

Alkali Anions. Preparation and Crystal Structure of a Compound Which Contains the Cryptated Sodium Cation and the Sodium Anion

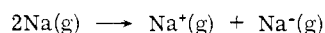
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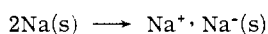
Abstract: When a saturated solution of sodium metal in ethylamine in the presence of a cation-complexing bicyclic diamine ether ("crypt") is cooled, crystals of $\text{Na}_2\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6$ form as thin hexagonal plates. The synthesis, analysis, crystal growth, and crystal structure of this compound are described. One of the sodium species is trapped in the "crypt" and the other is outside. The compound crystallizes in the rhombohedral system ($R\bar{3}2$) with three molecules per unit cell (hexagonal axes). The structure was solved by Patterson methods and refined by full-matrix least-squares calculations. The observed structure and distances are in full agreement with a model in which a sodium cation is trapped in the crypt and a sodium anion is outside.

Accustomed as we are to the +1 oxidation state of alkali metals in their compounds, this report of a new solid compound which contains sodium in the -1 oxidation state requires convincing substantiation. While the method of preparation, analysis, and properties are all consistent with the presence of Na^- , we believe that the crystal structure provides the most convincing evidence that the sodium anion is indeed present. In this paper we describe the synthesis, analysis, crystal growth, and crystal structure of a stoichiometric compound in which the cation, Na^+ , is trapped in a "crypt" and the counterion, Na^- , is outside. Some of the properties have been described in a preliminary communication.¹

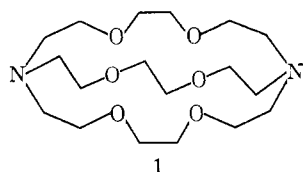
It has been known for some time that alkali anions are stable in the gas phase. Indeed, the electron affinity of the sodium atom is +0.54 eV.^{2,3} Although the process



is endothermic by 4.54 eV, an estimate of the crystal energy of the *hypothetical* salt $\text{Na}^+ \cdot \text{Na}^-$ indicates that the process



is endothermic by only about 0.8 eV. (The crystal energy was estimated by scaling that of $\text{Na}^+ \cdot \text{I}^-$ to the interatomic distance in metallic sodium.) Stabilization of the cation by complex formation could, therefore, make up the energy deficit and lead to a stable salt of the sodium anion. Alternatively, if Na^+ were trapped in a cage which kinetically inhibited its release, the formation of solid sodium might be prevented. Such considerations led us to explore the use of the bicyclic polyoxadiazine, **1** (2,2,2-crypt), as a complexing agent for this purpose.

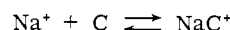


It has been evident for several years that species of stoichiometry M^- are present in metal-amine and metal-ether

solutions. In fact, such species were proposed many years ago in order to explain the magnetic and electrochemical properties of metal-ammonia solutions.⁴⁻⁶ However, in this case, the absence of specific metal-dependence has not permitted distinction among a number of alternative structures, including a loose ion cluster,⁷ $\text{e}^- \cdot \text{M}^+ \cdot \text{e}^-$, an ion pair with the dielectron,^{4,8} $\text{M}^+ \cdot \text{e}_2^{2-}$, and a spherically symmetric anion,⁶ M^- . By contrast, solutions of the alkali metals in amines and ethers give metal-dependent absorption bands^{9,10} of M^- , which suggests that the alkali metal plays more than a mere "bystander" role.

By comparing the temperature and solvent dependence of the optical bands in metal-amine solutions with the charge-transfer-to-solvent (ctts) bands of I^- , Matalon, Golden, and Ottolenghi¹¹ assigned the metal-dependent band to the alkali anion, M^- . This assignment is in accord with the diamagnetic nature of the species,^{12,13} its conductivity,^{14,15} the Faraday effect,¹⁶ the oscillator strength,¹⁷ photolysis studies,^{13,18-20} and the kinetics of its formation from M^+ and e^-_{solv} .^{21,22} The prominent role played by the particular alkali metal in determining the formation and properties of M^- suggests that it may best be described as a centrosymmetric anion with both electrons in the outer s orbital. However, its description as a "tight ion pair" of M^+ with e_2^{2-} , as a "tight ion cluster," $\text{e}^- \cdot \text{M}^+ \cdot \text{e}^-$, or as a solvated cation with two electrons in an expanded orbital could not be ruled out on the basis of the solution properties. The evidence given in the present paper that Na^- can exist free of solvent in a crystal, greatly strengthens the viewpoint that M^- in solution is a "true" solvated alkali anion. Recent ²³Na nmr studies of Na^- in solution appear to confirm this assignment.²³

We have recently shown^{9,24-26} that cyclic and bicyclic polyethers which form "crown"²⁷ and "cryptate"²⁸ complexes with alkali cations greatly enhance the solubility of the alkali metals in amines and ethers. For example, the absence of any blue color when pure ethylamine is allowed to contact a freshly deposited sodium mirror indicates a solubility of less than $10^{-6}M$. However, in the presence of 2,2,2-crypt (**1**), solutions as concentrated as 0.4 M in total sodium can be prepared. This solubility enhancement indicates a complexation constant of at least 10^{10} for the process

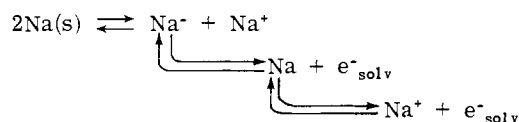


in ethylamine. This value is reasonable in view of the values in water (10^4) and in methanol ($>10^8$).^{29,30} As indicated

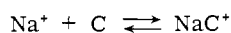
earlier, it is just such stabilization of the cation which might lead to the isolation of a salt of Na^- .

