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Preparation and Stereochemistry of Bis(1,10-phenanthroline)- and Bis(2,2′-bipyridine)chromium(III) Complexes Containing 2,2′-Bipyridine *N,N′*-Dioxide or Its 3,3′-Dimethyl Derivative

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Bis(1,10-phenanthroline)- and bis(2,2′-bipyridine)chromium(III) complexes containing a seven-membered chelate ligand, 2,2′-bipyridine *N,N′*-dioxide(bpdo) or 3,3′-dimethyl-2,2′-bipyridine *N,N′*-dioxide(mbdo) were prepared. Each complex gave only one of two possible pairs of enantiomers resolved by SP-Sephadex column chromatography. On the basis of the circular dichroism spectra, molecular models, and recovery of the optically active free mbdo ligand from the resolved mbdo complexes, it was found that all the enantiomeric pairs consist of $\Delta(\delta)$ and $\Lambda(\lambda)$ isomers involving the skew dioxide chelate ligands in the *ob* configuration.

A seven-membered, skew chelate conformation of 2,2′-bipyridine *N,N′*-dioxide (bpdo) in metal complexes has been confirmed by X-ray analysis of $[La(bpdo)_4](ClO_4)_3$.1) The skew conformation can exist in a pair of enantiomers, δ and λ (Fig. 1). We found that tris-type chromium(III) complexes with bpdo2) and its derivative, 3,3′-dimethyl-2,2′-bipyridine *N,N′*-dioxide (mbdo)3) give one and three diastereomers, respectively, of four possible ones, *lel*$_3$($\Delta(\lambda\lambda\lambda)$, $\Lambda(\delta\delta\delta)$), *lel*$_2$*ob*($\Delta(\lambda\lambda\delta)$, $\Lambda(\delta\delta\lambda)$), *lelob*$_2$($\Delta(\lambda\delta\delta)$, $\Lambda(\delta\lambda\lambda)$), and *ob*$_3$($\Delta(\delta\delta\delta)$, $\Lambda(\lambda\lambda\lambda)$). Δ and Λ denote the absolute configuration of a chromium(III) ion and *lel* and *ob* the diastereoisomerism of a complex with skew chelate rings analogous to that in $[M(en)_3]^{n+}$ (en=ethylenediamine).4) The number of diastereomers formed in the dioxide complexes is related to whether a dioxide chelate ring can change the skew conformation between δ and λ.

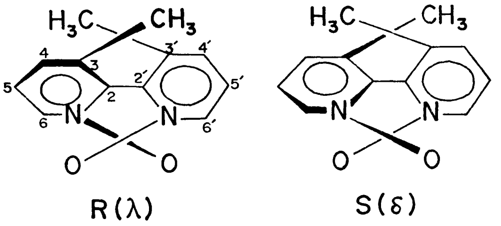

Fig. 1. A pair of enantiomers of mbdo.

This paper describes the preparation and stereochemistry of bis-phen and bis-bpy chromium(III) complexes containing bpdo or mbdo, where phen and bpy denote 1,10-phenanthroline and 2,2′-bipyridine, respectively. Since both phen and bpy ligands form planar chelate rings upon coordination to a metal ion, each of the complexes can have two diastereomers, *lel*($\Delta(\lambda)$, $\Lambda(\delta)$) and *ob*($\Delta(\delta)$, $\Lambda(\lambda)$). Bis(α-diimine) metal complexes containing a seven-membered chelate ligand do not seem to have been reported except for $[Co(bpy)_2(2,2'\text{-diaminobiphenyl})]^{3+}$ whose stereochemistry was not fully characterized because of instability.5)

Experimental

The new complexes are photosensitive causing hydrolysis and the following procedures should be carried out in the dark.

