"Side-On" Dinitrogen–Transition Metal Complexes. The Molecular Structure of $\{C_6H_5[Na{\cdot}O(C_2H_5)_2]_2[(C_6H_5)_2Ni]_2N_2NaLi_6(OC_2H_5)_4{\cdot}O(C_2H_5)_2\}_2$

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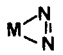
Abstract: The preparation of compound $\{C_6H_5[Na{\cdot}O(C_2H_5)_2]_2[(C_6H_5)_2Ni]_2N_2NaLi_6(OC_2H_5)_4{\cdot}O(C_2H_5)_2\}_2$ is presented, together with the determination of its structure by single-crystal x-ray diffraction techniques. The compound crystallizes in space group $P\bar{1}$, cell dimensions: $a = 15.775$ (4), $b = 18.689$ (5), $c = 23.607$ (5) Å; $\alpha = 66.02$ (2)°, $\beta = 66.39$ (2)°, $\gamma = 78.87$ (2)°; $Z = 2$; $R = 0.079$ for 9312 reflections, 4750 unobserved. A pseudocenter of symmetry is located between two $[(C_6H_5)_2Ni]_2N_2$ units, in which the N_2 ligands bridge "side-on" to nickel atoms of a $[(C_6H_5)_2Ni]_2$ system. This unit is furthermore stabilized by a $(C_6H_5)[NaO(C_2H_5)_2]_2$ bridge. The two $[(C_6H_5)_2Ni]_2N_2$ units are linked by two Na atoms and two $Li_6(OC_2H_5)_4{\cdot}O(C_2H_5)_2$ conglomerats. On the opposite side of the NiN_2 entity the nitrogen interacts with sodium. The lone pair electrons of the dinitrogen are pointed towards the midpoint of two Li-Li systems. Each of the phenyl rings of the $[Ni(C_6H_5)_2]_2$ interacts with Na and Li atoms, forming several multicenter two-electron bonds. The important average bond lengths (Å) are: N-N, 1.359 (18); N-Ni, 1.97 (3); N-Li, 2.05 (5); Ni-Ni, 2.749 (7); Li-Ni, 2.63 (5); Li-C, 2.42 (5); Na-Na, 3.191; Na-Ni, 2.96 (2); Na-N, 2.61 (3).

Complexes of dinitrogen are of considerable interest as models for biological nitrogen fixation as well as intermediate species in synthetic applications, especially in organic chemistry. Most of the reactions with a few of these compounds are of the protolysis type[1] although some examples of reaction with organic molecules (i.e., alkylhalides[2]) are also known. In recent years much work has been devoted to this field, and numerous reviews on the subject have been published.[3] Bonding of dinitrogen to transition metals may be postulated to proceed via several stereochemical possibilities, which may be divided into the "end-on" (**1–2**) and "side-on" categories (**3–4**). Most examples of stable dinitrogen complexes have been found to belong to category **1**.

$M{-}N{\equiv}N$ **1**

$M{-}N{\equiv}N{-}M$ **2**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Typical for this class of compounds is an only slightly elongated N-N bond length (1.11–1.12 Å) as compared to free dinitrogen (1.0976 Å), and only a few compounds[4] have been reported and fully characterized to show chemical reactivity in the above described sense. In only few of these well-defined compounds, however, does the dinitrogen seem to be sufficiently activated to be readily reduced to lower oxidation states. Similar comment can be made for the few examples of compounds of category **2**, in which two transition metals are bonded "end-on" to dinitrogen.[5] One compound of this type, $ReCl(P(CH_3)_2C_6H_5)_4{-}N_2{-}MoCl_4(OCH_3)$, is reported to exhibit a remarkable lengthening of the N-N bond (1.21 Å).[6]

The first isolated and characterized[7] compound of category **4** with "side-on" bonded dinitrogen, $\{[(C_6H_5Li)_3Ni]_2N_2{\cdot}2[O(C_2H_5)_2]\}_2$ (I), shows an even greater lengthening of the dinitrogen bond (1.34 Å).[8] This change upon complexation is reflected in the chemical reactivity of this class of compounds too, in which the "side-on" positions of the dinitrogen are occupied by two transition metals and the "end-on" positions by lithium atoms or lithium atom clusters. Supposedly the transition metals and lithium atoms interact synergetically to weaken the N-N bond. To extend the generality of this interaction, we have investigated the replacement of lithium by sodium in this type of compound.

Compound I was prepared by passing N_2 over an ethereal solution of phenyllithium and *all-trans*-1,5,9-cyclododecatrienenickel (CDTNi). When the phenyllithium in this formula is replaced by a mixture of LiC_6H_5/NaC_6H_5 (1/3–4), the reaction yields an orange crystalline powder (II), which has a $Ni{:}C_6H_5$ ratio of 1:3, a Li:Na ratio of 1:4, and a $N_2{:}Ni$ ratio of 1:2. II also contains variable amounts of diethyl ether. Out of the filtrate of II, crystals (III) were formed on standing at 0°C. In order to gain more information about the stereochemistry of such dinitrogen, organometallic compounds, we have investigated III by single-crystal x-ray diffraction methods.

Experimental Section

Unless specially noted, all preparations were made under argon. The solvents, pentane and diethyl ether, were dried over sodium tetraethylaluminate and freshly distilled before use. The analyses for nickel were made titrimetrically. Lithium and sodium analyses were made by flame spectroscopy. Total alkali content of the phenylsodium-phenyllithium mixture was determined by titration with 0.1 *N* HCl solutions.

The total alkali content of the nickel containing compounds could not be analyzed in this way. First they had to be decomposed with ethanol, the nickel precipitate being removed from the filtrate before titration.

Except in the working up stage, a literature method[9] was followed in the preparation of the $NaC_6H_5{-}LiC_6H_5$ mixture. $Hg(C_6H_5)_2$ (9 g, 25 mmol), LiC_6H_5 (4.2 g, 50 mmol), and Na (10 g) were stirred in 500 ml of ether for 3–5 hr at room temperature. The mixture was filtered to remove insoluble materials, and the filtrate was cooled to −78°C. A colorless crystalline precipitate (IV) (4.5 g) was obtained which was washed with precooled ether and pentane and vacuum dried at room temperature. The total alkali content was in agreement with the flame spectroscopic measurements. Based on the weight percentages of Na (16.7%) and Li (1.5%), the mixture has the empirical formula $(NaC_6H_5)_{3.36}(LiC_6H_5)_{1.0}{\cdot}0.6O(C_2H_5)_2$. Mixture IV (7.46 g, 70 mmol of alkaliphenyl) was added to (CDT)Ni[10] (4.62 g, 21 mmol) in 80 ml of ether at −78°C. The flask was evacuated, and N_2 was entered. The reaction mixture was allowed to warm up to 0°C. With vigorous stirring a measured quantity of N_2 (10 mmol) was absorbed in about 1 hr. During this stage a yellow red powder (II)

(6.4 g), which contained 64% of the nickel present, precipitated from the solution. II was separated from solution by filtration, washed with pentane, and dried under vacuum at 0°C. Based on Ni, Na, Li, and total alkali analyses, II has the composition $\{[(NaC_6H_5)_{2.44}(LiC_6H_5)_{0.67}]Ni\}_2N_2{\cdot}2.8O(C_2H_5)_2$. Reaction of a slurry of II in THF with an excess of CO yields 98% of the calculated amount of N_2. At the end of the reaction, all of the starting material (II) had gone into solution. Seventy percent (GC) of the calculated amount of diethyl ether was recovered when a measured quantity of II was decomposed with ethanol. The filtrate of II was placed in a refrigerator at 0°C for several weeks. Slowly crystals were formed from this solution. Treatment of this product with CO yielded both N_2 and ethylene.

