Subtle Coligand Effects on Chelation of (Benzyl-1-propenylmalonato)platinum(II) Complexes

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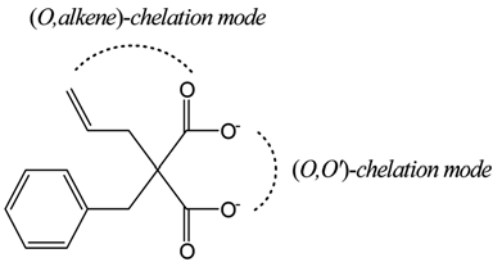
Studies on the linkage isomers of ambidentate ligands are increasingly important in molecular dynamical materials. Such results have been extended beyond the initial studies to diverse areas as quantum mechanical calculations, molecular switches, isomeric catalysts, the design of therapeutic reagents, the imaging agents in the body, and the separation of diastereomers. Although the coordination modes of ambidentate ligands may be vaguely predicted *via* electronic and steric effects, the coordination modes are sensitive to various factors such as central metals, oxidation states, coligands, reaction time, temperature, the solvent properties, etc.[1–9] In some cases, the steric factor plays an important role in determining the relative stability of the linkage isomers.[10] According to a previous report, an isomerism between the (*O,O′*)- and (*O,alkene*)-chelates was observed for diallylmalonatoplatinum(II) complexes.[11]

In order to scrutinize the coligand effects on the coordination chemistry of similar ambidentate ligands in platinum(II) complexes, benzyl-1-propenylmalonate (BPM) has been used as an anionic ambidentate ligand in this work. The ligand may coordinate to the platinum atom *via* either (*O,O′*) or (*O,alkene*) mode. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA), *N,N′*-dimethylethylenediamine (DMEDA), and ethylenediamine (en) were employed in order to examine the coligand effects on the coordination chemistry of BPM. Here we report the synthesis and structural properties of new platinum(II) complexes.



BPM

Experimental Section

Materials and Measurements. Potassium tetrachloroplatinate(II) was used as received from Kojima. TMEDA, DMEDA, and en were purchased from Aldrich. Diethyl benzyl-1-propenylmalonate (BPM) was prepared by the literature procedure[12] and then hydrolyzed with 1.5 eq. of $Ba(OH)_2 \cdot 8H_2O$ in 95% methanol to obtain the barium salt. *cis*-(Diamine)platinum(II) sulfates were also prepared by literature methods.[14-16] Elemental analyses were performed by the Advanced Analysis Center at KIST. The infrared spectra in the 5000-400 cm^{-1} region were measured as KBr pellets on a Perkin-Elmer 16F PC model FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-300 NMR spectrometer operating at 300.00 MHz (^1H) and 75.48 MHz (^{13}C), respectively, in pulse mode with Fourier transform. The chemical shifts were relative to $SiMe_4$ (^1H and ^{13}C) as an internal standard for the indicated nuclei.

Synthesis of *cis*-[Pt(BPM)(TMEDA)]. To a solution of *cis*-(TMEDA)$PtSO_4 \cdot H_2O$ (0.85 g, 2.0 mmol) in water (50 mL) was added $Ba(BPM) \cdot 2H_2O$ (0.81 g, 2.0 mmol) in water (50 mL), and then the resulting mixture was stirred for 3 h at room temperature. After barium sulfate was filtered off, the filtrate was evaporated to dryness. The crude white solid was recrystallized from a mixture of water and methanol (1 : 1) to obtain colorless crystals suitable for X-ray crystallography (72% yield). Anal. Found (Calcd) for $C_{19}H_{28}N_2O_4Pt \cdot H_2O \cdot 1/2CH_3OH$: C, 40.40 (40.55); H, 5.48 (5.58); N, 4.81 (4.85). IR (KBr, cm^{-1}): $\nu(COO)_{asym}$, 1640, 1616; $\nu(COO)_{sym}$, 1389. ^1H NMR (D_2O, ppm): 2.25 (s, NCH_3, 6H), 2.32 (d, NCH_2, 2H, J = 9.6 Hz), 2.49 (s, NCH_3, 6H), 2.52-2.59 (m, NCH_2 and CH_2, 4H), 3.07 (s, $PhCH_2$, 2H), 4.87-4.96 (m, $=CH_2$, 2H), 5.45-5.57 (m, =CH, 1H), 7.02-7.30 (m, Ph, 5H). ^1H NMR (Me_2SO-d_6, ppm): 2.12 (s, NCH_3, 6H), 2.35 (d, NCH_2, 2H, J = 8.2 Hz), 2.47 (s, NCH_3, 6H), 2.57-2.65 (m, NCH_2 and CH_2, 4H), 3.28 (s, $PhCH_2$, 2H), 4.76-4.92 (m, $=CH_2$, 2H), 5.42-5.54 (m, =CH, 1H), 7.00-7.28 (m, Ph, 5H). ^{13}C NMR (D_2O, ppm): 181.3, 137.7, 134.0, 130.1, 129.4, 127.8, 118.59, 65.9, 64.8, 52.0, 51.7, 45.9, 44.8, 30.7.

