Three Types of Diastereomeric Salts Containing Tris-(2,2'-bipyridine)metal(II) Complex and d-Tartrate Ions

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Three types of diastereomeric salts have been newly recognized for the systems containing divalent tris-2,2'-bipyridine complex ($[M(bpy)_3]^{2+}$ and d-tartrate (d-tart^{2-}) ions. The first is Λ-$[M(bpy)_3]_2Cl_2$ (d-tart)nH_2O, which is obtained by adding a large excess of $(NH_4)_2$·d-tart to the solution of racemic $[M(bpy)_3]Cl_2$, where M is divalent metal ions, Fe(II), Co(II), Ni(II), and Ru(II). The second is $Na_{1/2}$-{Δ-$[M(bpy)_3]$}$Cl_{1/2}$(d-tart)nH_2O, which is formed by using Na_2·d-tart instead of $(NH_4)_2$·d-tart. The addition of $(NH_4)_2$·d-tart to the Cl^--ion-free solution of the complex gave the third diastereomeric salt, $[M(bpy)_3]$d-tart·nH_2O. The recognition of the existence of these different types of diastereomeric salts has resolved the confusion concerning the absolute configuration of the complexes in these diastereomeric salts, which were all considered to have the formula, $[M(bpy)_3]$d-tart·nH_2O.

Since Werner prepared the diastereomeric salt of tris(2,2'-bipyridine)iron(II) complex and d-tartrate ions and gave it the formula, $[Fe(bpy)_3]$d-tart [1], diastereomeric salts of a similar formula, $[M(bpy)_3]$d-tart·nH_2O have been prepared for several divalent metal ions, Ni(II) [2], Ru(II) [3], Os(II) [4] and Co(II) [5]. As to the absolute configuration of the complexes in these diastereomeric salts, Mason and Peart [6] assigned the Λ-configuration to these complexes (except the labile Co(II) complex) from the excitation analysis of their absorption and CD spectra. Thus, it was concluded that $[M(bpy)_3]^{2+}$ has the Λ-configuration when it forms a diastereomeric salt with d-tart^{2-}. However, we have noticed one exception, for the case of Co(II). The recent crystal structure analysis by Kobayashi *et al.* [7] established the Λ-configuration of $(-)_{589}$-$[Co(bpy)_2]^{3+}$ which can be obtained by oxidation of the diastereomeric salt, $[Co(bpy)_3]$d-tart·nH_2O [5]. Since the inversion of the absolute configuration of the complex cannot be considered to take place during the oxidation, it must be concluded that $[Co(bpy)_3]^{2+}$ has also the Δ-configuration when it is included in the diastereomeric salt with d-tart^{2-}.

In addition, we have noticed in Jaeger's paper [8] a noteworthy description about the formation of diastereomeric salts containing $[Ni(bpy)_3]^{2+}$ and d-tart^{2-}: "While the addition of a large excess of $(NH_4)_2$·d-tart to the solution of racemic $[Ni(bpy)_3]$-Cl_2 produces crystals containing Λ-$[Ni(bpy)_3]^{2+}$ and d-tart^{2-}, the addition of an equivalent amount of Ag^2·d-tart gives crystals containing Δ-$[Ni(bpy)_3]^{2+}$ and d-tart^{2-}". It was considered by Jaeger that the high concentration of d-tart^{2-} favoured the deposition of the diastereomeric salt Λ-d, while the low concentration of d-tart^{2-} favoured the deposition of the salt Δ-d. This interpretation seems unnatural. Rather, it is more reasonable to consider that different preparative conditions give different types of diastereomeric salts. Hitherto, the composition of these diastereomeric salts have been considered to be $[M(bpy)_3]$d-tart·nH_2O without any careful inspection of analytical data. However, the X-ray crystal analysis by Wada *et al.* [9] revealed that the diastereomeric salt of Λ-$[Ni(bpy)_3]^{2+}$ and d-tart^{2-} which was prepared according to Morgan and Burstall [2] also contains Cl^- and has the composition, $[Ni(bpy)_3]_2Cl_2$(d-tart)nH_2O. The same composition is presumed for the diastereomeric salts of the other metal ions, when they are prepared in the same way using a large excess of $(NH_4)_2$·d-tart as a resolving agent. However, this composition cannot be obtained for the diastereomeric salt prepared by using Ag_2·d-tart, because Cl^- is removed from the solution. The diastereomeric salt obtained here is presumed to have the composition of $[Ni(bpy)_3]$d-tart·nH_2O. This is a different type of diastereomeric salt. Thus, it is not surprising that it may contain the complex with an absolute configuration opposite to that found in Λ-$[Ni(bpy)_3]_2Cl_2$(d-tart)nH_2O.

