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Note

The solid-state thermal dissociation of *cis*- and *trans*-potassium bis(iminodiacetate)cobaltate(III) 2-hydrate

E. L. Simmons and W. W. Wendlandt

Thermochemistry Laboratory, Department of Chemistry, University of Houston, Houston, Texas 77004 (U. S. A.)

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Mori *et al.*[1], reported the preparation of the purple colored *cis*-potassium bis(iminodiacetate)cobaltate(III), *cis*-$K[Co(IDA)_2]$, in 1962. That same year, Hidaka *et al.*[2], prepared both the *cis*- and the brown colored *trans*-isomers. The configuration of the *cis*- and *trans*-isomers were assigned on the basis of the comparison of the visible spectra with those of known compounds. It was concluded that the *trans*-isomer was probably the facial rather than the meridional isomer on the basis of bond strain considerations. Later, Legg and Cooke[3] using NMR data, showed that the ligand, IDA, does favor the facial configuration[3,4]. It was also shown[4] from visible spectral evidence that steric repulsion between the adjacent nitrogen atoms is involved in the *cis*-compound. Thus, the *trans*-isomer is more stable.

In this investigation the solid-state thermal oxidation–reduction reactions of *cis*- and *trans*- $K[Co(IDA)_2]\cdot 2H_2O$ were investigated by TG, magnetic susceptibility, mass spectrometry, and DSC measurements. The reaction enthalpies were determined and a possible reaction mechanism suggested.

EXPERIMENTAL PART

Preparation and analysis of the compounds

The complexes, *cis*- and *trans*-$K[Co(IDA)_2]\cdot 2H_2O$, were prepared by a previously published method[5]. The water content of the compounds was determined by TG mass-loss measurements. The cobalt content was determined by pyrolyzing the samples at 800°C, leaching out the potassium salts with water, reignition, and weighing the residue as Co_3O_4. The results of the analyses were: H_2O: theor., 9.09%; found, 10.1% (*cis*-), 9.5% (*trans*-); Co: theor., 14.87%; found, 15.5% (*cis*-), 15.2% (*trans*-).

Thermogravimetric studies

The thermogravimetric studies were carried out by the use of a DuPont Model 950 Thermogravimetric Analyzer. The furnace atmosphere was air and a heating rate of 10°C/min was employed. Sample sizes ranged in mass from 4–5 mg.

Mass spectrometric studies

A Hitachi Perkin–Elmer RMU-6H mass spectrometer was used to obtain the mass spectra of the evolved gases during the thermal dissociation reactions.

Reaction enthalpies

The reaction enthalpies were determined using a Perkin–Elmer Model DSC-1B differential scanning calorimeter. From 3–6 mg of sample were used and the heating rate was 10°C/min. The heat of fusion of indium (6.8 cal/g) was used as the standard. Areas under the DSC peaks were measured with a planimeter.

Magnetic susceptibility

The magnetic susceptibilities of the reaction products of *cis*- and *trans*-$K[Co(IDA)_2]\cdot 2H_2O$ were obtained by the Faraday method. Sample sizes ranged in mass from 0.5–1 mg. The compound, $(NH_4)_2Fe(SO)_4)_2\cdot 6H_2O$, was used as the reference material.

RESULTS AND DISCUSSION

The thermogravimetric curves for *cis*- and *trans*-$K[Co(IDA)_2]\cdot 2H_2O$ are given in Fig. 1. In both cases the hydrate-bound water was lost between 50 and 110°C. A mass loss corresponding to a decrease in molecular weight of about 44 amu occured at 260°C for the *cis*-isomer and at about 290°C for the *trans*-isomer. In both cases, a brown-colored compound was obtained after the mass loss. Magnetic susceptibility measurements showed that the cobalt ion in this material was in the divalent state. The brown cobalt(II) compound or mixture decomposed at about 330°C.

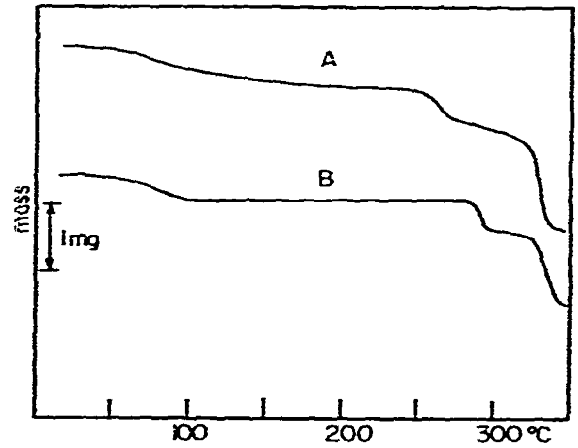
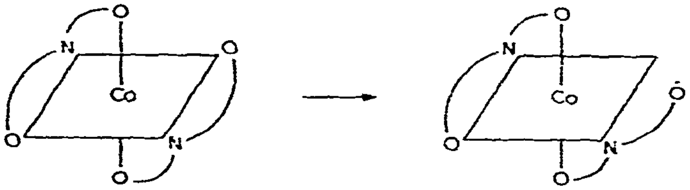


Fig. 1. Thermogravimetric curves for (A) *cis*-$K[Co(IDA)_2]\cdot 2H_2O$, and (B) *trans*-$K[Co(IDA)_2]\cdot 2H_2O$.