Another factor which might be of importance is the rate of release of Na^+ from the crypt. Extrapolation of the rate data for ethylenediamine³¹ suggests that the average lifetime of Na^+ in a cryptate complex at -78° could be as long as 1 min or more.

The composition of metal solutions in the presence of crypt is to some extent controllable. The overall equilibrium scheme may be described by²⁵



together with the complexation equilibrium



By using a mole ratio of metal to crypt of at least two, the formation in amines and ethers, of monomers (Na) and solvated electrons, can be largely prevented. In this case, the solution stoichiometry, as indicated by the optical and magnetic properties, is dominated by NaC^+ and Na^- . On the other hand, when the mole ratio of metal to crypt is less than two, substantial concentrations of e^-_{solv} can be obtained.⁹

With these considerations in mind, we began several years ago to examine the solids which are produced either by solvent evaporation or by cooling two types of solutions. The first kind of solution was prepared in such a way that the major species present were MC^+ and e^-_{solv} . The blue, strongly paramagnetic solids obtained in this way have not yet been fully characterized. The second type of solution contained largely MC^+ and M^- . In the case of sodium solutions in ethylamine, the gold colored crystals which are the subject of this paper formed spontaneously when a saturated solution was cooled.

Preparation and General Properties

The complexing agent, **1**, was synthesized in our laboratory by a modification³² of the procedure of Lehn and coworkers.²⁹ Since high purity is required in order to form stable metal solutions, the 2,2,2-crypt was further purified by vacuum sublimation followed by over 100 passes with a zone-melting apparatus. The final material was snow-white and melted at 68° . The pmr spectrum consisted of two triplets at 2.65 and 3.65 ppm and a singlet at 3.78 ppm as expected for the pure compound.³⁰

Ethylamine was first dried with calcium hydride, then vacuum distilled onto Na-K alloy. After several days storage over this alloy as the blue solution, the solvent was vacuum distilled into a storage bulb. We recognize³³ that this procedure does not remove certain impurities such as ammonia, methylamine, etc., but for our purposes these substances are not detrimental. General vacuum and solution-handling techniques have been described elsewhere.⁹

Weighed quantities of 2,2,2-crypt were placed into a Pyrex vessel which was separated from a metal-containing side arm by a coarse frit. After evacuation to 10^{-5} Torr, sodium was distilled into the side arm through several constrictions and heated to form a mirror. Ethylamine was then distilled onto the 2,2,2-crypt and the make-up vessel was removed from the vacuum line and cooled to -78° . The solution was poured through the frit onto the sodium mirror where a dark blue solution formed immediately. After several minutes, the solution was warmed and allowed to flow through the frit. A gold colored solid formed when the blue solution was cooled again to Dry Ice temperatures. The solid formed by such rapid cooling is microcrystalline as shown by the X-ray powder pattern which was observed when some of the powder was allowed

to form in an X-ray capillary. In order to ensure that the solution stoichiometry was $\text{NaC}^+ \cdot \text{Na}^-$, the supernatant liquid was repeatedly poured through the frit onto the sodium mirror. This was followed by repeated distillation of ethylamine from the solution onto the sodium until a blue solution could no longer be formed.

After evaporation of the ethylamine which had been poured away from the crystals, some blue coloration remained on and near the crystals. This was removed by washing the crystals with either *n*-hexane or diethyl ether. The crystals are very slightly soluble in the latter solvent but show no evidence of solubility in the former. Washed crystals appear to be indefinitely stable when stored in a freezer at -10° but show signs of irreversible darkening when stored for several days at room temperature and when held for short periods at elevated temperatures. The crystals melt with decomposition at 83° to yield gray particles suspended in a clear fluid. Proton nmr studies on thermally decomposed samples dissolved in deuterated chloroform showed only the peaks expected for 2,2,2-crypt, indicating that this structure remains intact. When thermally decomposed samples are cooled and dissolved in either ethylamine or ammonia, dark blue solutions are obtained, indicating that the metal is not completely oxidized by the decomposition. Therefore it is likely that the melting process is accompanied by loss of Na^+ from the crypt with the subsequent formation of sodium metal. We cannot, however, rule out partial decomposition of the organic structure by reaction with sodium.

The integrity and stoichiometry of the compound were tested in several ways as previously reported.¹ These tests leave no doubt that the material is a stoichiometric compound with the formula $\text{Na}_2\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6$ corresponding to two atoms of sodium for each 2,2,2-crypt molecule. Although the appearance of the crystals suggests a metallic nature, packed powders show conductance behavior characteristic of a semiconductor rather than a metal.¹ The absence of an esr signal indicates that the electron spins are paired although static susceptibility measurements will be required to confirm this.

Preparation of Single Crystals

After several attempts to grow single crystals by solvent evaporation had failed, slow cooling of saturated solutions was selected as the crystal-growing technique. The most effective procedure was found to be overnight cooling from about $+12$ to -28° . Higher initial temperatures or slower initial cooling resulted in solution decomposition while low solubility precluded lower initial temperatures. The crystals formed as thin hexagonal plates on the walls of the vessel. By using tubes with flat sides rather than a circular cross-section, larger crystals could be grown. After pouring away the ethylamine, the crystals were washed with purified *n*-hexane.