***cis*-[Pt(BPM)(DMEDA)].** This compound was prepared by the same procedure. Yield: 70%. Anal. Found (Calcd) for $C_{17}H_{25}N_2O_4Pt \cdot 2H_2O$: C, 36.40 (36.94); H, 5.38 (5.29); N, 5.01 (5.07). IR (KBr, cm^{-1}): $\nu(COO)_{asym}$, 1652, 1629, 1597; $\nu(COO)_{sym}$, 1376, 1332, 1280, 1252. ^1H NMR (D_2O, ppm): (major, (*O,O′*)-isomer) 2.22 (s, NCH_3, 3H), 2.25-2.36 (m, NCH_2, 2H), 2.54 (s, NCH_3, 3H), 2.56-2.62 (m, NCH_2 and CH_2, 4H), 3.17 (s, $PhCH_2$, 2H), 4.86-4.95 (m, $=CH_2$, 2H),

Table 1. Crystallographic Data for *cis*-[Pt(BPM)(TMEDA)]

Formula	$C_{38}H_{56}N_4O_8Pt_2 \cdot 2H_2O \cdot CH_3OH$
Fw	1155.12
λ, Å	0.71073
space group	monoclinic, $P2(1)/n$
a, Å	9.777(2)
b, Å	17.416(4)
c, Å	26.429(6)
β, deg	99.22(2)
V, Å^3	4442(2)
Z	4
d_{calcd}, gcm^{-3}	1.727
abs coeff, mm^{-1}	6.351
Data / restraints / parameters	5682 / 0 / 505
Final R indices [I > 2sigma(I)]	R1 = 0.0439, wR2 = 0.1055
R indices (all data)	R1 = 0.0458, wR2 = 0.1072

5.45-5.60 (m, =CH, 1H), 7.10-7.40 (m, Ph, 5H); (minor, (*O,alkene*)-isomer) 1.48-1.60 (m, CH_2, 1H), 2.04 (s, NCH_3, 3H), 2.24-2.67 (m, NCH_2 and CH_2, 3H), 2.49 (s, NCH_3, 3H), 3.11 (s, $PhCH_2$, 2H), 4.12 (d, =CH_2, 1H, J = 15.25 Hz), 4.74 (d, =CH_2, 1H, J = 7.92 Hz), 5.23-5.42 (m, =CH, 1H), 7.10-7.40 (m, Ph, 5H). ^{13}C NMR (D_2O, ppm): 182.5 (C=O, uncoordinated to Pt), 177.6 (C=O, coordinated to Pt), 140.3, 135.2, 131.6, 130.3, 128.7, 120.6, 98.2 (C=C, coordinated to Pt), 79.5 (C=C, coordinated to Pt), 68.2, 65.3, 54.0, 52.7, 46.2, 44.8, 31.2, 29.5.

***cis*-[Pt(BPM)(en)].** This compound was prepared by the same procedure. Yield: 76%. Anal. Found (Calcd) for $C_{15}H_{20}N_2O_4Pt \cdot 2H_2O$: C, 34.40 (34.42); H, 4.38 (4.62); N, 5.31 (5.35). IR (KBr, cm^{-1}): $\nu(COO)_{asym}$, 1629, 1570; $\nu(COO)_{sym}$, 1352, 1272, 1236. ^{1}H NMR (D_2O, ppm): (major, (*O,alkene*)-isomer) 1.68 (dd, CH_2, 1H), 2.56-2.98 (m, NCH_2 and CH_2, 5H), 2.94 (d, $PhCH_2$, 1H, J = 13.59 Hz), 3.26 (d, $PhCH_2$, 1H, J = 13.32 Hz), 4.23 (d, =CH_2, 1H, J = 15.09 Hz), 4.93 (d, =CH_2, 1H, J = 7.65 Hz), 5.56-5.69 (m, =CH, 1H), 7.15-7.48 (m, Ph, 5H); (minor, (*O,O'*)-isomer) 2.56-2.98 (m, NCH_2 and CH_2, 5H), 3.26 (s, $PhCH_2$, 2H), 5.10-5.22 (m, =CH_2, 2H), 5.70-5.83 (m, =CH, 1H), 7.15-7.48 (m, Ph, 5H).

