Table VI. Sodium-Potassium Competition

Temp, °C	% Na	% K	Mole ratios	
			Na:K	Amine:salt
−15	2.39 ± 0.03	0.896 ± 0.01	4.5	2.90
30	2.70 ± 0.02	0.346 ± 0.02	13.3	3.01
40	2.81 ± 0.08	0.258 ± 0.08	18.5	2.93

change in conductance was observed for these salts upon addition of the diamine.

Acknowledgment. Financial support of this work by the Research Corp. and by the Office of Saline Water, U. S. Department of the Interior, is gratefully acknowledged.

Registry No. I, 42282-63-3; NaCl(I)$_3$, 42343-70-4; NaBr(I)$_3$, 42343-74-8; NaI(I)$_3$, 42343-75-9; NaCN(I)$_3$, 42343-72-6; NaN$_3$(I)$_3$, 42343-77-1; NaNO$_2$(I)$_3$, 42396-98-5; NaNO$_3$(I)$_3$, 42343-71-5; KCl(I)$_3$, 42396-99-6; KI(I)$_3$, 42397-00-2; RbCl(I)$_3$, 42397-01-3; RbI(I)$_3$, 42343-79-3; CsI(I)$_3$, 42343-80-6; CsN$_3$(I)$_3$, 42343-81-7; AgNO$_3$(I)$_3$, 42294-78-0; TlClO$_4$(I)$_3$, 42343-82-8.

Contribution from the Physics Department, Clemson University,
Clemson, South Carolina 29631

Solid Coordination Compounds of Alkali Metal Salts with a Neutral Atomatic Amine. II. Crystal Structures

LANCE A. DUVALL and DONALD P. MILLER*

Received May 23, 1973

The crystal and molecular structures of adducts of racemic DPB (DPB = *p,p'*-diamino-2,3-diphenylbutane, $C_{16}H_{20}N_2$) with sodium chloride, sodium nitrate, and sodium cyanide have been determined using data collected with a counter diffractometer. The ratio of DPB to salt is 3:1. The Na(DPB)$_3$Cl structure was solved using direct methods and was refined by full-matrix least squares using 1216 reflections to a conventional $R = 0.082$ and weighted $R_w = 0.070$. The adduct crystallizes in space group $R\bar{3}c$ with hexagonal unit cell dimensions $a = 21.172$ (2) Å, $c = 17.004$ (4) Å; $\rho_{obsd} = 1.178$ (5) g/cm^3, $\rho_{calcd} = 1.176$ g/cm^3 for $Z = 6$. Five of the ten hydrogens in the asymmetric unit were located in a difference map and were included in the refinement. The nitrogens of the amines are hexacoordinated to the sodium ions with a bond length of 2.608 (3) Å. The Na(DPB)$_3$NO$_3$ and Na(DPB)$_3$CN structures were refined using the general positions from the sodium chloride adduct structure as an initial model. The use of limited sets of data led to conventional and weighted residuals of $R = 0.113$ and $R_w = 0.072$ for the sodium nitrate adduct and $R = 0.117$ and $R_w = 0.076$ for the sodium cyanide adduct.

Introduction

There has been considerable interest recently in the structure of nonionic organic molecules which are capable of forming metal cation complexes. The crystal structures of the crown complexes RbNCS(dibenzo-18-crown-6) and NaNCS(dibenzo-18-crown-6) have been reported by Bright and Truter.[1] The crystal structures of the rubidium cryptates[2,3] and the barium cryptates[4] have been reported by Metz, Moras, and Weiss. The structure of a metal cation complex, reported in 1966 by Marullo and Lloyd,[5] has now been solved. Marullo and Lloyd[5] described the first example of the precipitation of simple salts of alkali metals from an aqueous solution by compound formation with a nonionic ligand, racemic *p,p'*-diamino-2,3-diphenylbutane (DPB), $C_{16}H_{20}N_2$. They found chemical and infrared spectral evidence of a hexacoordinated bond between the cation and the amine of the DPB molecule. Other questions remained, however. Is the DPB molecule in extended, partially eclipsed, or eclipsed conformation? Is the nitrogen coordination about the sodium completely octahedral? What are the conformations of the several anions? Structure determinations of three of the reported adducts have provided detailed answers to these questions. Discussion of bonding is presented in the previous paper.[6]

