Inorganica Chimica Acta, *158* (1989) 33–36

Investigation of the Structure and Reactivity of Cobalt(III) Carbonato Complexes by Using EHMO Calculation

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(Received August 3, 1988)

Abstract

Extended Hückel molecular orbital (EHMO) calculations on modified structures of $[CoCO_3(NH_3)_4]^+$ have been performed to investigate the influence of the strain caused by a chelated carbonato ligand on the complex structure and on the decarboxylation of carbonato cobalt(III) complexes with tetraamine ligands ($[CoCO_3(N)_4]^+$ type). It was suggested that the CO_3^{2-} chelation enlarges the N–Co–N angle (θ) *trans* to the O–Co–O angle to some extent and in the most stable structure the angle θ of $[CoCO_3(NH_3)_4]^+$ is about 94°, which is slightly larger than the octahedral angle (90°). The existence of d electrons in the d_{xy} orbital seems to be a key point for controlling the N–Co–N angle in this type of complex. Furthermore, the difference in decarboxylation rate between *trans*-$[CoCO_3(NH_3)_2en]^+$ and *trans*-$[CoCO_3(NH_3)_2tn]^+$, in which en and tn refer to ethylenediamine and trimethylenediamine, respectively, was examined on the basis of the calculated potential energies of the structure-modified $[CoCO_3(NH_3)_4]^+$ as a model compound.

Introduction

It is well-known that the d^6 cobalt(III) complex does not display a striking structural deformation from octahedral geometry. One of the exceptions is the cobalt(III) carbonato complex with a CO_3^{2-} chelate, which shows a great deviation of the O–Co–O bond angle of 70° from the octahedral one (90°). This is due to the steric restriction of the chelated carbonato ligand of a four membered ring [1]. This deformation should supply some strain for the cobalt(III) complex and influence the structure around the cobalt ion and the reactivity concerning this complex. From this viewpoint, some experimental approaches have already been carried out. The structure of carbonatotetraamminecobalt(III), $[CoCO_3(NH_3)_4]^+$, was reinvestigated by X-ray analysis and the *trans* influence of a chelated carbonato ligand was discussed [2]. In this investigation, any distinct influence was not detected in the Co–N bond length *trans* to the Co–O bond. Then, the dissociative reaction of CO_3^{2-} (so-called decarboxylation) in some carbonatocobalt(III) complexes with tetraamine ligands ($[CoCO_3(N)_4]^+$ type complexes) was examined [3]. It was reported there that the reaction rate is correlated to the magnitude of the N–Co–N bond angle *trans* to the O–Co–O angle (part of a carbonato chelation). In these investigations, however, all discussions were based on speculation about the strain caused by a carbonato ligand, and were not on the basis of molecular orbital consideration.

On the other hand, the structures and reactivities of many metal complexes have recently been examined by means of the extended Hückel MO (EHMO) calculation [4]. It has been reported that the results of these calculations are quite informative on the correlation between potential energies and bond angles of the metal complexes despite the approximate nature of the computational method. In the present work, we investigate the influence of the strain of a carbonato ligand on the structure of $[CoCO_3(NH_3)_4]^+$, especially on the bond angle N–Co–N, and on the decarboxylation of cobalt(III) carbonato complexes with tetraamine ligands ($[CoCO_3(N)_4]^+$ type) by using the extended Hückel MO calculation.

Calculational Details

All calculations were performed by use of the extended Hückel method described by Hoffmann. Program number QCPE #0344 from the Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, was used at the Computer Center of Institute for Molecular Science. The off-diagonal elements H_{ij} were calculated by a weighted Wolfsberg–Helmholtz formula with the standard K value of 1.75. The Coulomb integrals and orbital exponents for Co are listed in Table 1 [5] and the parameters for C, N, O and H are the standard ones. Charge iterations were performed on $[CoCO_3(NH_3)_4]^+$ assuming a linear charge dependence for

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TABLE 1. Parameters Used in Extended Hückel Calculations

Atom	Orbital	H_{ii} (eV)	Exponents[a]		Coefficients[a]	
			ζ_1	ζ_2	C_1	C_2
Co	3d	−13.18	5.55	2.10	0.568	0.606
	4s	−9.21	2.00			
	4p	−5.29	2.00			

[a] Coefficients and exponents in a double-ζ expansion.

