# Preparation and Stereochemistry of (Acetylacetonato)(2,2′-bipyridine)-chromium(III) Complexes with 2,2′-Bipyridine *N,N′*-Dioxide or Its 3,3′-Dimethyl Derivative

Hideaki KANNO,* Shunji UTSUNO, and Junnosuke FUJITA†
Department of Chemistry, Faculty of Science, Shizuoka University, Oya, Shizuoka 422
†Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464
(Received December 3, 1985)

**Synopsis.** Four new mixed-ligand chromium(III) complexes, $[Cr(acac)(bpy)(L)]^{2+}$ and $[Cr(bpy)(phen)(L)]^{3+}$, where L denotes a seven-membered chelate ligand, 2,2′-bipyridine *N,N′*-dioxide (bpdo) or its 3,3′-dimethyl derivative (mbdo), were prepared and resolved. All of the complexes formed only one of two possible racemic pairs of diastereomers. The pair was assigned to have an *ob*($\Delta(\delta)$, $\Lambda(\lambda)$) structure on the basis of the circular dichroism spectra and the absolute configuration of optically active mbdo recovered from the resolved complex.

2,2′-Bipyridine *N,N′*-dioxide (bpdo)[1] and 3,3′-dimethyl-2,2′-bipyridine *N,N′*-dioxide (mbdo)[2] form a skew seven-membered chelate ring, $\delta$ and $\lambda$, upon coordination (Fig. 1). Recently, we found that the conformations of these dioxide ligands (L) in mixed-ligand chromium(III) complexes are greatly influenced by the other ligands in the complex. Thus, $[Cr(en)_2(bpdo)]^{3+}$ [3] and $[Cr(acac)_2(L)]^{+}$ [4] formed only a *lel*($\Delta(\lambda)$, $\Lambda(\delta)$) isomer, whereas $[Cr(bpy\text{ or }phen)_2(L)]^{3+}$ [5] formed an *ob*($\Delta(\delta)$, $\Lambda(\lambda)$) isomer of two possible ones, *lel* and *ob*. Here, en, acac, bpy, and phen denote ethylenediamine, acetylacetonate(−1), 2,2′-bipyridine, and 1,10-phenanthroline, respectively. An examination using molecular models indicated that such a difference in selectivity comes from steric interactions among the ligands in the complex.

In this paper, we report on the preparation and stereochemistry of chromium(III) complexes which consist of three different bidentate ligands, $[Cr(acac)(bpy)(L)]^{2+}$ and $[Cr(bpy)(phen)(L)]^{3+}$. Since acac, bpy, and phen form planar chelate rings in a complex, these complexes can have two racemic pairs of diastereomers, *lel* and *ob*.

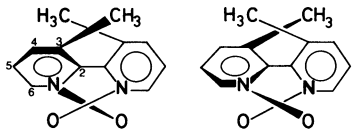


Fig. 1. A pair of enantiomers of mbdo.

## Experimental

Since the new complexes are photosensitive causing hydrolysis, the following experiments were carried out in the dark.

**Preparation of $[Cr(acac)_2(bpy)]Cl\cdot 2.5H_2O$.** The complex was prepared according to a method similar to that for $[Cr(acac)_2(phen)]ClO_4$.[6] An aqueous ethanol solution (90%, 300 cm³) containing $[Cr(acac)_3]$ (3.0 g, 8.6 mmol), bpy (4.0 g, 25.6 mmol), and concd HCl (3 cm³) was kept at 80 °C for 2 d with stirring. The resulting solution was evaporated under reduced pressure to give pink crystals. They were collected by filtration, washed with 2 mol dm⁻³ HCl and acetone, and recrystallized from hot water. Yield: 1.9 g (45%). Found: C, 49.19; H, 5.30; N, 5.68%. Calcd for $C_{20}H_{22}N_2O_4ClCr\cdot 2.5H_2O$: C, 49.34; H, 5.59; N, 5.75%.

