

of which only four are observed at X band for copper butyrate, *viz.*

$$H_{x2}^2 = (g_e/g_x)^2(H_0 + D' - E')(H_0 - 2E') \quad (2)$$

$$H_{y2}^2 = (g_e/g_y)^2(H_0 + D' + E')(H_0 + 2E') \quad (3)$$

$$H_{z1}^2 = (g_e/g_z)^2[(H_0 - D')^2 - E'^2] \quad (4)$$

$$H_{z2}^2 = (g_e/g_z)^2[(H_0 + D')^2 - E'^2] \quad (5a)$$

where $H_0 = h\omega_0/g_e\beta$, $D' = D/g_e\beta$, $E' = E/g_e\beta$, and $g_e = 2.0023$. Since $(H_0 + D')^2 \gg E'^2$, eq 5a can be replaced by (5b) to good accuracy. Combining eq 4 and 5a, we obtain

$$H_{z2} \simeq (g_e/g_z)(H_0 + D') \quad (5b)$$

after rearrangement

$$D' = (g_z/g_e)^2(H_{z2}^2 - H_{z1}^2)/4H_0 \quad (6)$$

By setting $g_x = g_y = g_{\perp}$, we now have four unknowns (D' , E' , g_z , g_{\perp}) and four resonance fields (H_{x2} , H_{y2} , H_{z1} , H_{z2}). The parameters were determined by an iterative procedure beginning with eq 5b and 6 (yielding D' and g_z), then using eq 4 (yielding an initial E'), and finally using eq 2 and 3 (yielding final E' and g_{\perp}). The final parameters checked with eq 2-5a well within the stated errors.¹¹

We obtain reliable parameters, particularly D and g_z , by this procedure. The fractional error in E is given by $|\delta E/E| \simeq (H_{x2}^2 + H_{y2}^2)(g_x - g_y)/2(H_{y2}^2 - H_{x2}^2) = 5.6(g_x - g_y)$. Of all the alkanates the acetate has the largest known rhombic component in g_{\perp} ($g_z - g_y = 0.040$).¹⁴ The axial symmetry approximation in g perhaps introduces 20-30% error in E while the error introduced in g_{\perp} [$= (g_x + g_y)/2$] is small, ± 0.002 .

We now examine the zero-field splitting parameter D in some detail. The magnetic dipole interaction D_{dd} and the pseudo dipolar term D_{pseudo} both contribute to the experimental D value, $|D_{exptl}| \simeq |D_{dd} + D_{pseudo}|$. For several vanadyl and copper dimers the magnetic dipole interaction dominates^{8,9} ($D_{exptl} \simeq D_{dd}$) whereas the opposite is true for the copper chloride-pyridine N -oxides¹⁵ ($D_{exptl} \simeq D_{pseudo}$); the copper alkanates are intermediate.

At the short Cu-Cu distance (2.64 Å) of copper acetate,¹⁶ a reasonable calculation of D_{dd} must take some account of the spin-density distributions on each half of the dimer. Using a covalent model which places 5% of the spin density on each of the four in-plane oxygen atoms and the remaining spin at four points representing the copper $d_{x^2-y^2}$ orbital (see ref 9 for a similar calculation), we estimate $D_{dd} \simeq -0.12 \text{ cm}^{-1}$ for the alkanates. This value is considerably smaller than the previous estimate of -0.20 cm^{-1} based on a simple two-center calculation.^{9,17}

The pseudo dipolar term is given approximately by the relationship²

$$D_{pseudo} \simeq -J'[(g_z - 2.002)^2/4 - (g_{\perp} - 2.002)^2]/8$$

where J' is an "average" exchange interaction, unknown in magnitude and sign, of excited electronic states. For copper butyrate we estimate D_{pseudo} to be

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+0.45 or -0.21 cm^{-1} depending on the relative sign of D_{exptl} and D_{dd} ($D_{pseudo} \simeq 0.12 \pm 0.33 \text{ cm}^{-1}$). The corresponding approximate J' values are -140 cm^{-1} (antiferromagnetic) or $+65 \text{ cm}^{-1}$ (ferromagnetic) compared to the antiferromagnetic exchange interaction, $J = -339 \text{ cm}^{-1}$, of the ground state.¹² Reduction in magnitude of excited-state exchange interactions relative to the ground-state value has also been noted for the copper chloride-pyridine N -oxide complexes.¹⁵