H_{ii}s ($H_{ii} = H_{ii}^{\circ} + 2q$). Geometrical assumption included are as follows: Co–N, 1.98; Co–O, 1.94; N–H, 1.02; C–O, 1.34; C=O, 1.23 Å; O–Co–O, 70°; N–Co–N (*trans* to O–Co–O), valuable; N–Co–N (*cis* to O–Co–O), 90°; Co–O–C, 90°; O–C–O, 110°; O–C=O, 125°; NH_3 is assumed to be tetragonal geometry.

Results and Discussion

Structure of [$CoCO_3(NH_3)_4$]$^+$

Quantitative EHMO calculations were performed on the $[CoCO_3(NH_3)_4]^+$ complex modified in structure within the C_2 symmetry. We are interested in the influence of CO_3^{2-} coordination on the N–Co–N geometry *trans* to O–Co–O. Therefore, the N–Co–N angle θ, which is shown in Fig. 1, is taken as a variational parameter and is varied from 70° to 110°. The relationship of the potential energy for modified structures of this complex with bond angle θ is shown in Fig. 2. It is apparent in this Figure that the energy minimum is at a bond angle of 94°. The deformation of the angle from the octahedral one (90°) is not so drastic for this carbonato cobalt(III) complex but the N–Co–N angle is slightly larger than 90°. The structure of $[CoCO_3(NH_3)_4]Br$ has already been determined experimentally by X-ray analysis [1, 2]. The bond angle θ (N–Co–N) in crystals of bromide salts was reported to be 95(1)° (average of the data in refs. 1 and 2). This value of θ is quite similar to that at the energy minimum which is estimated here by EHMO calculation. Thus, it is concluded that the N–Co–N angle (*trans* to O–Co–O) is slightly enlarged by the coordination of CO_3^{2-} with a small O–Co–O bond angle.

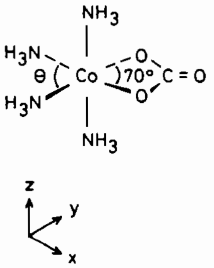


Fig. 1. Molecular geometry of $[CoCO_3(NH_3)_4]^+$. The coordinate system is also shown.

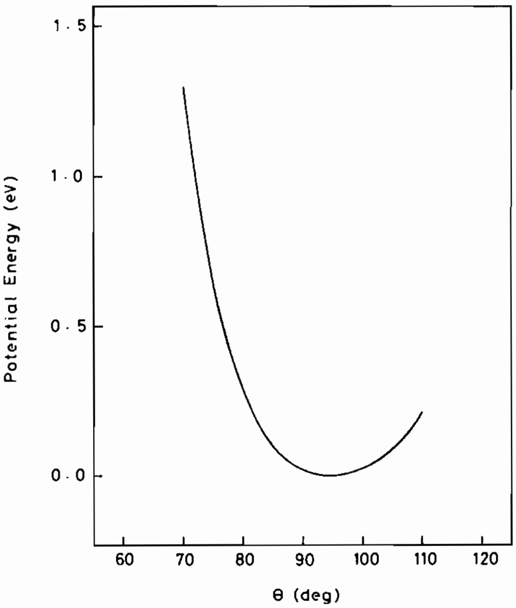


Fig. 2. Potential energy curve of $[CoCO_3(NH_3)_4]^+$ as a function of N–Co–N angle θ.