A number of crystals of this product were mounted in glass capillaries under argon. Weissenberg and precession photographs indicated that each crystal belongs to the triclinic system. One crystal, a platelet with the dimensions 0.29 × 0.24 × 0.43 mm, was then transferred to a Nonius CAD-4 automated diffractometer equipped with a graphite monochromator and a molybdenum tube, λ(Mo Kα) 0.71069 Å. The crystalline quality was checked by ω scans of several reflections. Refined unit cell dimensions were derived from the average of the plus and minus θ values of 60 centered reflections. The unit cell constants are a = 15.775 (4) Å, b = 18.689 (5) Å, c = 23.607 (5) Å, α = 66.02 (2)°, β = 66.39 (2)°, and γ = 78.87 (2)°. The calculated density is 1.191 g/cm^3 assuming two $\{C_6H_5[Na{\cdot}O(C_2H_5)_2]_2[(C_6H_5)_2Ni]_2N_2NaLi_6(OC_2H_5)_4{\cdot}O(C_2H_5)_2\}_2$ (III) (molecular weight 2088.38). The extreme sensitivity of the compound to oxygen and moisture prevented an experimental determination of the density.

Intensity data were collected by the θ–2θ scan technique. A total of 11032 reflections were measured in overlapping shells of 2θ. The data collection program automatically selected scan speeds in order to keep the total number of counts constant (6000). The centering of three reflections was monitored periodically during data collection. The average of the intensities of these reflections varied randomly between 92 and 102% of their initial values.

The intensities were reduced to structure factor amplitudes F_o's by a Lorentz-polarization correction which took into account the polarization of the x-ray beam by the monochromator. A correction for the fluctuation of the standard reflections was also applied. No absorption correction was deemed necessary, μ(Mo Kα) = 7.19 cm^{-1}. Averaging of the multiply measured reflections yielded 9312 unique data, of which 4750 intensities, I, obeyed the relation $I > 2\sigma(I)$ where

$$\sigma^2(I_0) = \sigma^2(I_0)_{\mathrm{Poisson}} + 0.03^2 I^2$$

A sharpened Patterson map was calculated. This map had a very large peak at ½, ½, ½ which indicated that the unit cell is pseudo-body centered. Indeed the F_o's with $h + k + l = 2n + 1$ were found to be weaker, in general, than the other reflections. Therefore we assumed that the unit cell had a pseudocenter of symmetry at ¼, ¼, ¼. Positions for the four Ni atoms, Na1, and Na2 were derived from the vector distribution. A subsequent electron density map revealed the remaining Na atom positions. The other nonhydrogen atoms were located from a series of Fourier syntheses, the ethyl groups of the ether molecules being located last. The ethyl groups of ether oxygen atoms $O_{et}5$ and $O_{et}6$ appear to be disordered.

The structure was refined by block-diagonal least-squares methods. The function minimized was $w(||F_o| - |F_c||)$, where weights. w, equal $1/\sigma^2(|F_o|)$. Neutral atom scattering factors for Ni, Na, O, N, C, and Li were taken from the compilation of Cromer,[11] and the best spherical scattering factors were used for H.[12] Anomalous dispersion corrections were applied to the scattering factors of Ni and Na.[13] With the Ni and Na atoms anisotropic and the remaining atoms isotropic (ethyl groups of $O_{et}5$ and $O_{et}6$ with half occupancies), the refinement converged to

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.129$$

and

$$R = [\Sigma w(||F_o| - |F_c||)/\Sigma w|F_o|^2]^{1/2} = 0.154$$

A difference Fourier synthesis revealed alternative positions for the ethyl carbon atoms of $O_{et}5$ and $O_{et}6$. Carbon atoms of 0.5 occupancies were assigned to these positions. The coordinates of the 50 phenyl hydrogen atoms were calculated assuming sp^2 hybridization for the C atoms. In some cases these calculated positions could be verified by the difference electron density distribution. Locations for 21 of the remaining 100 H atoms of the ethyl groups were derived from the difference density map. Further refinement with all Ni, Na, O, N, and C atoms anisotropic and the Li atoms isotropic (the H atom parameters not being refined) reduced R and R_w to 0.079 and 0.095, respectively. These summations ignore 16 strong reflections which showed disagreement in $|F_o|$ and $|F_c|$ ($|F_c|$ greater than $|F_o|$ by more than 25%). The number of observations, 4734, is unfavorable for the number of parameters, 1255. The final position and temperature parameters are listed in Tables I and II. The numbering scheme is defined by Figure 2. The carbon atoms that are not shown are numbered Cl, Cln, Cn (l = 1, 6 and n = 1, 9) for the phenyl groups CnO1, CnO2 for the ethoxy groups, and C_{et} and O_{et} for the carbon and oxygen atoms, respectively, of the ether ligands. Selected bond distances and angles are given in Table III.

Description and Discussion of the Molecular Structure

Crystals of III consist of independent molecules of formula $\{C_6H_5[Na{\cdot}O(C_2H_5)_2]_2[(C_6H_5)_2Ni]_2N_2NaLi_6(OC_2H_5)_4{\cdot}O(C_2H_5)_2\}_2$. The presence of ethoxy groups in III was surprising. Undoubtedly they were introduced into the filtrate of II via an ether cleavage reaction of the type

$$NaC_6H_5 + (C_2H_5)_2O \rightarrow NaOC_2H_5 + C_6H_6 + C_2H_4$$

Significantly, ethylene was also liberated by decomposition of the material from which III was obtained. Since we did not find ethylene in the structure of III, the reaction product may not be homogeneous. A clue to the type of impurity present is given by our recent structural investigation of $Na_4{\cdot}5OC_4H_8[(C_6H_5)_2NiC_2H_4]_2$,[14] in which the ethylene also results from an ether cleavage reaction.[15]

In III, two distinct $[(C_6H_5)_2Ni]_2N_2$ entities are linked together by an involved network of bonds to Na1 and Na2 as well as by two $Li_6(OC_2H_5)_4{\cdot}O(C_2H_5)_2$ nests. On the outer side of this cage system two μ-$(C_6H_5)[Na{\cdot}O(C_2H_5)_2]_2$ moieties are bonded to the $[(C_6H_5)_2Ni]_2N_2$ species by Na–C and Na–Ni bonds. While no crystallographic symmetry is imposed on the molecule, the molecular symmetry is approximately C_{2h}. as was indicated by the Patterson synthesis. This pseudocenter of symmetry is located at a point midway between Na1 and Na2. Na1, Na2, Li9–Li12, O1, O3, O5, O8, $O_{et}5$, and $O_{et}6$ lie close to the mirror plane. The twofold axis passes through the midpoints of the dinitrogen ligands and the 1,4 carbon atoms of the two phenyl groups which bridge the outer Na atoms. If we disregard the ethyl groups as well as $O_{et}5$ and $O_{et}6$, the molecular symmetry is roughly D_{2h}. The second mirror plane is defined by the best plane through the four Ni and six Na atoms (±0.25 Å), and the third mirror plane contains the dinitrogen ligands, O2, O4, O6, O7, and the two phenyl rings which bridge the outer Na atoms. As we will show later, the structure obeys neither D_{2h} nor C_{2h} symmetry exactly. Figure 1 is a reproduction of the nonhydrogen atoms in the molecule, except the ether group of $O_{et}6$. In Figure 2, a stereodrawing of the inner core is presented.

