averaging 115.8 ± 3.7°. There appear to be no significant distortions of the methyl groups from positions predicted from an idealized icosahedral geometry. Individual C–CH_3 bond lengths are: C(1)–CH_3(1) = 1.553 ± 0.014 Å, C(2)–CH_3(2) = 1.547 ± 0.014 Å, C(1′)–CH_3(1′) = 1.511 ± 0.014 Å, C(2′)–CH_3(2′) = 1.577 ± 0.017 Å. The average value of 1.547 ± 0.028 Å is not significantly different from the C(sp^3)–C(sp^3) distance of 1.5445 Å in diamond.[30]

Intermolecular Contacts

The packing of (3,4′)-$[(CH_3)_2B_9C_2H_9]Ni^{IV}$ molecules within the unit cell is shown in Figure 2, which shows the view down c. Enantiomers are related to one another by an n-glide plane at $y = 0.25$, and by centers of symmetry at (0 or 0.5, 0 or 0.5, 0 or 0.5).

The individual molecules are separated by normal van der Waals distances. Quantitative data on intermolecular contacts are shown in Table VIII. Closest approaches (of each type) are methyl carbon···hydrogen = 3.17, boron···hydrogen = 3.34, and hydrogen···hydrogen = 2.65 Å. It should be emphasized, however, that hydrogen atoms of the methyl groups have not been included in these calculations.

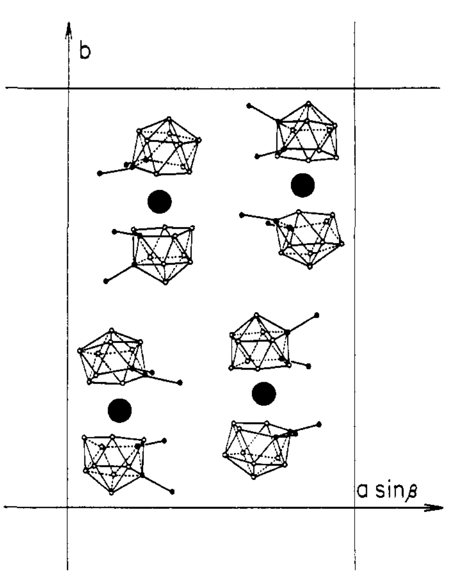

Figure 2. Packing of (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$ molecules in the unit cell, viewed down c.

Acknowledgments. We wish to thank Professor M. F. Hawthorne and Mr. L. F. Warren for providing us with the crystalline sample.

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[30] "Interatomic Distances, Supplement," Special Publication No. 18, The Chemical Society, London, 1965, p S14s.

Crystal and Molecular Structure of Bis-(3)-1,7-dicarbollylnickelate(II) Dianion

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Abstract: The crystal and molecular structure of $[CH_3N(C_2H_4)_3NCH_3][Ni(neo\text{-}C_2B_9H_{11})_2]$ has been determined from a single-crystal X-ray diffraction study. The orthorhombic cell Fdd2 with $a_0 = 16.95$ (3), $b_0 = 24.52$ (7), and $c_0 = 11.63$ (4) Å contains only eight formula units ($\rho = 1.30$ g/cm^3); thus both the organic dication and carbametallic dianion are crystallographically required to possess twofold axes of symmetry. The structure was solved using 622 unique nonzero reflections collected by a film method, and refined by least-squares techniques to a final R factor of 10.5% based on F. While the carborane cages in the previously reported bis-(3)-1,2-dicarbollylnickelate(II) ion were grossly slipped with respect to one another to give an allyl-like structure, that distortion is nearly absent in the compound reported here. Although the (3)-1,7- and (3)-1,2-dicarbollide ions have the same symmetry, the atom charges in the former are believed to be more uniformly distributed. Thus, it appears that ligand asymmetry is a definite factor in the stereochemistry of the electron-rich metallobisdicarbollyls. A further feature of the structure is that the carborane cages are not related by a center of symmetry but, rather, have taken on an intermediate rotamer configuration. Although the N,N′-dimethyltriethylenediammonium ion possesses three different twofold axes of symmetry, none of them was found to lie along a crystallographic twofold axis. Thus, for no obvious reason, the organic dication is disordered.

