nitrosobenzene is in doubt because of the dimer–monomer equilibrium and because of possible conjugation effects,[28] examination of other regions of the infrared spectrum of the complex does not aid in ascertaining the mode of coordination.

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(28) K. Nakamoto and R. E. Rundle, *J. Am. Chem. Soc.*, **78**, 1113 (1956).

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# Deprotonation of 2-Aminoethanethiol Complexes of Nickel(II) and Palladium(II)

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The complexes $M(SC_2H_4NH_2)_2$ (M = Ni, Pd) are not deprotonated by anhydrous liquid ammonia at −33.5° but undergo successive deprotonation upon treatment with 1 and 2 molar equiv of amide ion in ammonia. The reprotonation and methylation of the resulting species are described and interpreted in relation to infrared spectral data.

Deprotonation of ethylenediamine complexes of several transitional metal ions has been reported from this laboratory;[1] these studies have recently been extended to glycine, alanine,[2] *o*-aminophenolato, and *o*-aminothiophenolato complexes.[3] We report here the results of an investigation of the deprotonation of 2-aminoethanethiolato complexes of nickel(II) and palladium(II) in liquid ammonia.

## Experimental Section

**Materials and Methods.**—All chemicals were reagent grade and used without further purification with the exception of methyl iodide, which was dried over $P_4O_{10}$ and fractionally distilled prior to use. 2-Aminoethanethiol hydrochloride[4] was kindly donated by Evans Chemetics, Inc., Houston, Texas. The reactions in liquid ammonia were carried out as previously described.[5] All hygroscopic samples were handled in a drybox filled with helium which was maintained free of oxygen by continuous exposure to liquid Na–K alloy. Only standard methods of analysis were employed.

Infrared spectra were recorded as Nujol or halocarbon mulls between NaCl or CsI disks with Beckman IR-7 (4000–600 $cm^{-1}$) and Beckman IR-11 (600–200 $cm^{-1}$) spectrophotometers.

X-Ray diffraction data were obtained using Cu K$\alpha$ radiation (Ni filter) at 35 kV and 15 mA. Exposure times were 8–12 hr; relative intensities were estimated visually. The data are listed immediately following analytical data.

**$Ni(SC_2H_4NH_2)_2$ and $Pd(SC_2H_4NH_2)_2$** were prepared as described by Jicha and Busch.[6] *Anal.* Calcd for $Ni(SC_2H_4NH_2)_2$: C, 22.77; H, 5.73; Ni, 27.83. Found: C, 23.32; H, 5.98; Ni, 28.2. X-Ray diffraction data: 6.25 (0.9), 5.14 (0.6), 4.83 (0.5), 3.72 (0.9), 2.95 (0.4), 2.70 (0.7), 2.68 (0.6), 1.95 (0.3). Calcd for $Pd(SC_2H_4NH_2)_2$: C, 18.78; H, 4.68; Pd, 41.13. Found: C, 18.38; H, 4.67; Pd, 40.7. X-Ray diffraction data: 6.34 (1.0), 5.18 (0.6), 4.90 (0.5), 3.74 (0.9), 3.16 (0.4), 2.96 (0.5), 2.70 (0.3), 2.10 (0.1).

**Behavior of $Ni(SC_2H_4NH_2)_2$ and $Pd(SC_2H_4NH_2)_2$ toward Liquid Ammonia at −33.5°.**—Samples (0.50 g) of bis(2-aminoethanethiolato)nickel(II) and of bis(2-aminoethanethiolato)palladium(II) were suspended in liquid ammonia (*ca.* 25 ml) at −33.5° and stirred for 2 hr. The ammonia was then filtered off under reduced pressure and the remaining solids collected. The infrared spectra and X-ray diffraction data for these solids were identical with those of the starting materials.

