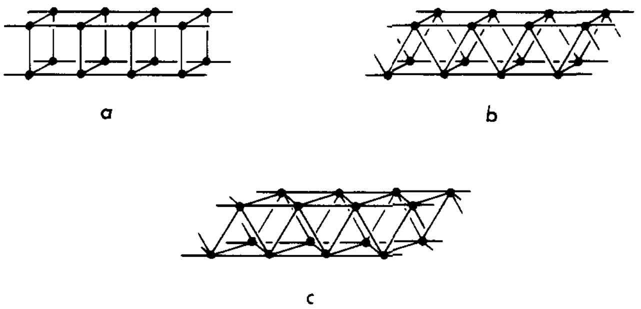

Figure 18. Tubes with a single-link members running lengthwise and circumferentially: (a) a tube with four units at each junction, (b) a tube with five units at each junction, and (c) a tube with six units at each junction.

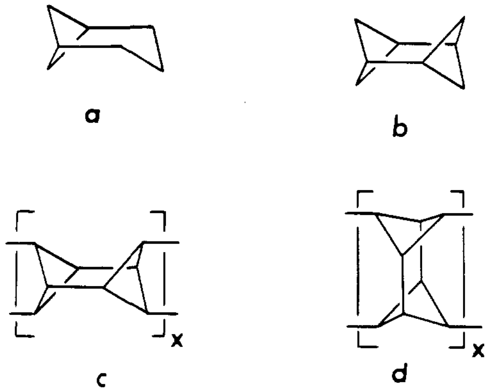

Figure 19. The structures of (a) norpinane, (b) tricyclo[3.1.1.1^{2,4}]-octane, (c) the hypothetical narsarsukite-type polymer, and (d) the hypothetical litidionite-type polymer.

litidionite, and miserite types will be found in silicates other than those in which they are now known. Since the litidionite tube has been found in several silicates and since the relationships between it and several linear silicates are strong, it is particularly likely that this tube will be found in other silicates.

It also appears likely that new types of silicate tubes will be found soon. Among the most likely to be found are those having the 8_2:6, 8_2:4,8, and 6_2:4,6,8 latticework tubes as parents since these latticework tubes are like those which are parents of the litidionite and miserite tubes. The probability of finding the silicate tube whose parent is the 8_2:6 tube is further enhanced because of the close relationships that exist between it and known silicate bands.

As is evident latticework tubes of the types described cannot simultaneously have continuous single-link members running lengthwise and circumferentially. Tubes of this type are, however, found among those having four, five, and six members radiating from a junction (Figure 18).

Finally, it is probable that in some cases organic tubes having carbon or carbon-heteratom frameworks like those discussed can be made. Thus, since norpinane can be made,[64] it seems likely that tricyclo[3.1.1.1^{2,4}]octane can be made and, hence, that narsarsukite-type and perhaps litidionite-type tubes can be made (Figure 19).[65] Such polymeric systems should have very interesting properties.

Acknowledgment. We wish to thank Dr. Kenneth Wynne and Dr. Kerro Knox for helpful discussions. We also gratefully acknowledge support of this work by the Dow-Corning Corp., the B. F. Goodrich Corp., and the Office of Naval Research.

Registry No. Litidionite, 12417-65-1.

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(65) The litidionite-type tube having a carbon framework would be strained to an appreciable extent.

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Theoretical Study on Dinitrogen Complexes. Position of the Third Protonation and the Reduction Mechanism

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Received September 9, 1981

This paper concerns itself with the position of the third protonation of the dinitrogen ligand and its reduction mechanism. It is considered that two kinds of isomers, $NHNH_2$ and N_2H_3 complexes, give N_2H_4 and NH_3 as reduction products, respectively. Though the N–N bond is weakened by the third protonation at the terminal nitrogen atom of the N_2H_2 complex, it does not lead to cleavage of the bond. On the other hand, it is calculated that $NHNH_2$ is released from the $NHNH_2$ complex by attack at the nitrogen atom attached to Cr. $NHNH_2^+$ decomposes to give NHNH and H^+, and then, two molecules of NHNH react to form N_2 and N_2H_4.