Experiment, Solution, and Refinement

Collection and Reduction of X-Ray Data. Clear, well-formed crystals of the adducts were obtained from N. P. Marullo; a description of their preparation can be found in the literature.[7] The external morphology of the crystals exhibits the symmetry elements of the class $R\bar{3}2/m$. Buerger precession photographs (*hk*0, *hk*1, *hk*2, *hk*3) using Cu $K\bar{\alpha}$ radiation revealed trigonal symmetry with reflections limited to those satisfying the conditions hkl, $-h + k + l = 3n$; hhl, $l = 3n$; and $h\bar{h}l$, $h + l = 3n$, $l = 2n$, which identifies the space group as either $R\bar{3}c$ (D_{3d}^6, No. 167) or $R3c$ (C_{3v}^6, No. 161). $R\bar{3}c$ was chosen because the external morphology indicated the presence of inversion symmetry. The following discussion will detail the data collection process used for the sodium chloride structure; the treatment of the other adducts was essentially identical except that only those reflections whose peak intensity was at least 1/1000th of the peak intensity of the strongest reflection were measured. Table I lists the pertinent physical data for all the adducts. A sodium chloride adduct crystal was cleaved normal to the *c* axis to produce a sample of approximate dimensions 0.15 mm × 0.15 mm × 0.13 mm for intensity data collection. The crystal was mounted on an automatic three-circle diffractometer, designed and built in our laboratory. The crystal was aligned so that the *c* axis (coincident with the needle axis of the crystal) was approximately 1° out of allignment with the ϕ axis in order to minimize multiple reflections. The unit cell parameters were determined using Cu $K\bar{\alpha}$ radiation (1.5418 Å) by least-squares refinement based on 12 accurately centered reflections. The density was measured using a bromobenzene-chlorobenzene linear density gradient column calibrated with aqueous solutions of potassium iodide. The calculated and measured densities are in agreement for

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(3) B. Metz, D. Moras, and R. Weiss, *Chem. Commun.*, 217 (1970).

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(5) N. P. Marullo and R. A. Lloyd, *J. Amer. Chem. Soc.*, **88**, 1076 (1966).

(6) N. P. Marullo, J. F. Allen, G. T. Cochran, and R. A. Lloyd, *Inorg. Chem.*, **13**, 115 (1974).

(7) G. T. Cochran, J. F. Allen, and N. P. Marullo, *Inorg. Chim. Acta*, 1, 109 (1967).

Table I. Physical Data for Adducts of DPB[a]

	NaCl adduct	$NaNO_3$ adduct	NaCN adduct
Habit	Colorless hexagonal prisms	Colorless hexagonal prisms	Colorless hexagonal prisms
Crystal size	0.13 mm (*c* axis) × 0.15 mm (max dimension in *ab* plane)	0.10 mm (*c* axis) × 0.18 mm (max dimension in *ab* plane)	0.20 mm (*c* axis) × 0.17 mm (max dimension in *ab* plane)
Space group	$R\bar{3}c$	$R\bar{3}c$	$R\bar{3}c$
a, Å	21.172 (2)	21.250 (4)	21.202 (5)
c, Å	17.004 (4)	17.332 (5)	17.170 (5)
γ, deg	120	120	120
V, Å^3	6600.74	6777.73	6684.08
Z	6	6	6
ρ_{calcd}, g/cm^3	1.176	1.184	1.147
ρ_{obsd}, g/cm^3	1.178 (5)	None	None
μ(Cu Kα), cm^{-1}	11.73	6.85	6.20
No. of reflections	1216	774	771
Max (sin θ)/λ	0.5313	0.4586	0.4586

[a] Numbers in parentheses are esd's in the last figure quoted for all tables.

Table II. Final Positions[a] and Thermal Parameters[b]