$[Cr(phen)_2(bpdo)]^{3+}$ and $[Cr(phen)_2(mbdo)]^{3+}$. $[CrCl_2(phen)_2]Cl\cdot 2H_2O$6) (2.0 g, 3.6 mmol) was added to an aqueous solution (50 cm^3) containing $bpdo\cdot H_2O$7) (0.75 g, 3.6 mmol) or racemic mbdo3) (0.9 g, 4.2 mmol). The solution was adjusted to pH *ca.* 2 with hydrochloric acid in order to avoid the formation of hydroxo complexes, kept at 85 °C with stirring for 6 h, and cooled to room temperature. The resulting solution was diluted with water (0.5 dm^3) and passed through a short column (ϕ 2.7×5 cm) of SP-Sephadex C-25. The resin which adsorbed the red orange product was loaded on a column (ϕ 2.7×80 cm) of SP-Sephadex C-25 and the complexes were eluted with an aqueous 0.2 mol/dm^3 Na_2SO_4 solution adjusted to pH 2 with hydrochloric acid. The column showed two bands, red and orange, the red band being eluted faster than the orange one. The red eluate was found to involve $[Cr(H_2O)_2(phen)_2]^{3+}$ from the absorption spectrum.8) The orange eluate was diluted with water and poured again on a small column (ϕ 2.7×3 cm) of SP-Sephadex C-25, and the complex adsorbed was eluted with an aqueous 0.5 mol/dm^3 $NaClO_4$ solution. The eluate gave an orange precipitate on standing at room temperature, which was collected and washed with a small amount of water. Recrystallization from hot water gave orange needle crystals. Yield: bpdo-complex, 0.7 g (22%); mbdo-complex, 0.6 g (17%).

$[Cr(bpy)_2(bpdo)]^{3+}$ and $[Cr(bpy)_2(mbdo)]^{3+}$. Orange needle crystals of the complexes were obtained by the same method as that for the corresponding phen complexes using $[CrCl_2(bpy)_2]Cl\cdot 2H_2O$9) (2.7 g, 5.3 mmol) and $bpdo\cdot H_2O$ (1.2 g, 5.8 mmol) or racemic mbdo (1.3 g, 6.0 mmol). Yield: bpdo-complex, 1.9 g (41%); mbdo-complex, 0.9 g (18%).

Each of the phen and bpy complexes gave only one diastereomer, no indication for the formation of another isomer being detected on column chromatography.

Resolution of the Complexes. All the complexes were completely resolved by SP-Sephadex column chromatography. Each complex was loaded on a column (ϕ 2.7×130 cm) of SP-Sephadex C-25. By elution with a 0.15 mol/dm^3 sodium $(+)_{589}$-tartratoantimonate(III) solution, the column gave two separate bands of $(+)_{589}$- and $(-)_{589}$-isomers, the former being eluted faster. Each isomer was isolated as perchlorate and recrystallized from hot water by the same method as that for the racemate. Analytical data of the racemic and optically active complexes are given in Table 1.

Recovery of mbdo from the Complexes. The optically active free mbdo ligand was recovered from $(-)_{589}$-$[Cr(phen)_2(mbdo)]^{3+}$ and $(-)_{589}$-$[Cr(bpy)_2(mbdo)]^{3+}$ by the same method as that for $[Cr(mbdo)_3]^{3+}$.3) Both mbdo recovered gave positive rotation at 589 nm.

Measurements. Absorption and circular dichroism (CD) spectra of the complexes in aqueous solutions were obtained

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TABLE 1. ANALYTICAL DATA

Complexes	C/%	H/%	N/%
$[Cr(phen)_2(bpdo)](ClO_4)_3$	45.48 (45.42)	2.59 (2.70)	9.41 (9.35)
$(-)_{589}$-$[Cr(phen)_2(bpdo)](ClO_4)_3\cdot 3H_2O$	42.91 (42.85)	2.85 (3.18)	9.19 (8.82)
$[Cr(phen)_2(mbdo)](ClO_4)_3\cdot 2H_2O$	44.97 (44.89)	2.99 (3.36)	8.97 (8.73)
$(-)_{589}$-$[Cr(phen)_2(mbdo)](ClO_4)_3\cdot 2H_2O$	44.84 (44.89)	2.70 (3.36)	8.97 (8.73)
$[Cr(bpy)_2(bpdo)](ClO_4)_3\cdot H_2O$	41.63 (41.46)	2.71 (3.02)	9.50 (9.67)
$(-)_{589}$-$[Cr(bpy)_2(bpdo)](ClO_4)_3\cdot H_2O$	41.28 (41.46)	3.05 (3.02)	9.22 (9.67)
$[Cr(bpy)_2(mbdo)](ClO_4)_3\cdot 3H_2O$	41.22 (41.19)	3.18 (3.68)	8.73 (9.01)
$(-)_{589}$-$[Cr(bpy)_2(mbdo)](ClO_4)_3\cdot 5H_2O$	39.28 (39.66)	3.56 (3.96)	8.74 (8.67)

