

It was anticipated that the far-infrared spectra of the deprotonated complexes would reflect the effect of deprotonation upon the metal-nitrogen bond. It has been demonstrated that the complexes $M(SC_2H_4NH_2)_2$ possess the *cis* configuration.^{8,9} Hence, four bands due to the $\nu(M-N)$ and $\nu(M-S)$ vibrations were anticipated. The $\nu(M-N)$ modes have been assigned to the pair of bands occurring at *ca.* 450–550 cm^{-1} . Similarly, two bands at *ca.* 300–385 have been assigned to the $\nu(M-S)$ mode. Unfortunately, the singly deprotonated complexes $K[M(SC_2H_4NH)(SC_2H_4NH_2)]$ did not give well-resolved spectra in this region. However, the spectra of the doubly deprotonated complexes in this region were somewhat better resolved even though the band intensities were significantly less when compared with the corresponding bands in the parent complexes. It has been previously noted that deprotonation generally results in an increase in the $\nu(M-N)$ vibration.^{2,10,11} Similar behavior was observed in the spectrum of $K_2[Pd(SC_2H_4NH)_2]$; the metal-nitrogen stretching modes shifted from 533 and 453 cm^{-1} to 537 and 468 cm^{-1} in going from the parent complex to the deprotonated complex. A different behavior was exhibited by $K_2[Ni(SC_2H_4NH)_2]$. In this instance, the

asymmetric $\nu(M-N)$ mode decreased in frequency from 550 to 507 cm^{-1} . Consequently, no definitive conclusions can be drawn at present regarding the effect of deprotonation of the $\nu(M-N)$ vibrations and the metal-nitrogen bond. It may be noted that a similar trend was observed for those bands assigned to the $\nu(M-S)$ vibration. The remaining bands observed in the far-infrared region have been assigned to various ring deformations.

The complex $K[Pd(SC_2H_4NH)(SC_2H_4NH_2)]$ reacted with methyl iodide at 25° with the loss of 1 mol of ligand to form the thioether complex $PdI_2(CH_3SC_2H_4NH_2)$. This complex is characterized by bands in the infrared region at 1558 and 1568 cm^{-1} which may be assigned to $\delta(NH_2)$ vibrations. The observation that S-methylation of the ligand has occurred is not surprising since Busch and coworkers⁸ isolated the same complex from the reaction of $Pd(SC_2H_4NH_2)_2$ with methyl iodide in *N,N*-dimethylformamide.

When $K_2[Pd(SC_2H_4NH)_2]$ was allowed to react with methyl iodide at 25° in the absence of moisture, the same product was isolated. This result is surprising since the related complex $K_2[Pd(o-SC_6H_4NH)_2]^3$ reacts with methyl iodide with concomitant S- and N-methylation of the coordinated ligand to form $PdI_2(o-CH_3SC_6H_4NHCH_3)$.

Acknowledgments.—This work was supported by the Robert A. Welch Foundation and the U. S. Atomic Energy Commission.

(8) D. H. Busch, D. C. Jicha, M. C. Thompson, J. W. Wrathall, and E. Blinn, *J. Am. Chem. Soc.*, **86**, 3642 (1964).

(9) M. C. Thompson and D. H. Busch, *ibid.*, **86**, 3651 (1964).

(10) G. W. Watt and J. K. Crum, *ibid.*, **87**, 5366 (1965).

(11) G. W. Watt, P. W. Alexander, and B. S. Manhas, *ibid.*, **89**, 6483 (1967).

CONTRIBUTION FROM THE WILLIAM A. NOYES LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Contact Shift Studies of Nickel(II)-2,3-Diaminobutane Complexes^{1a}

BY RONALD J. FITZGERALD^{1b} AND RUSSELL S. DRAGO

Received January 29, 1969

The proton nmr contact shifts of the diastereoisomeric complexes $[Ni(meso-bn)_3]Cl_2 \cdot 2H_2O$ and $[Ni(d-bn)_3]Cl_2 \cdot 2H_2O$ (*bn* = 2,3-diaminobutane) have been investigated to ascertain more exactly what factors contribute to the difference in chemical shifts, required in principle, for diastereoisomers. This system is of particular interest because it can be investigated under conditions where there is no equilibrium between various species and the pseudocontact shift contributions are expected to be negligible. Thus, we can observe effects in the nmr spectra arising from the Fermi contact interaction for the diastereoisomers and thereby gain information about differences in the metal-ligand interaction. Only the methyl protons are detected in the nmr spectra of these complexes and within experimental error no differences exist in the contact shifts of the diastereoisomers. In view of sensitivity of the contact shift to bonding interactions the metal-ligand bond strengths must be of comparable magnitude in the two isomers and other factors are needed to account for the large differences in the stability constants of the diastereoisomers and reported chemical shift differences in many other diastereoisomers. Possible contributions to these phenomena are discussed. Spectral data are presented to substantiate our claim that these tris complexes undergo an octahedral \leftrightarrow square-planar dissociation similar to that observed for "Lifschitz salts," unless excess ligand is present.

Introduction

There has been much recent interest in the use of nmr methods to solve problems involving optical activity.

