665. *Alkali-metal–Amine Solutions. Spectroscopic and Magnetic Studies.*

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One or both of two intense electronic absorption bands in the visible and the infrared region, respectively, are invariably found in dilute solutions of alkali metals in amine solvents. Which band predominates and the precise position of the absorption maximum depend upon the solvent, the metal, and the temperature. Solutions showing only the visible band are not paramagnetic, whereas paramagnetism is found whenever the infrared band is detectable. In agreement with current theory, it is postulated that electrons are solvated, either singly or as pairs, and that the intense absorption band is caused by the transition of an electron to a discrete excited state defined by the solvent shell. Allocation of the visible and the infrared bands to excitations from paired and unpaired electrons respectively, and the factors affecting the pairing and unpairing of electrons, are discussed, together with the effect of changes in environment on the absorption maxima.

IT has been established that alkali metals dissolve reversibly in liquid ammonia to give true, rather than colloidal, solutions. The precise nature of these solutions has been investigated in several ways. Conductivity studies [1] have shown that these solutions have an equivalent conductance greater than that found for any salt in liquid ammonia; in very dilute solutions the conductance is about three times that of a salt in liquid ammonia, while in concentrated solutions the conductance closely approaches that of a metal. These results have been interpreted as a dissociation of the metal atoms into metal ions and solvated electrons, $M \rightleftharpoons M^+ + e$, the high conductivity of the dilute solution being attributed to the abnormal mobility of solvated electrons. Further information on the nature of solvated electrons is provided by density measurements,[2] which show that solutions of metals are less dense than pure ammonia to the extent of at least 70 $Å^3$ per alkali-metal atom dissolved, and by measurements of magnetic susceptibility [3] and paramagnetic resonance absorption.[4] Magnetic measurements show that paramagnetic species are present at low concentrations, but that the solutions become increasingly diamagnetic as they become more concentrated, and that, further, the paramagnetism increases with increase in temperature. Since the characteristic spectra of the metal atoms cannot be detected, these changes in paramagnetism are generally attributed to the presence of electrons solvated either singly or in pairs. The metal atoms are completely ionised and the resulting cations and electrons are stabilised by solvation. If the electrons are separately solvated, they will be paramagnetic, whereas they will be diamagnetic if they are solvated in pairs.

In the model described by Kaplan and Kittel,[5] based on the investigations by Hutchinson *et al.*,[4] the solvated electrons exist in delocalised molecular orbitals on all the solvent protons surrounding cavities which the electrons create in the solvent. The molecular orbitals are described by a wave function of the type

$$\Psi = p^{-\frac{1}{2}} \sum_{i=1}^{p} \psi_i$$

where p is of the order of 50, and ψ_i represents the 1*s* atomic orbital on the *i*th proton together with a small contribution from higher-energy states. In an alternative

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[1] Kraus, *J. Amer. Chem. Soc.*, 1921, **43**, 749.

[2] Lipscomb, *J. Chem. Phys.*, 1953, **21**, 52.

[3] Freed and Sugarman, *ibid.*, 1943, **11**, 354.

[4] Hutchinson and Pastor, *Rev. Mod. Phys.*, 1953, **25**, 285; *J. Chem. Phys.*, 1953, **21**, 1959; Hutchinson, *J. Phys. Chem.*, 1953, **57**, 546.

[5] Kaplan and Kittel, *J. Chem. Phys.*, 1953, **21**, 1429.

description, Platzman[6] considers the electron to be bound in the lowest discrete state of the potential created by the oriented solvent molecules. In both these models, the solvated electron is quite independent of the cation.

Recently, Becker *et al.*[7] have suggested that no cavities exist, but that the electron is associated only with the protons of the solvent molecules orientated around the cation. Our results suggest that, although the cation influences the solvation of the electron, the extreme position proposed by Becker is unlikely in dilute solutions.