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{13}$	$2U_{23}$
				NaCl Adduct					
N	440 (2)	1121 (2)	0931 (3)	38 (3)	49 (3)	85 (3)	30 (2)	−13 (3)	−27 (3)
C(1)	1195 (3)	1613 (3)	0865 (3)	63 (3)	43 (3)	57 (5)	58 (3)	−9 (3)	−17 (3)
C(2)	1688 (3)	1579 (3)	1390 (3)	66 (5)	51 (3)	48 (5)	61 (3)	−6 (3)	−7 (3)
C(3)	2446 (3)	2037 (3)	1285 (4)	61 (5)	51 (3)	23 (3)	54 (3)	−9 (3)	0 (3)
C(4)	2719 (3)	2528 (3)	0659 (4)	58 (3)	39 (3)	70 (5)	54 (3)	13 (3)	−3 (3)
C(5)	2230 (3)	2577 (3)	0159 (3)	73 (5)	58 (3)	60 (5)	78 (3)	−3 (3)	7 (3)
C(6)	1483 (3)	2131 (3)	0253 (4)	61 (5)	54 (3)	62 (5)	61 (3)	−16 (3)	0 (3)
C(7)	3542 (3)	3010 (3)	0532 (4)	48 (3)	56 (3)	91 (5)	48 (3)	32 (3)	−7 (3)
C(8)	3937 (3)	2550 (3)	0564 (5)	78 (5)	73 (3)	180 (9)	109 (3)	47 (5)	14 (5)
H[C(2)]	1420 (40)	1150 (40)	1740 (40)	119	119	119	119	0	0
H[C(3)]	2810 (40)	2010 (40)	1780 (50)	119	119	119	119	0	0
H[C(5)]	2390 (40)	3020 (40)	−0310 (50)	119	119	119	119	0	0
H[C(6)]	1070 (50)	2160 (50)	−0140 (50)	119	119	119	119	0	0
H[C(7)]	3730 (40)	3210 (40)	−0020 (40)	119	119	119	119	0	0
Na	0000	0000	0000	44 (2)	44 (2)	69 (3)	44 (2)	0	0
Cl	0000	0000	2500	70 (2)	70 (2)	50 (3)	68 (2)	0	0
				$NaNO_3$ Adduct					
N(1)	0474 (4)	1186 (4)	0866 (5)	36 (7)	39 (7)	94 (8)	17 (5)	6 (6)	−32 (6)
C(1)	1253 (6)	1663 (5)	0816 (7)	58 (9)	34 (8)	70 (11)	45 (8)	3 (9)	−42 (8)
C(2)	1710 (6)	1598 (6)	1401 (6)	75 (9)	58 (8)	67 (11)	85 (8)	84 (9)	−38 (8)
C(3)	2494 (7)	2067 (6)	1322 (7)	70 (9)	48 (8)	64 (11)	48 (8)	38 (8)	0 (8)
C(4)	2776 (7)	2547 (6)	0658 (8)	82 (9)	39 (8)	87 (12)	79 (8)	19 (9)	−16 (8)
C(5)	2300 (7)	2620 (6)	0117 (7)	79 (9)	60 (8)	58 (9)	68 (8)	16 (8)	−19 (8)
C(6)	1534 (7)	2173 (6)	0200 (7)	99 (12)	34 (8)	62 (11)	51 (8)	36 (8)	3 (8)
C(7)	3613 (5)	3033 (6)	0512 (8)	31 (8)	74 (12)	152 (15)	51 (8)	6 (9)	−78 (9)
C(8)	3964 (6)	2548 (6)	0563 (8)	63 (9)	68 (9)	213 (15)	117 (8)	42 (9)	0 (9)
Na	0000	0000	0000	55 (7)	55 (7)	70 (9)	55 (7)	0	0
N(2)	0000	0000	2500	79 (15)	79 (15)	33 (12)	79 (14)	0	0
O	0605 (4)	0000	2500	65 (5)	106 (9)	164 (14)	106 (9)	0 (9)	0 (9)
				NaCN Adduct					
N(1)	444 (7)	1136 (7)	0929 (8)	32 (10)	51 (10)	90 (1)	24 (9)	−3 (9)	−45 (9)
C(1)	1220 (1)	1620 (9)	0860 (1)	9 (2)	26 (14)	75 (1)	55 (14)	16 (14)	−16 (13)
C(2)	1690 (1)	1596 (9)	1440 (1)	72 (15)	59 (15)	60 (1)	89 (14)	−10 (14)	−51 (11)
C(3)	2470 (1)	2050 (1)	1320 (1)	56 (15)	34 (14)	119 (3)	44 (12)	28 (14)	26 (14)
C(4)	2760 (1)	2537 (9)	0680 (1)	9 (2)	31 (14)	75 (1)	85 (14)	−10 (14)	−35 (13)
C(5)	2270 (1)	2600 (9)	0100 (1)	9 (2)	20 (14)	75 (1)	85 (14)	−28 (14)	−42 (13)
C(6)	1490 (1)	2130 (1)	0240 (1)	55 (15)	39 (14)	90 (1)	48 (12)	−16 (14)	−38 (13)
C(7)	3594 (9)	3030 (1)	0500 (1)	18 (12)	51 (15)	194 (3)	7 (12)	16 (14)	−64 (2)
C(8)	3954 (9)	2552 (9)	0570 (1)	21 (15)	59 (15)	224 (3)	113 (14)	32 (2)	−22 (14)
Na	0000	0000	0000	48 (7)	48 (7)	90 (1)	48 (7)	00	00
C(9)	0000	0000	2306	256	256	9	263	00	00
N(2)	0000	0000	2669	331	331	45	273	00	00