(1) (a) Presented in part before the Division of Inorganic Chemistry, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969. (b) Abstracted in part from the Ph.D. thesis of R. Fitzgerald, University of Illinois, 1968; National Institutes of Health Pre-doctoral Fellow, 1966–1968.

The chemical shift differences, required in principle for diastereoisomers, are often observable but not always resolvable in diamagnetic complexes. Spees, *et al.*,² have studied the conformation of chelate rings in Co(III) complexes and nmr methods have been widely

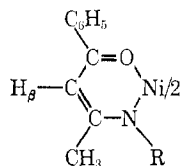
(2) S. T. Spees, Jr., L. J. Durham, and A. M. Sargeson, *Inorg. Chem.*, **5**, 2103 (1966).

used³ to elucidate the structures of *meso* and racemic forms of complexes. The causes of the observed differences may arise from different metal-ligand bond strengths or neighbor anisotropies.

Contact shifts, which are present in paramagnetic complexes, should accentuate these differences in chemical shifts if the metal-ligand interaction is varying. The general theory and interpretation of nmr contact shifts, as well as pseudocontact shift contributions, have been discussed in several recent review articles.^{4,5}

Holm and coworkers have been especially active in studying diastereoisomeric mixtures of nickel(II) complexes that undergo square-planar \leftrightarrow tetrahedral equilibria.⁶ In such systems the difference in the contact shifts, $\Delta\Delta\nu$, may be a function of both ΔA_n and $\Delta\Delta G$. Here $\Delta A_n = A_n(\text{act.}) - A_n(\text{meso})$ and represents the difference in the nuclear spin-electron spin coupling constant for the diastereoisomers (assuming $g_{\text{act}} = g_{\text{meso}}$); $\Delta\Delta G = \Delta G_{\text{act}} - \Delta G_{\text{meso}}$ and represents the difference in the free energy for the stereochemical rearrangement of these four-coordinate complexes. Holm has shown that the contact shift differences $\Delta\Delta\nu$ are always larger for such systems than for complexes with similar ligands, but which exist only in the paramagnetic form. On the basis of such evidence, he has concluded that for a wide variety of complexes which exhibit this spin-paired \leftrightarrow spin-free equilibria the difference in the contact shift, $\Delta\Delta\nu$, is chiefly a function of the free energy change $\Delta\Delta G$.

However, in contrast to these well-studied systems, there is a paucity of nmr results^{6c,7,8} for the diastereoisomers of paramagnetic complexes which do not undergo spin-paired \leftrightarrow spin-free type equilibrium. Holm and coworkers^{6c} have studied tetrahedral bis(β -ketoamine)nickel(II) complexes of the type

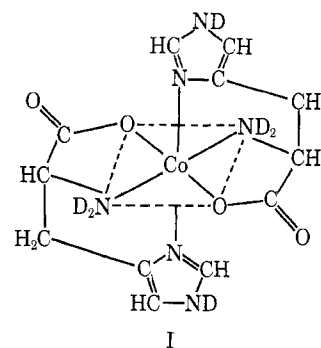


where $R = \text{sec-C}_4\text{H}_9$, $-\text{C}(\text{CH}_3)\text{HCH}_2\text{C}_6\text{H}_5$ (Amp), $-\text{C}(\text{CH}_3)\text{H}_2\text{C}_6\text{H}_5$. The difference in the contact shifts, $\Delta\Delta\nu$, changed greatly upon changing R with $\text{C}_6\text{H}_5\text{C}_2\text{H}_5 \gg \text{sec-C}_4\text{H}_9 > \text{Amp} \cong 0$. These differences seemed to reflect differences in the diamagnetic $\text{Zn}(\text{II})$ di-

astereoisomers,⁹ but the authors offered no other explanation for this observed variance in $\Delta\Delta\nu$ upon change of R , except for $R = \text{C}_6\text{H}_5\text{C}_2\text{H}_5$; *vide infra*.

Recently, Pignolet and Horrocks^{8,9a} have studied tetrahedral dihalogenobis(phosphine) complexes of cobalt(II) and nickel(II) that do not undergo tetrahedral \leftrightarrow square-planar equilibrium. They observed small differences in the contact shifts of the active (+,+) or (-,-) and the *meso* (+,-) complex. They attributed these differences to differences in the hyperfine coupling constants; *i.e.*, $A_i(\text{active}) \neq A_i(\text{meso})$. The shifts showed a solvent dependence which the authors attributed to a subtle change in geometry.

McDonald and Phillips⁷ studied the bis(hist.dine)-cobalt(II) complexes. At pH 5.0-10.5 the hist.dine ligand is tridentate and the geometry of the complex is roughly octahedral (see I). They attributed the much



larger contact shifts observed for $\text{Co}^{\text{II}}(\text{DL-his})_2^{2+}$ (his = histidine) to be due to the greater thermodynamic stability of this complex over either $\text{Co}^{\text{II}}(\text{DD-his})_2^{2+}$ or $\text{Co}^{\text{II}}(\text{LL-his})_2^{2+}$. They analyzed the stability of these complexes by examining the intensity ratios of analogous resonances of the DL and DD + LL forms, as they varied the proportion of D-histidine. They then compared these ratios with statistical ratios expected for random distribution. In all cases, the concentration of the DL form was greater than the statistical ratio and from the values of the equilibrium constants they calculated the free energy difference to be $\Delta G \cong 0.7$ kcal/mol.