As in the structure of I, the most important interactions of the dinitrogen ligands are with Ni and Li atoms. The geometry of these interactions is shown in Figure 3. The N_2 species is bonded "side-on" to both nickel atoms of a $[(C_6H_5)_2Ni]_2$ system. The lone pairs of the N_2 atoms are directed towards the midpoint of the bond between two Li atoms. In this respect the geometry is different in compound I in which one N atom was below the midpoint of a Li_3 triangle and the other N atom bonded "end-on" to a single Li atom. If we consider only the midpoint of the N_2 moiety and the two phenyl carbon atoms that are bonded to each Ni atom, the coordination about each Ni atom is trigo-

Table I. Final Atomic Coordinates and Their Standard Deviations (*10000)

Atom	x	y	z	Atom	x	y	z
Ni1	339 (1)	−2242 (1)	−1452 (1)	C74	1455 (17)	1146 (12)	−1944 (11)
Ni2	4627 (1)	−2791 (1)	−3548 (1)	C75	693 (17)	703 (13)	−1514 (10)
Ni3	1050 (1)	−898 (1)	−2505 (1)	C76	606 (13)	−91 (10)	−1697 (9)
Ni4	3936 (1)	−4100 (1)	−2435 (1)	C81	3614 (10)	−5047 (7)	−2487 (7)
Na1	2878 (4)	−1734 (3)	−3145 (3)	C82	3246 (11)	−5697 (9)	−1933 (8)
Na2	2107 (4)	−3250 (3)	−1847 (3)	C83	2944 (14)	−6367 (10)	−1915 (9)
Na3	6475 (5)	−3485 (4)	−4079 (4)	C84	3117 (14)	−6367 (10)	−2537 (11)
Na4	−1429 (5)	−1576 (4)	−759 (3)	C85	3492 (14)	−5773 (10)	−3130 (10)
Na5	5410 (5)	−5300 (4)	−2723 (4)	C86	3737 (12)	−5064 (10)	−3123 (8)
Na6	−640 (5)	153 (4)	−2318 (4)	C91	4551 (10)	−4560 (8)	−1773 (7)
N1	3830 (8)	−2988 (7)	−2647 (6)	C92	5503 (11)	−4496 (6)	−1933 (8)
N2	1177 (8)	−2000 (6)	−2340 (5)	C93	5875 (12)	−4846 (10)	−1416 (10)
N3	1540 (8)	−1830 (6)	−1977 (5)	C94	5371 (14)	−5175 (11)	−801 (9)
N4	3428 (8)	−3190 (6)	−2971 (5)	C95	4453 (12)	−5274 (10)	−608 (8)
O1	1319 (6)	−3904 (5)	−2190 (4)	C96	4066 (11)	−4941 (9)	−1117 (8)
O2	2301 (6)	−3510 (5)	−3686 (4)	C101	1041 (9)	−4618 (9)	−1666 (7)
O3	2346 (6)	−1784 (5)	−3945 (4)	C102	1252 (12)	−4739 (9)	−1063 (8)
O4	547 (6)	−2632 (5)	−3151 (5)	C201	2618 (12)	−3837 (10)	−4200 (8)
O5	3747 (6)	−1091 (5)	−2852 (5)	C202	2500 (16)	−3228 (12)	−4836 (9)
O6	4475 (6)	−2372 (5)	−1841 (4)	C301	2543 (11)	−1086 (9)	−4512 (7)
O7	2776 (7)	−1406 (5)	−1401 (5)	C302	2044 (18)	−1020 (12)	−4962 (10)
O8	2626 (7)	−3158 (5)	−1030 (4)	C401	−319 (12)	−2534 (10)	−3274 (8)
$O_{et}1$	−965 (10)	1463 (8)	−2868 (7)	C402	−110 (14)	−2400 (14)	−3998 (11)
$O_{et}2$	−2657 (9)	−1854 (8)	281 (6)	C501	4233 (12)	−450 (9)	−3432 (8)
$O_{et}3$	7764 (9)	−2972 (8)	−5073 (7)	C502	3944 (14)	−278 (11)	−3997 (9)
$O_{et}4$	5708 (9)	−6641 (7)	−2126 (7)	C601	5277 (10)	−2637 (10)	−1627 (8)
$O_{et}5$	4953 (9)	−436 (7)	−2286 (6)	C602	5022 (14)	−2771 (17)	−933 (9)
$O_{et}6$	287 (8)	−4592 (7)	−2862 (6)	C701	2521 (12)	−899 (10)	−1014 (8)
C1	598 (10)	−363 (8)	−3230 (7)	C702	2978 (17)	−1242 (11)	−464 (10)
C2	995 (10)	313 (9)	−3757 (7)	C801	2212 (13)	−3707 (9)	−356 (8)
C3	735 (12)	715 (10)	−4310 (8)	C802	2456 (17)	−3662 (14)	159 (9)
C4	−2 (12)	424 (10)	−4341 (8)	$C_{et}1$	−2098 (19)	1359 (18)	−3173 (18)
C5	−380 (12)	−210 (10)	−3866 (9)	$C_{et}2$	−1537 (20)	1835 (20)	−3166 (19)
C6	−144 (11)	−612 (9)	−3312 (8)	$C_{et}3$	−303 (20)	2032 (14)	−2946 (13)
C11	−2084 (11)	−230 (11)	−1313 (9)	$C_{et}4$	−585 (21)	2268 (17)	−2439 (16)
C12	−2918 (14)	−518 (12)	−1203 (10)	$C_{et}5$	−3165 (17)	−2866 (14)	125 (11)
C13	−3820 (14)	−209 (15)	−948 (12)	$C_{et}6$	−3455 (16)	−2248 (16)	432 (11)
C14	−3885 (17)	416 (15)	−841 (13)	$C_{et}7$	−2993 (18)	−1280 (13)	598 (11)
C15	−3137 (18)	746 (14)	−898 (11)	$C_{et}8$	−2080 (20)	−982 (14)	453 (13)
C16	−2262 (16)	400 (13)	−1153 (10)	$C_{et}9$	7763 (23)	−3029 (18)	−6028 (14)
C21	6855 (13)	−4911 (11)	−3667 (9)	$C_{et}10$	7503 (19)	−2497 (14)	−5680 (11)
C22	7495 (13)	−5236 (12)	−3343 (11)	$C_{et}11$	8724 (15)	−3112 (15)	−5152 (14)
C23	8291 (15)	−5627 (14)	−3549 (13)	$C_{et}12$	8883 (21)	−3465 (16)	−4534 (15)
C24	8549 (17)	−5655 (16)	−4180 (14)	$C_{et}13$	5885 (21)	−6941 (18)	−3059 (15)
C25	8052 (22)	−5370 (18)	−4553 (14)	$C_{et}14$	5966 (23)	−7223 (14)	−2417 (17)
C26	7226 (14)	−5052 (13)	−4233 (12)	$C_{et}15$	5761 (18)	−6878 (15)	−1427 (13)
C31	120 (10)	−2366 (8)	−520 (7)	$C_{et}16$	6670 (22)	−6846 (17)	−1468 (15)
C32	−318 (12)	−3016 (9)	22 (7)	$C_{et}51$	5898 (24)	−663 (24)	−2647 (26)
C33	−445 (13)	−3116 (10)	647 (8)	$C_{et}52$	6580 (27)	−627 (25)	−2571 (22)
C34	−116 (15)	−2572 (12)	789 (8)	$C_{et}53$	4681 (26)	232 (28)	−2031 (20)
C35	286 (13)	−1951 (10)	274 (8)	$C_{et}54$	4518 (37)	1027 (31)	−2432 (23)
C36	420 (11)	−1804 (9)	−370 (7)	$C_{et}51^*$	5839 (34)	−266 (35)	−2892 (29)
C41	4860 (9)	−2825 (9)	−4403 (7)	$C_{et}52^*$	6495 (30)	−302 (34)	−2996 (25)
C42	5120 (12)	−3502 (11)	−4575 (9)	$C_{et}53^*$	4519 (38)	729 (28)	−1954 (23)
C43	5313 (15)	−3468 (12)	−5237 (10)	$C_{et}54^*$	4711 (44)	553 (36)	−2523 (24)
C44	5218 (16)	−2810 (15)	−5700 (10)	$C_{et}61$	737 (34)	−5279 (35)	−3326 (25)
C45	4988 (14)	−2134 (14)	−5607 (9)	$C_{et}62$	930 (30)	−5353 (19)	−2834 (22)
C46	4809 (12)	−2142 (11)	−4944 (8)	$C_{et}63$	−772 (27)	−4523 (20)	−2613 (22)
C51	5698 (9)	−2278 (8)	−3686 (7)	$C_{et}64$	−1279 (33)	−4999 (35)	−2250 (27)
C52	6244 (10)	−2515 (10)	−3273 (8)	$C_{et}64^*$	−780 (35)	−4854 (32)	−2189 (26)
C53	6988 (11)	−2135 (10)	−3423 (8)	$C_{et}61^*$	804 (45)	−5866 (34)	−2760 (37)
C54	7283 (11)	−1520 (10)	−3966 (9)	Li1	3185 (19)	−2762 (16)	−3856 (13)
C55	6804 (13)	−1236 (10)	−4407 (8)	Li2	1782 (17)	−2207 (14)	−1147 (12)
C56	6029 (11)	−1620 (10)	−4259 (8)	Li3	1133 (18)	−1637 (15)	−3269 (13)
C61	−755 (10)	−2722 (9)	−1353 (7)	Li4	526 (18)	−2914 (15)	−2247 (13)
C62	−1387 (11)	−2276 (9)	−1677 (7)	Li5	4484 (20)	−2077 (17)	−2746 (14)
C63	−2125 (11)	−2617 (11)	−1645 (9)	Li6	2552 (18)	−3954 (16)	−2837 (13)
C64	−2314 (13)	−3360 (12)	−1317 (11)	Li7	3848 (17)	−3317 (14)	−1688 (12)
C65	−1723 (12)	−3820 (11)	−1003 (10)	Li8	2492 (18)	−1001 (15)	−2212 (13)
C66	−963 (11)	−3494 (9)	−1017 (9)	Li9	4061 (16)	−1201 (13)	−2082 (11)
C71	1211 (11)	−35 (8)	−2284 (8)	Li10	1045 (20)	−3725 (17)	−2965 (14)
C72	1918 (13)	461 (10)	−2654 (9)	Li11	1625 (18)	−2531 (15)	−3887 (13)
C73	2069 (16)	1120 (11)	−2547 (11)	Li12	3388 (20)	−2361 (17)	−1136 (14)

