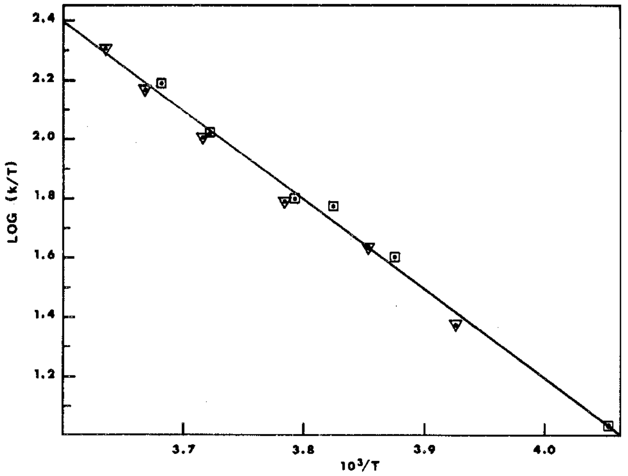

Figure 3. Plot of log (k/T), where $k = 1/\tau_M$, *vs.* $10^3/T$ for acetone solutions containing: □, 0.0252 *M* $[Ni(LUNO)_4](ClO_4)_2$ and 6.40 *M* LUNO; ▽, 0.0431 *M* $Ni[LUNO]_4(ClO_4)_2$ and 6.20 *M* LUNO.

Ni(II) complexes[8,11-14] where a dissociatively controlled mechanism is undoubtedly operating. Also the values of $1/\tau_M$ calculated in the present study do not show any detectable dependence on the ligand/complex ratio which is also consistent with a dissociative rate-controlling step.[8,11-14]

In view of the remote but finite possibility that the behavior of the chemical shift and line width data can be interpreted in terms of five exchanging ligands, calculations were carried out under this assumption using eq 1. This analysis produces a paramagnetic shift of 825 ± 75 Hz for the methyl protons at 25° and the following kinetic parameters: $1/\tau_M$ (0°) = 4.9×10^4 sec^{-1}, $\Delta H^\ddagger \simeq 18$ kcal/mol, and $\Delta S^\ddagger \simeq 29$ eu.

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Registry No. $[Ni(LUNO)_4](ClO_4)_2$, 22455-33-0; $Ni(LUNO)_5(ClO_4)_2$, 40959-52-2; LUNO, 1073-23-0.

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Complexes Containing Multidentate Ligands. IV.[1] Unique Bis(S-dealkylation) Reactions of Bis(*o*-diphenylarsinophenylthio)alkanes Catalyzed by Nickel(II) Salts

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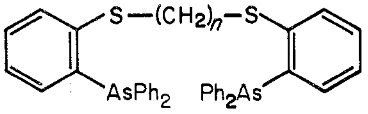
As part of a program initiated to study the effects of altering chelate chain length in multidentate ligand systems we have studied the reaction of nickel(II) salts with 1,2-bis(*o*-diphenylarsinophenylthio)ethane (C_2) (first prepared by Venanzi and coworkers[2]) and the 1,3-propane (C_3) and 1,4-butane (C_4) analogs. We wish to report here the spontaneous bis(S-dealkylation) of these ligands upon reaction with nickel(II) salts in an acetone–ethanol mixture at 30°.



C_2, $n = 2$
C_3, $n = 3$
C_4, $n = 4$

Experimental Section

The Ligands. 1,2-Bis(*o*-diphenylarsinophenylthio)ethane (C_2) was prepared according to the method of Cannon, Chiswell, and Venanzi.[2] The C_3 and C_4 ligands were prepared by analogous methods.

The Complexes. The ligand (0.001 mol) in acetone (10 ml) was mixed with the nickel(II) salt (0.001 mol) in ethanol with stirring. At room temperature no reaction was apparent even with continued stirring, but on warming gently to 30° a deep blue-purple color developed, followed almost at once by the deposition of green crystals. These were filtered, washed with ethanol, and dried *in vacuo* over P_4O_{10}. From the hydrated and anhydrous NiX_2 (X = ClO_4, NO_3, Cl, Br) salts used all products had identical carbon and hydrogen analyses. *Anal.* Calcd for $NiC_{36}H_{28}As_2S_2$: C, 58.9; H, 3.8. Found: C, 59.1; H, 4.0. Yields were ~80%.

$Ni[o\text{-}C_6H_4(AsPh_2)S]_2$. Nickel(II) perchlorate hexahydrate (0.001 mol) in ethanol (10 ml) was added to a solution of *o*-mercaptophenyldiphenylarsine (0.002 mol) in hot ethanol (20 ml) with stirring. No deep blue-purple color was seen, but the green solution yielded green crystals on cooling. *Anal.* Calcd for $NiC_{36}H_{28}As_2S_2$: C, 58.9; H, 3.8. Found: C, 59.0; H, 4.0.

Physical Measurements. Magnetic measurements, infrared and visible–ultraviolet spectra, and conductivity measurements were obtained as previously described.[3]

Results and Discussion

Although Cannon, *et al.*,[2] have reported some palladium(II) complexes of C_2, no first transition series complexes have been isolated of C_2, C_3, or C_4. When these ligands are mixed with $Ni(H_2O)_6(ClO_4)_2$ in an ethanol–acetone mixture at room temperature, there is no apparent reaction until the solution is warmed to 30°, after which an intense blue-purple color is formed. This is followed almost immediately by the precipitation of a green microcrystalline material. An infrared spectrum of this material indicated that there were no ClO_4^- groups present in this complex by the complete absence of the characteristic ClO_4^- absorptions at ~1100 and ~630 cm^{-1}.[4] An early suspicion that reduction of ClO_4^- to Cl^- ion was taking place (perchlorate reduction by phosphines is now well established[5]) was shown not to be true when it was discovered that all nickel(II) salts used (the chloride, bromide, and nitrate) yielded the same green complex with identical analyses and infrared and electronic spectra.