A large number of transition metal derivatives of the (3)-1,2-dicarbollide ion have been synthesized and structurally characterized by single-crystal X-ray diffraction studies.[1] The stereochemistry of these compounds is of two distinct forms.

First, as exemplified by $[\pi\text{-}C_5H_5]Fe[\pi(3)\text{-}1,2\text{-}C_2B_9H_{11}]$,[2] there are symmetrical π-sandwich structures which are extant when the metal in its "formal" valence possesses seven or fewer d electrons.

Second, for those compounds which formally contain d^8 or d^9 metal ions, a slipped π-sandwich or π-allyl stereochemistry is observed.[3]

A part of a continuing effort to learn more about the distortions in the electron-rich (d^7–d^9) series of compounds, the structure determination of the Ni^{2+} (d^8) complex of (3)-1,7-dicarbollide ion was undertaken.

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[1] M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

[2] A. Zalkin, D. H. Templeton, and T. E. Hopkins, *J. Amer. Chem. Soc.*, **87**, 1818 (1965).

[3] R. M. Wing, *ibid.*, **90**, 4828 (1968).

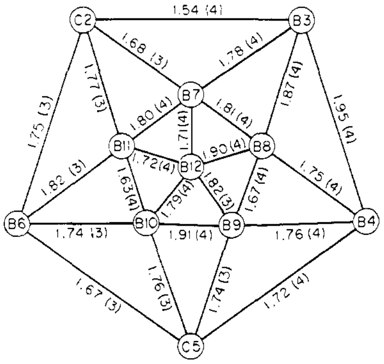

Figure 1. Bond lengths in the (3)-1,2-dicarbollyl cage.

The ligand, a geometrical isomer of the (3)-1,2-dicarbollide ion, is distinguished from the latter in that its carbon atoms (which still remain in the open five-atom face) are separated by a boron atom. It was felt that this change might make the relative electron-donating ability of the face carbon and boron atoms nearly equal. The evidence reported here indicates this hypothesis to be nearly correct.

Experimental Section

Red needles of $[CH_3N(C_2H_4)_3NCH_3]\ Ni(C_2B_9H_{11})_2$ were provided by Mr. D. V. Howe and Professor M. F. Hawthorne of this department. A single crystal (0.15 × 0.15 × 0.8 mm) was selected and mounted in a borosilicate capillary.

Precession (Mo Kα; λ 0.7107 Å) and Weissenberg (Cu Kα; λ 1.5418 Å) photographs indicated that the crystal was orthorhombic with a_0 = 16.95 (3), b_0 = 24.52 (7), and c_0 = 11.63 (4) Å. Systematic absences for *hkl* when the indices were not all even or all odd indicated a face-centered cell. Further absences in the 0*kl* zone for $k + l \neq 4n$ and in the *h*0*l* zone for $h + l \neq 4n$ lead unambiguously to Fdd2 (No. 43) as the space group.

Since the compound was very unstable and limited in supply, no analysis was available. However, the expected composition fit the unit cell volume and density data (ρ = 1.30 (2) g/cm^3; flotation in 1-bromobutane) very well for eight formula units per cell (calcd 8.06).

Reflections were collected for the layers *hk*0 through *hk*8 out to sin θ = 0.95 on a Nonius integrating Weissenberg camera using Ni-filtered Cu radiation. The film pack consisted of three films with relative speeds of 9:3:1. The attenuation of the X-ray intensity in each film was such that the normalized intensities were *ca* 100:10:1. The individual spot intensities along with a background for each spot were read from the expanded side of the films using a Nonius microdensitometer. Of the 800 unique reflections accessible, 622 were found to have intensities above background. They were corrected for Lorentz and polarization effects, but not for absorption ($\mu r \sim 0.08$). Empirical spot shape[4] corrections were made to the low angle reflections of the upper levels. The maximum number of corrections was to six reflections on the seventh level. The data from the different levels were put on a common scale during refinement.

