observed distance of 2.44 Å. Similarly, the Pt–O distance of 1.99 Å compares well with Pt^{2+} (IV) + (O^{2-}) = 2.00 Å. The sp^2 hybridization of the oxygen atoms accounts readily for the planar-triangular bonding to Pt. The Pt–Pt distance indicates metallic bonding (Pt–Pt in Pt metal is 2.80 Å).

In $CaPt_2O_4$ the situation seems to be more complex. The Pt atoms are not equidistant but slightly paired, although we presume that all the bonds have metallic character. The Ca^{2+} ions again fit very well in the oxygen channels, as shown by the Ca–O bond length of 2.48 Å (the sum of the ionic radii is 2.52 Å). The oxygen coordination around the Pt is slightly distorted from square planarity, but hardly significantly so. The Pt lies 0.15 (5) Å from the plane defined by the four-coordinated oxygen atoms. As in the general bronze structure, chains of alternating Ca and O atoms run diagonally through the crystal.

Most unusual is the coordination of Pt around oxygen. It was this feature that prompted us to calculate the difference Fourier synthesis and to vary the Pt occupancy factor (as described above) in order to see if some electron density might be found in the channels of the structure. The resulting bonding shows each oxygen atom connected to two platinum atoms, with the angle between them close to 120° [110

(3)°]. This suggests that some electron density centered on the oxygen is pointing toward the position where Pt would be found in the bronze structure. Although such bonding for oxygen is not uncommon (*e.g.*, H_2O) it is highly unusual in a metal oxide. As mentioned before, metallic bonding between the platinum atoms is found in both $Cd_{0.3}Pt_3O_4$ and $CaPt_2O_4$. We are currently investigating some of the physical properties of these and other bronzes in order to look for evidence of metallic behavior in these materials. The results of this study together with details on the preparation and catalytic behavior of the bronzes will be the subjects of future publications.

Contribution from the Department of Chemistry and Geology, Clemson University, Clemson, South Carolina 29631

Solid Coordination Compounds of Alkali Metal Salts with a Neutral Aromatic Amine.[1] I. Molecular Structure and Bonding

N. P. MARULLO,* J. F. ALLEN, G. T. COCHRAN, and R. A. LLOYD

Uni-univalent metal salts, including alkali metal salts, are precipitated from aqueous solution by complexation with racemic *p,p'*-diamino-2,3-diphenylbutane. The stoichiometry and infrared and solution properties of these compounds are presented and discussed in terms of coordination compounds in which the metal ion is octahedrally coordinated by six amino nitrogen atoms to give an infinite three-dimensional polymeric structure. Evidence is presented for strong metal ion–amino nitrogen bonding as well as interaction between the anion and amino hydrogens. Both of these attractive interactions are attributed to ion dipole forces. Evidence is also presented which strongly indicates that there is little anion–cation interaction.

Introduction

In a previous communication,[1] we reported initial results on the precipitation of simple alkali metal salts such as sodium chloride from aqueous solution by complexation with racemic *p,p'*-diamino-2,3-diphenylbutane (I). The stoichiometry, constant composition, and infrared spectrum of the NaCl adduct with I was interpreted in terms of a structure in which six nitrogen atoms from six amino groups are octahedrally coordinated about the sodium. This is unusual since of the alkali metals only lithium salts are known to form isolable coordination compounds with nitrogen donor ligands. The more stable are those where the ligand is ammonia, and replacement of ammonia with amines decreases their stability. It is therefore surprising that I, a weakly basic and bulky aromatic amine, can exhibit bonding with sodium.

Unlike nitrogen, there are many examples of oxygen donor ligands which effectively coordinate with alkali metal cations. Some notable recent examples are the macrocyclic ethers

(crown ethers) (II)[2] and the macroheterobicyclics (cryptates) (III).[3] Subsequent to our initial report methylenedianiline (IV), a closely analogous compound of I, was reported to form isolable compounds with alkali metal salts.[4]

I

II   III
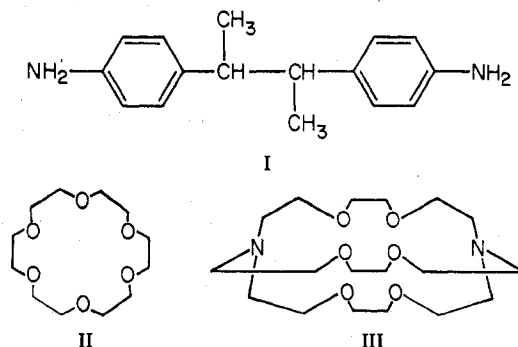
(1) (a) A preliminary account of a portion of this work has been reported: N. P. Marullo and R. A. Lloyd, *J. Amer. Chem. Soc.*, **88**, 1076 (1966). (b) Abstracted in part from the Master's thesis of R. A. Lloyd and Ph.D. thesis of G. T. Cochran, Clemson University, 1967.