Spectra.—Examination of the available spectroscopic data[8-13] for dilute solutions of the alkali and alkaline-earth metals in ammonia, amines, and mixed solvents shows the presence of one or both of two characteristic and very intense electronic absorption bands, one in the visible (~6500 Å) and the other in the infrared (~15,000 Å) region. A less intense, but continuous, absorption is also found, starting at about 5500 Å and extending into the ultraviolet. Apparently, the only exception to this generalisation is found in the spectra of some solutions of potassium, where there is an absorption peak at about 8000 Å; this exception is discussed below. The existing data, together with the results obtained in the present study, are summarised in Table 1.

Nature of the Absorption.—The concept that one species is responsible for both bands can be discarded, since often only one band is detectable, whilst in other cases a change of temperature increases one band at the expense of the other—a fact which implies the presence of two different absorbing species in equilibrium. Thus three problems present themselves: (*a*) What is the nature of the absorbing species? (*b*) What is the change induced when light is absorbed? (*c*) What are the reasons for the marked effect of slight changes in environment on the relative amounts of each absorbing species and on the precise positions of the band maxima?

(*a*) Blade and Hodgins[10] attribute the existence of two bands to the variation in physical arrangement of the solvent molecules around the periphery of cavities containing single electrons, and suggest that with amines there are traps or cavities containing single electrons in which the hydrogen atoms of either amino-groups only or both amino- and hydrocarbon groups are oriented inwards. These are termed amine traps and aliphatic traps respectively. The 15,000 Å peak is then attributed to amine traps and the 6500 Å peak to aliphatic traps. This theory clearly cannot account for the appearance of the visible peak in ammonia solutions at low temperatures and high concentrations, and it is also difficult to see why all possible intermediate arrangements of N–H and N–Me groups around the cavity are not just as likely as the two extremes postulated. In any case, on the basis of Kaplan and Kittel's interpretation,[5] the orientation of N–Me bonds around the cavity could only mean that fewer protons are available to contribute to the delocalised molecular orbital, since C–H bonds would not be sufficiently polar for the hydrogen atoms to contribute appreciably.

Platzman and Frank[14] also only consider single solvated electrons, and propose that the observed absorption bands are part of a series of transitions. This theory, again, does not explain why when both bands are observed in one solution a change in temperature favours one at the expense of the other.

We suggest that, since magnetic studies[4] show that the energies of paired (e_2) or unpaired (e_1) solvated electrons are very similar, the most reasonable explanation of the two main bands is that they are caused by e_2 and e_1 species severally. The paramagnetic-resonance results obtained by Hutchinson and Pastor[4] for liquid-ammonia solutions, and

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[6] Platzman, unpublished results, quoted in footnote to p. 423 of ref. 14.

[7] Becker, Landquist, and Alder, *J. Chem. Phys.*, 1956, **25**, 971.

[8] Gibson and Argo, *J. Amer. Chem. Soc.*, 1918, **40**, 1327.

[9] Vogt, *Naturwiss.*, 1948, **35**, 298.

[10] Blade and Hodgins, *Canad. J. Chem.*, 1955, **33**, 411.

[11] Jolly, U.S. Atomic Energy Comm. Nat. Sci. Foundation, Washington D.C., 1952, U.C.R.L. 2008, 3.

[12] Bosch, *Z. Physik*, 1954, **137**, 89.

[13] Hohlstein and Wannagat, *Z. anorg. Chem.*, 1956, **288**, 193.

[14] Platzman and Frank, *Z. Physik*, 1954, **138**, 411.

those obtained by us for solutions in methylamine, ethylenediamine, and propylenediamine (see Table 2) strongly suggest that the infrared band is a property of the e_1 species and the visible band of the e_2 species. Thus solutions which show only the visible band are not detectably paramagnetic, although the total metal concentration (*ca.* 10^{-3}M) would give an unpaired-electron concentration many hundreds of times greater than the minimum which can be detected. When both bands are observed, or only that in the infrared region, then paramagnetic resonance absorption is always found.