The atomic scattering power of nickel was corrected for the real and imaginary parts of the anomalous dispersion,[5] and the atomic scattering powers of Ni$^+$, along with neutral N, C, B, and H, were taken from standard tables.[6]

All calculations[7] were executed on an IBM 360-50 computer having a 256K byte memory. In the least-squares refinement the function $\Sigma w(|F_o| - |F_c|)$ was minimized and in the last six cycles the weights were: $w = (40 + F_o + F_o^2/250)^{-1}$.

Solution of the Structure

Since there are only eight nickel atoms in the cell they must occupy the special 8a equipoint of Fdd2. The *z* coordinate must be arbitrarily set to fix the origin. Therefore the nickel was placed at $^1/_4$, $^1/_4$, $^1/_4$ for convenience. An electron density map was then computed resulting in the expected, but nevertheless confusing, false center of symmetry. A careful search in the vicinity of the nickel indicated four carborane cages. Each pair of atoms correctly related by the twofold axis at $^1/_4$, $^1/_4$, *z* was then reflected into yet another pair by a false mirror at *x*, $^1/_4$, *z*. One of the four cages was arbitrarily selected to be least-squares refined as a C_{5v}-B_{11} icosahedral group. Three cycles of refinement of the group parameters,[8] the nickel temperature factor, and the nine film scale factors gave $R_1 = 0.22$ ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$).

A Fourier map computed at this point now had the correct symmetry. Besides the indication that the C_{5v} group was only a fair approximation to the cage, only the nitrogen and methyl carbon atoms of the organic dication were readily apparent. These two atoms were included with the individual cage atoms (assumed to be all boron atoms) in four cycles of refinement, reducing R_1 to 0.17. Both on the basis of temperature factors and of bond distances, the identity of the cage carbon atoms was now apparent, but no action was taken at this point.

A difference electron density map was computed and the six carbon atoms from the three missing ethylene linkages still could not be found in the expected places. However, 12 peaks ranging in size from 2 to 3 e/Å^3 were found in places proper for ethylene carbons, assuming that the cation was rotated about the N–CH_3 bond *ca.* 30° away from that orientation which would allow one of its molecular twofold axes to be coincident with the crystallographic twofold axis. Thus, for no obvious reason the N,N′-dimethyltriethylenediammonium ion is disordered. Six unique ethylene carbon atoms (each at half weight) were now added to the least-squares refinement calculations. Seven cycles, in which all positional (except nickel) and thermal parameters (nickel anisotropic) and the nine film scale factors were varied, reduced the residue R_1 to 0.116. The identity of the cage carbons remained the same, and those two atoms, B(2) and B(5), were now assigned carbon scattering powers.

A final difference Fourier had its most prevalent features at the expected cage hydrogen atom locations, and those 11 atoms were included in the calculations but not refined. Three more cycles of refinement resulted in a final value for R_1 of 0.105 and for R_2, 0.143 ($R_2 = \Sigma w \cdot (|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$. The standard deviation of an observation of unit weight is 0.97.

The observed and final calculated structure factors have been deposited with NAPS.[9]

Atom coordinates and temperature factors are listed in Table I. Derived bond lengths are given in Table II

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[4] A. K. Singh, *Z. Kristallogr.*, **124**, 378 (1967).

[5] D. H. Templeton in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 214.

[6] J. A. Ibers, ref 5, p 202.

[7] The programs used were Zalkin's FORDAP Fourier summation program, Busing, Martin, and Levy's ORFLS full-matrix least-squares program as modified by Doedens for group refinement, Johnson's ORTEP drawing program, and Woods's MGEOM distance, angle, and plane program.

[8] C. Scheringer, *Acta Crystallogr.*, **16**, 546 (1963).

[9] A table of the observed and calculated structure amplitudes of $CH_3N(C_2H_4)_3NCH_3][Ni(\textit{neo}\text{-}C_2B_9H_{11})_2]$ has been deposited as Document No. NAPS-00852 with the ASIS National Auxiliary Pubication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $3.00 for photocopies or $1.00 for microfiche. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

and Figure 1. Some bond angles and best planes are given in Tables III and IV. Labeling of the atoms is the same in the tables and figures, except for the carborane carbons.