Literature D_{exptl} values for the acetate,¹⁴ propionate,⁷ butyrate,¹⁰ benzoate,⁶ monochloroacetate-2.5-water,¹⁸ and monochloroacetate monohydrate¹⁰ all fall in the narrow range 0.327 - 0.350 cm^{-1} (except for the cyanoacetate⁵ with $D_{exptl} = 0.39 \pm 0.01 \text{ cm}^{-1}$). Within experimental error, assuming a common J' value (-140 cm^{-1}) and $D_{dd} = -0.12 \text{ cm}^{-1}$, variations in g of the respective compounds can readily account for the differences in D_{exptl} . g_z values range from 2.34 to 2.40, and g_{\perp} values, from 2.06 to 2.08. Note that variations in g should have a more pronounced effect on D_{pseudo} than on D_{dd} .

Differences in the rhombic component of the crystalline field are evidenced by variations in E from $<0.001 \text{ cm}^{-1}$ for the propionate⁷ to $0.0147 \pm 0.0003 \text{ cm}^{-1}$ for the benzoate.⁶ The acetate¹⁴ and butyrate are intermediate with $E = 0.007 \pm 0.003$ and $0.011 \pm 0.003 \text{ cm}^{-1}$, respectively. Several other carboxylates have been studied by Lewis, *et al.*¹⁹

Acknowledgment.—The author wishes to thank Professor Melvin W. Hanna for the use of his laboratory and magnetic resonance facilities and Professor R. Linn Belford for helpful discussions.

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The Kinetics of Interaction of Nickel(II) and Cobalt(II) with Bis(2-pyridylmethyl)amine

BY COLIN D. HUBBARD

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The general features of the mechanism of formation of complexes of transition metal ions in aqueous medium have been thoroughly discussed.¹⁻⁴ More recently, determinations have been made of some of the more subtle effects in the formation process arising from variations in the ligand which replaces the coordinated water of the metal ion. Chelate ring size is important if coordinated water is sufficiently labile;^{5,6} substitution

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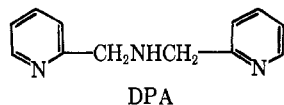
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(6) A. Kowalak, K. Kustin, R. F. Pasternack, and S. Petrucci, *ibid.*, **89**, 3126 (1967).

in coordinated ligands affects the replacement of Ni(II)-bound water in a manner which may be correlated by a Hammett linear free energy equation;⁷ and the rate of replacement of coordinated water from nickel-polyamine complexes increases as the number of coordinated nitrogens in the complex is increased.⁸

Investigations of the effect of charge on a ligand upon its reactivity have yielded the anticipated general result that anionic ligands react more rapidly and cationic ligands react more slowly than those that are uncharged.^{2,9}

Bis(2-pyridylmethyl)amine or di(2-picoly)amine (in the neutral form abbreviated as DPA) possesses appropriate properties for a study of the effect of protonation of ligand upon the reaction rate of metal complex formation. This ligand exists as a mixture of neutral



and monoprotonated forms in the neutral pH region¹⁰ and reacts to form two identical chelate rings.

Experimental Section

Materials.—Bis(2-pyridylmethyl)amine was prepared as a trihydrochloride according to a literature method.¹¹ *Anal.* Calcd for C₁₂H₁₃N₃·3HCl: C, 46.70; H, 5.23; N, 13.61. Found: C, 46.78; H, 5.30; N, 13.66. Other materials used were reagent grade commercial products.

