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CONFORMATIONAL INVERSION OF 2,2'-BIPYRIDYL N,N'-DIOXIDE (bpdo) CHELATE RINGS IN THE $[Cr(acetylacetonato)(bpdo)_2]^{2+}$ ION

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The $[Cr(acetylacetonato)(bpdo)_2](ClO_4)_2 \cdot H_2O$ complex (bpdo= 2,2'-bipyridyl N,N'-dioxide) crystallizes in the lel_2 ($\Delta(\lambda\lambda)$, $\Lambda(\delta\delta)$) isomer. This isomer isomerizes to the lel·ob ($\Delta(\lambda\delta)$, $\Lambda(\delta\lambda)$) isomer in aqueous solution with the rate constant of 3.31×10^{-3} s^{-1} at 295.2 K, the rate constant for racemization ($\Delta \rightleftarrows \Lambda$) being 1.08×10^{-4} s^{-1} at 295.2 K.

2,2'-Bipyridyl N,N'-dioxide (bpdo) forms a pair of chiral seven-membered chelate rings, δ and λ upon coordination (Fig. 1).[1] A bpdo chelate ring will be flexible and change its conformation ($\delta \rightleftarrows \lambda$) with ease.[2] This letter is concerned with the conformational inversion of bpdo chelate rings in $[Cr(acac)(bpdo)_2]^{2+}$ (acac= acetylacetonate ion). Since the acac chelate ring is assumed to be planar, this complex can have three racemic pairs of diastereomers (conformational isomer), lel_2 ($\Delta(\lambda\lambda)$, $\Lambda(\delta\delta)$), lel·ob ($\Delta(\lambda\delta)$, $\Lambda(\delta\lambda)$), and ob_2 ($\Delta(\delta\delta)$, $\Lambda(\lambda\lambda)$), where lel and ob denote the λ (or δ) ligand in the Δ (or Λ) and Λ (or Δ) complexes, respectively.[2]

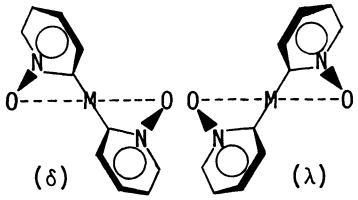

Fig. 1. Conformation of bpdo.

The $[Cr(acac)(bpdo)_2]^{2+}$ complex was prepared by heating a mixture of $[Cr(acac)_3]$ and bpdo (1:2) in 90% ethanol adjusted to pH 2 with HCl, purified by SP-Sephadex C-25 column chromatography, and isolated as perchlorate. Found: C, 40.51; H, 2.91; N, 7.24%. Calcd for $[Cr(acac)(bpdo)_2](ClO_4)_2 \cdot H_2O$: C, 40.33; H, 3.39; N, 7.53%. The complex was resolved with $K_2[Sb_2(d\text{-tartrato})_2] \cdot 3H_2O$. The less soluble complex d-tartratoantimonate was converted into perchlorate by treating with $NaClO_4$ and a small amount of cold water. Found: C, 40.41; H, 2.94; N, 7.36%. Calcd for $(-)_{589}$-$[Cr(acac)(bpdo)_2](ClO_4)_2 \cdot H_2O$: C, 40.33; H, 3.39; N, 7.53%. The complex in aqueous solution is photosensitive causing hydrolysis and all the experiments should be carried out in the dark.

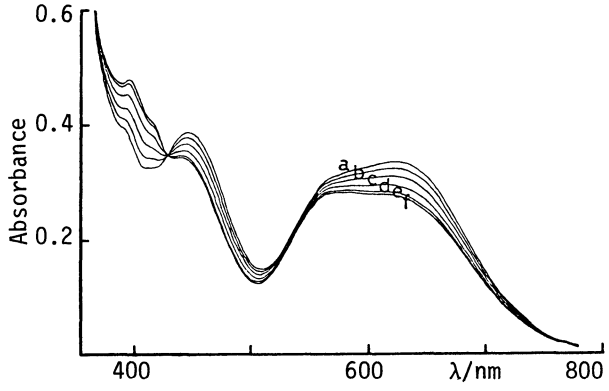

Fig. 2. Absorption spectral change of $[Cr(acac)(bpdo)_2](ClO_4)_2 \cdot H_2O$ in aqueous solution (pH 7) at 291.2 K. Reaction time (min): a, 1; b, 3; c, 6; d, 12; e, 24; f, ∞.