**Preparation and Resolution of [Cr(acac)(bpy)(bpdo or mbdo)]$(ClO_4)_2$.** An aqueous 0.2 mol dm⁻³ HCl solution (50 cm³) containing $[Cr(acac)_2(bpy)]Cl\cdot 2.5H_2O$ (2.0 g, 4.1 mmol) was kept at 60 °C for 2 d with stirring. To the resulting solution, $NaClO_4$ (2.5 g) and $bpdo\cdot H_2O$[7] (1.2 g, 5.8 mmol) or racemic mbdo[2] (1.3 g, 6.0 mmol) were added. The solution was again kept at 60 °C for 8 h with stirring to give reddish-brown crystals. They were collected by filtration, washed with cold water, and recrystallized from hot water. Yield: the bpdo complex, 1.1 g (41%); the mbdo complex, 1.3 g (43%). Found for the bpdo complex: C, 42.99; H, 3.31; N, 7.99%. Calcd for $C_{25}H_{23}N_4O_{12}Cl_2Cr$: C, 43.24; H, 3.34; N, 8.07%. Found for the mbdo complex: C, 44.78; H, 3.76; N, 7.68%. Calcd for $C_{27}H_{27}N_4O_{12}Cl_2Cr$: C, 44.89; H, 3.77; N, 7.76%. Each complex gave only one racemic pair of diastereomers, no indication for the formation of another isomer being detected on column chromatograms.

The complexes were resolved by SP-Sephadex C-25 column chromatography. The perchlorate of each complex (0.08 g) was loaded on a column ($\phi$2.2×130 cm) of SP-Sephadex and eluted with a 0.15 mol dm⁻³ $Na_2SO_4$ solution. Although only one band was observed on the column, the front and rear fractions of the band showed positive and negative rotations at 546 nm, respectively. The fractions which showed a constant specific rotation were combined, diluted with water, and poured again on a small column ($\phi$2.2×3 cm) of SP-Sephadex. The adsorbed complex was eluted with a 2 mol dm⁻³ NaCl solution. The eluate was mixed with $NaClO_4$ to give reddish-brown crystals. They were collected by filtration, washed with a small amount of cold water, and recrystallized from hot water. Found for the $(+)_{546}$-isomer of the bpdo complex: C, 43.14; H, 3.33; N, 8.03%. Calcd for $C_{25}H_{23}N_4O_{12}Cl_2Cr$: C, 43.24; H, 3.34; N, 8.07%. Found for the $(+)_{546}$-isomer of the mbdo complex: C, 44.66; H, 3.73; N, 7.68%. Calcd for $C_{27}H_{27}N_4O_{12}Cl_2Cr$: C, 44.89; H, 3.77; N, 7.76%.

**Preparation and Resolution of [Cr(bpy)(phen)(bpdo or mbdo)]$(ClO_4)_3\cdot H_2O$.** The complexes were prepared by a method similar to that for $[Cr(phen)_2(bpdo)](ClO_4)_3$[5] using $[Cr_2(OH)_2(bpy)_2(phen)_2](NO_3)_4\cdot 6H_2O$[8] and the dioxide ligand. The complexes were obtained as orange crystals. Yield: the bpdo complex, 34%; the mbdo complex, 27%. Found for the bpdo complex: C, 42.98; H, 2.69; N, 9.48%. Calcd for $C_{32}H_{24}N_6O_{14}Cl_3Cr\cdot H_2O$: C, 43.04; H, 2.93; N, 9.41%. Found for the mbdo complex: C, 44.10; H, 2.98; N, 9.00%. Calcd for $C_{34}H_{28}N_6O_{14}Cl_3Cr\cdot H_2O$: C, 44.34; H, 3.28; N, 9.12%. Each complex gave only one racemic pair of diastereomers, no indication for the formation of another isomer being detected on column chromatograms.

The complexes were completely resolved by SP-Sephadex column chromatography using a 0.15 mol dm⁻³ $Na_2[Sb_2((+)_{589}\text{-tart})_2]$ solution as an eluent. The $(+)_{589}$-isomer was eluted faster from the column. The optically

active complex was isolated as the perchlorate by the same method as that for $(-)_{589}$-[Cr(phen)$_2$(bpdo)]$^{3+}$.[5] Found for the $(-)_{589}$-isomer of the bpdo complex: C, 43.15; H, 2.74; N, 9.41%. Calcd for $C_{32}H_{24}N_6O_{14}Cl_3Cr \cdot H_2O$: C, 43.04; H, 2.93; N, 9.41%. Found for the $(-)_{589}$-isomer of the mbdo complex: C, 44.13; H, 2.98; N, 9.10%. Calcd for $C_{34}H_{28}N_6O_{14}Cl_3Cr \cdot H_2O$: C, 44.34; H, 3.28; N, 9.12%.