( ): Calcd, bpdo=$C_{10}H_8N_2O_2$, mbdo=$C_{12}H_{12}N_2O_2$.

with a Hitachi 323 spectrophotometer and a Jasco J-40 spectropolarimeter, respectively. Optical rotations were measured with a Jasco DIP-4 polarimeter.

Results and Discussion

Each of the four new complexes, $[Cr(L)_2(bpdo)]^{3+}$ and $[Cr(L)_2(mbdo)]^{3+}$ (L=phen, bpy) gives only one pair of enantiomers stereoselectively by the reaction of the corresponding dichloro complex with the dioxide ligand in water, although there are two possible pairs of enantiomers, *lel*($\Delta(\lambda)$, $\Lambda(\delta)$) and *ob*($\Delta(\delta)$, $\Lambda(\lambda)$) (Fig. 1). The enantiomers are completely resolved by SP-Sephadex column chromatography using sodium $(+)_{589}$-tartratoantimonate(III) as an eluent. The complexes in aqueous solutions are stable in the dark, undergoing gradual hydrolysis in the light.

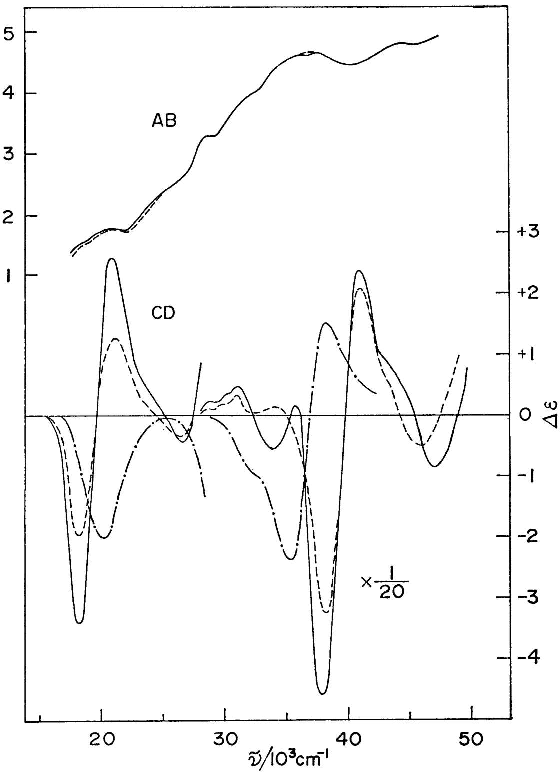

Fig. 2. Absorption and CD spectra of $(-)_{589}$-$[Cr(phen)_2(mbdo)]^{3+}$ (——) and $(-)_{589}$-$[Cr(phen)_2(bpdo)]^{3+}$ (-----), and CD spectrum of Δ-$[Cr(ox)(phen)_2]^+$ (–•–•–).[12)]