It has been a few years since the N_2 ligand in dinitrogen complexes of Mo and W was reduced to NH_3 and N_2H_4.[1] Complexes attached by one or two protons are considered to be intermediates of the reduction.[2] The features of protonation of the dinitrogen ligand are (1) the weakening of the N–N bond and (2) the reinforcement of the M–N one.[3] This trend was discussed on the basis of results of ab initio calculations of model complexes and the orbital-mixing rule.[4] In

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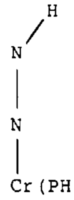
0020-1669/82/1321-2816$01.25/0

order to produce the reduction products from diprotonated complexes (N_2H_2), further protonation is needed at the terminal nitrogen (N_T) or that attached to the central metal (N_A). Takahashi et al. found that the third proton attacks the central metal to form a seven-coordinate intermediate.[5] They proposed the fourth protonation to reduce the protonated N_2 ligand. Chatt et al., on the other hand, expected for NH_3 formation that the fourth protonation occurred at N_T, following the attack of the third protonation at N_A.[6] They also considered that the $NHNH_2$ complex was likely to be an intermediate along the route of N_2H_4 formation.[3] It is, therefore, the key to the reduction where the protonation occurs in the N_2H_2 complex. In this preliminary study on Cr complexes, $[Cr(PH_3)_4NHNH_2]^{3+}$ and $[Cr(PH_3)_4N_2H_3]^{3+}$ (hereafter, they are represented by $NHNH_2$ and NH_3 complexes, respectively) as model complexes of Mo and W analogues are calculated to make clear the position of the third protonation and the reduction mechanism.

The GAUSSIAN-76 program is used for all calculations.[7] The basis set of Cr given by Roos et al. (12s6p4d) is contracted to [5s2p2d], and 4p-type orbitals are added.[8] STO-3G minimal basis sets are used for ligand atoms. Five-coordinated geometries are adopted for the simplicity of calculations. They are shown in **1**–**6**, where the $Cr(PH_3)_4$ fragment has the C_4 symmetry. It is considered that the change of the M–N and N–N bond lengths due to protonation affects very much the mechanism that the reduction of the N_2 ligand goes through. On the other hand, M–P and N–H lengths are not expected to have much influence on the reduction. Therefore, M–N and N–N lengths and MNN and NNH angles are optimized, whereas M–P (2.53 Å) and N–H (1.05 Å) bond lengths are fixed in all calculations.



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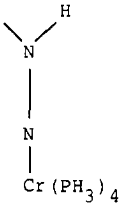

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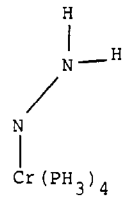

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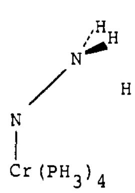

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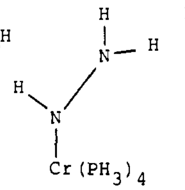

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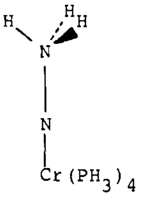

6

Results and Discussion

The N_2H_n (n = 1 or 2) fragments of N_2H and N_2H_2 complexes are optimized prior to the consideration of the position of the third protonation. Cr–N and N–N bond lengths optimized for the former complex are 1.742 and 1.249 Å, respectively. The NNH angle is estimated to be 108.7°. Those values for the N_2H_2 complex are 1.868 Å, 1.273 Å, and 121.7°, respectively. The complex with the geometry **3** is calculated to be the most stable one, where the NH_2 plane is in the xz plane and the CrNN angle (θ) is 148.8° (total energy = −2503.836 70 au). However, the energy difference between **2** and **3** is only 0.00158 au. On the other hand, **4**, in which the NNH_2 plane 0.001 58 out of the xz plane, becomes unstable with the decrease of the CrNN angle; i.e., total energies of those geometries with θ = 150.0 and 120.0° are −2503.834 00 and −2503.804 90 au, respectively. Therefore, it is considered that the N_2H_2 complex has the geometry **3**. The crystallographic analysis determined the angles for N_2H_2 and N_2R_2 complexes to be about 170.0 and 148.0°.[3] Though these experimental results are consistent with that of the present calculations, it seems to be overestimated. This is probably attributed to the limitation of basis sets used for calculations or to the difference of the central metal.