Table I. Final Positional and Thermal Parameters for $[CH_3N(C_2H_4)_3NCH_3][Ni(C_2B_9H_{11})_2]$

Atom	x/a	y/b	z/c	B^a
Ni	0.25	0.25	0.25	
CB(2)	0.383(1)	0.2828(7)	0.237(2)	2.7(4)
B(3)	0.358(2)	0.2567(10)	0.352(3)	3.1(5)
B(4)	0.311(2)	0.1848(12)	0.328(3)	3.4(6)
CB(5)	0.313(1)	0.1831(8)	0.179(2)	2.0(4)
B(6)	0.343(1)	0.2432(8)	0.127(2)	1.6(4)
B(7)	0.457(1)	0.2498(12)	0.304(3)	3.4(6)
B(8)	0.411(2)	0.1900(10)	0.366(3)	3.3(5)
B(9)	0.387(1)	0.1496(9)	0.256(3)	2.9(4)
B(10)	0.407(2)	0.1879(10)	0.115(3)	3.3(5)
B(11)	0.449(1)	0.2453(10)	0.150(3)	2.7(5)
B(12)	0.475(1)	0.1902(9)	0.232(3)	3.2(4)
C(1)	0.654(2)	0.245(1)	0.211(3)	2.1(7)
C(2)	0.691(3)	0.202(2)	0.211(5)	5.1(12)
C(3)	0.766(2)	0.287(1)	0.344(4)	1.6(6)
C(4)	0.802(3)	0.228(2)	0.344(5)	4.8(11)
C(5)	0.771(3)	0.299(2)	0.126(5)	3.7(10)
C(6)	0.821(2)	0.243(2)	0.134(4)	2.8(7)
C(7)	0.833(1)	0.1506(9)	0.220(2)	3.9(5)
N	0.788(1)	0.2026(6)	0.225(2)	2.7(3)
H(2)	0.37	0.32	0.225	
H(3)	0.33	0.28	0.44	
H(4)	0.28	0.17	0.39	
H(5)	0.28	0.165	0.13	
H(6)	0.31	0.245	0.04	
H(7)	0.50	0.28	0.36	
H(8)	0.43	0.17	0.46	
H(9)	0.395	0.105	0.24	
H(10)	0.42	0.16	0.03	
H(11)	0.48	0.28	0.10	
H(12)	0.525	0.17	0.24	

[a] Nickel: $B_{ij} = 4b_{ij}/a_i^*a_j^*$; $B_{11} = 1.9$ (1), $B_{22} = 2.1$ (1), $B_{33} = 2.5$ (1), $B_{12} = 1.2$ (1), $B_{13} = B_{23} = 0.0$.

Table II. Selected Bond Lengths in $[CH_3N(C_2H_4)_3NCH_3][Ni(C_2B_9H_{11})_2]$

Anion		Cation	
Ni–CB(2)	2.39(2)	N(4)–C(7)	1.49
Ni–B(3)	2.18(3)	N(4)–C(2)	1.66
Ni–B(4)	2.11(3)	N(4)–C(4)	1.54
Ni–CB(5)	2.12(2)	N(4)–C(6)	1.56
Ni–B(6)	2.14(2)	C(1)–C(2)	1.24
		C(3)–C(4)	1.58
⟨C–B⟩	1.70(8)	C(5)–C(6)	1.62
		C(1)–N(4)*	1.64
⟨B–B⟩	1.79(9)	C(3)–N(4)*	1.68
		C(5)–N(4)*	1.53
⟨Cage–H⟩	1.1(1)		
		⟨N–C⟩	1.57(8)
		⟨C–C⟩	1.48(20)

Discussion

The carbametallic anion is shown in Figure 2. That it is very nearly of the symmetrical π-sandwich variety is the most striking aspect of this structure. This is made clear by reference to Figure 3, which shows the nickel and five face atoms of one cage projected onto the plane defined by B(3), B(4), and B(6). The nickel atom is shifted 0.15 Å off center. When compared to the 0.6-Å shift observed for the isoelectronic Cu(III) bis-(3)-1,2 dicarbollyl anion and 0.6 Å estimated for the Ni(II) bis-(3)-1,2 dicarbollyl dianion[3] the present structure seems to belong to the π-sandwich rather than π-allyl classification.