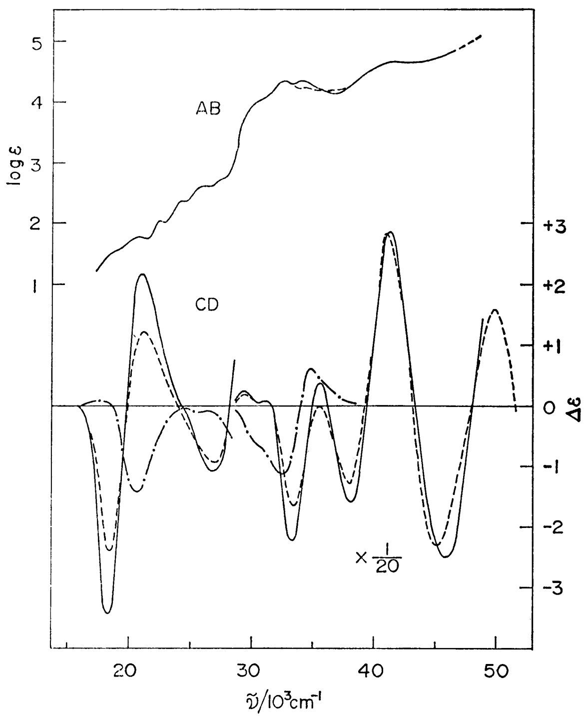

Fig. 3. Absorption and CD spectra of $(-)_{589}$-$[Cr(bpy)_2(mbdo)]^{3+}$ (——) and $(-)_{589}$-$[Cr(bpy)_2(bpdo)]^{3+}$ (-----), and CD spectrum of Δ-$[Cr(ox)(bpy)_2]^+$ (–•–•–).[12)]

Absorption and CD spectra of $(-)_{589}$-$[Cr(phen)_2(L)]^{3+}$ are shown in Fig. 2 and those of $(-)_{589}$-$[Cr(bpy)_2(L)]^{3+}$ in Fig. 3 (L=bpdo, mbdo). The spectral data are given in Table 2. The absorption spectra of the bpdo and mbdo complexes are nearly the same over the whole region. The bands at 20750 cm^{-1} with a shoulder (18500 cm^{-1}) and *ca.* 20850 cm^{-1} with a shoulder (18900 cm^{-1}) for the phen and bpy complexes, respectively, can be assigned to the first absorption band ($^4T_{2g}\leftarrow{}^4A_{2g}$), although the assignments are somewhat ambiguous because of adjacent strong charge-transfer bands. These first absorption bands are shifted to small wavenumbers by 450—500 cm^{-1} from those of the corresponding oxalato complexes.[10)] In the ultraviolet region, all the complexes show complicated spectra due to absorptions arising from intramolecular transitions of the ligands and charge-transfer transitions from the ligands to a Cr(III) ion.

The CD spectra of all the $(-)_{589}$-isomers show a very similar pattern in the region of the first absorption band. The bpdo and mbdo complexes give similar CD spectra over the whole region. This suggests that all the $(-)_{589}$-isomers have the same absolute configuration including chirality of a skew dioxide chelate ring. The CD spectra of the dioxide complexes are compared with those of Δ-$[Cr(ox)(phen)_2]^+$ and Δ-$[Cr(ox)(bpy)_2]^+$ in Figs. 2 and 3, respectively. The absolute configurations

TABLE 2. ABSORPTION AND CD SPECTRAL DATA

	Absorption $\tilde{\nu}/10^3$ cm^{-1} (log ε)	CD $\tilde{\nu}/10^3$ cm^{-1} ($\Delta\varepsilon$)
$(-)_{589}$-[Cr(phen)$_2$-(bpdo)]$^{3+}$	13.92 ($\bar{1}$.91)	13.77 (−0.013)
	14.62 ($\bar{1}$.99)	14.27 (−0.013)
	18.5 (1.5) sh	18.15 (−1.94)
	20.75 (1.75)	21.16 (+1.28)
	28.41 (3.32)	26.32 (−0.34)
	32.5 (4.1) sh	28.41 (+2.82)
	36.4 (4.6) sh	29.85 (+3.96)
	37.24 (4.63)	30.86 (+6.74)
	40.8 (4.6) sh	34.36 (+2.57)
	44.54 (4.86)	38.02 (−64.6)
		40.90 (+40.2)
		42.5 (+17) sh
$(-)_{589}$-[Cr(phen)$_2$-(mbdo)]$^{3+}$	13.79 ($\bar{1}$.91)	13.74 (−0.014)
	14.64 ($\bar{1}$.99)	14.24 (−0.014)
	18.5 (1.6) sh	18.15 (−3.44)
	20.75 (1.77)	21.05 (+2.60)
	28.37 (3.30)	26.39 (−0.43)
	32.5 (4.1) sh	28.49 (+4.76)
	36.23 (4.62)	29.9 (+6.7) sh
	37.31 (4.63)	30.86 (+10.5)
	44.54 (4.84)	33.78 (−11.6)
		35.65 (+3.62)
		37.88 (−91.5)
		40.82 (+48.0)
		43.96 (+13.6)
		46.95 (−17.7)
$(-)_{589}$-[Cr(bpy)$_2$-(bpdo)]$^{3+}$	13.89 ($\bar{1}$.60)	13.77 (−0.010)
	14.62 ($\bar{1}$.71)	14.27 (−0.014)
	18.9 (1.6) sh	18.28 (−2.37)
	20.88 (1.78)	21.28 (+1.22)
	22.32 (2.03)	26.67 (−0.92)
	23.92 (2.36)	29.41 (+4.40)
	25.50 (2.56)	31.25 (+1.52)
	27.1 (2.7) sh	33.28 (−33.9)
	30.3 (4.0) sh	37.88 (−25.8)
	32.26 (4.34)	41.07 (+56.7)
	34.3 (4.3) sh	44.84 (−45.7)
	40.98 (4.63)	50.00 (+32.2)
$(-)_{589}$-[Cr(bpy)$_2$-(mbdo)]$^{3+}$	13.79 ($\bar{1}$.54)	13.81 (−0.014)
	14.58 ($\bar{1}$.63)	14.21 (−0.018)
	18.9 (1.6) sh	18.32 (−3.42)
	20.83 (1.76)	21.14 (+2.20)
	22.27 (2.02)	26.81 (−1.05)
	23.89 (2.36)	29.33 (+4.82)
	25.48 (2.57)	31.01 (+0.67)
	27.0 (2.7) sh	33.17 (−45.1)
	30.5 (4.0) sh	35.59 (+7.33)
	32.25 (4.33)	38.10 (−31.6)
	33.78 (4.34)	41.32 (+57.6)
	41.24 (4.63)	46.08 (−50.5)