X-ray Crystallography. All the crystallographic data were obtained on an Enraf-Nonius CAD 4 automatic diffractometer with graphite-monochromated molybdenum radiation Mo Kα radiation (λ = 0.71073 Å) at ambient temperature of 23(2) °C. Preliminary diffractometric investigation indicated monoclinic system. Accurate cell dimensions were obtained from the setting angles of 25 well-centered reflections by using a least-square procedure. During the data collection, three standard reflections monitored after every hour did not reveal any systematic variation in intensity. The structure was solved by a direct method, followed by successive difference Fourier synthesis. The nonhydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. All calculations were carried out on a personal computer with use of SHELXS 86 or SHELXL 97.[13] Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC- 273239). The data can be obtained free of charge *via http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi* (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Synthesis. The reaction of [(N-N)Pt(II)] sulfates with barium salts of the BPM ligand in aqueous solution at room temperature produced the products in high yields (70-76%) with precipitation of barium sulfate. Recrystallization of the compounds in a solvent pair of water and methanol resulted in colorless crystalline solid products. The products are stable, and moderately soluble in water and in polar organic solvents such as methanol, ethanol, dimethylformamide, and dimethyl sulfoxide.

$$Pt(N\text{-}N)(SO_4) + BaBPM \xrightarrow[H_2O]{} cis\text{-}[Pt(BPM)(N\text{-}N)] + BaSO_4\downarrow$$

N-N = TMEDA, DMEDA, en

Crystal Structure. The X-ray crystal structure of *cis*-[Pt(BPM)(TMEDA)] is depicted in Figure 1, and relevant bond distances and angles are listed in Table 2. There are two independent molecules (1 and 2) in an asymmetric region of a monoclinic unit cell and the structures of the two molecules are the same within error of being identical. Molecule 1 and its labeling scheme are shown in the figure. As expected, the local geometry around the platinum(II)

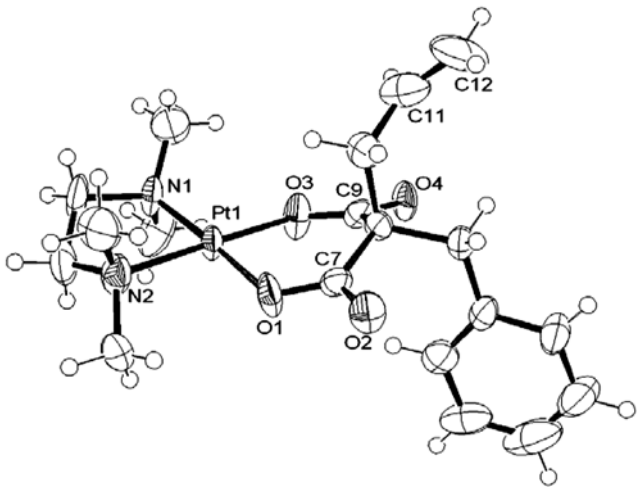


Figure 1. Crystal structure of *cis*-[Pt(BPM)(TMEDA)] showing the atomic labeling scheme and thermal ellipsoids at the 50% level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *cis*-[Pt(BPM)(TMEDA)]

Pt(1)-O(3)	2.004(7)	Pt(1)-O(1)	2.012(7)
Pt(1)-N(1)	2.039(9)	Pt(1)-N(2)	2.059(9)
Pt(2)-O(5)	1.995(8)	Pt(2)-O(7)	2.001(7)
Pt(2)-N(3)	2.026(9)	Pt(2)-N(4)	2.046(9)
C(11)-C(12)	1.30(2)	C(16)-C(17)	1.33(2)
O(3)-Pt(1)-O(1)	92.4(3)	O(3)-Pt(1)-N(1)	90.9(3)
O(1)-Pt(1)-N(1)	176.6(3)	O(3)-Pt(1)-N(2)	175.2(4)
O(1)-Pt(1)-N(2)	90.7(4)	N(1)-Pt(1)-N(2)	86.0(4)
O(5)-Pt(2)-O(7)	92.8(3)	O(5)-Pt(2)-N(3)	90.3(3)
O(7)-Pt(2)-N(3)	176.9(3)	O(5)-Pt(2)-N(4)	176.5(3)
O(7)-Pt(2)-N(4)	90.4(3)	N(3)-Pt(2)-N(4)	86.5(4)