The Δ-configuration of the Co(II) diastereomeric salt might also be attributed to the formation of a diastereomeric salt different from the above. Indeed, Na_2·d-tart was used instead of $(NH_4)_2$·d-tart in the case of the Co(II) diastereomeric salt. This might possibly lead to a different type of diastereomeric salt.

Based on these considerations, preparation of diastereomeric salts containing divalent tris-2,2'-bipyridine complex and d-tart^{2-} ions was re-examined using $(NH_4)_2$·d-tart and Na_2·d-tart too in the presence and absence of Cl^- ions.

As expected, the addition of $(NH_4)_2$·d-tart to the solution of $[M(bpy)_3]Cl_2$ produced the diastereomeric salt containing Cl^-, Λ-$[M(bpy)_3]_2Cl_2$ (d-tart)nH_2O in all cases (M = Fe(II), Co(II), Ni(II), and Ru(II)). The addition of Na_2·d-tart surprisingly

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TABLE I Crystallographic Data. Crystals (1) to (4) are of the Composition Λ-$[M(bpy)_3]_2Cl_2$(d-tart)$\cdot nH_2O$, (5) to (8) are $Na_{1/2}\{\Delta$-$[M(bpy)_3]\}Cl_{1/2}$(d-tart)$\cdot nH_2O$, (9) to (10) are Δ-$[M(bpy)_3]$d-tart$\cdot nH_2O$, (11) to (13) are rac-$[M(bpy)_3]$d-tart$\cdot nH_2O$, and Crystal (14) is Racemic-$[Ni(bpy)_3]SO_4\cdot 7.5H_2O$.

Crystal	Metal	a/A	b/A	c/A	$\beta/^\circ$	Space group	Z	R
(1)	Fe(II)	23.587(5)	13.083(3)	22.609(5)	102.63(2)	C2	4	0.081
(2)	Co(II)	23.44(1)	13.15(1)	22.86(1)	103.56(4)	C2	4	–
(3)[a]	Ni(II)	23.600(1)	13.199(1)	23.099(1)	103.68(2)	C2	4	0.096
(4)	Ru(II)	23.549(4)	13.205(2)	22.894(3)	103.28(3)	C2	4	0.068
(5)	Fe(II)	22.55(1)	13.27(1)	12.80(1)	104.99(4)	C2	4	–
(6)	Co(II)	22.607(5)	13.429(2)	12.823(2)	104.67(2)	C2	4	0.070
(7)	Ni(II)	22.547(4)	13.387(2)	12.826(2)	104.50(1)	C2	4	[c]
(8)	Ru(II)	22.712(5)	13.334(3)	12.765(3)	105.28(2)	C2	4	[c]
(9)	Co(II)	12.976(2)	–	49.012(4)	–	$P4_1$ or $P4_3$	4	–
(10)	Ni(II)	23.274(3)	13.070(1)	12.763(1)	109.95(1)	P2	2	[c]
(11)	Fe(II)	25.573(6)	13.558(3)	24.486(5)	115.82(2)	$P2_1$	2	[c]
(12)	Ni(II)	25.631(9)	13.720(8)	24.416(8)	115.34(2)	$P2_1$	2	–
(13)	Ru(II)	25.76(3)	13.68(3)	24.34(3)	115.74(9)	$P2_1$	2	–
(14)[b]	Ni(II)	22.703(1)	13.550(1)	24.727(1)	115.13(2)	C2/c	8	0.099

[a] A. Wada, C. Katayama and J. Tanaka, *Acta Crystallogr., Sect. B, 32,* 3194 (1976). [b] A. Wada, N. Sakabe and J. Tanaka, *ibid., Sect. B, 32,* 1121 (1976). [c] Analysis in progress.

gave a different type of diastereomeric salt, containing Na^+ and Cl^-, $Na_{1/2}\{\Delta$-$[M(bpy)_3]\}_{1/2}$(d-tart)nH_2O. The existence of Na^+ and Cl^- was confirmed in the crystal structure determination. The addition of $(NH_4)_2\cdot$d-tart to the solution of racemic $[M(bpy)_3]$-d-tart gave $[M(bpy)_3]$d-tart$\cdot nH_2O$, which contained the racemic mixture of the complex in some cases and the Δ-complex in others. Thus, we have newly recognized the existence of three different types of diastereomeric salts containing $[M(bpy)_3]^{2+}$ and d-tart^{2-}, which can resolve the confusion concerning the absolute configuration of the complex included.