In view of these differences in results, we have undertaken the study of the diastereoisomeric six-coordinate complexes $\text{Ni}(\text{meso-bn})_3^{2+}$ and $\text{Ni}(d\text{-bn})_3^{2+}$ in an effort to ascertain more exactly what factors contribute to the contact shifts. These complexes may be studied under conditions where there is no equilibrium between species in solution and, very importantly, pseudocontact shift contributions are expected to be negligible. Hence, there is no ambiguity in attributing observed differences in $\Delta\Delta\nu$ to differences in ΔA_n , *i.e.*, Fermi contact contributions. In the previously described works contributions to the ob-

(3) N. F. Curtis, *Chem. Commun.*, 881 (1966), and references therein.

(4) D. R. Eaton and W. D. Phillips in "Advances in Nuclear Magnetic Resonance," Vol. 1, J. S. Waugh, Ed., Academic Press, Inc., New York, N. Y., 1965, pp 103-148.

(5) E. DeBoer and H. VanWilligen in "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. 1, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, New York, N. Y., 1967, pp 111-161.

(6) (a) R. H. Holm, A. Chakrovorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964); (b) A. Chakrovorty and R. H. Holm, *ibid.*, **86**, 3999 (1964); (c) R. E. Ernst, M. J. O'Connor, and R. H. Holm, *ibid.*, **89**, 6104 (1967); (d) M. J. O'Connor, R. E. Ernst, and R. H. Holm, *ibid.*, **90**, 4561 (1968); (e) R. E. Ernst, M. J. O'Connor, and R. H. Holm, *ibid.*, **90**, 5735 (1968).

(7) C. C. McDonald and W. D. Phillips, *ibid.*, **85**, 3736 (1963).

(8) L. H. Pignolet and W. D. Horrocks, Jr., *Chem. Commun.*, 1012 (1968).

(9) R. H. Holm, R. E. Ernst, D. H. Gerlach, M. J. O'Connor, and J. Schoenburn, to be submitted for publication.

(9a) NOTE ADDED IN PROOF.—In a recent communication [*J. Am. Chem. Soc.*, **91**, 3976 (1969)], Pignolet and Horrocks now attribute the multiplicity of observed nmr peaks to be due to a mixture of phosphine and phosphine oxide complexes in solution, rather than diastereoisomeric "doubling" as they had originally claimed.

served shifts from either or both of these effects exist.

The complex $\text{Ni}(\text{bn})_3^{2+}$, which is closely related to the so-called "Lifschitz salts," was first successfully prepared by Frejka and Zahlova in 1930.¹⁰ They synthesized a wide variety of salts with the general formula $[\text{Ni}(\text{bn})_3]\text{X}_2 \cdot y\text{H}_2\text{O}$ ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NO}_3^-, \text{SCN}^-$; $y = 1, 1, 4, 1, 0$, respectively). They prepared these violet or red-violet complexes by adding the appropriate hydrated nickel salt to the 2,3-diaminobutane. The reactions, in general, proceed slowly and the product is recrystallized from water. They apparently made no attempt to separate the diastereoisomers of 2,3-diaminobutane so their ligand must be some mixture of *meso*- and *rac*-2,3-diaminobutane.

Experimental Section

Apparatus. a. Nmr Spectra.—The nmr spectra were obtained with a Varian HA-100 spectrometer. The concentration of complex was $\sim 0.1 M$. Chemical shift measurements were made using a side-band technique. All chemical shifts are reported relative to TMS.

b. Visible and Near-Infrared Spectra.—All near-infrared and visible spectra were measured using a Cary recording spectrophotometer, Model 14 RI.

c. Optical Activity Measurements.—All measurements of optical activity were made on an ETL-NPL automatic polarimeter, Type 143A, using a 0.1-dm cell. This instrument was calibrated using solutions containing known amounts of sucrose, $[\alpha]^{25\text{D}} + 66.8 \pm 0.2^\circ$.

Reagents and Solutions.—Hydrated nickel(II) chloride (Baker), *meso*- and *dl*-2,3-diaminobutane (Wyandotte), concentrated hydrochloric acid (Baker and Adamson), anhydrous methanol (Mallinckrodt), anhydrous ethanol (U.S.I.), anhydrous sodium methoxide (Matheson Coleman and Bell), potassium chloride (Fisher), and *d*-tartaric acid (Eastman Organics) were used without further purification.

Separation and Resolution of 2,3-Diaminobutane.—In general, we have used the procedures of Dickey, *et al.*,¹¹ together with modifications introduced by Hall and Douglas.¹² The 2,3-diaminobutane when obtained commercially is some physical mixture of the *meso* and racemic compounds. The *meso*:racemic ratio varies with the method of preparation, but it is usually 1:4.¹³

a. Separation of *meso*- and *dl*-2,3-Diaminobutane.—The diamine was neutralized by adding concentrated hydrochloric acid dropwise to an aqueous solution of the diamine cooled in an ice bath. The solution was then evaporated almost to dryness, and the dihydrochloride salt was filtered and when necessary washed with small amounts of anhydrous ether. This salt was then fractionally recrystallized five times from aqueous methanol (95%) and then anhydrous methanol. The less soluble salt is the *meso* form. The reported solubilities¹¹ are: 0.9 g of *meso*-bn \cdot 2HCl/100 ml of CH_3OH and 7.0 g of *dl*-bn \cdot 2HCl/100 ml of CH_3OH at 22° .

