazabutadiene complexes belonging to either one of these extreme descriptions. For the compounds belonging to class A, the N^{α}–N^{β} distances are expected to be shorter than the distance between the N^{β} atoms. However, this difference between N^{α}–N^{β} and N^{β}–N^{β} bond lengths will become less distinct because of conjugation within the NiN_4 system. This effect is enhanced when aryl groups are connected to the N^{α} atoms. For compounds in which canonical form B represents the predominant tetraazabutadiene–metal interaction, the reverse is expected, i.e., a short N^{β}–N^{β} distance and longer N^{α}–N^{β} distances. Indeed the N–N distances in the tetraazabutadiene–metal complexes studied so far by X-ray structure determinations seem to support these ideas. The crystal structure of 1,4-bis(*N*-ethyl-1,2-dihydrobenzothiazol-2-ylidene)tetrazene,[16] which contains a NN=NN fragment, can be used as a model for obtaining reasonable estimates for N=N and N—N bond distances, which amount to 1.257 (4) and 1.400 (4) Å, respectively. Accordingly, the $[Ir[1,4\text{-}(4\text{-}FC_6H_4)_2N_4](CO)(PPh_3)_2]^+BF_4^-$ complex with a N^{β}–N^{β} separation of 1.270 (16) Å and N^{α}–N^{β} distances of 1.350 (16) and 1.400 (16) Å can therefore be clearly seen to be a representative of class B.[17] The N–N separations of 1.328 (3) and 1.309 (3) Å found in III are intermediate between those of N=N and N—N bond lengths. This strongly suggests that this complex is a representative of type A in which electron delocalization via the conjugated π system of the aryl rings and N_4 skeleton has led to some equalization of the N–N distances owing to multiple bond character in the N_4 unit. The final[7o] data furthermore show that the N^{β}–N^{β} distance tends to be slightly shorter than the N^{α}–N^{β} distances, which suggests that canonical form B contributes to a little extent to the overall bonding.

Support for the view that in $[Ni(Ar_2N_4)_2]$ the nickel atom coordinates to two neutral ligands having a conjugated π system comes from the observation that the aryl rings in the Ar_2N_4 unit are coplanar with each other and with the NiN_4 ring. This planarity is to be expected in the case of π delocalization throughout the coordinated ligand system. Such coplanarity is not observed in tetraazabutadiene–metal complexes of type B. For example, in $[Ir[1,4\text{-}(4\text{-}FC_6H_4)_2N_4](CO)(PPh_3)_2]^+BF_4^-$ the aryl rings are 66 and 131° out of the MN_4 plane,[7b] in $[Ni[1,4\text{-}(4\text{-}MeC_6H_4)_2N_4](\eta^5\text{-}C_5H_5)]$ (N^{β}–N^{β} = 1.278 (3) Å) the aryl rings are 45 and 135° out of the MN_4 plane,[14] and in $[Co[1,4\text{-}(C_6F_5)_2N_4](\eta^5\text{-}C_5H_5)]$ (N^{β}–N^{β} = 1.279 (2) Å) the aryl rings are also reported to be twisted out of the MN_4 plane.[7c]

Another distinctive feature of the structure of III is the pseudotetrahedral coordination around the metal, with both Ar_2N_4 ligands perpendicular to each other. The distortion from the ideal tetrahedral angles is the result of the bite angle of the Ar_2N_4 ligand which lies in the range characteristic for bidentate ligands in five-membered chelate rings. These three structural features, i.e., the equal N–N distances, the flat Ar_2N_4 system, and the pseudotetrahedral geometry, indicate that III is best described as an 18e Ni^0 species having canonical form A mainly contributing to the bonding.

The infrared isocyanide stretching frequency can be used as a measure for the π-acceptor properties of unsaturated ligands in $[Ni(t\text{-}BuNC)_2L_2]$ complexes, as demonstrated by Ibers and Ittel.[18] The values of ν(NC) as found for V (2168 and 2146 cm^{-1}) show the tetraazabutadiene ligand to be a very strong π acceptor. For the $[Ni(Ar_2N_4)L_2]$ complexes this implies that the aryl tetraazabutadiene ligand probably shows a tendency toward form B (Figure 1) in the presence of less electron-withdrawing coligands but adopt form A if the coligands are equally strong π acceptors, i.e., in $[Ni(Ar_2N_4)_2]$. In this respect it is interesting to note that Trogler[7r] finds that the π-acceptor ability of the Me_2N_4 unit is comparable to that of two carbon monoxides in $[Fe[1,4\text{-}(Me)_2N_4](CO)_3]$ for which the preliminary results of an X-ray structure determination suggest this compound to contain equal N^{α}–N^{β} and N^{β}–N^{β} bond lengths of 1.32 Å.[7a]