[a] The listed positions are multiplied by 10^4. [b] The listed U_{ij}'s are in Å^2 and are multiplied by 10^3. The form of the temperature factor expression is $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}a^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^{*2}hk + 2U_{13}a^{*}c^{*}hl + 2U_{23}a^{*}c^{*}kl)]$.

$Z = 6$. The asymmetric unit included half of a DPB molecule and one anion–cation pair. The ion positions must be along the threefold axes while the DPB half-molecule atoms are each in a general position.

Intensities were measured using a NaI(Tl) scintillation counter and Ni-filtered Cu K$\bar{\alpha}$ radiation. The pulse height discriminator was set to pass 90% of the Cu K$\bar{\alpha}$ peak. The scans were made using the θ–2θ technique with a scan rate of 3°/min. The background was measured for 20 sec at the beginning and end of each scan and subtracted from the total count to yield the corrected net count. Because there was some uncertainty as to whether the glide symmetry was present, data were collected for $R\bar{3}$ symmetry. All unique reflections in the range $2\theta = 0, 90°$ were collected; a number of stronger reflections, those whose peak intensity was at least 1/1000th of the peak intensity of the strongest recorded intensity in the range

Table III. Interatomic Distances (Å)[a]

Atom pairs	NaCl adduct	$NaNO_3$ adduct	NaCN adduct
N(1)-C(1)	1.41 (1)	1.45 (2)	1.45 (3)
C(1)-C(2)	1.40 (1)	1.46 (2)	1.45 (4)
C(2)-C(3)	1.41 (1)	1.46 (3)	1.47 (3)
C(3)-C(4)	1.40 (1)	1.45 (3)	1.42 (4)
C(4)-C(5)	1.38 (1)	1.42 (3)	1.45 (4)
C(5)-C(6)	1.39 (1)	1.42 (3)	1.45 (4)
C(1)-C(6)	1.40 (1)	1.42 (3)	1.42 (4)
C(4)-C(7)	1.53 (1)	1.57 (3)	1.58 (4)
C(7)-C(8)	1.57 (1)	1.55 (3)	1.55 (4)
C(7)-C(7)′	1.57 (1)	1.57 (3)	1.59 (4)
N(1)-Na	2.608 (5)	2.661 (9)	2.64 (1)
N(1)-Cl	3.378 (5)		
Na-Cl	4.251 (1)		
C(2)-H[C(2)]	0.97 (4)[b]		
C(3)-H[C(3)]	1.20 (4)[b]		
C(5)-H[C(5)]	1.14 (4)[b]		
C(6)-H[C(6)]	1.12 (4)[b]		
C(7)-H[C(7)]	1.03 (4)[b]		
N(2)-O		1.29 (1)	
Na-N(2)		4.333 (1)	
N(1)-O		3.89 (1)	

[a] The symmetry transformation which produces the second half of the DPB molecule from the asymmetric unit generates the position C(7)′ from the position C(7). [b] Estimated C-H bond errors are based on estimated hydrogen positions located on difference *E* maps which had grids of approximately 0.01 Å. Positions were estimated to within the difference peak ±0.04 Å for ring hydrogens.