Table II. Final Thermal Parameters (*1000)

Atom	$U_{1,1}$	$U_{2,2}$	$U_{3,3}$	$U_{1,2}$	$U_{1,3}$	$U_{2,3}$	Atom	$U_{1,1}$	$U_{2,2}$	$U_{3,3}$	$U_{1,2}$	$U_{1,3}$	$U_{2,3}$
Ni1	52	61	64	−3	−36	−37	C73	192	81	192	−18	−156	−20
Ni2	55	70	55	−6	−37	−35	C74	243	123	188	8	−173	−73
Ni3	66	52	69	4	−51	−35	C75	222	149	141	72	−125	−109
Ni4	62	55	66	1	−47	−36	C76	131	105	106	47	−79	−82
Na1	60	65	70	0	−48	−37	C81	65	30	90	0	−41	−43
Na2	67	61	68	−5	−40	−38	C82	77	61	116	−5	−46	−51
Na3	84	99	113	10	−47	−67	C83	133	76	118	−17	−56	−29
Na4	90	104	103	22	−58	−64	C84	125	79	193	−13	−90	−68
Na5	84	88	129	16	−64	−68	C85	172	84	160	0	−119	−80
Na6	96	114	113	29	−62	−70	C86	113	95	93	27	−66	−61
N1	73	78	75	−13	−61	−40	C91	81	38	60	11	−43	−35
N2	64	48	69	9	−53	−30	C92	79	66	125	10	−73	−47
N3	67	59	63	9	−46	−41	C93	97	94	192	27	−127	−74
N4	81	57	59	−7	−50	−30	C94	171	107	96	34	−100	−45
O1	60	53	66	−16	−36	−27	C95	108	112	87	9	−53	−55
O2	58	70	73	−19	−37	−43	C96	107	72	93	33	−79	−53
O3	68	67	48	1	−46	−24	C101	43	71	82	1	−36	−28
O4	67	72	93	−0	−70	−40	C102	121	69	79	−34	−64	−12
O5	62	55	78	1	−48	−29	C201	111	88	90	12	−35	−78
O6	61	76	71	−3	−46	−47	C202	207	143	96	15	−98	−72
O7	79	74	81	17	−66	−56	C301	85	85	70	24	−52	−50
O8	80	55	69	−7	−52	−28	C302	252	127	133	−21	−165	−1
$\mathrm{O_{et}}1$	148	105	161	13	−61	−56	C401	98	86	111	8	−66	−60
$\mathrm{O_{et}}2$	127	128	112	2	−58	−50	C402	125	212	155	−8	−110	−90
$\mathrm{O_{et}}3$	111	136	183	−3	−35	−74	C501	125	54	91	−16	−71	−23
$\mathrm{O_{et}}4$	100	98	198	2	−61	−63	C502	144	118	96	−13	−88	−34
$\mathrm{O_{et}}5$	118	115	139	−8	−77	−72	C601	55	121	94	−7	−62	−48
$\mathrm{O_{et}}6$	112	124	136	−47	−52	−77	C602	106	340	86	44	−85	−63
C1	73	54	51	−16	−36	−14	C701	116	78	106	−23	−61	−51
C2	78	72	73	−1	−56	−42	C702	265	107	153	−2	−178	−68
C3	89	87	85	−18	−31	−37	C801	156	53	72	−6	−55	−26
C4	104	79	73	−2	−63	−7	C802	215	208	81	−47	−108	−40
C5	110	85	121	−11	−101	−25	$\mathrm{C_{et}}1$	170	266	457	19	−122	−285
C6	85	82	83	−29	−56	−17	$\mathrm{C_{et}}2$	180	265	399	156	−153	−76
C11	67	121	104	21	−39	−73	$\mathrm{C_{et}}3$	253	119	188	−32	−31	−22
C12	149	136	132	50	−88	−94	$\mathrm{C_{et}}4$	231	203	325	39	−178	−121
C13	95	215	201	−4	−84	−103	$\mathrm{C_{et}}5$	183	174	153	−56	−41	−98
C14	185	222	221	129	−147	−152	$\mathrm{C_{et}}6$	146	226	121	−21	−39	−3
C15	223	174	125	93	−88	−119	$\mathrm{C_{et}}7$	237	146	159	7	−100	−114
C16	168	161	132	10	−77	−76	$\mathrm{C_{et}}8$	279	190	266	104	−203	−201
C21	124	130	120	25	−85	−80	$\mathrm{C_{et}}9$	281	239	213	−59	−30	−149
C22	85	137	208	15	−67	−115	$\mathrm{C_{et}}10$	235	147	121	−47	−67	−39
C23	121	172	263	19	−124	−100	$\mathrm{C_{et}}11$	87	191	286	−46	−29	−88
C24	154	209	224	24	−6	−143	$\mathrm{C_{et}}12$	230	203	253	−1	−133	−97
C25	271	311	205	−26	−66	−212	$\mathrm{C_{et}}13$	266	267	301	111	−218	−198
C26	118	181	200	32	−68	−151	$\mathrm{C_{et}}14$	283	112	390	44	−60	−176
C31	70	55	65	8	−33	−24	$\mathrm{C_{et}}15$	187	169	188	2	−71	−58
C32	104	95	48	−29	−29	−37	$\mathrm{C_{et}}16$	267	212	261	30	−131	−162
C33	127	70	88	−9	−30	−32	$\mathrm{C_{et}}51$	46	106	306	6	−71	−24
C34	181	140	41	9	−26	−52	$\mathrm{C_{et}}52$	131	162	211	−6	−155	−87
C35	126	110	58	−19	−36	−57	$\mathrm{C_{et}}53$	92	235	146	−12	−4	−166
C36	101	68	73	−21	−33	−52	$\mathrm{C_{et}}54$	229	234	142	134	−99	−116
C41	40	72	46	−19	−22	19	$\mathrm{C_{et}}51$*	128	287	293	120	−115	−185
C42	82	125	112	−15	−17	−91	$\mathrm{C_{et}}52$*	84	292	229	−4	−10	−196
C43	149	143	145	−19	−63	−103	$\mathrm{C_{et}}53$*	242	178	156	−34	6	−145
C44	151	253	101	12	−72	−101	$\mathrm{C_{et}}54$*	325	287	141	137	−125	−161
C45	112	221	88	12	−79	−21	$\mathrm{C_{et}}61$	146	300	174	−138	−51	−57
C46	92	145	84	8	−39	−77	$\mathrm{C_{et}}62$	200	46	242	13	−163	−90
C51	43	49	66	−39	−19	−22	$\mathrm{C_{et}}63$	136	70	217	−94	−106	1
C52	47	114	92	−13	−36	−60	$\mathrm{C_{et}}64$	162	380	308	−195	40	−299
C53	70	124	81	−33	−50	−33	$\mathrm{C_{et}}64$*	176	269	232	40	−163	−164
C54	67	102	119	−31	−35	−53	$\mathrm{C_{et}}61$*	230	168	409	39	−128	−126
C55	123	76	85	−10	−50	−9	Li1	71					
C56	59	113	103	−37	−37	−60	Li2	54					
C61	61	88	65	−10	−24	−40	Li3	63					
C62	79	89	53	−14	−21	−40	Li4	62					
C63	66	131	139	−2	−62	−77	Li5	76					
C64	90	147	216	−6	−84	−120	Li6	66					
C65	85	101	163	−25	−24	−85	Li7	54					
C66	71	65	154	−12	−47	−56	Li8	61					
C71	118	24	100	−10	−97	−1	Li9	44					
C72	131	73	145	10	−107	−57	Li10	80					
							Li11	60					
							Li12	76					