Although, in a good vacuum system, the crystals have a bright gold appearance, they are extremely reactive toward air and moisture. Partial reaction leaves a white coating on the crystals. Although *n*-hexane does not perceptibly dissolve the compound, the rapid degradation of crystals which were held to the X-ray capillary walls by a film of *n*-hexane indicates that this liquid probably breaks up the crystal structure. As mentioned above, the crystals are not indefinitely stable even in a good vacuum system at room temperature and above.

All of these factors made it extremely difficult to isolate single crystals of suitable quality for X-ray structure determination. A number of methods were attempted. Crystals were washed into the capillary with *n*-hexane in a closed system. When this failed, we attempted to grow crystals in the capillary tube. Then an inert atmosphere box was used to transfer the crystals into capillaries and *n*-hexane was used to hold the crystals onto the walls. Although this looked promising, the crystal degradation noted above eventually yielded a powder pattern. Finally, the crystals were transferred into the capillary in an inert atmosphere box. Paraffin oil (which had been dried over Na-K alloy) was used to hold the crystal onto the wall of the capillary. After sealing the capillary with heat-shrink tubing and removing it from the inert atmosphere box, the system was pumped out and the glass capillary was sealed off under vacuum. In this way, several satisfactory crystals were obtained.

However, even the technique finally adopted has its faults. The compound, as noted, is extremely reactive and the crystals are de-

graded by any impurities in the inert atmosphere box, on the capillary walls, or in the solvents used. Temperature changes may also alter the crystal quality. The crystals were grown at -28° , isolated in the inert atmosphere box at 25° , stored at -80° , and subjected to X-rays at room temperatures and above. Problems may also have occurred because of slight movements of the crystal in the paraffin oil. Furthermore, there were many problems with twinning and unfavorable crystal dimensions. (As noted earlier, the crystals grow in thin hexagonal plates.) Unfortunately, the crystal size and shape could not be determined while it was in the inert atmosphere box but only after it had been sealed in the capillary. Thus, even though nearly a hundred crystals were isolated, only three crystals satisfied all of the necessary conditions for X-ray structure determination.

Space Group Determination and Crystal Selection

Preliminary X-ray investigations were carried out on a G. E. XRD-5 diffractometer equipped with a single-crystal orienter. All X-ray studies were conducted on crystals mounted in glass capillaries and at room temperature ($\sim 22^\circ$). Plots of the intensity-weighted reciprocal lattice revealed the diffraction symmetry to be $R\bar{3}m$. Of the three possible space groups $R\bar{3}m$, $R3m$ and $R32$, the choice of $R32$ (No. 155) was confirmed by the solution and refinement of the structure.

Because a noticeable loss of intensity was observed during preliminary investigations and most of the crystals were of insufficient quality for data collection purposes, several crystals were inspected before suitable ones for data collection could be found. Two crystals were chosen on the basis of their ω scans, which showed single and symmetric peaks having widths from background to background of 2.2° for crystal I and 1.5° for crystal II. In addition, measurable intensities were observed beyond $0.45 \text{ \AA}^{-1} \sin \theta / \lambda$.

The use of a second crystal was prompted by the 35% decay which occurred during the data collection of crystal I and from the unusually large anisotropic thermal parameters derived from the refinement of the structure. Although there was a significant improvement in reducing the decomposition (6% decomposition) during data collection with crystal II, there was no significant change observed in the refined parameters. Even though decomposition and the large thermal parameters precluded the determination of all the structural details of the complex, the overall features of the crystal structure could be conclusively determined. Unless specifically stated, all parameters given were obtained from crystal II. Crystal data are given in Table I. (See paragraph at end of paper regarding supplementary material.)

Data Collection (Crystal I) and Solution of Structure

Different data collection procedures for the two crystals were employed. For crystal I, intensity data were collected to the limit $2\theta = 50^\circ$ (Mo $K\alpha_1$, λ 0.70926 \AA) by the ω -scan technique with a scan range of 2.5° and a scan rate of $1^\circ/\text{min}$ using a Picker-FACS I diffractometer equipped with a graphite monochromator. Individual background measurements were made at the end points of the scan. The counting system employed a scintillation counter with pulse height discrimination. Intensities of three periodically monitored reflections (300, $\bar{1}20$, 0015) decreased by $\sim 35\%$ during the 3 days of data collection which indicated severe decomposition of the crystal.

The intensity data were reduced to structure factor amplitudes in a conventional manner.³⁴ Corrections for Lorentz and polarization effects, as well as a decay correction which was a linear function of time and assumed the decomposition to be isotropic, were applied to the data. No absorption correction was applied. Of the 480 independent reflections measured, only 221 were greater than $2\sigma(I)$ and used in the subsequent solution and first refinement of the structure. The crystal structure was deduced from the three-dimensional Patterson map.