TABLE 1. *Absorption spectra of dilute solutions of metals in amine solvents.*

Solvent	Metal	Temp.*	Range investigated (Å)	Absorption max. (Å)	Comments †	Ref.
NH_3	Li	−65° to RT	4000—7500	—	A	8
	Li	—	4000—20,000	18,000	—	9
	Li	− 70	4000—20,000	14,900	T.	10
	Li	−253	4000—25,000	5850; 12,500	B	12
	Na	−65 to RT	4000—7500	—	A	8
	Na	—	4000—20,000	18,000	—	9
	Na	—	10,000—25,000	15,000	—	11
	Na	− 60	4000—20,000	14,700	T.	10
	Na	−253	4000—25,000	5900; 12,500	B	12
	K	−65 to RT	4000—7500	—	A	8
	K	−70	4000—20,000	15,000	—	10
	Mg	−65 to RT	4000—7500	—	A	8
	Ca	−65 to RT	4000—7500	—	A	8
$MeNH_2$	Li	−60	4000—20,000	13,500	—	10
	Li	—	4000—16,000	7100; 13,000	—	13
	Na	−60	4000—20,000	6400	—	10
	Na	−70 to RT	4000—7500	6500	—	8
	Na	—	4000—16,000	6900	—	13
	K	−60	4000—20,000	6540; 8200	—	10
	K	−70 to RT	4000—7500	6500	—	8
	Ca	−60	4000—20,000	12,800	—	10
$EtNH_2$	Li	−40	4000—20,000	14,200	—	10
	Li	—	4000—16,000	6800	—	13
	Na	—	4000—16,000	6800	—	13
	K	−60	4000—20,000	6450	—	10
$(\cdot CH_2\cdot NH_2)_2$	Na	RT	4000—10,000	6700	—	‡
	K	RT	4000—10,000	6700	—	‡
$NH_2\cdot CHMe\cdot CH_2\cdot NH_2$	Na	RT	4000—10,000	6600	—	‡
	K	RT	4000—10,000	6700	Also small shoulder at 8200 Å	‡
NH_3–$MeNH_2$						
(90—80% $MeNH_2$)	Li	—	4000—16,000	7400—7500; 13,000	—	13
(70% $MeNH_2$)	Li	—	,,	13,000	—	13
(90% $MeNH_2$)	Na	—	,,	7000	—	13
(80—70% $MeNH_2$)	Na	—	,,	7200; 13,200—12,500	—	13
(60—0% $MeNH_2$)	Na	—	,,	12,500—12,000	—	13
(50% $MeNH_2$)	Na	−70	4000—20,000	13,300	—	10
NH_3–$MeNH_2$ (50%)	K	−60	4000—20,000	14,000	—	10
NH_3–$EtNH_2$						
(90—70% $EtNH_2$)	Li	—	4000—16,000	7000—7200; 13,000	—	13
(60% $EtNH_2$)	Li	—	,,	12,500	—	13
(90—80% $EtNH_2$)	Na	—	,,	7000	—	13
(70—60% $EtNH_2$)	Na	—	,,	7000—7500; 13,000	—	13
(50% $EtNH_2$)	Na	—	,,	12,500	—	13

* RT = room temperature. † A = absorption increases with temperature; B = thin films, concentrated; T = temperature-dependent. ‡ This paper.

Support for this allocation of the visible and infrared bands to the e_2 and e_1 species is provided by the Hutchinson and Pastor's magnetic measurements of liquid-ammonia solutions, which show that e_2 is favoured as the temperature is lowered, while Blade and Hodgins [10] find that the visible band of a solution in a mixed ammonia–methylamine solvent is favoured at the expense of the infrared band at lower temperatures (thus agreeing with the qualitative observations by Ogg [15] on analogous solutions in liquid ammonia).

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[15] Ogg, *J. Chem. Phys.*, **1946**, **14**, 114.