Table IV. Interatomic Angles (deg)

Atoms	NaCl adduct	Atoms	NaCl adduct
N(1)-C(1)-C(2)	120.6 (1)	C(1)-C(2)-H[C(2)]	109.0 (2)
C(1)-C(2)-C(3)	120.3 (4)	C(3)-C(2)-H[C(2)]	129.9 (2)
C(2)-C(3)-C(4)	121.0 (3)	C(2)-C(3)-H[C(3)]	115.3 (5)
C(3)-C(4)-C(5)	118.5 (1)	C(4)-C(3)-H[C(3)]	124.3 (4)
C(4)-C(5)-C(6)	121.3 (4)	C(4)-C(5)-H[C(5)]	124.3 (1)
C(5)-C(6)-C(1)	121.1 (1)	C(6)-C(5)-H[C(5)]	114.0 (1)
N(1)-C(1)-C(6)	121.5 (4)	C(5)-C(6)-H[C(6)]	122.9 (5)
C(6)-C(1)-C(2)	117.8 (3)	C(1)-C(6)-H[C(6)]	116.0 (2)
C(3)-C(4)-C(7)	121.0 (1)	C(4)-C(7)-H[C(7)]	119.1 (5)
C(5)-C(4)-C(7)	120.5 (4)	C(8)-C(7)-H[C(7)]	93.9 (6)
C(4)-C(7)-C(8)	111.3 (1)	C(7)′-C(7)-H[C(7)]	109.0 (1)
C(8)-C(7)-C(7)′	112.5 (1)		
C(4)-C(7)-C(7)′	110.1 (1)		

Atoms	$NaNO_3$ adduct	NaCN adduct
N(1)-C(1)-C(2)	118.3 (4)	115.1 (5)
C(1)-C(2)-C(3)	117.3 (5)	115.5 (4)
C(2)-C(3)-C(4)	118.9 (2)	122.1 (5)
C(3)-C(4)-C(5)	121.7 (1)	121.6 (1)
C(4)-C(5)-C(6)	119.4 (4)	115.3 (2)
C(5)-C(6)-C(1)	119.3 (5)	122.4 (9)
N(1)-C(1)-C(6)	118.5 (5)	105.2 (4)
C(6)-C(1)-C(2)	123.2 (2)	122.8 (5)
C(3)-C(4)-C(7)	121.5 (4)	123.7 (1)
C(5)-C(4)-C(7)	116.8 (3)	114.7 (2)
C(4)-C(7)-C(8)	108.6 (2)	108.2 (2)
C(4)-C(7)-C(7)′	106.7 (3)	105.4 (1)
C(8)-C(7)-C(7)′	111.5 (2)	109.9 (1)
C(1)-N(1)-Na	112.9 (4)	

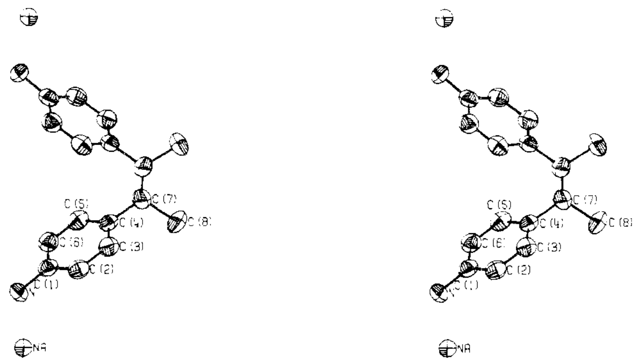

Figure 1. Stereographic view of DPB molecule. The ellipsoids enclose 50% probability of thermal motion.

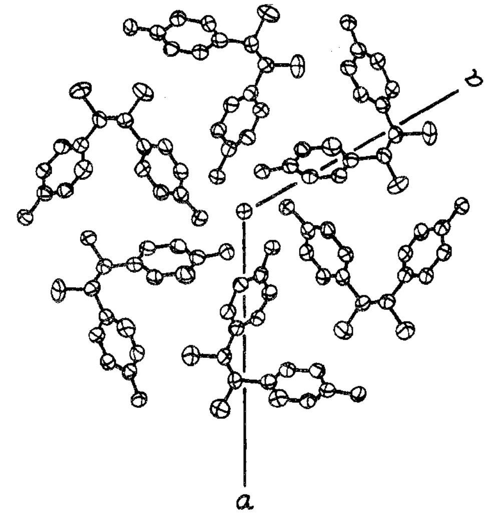

Figure 2. Section of crystal ±0.17*c* projected onto the *ab* plane. The ellipsoids enclose 50% probability of thermal motion.

$2\theta = 90, 110°$ were also collected. All intensities were collected at approximately 22°. Of a total of 1383 unique intensities collected, 113 were rejected because their corrected net count was negative. No other intensities were discarded.

The 440 reflection was remeasured periodically during data collection in order to check for instabilities in the crystal and in the diffractometer system. No significant change in the measured intensity of the 440 reflection was observed during data collection.

