CHEMISTRY LETTERS, pp. 833-836, 1974. Published by the Chemical Society of Japan

THERMAL ELECTRON TRANSFER REACTION OF SOME BIGUANIDE-COBALT(III) COMPLEXES IN SOLID PHASE

Ryokichi TSUCHIYA, Akira UEHARA, Kenji OTSUKA
and Eishin KYUNO
Department of Chemistry, Faculty of Science, Kanazawa University,
Kanazawa 920

The thermal reduction from Co(III) to Co(II) in the biguanide mixed complexes, trans-$[Co(CH_3NH_2)_2(bgH)_2]Br_3 \cdot H_2O$ and trans-$[Co(py)_2(bgH)_2]ClBr_2 \cdot 2.5H_2O$, was investigated in solid phase. These Co(III) octahedral complexes were found to undergo an electron transfer and converted to Co(II) square-planar complexes upon heating retaining the metal-biguanide bonds.

It is already known that biguanide, $H_2NC(NH)NHC(NH)(NH_2)$, (bgH), combines with many kinds of transition metal ions to give, in general, two series of complexes, $[Mbg_2]$ or $[M'bg_3]$ and $[M(bgH)_2]X_2$ or $[M'(bgH)_3]X_3$, where M and M' are bivalent and tervalent metal ions, respectively, and X is a univalent anion. Various formulas for their coordination structures have been proposed by many authors,[1)] but it seems that pronounced resonance among a number of alternative structures of the chelate rings exists in them.

Owing to the presence of such resonance, we can expect not only a considerable stabilization in six-coordinate biguanide cobalt(III) complexes containing two unidentate amine ligands in trans sites, but also the easy occurrence of a square planar structure in bis(biguanide)cobalt(II) complexes.

In general, when cobalt(III) complexes are heated in solid phase, the central metal ion is easily reduced even in a comparatively mild condition, and complicated decomposition occurs until the bonds between ligand and metal ion are completely broken.

Nevertheless, it is possible to expect that the special resonance effect described above will play an important role for the extra stabilization of the thermal product such as bis(biguanide)cobalt(II) complex.

In the present paper, we shall report on the unique thermal electron transfer process in the mixed biguanide cobalt(III) complexes to form biguanide cobalt(II) complexes without the rupture of the bonds between metal ion and biguanide, the coordination structure being changed from octahedral to square planar.

Preparation of Complexes trans-$[Co(CH_3NH_2)_2(bgH)_2]Br_3 \cdot H_2O$ (I) and trans-$[Co(py)_2(bgH)_2]ClBr_2 \cdot 2.5H_2O$ (II) were prepared by the methods used for the corresponding ammine complexes with slight modification. Found for complex (I): C, 12.70; H, 4.61; N, 28.23%. Calcd for trans-$[CoC_6H_{24}N_{12}]Br_3 \cdot H_2O$: C, 12.42; H, 4.48; N, 28.92%. Found for complex (II): C, 25.25; H, 4.84; N, 25.24%. Calcd for trans-$[CoC_{14}H_{24}N_{12}]ClBr_2 \cdot 2.5H_2O$: C, 25.47; H, 4.40; N, 25.47%.

Measurements The derivatograms for the complexes were obtained with a MOM Derivatograph Typ-OD-102. In order to obtain the informations on the complexes under heating, their electronic and IR spectra were measured with a Hitachi EPU-2A spectrophotometer in powdered state and with both JASCO Model IR-G and IR-F spectrophotometers in mull state, respectively. The magnetic susceptibilities of the complexes were measured by Gouy method at room temperature. The conductivity of the complexes was measured with a Yokogawa BV-Z-12A Universal Bridge, from which the molar conductivity was calculated.

Results and Discussion The thermogravimetric curve(TG) for the complex (I) is shown in Fig. 1. It can be seen that one mole of lattice water is liberated up to 130°, and then two moles of methylamine and 1/2 mole of bromine gas are evolved at the same time. The derivatogram of the complex (II) is shown in Fig. 2. Here, two moles of the lattice water are liberated first up to 80°, followed by evolution of 1/2 mole of the remaining water. Finally, two moles of pyridine and 1/2 mole of bromine gas are generated in the range of 190-200°. In both cases, the color change of the complexes, red-to-greenish yellow, was observed and the products were stable without any mass loss in TG curve up to ca. 240°. In these last steps, the complexes (I) and (II) both undergo an electron transfer to give the cobalt(II) complexes containing biguanide in the same way as the starting materials.

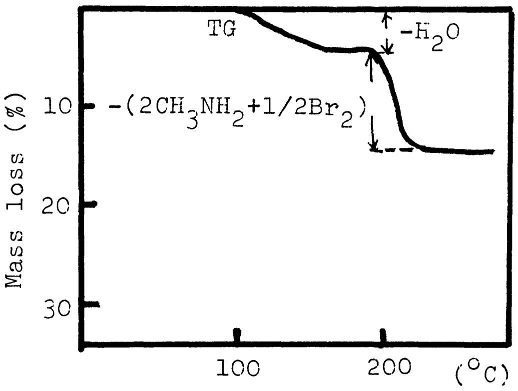

Fig. 1. TG curve for the complex (I).