(2) D. J. Sam and H. E. Simmons, *J. Amer. Chem. Soc.*, **94**, 4024 (1972), and references cited therein.
(3) J. M. Lehn and J. P. Sauvage, *Chem. Commun.*, 440 (1971), and references cited therein.
(4) T. C. Shields, *Chem. Commun.*, 832 (1968).

NH$_2$—⟨benzene⟩—CH$_2$—⟨benzene⟩—NH$_2$

IV
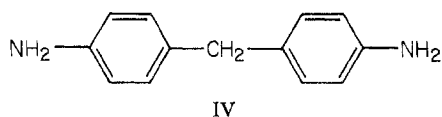
The ability of compounds such as II and III to complex alkali and alkaline earth cations has led to many biological and chemical studies. The principal motives of these studies have been to ascertain those factors which are responsible for and contribute toward complexation particularly as they might relate toward an understanding of the mechanism of active transport of cations through membranes. The ability of I to selectively complex alkali metal cations is of interest for similar reasons. Furthermore, physiological systems contain many different kinds of molecules having amino functions which have been generally thought to be ineffective as ligands for complexation with alkali metals.

The purpose of this report is to describe some of the properties of complexes of I with a variety of uni-univalent metal salts. Discussion of these properties is directed toward formulating a plausible structure for the adducts as well as to establish the interactions which are responsible for their formation.

Results and Discussion

Listed in Table I are the solid adducts of racemic *p,p'*-diamino-2,3-diphenylbutane (I) and a variety of uni-univalent metal salts which have been prepared by precipitation from aqueous alcohol (see Experimental Section). In all cases the adducts have the empirical formula M$^+$(I)$_3$X$^-$ and are well-defined crystalline solids. Also tabulated are the melting points, per cent yield (no attempts were made to maximize yields), and the N–H stretching frequencies.

Solid adducts could not be prepared from a variety of lithium salts or from sodium formate, acetate, thiocyanate, perchlorate, sulfide, or fluoride. Furthermore, no adduct formation was obtained with the dipositive ions such as calcium, magnesium, or barium except for those which are known to coordinate strongly with nitrogen, such as zinc and cadmium.

The apparent inability of I to precipitate lithium salts is unexpected since, of the alkali metals, lithium generally undergoes coordination best. One rationalization is that the arrangement of the requisite number of large units of I about the small lithium ion results in too much nonbonded repulsion for stable adduct formation to occur. Another is that the hydration energy of Li$^+$ is too large to allow complete replacement of water by I. It will be shown that adduct formation between I and salts not only appears to require hexacoordination but that the amine groups occupy all six coordination sites. Compound IV however has been reported[4] to form 3:1 adducts with lithium halide as well as sodium halide. If a steric argument is to have validity, it should therefore relate to a critical involvement of unfavorable methyl–methyl or methyl–hydrogen repulsion interactions upon adduct formation since the basicity or availability of the nitrogen lone pairs of I or IV should be very nearly identical.

The selectivity of I for alkali metals over that of the alkaline earths is exemplified by the fact that only NaCl is precipitated by I when I is added to a solution containing both sodium and barium chloride. This selectivity differs from that determined for the cryptates.[3] For example, the stability constant (log K_s) for the sodium cryptate (5.4) is smaller than that for the barium cryptate (6.3) even when the estimated cavity size of the cryptate, 1.15 Å, is nearly the same as the Na$^+$ ionic radius (1.12 Å) but smaller than that of Ba^{2+} (1.49