Table III. Selected Bond Distances (Å) and Angles (deg)

N1–Li5	2.05 (3)
N1–Li7	2.10 (3)
N2–Li3	2.04 (3)
N2–Li4	2.05 (3)
N3–Li2	1.97 (3)
N3–Li8	2.12 (3)
N4–Li1	2.08 (3)
N4–Li6	2.02 (3)
av	2.05 (5)
N1–N4	1.36 (2)
N2–N3	1.36 (2)
av	1.36 (0)
Ni1–Li2	2.67 (3)
Ni1–Li4	2.55 (3)
Ni2–Li1	2.64 (3)
Ni2–Li5	2.65 (3)
Ni3–Li3	2.64 (3)
Ni3–Li8	2.58 (3)
Ni4–Li6	2.64 (3)
Ni4–Li7	2.67 (3)
av	2.63 (4)
Ni1–Na2	3.083
Ni2–Na1	3.121
Ni3–Na1	3.118
Ni4–Na2	3.097
av	3.105 (18)
Na3–C41	2.86
Na3–C51	2.68
Na4–C31	2.74
Na4–C61	2.84
Na5–C81	2.64
Na5–C91	2.85
Na6–C1	2.64
Na6–C71	2.90
Na3–O_{et}3	2.38 (2)
Na4–O_{et}2	2.37 (2)
Na5–O_{et}4	2.39 (2)
Na6–O_{et}1	2.33 (2)
av	2.37 (3)
Na1–Li1	2.89
Na1–Li3	2.85
Na1–Li5	2.92
Na1–Li8	2.86
Na2–Li2	2.89
Na2–Li4	2.88
Na2–Li6	2.92
Na2–Li7	2.89
av	2.89 (3)
Li1–C41	2.44
Li2–C31	2.45
Li3–C1	2.40
Li4–C61	2.36
Li5–C51	2.40
Li6–C81	2.46
Li7–C91	2.42
Li8–C71	2.45
Li1–O2	1.98 (3)
Li1–O3	2.03 (3)
Li2–O7	2.11 (3)
Li2–O8	1.99 (3)
Li3–O3	1.99 (3)
Li3–O4	2.10 (3)
Li4–O1	2.01 (3)
Li4–O4	1.97 (3)
Li5–O5	1.96 (3)
Li5–O6	1.97 (3)
Li6–O1	1.95 (3)
Li6–O2	2.01 (3)
Li7–O6	2.03 (3)
Li7–O8	1.99 (3)
Li8–O5	1.98 (3)
Li8–O7	1.96 (3)
Li9–O5	1.99 (3)
Li9–O6	2.07 (3)
Li9–O7	2.01 (3)
Li10–O1	1.93 (4)
Li10–O2	2.01 (3)
Li10–O4	1.98 (3)
av	2.00 (5)
N1–Ni2	1.91 (1)
N1–Ni4	1.92 (1)
N2–Ni1	1.90 (1)
N2–Ni3	1.92 (1)
N3–Ni1	1.90 (1)
N3–Ni3	1.92 (1)
N4–Ni2	1.91 (1)
N4–Ni4	1.92 (1)
av	1.91 (1)
Ni1–Ni3	2.744 (3)
Ni2–Ni4	2.754 (3)
av	2.749 (7)
Ni1–C31	2.01 (2)
Ni1–C61	1.99 (2)
Ni2–C41	1.93 (2)
Ni2–C51	1.95 (1)
Ni3–C1	1.94 (2)
Ni3–C71	1.97 (2)
Ni4–C81	2.00 (1)
Ni4–C91	1.98 (2)
av	1.97 (3)
Ni1–Na4	2.944
Ni2–Na3	2.947
Ni3–Na6	2.984
Ni4–Na5	2.976
av	2.963 (20)
Na3–C42	2.83
Na3–C52	3.00
Na4–C32	3.23
Na4–C62	2.93
Na5–C82	3.04
Na5–C92	2.98
Na6–C6	3.00
Na6–C76	2.85
Na1–O3	2.39 (1)
Na1–O5	2.42 (1)
Na2–O1	2.43 (1)
Na2–O8	2.45 (1)
av	2.42 (2)
Na3–C21	2.48 (2)
Na4–C11	2.55 (2)
Na5–C21	2.44 (2)
Na6–C11	2.50 (2)
av	2.49 (5)
Na3–Na5	3.693
Na4–Na6	3.709
av	3.701
Na1–Na2	3.191
Li1–C46	2.82
Li2–C36	2.43
Li3–C6	2.50
Li4–66	2.84
Li5–C52	2.67
Li6–C86	2.62
Li7–C96	2.79
Li8–C72	2.62
Li9–O_{et}5	1.98 (3)
Li10–O_{et}6	2.08 (4)
av	2.03 (7)
Li11–O2	1.91 (3)
Li11–O3	1.90 (3)
Li11–O4	1.85 (3)
Li12–O6	1.86 (3)
Li12–O7	1.95 (3)
Li12–O8	1.97 (3)
av	1.89 (5)
Li12–Li2	2.50
Li12–Li7	2.46
Li12–Li9	2.42
Li11–Li1	2.44
Li11–Li3	2.47
Li11–Li10	2.41
Li10–Li4	2.52
Li10–Li6	2.45
Li9–Li5	2.53
Li9–Li8	2.55
av	2.48 (5)
Li8–Li2	2.60
Li7–Li5	2.61
Li6–Li1	2.52
Li4–Li3	2.62
av	2.58 (4)
C1–C2	1.39
C2–C3	1.40
C3–C4	1.41
C4–C5	1.29
C5–C6	1.38
C6–C1	1.44
av	1.39 (5)
C11–C12	1.40
C12–C13	1.41
C13–C14	1.27
C14–C15	1.37
C15–C16	1.41
C16–C11	1.32
av	1.36 (6)
C31–C32	1.39
C32–C33	1.34
C33–C34	1.43
C34–C35	1.32
C35–C36	1.36
C36–C31	1.44
av	1.38 (5)
C51–C52	1.43
C52–C53	1.34
C53–C54	1.31
C54–C55	1.40
C55–C56	1.39
C56–C51	1.39
av	1.38 (4)
C71–C72	1.35
C72–C73	1.43
C73–C74	1.38
C74–C75	1.37
C75–C76	1.42
C76–C71	1.42
av	1.40 (3)
C91–C92	1.41
C92–C93	1.43
C93–C94	1.29
C94–C95	1.36
C95–C96	1.43
C96–C91	1.36
av	1.38 (5)
C101–C102	1.52 (3)
C201–C202	1.53 (3)
C301–C302	1.51 (3)
C401–C402	1.53 (3)
C501–C502	1.48 (3)
C601–C602	1.44 (3)
C701–C702	1.58 (3)
C801–C802	1.45 (3)
av	1.48 (7)
C_{et}1–C_{et}2	1.38 (5)
C_{et}3–C_{et}4	1.32 (5)
C_{et}5–C_{et}6	1.51 (4)
C_{et}7–C_{et}8	1.51 (4)
C_{et}9–C_{et}10	1.44 (4)
C_{et}11–C_{et}12	1.44 (5)
C_{et}15–C_{et}16	1.41 (5)
C61–Ni1–C31	103.4 (7)
C51–Ni3–C41	104.2 (7)
C71–Ni–C1	103.1 (7)
C91–Ni4–C81	102.5 (6)
av	103.3 (7)
C61–Ni1–N3	150.0 (6)
C61–Ni1–N2	108.2 (6)
C31–Ni1–N3	106.0 (6)
C31–Ni1–N2	147.6 (6)
C51–Ni2–N4	147.7 (6)
C51–Ni2–N1	106.3 (6)
C41–Ni2–N4	107.7 (6)
C41–Ni2–N1	149.4 (6)
C71–Ni3–N3	106.5 (6)
C71–Ni3–N2	147.9 (6)
C1–Ni3–N3	149.8 (6)
C1–Ni3–N2	109.0 (6)
C91–Ni4–N4	148.5 (6)
C91–Ni4–N1	107.1 (6)
C81–Ni4–N4	108.6 (6)
C81–Ni4–N1	149.9 (6)
O3–Li1–O2	98.7 (1.4)
C21–C22	1.41
C22–C23	1.34
C23–C24	1.40
C24–C25	1.30
C25–C26	1.38
C26–C21	1.34
av	1.36 (4)
C41–C42	1.42
C42–C43	1.44
C43–C44	1.30
C44–C45	1.33
C45–C46	1.47
C46–C41	1.41
av	1.40 (7)
C61–C62	1.43
C62–C63	1.39
C63–C64	1.31
C64–C65	1.37
C65–C66	1.43
C66–C61	1.36
av	1.38 (6)
C81–C82	1.38
C82–C83	1.40
C83–C84	1.38
C84–C85	1.37
C85–C86	1.46
C86–C81	1.45
av	1.41 (4)
O1–C101	1.39 (2)
O2–C201	1.45 (2)
O3–C301	1.41 (2)
O4–C401	1.47 (2)
O5–C501	1.44 (2)
O6–C601	1.47 (2)
O7–C701	1.47 (2)
O8–C801	1.45 (2)
av	1.45 (5)
O_{et}1–C_{et}2	1.29 (4)
O_{et}1–C_{et}3	1.54 (3)
O_{et}2–C_{et}6	1.43 (3)
O_{et}2–C_{et}7	1.45 (3)
O_{et}3–C_{et}10	1.52 (3)
O_{et}3–C_{et}11	1.43 (3)
O_{et}4–C_{et}14	1.43 (3)
O_{et}4–C_{et}15	1.56 (4)
O_{et}5–C_{et}51	1.47 (5)
O_{et}5–C_{et}53	1.52 (5)
O_{et}6–C_{et}62	1.57 (4)
O_{et}6–C_{et}63	1.53 (5)
C_{et}13–C_{et}14	1.44 (6)
Ni4–N1–Ni2	92.0 (6)
Ni1–N2–Ni3	92.0 (5)
Ni1–N3–Ni3	91.8 (5)
Ni4–N4–Ni2	92.1 (5)
av	92.0 (1)
Li7–N1–Li5	77.9 (1.3)
Li4–N2–Li3	79.0 (1.2)
Li2–N3–Li3	79.0 (1.2)
Li1–N4–Li6	75.0 (1.3)
av	77.7 (1.9)
O_{et}3–Na3–C21	103.7 (7)
O_{et}2–Na4–C11	95.4 (6)
O_{et}4–Na5–C21	103.7 (7)
O_{et}1–Na6–C11	102.3 (7)
av	101.3 (4.0)
O5–Na1–O3	149.7 (5)
O8–Na2–O1	152.2 (4)
Li1–O2–Li6	78.3 (1.3)
Li3–O4–Li4	79.5 (1.2)
Li5–O6–Li7	81.4 (1.3)
Li2–O7–Li8	79.3 (1.2)
Na4–C11–Na6	94.5 (7)
Na3–C21–Na5	97.3 (8)
av	95.9 (2.0)