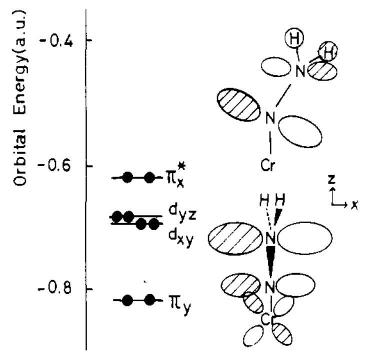

Figure 1. MO diagram and shape of molecular orbitals of $[Cr(PH_3)_4N_2H_2]^{2+}$.

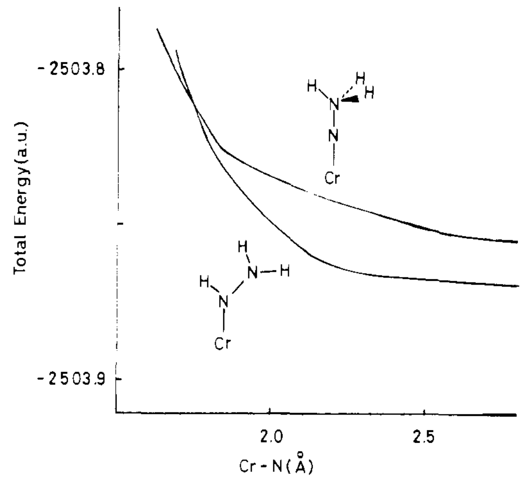

Figure 2. Potential curves of $[Cr(PH_3)_4NHNH_2]^{3+}$ and $[Cr(PH_3)_4N_2H_3]^{3+}$ as a function of the Cr–N bond length.

The position of the protonation of the N_2H_2 complex is largely influenced by its molecular orbitals (MO's). Figure 1 shows the MO diagram of the complex. HOMO of **2** (π^*_x) has a large p_x coefficient of N_A, and π_y is the MO expanded around N_T as shown in the figure. The former orbital lies at a position much higher (0.2 au) than the latter. Therefore, the third protonation is expected to occur at N_A rather than N_T.

So that the position of the third protonation can be considered, $[Cr(PH_3)_4NHNH_2]^{3+}$ (**5**) and $[Cr(PH_3)_4N_2H_3]^{3+}$ (**6**) are calculated. Figure 2 represents the potential curves of them in lengthening the Cr–N bond after the other lengths and angles are optimized.[9] As expected by the MO diagram of the N_2H_2 complex, **5** is more stable than **6** at the Cr–N bond

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(9) Optimized bond length and angles are as follows: (a) $NHNH_2$, N–N = 1.163 Å, ∠CrNH = 113.2°, ∠CrNN = 111.8°; (b) N_2H_3, N–N = 1.434 Å, ∠NNH = 111.9°.

length of more than 1.8 Å. It is known the N_2H_2 complex gives two types of reduction products, NH_3 and N_2H_4.[2] Therefore, **5** is concerned with the formation of the N_2H_4 complex and **6** will give NH_3.

In the case of the $NHNH_2$ complex, Figure 2 shows that the third protonation to N_A has the $NHNH_2$ fragment released. The net charge of the fragment with $r_{Cr-N} = 2.57$ Å is calculated to be 1.053+ ($NHNH_2^+$), which shows two electrons to be transferred from the metal moiety, $Cr(PH_3)_4$. The $NHNH_2^+$ released will decompose to give NHNH and H^+. It should be noted here that the experimental results showed that two molecules of NHNH react to form N_2 and N_2H_4.[10] The reaction is theoretically discussed by Yamabe et al.[11] on the basis of MINDO/3 calculations. Therefore, equimolar N_2H_4 and N_2 are expected to be evolved when the reduction goes through this mechanism. $WCl_3H(PMePh_2)_2(NNH_2)$ in methanol solution gives almost equimolar N_2H_4 and N_2 as the reduction products.[3] For this reaction, the $NHNH_2$ complex is considered to be along the route to N_2H_4. The mechanism mentioned above will account for the proportion of the products from the W complex. However, it is necessary to note that the effect of the trans ligand is neglected in the calculations.