Data Collection (Crystal II)

Three-dimensional intensity data for crystal II were collected on a different Picker FACS I diffractometer by a "wandering" ω -step-scan procedure^{35,36} using Cu $K\alpha$ radiation (λ 1.54178 \AA) with a balanced Ross filter pair (Ni/Co). Six steps were measured

Table I. Crystal Data for $\text{NaC}^+ \cdot \text{Na}^-$ ^a

Crystal system: rhombohedral
Diffraction symmetry: $R\bar{3}m$
Space group: $R32$ (No. 155) hexagonal setting
$a = 8.83$ (1) \AA , $V = 1976.0$ \AA^3
$c = 29.26$ (2) \AA , $Z = 3$
Formula wt ($\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_8\text{Na}_2$): 422.48
$\rho_{\text{calcd}} = 1.064$ g/cm^3 ; $F(000) = 684$ electrons
λ 1.5418 \AA ; $2\theta_{\text{max}} = 120^\circ$
Number of reflections measured: 411
Number of reflections used in refinement: 305

^a Estimated standard deviation of the last significant digit is given in parentheses.

at 0.30° increments on ω from -0.75 to 0.75° and the largest four measurements were summed to give the total intensity. If the peak maximum did not occur at the calculated ω value, one or two additional steps were taken to assure centering of the scan in the detector window. A single background measurement was made at the position of maximum intensity. The counting system was the same as for crystal I.

Intensities of three periodically monitored reflections showed a 6% decrease during the 6 hr of data collection. Corrections for this nominal decay and for an absorption effect by an empirical method³ were applied to these data. Relative structure factor amplitudes were calculated which included Lorentz and polarization corrections. Splitting effects for $\alpha_1 - \alpha_2$ were avoided by collecting data for 2θ less than 120° . Of the 411 measured independent reflections, 308 (75%) were greater than $2\sigma(I)$ and were used in the refinement of the structure.

Refinement of the Structure

Initial values for the refinement of the second data set were taken from the refined positional parameters obtained from the data of crystal I and from arbitrarily assigned isotropic temperature values for the individual atoms.

Four cycles of full-matrix least-squares refinement reduced the conventional R value to 0.14. After the isotropic thermal parameters had been converted to anisotropic values with appropriate restraints applied for atoms in special positions (Na^+ , Na^- , and N), the refinement converged in six cycles with an R value of 0.094. A difference Fourier map did not reveal discernible positions for the hydrogen atoms, so that these atoms were not included in the refinement. This final difference map had no features other than a randomly fluctuating background of $0.3 \text{ e}^-/\text{\AA}^3$. Final atomic parameters are given in Table II with the estimated standard deviations obtained from the inverse matrix of the final least-squares cycle. Atomic scattering factors used were those of Cramer and Waber.³⁸ Because there is no scattering factor available for Na^- , the form factors for neutral sodium were used for both species.

The crystal structure is composed of NaC^+ and Na^- ions held together presumably by electrostatic forces, while the molecule has 32 symmetry as required by the crystallographic symmetry. The disposition of the sodium species in the crystal structure can be described as hexagonal-closest-packing with the separation of layers being $1/2$ of a cell edge along the c axis or 4.88 \AA and a sodium (Na^+)-sodium (Na^-) nearest neighbor distance of 7.06 \AA .

The geometry of the "crypt" is illustrated by the stereoscopic drawing shown in Figure 1. Coordination about the sodium cation is very nearly bicapped trigonal antiprismatic, such that the trigonally oriented oxygen atoms are staggered with respect to the nearest layer at anions. Although this arrangement is enhanced by the electrostatic interactions between oxygen atoms and sodium anions, a more dominant effect is probably due to changes in the "crypt" cavity with changes in size of the cations. As the size of the alkali cations decreases from Cs^+ , Rb^+ , K^+ to Na^+ , the oxygen coordination changes from trigonal prismatic in CsC^+ ,³⁹ RbC^+ ,⁴⁰ and KC^+ ⁴¹ to trigonal antiprismatic in the present structure and in the NaC^+I^- structure.⁴² Even between the latter two structures, the "crypt" shows its flexibility by changing its shape somewhat. These differences may be demonstrated by comparing the torsional angles of the strands given in Table III. The ability of the "crypt" to be flexible in accommodating larger cations and different crystal fields is probably one of the reasons for the ease of

Table II, Final Parameters of $\text{NaC}^+ \cdot \text{Na}^-$ ^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Na ⁺	0.0	0.0	0.0
Na ⁻	0.3333	0.6667	0.1667
N	0.0	0.0	0.0928 (4)
O	0.308 (1)	0.176 (1)	0.0347 (3)
C1	0.184 (2)	0.090 (5)	0.1076 (3)
C2	0.321 (2)	0.182 (4)	0.0829 (3)
C3	0.391 (2)	0.350 (2)	0.0197 (5)

Atom	Anisotropic Thermal Parameters					
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na ⁺	0.026 (1)	0.026 (1)	0.0020 (1)	0.013 (1)	0.0	0.0
Na ⁻	0.042 (2)	0.042 (2)	0.0039 (2)	0.021 (1)	0.0	0.0
N	0.034 (2)	0.034 (2)	0.0019 (2)	0.017 (1)	0.0	0.0
O	0.028 (2)	0.034 (2)	0.0027 (1)	0.013 (2)	0.0001 (4)	-0.0005 (5)
C1	0.034 (3)	0.083 (8)	0.0022 (2)	0.013 (6)	-0.0027 (6)	0.001 (1)
C2	0.033 (3)	0.093 (8)	0.0019 (2)	0.015 (6)	-0.0003 (6)	0.002 (1)
C3	0.040 (5)	0.050 (5)	0.0043 (4)	-0.000 (4)	-0.0027 (11)	0.002 (1)