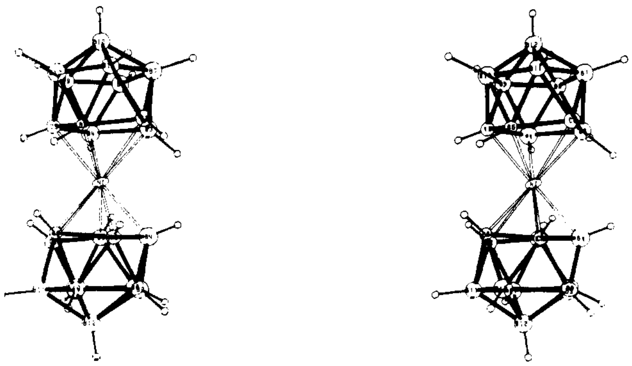

Figure 2. A stereo-pair of the nickel bis-(3)-1,7-dicarbollyl) dianion.

Table III. Average Bond Angles (deg) in $[CH_3N(C_2H_4)_3NCH_3][Ni(C_2B_9H_{11})_2]$

Angle	Number	Range	Average
	Carbametallic Triangular Faces		
C–Ni–B	4	39–48	44(4)
B–Ni–B	1		54(1)
C–B–B	12	53–62	58(3)
B–C–B	6	61–67	63(4)
B–B–B	27	53–66	60(4)
	Carbametallic Pentagonal Rings		
C–B–B	15	99–111	106(3)
B–C–B	7	108–117	113(3)
C–B–C	1		110(1)
B–B–B	22	102–114	107(4)
	Organic Dication		
C–N–C	12	105–119	109(4)
N–C–C	6	106–119	112(5)

Table IV. Some Best Least-Squares Planes in $[CH_3N(C_2H_4)_3NCH_3][Ni(C_2B_9H_{11})_2]^a$

Plane $1^{b,d}$			Plane $2^{c,e}$		
Atom	Weight	Distance from plane, Å	Atom	Weight	Distance from plane, Å
CB(2)	12	−0.08	B(7)	11	−0.04
B(3)	11	0.06	B(8)	11	0.05
B(4)	11	0.01	B(9)	11	−0.04
CB(5)	12	−0.07	B(10)	11	0.03
B(6)	11	0.09	B(11)	11	0.00
Ni	0	1.61	Ni	0	3.11
B(7)	0	−1.55	B(12)	0	−0.97
B(8)	0	−1.45	CB(2)	0	1.43
B(9)	0	−1.53	B(3)	0	1.56
B(10)	0	−1.47	B(4)	0	1.51
B(11)	0	−1.51	CB(5)	0	1.42
B(12)	0	−2.47	B(6)	0	1.59

[a] Cartesian coordinates with $x \parallel a_0$, etc. [b] Plane 1: $-0.905X + 0.425Y + 0.020Z = -2.785$. [c] Plane 2: $-0.902X + 0.431Y + 0.021Z = -4.235$. [d] CB(2)–B(3)–B(4)–CB(5)–B(5) nonplanar at better than the 0.999 confidence level. [e] B(7)–B(8)–B(9)–B(10)–B(11) nonplanar at the 0.99 confidence level.

There are, however, several structural features which distinguish the present structure from an idealized symmetric π-sandwich stereochemistry.

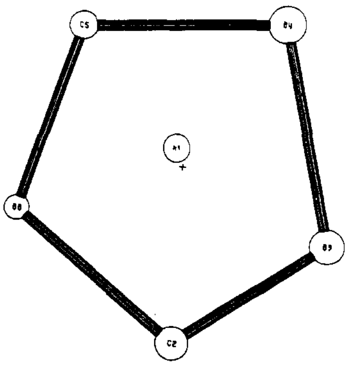

Figure 3. A projection of the nickel atom onto the plane defined by B(3), B(4), and B(6).