The absence of any anions in the resulting complexes pointed to the fact that the nickel(II) ion was complexed

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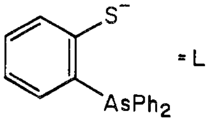
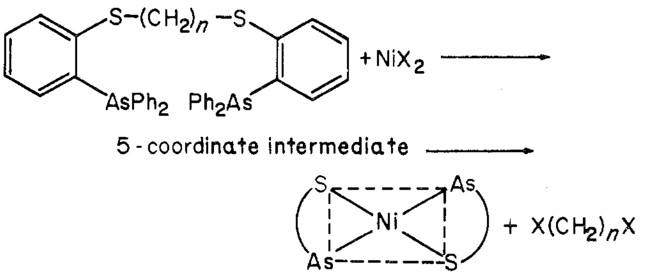
to a dinegative ligand (or ligands). The most obvious explanation was that the ligand had S-dealkylated and that two arsinosulfide ligands (L, I) were coordinated. This ex-



I

planation was confirmed by the analytical data, and further confirmation was obtained by the isolation of identical products from the reaction of *o*-mercaptophenyldiphenylarsine (LH) with the nickel(II) salts.

The [NiL_2] complexes derived from either C_2, C_3, C_4, or LH all have identical infrared and electronic spectra, are nonelectrolytes in nitromethane, nitrobenzene, and dichloroethane, and are diamagnetic. It is known that arsinosulfide ligands form trans square-planar complexes,[6] and because the [NiL_2] complexes prepared here from the quadridentate and bidentate ligands are alike in all respects, it is most likely that the [NiL_2] complexes prepared from the C_2, C_3, and C_4 ligands are *trans*-[NiL_2] species. The path of the reactions may be thus illustrated



Molecular models indicate that all the ligands fit more comfortably around a square-pyramidal structure than a planar structure, and the intense blue-purple color obtained upon initial reaction is reminiscent of the colors of low-spin pentacoordinate nickel(II) complexes with heavy donor atoms.

The visible spectra of reaction mixtures warmed to 30°, which had developed the blue-purple color, exhibit a broad band at *ca.* 19 kK, which is in the range accepted for low-spin square-pyramidal nickel(II) complexes.[7] Extreme difficulty was experienced in obtaining spectra of the blue-purple solutions; rapid precipitation of the green dealkylated complex continuously altered the intensity of absorption. Nevertheless, a laborious process of running small regions of the visible spectrum did build up a composite spectrum which indicated a band at *ca.* 19 kK. Dealkylation of the pentacoordinate intermediate followed by a slight rearrangement yields the complexes isolated. The visible spectra of the [NiL_2] complexes are, as expected, identical and consist of a symmetrical absorption at 24,180 cm^{-1} (ϵ 680) and a band at 15,380 cm^{-1} (ϵ 290) accompanied by a shoulder at 14,300 cm^{-1}.

Evidence of the bis(dealkylation) has been obtained by glc identification of 1,2-dichloroethane and 1,3-dichloropropane in the solution obtained from the reaction of $NiCl_2$ with C_2 and C_3.[8] It is interesting to speculate on the fate of the $X(CH_2)_nX$ ($X = ClO_4$, NO_3) compounds formed during these reactions, but we have not followed this aspect of these reactions.

A number of attempts were made to isolate the blue-purple intermediates in the C_2, C_3, and C_4 ligand reactions. However, even careful control of the temperature of the reaction did not allow for any success. It is thus concluded that the initial reaction between NiX_2 and the quadridentate ligands is followed immediately by bis(dealkylation).

The S-dealkylation of a number of chelates containing thioether groups is known,[9-12] and these have usually employed heavy metal ions such as Au(III)[9] or Pd(II).[10] Two examples of S-dealkylation with nickel(II) halides are known,[11,12] but these, like the other examples,[9,10] have employed high-boiling solvents and long reflux times. Moreover, these are all examples of mono(S-dealkylation).

The present study has provided the first example of facile (30°) bis(S-dealkylation).

Registry No. Ni[o-$C_6H_4(AsPh_2)S]_2$, 41184-54-7; C_2, 16825-42-6; C_3, 41178-30-7; C_4, 41178-31-8; nickel, 7440-02-0; *o*-mercaptophenyldiphenylarsine, 16823-73-7.

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A New Synthesis of NF_4^+ Salts and Its Mechanistic Interpretation Involving a New and Exceptionally Powerful Oxidizing Species

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Complex fluoro cations are generally prepared through fluorine abstraction from the parent molecule by means of a strong Lewis acid. This was first demonstrated in 1949 by Woolf and Emeleus[1] for BrF_3.

$$BrF_3 + SbF_5 \rightarrow BrF_2^+SbF_6^- \tag{1}$$

In the case of NF_4^+ salts, this approach was impossible since the parent molecule NF_5 is unknown and unlikely to exist owing to the validity of the octet rule for first row elements such as nitrogen and fluorine. The synthesis of NF_4^+ from NF_3 and F^+ is preempted by the fact that fluorine is the most electronegative element and, hence, F^+ should be extremely difficult, if not impossible, to prepare by chemical means. In 1965, Christe and coworkers experimentally confirmed that NF_4^+ salts can be prepared from NF_3, F_2, and a strong Lewis acid in the presence of an activation energy source.[2] Presently, three methods are known which are capable of producing NF_4^+ salts. These are (1) glow discharge at low temperature,[3,4] (2) heating under high pressure,[5,6]

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