The intensities were used to generate structure factor amplitudes $|F_o| = (I_0/Lp)^{1/2}$, where Lp is the Lorentz-polarization correction. The estimated standard deviation for the structure factor amplitudes was taken as $\sigma_F = (\sigma_{pk}{}^2/4LpI_0)^{1/2}$, where $\sigma_{pk} = (N_T + N_{b_1} + N_{b_2})^{1/2}$; N_T is equal to the total count, and N_{b_1} and N_{b_2} are the background counts at the ends of the scanning interval. No correction for absorption was made; $\mu = 11.73$ cm^{-1} for Cu K$\bar{\alpha}$ and the factor for absorption along the largest dimension of the crystal is about 2.1% larger than that for absorption through the smallest dimension.

All of the crystals used for intensity data collection were repeatedly dipped into liquid nitrogen to produce a better mosaic character so as to reduce the possible effects of secondary extinction. After the first cycle of least-squares refinement, the observed and calculated structure factor magnitudes were compared, and no evidence of secondary extinction was found.

Solution and Refinement of Structure. The measured structure factors (*F*'s) for the sodium chloride adduct were put on a normalized basis (*E*'s). The *E*'s were then used in a modification of Long's program[8] to determine phases. The signs for a set of 177 *E*'s, 133 positive and 44 negative, reflected the contribution of the ions in the special positions. An *E* map computed from the set of 177 *E*'s revealed the positions of all the nonhydrogen atoms. The positions were refined by a least-squares method. Scattering factors, from ref 9, for singly ionized sodium and chlorine were used. The anomalous dispersion coefficient $\Delta f''$ is less than 10% of the chlorine scattering factor at the limit of the data sphere. No corrections for anomalous dispersion were included. Three cycles of least-squares refinement on the positions found in the *E* map gave $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.122$ and $R_w = \{\Sigma w(F_o - F_c)^2/\Sigma wF_o{}^2\}^{1/2} = 0.104$ $(w_i = 1/\sigma_i{}^2)$. Anisotropic temperature factors were introduced for all nonhydrogen atoms, and two additional cycles were run. The resulting residuals were $R = 0.096$ and $R_w = 0.081$, and the decreases in both were found significant at the 0.5% level, using Hamilton's criterion.[10] In computing the degrees of freedom it was assumed that only half of the observed reflections were unique since glide-related pairs were present throughout the data; therefore the number of observations was assumed to be 608 in determining the level of significance. A difference Fourier synthesis was computed and eight of the ten

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(8) R. E. Long, Ph.D. Thesis, University of California, Los Angeles, Calif., 1965.

(9) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962.

(10) W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

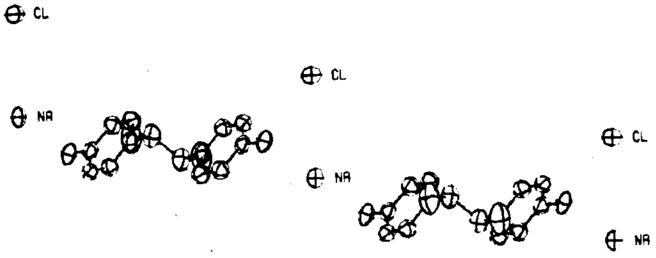


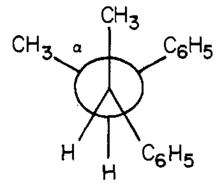
Figure 3. Section parallel to the (010) plane. Only two DPB are shown; other atoms have been deleted. The ellipsoids enclose 50% probability of thermal motion.