We have determined the crystal structures of these three types of diastereomeric salts. The crystallographic data are listed in Table I. The detailed results and discussion of these crystal structures will be published in the near future.

Preparation

Typical examples of preparation of the three types of diastereomeric salts are described.

1) Λ*-*$[Fe(bpy)_3]_2Cl_2$*(d-tart)*$\cdot 11H_2O$

Sixty grams of $(NH_4)_2\cdot$d-tart were added to the solution of 2.5 g of $[Fe(bpy)_3]Cl_2$ in 130 ml of water. The solution was kept at room temperature for a few days. Dark red rod-like crystals were obtained. Found:C, 51.46; H, 5.02; N, 11.28%. Calcd. for $[Fe(C_{10}H_8N_2)_3]_2Cl_2(C_4H_4O_6)\cdot 11H_2O$: C, 52.44; H, 5.09; N, 11.47%.

The diastereomeric salts of Ru(II), Co(II), and Ni(II) were also obtained in a similar way. The absolute configuration of the complexes in these salts was assigned as Λ by X-ray analysis. It was also assigned as Λ by the excitation analysis of the CD spectrum.

2) $Na_{1/2}\{\Delta$*-*$[Co(bpy)_3]\}Cl_{1/2}$*(d-tart)*$\cdot 6.5H_2O$

According to Ferguson's method [5], a mixture of 0.48 g of $CoCl_2\cdot 6H_2O$ and 1.58 g of 2,2′-bipyridine was dissolved in 35 ml of degassed hot water. To this solution was added 12 g of $Na_2\cdot$d-tart$\cdot 2H_2O$. Oily material which was deposited was filtered off. As the filtrate was cooled to room temperature, a small amount of powder came out. This was filtered off. The filtrate was placed in a dessicator for several days. The title compound came out as pale yellow needles. The presence of Na^+ and Cl^- was confirmed by the X-ray analysis. Found: C, 49.21; H, 4.97; N, 10.13%. Calcd. for $Na_{1/2}$-$[Co(C_{10}H_8N_2)_3]Cl_{1/2}(C_4H_4O_6)\cdot 6.5H_2O$: C, 49.69; H, 5.03; N, 10.23%. The diastereomeric salts of Fe(II), Ru(II), and Ni(II) were also obtained in a similar way. The chirality of the complexes in these salts was assigned as Δ in all cases by X-ray analysis, as well as the excitation analysis of the CD spectrum.

3) Δ*-*$[Ni(bpy)_3]$*d-tart*$\cdot 5H_2O$ *and racemic-*$[Ni(bpy)_3]$*-d-tart*$\cdot 6H_2O$

A mixture of 1.68 g of $NiSO_4\cdot 7H_2O$ and 2.81 g of 2,2′-bipyridine was dissolved in 50 ml of water. To this solution was added the freshly prepared precipitate Ba$\cdot$d-tart from 1.5 g of $BaCl_2\cdot 2H_2O$ and 1.4 g of $Na_2\cdot$d-tart$\cdot 2H_2O$. The mixture was heated to *ca.* 70 °C and stirred for 30 min. The precipitate $BaSO_4$ was filtered off. To the filtrate was added 21 g of $(NH_4)_2\cdot$d-tart. The solution was left at room temperature overnight. Pink needles were deposited together with colourless crystals of $(NH_4)_2$·d-tart. Found: C, 52.90; H, 4.83; N, 10.79%. Calcd. for $[Ni(C_{10}H_8N_2)_3](C_4H_4O_6)\cdot 5H_2O$: C, 53.35; H, 5.00; N, 10.98%. The chirality of the complex included was assigned as Δ from the CD spectrum pattern.

After filtration of these crystals, the filtrate was left at room temperature overnight. Pink rod-like crystals were obtained. These crystals differ in appearance from the crystals of the first crop. Found: C, 52.06; H, 5.06; N, 10.82%. Calcd. for $[Ni(C_{10}H_8N_2)_3](C_4H_4O_6)\cdot 6H_2O$: C, 52.13; H, 5.15; N, 10.73%. The aqueous solution of a single crystal gave no CD spectrum. The X-ray analysis showed that these crystals belong to a system different from those of the first crop.

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