**$K[Ni(SC_2H_4NH)(SC_2H_4NH_2)]$.**—Bis(2-aminoethanethiolato)nickel(II) (4.75 g) was suspended in liquid ammonia (*ca.* 45 ml) at −33.5° and 1 molar equiv of $KNH_2$ in liquid ammonia (20 ml) was added slowly at −33.5°. After 3–4 hr, the reddish brown precipitate was washed with ammonia (10 ml) and dried *in vacuo* overnight. *Anal.* Calcd for $K[Ni(SC_2H_4NH)(SC_2H_4NH_2)]$: C, 19.29; H, 4.45. Found: C, 20.08; H, 4.82. X-Ray diffraction data: 9.40 (0.4), 8.67 (0.6), 8.15 (1.0), 6.25 (0.4), 3.72 (0.5).

**$K_2[Ni(SC_2H_4NH)_2]$.**—Bis(2-aminoethanethiolato)nickel(II) (2.14 g) was suspended in liquid ammonia (*ca.* 40 ml) at −33.5°, titrated with 2 molar equiv of $KNH_2$, and thereafter treated as described above. *Anal.* Calcd for $K_2[Ni(SC_2H_4NH)_2]$: C, 16.73; H, 3.51. Found: C, 16.55; H, 3.99. X-Ray diffraction data: 8.62 (1.0), 8.11 (0.3), 4.55 (0.4), 4.37 (0.4), 3.77 (0.2).

**$K[Pd(SC_2H_4NH)(SC_2H_4NH_2)]$.**—Similarly, bis(2-aminoethanethiolato)palladium(II) (2.89 g) was suspended in liquid ammonia (40 ml) at −33.5° and 1 molar equiv of $KNH_2$ in liquid ammonia (20 ml) was added slowly; the product was isolated as described above. *Anal.* Calcd for $K[Pd(SC_2H_4NH)(SC_2H_4NH_2)]$: C, 16.7; H, 3.71. Found: C, 15.95; H, 4.39. X-Ray diffraction data: 9.11 (0.9), 6.36 (1.0), 5.20 (0.2), 4.77 (0.2), 4.23 (0.4), 3.76 (0.7).

**$K_2[Pd(SC_2H_4NH)_2]$.**—In a similar manner, bis(2-aminoethanethiolato)palladium(II) was treated with 2 molar equiv of $KNH_2$ in liquid ammonia at −33.5°. *Anal.* Calcd for $K_2[Pd(SC_2H_4NH)_2]$: C, 14.35; H, 3.01. Found: C, 14.10; H, 3.05. X-Ray diffraction data: 9.01 (0.9), 7.10 (0.2), 5.57 (1.0), 4.73 (0.3), 4.49 (0.3), 3.39 (0.2), 3.24 (0.4).

**Reaction of $K[M(SC_2H_4NH)(SC_2H_4NH_2)]$ and $K_2[M(SC_2H_4NH)_2]$ with Water.**—Samples (0.50 g) of the singly and doubly deprotonated nickel(II) and palladium(II) complexes were each added to water (25 ml) and stirred for 8 hr. The products from these reactions were collected by filtration and thoroughly washed with water and ethanol. X-Ray diffraction and infrared spectral data for these materials showed them to be $Ni(SC_2H_4NH_2)_2$ and $Pd(SC_2H_4NH_2)_2$, respectively.

**Reaction of $K[Pd(SC_2H_4NH)(SC_2H_4NH_2)]$ with Methyl Iodide.**

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(1) G. W. Watt and D. G. Upchurch, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1966, pp 253–271.

(2) G. W. Watt and J. F. Knifton, *Inorg. Chem.*, **6**, 1010 (1967).

(3) G. W. Watt and J. F. Knifton, *ibid.*, **7**, 1443 (1968).

(4) To conform to earlier usage the $NH_2C_2H_4S^-$ ligand is abbreviated as bme, and bme-H denotes a deprotonated bme ligand.

(5) G. W. Watt and P. W. Alexander, *Inorg. Chem.*, **7**, 537 (1968), and references therein.

(6) D. C. Jicha and D. H. Busch, *J. Am. Chem. Soc.*, **1**, 872 (1962).