(*b*) It is often stated (see, *e.g.*, ref. 5) that the intense absorption associated with solvated electrons corresponds to the total ejection of an electron from the cavity composed of orientated solvent molecules into bulk, unorientated solvent (described as a conduction band). Similar theories have been invoked to describe the intense ultraviolet absorption of halide ions. However, Platzman and Frank [14] recently suggested that the electron in the excited state of a halide ion is still held by the orientated solvent shell, though more weakly. Indeed, one would expect an absorption continuum rather than a discrete band for a process involving total electron ejection.

Evidence for the nature of the act of light absorption in metal solutions is provided by the irradiation experiments of Linschitz, Berry, and Schweitzer,[16] who found that, when lithium in a glass of mixed ether, *iso*pentane, trimethylamine, and methylamine was irradiated, the strong visible absorption band was lost. These authors found that the band was discharged only when light of wavelength less than 5400 Å was used for irradiation, although the maximum absorption was at 6000 Å. A general increase in absorption in the near-infrared region, with a broad maximum at 12,500 Å was also observed. Our qualitative observation that when a blue glass of propylenediamine containing dissolved sodium is irradiated the blue colour is greatly diminished but never quite lost is in agreement with the work of Linschitz *et al.*

We can hence conclude that the two main absorption bands do not correspond to the ejection of an electron (paired or unpaired) from its cavity into a conduction band, but rather to its excitation into a higher-energy orbital still within the same cavity. We further suppose that the continuum observed below about 5500 Å corresponds to the total ejection of the electron into a conduction band. When this electron is forced out of its cavity completely, it is unable to return to its original state because of the rigidity of the solvent, but once the glass is allowed to soften, the electron can create a new cavity, so that the original absorption band returns. When one electron has been ejected from an e_2 cavity, then an e_1 cavity in effect remains, thus accounting in part for the increase in the infrared band observed by Linschitz.

(*c*) *Effect of Environmental Changes on the* $2e_1 \rightleftharpoons e_2$ *Equilibrium.*—It is apparent from Table 1 and from the results on mixed solvents reported by Blade and Hodgins,[10] that quite small changes in temperature, concentration, and the nature of the metal and solvent readily affect the equilibrium $2e_1 \rightleftharpoons e_2$, so that e_1 and e_2 must have very similar energies. Lowering the temperature or raising the concentration clearly favours the e_2 form. Solvents with relatively high dielectric constants (*e.g.*, NH_3) appear to favour e_1 formation irrespective of the metal, but in amine solvents e_1 formation occurs only when the metal ions have a high surface-charge density. It is perhaps significant that lithium is much more soluble in amines than either sodium or potassium, and that lithium alone of these metals forms appreciable amounts of e_1 cavities in such solvents. These trends are consistent and suggest that in amine solvents ion-pair formation may take place, so that the metal ion is close to the solvated electron and has a noticeable influence upon the type of cavity formed.

We are unable to explain the absorption band at 8500 Å which appears in relatively concentrated solutions of potassium in methylamine and propylenediamine. Since the band is reproducible but occurs only in these two solvents, it is unlikely to be caused by impurities in the metal. The band appears at such short wavelengths that it can hardly be caused by e_1 transitions (shifted by the effect of the metal ion) and in any case paramagnetic-resonance measurements show that the concentration of e_1 species is extremely small.

Effect of Environmental Changes upon the Position of Maximum Absorption and Band Width.—The results reported by Blade and Hodgins [10] show that subtle changes in environment have a marked effect, not only on the pairing of electrons, but also upon the

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[16] Linschitz, Berry, and Schweitzer, *J. Amer. Chem. Soc.*, 1954, **76**, 5833.

exact positions of maximum absorption and widths of both bands. The magnitude of the shift of maximum absorption does not give a direct measure of the change in energy of either the ground or the excited state, but of the change in energy of one in relation to the other. The various trends may be summarised: (*a*) Increase in temperature broadens the band and shifts it to longer wavelengths. For a given solvent, this effect is more pronounced for e_1 than e_2 bands. (*b*) Increase in concentration shifts the band to shorter wavelengths. This effect is more marked for e_2 than e_1 bands, and is greater in amine solvents than in ammonia. (*c*) Replacement of hydrogen atoms by methyl groups (*i.e.*, in amines) gives a shift to shorter wavelengths, and in mixed solvents the band lies between the two extremes. This gradual change indicates that in mixed solvents the hydrogen atoms of the N–H bonds of both amines and ammonia molecules can contribute directly to cavity formation.

