has been interpreted as being due to the relatively low-lying π^* ligand orbitals in bipyridyl which allow for considerable back-donation from the copper ion, the net effect of which is the lowering of the electron density on the copper ion. This delocalization of electron density should manifest itself kinetically but in a manner determined by the mechanism of the reaction. More specifically, lowering of electron density on the copper ion should serve to slow down an S_N1 process but enhance an S_N2(lim) process.[21] However, we find a value for k_{12} for reaction 16 which is identical with the value of k_2 determined by Kustin and Kirschenbaum for reaction 15. This implies that the rate-determining step involves both bond making and bond breaking and therefore falls into the S_N2 category. Kustin and Kirschenbaum[13] considered the internal conjugate base (ICB) mechanism suggested by Rorabacher[22] for nickel(II) complexation but, to be applicable, this variation of the S_N1 mechanism would necessitate a rate-determining step in which the rate constant is significantly larger than 10^9 sec^{-1}. These authors called attention to the fact that their results are explained at least as well by an S_N2 process. The similarities in k_{12} for ethylenediamine, α-alanine, and glycine can be interpreted as reflecting the similar nucleophilicities of these ligands. The reverse rate constants in turn reflect the relative difficulty in breaking bonds between the metal center and the leaving ligand.

We have extended our studies to the investigation of a ternary complex of cobalt(II) where less ambiguity exists concerning the mechanistic details for ligand substitution.[23]

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[21] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967.

[22] D. B. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966).

[23] Note Added in Proof.—Other evidence for an S_N2 mechanism for copper complexation reactions has been offered by Sharma and Leussing (D. Leussing, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, and private correspondence). In their study of $Cu(en)^{2+} + ser^- \rightleftarrows Cu(en)(ser)^+$, these workers obtain a forward rate constant of 6×10^8 M^{-1} sec^{-1}. The analogous reactions described here of $Cu(bipy)^{2+}$ with amino acid anions, studied at a temperature 12° below that of the Sharma and Leussing study, yield rate constants two to three times larger. Since, as has been shown, the presence of ethylenediamine in the inner coordination sphere of nickel(II) has a more pronounced labilizing effect on remaining water molecules than does bipyridyl,[24,25] these kinetic results suggest an associative rather than a dissociative mechanism for copper(II).

[24] A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **91**, 5001 (1969).

[25] M. Grant, H. W. Dodgen, and J. P. Hunt, *ibid.*, **92**, 2321 (1970).

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Elimination of Solvation Contributions to the Enthalpies of Adduct Formation in Weakly Polar Solvents. II. Adducts of Bis(hexafluoroacetylacetonato)copper(II)

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An earlier preliminary report on a procedure for eliminating solvent contributions to enthalpies measured in polar solvents has been extended to include the Lewis acid bis(hexafluoroacetylacetonato)copper(II), $Cu(hfac)_2$. In slightly polar, weakly basic solvents, solvation effects have been shown to cancel (within error limits) for the displacement reaction represented by the equation $AB + B' \rightarrow AB' + B$, where A is $Cu(hfac)_2$ and B and B′ are Lewis bases. This procedure can be applied to calculate the enthalpy of adduct formation between a Lewis base and $Cu(hfac)_2$ in the nonpolar solvent for a base which is insoluble in nonpolar solvents.

Introduction

Previous reports from our laboratory[1] have demonstrated that the enthalpies of the interaction of donor–acceptor systems in nonpolar solvents can be accurately estimated (to ±0.2 kcal mol^{-1}) with the double-scale equation[2]

$$-\Delta H = E_A E_B + C_A C_B \qquad (1)$$

where E and C are empirically determined parameters and the subscripts A and B refer to an acid and a base, respectively. The predictive and correlative power of this formula have been successfully tested in a variety of systems.[1-7] However, the range of systems which can be investigated is limited by the insolubility of donors, acceptors, or adducts in nonpolar systems. For example, the only transition metal compound which has been incorporated into the E and C scheme is a copper(II)–β-diketone chelate.[8] It is desirable to examine further the generality of eq 1 and enhance our knowledge of intermolecular interactions. It would be particularly interesting to extend our measurements to other transition metal compounds where π back-bond-

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[1] See G. C. Vogel, R. S. Drago, and T. Needham, *J. Amer. Chem. Soc.*, **93**, 6014 (1971), and references therein.