Table I. Adducts of I with Various Salts

Adduct	Mp, °C	% yield	N–H str, cm^{-1} Asym	Sym
I	84		3384	3294
NaCl	200–203	90	3329	3236
NaBr	206–210	81	3329	3233
NaI	225–227	41	3338	3251
NaCN	179–185	85	3344	3256
NaN$_3$	177–183	71	3320	3260
NaNO$_2$	174–179	59	3337	3258
NaNO$_3$	174–176	73	3322	3257
KCl	194–196	74	3353	3260
KI	203–204	52	3356	3267
RbCl	162–164	56	3365	3280
RbI	192–193	41	3370	3282
CsI	154–156	48	3373	3283
CsN$_3$	150–155	45	3372	3277
AgNO$_3$	213–217	74	3316	3258
TlClO$_4$	204–206	80	3371	3292

Å). An increase in the cavity size to 1.4 Å resulted in a log K_s for Na$^+$ of 3.9 compared to 9.5 for that of Ba^{2+}.

Included in the tabulation are the previously reported[5] adducts of I with Ag$^+$ and Tl$^+$. These adducts also have a stoichiometry of 3 units of I per unit of salt and represent one of the few examples of hexacoordinated Ag$^+$ and Tl$^+$. Since Ag$^+$ commonly undergoes two-coordination with amines, this result forcefully demonstrates that I acts as a ligand for uni-univalent salts only if it can octahedrally coordinate the metal ion. Additional support for this conclusion is that the meso stereoisomer of I, which does not precipitate simple alkali metal salts, gives the usual 1:1 complex with AgNO$_3$. Another pertinent point is that the solid adducts do not contain any detectable amount of water or alcohol. The infrared spectra of air-dried samples show no absorption due to water or alcohol nor is there any significant weight loss when the samples are heated *in vacuo*.

The infrared spectra of the adducts of simple salts are nearly identical with I except that the N–H stretching frequencies are more intense and shifted to lower frequencies. The important feature is that all the adducts, as in the case for I, have only two sharp N–H stretching frequencies. This signifies that the adducts have only one kind of amino group; that is, all six of the amino groups from three molecules of I experience the same environment. Inspection of Table I shows that both the asymmetric and symmetric N–H stretching frequencies vary with changes in either the anion or the cation; however, it is also evident that these shifts are more sensitive to changes in the cation rather than the anion. For example, a comparison of the chloride and iodide adducts of Na, K, and Rb gives a difference of 15, 7, and 2 cm^{-1} for the symmetric N–H stretch and a difference of 9, 3, and 5 cm^{-1} for the asymmetric stretch. On the other hand, the difference in the N–H symmetrical stretching frequency between I and the iodides of Na, K, Rb, and Cs is 43, 27, 12, and 11 cm^{-1}, respectively, and 54, 28, 14 and 11 cm^{-1} for the asymmetric stretch. We interpret this to mean that complexation results in substantial attractive interactions between the cation and the amino nitrogen and the magnitude of this interaction may even be larger than that between the anion and amino hydrogens. Furthermore, if the magnitude of change in N–H stretching frequency is a measure of the extent of bonding between the metal ion and the amino nitrogen, then this should follow the order Na > K > Rb > Cs. The values given above for the alkali metal iodides show this to be the case. Additional experimental support for this trend in

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

ability of the alkali metals toward complexation with I was obtained by carrying out competition experiments between sodium and potassium chloride and also between sodium and cesium iodide. When a solution containing I, NaCl, and KCl in a molar ratio of 4:1:1 was allowed to crystallize at 40°, the molar ratio of Na to K in the precipitate was 18.5 to 1. The selectivity of I over that for cesium was even more pronounced. Fractional crystallization of a solution containing the diamine (I) and iodides of ^{22}Na$^+$ and ^{137}Cs$^+$ in either a 4:1:1 or a 3:1:1 molar ratio gave initial fractions which contained only sodium and no detectable amount of radiocesium. Intermediate fractions contained both sodium and cesium, and pure cesium iodide adduct was obtained only after all the sodium had been precipitated.

If one takes the view that there is no metal–nitrogen interaction in these adducts and that the spectral characteristics are due to anion–amino hydrogen interactions which are modified by anion–cation interactions, then it is reasonable to expect that for a given anion the change in N–H stretching frequency should increase as the cation radii increase. As was shown above, exactly the opposite was found.