It is necessary to break the N–N bond for the production of NH_3 in the mechanism of the N_2H_3 complex. The N–N bonds optimized in the N_2H_2 and N_2H_3 complexes are 1.273 and 1.434 Å, respectively. Though the N–N bond is weakened by the third protonation, the bond does not break to form NH_3 at this stage. On the other hand, Figure 2 also shows that the N_2H_3 fragment of **6** is released from the complex. The net charge of the fragment with $r_{Cr-N} = 2.5$ Å is 1.073+ ($N_2H_3^+$), which confirms that it accepts two electrons from the metal fragment. However, the formation of NH_3 is not expected even though $N_2H_3^+$ is released from the N_2H_3 complex. On the other hand, it is known that the substitution of phosphine ligands with halogen atoms in the reduction of the ligand nitrogen molecule occurs. Therefore, further calculations including this effect are needed in order to account for the process of NH_3 and N_2H_4 formation as the reduction products.

Acknowledgment. Permission to use the FACOM M-200 computer at the Data Processing Center of Kyoto University is gratefully acknowledged. The authors also thank the Computer Center, Institute for Molecular Science, for the use of the HITAC M-200H computer. The work was carried out by Grant-in-Aid 510206 from the Ministry of Education.

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Mechanistic Information from Oxygen-17 NMR Measurements. Evidence for the Existence of Oxygen-Bonded (Sulfito)pentaamminecobalt(III) in Weakly Acidic Aqueous Solution

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Received October 20, 1981

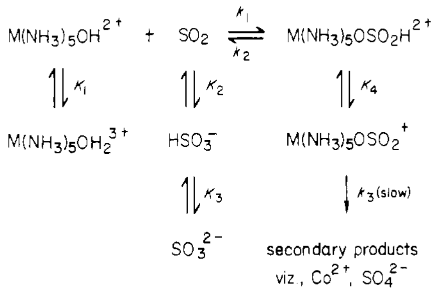
It has been suggested in the literature that $Co(NH_3)_5OH^{2+}$ reacts with SO_2 in aqueous solution to produce an O-bonded sulfito complex $Co(NH_3)_5OSO_2^+$, which on acidification releases SO_2 and forms the corresponding aquo complex. The kinetics of both processes suggested that no Co–O bond breakage is involved. ^{17}O-exchange experiments have now been performed with ^{17}O NMR and indicate that the earlier suggestions are correct.

Introduction

In contrast to numerous studies reported on the formation and stability of S-bonded sulfito complexes (see the literature cited in ref 1), very little has until recently been reported on the formation and reactivity of O-bonded sulfito complexes. A number of authors[2-7] have speculated on the possible formation of such species but, due to the lack of direct evidence in many cases, failed to illustrate their chemical significance.

Kinetic evidence for the formation of O-bonded sulfito complexes of the type $M(NH_3)_5OSO_2^+$ (M = Co(III), Rh(III), and Cr(III)) was reported recently.[1,8] In these studies the kinetics and mechanism of SO_2 uptake by the $M(NH_3)_5OH^{2+}$ species in weakly acidic medium and of the acid-catalyzed aquation (loss of SO_2) of $M(NH_3)_5OSO_2^+$ were investigated. Such reactions are very rapid and similar in nature to the corresponding CO_2 uptake/acid-catalyzed decarboxylation processes.[9-11] The suggested mechanism is outlined in Scheme I, in which the participating hydrogen ions

Scheme I



M ≡ Co(III), Rh(III), Cr(III)

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