[2] R. S. Drago and B. B. Wayland, *ibid.*, **87**, 3571 (1965).

[3] R. S. Drago, *Chem. Brit.*, **3**, 516 (1967).

[4] R. S. Drago and T. D. Epley, *J. Amer. Chem. Soc.*, **91**, 2883 (1969).

[5] R. S. Drago, N. O'Bryan, and G. C. Vogel, *ibid.*, **92**, 3924 (1970).

[6] M. S. Nozari and R. S. Drago, *ibid.*, **92**, 7086 (1970).

[7] G. C. Vogel and R. S. Drago, *ibid.*, **92**, 5347 (1970).

[8] W. Partenheimer and R. S. Drago, *Inorg. Chem.*, **9**, 47 (1970).

ing is felt to be important. In these systems, eq 1 may break down since the parameters are determined for systems which mainly σ bond.

Unfortunately, the number of strong Lewis-acid, nonionic, coordination compounds which are *believed* to undergo π back-bonding and which are soluble in nonpolar solvents is limited. Thus, it was highly desirable to develop a method which would enable one to measure the enthalpies of adduct formation of Lewis bases with these compounds in weakly polar solvents and attempt to convert these results to enthalpies expected in poorly solvating media. A method for carrying out this objective has been described for adducts of phenols.[9] In this procedure, the displacement reaction

$$AB + B' \longrightarrow AB' + B \qquad (2)$$

where A is the Lewis acid *m*-fluorophenol and B and B' the Lewis bases—the latter insoluble in nonpolar solvents, was investigated in weakly basic, polar solvents. Since in this reaction (eq 2), the acid remains fully complexed, it does not undergo specific interactions with the basic solvent. It was further demonstrated in the systems studied that nonspecific solvation of products and reactants canceled. Consequently, if the gas-phase enthalpy for the reaction

$$A(g) + B(g) \longrightarrow AB(g) \qquad (3)$$

is known, this can be algebraically added to eq 2, producing the gas-phase enthalpy for the reaction

$$B'(g) + A(g) \longrightarrow AB'(g) \qquad (4)$$

In practice, enthalpies measured in carbon tetrachloride or cyclohexane have been substituted for eq 3, producing the equivalent for B'. If B' was insoluble in CCl_4, the appropriate enthalpy could be obtained by measuring the displacement reaction (eq 2) in a weakly basic polar solvent with a base that is soluble in CCl_4. If the acid is held constant in a given polar solvent and a series of bases studied, the assumption that solvation contributions to the general eq 2 cancel is identical with the expectation that the enthalpies measured in the polar solvent will differ by a constant amount from those measured in an inert medium.[9]

The success of this approach on the phenol systems is encouraging, but could be fortuitous and limited to this type of acid and adduct. This prompted us to extend the range of acids investigated. Since we are particularly interested in investigating systems containing transition metal ions and since the data we previously reported are available to check our approach, the acid bis(hexafluoroacetylacetonato)copper(II) was selected for this study.

Experimental Section

Materials.—Eastman *o*-dichlorobenzene was dried over Linde 4A Molecular Sieves for at least 24 hr prior to use. Mallinckrodt reagent ethyl acetate (EtOAc), Aldrich triethylamine (Et_3N), and Baker Analyzed dimethyl sulfoxide (DMSO) were purified as previously described.[6,9] In all cases, the purity was checked by glpc analysis. Peninsular Chemresearch bis(hexafluoroacetylacetonato)copper(II) was sublimed twice at 90° (1 mm) and kept over fresh P_2O_5 in a desiccator overnight under vacuum.

All solutions were prepared under a dry, ultrapure nitrogen atmosphere. The glassware was kept in a desiccator and was flushed with nitrogen prior to use. In all runs, the acid was dissolved in the solvent by gently heating the volumetric flasks for an appropriate length of time. The solutions then were cooled down to room temperature by placing the containers in a desiccator for at least 3 hr. Due to the extreme hygroscopic nature of the acid, the solutions had to be transferred into the calorimeter cells inside a drybag. The calorimetric runs were also carried under a dry nitrogen atmosphere.