If the magnitude of the shift in N–H stretching frequencies results primarily from interaction between the cation and amino nitrogen, then the close correspondence of values observed for Na(I)$_3$NO$_3$ and Ag(I)$_3$NO$_3$ dictate that the magnitude and probably the nature of this interaction (ion dipole, dispersion, etc.) is substantially the same for both Na$^+$ and Ag$^+$. In view of the markedly different chemistry of Ag$^+$ compared to that of Na$^+$ this may seem to be an untenable conclusion. However, it should be remembered that Ag$^+$ is behaving in a very unusual way with I, *i.e.*, six-coordination rather than two-coordination. Indeed the similarity of Na$^+$ and Ag$^+$ in these adducts corresponds to the similarity in the effective ionic radii for six-coordinated Ag$^+$ (1.15 Å)[6] and Na$^+$ (1.12 Å)[7] and is therefore consistent with an ion dipole interaction between the cations and ligand I.

Hydrogen Bonding and Cation–Anion Interaction. In the preceding section, the magnitude of the N–H shift was shown to correlate with the nature of the cation and interpreted in terms of a cation–amino nitrogen interaction. This, however, does not mean that there is no anion–amino hydrogen interaction. Indeed, Table I shows that the N–H stretch does vary with changes in the anion. As will be shown shortly, these changes are probably not the result of changes in cation–anion interactions and therefore are consistent with anion–amino hydrogen interactions. Although it may be convenient to label this interaction as hydrogen bonding, the stoichiometry of the adducts and the fact that the infrared spectra of all the adducts give a single symmetric and antisymmetric stretch dictate that there be an equivalent interaction between the anion and each of the twelve amino hydrogens from six amino groups. It is unlikely that the interaction of each hydrogen with the anion would be of the magnitude commonly associated with hydrogen bonding. Instead it is suggested that this interaction is of the ion dipole type. This conclusion differs from that derived from the X-ray crystallographic structure of the closely related compound IV which has been reported to have two different kinds of amino hydrogens.[8] One set of six hydrogens from six mole-

Table II. Solubilities of NaCl Adduct at 25°

	Available		Dissolved		
	NaCl, g/l.	I, g/l.	NaCl, g/l.	I, g/l.	[I]:[NaCl]
Water	6.1	74.5	1.03	0.272	0.06
Methanol	6.1	74.5	2.30	38.0	3.9
Acetone	6.1	74.5	0.1	69.0	160
Ethyl acetate	5.9	73.3	0.1	47.3	115
Chloroform	6.2	76.0	0	55.0	
Carbon tetrachloride	6.8	82.5	0	1.82	

Table III. Solubility of Na(I)$_3$Cl in Organic Liquids

Solvent	Solubility, g of metal/l.
Ethylene dichloride	1.44×10^{-2}
o-Dichlorobenzene	$<5.0 \times 10^{-3}$
Chlorobenzene	8.25×10^{-3}
1-Hexanol	1.22×10^{-2}
Methyl isopropyl ketone	7.85×10^{-3}
Diglyme	$<5.0 \times 10^{-3}$
Cyclohexanone	1.74×10^{-2}

cules of IV being somewhat closer to the chloride ion[8a,c] are believed[8b] to take part in weak hydrogen bonding whereas the other set of six hydrogens are not involved in any specific interactions.

Examination of the infrared spectra of those adducts with certain polyatomic anions show that in no case are absorption bands observed which are characteristic of coordinated nitrate,[9] nitrite,[10] or perchlorate.[11] The infrared spectra for the adducts containing CN$^-$ and N$_3^-$ show that they have a high degree of ionicity. The C–N stretching frequency of the cyano group has been related to the extent to which it coordinates;[12] the greater the coordination the higher the stretching frequency. For example, the C–N stretch in K$_3$-[Fe(CN)$_6$] has been reported at 2125 cm^{-1},[13] compared to 2080 cm^{-1} for NaCN.[14] The C–N stretch for Na(I)$_3$CN appeared as a sharp intense bond at 2030 cm^{-1}, clearly indicating a degree of ionic character for the cyanide which is greater than that for NaCN. Similarly, for both the sodium and cesium azide adducts, the azide stretching frequencies of 2005 and 2003 cm^{-1}, respectively, are smaller than those of the corresponding simple sodium salts of 2128 and 2015 cm^{-1}. Furthermore, it is especially important to note that the large difference of 113 cm^{-1} in the N$_3^-$ stretch between NaN$_3$ and CsN$_3$ is reduced to a difference of only 2 cm^{-1} between Na(I)$_3$N$_3$ and Cs(I)$_3$N$_3$. This small difference in N$_3^-$ stretching frequency coupled with a corresponding large difference of 52 cm^{-1} for the asymmetric N–H stretch and the much higher affinity of Na$^+$ over Cs$^+$ for precipitation with I is interpreted in terms of an adduct in which the anion is effectively insulated and prevented from close interaction with the cation and the principal attractive interaction is between the cation and amino nitrogen.