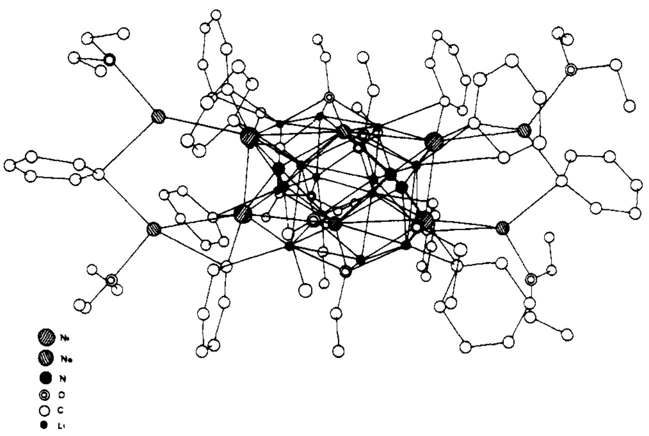

Figure 1. Geometrical arrangement of $\{C_6H_5[Na\cdot O(C_2H_5)_2]_2[(C_6H_5)_2Ni]_2N_2NaLi_6(OC_2H_5)_4\cdot O(C_2H_5)_2\}_2$. One ether molecule has been omitted from the drawing.

nal. The N_2 ligands lie approximately in the trigonal planes of both Ni atoms to which it is attached. The dihedral angles between the trigonal planes of Ni1 and Ni3 and of Ni2 and Ni4 are 101.6 and 100.7°, respectively. The Ni-C distances and the C-Ni-C angles average 1.97 (3) Å and 103.3 (7)°, respectively. The Ni-N distances average 1.911 (9) Å. The N-N distances are both 1.359 (18) Å. These dihedral angles, bond lengths, and bond angles are quite similar to those found in I. The Li-N distances average 2.05 (5) Å, and the Li-N-Li angles average 77.7 (2)°. The size of this angle supports the suggestion that Li-N bonding proceeds via the nitrogen lone pairs.

The above mentioned Ni coordination planes are so distorted that the Ni atoms are displaced about 0.05 Å towards the other Ni atom of the $[(C_6H_5)_2Ni]_2$ moieties. The Ni-Ni distances average 2.749 (7) Å, a value somewhat larger than that found in I, 2.687 Å. The dihedral angles between the planes defined by the phenyl rings and the trigonal plane of the nickel atom to which they are attached are 103.3, 105.5, 106.9, and 112.5° for the phenyl rings of C71, C41, C91, and C61 respectively. The other four dihedral angles are 133.6, 133.8, 134.2, and 142.6° for the phenyl rings of C81, C51, C1, and C31, respectively. These two groups of dihedral angles are distributed in such a way as to retain twofold symmetry in each $[(C_6H_5)_2Ni]_2$ fragment. The distribution between these two fragments obeys a twofold symmetry operator along the Na1-Na2 vector. Inspection of molecular models indicates that the conformations of the phenyl rings are determined by ion pair interactions with Li1 to Li8 and Na3 to Na6 as well as by nonbonded repulsions between the ortho H atoms of phenyl ligands on neighboring Ni atoms. Nonbonded repulsions between the phenyl groups and ethyl groups may also be important.

Each dinitrogen species also has a "side-on" interaction with Na1 and Na2 (Figure 5). These two sodium atoms thus bridge the two $[(C_6H_5)_2Ni]_2N_2$ moieties (Figure 2). These Na-N distances average 2.61 (3) Å. Na1 is displaced approximately 0.6 Å from the trigonal planes of Ni1 and Ni4; Na2 is similarly positioned with respect to the coordination planes of Ni2 and Ni3.

