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Synthesis and Crystal Structure of Cyclodimeric Ag(I) Complex with 2,3-Bis(2-pyridyl)pyrazine

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고리 이합체 2,3-비스(2-피리딜)피라진(트라이플루오르아세테이토) 은(I) 착물의 합성 및 결정 구조

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Abstract

The slow diffusion of 2,3-bis(2-pyridyl)pyrazine (bpp) with $Ag(CF_3CO_2)$ produces crystalline product suitable for X-ray crystallography. Crystallographic characterization of the crystal ($C_{32}H_{20}F_6N_8O_4Ag_2$: triclinic $P\bar{1}$, a=8.518(5) Å, b=9.546(2) Å, c=10.632(1) Å, α=81.11(1)°, β=87.61(3)°, γ=75.66(3)°, V=827.5(5) Å^3, Z=1, R=0.0431) has provided that the complex is a cyclic dimer $[Ag(bpp)(CF_3CO_2)]_2$. Each bpp ligand connects two tetrahedral silver(I) ions in a tridentate mode (Ag-N, 2.26(2)-2.43(2) Å), and the trifluoroacetato anion is bonded to each silver(I) atom in a monodentate fashion (Ag-O, 2.38(1); 2.39(2) Å). The skeletal cyclic dimer is stable up to 212°C, and drastically decomposes around this temperature.

요 약

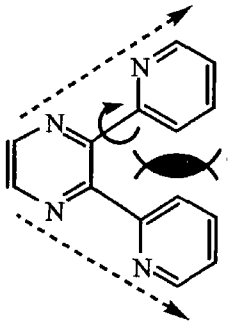
다양한 배위 형태가 가능한 2,3-비스(2-피리딜)피라진 (2,3-bis(2-pyridyl)pyrazine, bpp) 리간드를 $Ag(CF_3CO_2)$와 느린확산법으로 반응시켜 결정성 고체를 얻었다. 결정학적 ($C_{32}H_{20}N_8F_6O_4Ag_2$: triclinic $P\bar{1}$, a=8.518(5) Å, b=9.546(2) Å, c=10.632(1) Å, α=81.11(1)°, β=87.61(3)°, γ=75.66(3)°, V=827.5(5) Å^3, Z=1, R=0.0431) 방법에 의한 규명 결과 이 화합물의 구조는 고리형 이합체라는 사실이 밝혀졌다. 여기서 bpp 리간드는 하나의 사면체 은(I) 금속에 한 자리(monodentate)로 결합하고 다른 하나의 금속에 두 자리(bidentate)로 결합하여, 가교된(bridged) 세 자리 리간드 (tridentate)로 배위되어 있다 (Ag-N, 2.26(2)-2.43(2) Å). 트라이플루오르아세테이토 음이온은 한 자리 리간드로 각 은(I) 원자에 결합되어 있다. 열분석 결과 이 고리 이합체 구조는 212°C까지 안정하였다. 트라이플루오르아세테이토 음이온 및 bpp리간드는 212°C 근처에서 연속적으로 급격히 해리 분해되었다.

1. Introduction

A wide range of polypyridyl ligands that can bridge two or more remote metal centers and that also contain a delocalized π system have received considerable attention in recent coordination chemistry. Interest in metal complexes of such polypyridyl ligands has been stimulated by the possibility that desirable molecular materials such as electrical conductors,[1] molecular magnets,[2,3] host-guest molecules,[4-6] inorganic-organic composites,[7-9] and crystal bending materials[10] may be engineered. Modulation

of structural and physicochemical properties by means of chemical triggers is of central importance and topical subject.[11,12] Among the elegant efforts to find key factors, the use of a unique multifunctional ligand is worthy of close attention as a rational synthetic strategy.[13,14] In particular, a simple rotational process involving an inter-annular C-C bond between two aromatic rings has been widely used in construction of elaborate metal complexes.[15,16] 2,3-Bis (2-pyridyl)pyrazine (bpp)[17-19] is a potential tetradentate ligand possessing a magic angle, appropriate chelate sites, and conformational nonrigidity. Moreover, the ligand would not be constrained to a planar conformation owing to the presence of intrinsic crowdedness between the two pyridyl groups. In contrast to rigid polypyridyl systems, systematic studies on the metal complexes of the bpp ligand are relatively rare. In this context, it is worth scrutinizing their bonding modes and related properties dependent upon the coordination geometry of its silver(I) metal complex. First, the bpp is a non-innocent ligand that can form various different bonding modes. Second, the metal environment provided by the bpp ligand may serve as a model for structure-stability or structure-property relationship. Third, delicate tuning of the bonding mode can contribute to the development of metal complexes that exhibit desirable properties.