**Recovery of mbdo from the Complexes.** The optically active mbdo was recovered from $(+)_{546}$-[Cr(acac)(bpy)(mbdo)]$^{2+}$ and $(-)_{589}$-[Cr(bpy)(phen)(mbdo)]$^{3+}$ by the same method as that for [Cr(mbdo)$_3$]$^{3+}$.[2] Both recovered mbdo showed positive rotations at 589 nm.

**Measurements.** Absorption and circular dichroism (CD) spectra were recorded on a Shimadzu MPS-50L spectrophotometer and a Jasco J-40 spectropolarimeter, respectively. Optical rotations were measured with a Union PM-101 polarimeter.

## Results and Discussion

Each of the complexes, [Cr(acac)(bpy)(L)]$^{2+}$ and [Cr(bpy)(phen)(L)]$^{3+}$ (L=bpdo, mbdo), formed only one of two possible racemic pairs, *lel*($\Delta(\lambda)$, $\Lambda(\delta)$) and *ob*($\Delta(\delta)$, $\Lambda(\lambda)$). The bpy·phen complexes were completely resolved by SP-Sephadex column chromatography using Na$_2$[Sb$_2$((+)$_{589}$-tart)$_2$] as an eluent, but the acac·bpy complexes were not under the same chromatographic conditions. Their resolutions were achieved by SP-Sephadex column chromatography using an achiral eluting agent $Na_2SO_4$, although the columns showed only one band. All the active complexes in aqueous solutions were optically stable in the dark, but gradually hydrolyzed in the light.

The absorption and CD spectra of $(+)_{546}$-[Cr(acac)(bpy)(L)]$^{2+}$ and $(-)_{589}$-[Cr(bpy)(phen)(L)]$^{3+}$ are shown in Fig. 2. The spectral data in the region of the first absorption band are listed in the Table. The

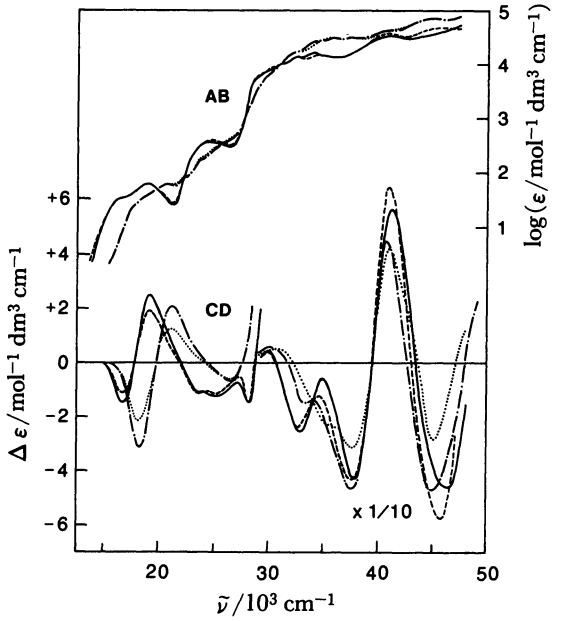


Fig. 2. Absorption (AB) and CD spectra of $(+)_{546}$-[Cr(acac)(bpy)(mbdo)]$^{2+}$ (——), $(+)_{546}$-[Cr(acac)(bpy)-(bpdo)]$^{2+}$ (– – – –), $(-)_{589}$-[Cr(bpy)(phen)(mbdo)]$^{3+}$ (–·–·–), and $(-)_{589}$-[Cr(bpy)(phen)(bpdo)]$^{3+}$ (·····) in water.

Table Absoption and CD Spectral Data in the Region of the First Absorption Band

| Complex | Absorption[a] | CD[a] |
|---|---|---|
| | $\tilde{\nu}$/10$^3$ cm$^{-1}$ (log $\varepsilon$) | $\tilde{\nu}$/10$^3$ cm$^{-1}$ ($\Delta\varepsilon$) |
| $(+)_{546}$-[Cr(acac)-(bpy)(mbdo)]$^{2+}$ | 16.9 (1.5)[b] | 17.06(−1.47) |
| | 19.23(1.77) | 19.53(+2.48) |
| $(+)_{546}$-[Cr(acac)-(bpy)(bpdo)]$^{2+}$ | 17.1 (1.5)[b] | 17.06(−1.14) |
| | 19.27(1.76) | 19.53(+1.89) |
| $(-)_{589}$-[Cr(bpy)-(phen)(mbdo)]$^{3+}$ | 18.7 (1.6)[b] | 18.35(−3.16) |
| | 20.70(1.76) | 21.32(+2.05) |
| $(-)_{589}$-[Cr(bpy)-(phen)(bpdo)]$^{3+}$ | 18.7 (1.5)[b] | 18.25(−2.13) |
| | 20.88(1.78) | 21.28(+1.24) |

a) Values of $\varepsilon$ and $\Delta\varepsilon$ are given in mol$^{-1}$ dm$^3$ cm$^{-1}$.
b) Shoulder.