Spectra and Kinetics Experiments.—Spectra were recorded with a Cary 14 spectrophotometer. These showed that the kinetics of complex formation could most suitably be monitored at 290 and 282 nm for the Ni(II) and Co(II) systems, respectively. At these wavelengths the complex absorbs significantly more than the ligand species. Formation of complexes was followed at 25° in a Durrum-Gibson stopped-flow spectrophotometer which has a Kel-F flow path. Reactions were run under pseudo-first-order conditions using a large excess of metal ion which ensures that only the 1:1 complex is formed. Both metal ion and ligand solutions were buffered to the desired pH with 0.01 M cacodylate buffer and the ionic strength was made up to 0.1 by use of sodium chloride. The signal amplitudes of first-order oscillogram traces were processed by a computer program¹² which yields the specific rate constant corresponding to each trace. Dividing the first-order rate constant by the total metal ion concentration yields k_t , the second-order complex formation rate constant. Reported values of k_t are an average of at least four individual determinations.

Results and Discussion

Potentiometric titration experiments have yielded the proton dissociation constants and several transition metal chelate formation constants of DPA.¹⁰ A pK of 7.30 characterizes the acceptance of a proton by the aliphatic moiety nitrogen, while the pyridine nitrogen atom protonations are associated with pK values of 2.60 and 1.12. The kinetics measurements have been conducted from pH 5.3 to 6.8, a range in which the proportion of the monoprotonated form (DPAH⁺) of the total ligand varies from about 99 to about 76% and in which the metal ions can be considered to be present as the hexaquo species.¹³ At pH 5.3 the proportion of diprotonated ligand is less than 0.2%

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and therefore in the pH range employed the assumption has been made that the ligand is present as either DPAH⁺ or DPA.

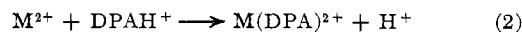
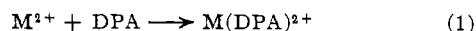
Table I is a summary of observed rate constants for

TABLE I
FORMATION OF Ni(II) AND Co(II) COMPLEXES
OF BIS(2-PYRIDYLMETHYL)AMINE AT 25°, I = 0.1

pH	[M ²⁺], mM	[DPA], mM	10 ⁻² k _t , M ⁻¹ sec ⁻¹
Nickel			
6.71	2.5	0.05	13.8
6.61	2.5	0.05	13.2
6.35	2.5	0.05	9.10
6.17	2.5	0.05	7.95
5.87	2.5	0.10	4.96
5.82	2.5	0.05	5.15
5.50	2.5	0.10	4.44
5.36	2.5	0.05	3.17
Cobalt			
6.70	1.25	0.05	542
6.61	1.25	0.05	438
6.36	1.25	0.05	301
6.16	2.5	0.05	246
5.81	2.5	0.05	100
5.37	1.25	0.05	54.9

metal complex formation as a function of pH.

The reactions and equilibrium involved in the pH range of measurement can be written as



where M is nickel or cobalt. From (3)

$$K_a = [H^+][DPA]/[DPAH^+] \quad (4)$$

That the proton is liberated in reaction 2 is indicated by the observation of a decrease in pH upon mixing metal ion and ligand in unbuffered solution. It is assumed that the proton liberation is very rapid compared with the measurements made.

The rate of production of metal complex M(DPA)²⁺ may be written

$$d[M(DPA)^{2+}]/dt = k_1[M^{2+}][DPA] + k_2[M^{2+}][DPAH^+] \quad (5)$$

k_1 and k_2 are the rate constants which characterize the reactions in (1) and (2). These can be separately determined graphically by use of the equation obtained by rewriting eq 5 as

$$d[M(DPA)^{2+}]/dt = k_1[M^{2+}][DPA] + k_2[M^{2+}][DPAH^+] \quad (6)$$

and by substituting (4) into (5) and (6)

$$k_1(1 + K_a/[H^+]) = k_2 + k_1K_a/[H^+] \quad (7)$$

A plot of the left-hand side of (7) vs. $K_a/[H^+]$ is shown in Figure 1 for the formation of complexes of Ni(II) (Figure 1a) and Co(II) (Figure 1b). The value of K_a employed in applying eq 7 is 5.0×10^{-8} and was obtained from measurements upon solutions of the same ionic strength, 0.1, and temperature, 25°, as used in this study. In each case the concentration of H⁺ was directly obtained from the measured pH of the mixed solution. The intercepts, which are k_2 values, and the slopes of the lines were determined by a least-squares analysis. Values obtained at 25° are $k_2 = 3.4 \times 10^2$ and $k_1 = 5.8 \times 10^8 M^{-1} sec^{-1}$ for the Ni(II)