Apparatus and Calculations.—The description of our calorimeter and the procedure has been previously reported.[6] The computer program for simultaneous determination of enthalpies and equilibrium constants has also been described.[4] In all instances, the reliability of the calculated quantities was checked by graphing K^{-1} *vs.* ΔH to demonstrate that the data points gave rise to lines with appreciably different slopes.

Results

The concentrations, volumes, and measured enthalpies are reported in Table I for various donors with $Cu(hfac)_2$. The experimental enthalpy H' is the total heat evolved, corrected for the heat of solution of the given donor at the corresponding donor concentration. The experimental values for the heats of solution of EtOAc and DMSO in *o*-dichlorobenzene have been previously reported.[9] The values for the heat of solution of triethylamine in *o*-dichlorobenzene and cyclohexane are equal to -0.19 and 0.26 kcal mol^{-1}. These values are constant over the entire donor concentration range employed within the experimental error.

TABLE I
CALORIMETRIC DATA FOR $Cu(hfac)_2$–BASE SYSTEMS IN *o*-DICHLOROBENZENE AT 25°

[Acid], *M*	[Base], *M*	Total soln volume, ml	Measd heat, cal
		o-Dichlorobenzene	
$Cu(hfac)_2$	EtOAc	solvent	H'
0.01922	0.00781	110.1	1.489
0.00933	0.02410	110.3	1.991
0.00956	0.14650	111.6	4.152
0.01874	0.25030	112.8	9.054
0.01877	0.01186	110.1	2.158
		o-Dichlorobenzene	
$Cu(hfac)_2$	DMSO	solvent	H'
0.009664	0.003153	110.1	2.380
0.009994	0.004200	110.1	3.186
0.009811	0.005823	110.1	4.372
0.009986	0.008381	110.1	5.936
		o-Dichlorobenzene	
$Cu(hfac)_2$	Et_3N	solvent	H'
0.01987	0.00067	110.0	0.957
0.01923	0.00254	110.0	3.599
0.01030	0.00682	110.1	8.920
0.01027	0.00678	110.1	8.656
0.00968	0.00758	110.1	9.476
0.00962	0.00415	110.1	5.368
		Cyclohexane	
$Cu(hfac)_2$	Et_3N	solvent	H'
0.01028	0.01001	110.2	15.897
0.00899	0.00842	110.1	13.463
0.00994	0.00586	110.1	9.644
0.00904	0.00797	110.1	12.598
0.00951	0.00713	110.1	11.685

In an earlier report,[8] the enthalpy of the interaction of $Cu(hfac)_2 + (C_2H_5)_3N$ in cyclohexane was reported as -16.9 ± 0.5 kcal mol^{-1}. In order to improve the accuracy, this enthalpy was remeasured and a value of -15.1 ± 0.2 kcal mol^{-1} was obtained. We attribute this large difference to the experimental difficulties associated with the accurate measurement of this enthalpy and the higher accuracy of our new modified

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[9] R. S. Drago, M. S. Nozari, and G. C. Vogel, *J. Amer. Chem. Soc.*, **94**, 90 (1972).

TABLE II

THERMODYNAMIC RESULTS FOR THE INTERACTION OF $Cu(hfac)_2$ WITH BASES IN A NONPOLAR AND A WEAKLY POLAR SOLVENT

	Nonpolar solvent[a]		*o*-Dichlorobenzene		
Donor	$-\Delta H$, kcal mol^{-1}	K, l. mol^{-1}	$-\Delta H$, kcal mol^{-1}	K, l. mol^{-1}	$\Delta(-\Delta H)$, kcal mol^{-1}
EtOAc	5.9 ± 0.3^b	195 ± 43^b	4.7 ± 0.3	35.1 ± 2	1.2
DMA	8.0 ± 0.2^b	$1,650 \pm 430^b$	6.6 ± 0.2^b	$\ldots^d$	1.4
DMSO	8.5 ± 0.3^b	$\ldots^d$	7.2 ± 0.2	3544 ± 507	1.3
Et_3N	15.1 ± 0.2	$25,113 \pm 1128$	13.4 ± 0.3	1589 ± 334	1.7
$(CH_3)_3NO$	12.8 ± 0.3^c	$\ldots^d$	11.4 ± 0.3	$\ldots^d$	