absorption spectra of the bpdo and mbdo complexes are nearly the same over the whole region. The bands at ca. 19000 cm$^{-1}$ with a shoulder (ca. 17000 cm$^{-1}$) for the acac·bpy complexes and at ca. 21000 cm$^{-1}$ with a shoulder (18700 cm$^{-1}$) for the bpy·phen complexes can be assigned to the first absorption band ($^4T_{2g} \leftarrow {}^4A_{2g}$). In the higher energy region, the complexes show complicated spectra due to absorptions of the three kinds of ligands. In this region, however, the spectra of the bpy·phen and acac·bpy complexes are very similar to the average of those of the corresponding bis-bpy and bis-phen complexes,[5] and bis-acac,[4] and bis-bpy complexes, respectively.

The CD spectra of the complexes are similar in pattern over the whole region. This suggests that all the isomers have the same absolute configuration, including the chirality of the skew dioxide chelate ring. The spectra are very similar to those of $\Delta(\delta)$-[Cr(bpy or phen)$_2$(L)]$^{3+}$,[5] but quite different from those of $\Delta(\lambda)$-[Cr(acac)$_2$(L)]$^+$.[4] Thus, all the isomers have the $\Delta(\delta)$ structure.

The free mbdo ligand is optically stable and can be recovered from the complex.[2] Both mbdo recovered from $(+)_{546}$-[Cr(acac)(bpy)(mbdo)]$^{2+}$ and $(-)_{589}$-[Cr-(bpy)(phen)(mbdo)]$^{3+}$ showed positive rotations at 589 nm. The $(+)_{589}$-mbdo ligand was assigned to the *S* configuration and forms a $\delta$ skew chelate ring in a complex.[2] This is consistent with the structure ($\Delta(\delta)$) of the complexes assigned on the basis of the CD spectra. Since the bpdo complexes give CD spectra similar to those of the corresponding mbdo complexes over the whole region, it is concluded that the bpdo complexes also form an *ob*($\Delta(\delta)$, $\Lambda(\lambda)$) isomer stereoselectively. While it is expected that [Cr(bpy)-(phen)(L)]$^{3+}$ forms the same *ob* isomer as [Cr(bpy or phen)$_2$(L)]$^{3+}$, the selectivity of [Cr(acac)(bpy)(L)]$^{2+}$ differs from that of [Cr(acac)$_2$(L)]$^+$ which gives only a *lel* isomer.[4] Molecular models indicate that in *lel*-[Cr(acac)(bpy)(L)]$^{2+}$ the 6(6′)-hydrogen atom of bpy comes very close to the 6(6′)-carbon (and hydrogen) atom of the dioxide. There is no such extreme proximity between the acac and dioxide ligands in both *lel* and *ob* forms. In the *ob* form, one of the pyridine rings of the dioxide is nearly parallel to the diimine ligand to form a stable structure. The selective formation of *ob*-[Cr(acac)(bpy)(L)]$^{2+}$ is attributable to such steric conditions.

This work was partially supported by a Grant-in-Aid for Scientific Research No. 60740330 from the Ministry of Education, Science and Culture.

**References**

1) A. Vinciguerra, P. G. Simpson, Y. Kakiuti, and J. V. Quagliano, *Inorg. Chem.*, **2**, 286 (1963); A. R. Al-Karaghouli, R. O. Day, and J. S. Wood, *Inorg. Chem.*, **17**, 3702 (1978).
2) H. Kanno, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **52**, 1408 (1979).
3) H. Kanno, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **52**, 761 (1979).
4) H. Kanno, S. Utsuno, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **57**, 3443 (1984).
5) H. Kanno, K. Kashiwabara, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **53**, 2881 (1980).
6) D. Banerjea, J. Roy, and S. Sarkar, *Indian J. Chem.*, **8**, 372 (1970).
7) I. Murase, *Nippon Kagaku Zasshi*, **77**, 682 (1956).
8) S. Kaizaki, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **43**, 3024 (1970); *Inorg. Chem.*, **12**, 135 (1973).