Structure. On the basis of the previous discussion and the stoichiometry of 3 units of I for each ion pair, it is reasonable to assume octahedral coordination of the amino groups about the cation. If the ligand I acts as a bidentate ligand, a mono-

(6) J. P. Jesson and E. L. Muetterties, "Basic Chemical and Physical Data," Marcel Dekker, New York, N. Y., 1969.

(7) M. F. C. Ladd, *Theor. Chim. Acta,* 12, 333 (1968).

(8) (a) J. W. Swardstrom, L. A. Duvall, and D. P. Miller, Paper O10, Proceedings of the American Crystallographic Association, Ames, Iowa, Aug 15–20, 1971; (b) J. A. J. Jarvis and P. G. Ocoston, *Chem. Commun.,* 1403 (1971); (c) J. W. Swardstrom, L. A. Duvall, and D. P. Miller, *Acta Crystallogr., Sect. B.,* 28, 2510 (1972).

(9) B. M. Gatehouse, S. E. Livingston, and R. S. Nyholm, *J. Chem. Soc.,* 3965 (1958).

(10) J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Wiley, New York, N. Y., 1960.
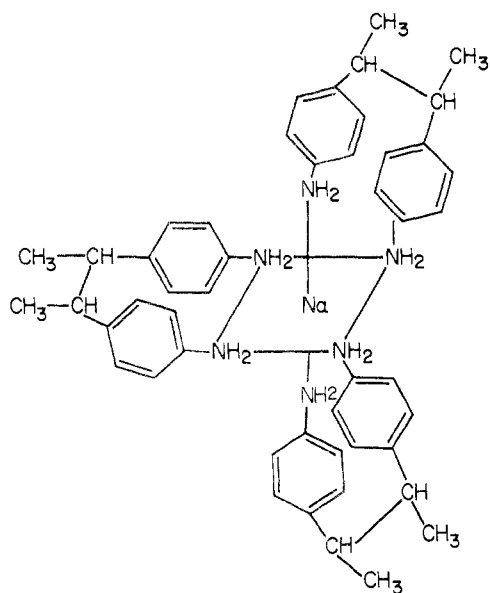
(11) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.,* 3091 (1961).

(12) F. M. El-Sayed and R. K. Sheline, *J. Inorg. Nucl. Chem.,* 6, 187 (1958).

(13) E. F. Herington and W. Kynaston, *J. Chem. Soc.,* 3555 (1955).

(14) W. D. Stalleup and D. Williams, *J. Chem. Phys.,* 10, 199 (1942).

meric structure V results, whereas if I bridges two metal ions a polymeric three-dimensional structure results.

V

The monomeric structure is unlikely since it should be considerably strained in a manner analogous to the [2.3]paracyclophanes. Based on the strain energies of paracyclophanes,[15] V should have a strain energy of about 60 kcal/mol. In addition, paracyclophanes exhibit characteristic intense infrared bands at 885 and 930 cm^{-1} [16] which are not present in the adducts. These considerations favor the relatively strainless polymeric structure.

Additional experimental evidence relative to the question of structure was sought by examining some solution properties of the adducts. The initial question which needed resolution was whether the adducts existed as such in solution or whether they underwent essentially complete dissociation. Dissolution of the polymeric structure requires its prior dissociation and resultant destruction of the adduct, whereas the monomeric structure is capable of existence in solution. Table II lists the solution characteristics of the NaCl adduct in several liquids.

Inspection of the last column of Table II shows that with the possible exception of methanol the ratio of I to salt in the supernatant was vastly different from that of the adduct. The relatively nonpolar solvents appeared to dissolve preferentially the amine from the solid whereas water preferentially dissolved the salt. Furthermore, the low concentration of salt dissolved in the organic solvents, methanol excluded, means that the amount of adduct as such dissolved in these solvents must be very small if it exists in solution at all.