[a] EtOAc, DMA, and DMSO measured in CCl_4; $(C_2H_5)_3N$, in cyclohexane. [b] Data from ref 9. [c] Predicted using eq 6. [d] K could not be measured.

TABLE III

Solvent	AB	+	B	→	AB′	+	B	$-\Delta H$, kcal/mol
CCl_4	$Cu(hfac)_2 \cdot EtOAc$	+	DMA	→	$Cu(hfac)_2 \cdot DMA$	+	EtOAc	2.1
o-$Cl_2C_6H_4$	$Cu(hfac)_2 \cdot EtOAc$	+	DMA	→	$Cu(hfac)_2 \cdot DMA$	+	EtOAc	1.9
CCl_4	$Cu(hfac)_2 \cdot EtOAc$	+	DMSO	→	$Cu(hfac)_2 \cdot DMSO$	+	EtOAc	2.6
o-$Cl_2C_6H_4$	$Cu(hfac)_2 \cdot EtOAc$	+	DMSO	→	$Cu(hfac)_2 \cdot DMSO$	+	EtOAc	2.5
Inert[a]	$Cu(hfac)_2 \cdot EtOAc$	+	Et_3N	→	$Cu(hfac)_2 \cdot Et_3N$	+	EtOAc	9.2
o-$Cl_2C_6H_4$	$Cu(hfac)_2 \cdot EtOAc$	+	Et_3N	→	$Cu(hfac)_2 \cdot Et_3N$	+	EtOAc	8.7
CCl_4	$Cu(hfac)_2 \cdot DMA$	+	DMSO	→	$Cu(hfac)_2 \cdot DMSO$	+	DMA	0.5
o-$Cl_2C_6H_4$	$Cu(hfac)_2 \cdot DMA$	+	DMSO	→	$Cu(hfac)_2 \cdot DMSO$	+	DMA	0.6
Inert[a]	$Cu(hfac)_2 \cdot DMA$	+	Et_3N	→	$Cu(hfac)_2 \cdot Et_3N$	+	DMA	7.1
o-$Cl_2C_6H_4$	$Cu(hfac)_2 \cdot DMA$	+	Et_3N	→	$Cu(hfac)_2 \cdot Et_3N$	+	DMA	6.8
Inert[a]	$Cu(hfac)_2 \cdot DMSO$	+	Et_3N	→	$Cu(hfac)_2 \cdot Et_3N$	+	DMSO	6.6
o-$Cl_2C_6H_4$	$Cu(hfac)_2 \cdot DMSO$	+	Et_3N	→	$Cu(hfac)_2 \cdot Et_3N$	+	DMSO	6.2

[a] Reaction of $Cu(hfac)_2$ with Et_3N carried out in cyclohexane; that of the acid, with DMSO, DMA, and EtOAc in CCl_4.

calorimeter. Another factor is the different values employed for the correction of heat of solution of $(C_2H_5)_3N$ in cyclohexane.

Discussion

In this report, we have extended our elimination of the solvation procedure (ESP) to include the transition metal Lewis acid bis(hexafluoroacetylacetonato)-copper(II). Earlier,[9] we showed that, for hydrogen-bonding acids, minimal solvation contributions were encountered for the general type of reactions represented by eq 2 in polar solvents as long as specific interactions of the donors and solvents could be avoided. To minimize specific interactions, the solvent employed should be basic for base displacement reactions. (Acidic solvents would form a specific complex with B and B′.)