Anal. Calcd for bn \cdot 2HCl: C, 29.7; H, 8.76. Found: C, 29.63; H, 8.47.

The dihydrochloride salts were decomposed by adding a slight excess of sodium methoxide in methanol to a methanolic solution of the salt. The diamine was then recovered by fractional distillation under reduced pressure, 60 mm.

b. Resolution of *dl*-2,3-Diaminobutane.—The acid tartrate of the racemic diamine was prepared by adding 6.0 g (0.068 mol) of *dl*-2,3-diaminobutane in 50 ml of absolute ethanol to a

warm solution containing 20.5 g (0.136 mol) of *d*-tartaric acid in 450 ml of absolute ethanol and 250 ml of water. After standing overnight, the white, less soluble diastereoisomer was filtered and washed with acetone. The salt was then recrystallized by dissolution in a warm ethanol-water (2:1) mixture which was then added to additional ethanol so that the final ethanol-water ratio was 3:1. This final solution was allowed to crystallize overnight and then was filtered. This procedure was repeated until this diastereoisomer had a constant solubility and gave a specific rotation of $[\alpha]^{25\text{D}} + 18.1^\circ$. The optically active bitartrate salt was transformed into the dihydrochloride salt by a reported method.¹⁴ The bitartrate was dissolved in the minimum amount of boiling water and added with stirring to a hot solution of potassium chloride (two times the number of moles of bitartrate salt), which is dissolved in the minimum amount of boiling water. The solution is cooled in an ice bath and the potassium hydrogen tartrate is filtered off. The solution is evaporated to approximately one-fourth its original volume with a stream of air and the dihydrochloride salt is then filtered off. The dihydrochloride is then recovered as noted previously.

Preparation of the Complexes. a. $[\text{Ni}(\textit{meso}\text{-bn})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$.—This compound was prepared by the standard method of making tris(propylenediamine)nickel(II) chloride dihydrate,¹⁵ except an appropriate amount of *meso*-bn was used, and in this case a larger excess of ligand must be used if the tris complex is to be obtained. If the complex is impure, it is recrystallized from an ethanol-water mixture containing excess diamine. A dark violet complex is obtained. *Anal.* Calcd for $[\text{Ni}(\textit{meso}\text{-bn})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$: C, 33.5; H, 9.39. Found: C, 33.65; H, 9.30.

b. $[\text{Ni}(\textit{d}\text{-bn})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$.—This complex was prepared in a manner analogous to that used to prepare the $[\text{Ni}(\textit{meso}\text{-bn})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ complex, except that *d*-bn is used. Again a violet complex is obtained. *Anal.* Calcd for $[\text{Ni}(\textit{d}\text{-bn})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$: C, 33.5; H, 9.39. Found: C, 33.73; H, 9.35.

Treatment of the Nmr Data. Our spectral data show that it is necessary to add excess 2,3-diaminobutane to these solutions in order to prevent the tris complex from dissociating according to eq 1. When this excess 2,3-diaminobutane is added to the solutions, peaks corresponding to the "free ligand" appear in the nmr spectrum. These peaks are shifted from the values obtained for the diamine in benzene. However, it is impossible to ascertain *a priori* whether this shift is due to (1) a hydrogen-bonding interaction with the water, (2) a slow exchange of free and coordinated ligand, or (3) some combination of (1) and (2); therefore, it is necessary to study the line width as a function of temperature, to determine what exchange region we are in.

The line width of the free amino peak as a function of temperature in the range 3–29° is plotted as the log of the line width at half-height, $\Delta\nu_{1/2}$, vs. reciprocal temperature, in Figure 1. A straight line having only a slight slope results. This non-variation of line width with temperature indicates that we are in the nonexchange region,¹⁶ on the nmr time scale, and the observed contact shifts will not be a function of added free ligand.

Results

1. Spectral Data.—The spectral data for the complexes and some data taken from ref 17 are given in Table I. The nature of the species in solution will be discussed later.

2. Nmr Data.—In the proton nmr spectrum, the complexed peaks appear as broad singlets. Despite repeated attempts, we were unable to locate the amino and methine peaks of both complexes. This is apparently due to severe broadening of these complexed

(10) J. Frejka and L. Zahlova, *Collection Czech. Chem. Commun.*, **2**, 639 (1930).

(11) F. H. Dickey, W. Fickett, and H. J. Lucas, *J. Am. Chem. Soc.*, **74**, 911 (1952).

(12) S. K. Hall and B. E. Douglas, *Inorg. Chem.*, **7**, 533 (1968).

(13) E. Strack and H. Schwaneberg, *Ber.*, **67B**, 1006 (1934).