A more quantitative estimate of the maximum amount of dissolved adduct in organic solvents was obtained by measuring the amount of dissolved metal employing radiotracer techniques. These results are listed in Table III.

The highest amount of dissolved sodium was found for the solvent cyclohexanone; however, this corresponds to a molar concentration of about only 7×10^{-4}. It is clear that if any adduct exists in these organic solvents, its concentration is small. Parenthetically it is interesting to note that the concentration of NaCl found when water was used as solvent

(1.03 g/l.) is considerably less than that which is available for dissolution and attests to the hydrolytic stability of Na(I)$_3$Cl. The AgNO$_3$ adduct is even more hydrolytically stable; the amount of dissolved Ag$^+$ in water was less than 5×10^{-3} g/l.

Only in the case of methanol was an approximate correspondence found between the stoichiometry of the solid adduct and the ratio of I to NaCl in solution. This along with the high concentration of NaCl found in methanol (larger than that for water) prompted examination of the uv spectral characteristics and conductance properties of some of the adducts in methanol. A methanol solution which was 10^{-4} *M* in dissolved Na(I)$_3$Cl had a λ_{max} of 293 nm which is identical with that of pure I dissolved in methanol and the molar absorptivity corresponded to 3 times that of I dissolved in methanol. Similarly the addition of stoichiometric amounts of I to methanol solutions of sodium, cesium, or thallium salts caused no measurable change in the molar conductances from that of the simple salts. These results demonstrate that there is no detectable amount of adduct in solution. It is therefore reasonable to conclude that the solid adducts have the infinite three-dimensional polymeric structure and that dissolution of the solid adduct requires its depolymerization.

Experimental Section

All melting points were determined in sealed capillary tubes. Infrared spectra were taken as Nujol or hexachlorobutadiene mulls using the Perkin-Elmer Model 221 equipped with sodium chloride optics.

Materials. Radioactive materials were obtained from Atomic Corp. of America. Cesium-137 (1 μCi in 5 ml of 1 *N* HCl), 10 μCi of iodine-131 in 5 ml of basic sodium bisulfite containing 0.1 mmol of sodium iodide, and 10 μCi of sodium-22 in 6 ml of 0.0002 *N* HCl were used as standard stock solutions.

All salts used were reagent grade and were dried at 110° prior to use except for cesium azide which was obtained and used as a 50% aqueous solution. *rac*- and *meso-p,p'*-diamino-2,3-diphenylbutane (I) were prepared as previously described.[17]

Preparation of Na(I)$_3$Cl. The diamine (I) and sodium chloride were weighed out in a 3:2 mole ratio, respectively, *i.e.*, 0.7211 g of I and 0.1169 g of sodium chloride. The diamine was dissolved in 9.0 ml of ethanol and the sodium chloride in 5.0 ml of deionized water. To the aqueous salt solution was added 1.0 ml of the sodium-22 solution. A 3.0-ml aliquot was withdrawn from the aqueous, labeled salt solution and added to the solution of I to give an approximate 3:1 mole ratio of the reactants. The remaining aqueous, labeled salt solution was retained for later use as a standard. Upon combination of the solutions of I and salt, a moderate precipitate occasionally formed which was disregarded and which redissolved when the mixture was heated to boiling and evaporated to about 8 ml. The solution was then cooled to room temperature with an associated formation of small, white crystals. The precipitate in contact with the mother liquor was refrigerated for 12 hr at 14°, filtered on sintered glass, washed with cool 3:1 ethanol–water solution, and then recrystallized from 3:1 ethanol–water solution. Evaporation of the filtrate to approximately 6 ml and subsequent treatment as described above yielded additional product. The total recrystallized product amounted to a 90.3% yield. The compound melted to a clear, light yellow liquid at 200–203°. Nonradioactive samples were prepared in the same way, except the sodium chloride was dissolved in 6.0 ml of water and no sodium-22 solution was added. This general procedure was used to prepare all the complexes listed in Table I.

