The Viscosities of Aqueous Solutions Containing Metal Complexes. III. Iminodiacetato and Methyliminodiacetato Complexes[1]

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(Received April 21, 1972)

The viscosities of aqueous solutions containing a metal chelate formed with iminodiacetic acid (H_2ida) or *N*-methyliminodiacetic acid (H_2mida) were measured with Cannon-Fenske capillary viscometers. Measurements were made in a Shibata viscosity bath maintained at 25±0.01°C. The Jones-Dole viscosity *B*-coefficient of each bis-ida chelate is lower than that of the corresponding bis-mida chelate, as may be expected. The *B*-coefficients for the mono-ida and mono-mida chelates were not determined accurately and will not be reported here. The *B*-value of *cis*(*N*)-[Co(ida)$_2$]$^-$ is higher than that of the *trans*-isomer. This is probably associated with the fact that the *cis*-isomer interacts with the solvent more strongly than the *trans*-isomer.

In the previous papers of this series, the viscosities of the luteo-type Co(III) and Co(II) complexes and the ethylenediaminetetraacetato (edta^{4-}) complexes[2a] and *trans*-1,2-cyclohexanediaminetetraacetato (cydta^{4-}) complexes were reported.[2b] The results showed, above all, that the *B*-coefficient of the Co(III) chelate formed with edta^{4-} or cydta^{4-} was much lower than those of the corresponding divalent metal chelates, and suggested that there might be a marked difference between the structures of [CoL]$^-$ and [ML]$^{2-}$ (L: edta^{4-} or cydta^{4-}; M: divalent metal ion). In order to study this problem in more detail, a viscosity study was made of aqueous solutions of metal chelates formed with iminodiacetic acid and *N*-methyliminodiacetic acid.

Experimental

Measurements. The viscosity *B*-coefficients of Co(III) and six divalent metal chelates were determined by means of Cannon-Fenske capillary viscometers with efflux times of ca. 520 and 600 sec respectively for distilled water. The viscosities and densities of the solutions were measured in a Shibata viscosity bath maintained at 25±0.01°C. The efflux times, measured with stopwatches to 0.1 sec, were easily reproducible to 0.2 sec.

Chelating Agents. Dotite H_2ida and Aldrich H_2mida were used. The analytical results for the C, H, and N contents showed these agents to be satisfactorily pure.

Complexes. The *cis*(*N*)- and *trans*(*N*)-potassium bis(iminodiacetato)cobaltates(III) were prepared following the method in the literature.[3] Divalent metal chelates of H_2ida and H_2mida were not isolated as crystals. Instead, solutions of these chelates were made up using metal nitrate (or chloride) and the K_2ida or K_2mida stock solutions.

Calculation. For each of the chelates studied, the relative viscosity, η/η_0, of aqueous solutions was expressed by the Jones-Dole equation:[4]

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc \qquad (1)$$

where η and η_0 are the viscosities of the solution and of water respectively, and where c is the molar concentration of the solute. The coefficients, A and B, which are constants characteristic of the solute, were fully discussed by Gurney.[5] The *B*-coefficient was evaluated by a plot of $((\eta/\eta_0)-1)/\sqrt{c}$ *vs.* $\sqrt{c}$. A straight line was obtained for each case studied at concentrations below 0.06 mol/l. The slope of the resulting straight line gives the value of the *B*-coefficient for the solute. Because it has been shown to be true, for a wide variety of solutions, that B is composed additively of contributions from each of the solute species present in a solution, the *B*-value of the complex ion is obtained by subtracting a relatively small correction for the co-existing ionic species.

Results and Discussion

As both H_2ida and H_2mida are tridentate chelating agents, two kinds of chelates are formed following these equations:

$$M + L \rightleftarrows ML \qquad (2)$$

$$ML + L \rightleftarrows ML_2 \qquad (3)$$

where M is a metallic cation and where L is ida^{2-} or mida^{2-}. Accordingly, there are two kinds of viscosity *B*-coefficients, B_{ML} and B_{ML_2}, to be measured. Though we tried to obtain both of them, only the latter was determined accurately. Concerning the coefficient, B_{ML}, for the mono-chelate, only a rough value could be estimated because of several difficulties involved. For instance, in the lower pH range the dissociation of the chelate ML, that is, the reverse reaction of Eq. (2), occurs. This might tend to increase the viscosity of the solution. Next, in the higher pH range hydroxo-complexes, which might be formed by base hydrolysis, should be taken into account, and the chelate ML_2 must be considered to be present in the solution following Eq. (3), even though the solution contains stoichiometrical quantities of the metal ion and ligand. Furthermore, the B_{ML}-value is lower than the B_{ML_2}-value, and so more concentrated solutions should be used for the viscosity measurements of the mono-chelate. However, because of the low solubility of ML, which has no ionic charge, accurate measurements were impossible.