Both rac- and $(-)_{589}$-$[Cr(acac)(bpdo)_2](ClO_4)_2$-

H_2O in aqueous solutions show a rapid absorption spectral change with an isosbestic point at 427 nm (Fig. 2). An aqueous solution of the $(-)_{589}$-isomer loses the optical activity in two steps with different rates, the first rapid (step A) and the subsequent slow (step B) steps (Fig. 3). In step A, the decrease in optical activity accompanies the spectral change, while no spectral change is observed in step B. These results suggest that step A involves only reaction of conformational inversion of bpdo chelate rings, $\delta \rightleftarrows \lambda$, and step B both reactions of this inversion and racemization of the complex, $\delta \rightleftarrows \lambda$ and $\Delta \rightleftarrows \Lambda$.

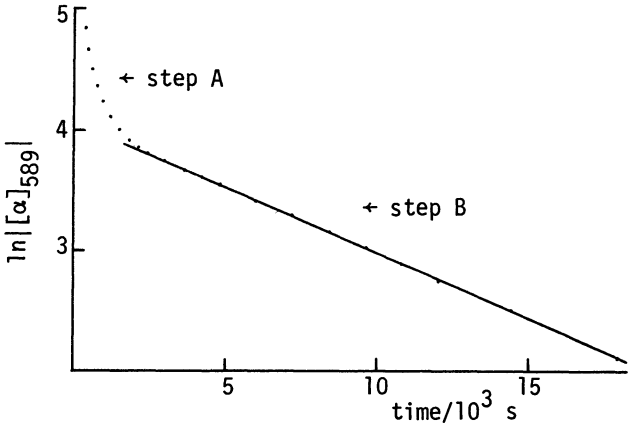

Fig. 3. Decrease in optical rotation of $(-)_{589}$-$[Cr(acac)(bpdo)_2](ClO_4)_2 \cdot H_2O$ with time in aqueous solution (pH 7) at 295.2 K.

The species corresponding to absorption spectra a and f in Fig. 2 were assigned by comparing these spectra with those of the 3,3'-dimethyl-2,2'-bipyridyl N,N'-dioxide (mbdo)[3] complexes. The mbdo chelate ring is not interconvertible between δ and λ.[3] The complex of rac-mbdo forms two isomers, I and II. Isomers I and II can be easily assigned to lel_2-$[Cr(acac)(R\text{- or }S\text{-mbdo})_2]^{2+}$ and lel·ob-$[Cr(acac)(R\text{-mbdo})(S\text{-mbdo})]^{2+}$, respectively, by comparing their properties with those of $[Cr(mbdo)_3]^{3+}$.[3] The ob_2 isomer is not formed probably because of a crowded structure as indicated by molecular models. Found for isomer I: C, 43.50; H, 3.90; N, 6.77%. Calcd for $[Cr(acac)(R\text{- or }S\text{-mbdo})_2](ClO_4)_2 \cdot H_2O$: C, 43.51; H, 4.16; N, 7.00%. Found for isomer II: C, 42.53; H, 4.46; N, 6.77%. Calcd for $[Cr(acac)(R\text{-mbdo})(S\text{-mbdo})](ClO_4)_2 \cdot 2H_2O$: C, 42.56; H, 4.31; N, 6.85%. Absorption spectra a and f of the bpdo complex quite resemble those of the lel_2 and lel·ob isomers of the mbdo complex. Thus it is concluded that $[Cr(acac)(bpdo)_2](ClO_4)_2 \cdot H_2O$ crystallizes in the lel_2 isomer and isomerizes to the lel·ob isomer in aqueous solution inverting the conformation of bpdo chelate rings.

The conformational isomerization was studied in aqueous solution of the complex (ca. 10^{-3} mol dm^{-3}) with ionic strength of 0.10 (NaCl) in the pH and temperature ranges of 1 - 7 and 289.0 - 307.8 K, respectively, and with or without addition of the free acac or bpdo ligand. The rates obeyed the first-order kinetic law and were independent of pH and concentrations of the free ligands. The first-order rate constant is $(3.31\pm0.09)\times10^{-3}$ s^{-1} at 295.2 K, and the values of the activation enthalpy and entropy are (75±4) $kJmol^{-1}$ and (-38±12) $JK^{-1}mol^{-1}$, respectively. For racemization ($\Delta \rightleftarrows \Lambda$) of the complex the first-order rate constant of $(1.08\pm0.06)\times10^{-4}$ s^{-1} at 295.2 K was also obtained by examining the decrease in optical rotation of the $(-)_{589}$-isomer in step B in Fig. 3.

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References

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