The effects closely parallel those reported for the same changes in environment on the first absorption band of the solvated iodide ion.[17] If either the e_1 or the e_2 bands represented the complete ejection of an electron from a cavity then one might have expected a reversal in the direction of the spectral shifts compared with those for iodide, since the ground state of the solvated electron resembles the excited state of the iodide ion. Since, however, the effects are very similar, the postulate that the excited electron is still held within the e_1 or the e_2 cavity is given further support.

It has been noted that the e_2 band in amine solvents is far more sensitive to changes in concentration than is the e_1 band in ammonia. This can probably be attributed to the combined effect of the higher charge density per cavity and the lower dielectric constant of the amine solvent which makes ion-pair formation significant despite the low concentrations.

EXPERIMENTAL

Purification of Materials.—Sodium and potassium were purified by distillation *in vacuo* into tubes sealed at one end, a modified version of the technique described by Dostrovsky and Llewellyn [18] being used. The samples of the metals taken for the distillation were cut under light petroleum from the centre of larger pieces.

Anhydrous ethylenediamine and propylenediamine were placed over potassium hydroxide pellets for some days, and then distilled through a 3 ft. column packed with glass helices. The middle fraction from the distillation was treated with sodium wire, and then distilled *in vacuo* on to freshly distilled alkali metal (sodium for ethylenediamine, potassium for propylenediamine); a permanent blue coloration was taken as a criterion of dryness.

Methylamine. An aqueous solution (30% w/w) was run on to pellets of sodium hydroxide; the liberated methylamine was passed through a column of glass wool mixed with moist, freshly precipitated mercuric oxide to remove traces of ammonia [19] and collected in a trap cooled with liquid oxygen. The amine was dried *in vacuo* with freshly crushed barium oxide and finally metallic sodium.

Preparation and Stability of Alkali-metal Solutions in Ethylenediamine and Propylenediamine.—The apparatus shown in Fig. 1 was used for the preparation of the metal solutions. A tube containing purified sodium or potassium was placed in *D*, which was then sealed off, and the system was evacuated through the B14 joint, *J*, and well flamed to remove traces of adsorbed moisture on the walls. When gently heated, the metal ran through the constrictions c_1 and c_2 and solidified in *B*; a thin film of the metal was then distilled on to the walls of *A* and the constriction c_3 sealed off. The diamine was condensed into *A*, *via J*, and the apparatus was sealed off at constriction c_4, leaving the metal and amine in an all-glass, highly evacuated system containing no taps or joints liable to introduce impurities. The amine was allowed to warm to room temperature in contact with the metal, and the resulting solution was freed from excess of metal by filtration through the sinter *S* into *E*; the filtration was assisted by gently warming tube *A* (with the hand), thus slightly increasing the vapour pressure of the amine in this section.

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[17] Smith and Symons, *J. Chem. Phys.*, 1956, **25**, 1074.
[18] Dostrovsky and Llewellyn, *J. Soc. Chem. Ind.*, 1949, **68**, 208.
[19] Hohlstein and Wannagat, *Z. anorg. Chem.*, 1956, **284**, 191.

Since lithium could not be melted through glass constrictions, a small portion of the metal was cut from the centre of a larger piece under light petroleum and while still wet with solvent was inserted into tube *A* against a counter-current of nitrogen; for this preparation, tube *D* and constrictions c_1, c_2, and c_3 were omitted from the apparatus. After evacuation, the solution was made up as before.