(14) J. C. Bailar, Jr., H. B. Jonassen, and A. D. Gott, *J. Am. Chem. Soc.*, **74**, 3131 (1952).

(15) H. M. State, *Inorg. Syn.*, **6**, 200 (1960).

(16) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 2686 (1964).

(17) D. L. Leussing, J. Harris, and P. Wood, *J. Phys. Chem.*, **66**, 1541 (1962).

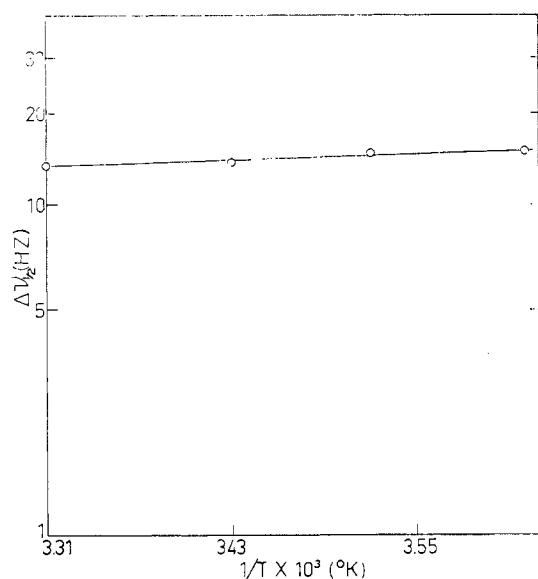


Figure 1.—Plot of the log of the width at half-height for the free amino proton *vs.* reciprocal temperature ($^{\circ}\text{K}$).

TABLE I
SPECTRAL DATA FOR
NICKEL(II)-2,3-DIAMINO BUTANE COMPLEXES

Compound	Solvent	ν_{max} , cm^{-1}	ϵ , M^{-1} cm^{-1}	Band assignment
$\text{Ni}(\text{meso-bn})_3^{2+}$ ^a	H_2O	10,929	8.3	${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$
		17,953	7.9	${}^3\text{A}_2 \rightarrow {}^3\text{T}_1(\text{F})$
		28,329	14.0	${}^3\text{A}_2 \rightarrow {}^3\text{T}_1(\text{P})$
$\text{Ni}(\text{meso-bn})_3^{2+}$	H_2O	10,929	8.5	${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$
		17,889	8.1	${}^3\text{A}_2 \rightarrow {}^3\text{T}_1(\text{F})$
		28,248	12.0	${}^3\text{A}_2 \rightarrow {}^3\text{T}_1(\text{P})$
		22,599		${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$
$\text{Ni}(\text{meso-bn})_3^{2+}$	$\text{H}_2\text{O} +$ excess bn	11,268	9.9	${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$
		18,484	10.2	${}^3\text{A}_2 \rightarrow {}^3\text{T}_1(\text{F})$
		29,240	14.2	${}^3\text{A}_2 \rightarrow {}^3\text{T}_1(\text{P})$
$\text{Ni}(\text{d-bn})_3^{2+}$	H_2O	10,929	9.1	${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$
		17,778	9.5	${}^3\text{A}_2 \rightarrow {}^3\text{T}_1(\text{F})$
		28,169	14.6	${}^3\text{A}_2 \rightarrow {}^3\text{T}_1(\text{P})$
		22,676		${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$
$\text{Ni}(\text{d-bn})_3^{2+}$	$\text{H}_2\text{O} +$ excess bn	11,416	11.8	${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$
		18,553	12.9	${}^3\text{A}_2 \rightarrow {}^3\text{T}_1(\text{F})$
		29,586	21.4	${}^3\text{A}_2 \rightarrow {}^3\text{T}_1(\text{P})$

^a Data taken from ref 17.

peaks. The failure to distinguish methyl groups in $\text{Ni}(\text{meso-bn})_3^{2+}$, which yields a poorly formed peak, is probably due to the extreme broadness of this peak, $\Delta\nu_{1/2} \approx 450$ Hz. We have assigned the observed peak to the methyl group on the basis of its similarity to the previously reported¹⁸ spectrum of the 1:1 complex of nickel(II) with ethylenediamine and the fact that the methyl group should be both more intense and have a narrower line width than any of the other peaks. Therefore, if any peak were to be detected, one would expect it to be the methyl peak.

Discussion

Nature of the Species in Solution.—The light purple complexes corresponding to the diastereoisomers $[\text{Ni}(\text{meso-bn})_3]^{2+}$ and $[\text{Ni}(\text{d-bn})_3]^{2+}$

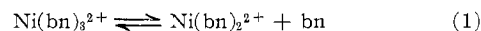
(18) R. S. Milner and L. Pratt, *Discussions Faraday Soc.*, **34**, 88 (1962).