The *B*-coefficients of the bis-chelate ML_2 studied here are listed in Table 1. The pH value of each solution

1) Presented at the Symposium on Coordination Chemistry of the Chemical Society of Japan, Kyoto, Oct. 1968, and Tokyo, Nov. 1970.

2) a) M. Yasuda, This Bulletin, **41**, 139 (1968). b) *ibid.*, **42**, 2547 (1969).

3) J. Hidaka, Y. Shimura, and R. Tsuchida, *ibid.*, **35**, 567 (1962).

4) G. Jones and M. Dole, *J. Amer. Chem. Soc.* **51**, 2950 (1929).

5) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Company, New Yrok (1953).

Table 1. Viscosity B-coefficients of iminodiacetato and methyliminodiacetato complexes (25°C)

Metal	B(ida)	B(mida)
Cu^{2+}	0.72	0.83
Ni^{2+}	0.73	0.85
Co^{2+}	0.72	0.84
Zn^{2+}	0.80	0.88
Cd^{2+}	0.90	—
Pb^{+2+}	0.75	—
Co^{3+}	*cis* 0.49	—
	trans 0.42	—

used for viscosity measurement was between 7~9; the higher pH range was used for the chelate with a lower stability constant. Since the ida^{2-} and $mida^{2-}$ chelates have rather large stability constants, it may be assumed that there is no appreciable change in the viscosity of the solution due to the dissociation of the chelate in the pH range studied.

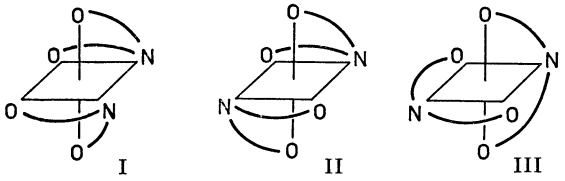

Fig. 1. The three possible geometric isomers of $[M(ida)_2]^{n-}$.

Three geometrical isomers are possible for the bis-chelate, $[M(ida)_2]^{n-}$ or $[M(mida)_2]^{n-}$, as is shown in Fig. 1. Two of them are *trans*(*N*)-forms, while the third is the *cis*(*N*)-form. However, only two isomers are isolated for Co(III)-ida chelates; one is *cis*(*N*) and the other is *trans*(*N*). The latter was assigned to Structure II by Hidaka *et al.* from the bond angles of a nitrogen atom of the ligand.[3] Later Cooke[6] tried several times to get the meridional *trans*-isomer (isomer III) by the elution of a mixture of the isomers from a Dowex 2-X8 anion-exchange resin in the chloride form, using NH_4Cl as the eluting agent. However, in no case was any evidence for a second *trans* isomer obtained. As he stated, the existence of this chelate can not be ruled out, and yet it is not considered that this chelate may be present appreciably. On the other hand, in the case of the bis-mida complexes of Co(III) the *trans*(*N*)-isomer alone is isolated.[6] The absence of the *cis*-isomer in this case and the dominance of the *trans*-isomer in the Co(III)-ida chelates were attributed to the presence of steric interactions between the amine groups in the *cis*-isomer. The values listed in Table 1 are, therefore, with the exception of Co(III) complexes, those for a mixture of *cis*- and *trans*-isomers which might be present in the solutions, although the values for the mida-chelates are considered to be practically those for the *trans*-isomers.

As may be seen from Table 1, the Jones-Dole viscosity *B*-coefficient of each ida-chelate is lower than that of the corresponding mida-chelate, as may be expected. The differences in *B*-values caused by the introduction of the methyl group on the amino nitrogen atom of ida^{2-} are 0.11~0.12 for Cu^{2+}, Ni^{2+}, and Co^{2+} complexes, and 0.08 for Zn^{2+}. That is, the differences are very much the same, except for the Zn^{2+} complex. However, as has been mentioned above, the differences may be caused by the *cis-trans* geometric effects as well as by the effect of the methyl group. Therefore, the lower value for the Zn^{2+} chelate can not be discussed easily. It is clear that there exists a definite difference between *cis*- and *trans*-$[Co(ida)_2]^-$. The higher value found for the *cis*-isomer is probably associated with the fact that this species interacts with the solvent more strongly than does the *trans*-isomer, evidently as a result of the permanent dipole moment associated with the *cis*-configuration.