Examination of the data in Table II indicates that, within the relatively large experimental errors inherent in the determination of the enthalpies on this system, solvation effects do cancel for reactions represented by eq 2, where A = $Cu(hfac)_2$. As in the *m*-fluorophenol system, the cancelation occurs even for combinations, B and B′, of polar and nonpolar donors, *e.g.*, $(CH_3)_2SO$ and $(C_2H_5)_3N$. Again, we obtain a cancelation of solvation effects, because there is a constant difference in the solvation of the complex and base in the nonpolar and polar solvents regardless of the base employed (the acid is not changed). The constant differences $\Delta(-\Delta H)$ in the two solvents are listed in Table II. The differences in the $\Delta(-\Delta H)$ values are well within the experimental error limits set on the enthalpies. The data in Table II are combined as previously described[9] to produce data for the displacement reactions which are presented in Table III. In all instances, the enthalpy of the reaction represented by eq 2 remains constant (within the experimental error) regardless of whether the reaction is carried out in a nonpolar solvent or *o*-dichlorobenzene. Thus, if one encounters a new base, B″, which is insoluble in inert solvents but is soluble in *o*-dichlorobenzene, the enthalpy of the displacement reaction (eq 2) should be determined with B″ and one of the bases in Table II in *o*-dichlorobenzene. The enthalpy of adduct formation of the base from Table II in CCl_4 or cyclohexane is then subtracted from the displacement reaction to produce the enthalpy of interaction of A with the base B″ in the nonpolar solvent. This approach can be expanded to permit study of many new coordination compounds which are insoluble in poorly solvating media but soluble in weakly polar solvents, provided checks are carried out on new systems to establish that they conform to the model. Needless to say, if the geometry of the adduct is considerably different in one solvent than in another this procedure is not valid. Wayland and Wishiewski[10] have recently suggested that axial and equatorial isomers may exist in these 1:1 adducts.

In order to determine the source of the constant difference in the two solvents, one needs to know the enthalpy of transferring the adduct[9] from nonpolar solvent to o-$Cl_2C_6H_4$, ΔH_C, in the scheme

$$\begin{tikzcd}
B(\text{inert solvent}) \arrow[d, "\Delta H_B"] & + & Cu(hfac)_2\text{-}(\text{inert solvent}) \arrow[r, "\Delta H_E"] \arrow[d, "\Delta H_A"] & B \cdot Cu(hfac)\text{-}(\text{inert solvent}) \arrow[d, "\Delta H_C"] \\
B(o\text{-}Cl_2C_6H_4) & + & Cu(hfac)_2(o\text{-}Cl_2C_6H_4) \arrow[r, "\Delta H_D"] & B \cdot Cu(hfac)_2\text{-}(o\text{-}Cl_2C_6H_4)
\end{tikzcd}$$

ΔH_A and ΔH_B are the differences between the heat of solvation of the acid and base in the inert solvent and *o*-dichlorobenzene. ΔH_E and ΔH_D are the enthalpies of interaction in the corresponding solvents. Unfortunately, however, in order to calculate ΔH_C, the ΔH_A values must be known. This is not possible in the present system because of the very slow rate of solution of $Cu(hfac)_2$ in *o*-dichlorobenzene (see the Experimental Section). If, as was previously the case,[9] the ΔH_A and ΔH_C values could have been determined, the source of the constant difference between

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(10) B. B. Wayland and M. D. Wishiewski, *Chem. Commun.*, 1025 (1971).

ΔH_C and ΔH_B for the various donors (1.4 kcal mol^{-1}) could be ascertained.

An immediate application of the procedure outlined above is to predict the enthalpy of adduct formation of bis(hexafluoroacetylacetonato)copper(II) with trimethylamine N-oxide in carbon tetrachloride. According to Table II, the reported value in o-dichlorobenzene should be corrected by

$$\Delta H[\mathrm{Cu(hfac)_2 \cdot base}]_{\mathrm{CCl_4}} = \Delta H[\mathrm{Cu(hfac)_2 \cdot base}]_{o\text{-}\mathrm{Cl_2C_6H_4}} - 1.4 \text{ kcal mol}^{-1} \quad (5)$$

producing a value of -12.8 kcal mol^{-1}.