TABLE I

INFRARED SPECTRAL DATA ($\text{cm}^{-1}$)

| Ni(bme)$_2$ | Pd(bme)$_2$ | K[Ni(bme)(bme-H)] | K$_2$[Ni(bme-H)]$_2$ | K[Pd(bme-H)-(bme)] | K$_2$[Pd(bme-H)$_2$] | Tentative assignments |
|---|---|---|---|---|---|---|
| 3196 vs | . . . | 3185 s | . . . | . . . | 3245 m | $\nu(NH_2)$, $\nu(NH)$ |
| 3160 vs | 3165 vs | 3151 s | 3180 m | 3160 m | 3190 m | |
| 3080 vs | 3080 s | 3080 s | . . . | 3090 m | 3090 m | |
| 2960 s | 2958 s | 2960 s | . . . | (2970) m | 2930 w | $\nu(CH_2)$ |
| (2940) m, sh | (2930) m, sh | . . . | . . . | . . . | 2888 m | |
| 2928 m | 2917 m | 2925 m | . . . | 2910 m | 2849 vw | |
| 2892 m | 2882 m | . . . | . . . | . . . | 2798 m | |
| 2873 m | 2861 m | 2870 m | 2859 s | 2860 m | 2768 m | |
| 2838 m | 2830 m | 2840 m | 2780 s | 2830 m | 2712 w | |
| 1578 s | 1578 s | 1576 m | . . . | 1577 m | . . . | $\delta(NH_2)$ |
| 1458 s | 1453 s | 1455 s | 1437 m | 1453 m | 1450 w | $\delta(CH_2)$ |
| 1382 m | 1382 w | 1381 m | 1340 w | 1379 w | 1378 w | |
| . . . | . . . | 1433 s | 1424 m | 1430 m | 1422 w | $\delta(NH)$ |
| 1309 m | 1303 w | 1307 w | 1309 w | (1300) vw | 1283 m | $\omega(CH_2)$ |
| 1272 s | . . . | 1272 s | 1267 m | 1267 m | 1251 vw | $\gamma(CH_2)$ |
| 1264 s | 1267 s | 1246 s | 1258 m | 1235 w | 1239 w | |
| 1247 s | 1244 s | 1237 s | . . . | 1243 w | . . . | $\omega(NH_2)$ |
| 1144 vs | 1143 vs | 1140 s | . . . | 1148 m | . . . | |
| 1115 m | 1117 w | 1123 s | 1124 s | 1118 w | 1105 vw | $\nu(C\text{–}N)$ |
| 1048 m | 1045 m, sh | 1047 s | 1048 vs | 1047 m | 1073 m | |
| 1060 m | 1057 m | . . . | . . . | . . . | . . . | $\gamma(NH_2)$ |
| 994 m | 995 w, sh | 979 | 993 w | 995 w | 1002 w | $\nu(C\text{–}C)$ |
| 924 m | 922 m | 925 m | 935 w | 922 w | 921 w | $\rho(CH_2)$ |
| 861 s | 858 m | 859 m | 869 w | 857 w | 854 w | |
| 761 m | 776 m | 757 m | . . . | 775 w | . . . | $\rho(NH_2)$ |
| 678 m | 671 m | 677 m | 681 w | . . . | 667 w | $\nu(C\text{–}S)$ |
| 550 s | 533 m | ? | 535 vw | ? | 537 w | $\nu(M\text{–}N)$ |
| 479 s | 453 w | ? | 507 w | ? | 468 w | |
| 382 s | 337 s | 380 vw | 366 w | ? | (350) vw | $\nu(M\text{–}S)$ |
| 338 s | 306 m | ? | 342 vw | ? | 316 vw | |
| 332 s | . . . | ? | 309 w | ? | (298) vw | $\delta(NCCS)$ |
| 293 s | 290 m | ? | 282 w | | | |
| | | 1188 w | 1185 w | 977 w | (1175) w | Other bands |
| | | (655) w | 635 w | (887) w | (975 )w | |
| | | (935) m, sh | 950 w | | (880) w | |

—Potassium (2-amidoethanethiolato)(2-aminoethanethiolato)-palladate(II) (0.50 g) was placed in a tube reactor and freshly distilled methyl iodide (*ca.* 25 ml) was added under reduced pressure. The tube was sealed and the mixture was stirred for 7 days. The tube was opened, excess $CH_3I$ was allowed to evaporate, and the product was leached with water (500 ml) to remove KI. After being washed with cold ethanol and ether, the reddish brown complex was dried *in vacuo*. *Anal.* Calcd for $PdI_2(CH_3SC_2H_4NH_2)$: C, 7.98; H, 2.01; N, 3.10; Pd, 24.3. Found: C, 7.78; H, 1.94; N, 3.10; Pd, 24.0.