Figure 2 also indicates that the potential energy of this complex rises up moderately in the region of more than 100° but rises up steeply in the region of less than 80°. This may be the reason why the cobalt(III) carbonato complex ($[CoCO_3(N)_4]^+$ type) with the angle θ of less than 80° has not yet been synthesized though the complex with the angle of more than 100° has already been prepared [6].

By contrast, in Fig. 3, a Walsh diagram for this system is drawn as a function of the N–Co–N angle. The HOMO is ϕ_1 (or ϕ_4 at 110°). ϕ_1 and ϕ_2 are derived from the d_{xz} or d_{yz} orbitals and ϕ_4 is from the d_{xy} orbital in the xy plane. Of all the occupied orbitals presented in Fig. 3, it is ϕ_4 and ϕ_5 that are noticeably changed in their energy according to the change of the bond angle θ. The energy of ϕ_4 rises up steeply with increase of the bond angle θ (>90°). That of ϕ_5, which is a bonding combination (σ orbital) of cobalt $d_{x^2-y^2}$ and p_x or p_y on the coordinated oxygens and nitrogens in the xy plane, goes down with increasing θ in the region of 70°–110°. Therefore, the potential energy of the complex seems to be correlated to these two orbitals. The d electrons in the d_{xy} orbital make the complex unstable in the region of more than 90°. The bonding electrons in the σ orbitals of the Co–N and Co–O bonds in the xy plane make it stable as the bond angle θ increases ($70° <$

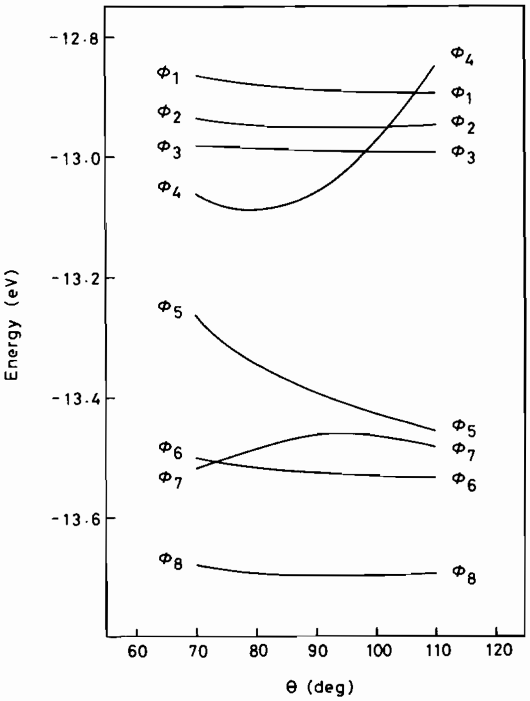
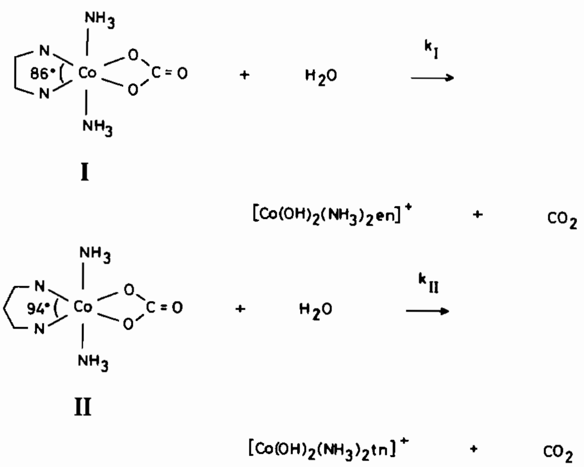


Fig. 3. Walsh diagram for $[CoCO_3(NH_3)_4]^+$.

$\theta < 110^\circ$). This means that, if the pseudo-octahedral complex of this type has no d electrons in the d_{xy} orbital [7], the N–Co–N angle of the complex should be enlarged to a greater extent (possibly more than 110°) though the potential energy of $[CoCO_3(NH_3)_4]^+$ which has d_{xy} electrons is minimum at the bond angle of θ 94°.