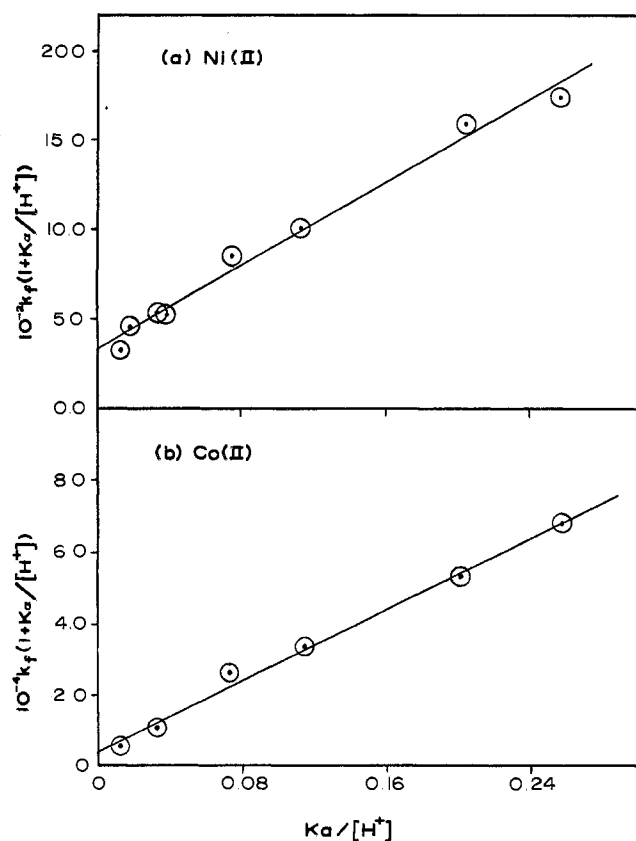
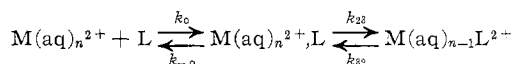


Figure 1.—Plot of $k_f(1 + K_o/[H^+])$ vs. $K_a/[H^+]$ at 25° and $I = 0.1$: (a) formation of $Ni(DPA)^{2+}$ and (b) formation of $Co(DPA)^{2+}$.

system and 4.8×10^3 and $2.5 \times 10^5 M^{-1} \text{sec}^{-1}$ for the same parameters in the $Co(II)$ system.

From the data and Figure 1, it may be concluded that both neutral and monoprotonated bis(2-pyridylmethyl)amine react with the metal ions to form complexes.

The general mechanism¹⁻⁴ for transition metal complex formation, shown here for a unidentate ligand L



is a scheme of two steps, the first of which is a diffusion-controlled association of reactants into an "outer-sphere" complex, and then the latter can lose a coordinated water molecule in a rate-determining step (k_{23}) with resulting penetration of the ligand into the inner sphere. It has been shown that $k_f = K_o k_{23}$ where $K_o = k_o/k_{-o}$. Additional steps for ligands of higher dentate number can be added to the mechanism, but in most cases within certain limits, the second-order rate constant is given by the same product. Results obtained above will be discussed within the framework of this mechanism.

Nickel.—The k_1 value for $Ni(II)$ is larger than that obtained for the somewhat similar $Ni(\text{terpy})^{2+}$ system ($k = 1.4 \times 10^3 M^{-1} \text{sec}^{-1}$)¹⁴ (terpy is the terdentate ligand, 2,2',2''-terpyridine). Differences in k_f can sometimes be interpreted as being a consequence of variations in the value of K_o , although in this case it is not easy to see why terpyridine is less strongly attracted to the aquometal ion by a factor of about 4.