sh: shoulder

of the oxalato complexes were assigned on the basis of the CD pattern in the regions of the first spin-allowed d-d,[11–13] the spin-forbidden d-d,[13] and the π*←π transitions.[11,12] There seems to be little similarity in CD spectra between the dioxide and the oxalato complexes. The dioxide complexes show two CD components of similar strength with opposite signs in the region of the first absorption band; it is not clear which component is dominant. In addition the complexes do not exhibit typical exciton CD bands in the region of the π*←π transitions of the phen (*ca.* 37000 cm^{-1}) or bpy (*ca.* 33000 cm^{-1}) ligand, although the spectra of the bpy complexes in this region somewhat resemble the spectrum of Δ-[Cr(ox)(bpy)$_2$]$^+$. Thus the absolute configuration of the dioxide complexes can not be assigned without ambiguity from the CD spectra in the region given. However, CD signs in the region of the spin-forbidden d-d transitions can be utilized for assigning the absolute configuration of chromium(III) complexes.

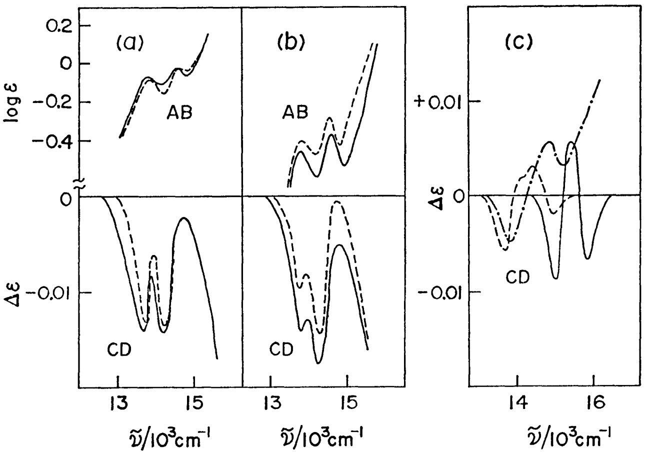

Fig. 4. Absorption and CD spectra in the region of the spin-forbidden d-d transitions. (a) $(-)_{539}$-[Cr(phen)$_2$(mbdo)]$^{3+}$ (——) and $(-)_{589}$-[Cr(phen)$_2$(bpdo)]$^{3+}$ (-----). (b) $(-)_{589}$-[Cr(bpy)$_2$(mbdo)]$^{3+}$ (——) and $(-)_{589}$-[Cr(bpy)$_2$(bpdo)]$^{3+}$ (-----). (c) Δ-[Cr(en)$_3$]$^{3+}$ (——),[13] Δ-[Cr(ox)(phen)$_2$]$^+$ in 70% HClO$_4$ (-·-·-),[13] and Δ-[Cr(ox)(bpy)$_2$]$^+$ (-----).[13]