Analytical Data and Procedure. The analytical data for the complexes listed in Table I, except those for the previously reported silver nitrate and thallium perchlorate,[5] are tabulated in Table IV. Unless specified otherwise, analyses for sodium and potassium were performed using a Perkin-Elmer Model 146 flame photometer. Analyses of complexes containing radio-labeled sodium, cesium, and iodine were performed in the following manner. A carefully weighed sample of approximately 15 mg of labeled complex was dissolved in 1.00 ml of 3:1 ethanol–water and counted along with the corresponding labeled standard solution. The 1.28-MeV γ radiation of sodium-22, 0.66-MeV γ radiation of cesium-137, and 0.364-MeV γ radiation

(15) D. J. Cram and J. M. Cram., *Accounts Chem. Res.*, 4, 204 (1971).

(16) D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.*, 73, 5691 (1951).

(17) C. G. Overberger, N. P. Marullo, and R. G. Hiskey, *J. Amer. Chem. Soc.*, 83, 1374 (1961).

Table IV. Analytical Data of Complexes[a]

Complex	%C Calcd	%C Found	%H Calcd	%H Found	%N Calcd	%N Found	% cation Calcd	% cation Found	% anion Calcd	% anion Found	% diamine (I) Calcd	% diamine (I) Found
NaCl	73.95	74.23	7.77	7.78	10.78	10.92	2.95	2.86[b]	4.55	4.53	92.50	92.25
							3.15	2.75[c]				
NaBr	69.97	69.79	7.34	7.42	10.20	10.28	2.79	2.77			87.53	87.66
NaI	66.19	66.11	6.95	7.04	9.65	9.81	2.64	2.67[b]	14.57	14.58[b]	82.79	82.21
NaCN	76.43	76.47	7.85	7.67	12.73	12.99	2.98	3.12			93.64	93.78
NaN$_3$	73.34	73.48	7.69	7.57	16.04	15.81	2.93	2.82			91.73	91.26
NaNO$_2$	72.96	73.04	7.65	7.78	12.41	12.62	2.91	2.90			91.26	91.22
NaNO$_3$	71.52	71.59	7.50	7.38	12.17	12.01	2.84	2.97			89.54	89.67
KCl	72.46	72.14	7.60	7.84	10.56	10.78	4.91	5.14			90.63	90.38
KI	64.99	65.14	6.82	7.00	9.48	9.42	4.11	4.02			81.23	81.30
RbCl	68.47	68.55	7.18	7.16	9.98	10.22					85.64	86.00
RbI	61.76	61.88	6.48	6.32	9.00	8.88					77.24	77.20
CsI	58.78	59.11	6.16	6.21	8.57	8.55	13.55	13.84[b]	12.93	12.97[b]	73.51	73.94
CsN$_3$	64.34	64.00	6.75	6.68	14.07	13.80					80.48	80.16

[a] Calculated values are based on a stoichiometry of 3 molecules of the diamine (I) per salt ion pair. [b] Determined radiochemically from labeled complex. [c] Determined gravimetrically as sulfate.

Table V. Analyses of Products Obtained in Competition Experiments

A. Iodine-131-Labeled Complexes

Sample no.	Mole ratio of diamine: NaI:CsI in soln	Mp, °C	% I	% amine	Mole ratio of diamine: salt (as I⁻) in complex
29A	2:0.1:1	225–227	14.42		
29D		154–156	13.05		
30A	2:0.1:1	225–227	14.51	80.09	2.92
30D		155–156.5	12.89	73.11	2.98

B. Initial Fractions Obtained from Mixtures of ^{22}NaI, ^{137}CsI, and Diamine

Sample no.	Mole ratio of diamine:NaI:CsI in soln	Mp, °C	% Na	% Cs	% amine	Mole ratio of diamine:salt (NaI) in complex
31A	4:1:3	225.5–228	2.49	<0.02	77.28	2.97
32A	4:3:1	226.5–228	2.67	<0.02	81.52	2.92
33A	3:1:1	225–226.5	2.84	<0.02	84.34	2.83

C. Cesium-137-Labeled Complexes

Sample no.	Mole ratio of diamine: NaI:CsI in soln	Mp, °C	% Cs	% amine	Mole ratio of diamine: salt (CsI) in complex
34A	6:1:1	226–227.5	0.88	84.20	
34D		152–156	13.55	75.19	3.07
35A	3:0.1:1	226.5–227.5	7.47	79.00	

of iodine-131 were counted using a well-type 2 × 2 in. NaI(Tl) crystal with a single-channel analyzer.