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Since only estimates can be made of some of the parameters involved in the calculation of K_o ,^{9,15} it is not practicable to attempt to compute the association constants in order to determine whether a difference of this order is manifest in this parameter. The rate constants characteristic of formation of certain nickel-polyamine complexes are higher than would be predicted from the general mechanism and higher than the value of k_f for the nickel-monoammine complex.¹⁶ These results and subsequently some others^{17,18} were explained by the internal conjugate base (ICB) mechanism. The relevant protonation constant for DPA¹⁰ (and also for terpy¹⁴) is smaller than the lower bound value which seems to be necessary for operation of the ICB mechanism¹⁶ and therefore it seems unlikely that the high value of k_1 obtained can be explained by this mechanism.¹⁹

Protonation of DPA has the effect of slowing down nickel complex formation by a factor of about 20 which is considerably less than that observed for the protonated and neutral forms of, for example, 2-aminomethylpyridine and aliphatic amino carboxylates in which cases the neutral species reactivity is greater by about 10^3 or more.²⁰ For the latter type an explanation based upon low reactivity of zwitterion forms has been suggested. Ligands such as ethylenediamine (en) and 2,2'-bipyridine, when protonated, react slightly less than 100 times as rapidly as their uncharged forms do with Ni^{2+} .²⁰ It was suggested that the amino-nickel bond first formed in the production of $Ni(\text{en})^{2+}$ is not particularly susceptible to dissociation; consequently, ring closure with proton elimination is facile. This argument would suggest that in the $DPAH^+$ system, the first nickel to pyridine N bond is relatively stable so that the subsequent ring closures and proton elimination can occur rapidly.

Cobalt.—DPA reacts with Co^{2+} about 10 times more rapidly than does terpy, although the value of k_1 , $2.5 \times 10^5 M^{-1} \text{sec}^{-1}$, is not exceptionally high; cf. 1,10-phenanthroline.²¹ It may be concluded, at least in comparison with terpy, that the cause of the apparent enhancement in K_o is more pronounced in the cobalt than in the nickel system. The relative reaction rate of the aquocobalt ion with DPA and with $DPAH^+$ is about 50, some 2.5 times the corresponding quantity for the nickel system. The difference in the $k_1:k_2$ ratio between the two metals can be attributed to either a variation in the metal-ligand or metal-protonated ligand interaction in the outer sphere or possibly to the protonated form of the ligand exerting influence upon the water expulsion rate in a different manner between the two aquo ions. In the latter situation, the presence of the charged form in the outer sphere may have a small retarding effect upon the rate of the first water molecule release, *i.e.*, upon k_{23} , which is greater in the

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(19) The ICB mechanism is also probably not significantly involved in the reaction of Co^{2+} with DPA. However, in this case the monohydroxycobalt(II) ion is slightly less basic than the corresponding nickel ion,¹⁸ and therefore conditions which appear to favor this mechanism begin to approach being realized.

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more labile cobalt system. Unfortunately, the kinetic behavior differences reported, although outside of experimental error, are quite small and therefore the reactivity variations are difficult to interpret quantitatively.

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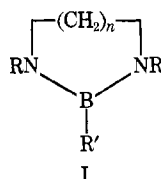
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Boron-Nitrogen Compounds. XXXVII.^{1a} Synthesis and Characterization of 2-Hydrido-1,3,2-diazaboracycloalkanes

BY EUGENE F. ROTHGERY,^{1b} PAUL J. BUSSE,
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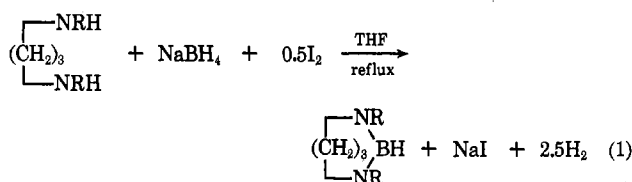
Although 1,3,2-diazaboracycloalkanes, I, have been known for some time, most of these heterocycles which have been prepared have been the *B*-alkyl and -aryl derivatives.² A few *B*-chloro compounds have also



been synthesized,^{3,4} and recently the remaining *B*-halo derivatives have been described.⁵ However, only one of the parent compounds with $R' = H$ has been reported.⁶ This latter compound was obtained from a transamination reaction of bis(dimethylamino)borane, $HB[N(CH_3)_2]_2$, with 1,3-diaminopropane. Some similar *B*-hydrido heterocycles have been prepared from the interaction of aromatic diamine monohydrochlorides with sodium tetrahydroborate,⁷ but this method failed to give the desired products when aliphatic diamines were treated with $NaBH_4$.