It is of interest to consider what approach could be taken for a system in which no adduct could be found that is soluble in CCl_4 or C_6H_{12}. Thus, although a solvation-free displacement reaction could be obtained, one could not find a solvation-minimized adduct formation reaction for any donor which could be subtracted to give the result for B′. A reliable spectroscopic method could be developed for estimating enthalpies from frequency shifts of donors (for example, the $-\Delta H$ vs. $\Delta\nu_{CO}$ relation[11] for ethyl acetate), and a CCl_4 equivalent enthalpy could be estimated from the frequency shift of the adduct (one would have to show that $\Delta\nu_{CO}$ was independent of the solvent employed). We should consider the eventuality that the enthalpy predicted from a spectroscopic correlation of the above type is in error. This introduces a constant error in all of the enthalpy values for this acid which would lead to incorrect E_A and C_A numbers for the acid. However, all the other base parameters in the correlation could predict enthalpies which are also off by approximately this constant amount. Thus, conclusions regarding trends in the importance of the base properties which influence the interaction would be valid. Clearly, other base displacement reactions in polar solvents could also be correctly predicted.

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[11] D. G. Brown, R. S. Drago, and T. F. Bolles, *J. Amer. Chem. Soc.*, **90**, 5706 (1968).

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Synthesis, Properties, and Electrochemical Studies of a Series of Nickel(II) Complexes with Related Macrocyclic Ligands of Varied Unsaturation

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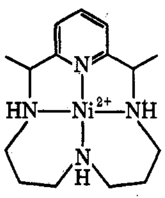
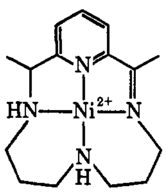
A complete series of nickel(II) complexes has been produced wherein a macrocyclic ligand containing four nitrogen donors varies stepwise from one unsaturated and three saturated donors through four unsaturated donors. The ligands are all derivatives obtained formally by hydrogenation or oxidative dehydrogenation of 2,12-dimethyl-1,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),2,11,13,15-pentaene (CR). Complexes of the parent ligand and the fully reduced ligand (CR + 4H) have been studied earlier. The monoene derivative $\mathrm{Ni(CR + 2H)^{2+}}$ was prepared both by reduction of $\mathrm{Ni(CR)^{2+}}$ and by aerial oxidation of $\mathrm{Ni(CR + 4H)^{2+}}$. $\mathrm{Ni(CR - 2H)^{2+}}$ was obtained by chemical oxidation of $\mathrm{Ni(CR)^{2+}}$. The electrochemical behavior of the entire series of complexes has been studied using both acetonitrile and methanol as solvents. A spectrum of oxidation states was obtained, ranging (formally) from 3+ to 1+ and zero, depending on the ligand. The effect of ligand unsaturation on the ease of electrochemical reduction and oxidation was most clearly seen in acetonitrile where simple reversible electron-transfer reactions prevailed. In methanol, electrochemical reductions were accompanied by hydrogenation processes. Here, for each complex, the total number of electrons involved in reduction was exactly enough to hydrogenate the imine functions present in the macrocyclic ring structure as well as to produce the same final product containing univalent nickel.

Introduction

As part of the short-range goals of our broad research program on the metal complexes of the new synthetic macrocyclic ligands, we are particularly concerned with developing and studying systems within which systematic variations in electronic structure can be produced. The complexes derived from condensation of 2,6-diacetylpyridine with γ,γ′-diaminodipropylamine in the presence of nickel(II) have provided a useful early example. Structures I–IV show the variation obtained in the ligands and permit easy establishment of a very simple system of abbreviations. Since its discovery by Curry[1] the complex of structure III has come to be known as $\mathrm{Ni(CR)^{2+}}$. It is the parent of the series of complexes and the other three are derivatives produced from it by oxidation or reduction.



(CR + 4H)
I



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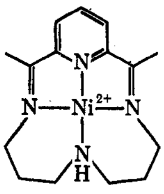

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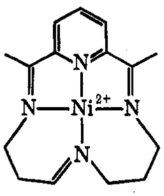
III



(CR − 2H)
IV

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[1] J. D. Curry, Ph.D. Dissertation, The Ohio State University, 1964.