FIG. 1. *Apparatus for preparation of metal–diamine solutions.*

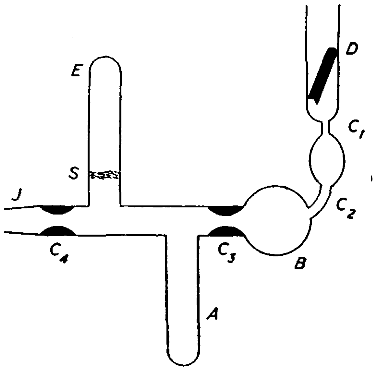


FIG. 2. *Apparatus for preparation of metal–diamine solutions for spectral studies.*

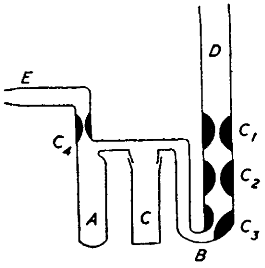
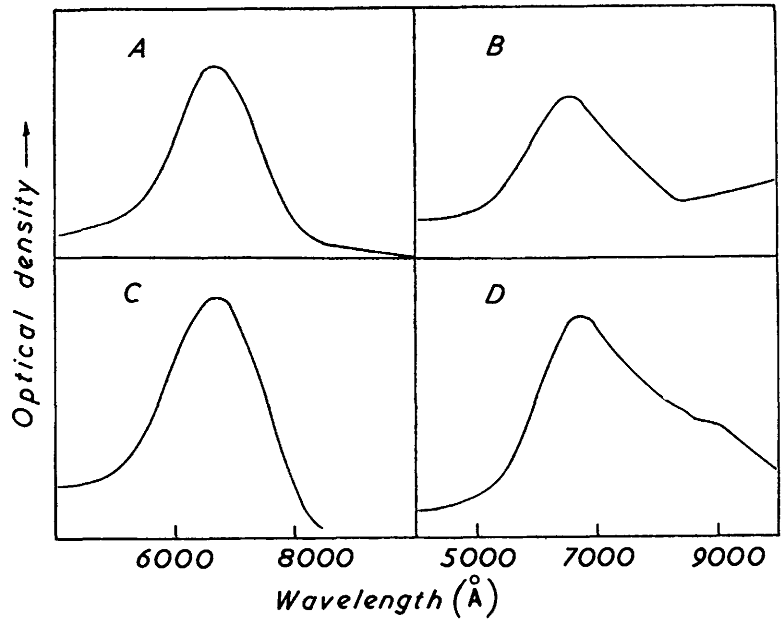


FIG. 3. *Absorption spectra.*



A, Sodium and, *B*, potassium in ethylenediamine.
C, Sodium and, *D*, potassium in propylenediamine.

Sodium, potassium, and lithium gave blue solutions in both diamines. Several independent studies for each metal–amine combination showed that in both solvents sodium and potassium formed very much more stable solutions than did lithium. Thus sodium and potassium solutions generally decomposed over a period of 6—12 hr. while the lithium solutions were stable for only 15—30 min. The rapid decomposition of the lithium solutions can probably be attributed in part to impurities in the metal.

Effect of Metals on the Stability of the Solutions.—In the hope that conductivity measurements could be made over a range of concentration, the effect of possible electrode metals on the stability of the solutions was investigated. A small strip of electrode metal was sealed into a side arm on tube *E*, and after evacuation and flaming of the apparatus the blue solutions were prepared as before and tipped on to the metal strip. With molybdenum, tungsten, and platinum the colour decayed within a minute or two; in view of this, conductivity studies were not attempted.

It seems that these transition metals catalyse the decomposition of the metal–amine solutions because of their ability to accept electrons.

Strength of the Metal–Amine Solutions.—Precise measurement of the concentration of the metal in the solutions is difficult, since some decomposition to amide appears to be inevitable, and any determination of the metal concentration will give only the sum of the metal in solution and that present as amide. Any metal determination thus represents the maximum upper limit. The total concentration of sodium in a freshly prepared saturated solution in ethylenediamine was estimated on a calibrated flame-photometer, and found to be 0·02 g.-atom/per l.