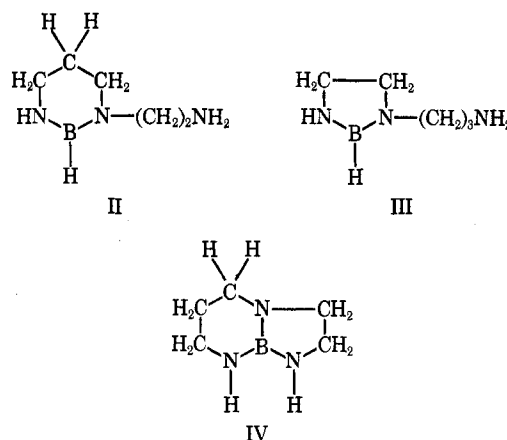
The present work reports on the synthesis of several 2-hydrido-1,3,2-diazaboracyclohexanes by the method illustrated in eq 1 which represents an extension of the procedure of Nainan and Ryschkewitsch⁸ for the preparation of borane adducts.

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- (7) J. Goubeau and H. Schneider, *Justus Liebigs Ann. Chem.*, **675**, 1 (1964).
- (8) K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Chem.*, **8**, 2671 (1969).



In an alternate procedure trimethylamine-borane was utilized as source of the borane and was found to serve equally well as sodium tetrahydroborate in the synthesis of 2-hydrido-1,3,2-diazaboracycloalkanes. This latter method yields trimethylamine as a by-product and thus facilitates the purification of the desired heterocycles.

Furthermore, *N*-(ω -aminoethyl)-1,3-diaminopropane, $H_2N(CH_2)_2NH(CH_2)_3NH_2$, was treated with sodium tetrahydroborate. Previously,⁹ this same amine had been treated with tris(dimethylamino)borane to yield 1,7,9,8-triazaborahydrindane, IV. In the present work it was possible to isolate a monocyclic intermediate. Two structures, II and III, can be suggested for the intermediate product. However, spectroscopic data clearly substantiate structure II. On heating II to 160° hydrogen is split off and IV is obtained in virtually quantitative yield.



Experimental Section

All diamines used in the present work were obtained from the Ames Laboratories, Milford, Conn.; they were dried over potassium hydroxide and were vacuum distilled before use. Elemental analyses were furnished by the Schwarzkopf Micro-analytical Laboratory, Woodside, N. Y. Infrared spectra of the materials were recorded on the neat liquids and/or vapor phases on a Perkin-Elmer Model 621 spectrophotometer. Raman spectra of the neat liquids were obtained with a Jarrell-Ash Raman spectrometer equipped with a He-Ne laser as exciting device through the courtesy of Dr. E. B. Bradley, Department of Electrical Engineering, University of Kentucky. Nuclear magnetic resonance spectra were recorded with a Varian HA60-IL and/or Model T-60 spectrometer; mass spectra were provided by the University of Kentucky Mass Spectroscopy Center and were obtained with a Hitachi Perkin-Elmer double-focusing spectrometer, Model RMU-6E.

All experiments were performed under rigorous exclusion of moisture in a prepurified nitrogen atmosphere. The cited yields represent only one or two experiments in most cases and no attempt has been made to improve the yields. Analytical data and physical constants of the products are summarized in Table I.

1,3-Dimethyl-2-hydridodiazaboracyclohexane (Typical Experiment).—*N,N'*-Dimethyl-1,3-diaminopropane (10.2 g, 0.10 mol) and sodium borohydride (4.2 g, 0.11 mol) were mixed with 75 ml of dry tetrahydrofuran in a dry, nitrogen-filled flask with a magnetic stirring bar. A solution of iodine (12.7 g, 0.10

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