The outer sodium atoms interact with a nickel atom and carbon atoms of three phenyl groups, of which two coordinate to a nickel atom and the other bridges two of the outer sodium atoms (Figure 4). Another Na coordination site is occupied by an ether oxygen atom. The Na-C(bridging phenyl) distances average 2.49 (5) Å, and the Na-O_{et} bond lengths average 2.37 (3) Å. The corresponding O_{et}-Na-C average bond angle is 101.3 (4.0)°. Longer Na-C distances are found for those carbon atoms of the phenyl groups bonded to Ni. Two different types of interactions are observed (Figure 4). In one case the interaction is only with the phenyl α-carbon atom (average 2.68 (5) Å). In the other case, Na-C(α) and Na-C(β) distances average 2.86 (3) and 2.88 (5) Å, respectively. Other Na-C distances are 3.00 Å or longer, and they represent, at the most, weaker interactions than those just mentioned. The average Na-Ni distance is 2.96 (2) Å. We propose that the interaction of the $[(C_6H_5)_2Ni]_2$ groups with the outer Na atoms is delocalized over the C(α)-Ni-C(α)-C(β) fragment. Interestingly an analogous interaction was found for the Li atom in $C(CH_6H_5)_3Li(CH_3)_2NCH_2CH_2N(CH_3)_2$,[16] the Ni atom in our case replacing the central C atom of the triphenylmethyl moiety.

Several other features of the phenyl bridges between the outer pairs of Na atoms deserve comment. The average Na-C-Na angle is 96 (2)°. The corresponding angles in the dimers of triphenylaluminum[17] and dimethyl(phenyl)aluminum[18] are 76.5 and 77.6°, respectively. In the aluminum compounds, as opposed to III, the bridge bonding is symmetric. The phenyl groups are not perpendicular to the plane of the bridge bonds. Dihedral angles of 111.1° for the planes Na3, C21, Na5 and C21 to C26 and of 115.6° for the planes Na4-C11-Na6 and C11 to C16 are observed. In the triphenylaluminum dimer, the corresponding dihedral angle is 84.4°.[17] Despite the differences in geometry between the Al-C(bridge)-Al residues and our Na-C(bridge)-Na fragments, we think that the bonding is still of the three-center two-electron type.

If we consider the metallic radii of Na, Li, and Ni as well as the covalent radii of nitrogen and oxygen,[19] Na1 and Na2 each has contacts with four Li atoms, one Na atom, four N atoms, and two O atoms which are short enough to indicate bonding interactions. The contacts to the O and N atoms undoubtedly are those of greatest structural importance. The Na-N distances were mentioned previously. The O-Na-O bond angles are 149.7° at Na1 and 152.2° at

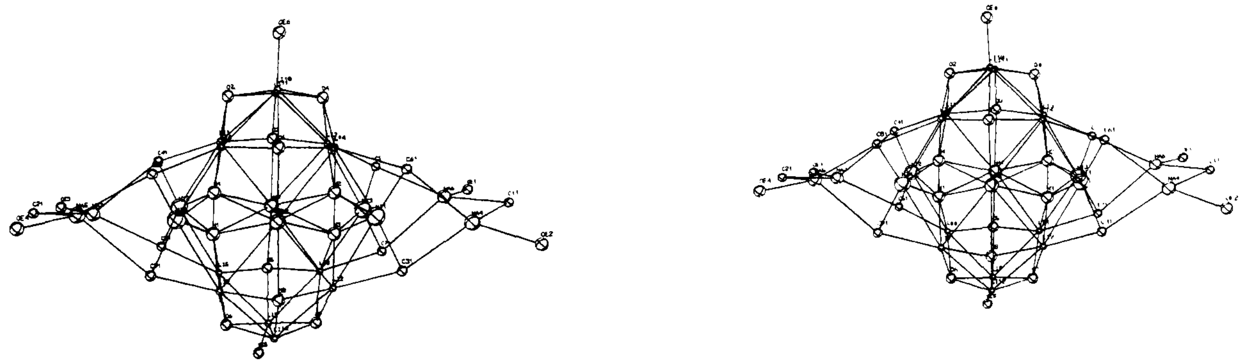

Figure 2. Stereoscopic reproduction of the inner core of $\{C_6H_5[Na\cdot O(C_2H_5)_2]_2[(C_6H_5)_2Ni]_2N_2NaLi_6(OC_2H_5)_4\cdot O(C_2H_5)_2\}_2$.

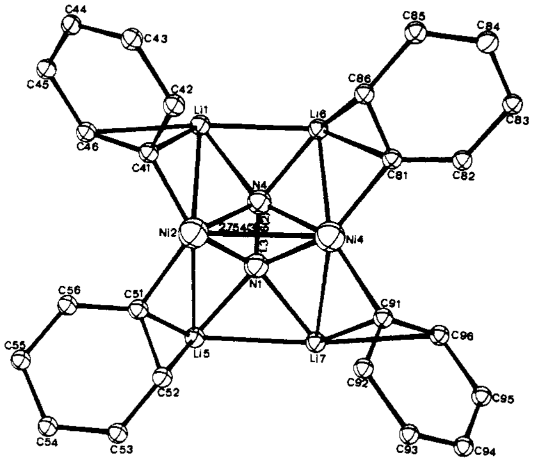

Figure 3. Section of the molecule of $\{C_6H_5[Na{\cdot}O(C_2H_5)_2]_2\text{-}[(C_6H_5)_2Ni]_2N_2NaLi_6(OC_2H_5)_4{\cdot}O(C_2H_5)_2\}_2$ showing the interaction of dinitrogen with nickel and lithium.

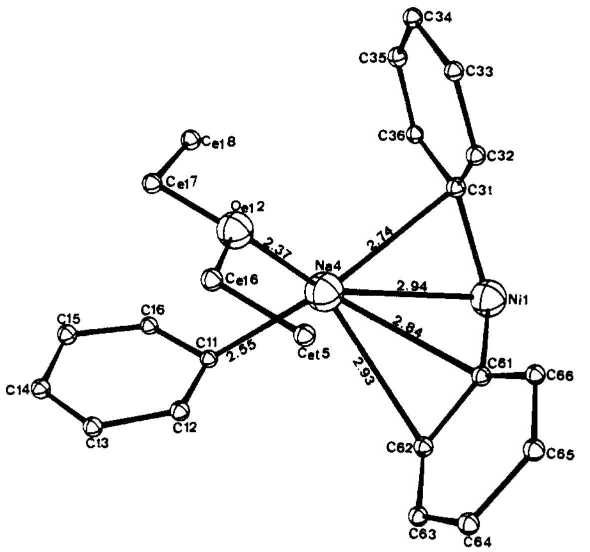

Figure 4. Section of the molecule of $\{C_6H_5[Na{\cdot}O(C_2H_5)_2]_2\text{-}[(C_6H_5)_2Ni]_2N_2NaLi_6(OC_2H_5)_4{\cdot}O(C_2H_5)_2\}_2$ showing the coordination geometry of the outer sodium atoms.

Na2. The positions of these Na atoms are consistent with the steric requirements of the oxygen atoms. Since these Na-O distances are all only somewhat longer than those of the outer Na atoms (2.42 (2) vs. 2.37 (3) Å), the large O-Na-O angles apparently do not greatly weaken the Na-O interactions. This fact is not surprising since the Na-O interaction is likely to be essentially ion-dipole in nature.

The bonds formed by Na1 and Na2 to O as well as the previously mentioned Li-N bonds hold the two $Li_6(OC_2H_5)_4{\cdot}O(C_2H_5)_2$ nests above and below the plane through the four Ni atoms. Four Li atoms may be divided into two sets of two each in that they are bonded to the same N atom and O atom by bonds of average length 2.05 and 2.00 Å, respectively.