Decarboxylation

Now, the decarboxylation of this type of complex is examined on the basis of the result obtained by EHMO calculation. We consider this carbonatotetraamminecobalt(III) complex to be a model compound of the following carbonatocobalt(III) complexes with tetraamine ligands. Dobbins and Harris have already reported the reaction rates of the CO_3^{2-} dissociation reaction (decarboxylation) of *trans*-$[CoCO_3(NH_3)_2en]^+$ (**I**) and *trans*-$[CoCO_3(NH_3)_2tn]^+$ (**II**) (en: ethylenediamine and tn: trimethylenediamine) [3]. These overall reactions are shown in Scheme 1. In these reactions, the rate constant is 1.5 times greater for the carbonato complex **I** which is coordinated *trans* to carbonate with ethylenediamine than for **II** which is coordinated *trans* to carbonate with trimethylenediamine ($k_I > k_{II}$). Dobbins and Harris concluded it to be probable on the basis of the following speculation: the N–Co–N angle *trans* to O–Co–O should be enlarged to more than 90° by the effect of the strain of a CO_3^{2-} coordination (O–Co–O = 70°), and so the en complex (**I**) which has a smaller N–Co–N bond angle than 90° is destabilized.



Scheme 1.

We examined the result of the above reaction rates in comparison with the structures and stabilities of both complexes. According to the literature, the angle of N–Co–N (*trans* to O–Co–O) is 94° for the tn complex (**II**) [8] but it becomes smaller and is 86° for the en complex (**I**) [9]. From the result of Fig. 2, we can predict that the en complex is less stable than the tn complex because the potential energy is minimum at 94° for a model compound. This leads to the conclusion that the rate of dissociation of CO_3^{2-} would be greater for the en complex (less stable complex in the ground state) if the energy of these two complexes is assumed to be approximately equivalent in the transition state which is probably free from the strain of a carbonato ligand. The difference in potential energy between the two structures (the angles of N–Co–N are 86° and 94°) is apparently quite small, about 0.1 eV (~2.0 Kcal/mol), but this energy difference roughly corresponds to a ratio of k_I/k_{II} (1.5). Thus, the EHMO calculation can predict that the tightening of the N–Co–N angle slightly accelerates the decarboxylation of this kind of carbonatotetraaminecobalt(III) complex.

The potential energy of the structure of this type of complex is possibly changed by the other influence of the ligands. This is because the difference in energy between the structures of a simple complex, such as depicted in Fig. 1, is of the magnitude of a few Kcal/mol and is similar in magnitude to the energy difference between some chelate conformations or to the energy of non-bonded interactions between some substituents. The angle of N–Co–N (*trans* to O–Co–O) of $[CoCO_3(tn)_2]^+$ is 94° [10] against this similarity in energy difference, while the angle of $[CoCO_3(py)_4]^+$ (py: pyridine) is 100° [6]; this may be due to the repulsion between the pyridine rings.

Therefore, discussions using the model complex of $[CoCO_3(NH_3)_4]^+$ should be valuable for decarboxylation of the complex without bulky ligands like pyridine, which was investigated by Dobbins and Harris. Here, the result obtained on the basis of their keen speculation was semiquantitatively estimated by the molecular orbital calculation.

Some of the calculated energy difference between other sets of parameters for Co within the extended Hückel framework are small. We also calculated the potential energies for some of the arbitrary structures within the C_1 symmetry. In all cases, the calculations show the same trends as obtained from the parameters and the symmetry (C_2) used here.

Acknowledgements

I wish to thank the Computer Center, Institute for Molecular Science, Okazaki National Research Institutes for the use of the HITAC M-680H computer and Library Program ICON. I also thank Dr K. Kitaura in Osaka City University, whose talk in a meeting aroused my interest in the EHMO calculation so much.

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