Structure in Solution. The structures of I–IV in solution were studied by ^1H and ^{13}C NMR spectroscopy. The spectra, which were temperature independent in the range from −80 to +25 °C, showed no evidence for the existence of equilibria or fluxional processes.[19]

Accordingly, no evidence has been obtained pointing to a deviation from the pseudotetrahedral structure to a more planar configuration in these $[Ni(Ar_2N_4)_2]$ complexes. This constitutes an interesting difference between tetraazabutadiene and 1,4-diaza-1,3-butadiene (RNC(H)C(H)NR, R-DAB) ligands. Nickel complexes of R-DAB ligands have structures containing a coordination geometry around nickel ranging from planar to pseudotetrahedral. tom Dieck[9] has ascribed these changes to a dependence of the conformation on the electronic properties of the R substituent; electron-withdrawing substituents promoting a more planar configuration.[20] No such electronic effects on the geometry have been observed in the (tetraazabutadiene)nickel complexes. Changes in the electronic properties of the substituent affect the yields and the nature of the products, vide infra, but not the geometry neither in our experiments nor in those reported in the literature. An explanation for these differences awaits a more sophisticated theoretical model for both types of ligand complexes.

Synthesis. In our experiments we found that the yields of $[Ni(Ar_2N_4)_2]$ dropped from about 20% to 1% on going from $4\text{-}MeC_6H_4$ to $4\text{-}ClC_6H_4$. Attempted reactions of $[Ni(COD)_2]$ with aryl azides containing stronger electron-withdrawing substituents such as $3,5\text{-}Cl_2C_6H_3$ and $4\text{-}NO_2C_6H_4$ afforded no products identifiable as $[Ni(Ar_2N_4)_2]$ or $[Ni(Ar_2N_4)(COD)]$. In this respect it is interesting to note that Stone et al.[7j] reported the synthesis of the latter compound, i.e., $[Ni[1,4\text{-}(C_6F_5)_2N_4](COD)]$ from the reaction of $C_6F_5N_3$ with $[Ni(COD)_2]$ at −30 °C. To date we have been unable to obtain tetraazabutadiene complexes from reactions of [Ni(C-

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(15) The same situation is encountered in *N,N*-dimethyl-*p*-nitrosoaniline hydrochloride hydrate.[25]

(16) Allman, R. *Acta Crystallogr.* **1967**, *22*, 246.

(17) This argument was originally brought up by Einstein and Sutton.[7b] In a subsequent publication Sutton proposed another canonical structure for the Ir complex.[7g]

(18) (a) Ittel, S. D. *Inorg. Chem.* **1977**, *16*, 2589. (b) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.

(19) For example, no evidence for the breakup of the tetraazabutadiene ligand into a nitrene and a coordinated azide at probe temperature was obtained. Such a process was suggested by Cenini but later revoked.[7m,l] However, recently we have shown that such processes, although being slow, take place at higher temperatures.[23]

(20) The structure of $[Ni(R\text{-}DAB)_2]^9$ is pseudotetrahedral for R = cyclohexyl. For R = $2,6\text{-}Me_2C_6H_3$, the angle between the two NiDAB planes is 44.5°.

OD)$_2$] with alkyl azides.[21] These results suggest that the electronic properties of the R group of the azide RN_3 have a decisive influence on the outcome of the reaction with [Ni(COD)$_2$]: (i) no reaction takes place if R is an alkyl group; (ii) with strongly electron-withdrawing aryl substituents such as C_6F_5, [Ni(Ar_2N_4)(COD)] is formed; (iii) with mildly electron-withdrawing or -donating aryl substituents, [Ni(Ar_2N_4)$_2$] complexes are found.

If the reactions of [Ni(COD)$_2$] with aryl azides proceed via [Ni(Ar_2N_4)(COD)] to [Ni(Ar_2N_4)$_2$], analogous to the sequence [Ni(Cp)$_2$] via [Ni(Ar_2N_4)(Cp)] to [Ni(Ar_2N_4)$_2$],[14] the substituent on Ar may steer the reaction in yet another direction. In reactions with [Pt(Ar_2N_4)(COD)] complexes we found that the COD moiety becomes susceptible to nucleophilic attack for Ar = 4-$NO_2C_6H_4$.[22] Moreover, the products from the latter reactions appeared to be more susceptible toward further reaction and decomposition than [Pt(Ar_2N_4)(COD)] itself. As the reactions of [Ni(COD)$_2$] with ArN_3 are very exothermic, as opposed to the slow reactions of [Pt(COD)$_2$] with ArN_3, the activation of the COD ligand in [Ni(Ar_2N_4)(COD)] (Ar = 4-$NO_2C_6H_4$ or 3,5-$Cl_2C_6H_3$) might very well provide a route to decomposition in the hot reaction mixture.