hydrogen positions in the asymmetric unit were tentatively located. Three of the positions did not yield chemically reasonable carbon-hydrogen bond lengths after being varied in the least-squares refinement and were discarded as being unreliable. The remaining five positions were added isotropically to the least-squares variables, and two additional cycles were performed. The final residuals were $R = 0.082$ and $R_w = 0.070$; the decrease in the residuals was significant at the 0.5% level. It has been found that the positions of the non-hydrogen atoms of the second half of the DPB molecule as determined from the least-squares refinement in $R\bar{3}$ symmetry could be generated to within their estimated standard deviations from the atoms of the first half of the molecule using the additional symmetry elements of $R\bar{3}c$. The refinement of the sodium chloride structure was terminated at this point. No attempt was made to determine the hydrogen positions for the sodium nitrate and the sodium cyanide adduct structures. The starting positions for the ions were chosen from symmetry considerations and the final position of the DPB molecule in the sodium chloride adduct structure was used as the initial position for the DPB molecule in the least-squares refinement of the remaining adduct structures. The refinement for the sodium cyanide adduct was performed in $R\bar{3}$ symmetry. The cyanide ion cannot be placed on the threefold axis so as to satisfy simultaneously the glide and inversion operators. The position of the cyanide anion would not converge (although no trouble was encountered with the remaining atoms in the structure). There are several possible reasons why this could occur. The atoms may be precisely located, but exchanging electron charge. They may be precisely located within each cell, but randomly disordered cell to cell. Or they may be tumbling about the special position $(0, 0, {}^1/_4)$. A Fourier map of the electron density was computed and revealed a large, diffuse spherical peak centered at the special position postulated for the center of the cyanide anion. In order to complete the refinement on the remaining positions, the cyanide anion position and isotropic temperature factors were fixed during the refinement. No unusual difficulties were experienced with the refinement of the sodium nitrate adduct structure. Observed and calculated structure factors for the three adducts are available.[11]

Computer Programs. Programs used in the structure determination include the Oak Ridge computer-controlled X-ray diffractometer program (W. R. Busing, R. D. Ellison, H. A. Levy, S. P. King, R. T. Rosenberry), for refining cell constants and collecting data; SAYREEQN (R. E. Long; revised and modified by K. F. Streib and C. Tsai), for determining the phases; ORFLS (W. R. Busing, K. O. Martin, H. A. Levy), for the least-squares refinement; ORFFE (W. R. Busing, K. O. Martin, H. A. Levy), for bond parameters and errors; ORTEP (C. K. Johnson), for diagrams of the structures.

Description of Structure

Fractional coordinates and thermal parameters are given in Table II. Tables III and IV give the pertinent interatomic distances and bond lengths. Figure 1 is a stereographic view of the DPB molecule in the configuration found in the sodium chloride adduct structure. The phenyl rings are tilted such that C(2) and C(3) are above C(1) and C(4) which are above C(5) and C(6). The other phenyl of the DPB is pitched in the opposite manner. Figure 2 is a section normal to the c axis of the sodium chloride adduct unit cell. The hexacoordination of the amine to the sodium ion at the center of the diagram is clearly evident. Three of the DPB are above the (001) plane. Alternating DPB are below the plane. The tilt of the phenyl ring with the [001] direction is 59, 60, and 61° for the NaCl, $NaNO_3$, and NaCN adducts. The butane is not in an eclipsed conformation. Rotation of the bond planes of the inner carbons from the methyl-methyl eclipsed position can be shown by Newman-type diagrams



$\alpha_{NaCl} = 54.9°$
$\alpha_{NaNO_3} = 58.3°$
$\alpha_{NaCN} = 58.6°$

The distance between end amine nitrogens is 8.12 Å. The conformation is more nearly staggered. The amines are grouped closely about the NaCl columns forming hexagonal-like channels running through the crystal along the [001] direction at 12.2 Å apart. These channels are in hexagonal array and the DPB molecules bridge between adjacent channels. This is shown in Figure 3, a section parallel to the (010) plane. Only the two DPB related by the inversion operation and three segments of the Na–Cl columns, which