The per cent diamine (I) of the complexes was determined spectrophotometrically with a Bausch and Lomb Spectronic 600. An amount of complex was dissolved in 3:1 ethanol–water which would give a diamine concentration in the range of $(0.5–1.0) \times 10^{-4}$ M assuming a stoichiometry of 3 units of diamine per unit of salt and complete dissociation of the complex. The pure diamine obeyed the Lambert–Beer law up to a concentration of 3×10^{-4} M in 3:1 ethanol–water and has a molar absorptivity of 2640 l. mol^{-1} cm^{-1} at 290 nm in this solvent.

Competition between Sodium and Cesium. The diamine (I) and cesium iodide were weighed out in a 1:1 mole ratio, the diamine being dissolved in 6.0 ml of ethanol, and the cesium was dissolved in 5.0 ml of deionized water to which was added 1.0 ml of the iodine-131 stock solution. A 3.00-ml aliquot of the aqueous labeled salt solution was added to the diamine solution to give a 2:0.1:1 mole ratio of diamine:sodium iodide:cesium iodide. Fractional crystallization at approximately 1-ml increments by evaporation down to a final volume of about 5 ml furnished products A–D. This same general procedure was employed in the preparation and treatment of samples having labeled sodium and cesium. Table V gives the results of these experiments. In the cesium analysis of samples 31–33 a correction was made for the high-level background of sodium-22 in the 0.662-MeV region due to Compton scattering of the 1.28-MeV sodium-22 photon.

Competition between Sodium and Potassium. To 0.24 g (1 mmol) of the diamine in 3 ml of ethanol was added 0.5 ml of an aqueous solution containing 0.25 mmol of sodium chloride and 0.25 mmol of potassium chloride. Six identical solutions made in the above manner were heated until clear and then two of each were placed in constant-temperature baths kept at 40, 30, and −15°. After

4 days the precipitate was filtered, washed once with cold aqueous alcohol, and dried. The sodium and potassium content was determined by flame photometry and the results are given in Table VI. The values given for sodium are the average for four trials while those for potassium are for six trials.

Solubility Measurements. The solubility data given in Table II were obtained as follows. Approximately 80 mg of complex and 1.00 ml of solvent were placed in a stoppered 2-ml centrifuge tube and kept at 25 ± 0.1° for 7 days. Four 100-μl aliquots were withdrawn from each tube. Two of these were diluted to 100 ml with aqueous ethanol and the diamine concentration was determined by quantitative ultraviolet spectroscopy as previously described. The other two aliquots were used for determination of the sodium concentration by flame photometry.

The solubility data given in Table III were obtained by adding sufficient labeled Na(I)$_3$Cl to 5 ml of each solvent to give a heterogeneous mixture. The samples were kept at 30 ± 0.1° for 8 days with frequent agitation. Aliquots of 1.00 ml were withdrawn and counted for sodium-22 as previously described. The sampling and counting procedures were repeated over 2-day intervals until the metal concentration remained constant.

Conductivity Measurements. Molar conductances were measured using an Industrial Instruments conductivity bridge, Model RC 16B2, and a Type L.C. conductivity cell. The cell electrodes were platinized by the method of Vogel.[18] A methanolic solution of diamine I $(3.02 \times 10^{-3}$ M) had a molar conductance of less than 2.14×10^{-3} ohm^{-1} cm^2 mol^{-1}. The molar conductances of NaCl $(1.01 \times 10^{-3}$ M), CsI $(1.10 \times 10^{-3}$ M) and TlClO$_4$ $(1.06 \times 10^{-3}$ M) in methanol were 97.0, 117.0, and 130.0 ohm^{-1} cm^2 mol^{-1}, respectively. No

(18) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," Longmans, Green and Co., Ltd., London, 1962, p 972.

Table VI. Sodium–Potassium Competition

Temp, °C	% Na	% K	Mole ratios Na:K	Mole ratios 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.

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*

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 ($hk0, hk1, hk2, hk3$) using Cu Kα 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 Kα 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

(1) D. Bright and M. R. Truter, *Nature (London)*, **225**, 176 (1970).

(2) B. Metz, D. Moras, and R. Weiss, *Proc. Int. Conf. Coord. Chem., 13th*, **2**, 85 (1970).

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

(4) B. Metz, D. Moras, and R. Weiss, *J. Amer. Chem. Soc.* **93**, 1806 (1971).

(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).