^a Estimated standard deviation of the last significant figure is given in parentheses. The form of the anisotropic temperature factor expression is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

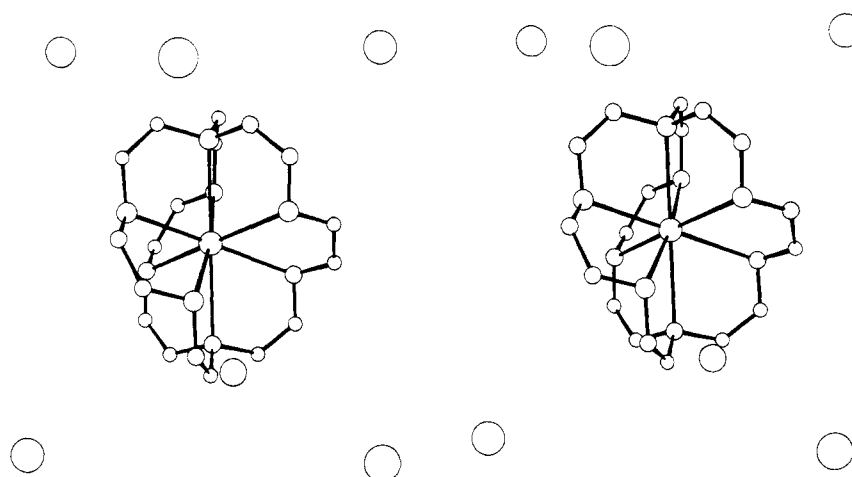


Figure 1. Stereoscopic view of the cryptated sodium cation with its six nearest sodium anions.

thermal decomposition of this complex and for the large thermal parameters observed for atoms in the "crypt."

Bond distances and angles for the cationic complex are given in Table IV. Even though some of these distances are consistently shorter than those expected, artificial shortening of interatomic distances and opening of bond angles often occur in structures with high thermal parameters. While the "true" uncertainties in these molecular parameters are higher than those formally calculated and are difficult to assess, it is reassuring that nearly identical parameters were obtained from the refinement of the data for crystal I. Differences between the two refinements for all parameters were within 3σ of one another.

Nonbonded distances of this structure are compared with related distances of the NaC^+I^- structure also given in Table IV. Favorable comparisons should be possible, since the expected size of the sodium and iodide anions are nearly the same (a more detailed size comparison is made later).

Valence electron distributions are difficult to obtain even with high quality X-ray data, so that no exhaustive proof of the presence of the Na^- ion was attempted with these data nor considered necessary in view of the analytical evidence and the close similarity of the present structure to that of the NaC^+I^- structure.

Conclusions

Obviously the two sodium moieties are in very different environments in the crystal. One is inside of the crypt at distances from the nitrogen and oxygen atoms which are characteristic of a trapped sodium cation. The other sodium species is outside of the crypt at a large distance from all other atoms. The displacement of the ether oxygen atoms in

Table III. Torsional Angles (deg)

	$\text{NaC}^+ \cdot \text{Na}^-$	$\text{NaC}^+ \cdot \text{I}^-$ ^a
N-C1-C2-O	-12.6	-49.4
C1-C2-O-C3	130.0	155.7
C2-O-C3-C3 (2) ^b	-155.8	-157.7
O-C3-C3 (2)-O (2) ^b	38.9	45.2

^a The molecular symmetry of the "crypt" in $\text{NaC}^+ \cdot \text{I}^-$ is (3)^b so that average values were used wherever possible for comparison.

^b The symmetries (2) and (3) are defined by (2) $\equiv y, x, \bar{z}$ and (3) $\equiv \bar{y}, x - y, z$, respectively.

the crypt chains indicates a repulsive interaction with the outside sodium, as expected.

The most convenient way to consider the atom placements is by comparison with the known crystal structure of sodium cryptate iodide, $[\text{Na}^+\text{C}_{18}\text{H}_{36}\text{O}_6\text{N}_2]\text{I}^-$, which was determined by Moras and Weiss.⁴² Although the sodium iodide complex crystallizes in the $P31c$ space group which does not have the twofold rotation axes of the present space group $R32$, it does have the threefold symmetry and a roughly equivalent placement of atoms including a sodium cation trapped in the crypt. Therefore, although the details of the chain conformations are different in the two cases, the ion-atom distances may still be compared.

As shown in Table IV, the $\text{Na}^+ \cdot \text{O}$ and the $\text{Na}^+ \cdot \text{N}$ distances in the present structure compare favorably with the corresponding distances in the iodide structure. This would