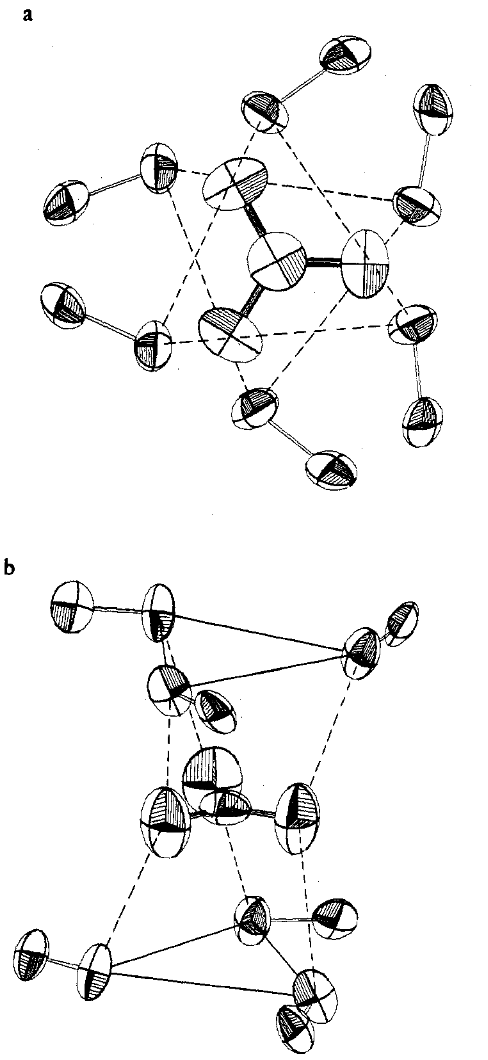


Figure 4. (a) Section of $NaNO_3$ adduct 0.25 ± 0.12c projected onto the ab plane. Heavy bonding connects the nitrate anion. Lighter bonding connects amine nitrogens to the first phenyl carbons. Dashed lines show amine nitrogen planes. (b) A side view of the above. Solid single lines define amine nitrogen planes. Dashed lines link amine nitrogens to nitrate oxygens.

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[11] See paragraph at end of paper regarding supplementary material.

extend through the structure along the [001] direction, are shown. There would be, for instance, a Cl atom below each Na equidistant to that above. The point symmetry of the Na is $\bar{3}$ with the nitrogens in antiprismatic coordination. The N-Na-N angles are 89.6, 89.8, and 89.6° for the three adducts. The Cl point symmetry is 32.

The crystal consists of approximately 8 Å layers of DPB molecules stacked in the [001] direction, interleaved by empty layers about 0.5 Å thick. This packing is consistent with the external morphology of the crystals which grow as needles along the [001] direction. The shortest interatomic distance measured between molecules in adjacent layers is a hydrogen-hydrogen separation of about 3.5 Å. When the structure is considered, using only the meso isomer, the layers of DPB molecules appear more closely packed. The minimum interatomic separation is 2-2.5 Å for hydrogens in adjacent layers.

In the nitrate adduct the anion array is in a plane parallel to the (001) at $z = {}^1/_4$. The nitrogen occupies the site (0, 0, ${}^1/_4$) in the center of an equilateral triangle of oxygens each 1.29 Å distant. The oxygens are in the {010} planes. Figure 4a is a section of the NO_3 environs $0.25 \pm 0.20c$ projected onto the (001) plane. Only the amine nitrogens and the first carbons of the DPB's are shown. Figure 4b is a different view of the anion. The NO_3 anion can be seen in the center of the figure. The coordination of the amine nitrogens is farther from octahedral than in the NaCl adduct. The N(1)-O distance is 3.89 Å. If one of the amine hydrogens were between the nitrogen and the oxygen, the O-H distance could be as short as 2.8 Å. Each oxygen would have two such hydrogens coordinated to it.

In the cyanide adduct, the carbon and nitrogen atoms could not be precisely located in the structure refinement. This and the large diffuse peak of electron density centered at (0, 0, ${}^1/_4$) in the Fourier map lead us to conjecture the cyanide anion as tumbling about that center. Either of the arrangements should result in an electron density peak elongated in the [001] direction. No such anisotropy was evident in the *F*-map peak.

The lack of success in resolving the positions of the amine hydrogens makes it difficult to conjecture on the role of hydrogen bonding in the DPB adducts. It was originally supposed that hydrogen bonds between the amines and the anions would be an important factor in the crystallization. The crystal structure of tris(4,4′-diaminodiphenylmethane)-sodium chloride has recently been determined.[12] One of each pair of amine hydrogens is located slightly below the amine nitrogen and away from the Na. The other is close to both the cation (2.60 (8) Å) and the chlorine anion (2.45 (8) Å). These two distances are within the van der Waals radii sum. The latter satisfies the Hamilton-Ibers criterion[13] for hydrogen bonding. This possibility is discussed further in the previous paper.[6]

Acknowledgment. We wish to thank Dr. W. R. Busing for helpful suggestions and the use of his programs, Dr. K. F. Streib for the Sayre equation program, and Dr. H. E. Vogel, who secured the support for this work.

Registry No. $Na(DPB)_3Cl$, 42343-70-4; $Na(DPB)_3NO_3$, 42343-71-5; $Na(DPB)_3CN$, 42343-72-6.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-120.

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(13) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, p 15.