A rough estimate of the concentration of metal in other solutions was then made by a comparison of the relative intensity of colour. On this basis, lithium is by far the most soluble of the alkali metals in either solvent; sodium and potassium in ethylenediamine and potassium in propylenediamine have similar solubilities, but sodium is only sparingly soluble in propylenediamine.

Absorption Spectra of Solutions of the Alkali Metals in Ethylenediamine and Propylenediamine.—Absorption spectra (3700—10,000 Å) were measured with a Unicam S.P. 600 spectrophotometer, the solutions being contained in fused silica cells (1 cm., equipped with standard C10 ground joints) which could be evacuated without distortion or breakage. Measurements below 3700 or above 10,000 Å were not reliable because of the strong absorption of the amine solvents. Unfortunately, cells thinner than 1 cm. could not be used, since they could not be evacuated and sealed.

The metal solutions were made in the apparatus shown in Fig. 2. The whole apparatus (except the cell *C*) was cleaned with hydrogen fluoride cleaning mixture [20] and dried for 12 hr. at 120°. The cell was cleaned with warm "Teepol," washed with pure acetone, and dried with warm air. The cell *C* was attached to the remainder of the apparatus with a trace of "Silicone" grease, and a tube of purified metal was placed in tube *D* which was then sealed. The whole apparatus was evacuated through joint *E*, and gently flamed (except cell *C*). After the apparatus had been pumped out for several hours, the metal was melted through constrictions c_1, c_2, and c_3 until a small globule appeared in *B*; the apparatus was then sealed at c_3. Sufficient solvent to fill cell *C* was then condensed in *A*, and the apparatus sealed at c_4; solvent was then carefully tipped into *C*, and its absorption compared with a "blank" cell containing boiled-out distilled water. A small portion of the solvent was tipped on to the globule of alkali metal in *B*, and the blue solution formed was carefully tipped back again into *C*. Gentle shaking gave a uniform dilute solution, whose absorption was again compared with the "blank" cell. The whole system, *A*, *B*, and *C* was designed to fit into a standard Unicam cell holder. All measurements were made at room temperature. The results for sodium and potassium in ethylenediamine and propylenediamine, shown graphically in Fig. 3, were obtained by subtracting the solvent absorption from that of the solution. Optical densities rather than extinction coefficients are recorded because of the difficulty of precisely estimating the concentration.

Paramagnetic Resonance Measurements on the Metal–Diamine Solutions.—The metal–diamine solutions were made in the usual manner, and tipped into a thin-walled Pyrex tube (3 mm.) so attached to the preparative apparatus that it could be placed directly into an H_{012} 3 cm. wavelength rectangular resonant cavity for paramagnetic-resonance measurements. The results

TABLE 2. *Paramagnetic-resonance absorption in metal–amine solutions at room temperature (metal concentration about* 2×10^{-3}M).

Metal	Amine	Magnitude of absorption	Metal	Amine	Magnitude of absorption
Na ...	$(\cdot CH_2 \cdot NH_2)_2$	Nil	Li	$MeNH_2$	Strong
K	,,	Very weak	K	,,	Weak
Na ...	$NH_2 \cdot CHMe \cdot CH_2NH_2$	Nil			
K	,,	Nil			

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[20] Crawley, *Chem. and Ind.*, **1953**, 1205.

obtained are summarised in Table 2. Concentrations were varied between 10^{-2} and 10^{-4}M, as judged from the intensity of the colour, and any absorption was found to increase with concentration. Experiments with lithium in methylamine showed that absorption was readily detected even in 10^{-4}M-solutions.

Irradiation Experiments.—Rapid cooling of a fairly deep blue solution of sodium in propylenediamine gave a clear, uncracked glass, the blue colour being undiminished in intensity. When this glass, immersed in liquid oxygen contained in an unsilvered Dewar flask was irradiated with light from a tungsten-filament lamp, the colour was slowly bleached, until, after about 4 hours' irradiation, only a faint blue colour remained. The original, deeper blue colour reappeared immediately when the glass softened. Repetition gave similar results, showing that no overall decomposition was occurring.

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