Table IV. Interatomic Distances and Angles^a

	NaC ⁺ Na ⁻	NaC ⁺ I ⁻ ^a
Bonded Distances (Å)		
Na ⁺ -N	2.72 (1)	2.75 (2)
Na ⁺ -O	2.57 (1)	2.58 (2)
N-C1	1.48 (2)	1.47 (2)
C1-C2	1.29 (2)	1.44 (3)
C2-O	1.41 (1)	1.44 (2)
O-C3	1.40 (2)	1.40 (5)
C3-C3 (2)	1.31 (3)	1.40 (4)
Nonbonded Distances		
Na ⁺ ...C1	3.45 (2)	3.53 (2)
Na ⁺ ...C2	3.46 (2)	3.46 (2)
Na ⁺ ...C3	3.34 (3)	3.39 (2)
O...O(2)	2.86 (2)	2.79 (2)
O...O (3)	4.09 (2)	4.07 (2)
O...O (3'2)	5.13 (2)	5.12 (2)
O...O (3'2)	3.38 (2)	3.53 (2)
N...N (2)	5.44 (2)	5.50 (2)
	A ⁻ = Na ⁻	A ⁻ = I ⁻
Na ⁺ ...A ⁻	7.06 (1)	7.40 (1)
A ⁻ ...N	5.54 (2)	5.39 (2)
A ⁻ ...O	5.72 (2)	5.22 (2)
Angles (deg)		
	NaC ⁺ Na ⁻	NaC ⁺ I ⁻
Na ⁺ -N-C1	107 (1)	110 (1)
C1-N-C1 (3)	112 (1)	109 (1)
N-C1-C2	128 (1)	113 (2)
C1-C2-O	120 (1)	117 (3)
C2-O-C3	107 (1)	100 (2)
O-C3-C3 (2)	121 (2)	116 (3)
O-Na ⁺ -O (2)	67.6 (3)	65.7 (4)
O-Na ⁺ -O (3)	105.4 (3)	104.4 (4)
O-Na ⁺ -O (3'2)	171.2 (3)	167.0 (4)
O-Na ⁺ -O (3'2)	82.0 (3)	86.6 (4)

^a Whenever possible average values of NaC⁺I⁻ ^{a1} were used for comparison purposes. The number in parentheses after the distances and angles refers to the estimated standard deviation of the last significant digit. The symmetries are defined as follows: $x, y, z \equiv I, \bar{x}, y - x, \bar{z} \equiv 3'2, y, x, \bar{z} \equiv 2, y - x, \bar{x}, z \equiv 3^2, \bar{y}, x - y, z = 3', x - y, \bar{y}, \bar{z} = 3^2$.

surely not be the case unless both structures had the same ion, Na⁺, trapped in the crypt. Therefore, *both* electrons associated with the pair of sodium atoms must be outside of the crypt.

The analogy of the outside sodium with an iodide anion is also appropriate in view of the distance comparisons given in Table IV. For example, the Na⁻-Na⁻ closest distance is 8.83 Å while the I⁻-I⁻ closest approach is 8.63 Å. Similarly, the Na⁻-N closest distance is 5.55 Å and the I⁻-N closest distance is 5.09 Å. Finally, the Na⁻-O distance is 5.76 Å while the I⁻-O distance is 5.19 Å. Thus, the outside sodium is similar to the iodide ion in its placement and distance from other atoms, except that the sodium anion appears to be somewhat larger than I⁻. In agreement with this assignment, the oxygen atoms are staggered away from the outside sodium as expected for a negatively charged sodium anion.

The ability of the strands of the complexing agent, 2,2,2-crypt, to twist in response to changes in the environment was noted by Moras and Weiss⁴² who described the changes in the conformation of the strands as the cation was changed from Na⁺ to K⁺. The present analysis further confirms the ability of the strands of the complexing agent to twist. Because of the antiprismatic structure of the crypt, all atoms (excluding hydrogen atoms) in the structure show a center of inversion through the central sodium except for the carbon atoms in the centers of the strands.

According to this structure, the sodium anion has a large effective radius, perhaps even larger than that of the iodide

ion. This may appear to be unreasonable to those who are accustomed to the sodium *cation* with its small radius. However, several estimates of the size expected for Na⁻ can be made. Matalon, Golden, and Ottolenghi,¹¹ by using Slater atomic radii, estimated the radius of Na⁻ (~2.25 Å) to be slightly greater than that of I⁻ (2.16 Å). We have calculated the radial distribution functions for the 3s electron in Na⁰ and for the two 3s electrons in Na⁻ by using the SCF wave functions of Clementi.^{43,44} The results give maxima at $r = 1.80$ and 2.10 Å for Na⁰ and Na⁻, respectively. While translation of this to atomic and ionic radii is arbitrary, if we scale the Na interatomic distance in metallic sodium by the ratio 2.1/1.8, a value of 2.17 Å is obtained for the radius of Na⁻.

All of the results obtained so far are consistent with the existence of a salt of the sodium anion. In view of the variety of complexing agents and metals which might be used, it is likely that many other compounds which contain alkali anions could be synthesized.

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Supplementary Material Available. A table of observed and calculated structure factor amplitudes $\times 10$ will appear following these pages in the microfilm edition of this volume of the journal. A denotes reflections with intensities less than $3\sigma(I)$ and an X denotes the four reflections omitted from the least-squares refinement. Photocopies of the supplementary material from this paper only or microfiche (105 \times 148 mm, 24 \times 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 \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-7203.