The viscosity *B*-values for the edta- and cydta-chelates have been reported by Charles[7] and by one of the present authors[2] respectively. The order of the *B*-values for each divalent metal is as follows:

$$[M(ida)_2]^{2-} < [M(mida)_2]^{2-} \sim [Medta]^{2-} < [Mcydta]^{2-}$$

This meets our expectations. Now, it may be noted that the bis(mida)-chelates have very much the same values as the corresponding edta-chelates. While the edta-chelates have an enforced *cis*(*N*)-configuration about the metal, the mida-chelates probably have the *trans*-configuration. Therefore, it may be supposed that each mida-chelate has a lower *B*-coefficient than the corresponding edta-chelate, because the $edta^{4-}$ anion is practically equivalent to two anions of $mida^{2-}$ from the standpoint of molecular size. Therefore, the equality in *B*-values between the edta- and bis(mida)-chelates might be explained as follows; for the divalent metal chelates, which are much less stable than the corresponding Co(III)-chelate, there is not so large a difference in *B*-values between the *cis*- and *trans*-configurations, or the special stability of the edta-complex, compared with that of the mida-complex, plays a part, or some other factors, for example, the geometric configuration, are related to it. In connection with the second point mentioned above, metals with a greater affinity for the ligand generally form chelates with smaller *B*-values, as has been reported previously.[2] This applies also to the ida- and mida-chelates, as may be seen from Fig. 2; the ordinates are the *B*-values of

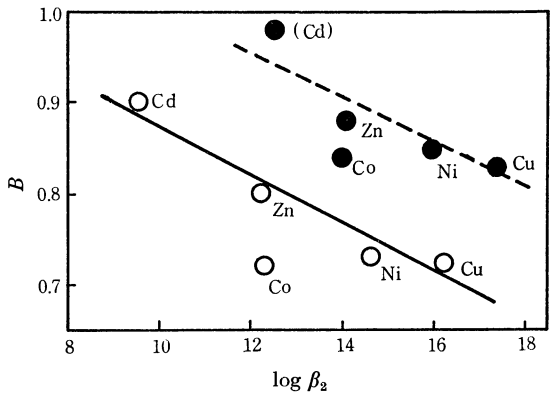

Fig. 2. Relation between the *B*-coefficient and the stability constant β_2: —○— ida-complex, —●— mida-complex.

6) D. W. Cooke, *Inorg. Chem.*, **5**, 1141 (1966).

7) R. G. Charles, *J. Amer. Chem. Soc.*, **78**, 3946 (1956).

the ida- or mida-chelates,[8] and the abscissas are the stability constants of these chelates.[9]

Finally, the *B*-coefficients of the Co(III) chelates will be discussed. The Co(III)-mida chelate, *trans*-K[Co(mida)$_2$], was prepared in a fashion analogous to that used for the *trans*-ida chelate, using an appropriate amount of H_2mida. However, its low solubility did not allow viscosity measurements. The *B*-values of the Co(III)-ida chelates are much lower than that of any of the divalent metal ida-chelates studied, as in the cases of the edta- and cydta-chelates. The solution of the *cis*-isomer showed no appreciable change in viscosity for at least 24 hr; thereafter the viscosity gradually decreased, probably because of the conversion of the *cis*- to the *trans*-configuration. It was unexpected that Co(III)-ida chelates have higher *B*-values than the Co(III)-edta chelate. This cannot be explained esaily, but we consider, at present, that the smaller *B*-value of the Co(III)-edta chelate might be caused by the extraordinary stability of the chelate, because chelates having higher stability constants have, in general, lower *B*-values, as has been mentioned above.

8) The *B*-value of the $[Cd(mida)_2]^{2-}$ anion (and also of $[Pb(mida)_2]^{2-}$) was not obtained because of its low solubility. Hence the value of $[Cdedta]^{2-}$ is plotted instead in Fig. 2, because $[M(mida)_2]^{2-}$ and $[Medta]^{2-}$ have very much the same *B*-coefficients for the divalent metal chelates studied.

9) a) S. Chaberek and A. E. Martell, *J. Amer. Chem. Soc.*, **74**, 5052 (1952). b) G. Schwarzenbach, G. Anderegg, W. Schneider, and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955).