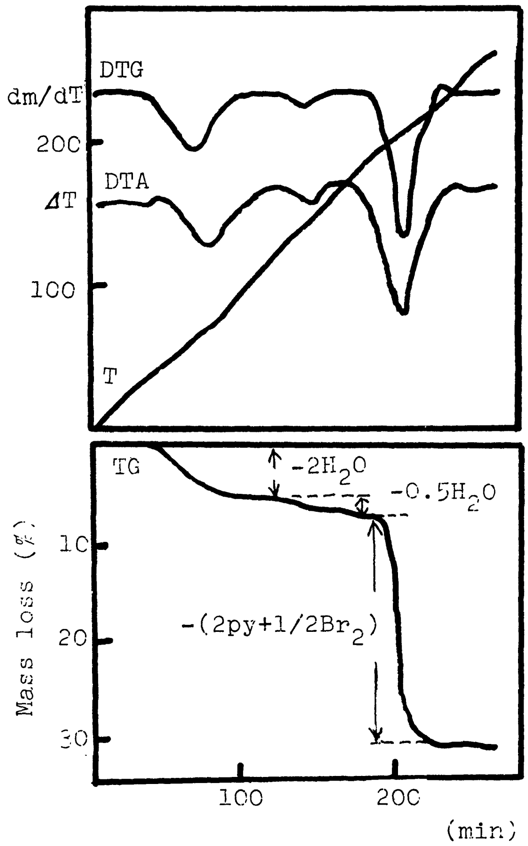

Fig. 2. Derivatogram for the complex (II).

The enthalpy change and the activation energy for deamination including those for electron transfer process were calculated to be $\Delta H=39$ kcal mol^{-1} and $E^{\ddagger}=73.2$ kcal mol^{-1} (from DTG) or 77.8 kcal mol^{-1} (from DTA), respectively.

Far-IR spectra for the complexes (I) and (II) are shown in Figs. 3 and 4, respectively. In the complex (I) before heating, two characteristic strong peaks are found at 510 and 490 cm^{-1}.2) The former is shifted to lower wave number side only by 5 cm^{-1}, but the latter certainly disappears just after the deamination. Therefore, the former is reasonably attributed to the stretching vibration of Co-N (biguanide), while the latter is assigned to that of Co-N (methylamine). Analogous explanation can be applied to the IR spectra for the complex (II) in Fig. 4. The bands at 640, 430 and 240 cm^{-1} 3) are assigned to the in-plane and out-of-plane ring deformations in pyridine and to the Co-N (pyridine) stretching, respectively, all of which disappear after the deamination. However, the band at 510 cm^{-1} remains even when further decomposition proceeds. These facts show that both complexes (I) and (II) give the stable cobalt(II) complexes without any rupture of the bonds between the central atom and the nitrogen atoms of the biguanide ligands after the deamination in spite of the occurrence of electron transfer.

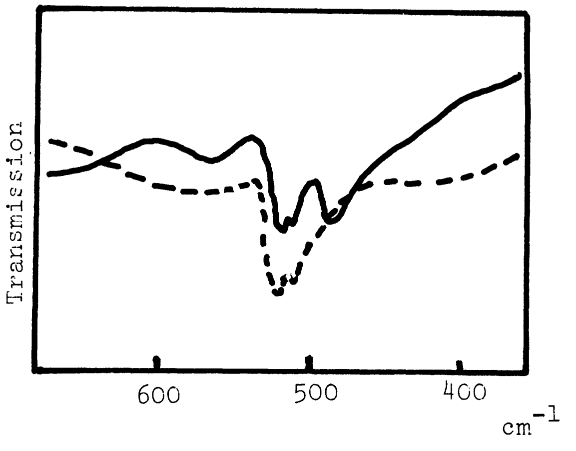

Fig. 3. Far-IR spectra of complex (I).
(———) at room temperature
(-----) after heating at 200°

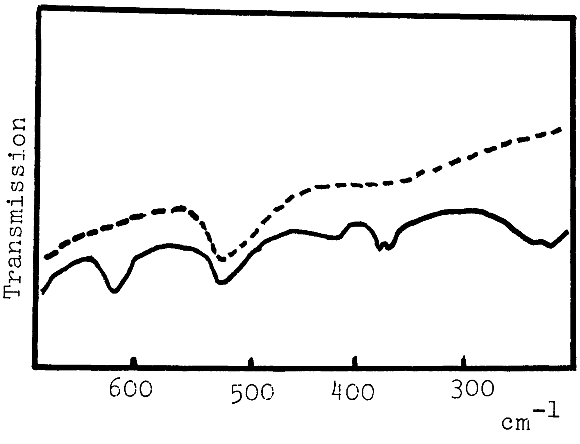

Fig. 4. Far-IR spectra of complex (II).
(———) at room temperature
(-----) after heating at 200°

The absorption spectra for both complexes in solid phase before and after the reactions are shown in Figs. 5 and 6. The absorption maxima at 58.6 and 85.0 x10^{13} sec^{-1} due to the d^6 low-spin six-coordinate cobalt(III) complex (I)4) turn to 44.2, 62.7 and 85.5x10^{13} sec^{-1} assigned to the square planar cobalt(II) complex after the reaction. Similarly, for the complex (II), the maxima at 57.8 and 85.0x10^{13} sec^{-1} are shifted to 45.0, 63.2 and 85.5x10^{13} sec^{-1}.