Reactivity. In contrast to the extreme sensitivity of the [Ni(R-DAB)$_2$] (vide infra) to hydrolysis and oxidation,[8] all reported tetraazabutadiene complexes show exceptional stability and the [Ni(Ar_2N_4)$_2$] complexes can even be refluxed for days in toluene in air without appreciable decomposition.

So far most reported reactions of tetraazabutadiene–metal complexes with nucleophilic or electrophilic reagents have not involved the R_2N_4 ligand itself; the only exceptions are reactions of [Pt[1,4-(4-$MeC_6H_4SO_2$)$_2N_4$](PPh$_3$)$_2$] with HCl, which resulted in formation of [Pt(PPh$_3$)$_2$Cl$_2$], ArN_3 and $ArNH_2$,[7m] and the photochemical reaction of [Co(Ar_2N_4)(η^5-C_5H_5)].[7q] The reaction of [Ni(Ar_2N_4)$_2$] with *t*-BuNC, which is the first example of substitution of a tetraazabutadiene by direct reaction with a neutral ligand, could only be accomplished under drastic conditions.

Recently we reported reactions in which a complete tetraazabutadiene ligand was transferred intact from [Ni(Ar_2N_4)$_2$] to another Ni or Pt center under mild conditions. Furthermore, we found that reactions of [Ni(Ar_2N_4)$_2$] with [Ni($Ar_2{}^*N_4$)$_2$] in boiling toluene involve extensive exchange and rearrangement processes, producing mixtures of [Ni(Ar_2N_4)$_2$] complexes containing all possible permutations in Ar* and Ar.[23]

Since the chemically reactive [Ni(Ar_2N_4)$_2$] complexes are formed during an exothermic reaction between [Ni(COD)$_2$] and ArN_3, it is apparent that the final yield will depend strongly on the importance of side reactions of the above mentioned type.

Conclusions

Bis(tetraazabutadiene)nickel complexes, [Ni(Ar_2N_4)$_2$], can be prepared for a limited number of Ar groups. Although the tetraazabutadiene ligand is a very strong π acceptor, the abovementioned complexes can best be described as 18eNi^0 species on the basis of their structural features and diamagnetism. Despite the surprising stability of these complexes, they exhibit some reactivity of the tetraazabutadiene moiety, including ligand transfer,[7p] ligand exchange and rearrangement,[23] and direct substitution by *t*-BuNC. The latter reaction is one of three reactions leading to [Ni(Ar_2N_4)(*t*-BuNC)$_2$]. The other two are (i) the reaction of [Ni(Ar_2N_4)(Cp)] with 2 equiv of *t*-BuNC at 25 °C[14] and (ii) the reaction between [Ni(Ar_2N_4)$_2$], *t*-BuNC, and [Ni(*t*-BuNC)$_4$], at 60 °C, which probably involves ligand transfer.[7p]

Acknowledgment. We thank Professor K. Vrieze for helpful discussions, Dr. D. M. Grove for criticizing the manuscript, Dr. J. Zwinselman and Mr. R. H. Fokkens for recording the FD mass spectra, and Dr. C. H. Stam for his kind assistance with the crystal structure determination.

Registry No. I, 73432-46-9; II, 73440-06-9; III, 73440-07-0; IV, 80997-17-7; V, 73440-08-1; VI, 78677-38-0; Ni(COD)$_2$, 1295-35-8; Ni(Cp)$_2$, 1271-28-9; Ni(*t*-BuNC)$_4$, 19068-11-2; 4-$MeC_6H_4N_3$, 2101-86-2; 4-$MeOC_6H_4N_3$, 2101-87-3; 3,5-$Me_2C_6H_3N_3$, 70334-59-7; 4-$ClC_6H_4N_3$, 3296-05-7.

Supplementary Material Available: Listings of structure factor amplitudes, least-square planes (Table V), fractional coordinates and isotropic thermal parameters for H atoms (Table VI), anisotropic thermal parameters (Table VII), and IR data of compounds I–VI (9 pages). Ordering information is given on any current masthead page.

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(21) The reactions of carbonyl–nickel complexes with alkyl azides did not produce tetraazabutadiene–nickel complexes, as described by Otsuka and Nakamura.[7i]

(22) Overbosch, P.; van Koten, G.; Grove, D. M.; Spek, A. L.; Duisenberg, A. J. M., submitted for publication in *Inorg. Chem.*

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