References and Notes

- J. L. Dye, J. M. Ceraso, M. T. Lok, B. L. Barnett, and F. J. Tehan, *J. Amer. Chem. Soc.*, **96**, 608 (1974).
- A. W. Weiss, *Phys. Rev.*, **166**, 70 (1968).
- W. H. E. Schwarz, *Chem. Phys. Lett.*, **10**, 478 (1971). (See this paper for earlier references to experimental and theoretical electron affinities of the alkali atoms.)
- W. Bingel, *Ann. Phys.*, **12**, 57 (1953).
- E. Arnold and A. Patterson, Jr., *J. Chem. Phys.*, **41**, 3089, 3098 (1964).
- S. Golden, C. Guttman, and T. R. Tuttle, Jr., *J. Amer. Chem. Soc.*, **87**, 135 (1965); *J. Chem. Phys.*, **44**, 3791 (1966).
- M. Gold, W. L. Jolly, and K. S. Pitzer, *J. Amer. Chem. Soc.*, **84**, 2264 (1962).
- J. L. Dye, *Pure Appl. Chem.*, **1** (1970).
- M. T. Lok, F. J. Tehan, and J. L. Dye, *J. Phys. Chem.*, **76**, 2975 (1972).
- For other references to optical properties of metal solutions see I. Hurley, T. R. Tuttle, Jr., and S. Golden, *Pure Appl. Chem.*, **449** (1970).
- S. Matalon, S. Golden, and M. Ottolenghi, *J. Phys. Chem.*, **73**, 3098 (1969).
- L. R. Dalton, J. D. Rynbrandt, E. M. Hansen, and J. L. Dye, *J. Chem. Phys.*, **44**, 3969 (1966).
- S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, **52**, 5555 (1970).
- R. R. Dewald and J. L. Dye, *J. Phys. Chem.*, **68**, 128 (1964).
- R. R. Dewald and K. W. Broull, *J. Phys. Chem.*, **74**, 129 (1970).
- T. R. Tuttle, Jr., *Chem. Phys. Lett.*, **20**, 371 (1973).
- M. G. DeBacker and J. L. Dye, *J. Phys. Chem.*, **75**, 3092 (1971).
- L. J. Gilling, J. G. Kloosterboer, R. P. H. Rettschnick, and J. D. W. Van-Voorst, *Chem. Phys. Lett.*, **8**, 457, 462 (1971).
- A. Gaathon and M. Ottolenghi, *Isr. J. Chem.*, **8**, 165 (1970).
- D. Huppert and K. H. Bar-Eli, *J. Phys. Chem.*, **74**, 3285 (1970).
- J. L. Dye, M. G. DeBacker, J. A. Eyre, and L. M. Dorfman, *J. Phys. Chem.*, **76**, 839 (1972).
- J. W. Fletcher, W. A. Seddon, J. Jevcak, and F. C. Sopchyshyn, *Chem. Phys. Lett.*, **18**, 592 (1973).
- J. M. Ceraso and J. L. Dye, *J. Chem. Phys.*, **61**, 1585 (1974).
- J. L. Dye, M. G. DeBacker, and V. A. Nicely, *J. Amer. Chem. Soc.*, **92**, 5226 (1970).
- J. L. Dye, M. T. Lok, F. J. Tehan, R. B. Coolen, N. Papadakis, J. M. Ceraso, and M. G. DeBacker, *Ber. Bunsenges. Phys. Chem.*, **75**, 659 (1971).

- (26) J. L. Dye in "Electrons in Fluids," J. Jortner and L. R. Kestner, Ed., Springer-Verlag, West Berlin, 1973, p 77.
- (27) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); **92**, 386 (1970).
- (28) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Lett.*, 2885, 2889 (1969).
- (29) J. M. Lehn, *Struct. Bonding (Berlin)*, **16**, 1 (1973).
- (30) J. M. Lehn and J. P. Sauvage, *Chem. Commun.*, 440 (1971).
- (31) J. M. Ceraso and J. L. Dye, *J. Amer. Chem. Soc.*, **95**, 4432 (1973).
- (32) J. L. Dye, M. T. Lok, F. J. Tehan, J. M. Ceraso, and K. J. Voorhees, *J. Org. Chem.*, **38**, 1773 (1973).
- (33) V. A. Nicely and J. L. Dye, *J. Chem. Phys.*, **53**, 119 (1970).
- (34) All calculations were carried out on a CDC-6500 computer. In addition to local programs, the following programs which include local modifications were used in this study: NUFACS, data reduction program by J. A. Ibers; UCLALS, full-matrix least-squares program; FOURR, Fourier program from XRAY 70 by J. M. Stewart; ORTEP, stereoscopic plotting program, C. Johnson.
- (35) H. W. Wyckoff, M. Doscher, D. Tsernoglou, T. Inagami, L. N. Johnson, K. D. Hardman, N. M. Allewell, D. M. Kelly, and F. M. Richards, *J. Mol. Biol.*, **27**, 563 (1967).
- (36) R. L. Vandlen and A. Tulinsky, *Acta Crystallogr., Sect. B*, **27**, 437 (1971).
- (37) A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, **24**, 351 (1968).
- (38) D. T. Cramer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
- (39) D. Moras, B. Metz and R. Weiss, *Acta Crystallogr., Sect. B*, **29**, 388 (1973).
- (40) R. Weiss, B. Metz, and D. Moras, "Proceedings of the 8th International Conference on Coordination Chemistry," Warsaw, Poland, Sept 1970.
- (41) D. Moras, B. Metz, and R. Weiss, *Acta Crystallogr., Sect. B*, **29**, 383 (1973).
- (42) D. Moras and R. Weiss, *Acta Crystallogr., Sect. B*, **29**, 396 (1973).
- (43) E. Clementi, "Tables of Atomic Functions," International Business Machines Corp., 1965.
- (44) E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, *Phys. Rev. A*, **133** 1274 (1964).