TABLE II
NMR CONTACT SHIFTS FOR
NICKEL(II)-2,3-DIAMINO BUTANE COMPLEXES

Complex	Group	$\Delta\nu$, Hz ^a	$\Delta\Delta\nu$, Hz ^b
$\text{Ni}(\text{meso-bn})_3^{2+}$	CH_3	-2422 ± 25	-29
$\text{Ni}(\text{d-bn})_3^{2+}$	CH_3	-2451 ± 25	

^a The contact shift, $\Delta\nu$, is calculated relative to the appropriate diamagnetic complex $\text{Co}(\text{bn})_3^{3+}$ (F. Woldbye, private communication). All chemical shifts are relative to TMS at 29° . $\Delta\nu = \nu_{\text{paramagnetic}} - \nu_{\text{diamagnetic}}$. ^b $\Delta\Delta\nu = \Delta\nu_{\text{d}} - \Delta\nu_{\text{meso}}$.

$(\text{meso-bn})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Ni}(\text{d-bn})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}]$ were prepared and isolated. Since the stability constants for these complexes in aqueous solution are nearly as large¹⁹ as those of $\text{Ni}(\text{en})_3^{2+}$ and their tendency to dissociate in slightly acidic aqueous solutions^{20,21} is much less than that of $\text{Ni}(\text{en})_3^{2+}$, one would expect these complexes to exist entirely as the tris complex in aqueous solution. Also, previously published spectral data¹⁷ for $\text{Ni}(\text{meso-bn})_3^{2+}$ gave no indication of dissociation in solution. However, our spectral data as presented in Table I indicate that a dissociation in solution, corresponding to eq 1, occurs.



The shift of the bands toward higher energy, in solutions containing excess amine, and the disappearance of the band near $22,625 \text{ cm}^{-1}$, which has been attributed¹⁷ to the square-planar complex, indicate that only the tris complex is present in aqueous solutions containing excess amine.

Finally, the stereochemistry of the complexes in solution should be discussed. There is both theoretical²² and experimental²³ evidence to indicate that in the $\text{Co}(\text{meso-bn})_3^{3+}$ complex one of the methyl groups is equatorial and the other is axial, regardless of the absolute configuration about the metal. Thus, there is an equal probability of the conformations $\Delta(\text{m,m,m})$ and $\Lambda(\text{m,m,m})$. However, in the case of the $\text{Ni}(\text{meso-bn})_3^{2+}$ complex, we failed to detect two different kinds of methyl groups.

For the $\text{M}(\text{d-bn})_3^{n+}$ complexes Woldbye²² has shown that the most stable conformation of the chelate ring is Λ , with the methyl groups equatorial and "1e1" or δ . There is experimental evidence²⁴ to indicate that $\text{Co}(\text{d-bn})_3^{3+}$ exists almost exclusively in the $\Lambda(\delta,\delta,\delta)$ configuration. However, our circular dichroism experiments failed to detect any reliable preference for the $\Lambda(\delta,\delta,\delta)$ configuration. Our measurement on the middle band showed $\Delta\epsilon = \epsilon_{\text{l}} - \epsilon_{\text{r}} = 0.003$, whereas a recent report by Treptow²⁵ gave $\Delta\epsilon = 0.035$ for the middle band of $\text{Ni}(\text{l-chn})_3^{2+}$ ($\text{l-chn} = \text{l-1,2-diaminocyclohexane}$). Without more extensive investigation, it is

(19) F. Basolo, Y. T. Chen, and R. K. Murman, *J. Am. Chem. Soc.*, **76**, 956 (1954).

(20) A. K. S. Ahmed and R. G. Wilkins, *Proc. Chem. Soc.*, 399 (1959).

(21) A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 2901 (1960).

(22) F. Woldbye, Proceedings of the 8th International Conference on Coordination Chemistry, Vienna, 1964, p 103.

(23) F. Woldbye, private communication.

(24) F. Woldbye, *Proc. Roy. Soc. (London)*, **A297**, 79 (1967).

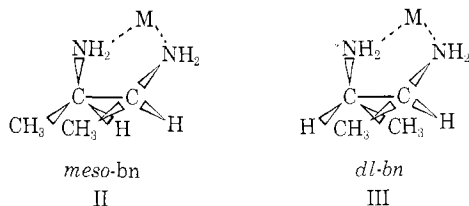
(25) R. S. Treptow, *Inorg. Chem.*, **7**, 1229 (1968).

difficult to say whether our measurements fail to detect preferential Λ or Δ absolute configurations or simply reflect the decrease in rotational strength that has been observed for some similar five-membered rings.²⁴

Interpretation of the Contact Shifts.—Peter²⁶ has examined the esr spectrum of $\text{Na}[\text{Ni}(\text{acac})_3]$ (acac = acetylacetonate) perturbed by axial and rhombic fields at 4.2°K and has concluded that $g_{\perp} \approx g_{\parallel}$. Therefore, even though our complexes possess an actual D_3 symmetry, the small anisotropy and the nondegenerate ground state should exclude the possibility of appreciable pseudocontact shifts.²⁷ We may, therefore, consider the observed shift to be Fermi contact in nature and draw conclusions about the bonding on this basis.