The Li atoms of one nest occupy six corners of a distorted cube, Na1 and Na2 being located at the corners of the remaining edges. An ethoxy O atom is 0.9 Å above the approximate center of each Li_4 face. The other ethoxy O atoms are located similarly over the Li_3 Na faces. A N atom is positioned above each Li_2Na_2 face. A total of 48 Li(Na)-N(O) bonding contacts are possible for two nests. The number of valence electrons available for these bonds is not obvious. If we assume that each atom is electronically neutral, that one electron of each N atom is used exclusively for N-N bonding, and that one electron of each O atom is used in its $O-C(C_2H_5)$ bond, then a total of 70 electrons would be available. Thus the Li(Na)-N(O) bonding must be multicentered in nature as well as electron deficient in the sense that there are not enough electrons available to form pair bonds for each Li(Na)-N(O) contact. The Li-O distances of those Li atoms which have short N-Li contacts are somewhat longer than those of the other Li atoms 2.00 (5) and 1.89 (5) Å, respectively. The Li-Li distances average 2.58 (5) Å when both of the Li atoms are bonded to N while the other Li-Li distances are somewhat shorter, 2.46 (5) Å. Those eight Li atoms which bond to N, also interact with the nearest of the four Ni atoms and α, β carbon atoms of the nearest of the eight phenyl groups bonded to Ni (Figure 5). The Li-Ni and Li-C(α) distances average 2.63 (5)

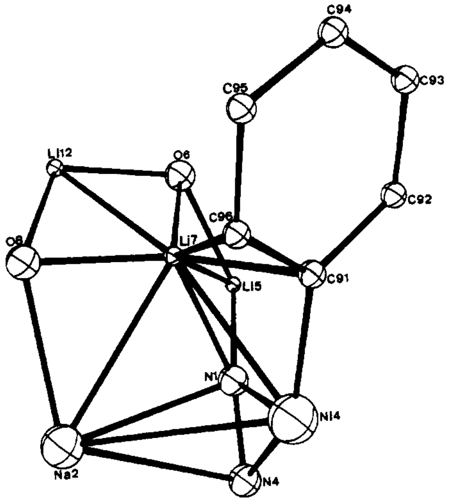

Figure 5. Section of the molecule of $\{C_6H_5[Na{\cdot}O(C_2H_5)_2]_2\text{-}[(C_6H_5)_2Ni]_2N_2NaLi_6(OC_2H_5)_4{\cdot}O(C_2H_5)_2\}_2$ showing the interactions of some lithium atoms with nitrogen.

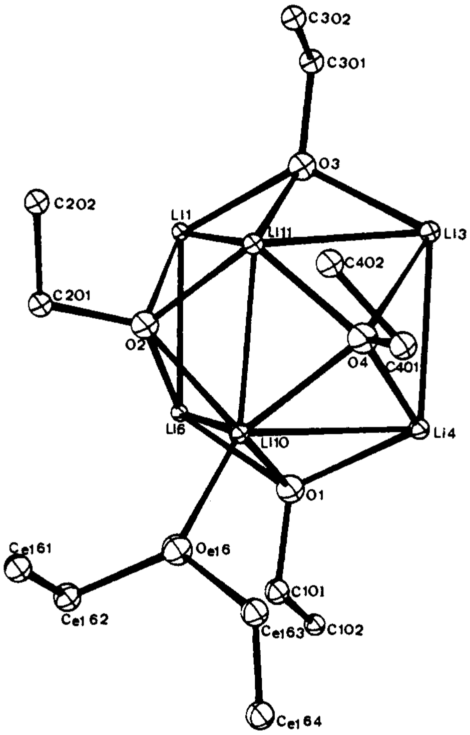

Figure 6. Section of the molecule of $\{C_6H_5[Na{\cdot}O(C_2H_5)_2]_2\text{-}[(C_6H_5)_2Ni]_2N_2NaLi_6(OC_2H_5)_4{\cdot}O(C_2H_5)_2\}_2$ showing the cage formed by several LiO_{et} groups.

and 2.42 (5) Å, respectively. The Li-C(β) distances vary widely from 2.46 (5) to 2.84 (5) Å.

As mentioned before the outer Na atoms also interact with the C(α,β) atoms of these phenyl groups. Interestingly, the Na-C(β) interactions are strong only for those four rings which form the smaller dihedral angles with the trigonal plane of the corresponding Ni atom. The Li-C(β) interactions are weaker, on the average, with these four phenyl groups. Shorter Li-C(β) bond lengths occur when the phenyl groups form larger dihedral angles with the relevant Ni trigonal plane. The stereochemistry of the bonding of the Li atoms to the Ni-C(α)-C(β) fragments bear similarity to that of Li atoms bonded to π-allylic fragments of benzyl and fluorenyl anions—the Ni atom replacing the carbon atoms of highest formal negative charge.[20] This Li, Ni, C(α), and C(β) interaction is similar to that shown by Na3 to Na6.

The Li atoms, which are not bonded to nitrogen atoms, form Li-O bonds to three ethoxy groups (see Figure 6). Two of these four Li atoms form an additional bond to an ether oxygen atom. In each nest, three of the ethoxy ethyl groups are oriented so that the open coordination site of the Li atoms, which do not bond to ether, are blocked. The remaining ethoxy groups shield the open coordination sites of Na1 and Na2. Whether or not the shielding of the Li and Na atoms by the ethyl groups is promoted by Li(Na)-H(CH_3) interactions is not clear; the orientation of these ethyl groups may be the result of minimization of steric interactions of these groups with the rest of the molecule.

As mentioned above average Li-Li distances of 2.46 (5) Å and 2.59 (5) Å as well as a Na1-Na2 distance of 3.191 Å are observed in this structure. These distances are considerably shorter than those reported for the metals, 3.039 and 3.716 Å, respectively.[19] Since in LiF the Li-Li distance is 2.85 Å, a Li-Li contact shorter than that observed in Li metal clearly is not sufficient evidence for a Li-Li bond. In any case we feel that the assumption of weak bonding interactions between the metal atoms in the nests is reasonable since this would reduce the repulsion between these atoms. However, the major concentration of bonding electron density in the nests is probably distributed between the metals and the nitrogen or oxygen atom contacts. This assumption is supported by the differences in the electronegativities of the atoms of the nests.[19]

Conclusion

As in I, each dinitrogen ligand of III is found to lie approximately on a line common to the nickel trigonal planes of two $Ni(C_6H_5)_2$ species. The N_2, Ni_2 bonding may be of the σ type (i.e., donation from the filled orbitals on N_2 to empty orbitals on Ni) and π type (i.e., back-donation from filled metal dπ orbitals to the two π^* orbitals of N_2). As mentioned recently, such interactions in trigonal nickel complexes obtain an additional stability since the σ bonding tends to strengthen the $d\pi(Ni) \rightarrow \pi^*(N_2)$ bond.[21] The Ni-N interaction is probably similar to that of the metal-C in binuclear complexes of acetylene or its derivatives such as in μ-tolane-dicobalthexacarbonyl[22] or in (bisacetylbismethylphenylhydrazone)dichloro-μ-ethyleneplatinum(II).[23] Negative charge on the N_2 ligands is stabilized by interactions with Na1 and Na2, which are located on the back side of each N_2, Ni bond. Additional charge stabilization results from the "end-on" three-center two-electron bonds Li-N-Li. While these types of interaction appear to be important for the stabilization of the "side-on" geometry of the N2, Ni bonding, comparison with the recently determined structure of I indicates that these interactions are not restricted to Li_2 and Na_2 entities but rather also Li and Li_3 species, and perhaps others are possible. This synergistic effect of transition and main group metals on dinitrogen clearly causes a considerable weakening of the N-N bond.

The delocalized interaction of the outer Na atoms with C(α'), Ni, C(α), C(β) fragments of the $(C_6H_5)_2Ni$ moieties and also the Li atoms with Ni, C(α), C(β) species are also of special interest. These bonding modes seem to be typical for main group, transition metal organometallic compounds and have been found recently in other examples.[24]

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