First, the five-atom face of the carborane cage is quite nonplanar, with the carbon atoms being bent away from the nickel back into the cage.

Second, the shape of the five-atom face is very irregular. There is one very short band (CB(2)–B(3) = 1.55 Å), and one very long band (B(3)–B(4) = 1.95 Å). Repeated attempts by least-squares refinement and by difference synthesis to place B(3) in a position which would equalize these bonds failed.

Third, both as a result of the small but real slip distortion, and the nonplanarity of the five-atom carborane face (CBBCB), C(2) is much farther from the nickel than the other four atoms (2.39 Å *vs.* 2.14 Å).

Distortions from ideal π-sandwich geometry such as those described above make a rational description of the molecule difficult. However, there can be little doubt of a strong tendency to adopt a symmetrical π-sandwich configuration.

Another interesting feature of the structure is the occurrence of a noncentrosymmetric rotamer form (Figure 2). Although the early structure determinations invariably turned up structures which had the carborane carbons *trans* to one another,[1] recent studies of the metallocarborane systems have revealed rotamer forms[10,11] as being important.

Further, dipole moment measurements on the neutral nickel systems imply an array of rotamer forms.[12] An interesting consequence of the dipolar nature of the nickel sandwiches is the formation of donor–acceptor complexes with aromatic donor molecules such as pyrene.[12] Structural results on these materials will be reported at a later date.[13]

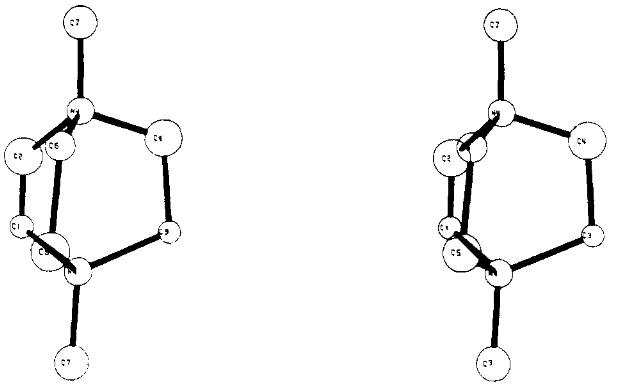

Figure 4. A stereo-pair of the N,N′-dimethyltriethylenediammonium ion.

Unfortunately, the organic dication N,N′-dimethyltriethylenediammonium ion was disordered; however, the gross features of the ion are evident (Figure 4). The idealized symmetry is D_3, as there seems to be a slight twisting of the ion about its threefold axis. This is in the direction of the expected strain-relieving distortion and puts the individual N–(C–C)$_2$–N six-atom rings into a twist boat conformation. The interionic distances are all of normal van der Waals size.

We conclude that ligand symmetry must be a prime consideration in any prediction of the stereochemistry of electron-rich metalloaromatics.[14]

Acknowledgments. I wish to thank Professor M. F. Hawthorne and Mr. David V. Howe for the crystalline sample, and the National Science Foundation for support of this research under Grant No. GP-8055.

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(10) D. St. Clair, A. Zalkin, and D. H. Templeton, *J. Amer. Chem. Soc.*, **92**, 1173 (1970).

(11) M. R. Churchill, K. Gold, J. N. Francis, and M. F. Hawthorne, *ibid.*, **91**, 1222 (1969).

(12) L. F. Warren Jr., and M. F. Hawthorne, *ibid.*, **92**, 1157 (1970).

(13) R. M. Wing and H. P. Calhoun, in preparation.

(14) Note Added in Proof. The symmetrical half-sandwich structure recently established for $Et_3PCu_5H_5$ (F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 7281 (1969)) constitutes further evidence that the slip distortion extant in some of the metallobisdicarbollyls has its origin in the asymmetry of the dicarbollyl cage.