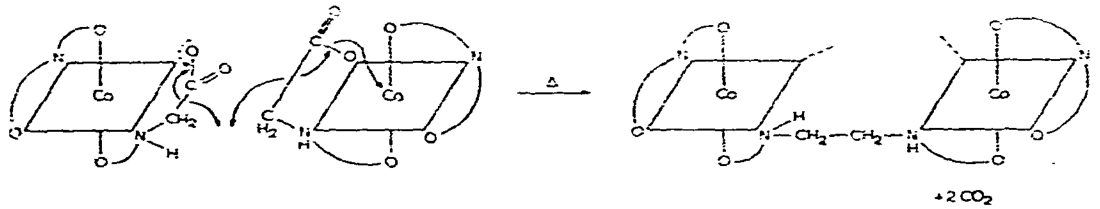
Mass spectrometric measurements showed that the gaseous products of the reduction reaction at 260°C for the *cis*-isomer and at 290°C for the *trans*-isomer was carbon dioxide. The empirical reaction stoichiometry was therefore as follows for both compounds:

$$KCoC_8O_8N_2H_{10} \rightarrow KCoC_7O_6N_2H_{10}+CO_2$$

A reaction mechanism which explains the reaction stoichiometry and the fact that the cobalt is reduced from the trivalent to the divalent state is as follows:



The free radical produced most likely reacts with an adjacent molecule in a manner similar to the following:



A mechanism of this type requires that the apparently vacant coordination sites be filled by partial bonds with carbonyl oxygens on adjacent molecules.

As expected, on the basis of steric repulsion[4], the *cis*-isomer is less stable thermally than the *trans*-isomer. The former undergoes the oxidation–reduction reaction at a temperature of 30°C lower than the latter. The difference in the stabilities of the complexes is also illustrated by the enthalpies of the oxidation–reduction reactions which were estimated from DSC measurements and are given in Table I. Both reactions are exothermic. In addition, a small exothermic peak was observed at about 240°C in the DSC curve for the *cis*-isomer. Since no mass loss occurs at that temperature, the peak was probably due to crystalline rearrangement.

TABLE I

ENTHALPIES OF THE SOLID-STATE OXIDATION–REDUCTION REACTIONS OF *cis*- AND *trans*-$K[Co(IDA)_2]\cdot 2H_2O$

Compound	ΔH *(kcal/mole)*
trans-$K[Co(IDA)_2]\cdot 2H_2O$	−6.0
cis-$K[Co(IDA)_2]\cdot 2H_2O$	−10.5
Difference	4.5

The area of this peak was included with that of the oxidation–reduction reaction at 260°C in order to calculate the reaction enthalpy. As can be seen, the reaction enthalpy for the *cis*-compound is 4.5 kcal/mole less than that of the *trans*-compound. Since both compounds apparently give identical reaction products, this value (4.5 kcal/mole) represents the approximate difference in the stabilities of the *cis*- and *trans*-isomers.

Both isomers are exceptionally stable for cobalt(III) complexes with mixed amine and carboxyl group oxygen ligands. An amine nitrogen is a stronger ligand than a carboxyl group oxygen; yet such complexes as $[Co(NH_3)_6]Cl_3$ and $[Co(en)_3]Cl_3$ undergo oxidation–reduction reactions at lower temperatures than the bis(iminodiacetate)-complexes. The former begins reduction of the cobalt(III) at about 175°C[6] and the latter at about 245°C[7]. The mixed amine and carboxyl group oxygen ligand complex, $[Co(en)_2C_2O_4]Cl$, undergoes reduction of the cobalt(III) at about 215°C[8]. Thus, in contrast to the above, the bis(iminodiacetate)-complexes are exceptionally thermally stable. This stability is undoubtedly due to the large chelate effect associated with the tridentate ligands.

Finally, it should be mentioned that the stoichiometry of the final decomposition step for both compounds in Fig. 1 has not been determined. The decomposition products above 330°C appear to be complicated mixtures. Also, the compounds undergo apparently different decomposition reactions in a nitrogen atmosphere than in an air atmosphere.

ACKNOWLEDGMENT

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