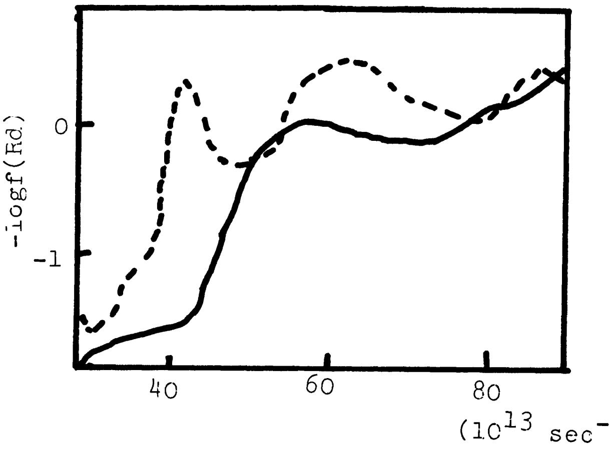

Fig. 5. Absorption spectra of complex (I) in solid phase.
(———) at room temperature
(-----) after heating at 200°

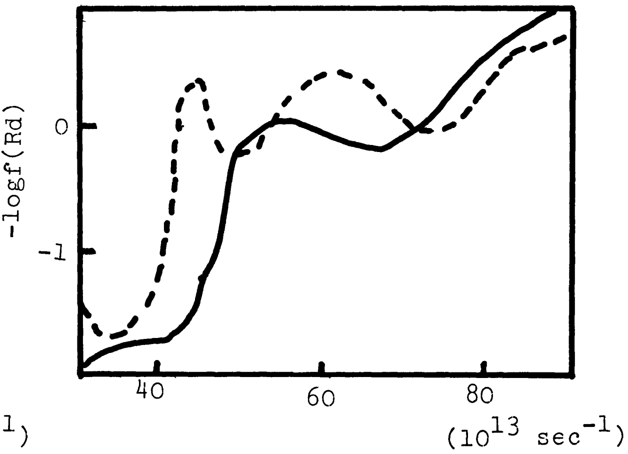

Fig. 6. Absorption spectra of complex (II) in solid phase.
(———) at room temperature
(-----) after heating at 200°

Molar conductivities of the reaction products of both the complexes (I) and (II) are 253 and 280 mho cm^{-1} in 1/10^3 molar solution, respectively, suggesting that they are 2:1-type complexes.

Magnetic moments of the reaction products of both the complexes (I) and (II) are 2.75 and 2.49 B.M., respectively.5) Therefore, it is concluded that the products have one free spin.6)

Proposed Thermal Reaction Process On the basis of the above results and discussion, the thermal reaction processes of the complexes (I) and (II) can be expressed by the following two sets of equations, respectively.

1. trans-$[Co(CH_3NH_2)_2(bgH)_2]Br_3 \cdot H_2O$ —— trans-$[Co(CH_3NH_2)_2(bgH)_2]Br_3 + H_2O$ (i)
   trans-$[Co(CH_3NH_2)_2(bgH)_2]Br_3$ —— $[Co^{II}(bgH)_2]Br_2 + 2\ CH_3NH_2 + 1/2\ Br_2$ (ii)
2. trans-$[Co(py)_2(bgH)_2]ClBr_2 \cdot 2.5H_2O$ —— trans-$[Co(py)_2(bgH)_2]ClBr_2 + 2.5\ H_2O$ (i)
   trans-$[Co(py)_2(bgH)_2]ClBr_2$ —— $[Co^{II}(bgH)_2]ClBr + 2\ py + 1/2\ Br_2$ (ii)

In each reaction (ii), it is noticeable that one electron transfer reaction from the counter bromide ion to the central cobalt(III) atom occurs to give a cobalt(II) complex: especially in the complex II, the electron transfer is considered to occur from the counter bromide ion, but not from the chloride ion owing to the electronegativity effect.

References

1) D. Sen, J. Chem. Soc., A1969, 2900.
2) D. B. Powell and N. Sheppard, J. Chem. Soc., 1956, 3108.
3) R. J. H. Clark and C. S. Williams, Inorg. Chem., 4, 350 (1956).
4) P Rây and A. N. Majumdar, J. Indian Chem. Soc., 23, 73 (1946).
5) P Rây and S. P. Ghosh, ibid., 20, 327 (1943).
6) Y. Nishida and S. Kida, Bull. Chem. Soc. Japan, 45, 461 (1972).

(Received May 20, 1974)