SHORT COMMUNICATIONS

Infrared Spectra of Glycols Coordinated to Metal Ions

By Akihisa Miyake

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Ethylene glycol has received attention in discussion of the infrared spectrum of polyethylene glycol¹⁾. Certain problems with regard to the rotational isomerism of this molecule still remain to be solved. It has been known that ethylene glycol forms coordination compound with cobalt or nickel ion²⁾. In an attempt to provide some new information on the vibrational assignments for this molecule, the infrared spectra of these coordination complexes were investigated.

Cobalt(II) chloride or nickel(II) chloride was dehydrated by heating at about 150°C. The coordination complexes were prepared by adding ethylene glycol to these dehydrated salts. There is a marked spectral difference between the free molecule and the molecule coordinated about a metal ion (Fig. 1). The coordinated ligand shows two kinds of spectra according to the water content of the dehydrated salts, both for cobalt and nickel. When the water contents of the salts exceed a value of about 15%, the complexes obtained from them (complex I) exhibit the spectrum shown in Fig. 1B. When the water contents are lower than this value, the complexes obtained (complex II) exhibit the spectrum shown in Fig. 1C. On the other hand, there is no difference between the cobalt and nickel complexes.

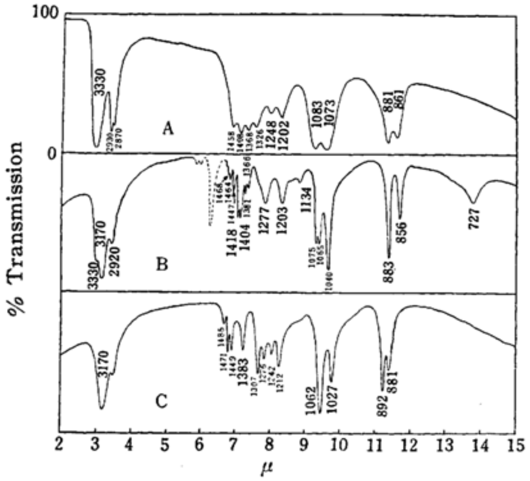

Fig. 1. Infrared spectra of ethylene glycol: (A) Liquid, (B) (C) metal complex (Nujol and polytrifluoroethylene mull, ---- water).

Two bands at 881 and 861 cm^{-1} in liquid ethylene glycol are undoubtedly assigned to the CH_2 rocking vibrations, because no other fundamental vibrations are expected in this region. The appearance of two CH_2 rocking bands indicates that ethylene glycol is present in the *gauche* form, because two CH_2 rocking bands (A and B types) are expected for the *gauche* form but only one (A_u type) for the *trans* form. The other CH_2 rocking vibration (B_g type) of the *trans* form is forbidden to appear in an infrared spectrum. An alternative interpretation is possible, however, assuming that two vibrations coalesce into a single band. In this way Kuroda and Kubo¹⁾ have assigned the band at 881 cm^{-1} to the *gauche* form and the band at 861 cm^{-1} to the *trans* form, considering that the two *gauche* vibrations overlap. Experimental results obtained in the present work provide data as to which one of these contradictory interpretations is more reasonable.

The number of absorption bands observed in the spectra of the complexes is a little larger than that observed for the liquid state. This indicates that the number of molecular forms present in the complex is at least not smaller than that present in the liquid. Thus, if the *trans* and *gauche* forms coexist in the liquid, they must also coexist in the complexes. Then the bands at 887 cm^{-1} (complex I) and 892 cm^{-1} (complex II) must be assigned to the *gauche* form, and the bands at

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1) Y. Kuroda and M. Kubo, *J. Polymer Sci.*, **26**, 323 (1957).

2) A. Grün and E. Boedecker, *Ber.*, **43**, 1051 (1910).

856 cm^{-1} (complex I) and 881 cm^{-1} (complex II) to the *trans* form. Relative intensities of these two bands attributed to different molecular forms do not change appreciably through the three states, liquid, complex I and complex II. Therefore, the assignment based on the coexistence of both *trans* and *gauche* forms leads to a very improbable conclusion that the equilibrium ratio of the two kinds of molecular form and hence the energy difference between them do not change through the three different states.