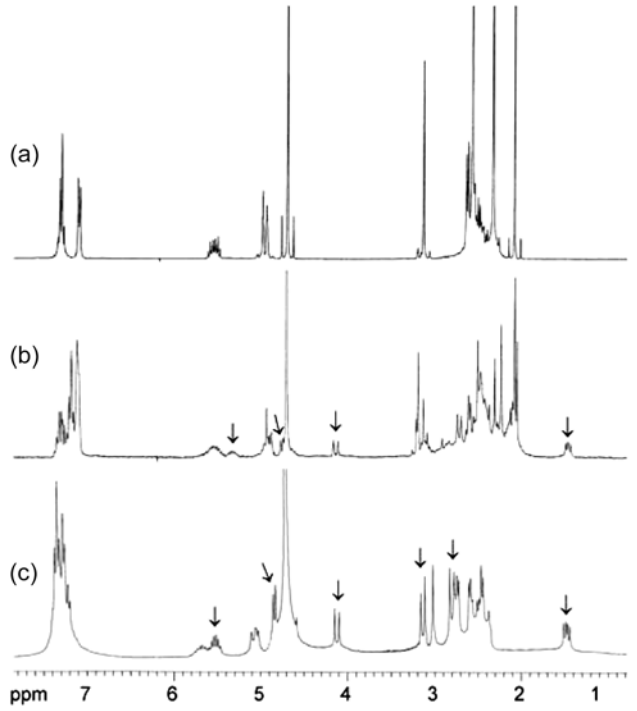


Figure 2. ^{1}H NMR spectra of (a) *cis*-[Pt(BPM)(TMEDA)], (b) *cis*-[Pt(BPM)(DMEDA)], and (c) *cis*-[Pt(BPM)(en)] in D_2O. The ↓ indicates (*O,alkene*)-chelate.

center approximates to a typical square planar arrangement with two nitrogen atoms in *cis* positions (N(1)-Pt(1)-N(2) = 86.0(4)°). The anionic BPM ligand was chelated the platinum atom in a (*O,O′*)-chelation through two carboxylate groups. Thus, the C(11)-C(12) distance of the alkene group (1.30(2) Å; the corresponding bond of molecule 2 = 1.33(2) Å) is close to that of the normal double bond (1.33 Å).[14] The bond lengths of C(7)-O(1) (1.27(1) Å) and C(9)-O(3) (1.28(1) Å) are longer than those of C(7)-O(2) (1.22(1) Å) and C(9)-O(4) (1.23(1) Å), being consistent with a typical monodentate carboxylate in other platinum(II) complexes.[15] The angle of O(1)-Pt(1)-O(3) (92.4(3)°) in a six-membered ring is splayed out compared to that of N(1)-Pt(1)-N(2) (86.0(4)°) in a five-membered ring.

Table 3. Distribution of chelation modes for BPM Compounds in D_2O

Compounds	Distribution (%)	
	O,O′-	*O,alkene*-
cis-[Pt(BPM)(TMEDA)]	100	0
cis-[Pt(BPM)(DMEDA)]	70	30
cis-[Pt(BPM)(en)]	30	70

Solution Behavior. The ^{1}H NMR spectrum of *cis*-[Pt(BPM)(TMEDA)] (Figure 2a) discloses that the BPM is coordinated to the platinum(II) in a (*O,O′*)-chelation mode in aqueous solution. That, only the (*O,O′*)-chelate species is obtained in the solid state, is retained without dissociation or isomerization in the solution. The NMR spectrum is not changed in dimethyl sulfoxide, indicating that the chelation mode is retained even in dimethyl sulfoxide solution. For the DMEDA analogue, ^{1}H NMR spectrum (Figure 2b) shows that the (*O,O′*) and (*O,alkene*) modes coexist in the ratio of 7 : 3 in D_2O solution (Table 3). The =CH protons of the BPM ligand appear as two distinct quartets in the range of 5.2-5.8 ppm, indicating that two species exist in aqueous solution. The $=CH_2$ protons are also observed as two distinguished sets. For (*O,O′*)-chelate, the $=CH_2$ protons of BPM appear as multiplet at 4.9 ppm. Otherwise, for (*O,alkene*)-chelate (indicated as ↓ in Figure 2b), the $=CH_2$ protons are shifted to the higher field and appear as two doublets at 4.12 ($^3J_{cis}$ = 15.25 Hz) and 4.74 ($^3J_{trans}$ = 7.92 Hz) ppm that are assigned as *cis*- and *trans*-protons to =CH, respectively. Thus, for the chemical shifts of (*O,alkene*) species, the methylene proton resonances of the BPM and N-N ligands are complicated due to the unsymmetrical ligation of the BPM ligand. The alkene resonances at 98.2 and 79.5 ppm are significantly shifted upfield compared to those of the potassium salt of BPM (139.3 and 117.8 ppm). Such results clearly indicate that the (*O,alkene*) chelation mode, as well as (*O,O′*) chelation, exists in aqueous solution. The NMR of the en analogue gives the mixture of (*O,O′*) and (*O,alkene*) chelation modes, but the ratio of 3 : 7 exists. The $=CH_2$ protons of BPM appear as two sets, a multiplet at 5.15 ppm and two doublets at 4.23 (J = 15.09 Hz) and 4.93 (J = 7.65 Hz) ppm, that is, (*O,O′*) and (*O,alkene*) chelation modes, respectively. Structural characterization of the platinum(II) compounds containing the BPM ligand has shown that a prominent coligand inductive effect on the coordination of the BPM ligand. Such a strong coligand inductive effect seems to be superior to the solvent and temperature effects, and consequently, the (*O,O′*) chelation mode of TMEDA analogue is locked irrespective of solvents.