Effect of Trans Ligands on Iodine-129 Mössbauer Parameters in Square-Planar Platinum(II) Complexes

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Abstract: The ^{129}I Mössbauer spectra of neutral and cationic compounds of the type *trans*- $^{129}\text{IQ}_2\text{PtX}$ ($\text{X} = \text{Me}, \text{CF}_3, \text{I}; \text{Q} = \text{Me}_2\text{PhP}$) and *trans*- $^{129}\text{IQ}_2\text{PtL}^+$ ($\text{L} = \text{P}(\text{OMe})_3, \text{P}(\text{OMe})_2\text{Ph}, \text{PPh}_3, \text{AsPh}_3, \text{EtNC}, p\text{-MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{NC}$) have been recorded. The ^{129}I e^2qQ values are very sensitive to the nature of the trans ligand. For example, the total range of $e^2qQ_{(7/2)}$ values is ~ 400 MHz, and the two isocyanide ligands give significantly different $e^2qQ_{(7/2)}$ values: -1038 ± 4 MHz (EtNC) compared to -1063 ± 4 MHz ($p\text{-MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{NC}$). The trans influence series is found to be $\text{Me} > \text{H} > \text{CF}_3 > \text{I}$ for the neutral compounds and $\text{P}(\text{OMe})_3 > \text{EtNC} > \text{P}(\text{OMe})_2\text{Ph} \sim p\text{-MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{NC} > \text{Ph}_3\text{As} > \text{Ph}_3\text{P}$ for the cationic complexes. This order is compared with those obtained from Pt-CH₃ nmr coupling constants, and Pt-Cl infrared stretching frequencies. Analysis of the spectra using the Williams-Bancroft analytical treatment leads to a $Q_{(5/2)}/Q_{(7/2)}$ value of 1.239 ± 0.007 , and statistically estimated errors (σ) in e^2qQ and η of ± 4 MHz and ± 0.03 , respectively.

Mössbauer spectroscopy has proved to be a very useful technique in the examination of bonding modes for a wide variety of molecules.^{1,2} We now wish to report the utilization of the 27.8-keV γ radiation from ^{129}I to elucidate the bonding in some square-planar platinum(II) complexes and in particular to examine the influence of ligands trans to the ^{129}I probe on the bonding of the iodine ligand.

The trans influence in transition metal complexes has been widely studied, using a variety of spectroscopic and other techniques, and is the subject of a recent review.³ The phenomenon has been most widely examined in platinum(II) complexes, and trans influence series have been established for a wide variety of ligands from infrared, nmr and nqr spectroscopic, and X-ray crystallographic parameters.³ The mechanism most widely invoked to explain the influence of a ligand to another trans to it in square-planar compounds is that postulated by Syrkin,⁴ where ligands trans to one another are considered to share the same hybrid orbital, which has predominantly 5d and 6s character. As a ligand L requires more d and s participation in the Pt-L bond; then the availability of these orbitals to the ligand trans to L is decreased, resulting in a weaker metal-ligand bond. The cis ligands use an independent s-d hybrid and will be affected to a lesser extent.

^{129}I Mössbauer spectra will yield less ambiguous results than those from some other Mössbauer isotopes, such as ^{119}Sn or ^{121}Sb , which have other ligands bonded to them. The parameters from the spectra of these latter elements will also reflect the bonding characteristics and structural distortions of the other ligands about the Mössbauer atom.

We have recorded the ^{129}I spectra and derived a number of spectroscopic and bonding parameters for three neutral compounds of the form *trans*- $^{129}\text{IQ}_2\text{PtX}$ ($\text{X} = \text{Me}, \text{CF}_3, \text{I}$) and six cationic complexes of the form *trans*- $^{129}\text{IQ}_2\text{PtL}^+$ ($\text{L} = \text{P}(\text{OMe})_3, \text{P}(\text{OMe})_2\text{Ph}, \text{PPh}_3, \text{AsPh}_3, \text{EtNC}, p\text{-MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{NC}$), where $\text{Q} = \text{Me}_2\text{PhP}$. The ^{129}I probe is found to be sensitive to the nature of the trans ligand and hence should be very useful in the future for studying subtle changes in iodine bonding. Since the completion of this work, the ^{129}I Mössbauer parameters for some platinum complexes of the type *cis*- and *trans*- $^{129}\text{I}_2\text{PtL}_2$ and *trans*- $^{129}\text{IHPtL}_2$ ($\text{L} = \text{neutral ligand}$) have been reported.^{5,6} A cis influence of ligands was obtained from the trans compounds, but the changes in parameters in the cis compounds are clearly due to both a cis and a trans influence.

The analysis of iodine Mössbauer spectra is still somewhat of a problem. Most recent workers have used numerical iterative methods⁷ to extract the ^{129}I Mössbauer parameters. However, the very large χ^2 values reported recently⁵ point out some of the problems associated with this method. For example, Q^*/Q —which is not yet accurately established—has to be assumed, and peak intensities have to be constrained to their expected values for random samples with no Goldanskii-Karyagin effects. In the present paper, we point out the significant advantages of the analytical method,⁸ outlined earlier, to extract our parameters. Excellent χ^2 values, a detailed analysis of the errors in the method, and the internal consistency checks which the method affords, strongly suggest that the Williams-Bancroft meth-