All the bands change their positions more or less on going from liquid to complex I and from complex I to complex II, indicating that some small differences in the molecular form are present among the three states. If the band at 881 cm^{-1} in liquid ethylene glycol is composed of two *gauche* vibrations, it is reasonably expected that these two separate from each other in the complexes because the CH_2 rocking frequencies are particularly sensitive to conformation[3]. Although the bands of the complexes at 887 and 892 cm^{-1} are much sharper than the band of the liquid at 881 cm^{-1}, there is no indication of such a separation. It is too accidental that the two *gauche* frequencies coincide through the three states.

From these considerations it is more reasonable to assign both the CH_2 rocking bands to the *gauche* form than to assign one of them to the *gauche* and the other to the *trans* form. The presence of only the *gauche* form is sufficient to account for the number of observed bands in the region 1500~800 cm^{-1}, ten for the liquid, fifteen for complex I, and thirteen for complex II. The number of fundamental frequencies expected to appear in this range are thirteen for the *gauche* form and six for the *trans* form.

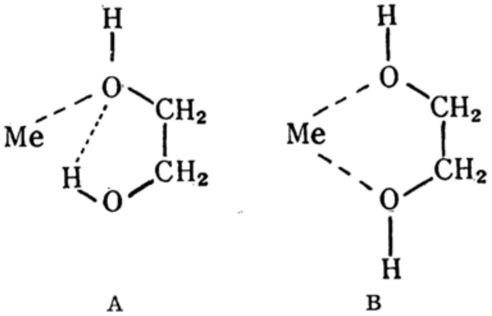

Fig. 2. Two types of coordination.

The ligand in complex I can be considered to coordinate in a manner shown in Fig. 2A. This is based on the existence of two OH bands (3330 and 3170 cm^{-1}) indicating the presence of two kinds of OH groups. [The OH frequencies of the coexisting water are higher (ca. 3400 cm^{-1}) even if they appear.] The ligand in complex II shows a single OH band and probably coordinates in a manner shown in Fig. 2B. Spectral features of the liquid ethylene glycol, especially the positions of the CH_2 rocking frequencies, are more close to those of complex I than to those of complex II. Thus one of the OH groups of ethylene glycol molecule seems to form an intramolecular hydrogen bond in the liquid state.

Besides ethylene glycol, diethylene glycol and triethylene glycol were also investigated. Again, there are significant changes of the spectra on passing from

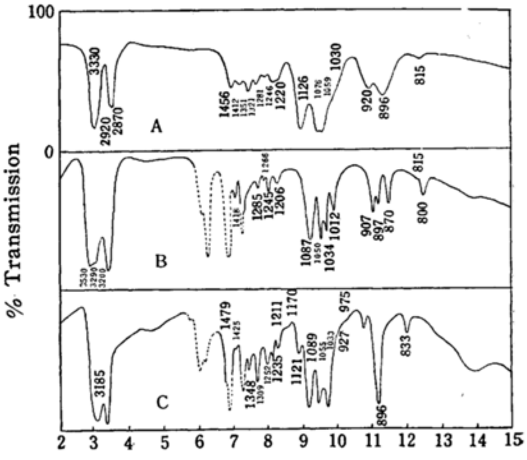

Fig. 3. Infrared spectra of diethylene glycol: (A) Liquid, (B) cobalt complex, (C) nickel complex (Nujol mull, ---- water and Nujol).

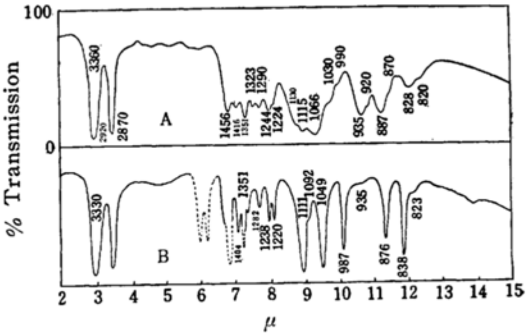

Fig. 4. Infrared spectra of triethylene glycol: (A) Liquid, (B) metal complex (Nujol mull, ---- water and Nujol).

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[3] I. Nakagawa and S. Mizushima, This Bulletin, 28, 589 (1955).

liquid to complex compound. In the case of triethylene glycol, there is no difference between the spectra of nickel and cobalt complexes. On the other hand, in the case of diethylene glycol, the spectrum of the nickel complex differs profoundly from that of the cobalt complex (Fig. 3).

Central Research Laboratories
Toyo Rayon Co.
Otsu, Shiga