In conclusion, the subtle coligand effect on the bonding mode of ambidentate ligand was observed in this study. In particular, the subtle properties between the (*O,O′*) and (*O,alkene*) modes appear to be associated with proximity in energy between the two chelation modes of the benzyl-1-propenylmalonate ligand. Various factors should be understood prior to molecular design of new platinum compounds that exhibit desirable molecular properties.

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References

1. Buckingham, D. A. *Coord. Chem. Rev.* **1994**, *135-136*, 587.
2. Appleton, T. G.; Pesch, F. J.; Wienken, M.; Menzer, S.; Lippert, B. *Inorg. Chem.* **1992**, *31*, 4410.
3. Ankersmit, H. A.; Witte, P. T.; Kooijman, H.; Lakin, M. T.; Spek, A. L.; Goubitz, K.; Vrieze, K.; van Koten, G. *Inorg. Chem.* **1996**, *35*, 6053.
4. Lanfredi, A. M. M.; Ugozzoli, F.; Camus, A.; Marsich, N.; Capelletti, R. *Inorg. Chim. Acta* **1993**, *206*, 173.
5. Bignozzi, C. A.; Chiorboli, C.; Indelli, M. T.; Scandola, F.; Bertolasi, V.; Gilli, G. *J. Chem. Soc., Dalton Trans.* **1994**, 2391.
6. Das, D.; Chaudhuri, N. R.; Ghosh, A. *Polyhedron* **1996**, *15*, 3919.
7. Parac, T.; Kostic, N. M. *J. Am. Chem. Soc.* **1996**, *118*, 5946.
8. Piao, L.; Kai, F.; Nirohata, M.; Matsuoka, Y.; Huang, H. *Polyhedron* **1996**, *15*, 3107.
9. (a) Clark, G. R.; Palenik, G. J. *Inorg. Chem.* **1970**, *9*, 2754. (b) Burmeister, J. L.; DeStefano, N. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1968.
10. (a) Burmeister, J. L.; DeStefano, N. J. *Inorg. Chem.* **1969**, *8*, 1546. (b) Burmeister, J. L.; Lim, J. C. *J. Chem. Soc., Chem. Commun.* **1969**, 1154.
11. (a) Lee, Y.-A.; Chung, Y. K.; Kim, K. M.; Sohn, Y. S. *Inorg. Chim. Acta* **1998**, *279*, 116. (b) Lee, Y.-A.; Chung, Y. K.; Sohn, Y. S. *Inorg. Chem.* **1999**, *38*, 531.
12. Marvel, C. S. *Org. Synth., Coll. III* **1955**, 705.
13. Sheldrick, G. M. *SHELX-97, A Program for Structure Determination and Refinement*; University of Göttingen: Germany, 1997.
14. Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 3rd ed.; Allyn and Bacon: Boston, MA, 1973; p 145.
15. (a) Lee, Y.-A.; Jung, O.-S.; Kang, S.-J.; Lee, K.-B.; Sohn, Y. S. *Inorg. Chem.* **1996**, *35*, 1641. (b) Bitha, P.; Morton, G. O.; Dunne, T. S.; Delos Santos, E. F.; Lin, Y.; Boone, S. R.; Haltiwanger, R. C.; Pierpont, C. G. *Inorg. Chem.* **1990**, *29*, 645.