The nmr isotropic contact shifts were given in Table II. We have observed at most a small difference, within the error limits of our experiment, $\Delta\Delta\nu = -29$ Hz. The stability constant measurements¹⁹ indicate that $\text{Ni}(\text{dl-bn})_3^{2+}$ should be more stable than $\text{Ni}(\text{meso-bn})_3^{2+}$ by approximately 3.90 kcal/mol at 25°. This small difference in contact shift is also in agreement with the spectrochemical data on this system (Table III). The value of the splitting parameter Dq can be used for certain similar ligands as a measure of the metal–ligand interaction, as for example in nickel(II)–amine complexes.²⁸ The slightly larger Dq value of 1142 cm^{-1} for *d*-bn compared to 1127 cm^{-1} for *meso*-bn is consistent with a slightly larger contact shift for *d*-bn compared to *meso*-bn. The slightly higher value of Dq found for the $\text{Ni}(\text{d-bn})_3^{2+}$ complex may be due to the fact that *d*-bn it is a slightly better base than *meso*-bn ($\Delta H_{\text{neut},d} = 20.6$ kcal/mol, $\Delta H_{\text{neut},\text{meso}} = -19.2$ kcal/mol).²⁹

Basolo, *et al.*,¹⁹ had proposed, on the basis of molecular models, that the complexes with *dl*-bn as a ligand are more stable than those with *meso*-bn as a ligand because of the internal strain imposed on the chelate ring by the crowding from having both methyl groups on the same side of the ring in *meso*-bn, as shown in structures II and III. The Dq and $\Delta\nu$ values found in our



study are comparable and in the same direction as the differences in ΔH_{neut} mentioned above and indicate this steric effect, if it does exist, has at most a minor effect on the metal–ligand bond strength. The difference in Dq is much less than that associated with replacing a hydrogen of ammonia with methyl (Table III).

(26) M. Peter, *Phys. Rev.*, **116**, 1432 (1959).

(27) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(28) R. S. Drago, D. W. Meek, R. Longhi, and M. D. Joesten, *Inorg. Chem.*, **2**, 1056 (1963).

(29) F. Basolo, R. K. Murman, and Y. T. Chen, *J. Am. Chem. Soc.*, **75**, 1478 (1953).

TABLE III

COMPARATIVE DATA FOR NICKEL(II)–AMINE COMPLEXES

Complex	Dq , cm^{-1}	ΔDq , cm^{-1}
$\text{Ni}(\text{NH}_3)_6^{2+}$	1053 ^a	
$\text{Ni}(\text{CH}_3\text{NH}_2)_3^{2+}$	993 ^a	60
$\text{Ni}(\text{d-bn})_3^{2+}$	1142	15
$\text{Ni}(\text{meso-bn})_3^{2+}$	1127	

^a R. S. Drago, D. W. Meek, R. Longhi, and M. D. Joesten, *Inorg. Chem.*, **2**, 1056 (1963).

This proposed steric effect should be much larger for phenyl groups substituted on the ethylenediamine carbon. Indeed, the failure to detect the formation of $\text{Ni}(\text{meso-stein})_3^{2+}$ (stein = stilbenediamine) in a 1:1 dioxane–water mixture¹⁹ and the reported failure to synthesize the tris complexes with *meso*-stein³⁰ as a ligand lent credence to this argument. However, the recently reported³¹ synthesis of $[\text{Ni}(\text{meso-stein})_3](\text{ClO}_4)_2$ has also cast doubt upon the existence of a substantial steric effect. Taken as a whole, the evidence indicates only a slight intrinsic difference in the metal–ligand bond strengths. The differences in stabilities, $\log K = 2.83 = \log K_{T,d} - \log K_{T,\text{meso}}$, of the $\text{Ni}(\text{bn})_3^{2+}$ complexes is practically impossible to interpret rigorously. In addition to the slight difference in metal–ligand bond strength many effects including some combination of entropy and/or solvent effects could lead to the observed differences in the stability constants.

Our findings are in sharp contrast to the nmr results on the cobalt(II)–histidine complexes⁷ where very much larger differences in the contact shifts have been attributed to a smaller difference in the free energy of the diastereoisomeric complexes. Although this larger shift could reflect to some extent differences in the delocalization mechanisms of these complexes, we feel that most probably these differences have been magnified by a pseudocontact interaction present in six-coordinate cobalt(II) complexes.

Large magnetic anisotropies are known to be present in six-coordinate cobalt(II) complexes.³² Pseudocontact shifts occur under conditions where there is a proper combination of magnetic anisotropy and geometric factors.

Jesson³³ has treated in detail the cases of cobalt(II) and nickel(II) chelate complexes in a trigonal field. Jesson calculated the dipolar (pseudocontact shift) contribution to the cobalt(II) complex and showed that this often amounted to several thousand hertz. There have been other precedents in the literature,³⁴ where pseudocontact shifts of several thousand hertz have been shown to exist for six-coordinate complexes of cobalt(II), but not for six-coordinate complexes of nickel(II). Therefore, we might reasonably expect a

(30) (a) I. Lifschitz and K. M. Dijkema, *Rec. Trav. Chim.*, **60**, 581 (1941);

(b) O. F. Williams and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 4464 (1959).

(31) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **7**, 1404 (1968).

(32) B. N. Figgis in "Introduction to Ligand Fields," Interscience Publishers, Inc., New York, N. Y., 1966, p 307.

(33) J. P. Jesson, *J. Chem. Phys.*, **47**, 582 (1967).