Kaizaki *et al.*[14] found that in tris-chelate chromium(III) complexes except for a few complexes such as those with biguanide or acetylacetonate, the smallest wavenumber CD band in the region of the spin-forbidden d-d transitions shows the same sign as that of a dominant CD band in the region of the first spin-allowed d-d transitions. The smallest wavenumber CD bands of all the $(-)_{589}$-dioxide complexes give a negative sign in the region of the spin-forbidden bands (Fig. 4). Thus dominant CD bands of the isomers in the region of the first spin-allowed band should be negative, and the isomers can be assigned to the Δ-configuration.[15] The Δ-isomers of [Cr(ox)(L)$_2$]$^+$ (L=phen, bpy) and a typical tris-chelate complex, [Cr(en)$_3$]$^{3+}$ (en=ethylenediamine) also give negative CD bands at the smallest wavenumber in the region of the spin-forbidden d-d transitions.

The $(-)_{589}$-dioxide complexes can have two diastereomers, Δ(δ)(*ob*) and Δ(λ)(*lel*). Since the free mbdo ligand is optically stable,[3] it was recovered from $(-)_{589}$-Δ-isomers of the phen and bpy complexes in order to know the absolute configuration. Both mbdo recovered show positive rotation at 589 nm. The $(+)_{589}$-mbdo

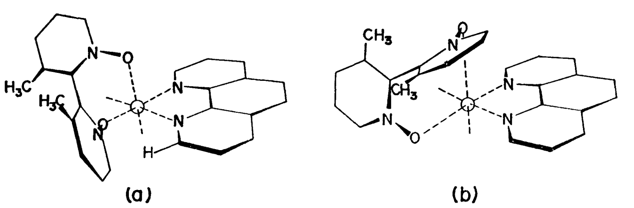

Fig. 5. Schematic drawing of the two diastereomers of Δ-$[Cr(phen)_2(mbdo)]^{3+}$; (a) $\Delta(\lambda)$(*lel*), (b) $\Delta(\delta)$(*ob*).

ligand is the same as that recovered from $(+)_{589}$-$[Cr(mbdo)_3]^{3+}$ which was assigned to the $\Lambda(\delta\delta\delta)(lel_3)$-configuration.[3] Thus the $(-)_{589}$-Δ-isomers involve mbdo of the $\delta(S)$ chirality to form a $\Delta(\delta)$(*ob*) diastereomer. Since the bpdo complexes give CD spectra similar to those of the mbdo complexes over the whole region, it is concluded that the bis-phen and bis-bpy chromium(III) complexes of these dioxides form only an *ob* isomer stereoselectively. Such stereoselectivity is in contrast with the fact that the stability of complexes with skew chelate rings decreases with an increase in the number of *ob* ligands.[4] The $[Co(en)_2(L)]^{3+}$ (L= 2,2′-diaminobiphenyl,[5,16] and its 6,6′-dimethyl derivative[16]) complexes, the ligands in which form skew seven-membered chelate rings similar to the dioxides, give only a *lel* isomer. The formation of only *ob* isomers for the dioxide complexes seems to be caused by steric interactions between the dioxide and the α-diimine ligands in the *lel* form. Figure 5 shows a schematic drawing of the two isomers of Δ-$[Cr(phen)_2((+)_{589}$-$mbdo)]^{3+}$ by Dreiding molecular models. In the $\Delta(\lambda)$(*lel*) form, each 2- (or 9-) hydrogen atom of the phen ligands comes very close to the 6- and 6′-carbon (and hydrogen) atoms of mbdo. On the other hand, there is no such extreme proximity among atoms of the ligands in the $\Delta(\delta)$(*ob*) form, each pyridine ring of mbdo becoming nearly parallel to each of the phen ligands to form a stable structure. Thus the bis-phen and bis-bpy complexes of bpdo and mbdo would give only one pair of *ob* enantiomers, $\Delta(\delta)$ and $\Lambda(\lambda)$, stereoselectively.

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