In similar experiments, $K[Ni(SC_2H_4NH)(SC_2H_4NH_2)]$ led to unstable products.

**Reaction of $K_2[Pd(SC_2H_4NH_2)]$ with Methyl Iodide.**—Potassium bis(2-amidoethanethiolato)palladate(II) was treated with methyl iodide as described above. The infrared spectrum and X-ray diffraction pattern for the reddish brown product were identical with these for $PdI_2(CH_3SC_2H_4NH_2)$. *Anal.* Calcd for $PdI_2(CH_3SC_2H_4NH_2)$: C, 7.98; H, 2.01. Found: C, 8.49; H, 3.01.

## Results and Discussion

The complexes $M(SC_2H_4NH_2)_2$ (M = Ni, Pd) react with 1 and 2 molar equivalents of $KNH_2$ in liquid ammonia at −33.5° according to

$$M(SC_2H_4NH_2)_2 + KNH_2 \longrightarrow K[M(SC_2H_4NH)(SC_2H_4NH_2)] + NH_3 \quad (1)$$

$$M(SC_2H_4NH_2)_2 + 2KNH_2 \longrightarrow K_2[M(SC_2H_4NH)_2] + 2NH_3 \quad (2)$$

The deprotonated products are moderately stable toward *dry* air but slowly react with any moisture in the air. Water reprotonates the complexes according to

$$2K[M(SC_2H_4NH)(SC_2H_4NH_2)] + 2H_2O \longrightarrow 2M(SC_2H_4NH_2)_2 + 2KOH \quad (3)$$

$$K_2[M(SC_2H_4NH)_2] + 2H_2O \longrightarrow M(SC_2H_4NH_2)_2 + 2KOH \quad (4)$$

Infrared spectral data are given in Table I together with tentative band assignments for the observed fundamental vibrations. Since the ligand $^{-}SC_2H_4NH_2$ is very similar to ethylenediamine, $H_2NC_2H_4NH_2$, band assignments between 4000 and 200 $\text{cm}^{-1}$ were made by taking into account previous infrared studies of related ethylenediamine complexes.[7]

Fundamental vibrations associated with the $NH_2$ and NH groups were readily assigned with the aid of deuteration and by noting the effect which deprotonation had on the infrared spectra. The $NH_2$ and NH stretching vibrations for the singly deprotonated complexes $K[M(SC_2H_4NH)(SC_2H_4NH_2)]$ could not be differentiated, but a new band at *ca.* 1435 $\text{cm}^{-1}$ was observed in their spectra and assigned to the NH bending mode. As expected, the doubly deprotonated complexes $K_2[M(SC_2H_4NH)_2]$ did not exhibit any $NH_2$ vibrations (Table I).

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(7) (a) D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **17**, 68 (1961) (b) G. W. Watt and D. S. Klett, *Inorg. Chem.*, **5**, 1279 (1966).

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 coworkers[8] 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 $K_2[Pd(o\text{-}SC_6H_4NH)_2]^3$ reacts with methyl iodide with concomitant S- and N-methylation of the coordinated ligand to form $PdI_2(o\text{-}CH_3SC_6H_4NHCH_3)$.

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[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).

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# Contact Shift Studies of Nickel(II)–2,3-Diaminobutane Complexes[1a]

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The proton nmr contact shifts of the diastereoisomeric complexes $[Ni(meso\text{-}bn)_3]Cl_2\cdot 2H_2O$ and $[Ni(d\text{-}bn)_3]Cl_2\cdot 2H_2O$ (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 ↔ 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. 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

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[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 Predoctoral Fellow, 1966–1968.

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