(34) J. Happe and R. L. Ward, *ibid.*, **39**, 1211 (1963).

large pseudocontact shift contribution in the six-coordinate cobalt(II)-histidine complexes. In this case, the observed $\Delta\Delta\nu$ differences do not necessarily reflect a different metal ion-ligand interaction, *i.e.*, Fermi contact difference.

Our results are in agreement with those reported by Holm, *et al.*,^{6c} for the nickel(II)-substituted bis(β -ketoamines), except when a $C_6H_5C_2H_5$ group is substituted. Since the *meso*-Ni($C_6H_5C_2H_5-C_6H_5HCH_3$)₂ complex exhibits anomalous behavior at low temperatures, which suggest hindered rotation about the N-C bond, it is probable that such steric factors enhance $\Delta\Delta\nu$ in this complex. If our results for "octahedral" nickel(II) systems can be extrapolated to tetrahedral nickel(II) systems, then our results support Holm's proposal^{6c} that the large differences in the contact shifts of diastereoisomeric nickel(II) complexes that undergo planar \leftrightarrow tetrahedral equilibrium are due chiefly to difference in the free energy, $\Delta\Delta G$. They are also in agreement with the relatively small differences in $\Delta\Delta\nu$, recently reported by Pignolet and Horrocks⁸ for the pseudotetrahedral dihalogenobis(phosphine) complexes of nickel(II) and cobalt(II). However, rigorous interpretation of these data⁸ is clouded by the fact that appreciable pseudocontact shift contributions may also be present in "tetrahedral" nickel(II) systems.³⁵

Recently Holm and coworkers^{6d} reported nonidentical resonances for the diastereoisomers $\Delta(+,+)$, $\Delta(-,-)$ and $\Delta(+,-)$, $\Delta(-,+)$ of pseudotetrahedral

complexes possessing a large activation energy for racemization. However, in agreement with an earlier report,^{6c} we were unable to detect a separate nmr resonance for different absolute configurations $\Lambda(d,d,d)$ and $\Delta(d,d,d)$. This may be due to rapid racemization—the lifetime has been recently estimated^{6c} to be 10^{-3} sec—or small differences in the shifts which are obscured by the broad, ill-resolved peaks.

In conclusion, our results show that chemical shift differences between diastereoisomers are enhanced either not at all or at most within the error limits of our measurement by a Fermi contact interaction. This enhancement is not as large as in previously reported cases⁷ where other factors may contribute to the observed chemical shift difference. In view of the sensitivity of the contact shift experiment, it appears that in the complexes studied here there is at most a very slight difference in the metal-ligand interaction of the diastereoisomers. In diamagnetic complexes neighbor anisotropies are probably more significant in accounting for differences in many of the systems studied.

Acknowledgment.—The authors acknowledge with thanks the financial support of this research by the National Science Foundation through Grant GP-5498. We are also indebted to Dr. W. Keith Langdon and Wyandotte Chemicals Corp., Wyandotte, Mich. 48192, for supplying us with the 2,3-diaminobutane used in these experiments. Thanks are due also to Professor John C. Bailar, Jr., for helpful discussions pertaining to the preparation and resolution of these complexes.

(35) J. P. Jesson, *J. Chem. Phys.*, **47**, 579 (1967).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA 55455

Inorganic Condensation Reactions. The Hydrolysis of Dimethylgold(III) and the Growth of Tetrakis(dimethylgold hydroxide)¹

BY SIMON J. HARRIS² AND R. STUART TOBIAS

Received March 19, 1969

The hydrolysis of the cation $(CH_3)_2Au(OH_2)_2^+$ has been studied in a 0.3 M (Na)ClO₄ medium at 25° by potentiometric measurements using glass electrodes. The only significant species aside from the aquo ion up to pH *ca.* 8 is the dimer $[(CH_3)_2AuOH]_2$, and the formation constant is $\log^* \beta_{22} = -9.794 \pm 0.003$. This product is presumed to be structurally analogous to trimethylsilyloxydimethylgold(III). The tetrameric molecule which has been identified in crystals of dimethylgold(III) hydroxide precipitated from aqueous solution is not present in significant concentrations. The equilibrium between $(CH_3)_2Au(OH_2)_2^+$ and $[(CH_3)_2AuOH]_2$ is rapid and reversible, but above pH 8 reaction appears to proceed very slowly.

Introduction

Hydrolysis reactions of metal ions have interested chemists for many years. There have been many efforts made to correlate information on the structures of the aquo cation, the hydrolyzed species in solution, and the hydroxide precipitate which eventually is obtained. In spite of this, the course of these reactions

is still little understood. In most cases, the hydration numbers of the cations, *i.e.*, their coordination numbers with respect to oxygen in solution, are not known and the stoichiometry deduced for the soluble hydrolysis products generally shows no obvious relationship to the structure of solid products precipitated from the solutions. With the exception of Bi(III) and Pb(II), direct evidence bearing on the structures of the soluble hydrolysis products is lacking. With hydrolyzed bismuth and lead solutions where the cation stoichi-

(1) Research sponsored by AFOSR(SRC)-OAR, USAF Grant No. AF-AFOSR-691-67.

(2) Research fellow in chemistry.