In this paper, we investigate the bonding of the bpp ligand to $Ag(CF_3CO_2)$, and describe its structure and related thermal properties.



bpp

2. Experimental Section

Materials and Measurements. Commercially available reagent-grade $Ag(CF_3CO_2)$ was used without further purification. 2,3-Bis(2-pyridyl)pyrazine (bpp) was prepared according to the procedure of Goodwin and Lions.[17] Infrared spectra were obtained on a Perkin Elmer 16F PC FTIR spectrophotometer with samples prepared as KBr pellets. Elemental analyses (C, H, N) were carried out at the Advanced Analysis Center at KIST (Korea Institute of Science and Technology). Thermal analyses were performed on a Stanton Red Croft TG 100 with a scanning rate of 10°C/min.

Preparation of $[Ag(bpp)(CF_3CO_2)]_2$. An acetone solution (3 mL) of $Ag(CF_3CO_2)$ (22 mg, 0.1 mmol) was slowly diffused into a chloroform solution (3 mL) of bpp (23 mg, 0.1 mmol). Thin yellow crystals suitable for X-ray crystallography formed at the interface and were obtained in a week in 80% yield. Anal. Calcd for $C_{32}H_{20}N_8F_6O_4Ag_2$: C, 42.72; H, 2.21; N, 12.31. Found: C, 42.90; H, 2.32; N, 12.30. IR (KBr, cm^{-1}): 1686 (s), 1586 (s), 1566 (m), 1481 (m), 1434 (m), 1397 (s), 1213 (s), 1143 (s), 1108 (s), 1038 (s), 993 (m), 839 (w), 794 (s), 749 (m), 724 (m), 664 (w), 629 (m), 570 (m), 415 (m).

X-ray Crystallography. Each crystal was wedged in a Lindemann capillary with mother solvent. All the X-ray data were collected on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated MoKα (λ=0.71073 Å) at ambient temperature. Unit cell dimensions were based on 25 well-centered reflections by using a least-squares procedure. During the data collection, three standard reflections monitored every hour did not show any significant intensity variation. All data were collected with the ϖ/2θ scan mode. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical ψ-scan method. The structures were solved by the Patterson method (SHELXS-86), and were refined by full-matrix least-squares techniques (SHELXL-97).[20] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were added at calculated positions. The crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1, and positional parameters and thermal ellipsoids are listed in Table 2.

Table 1. Crystal data and structure refinement for [Ag(bpp)(CF_3CO_2)]$_2$

Empirical	$C_{32}H_{20}Ag_2F_6N_8O_4$
Formula weight	910.29
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	a=8.518(5) Å α=81.11(1) deg. b=9.546(2) Å β=87.61(3) deg. c=10.632(1) Å γ=75.66(3) deg.
Volume	827.5(5) Å^3
Z, Calculated density	1, 1.827 mg/m^3
Absorption coefficient	1.268 mm^{-1}
F(000)	448
Crystal size	0.30×0.20×0.20 mm
2θ range for data collection	3.88 to 47.98 deg.
Index ranges	$0\le h\le 9$, $-10\le k\le 10$, $-12\le l\le 12$
Reflections collected/ unique	2338/2338 [R(int)=0.0000]
Completeness to 2θ=23.99	83.8%
Data/restraints/ parameters	2338/3/469
Goodness-of-fit on F^2	1.094
Final R indices [I>2σ(I)]	$R1$=0.0429, $wR2$=0.1082
R indices (all data)	$R1$=0.0434, $wR2$=0.1091
Largest diff. peak and hole	1.079 and -0.967 e.A^{-3}

$R1=\sum||Fo|-|Fc||/\sum|Fo|$
$wR2=\sum w(Fo^2-Fc^2)^2/\sum wFo^4)^{1/2}$

3. Results and Discussion

Synthesis. The reaction of a noninnocent bpp ligand with Ag(CF_3CO_2) in appropriate solvents afforded a cyclodimeric product of [Ag(bpp)(CF_3CO_2)]$_2$. The reaction was not significantly affected by the change of the mole ratio (bpp/silver=1-3) or by the method of diffusion. Thus, several attempts gave the same results, indicating that the products are favorable species irrespective of the mole ratio and the method of diffusion. This product is a discrete molecule as established by the following X-ray crystal characterization, instead of possible coordination polymers. It is air- and light-stable crystalline solids. The [Ag(bpp)(CF_3CO_2)]$_2$ is slightly soluble in

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for [Ag(bpp)(CF_3CO_2)]$_2$

	x	y	z	U(eq)
Ag(1)	3472(1)	8033(1)	449(1)	52(1)
Ag(2)	743(1)	10210(1)	3767(1)	52(1)
N(1)	4620(2)	7454(18)	2457(18)	38(4)
N(2)	1680(2)	7089(18)	1821(16)	39(4)
N(3)	5170(3)	7849(19)	4910(2)	78(7)
N(4)	1120(2)	8436(17)	5421(16)	39(4)
N(5)	2486(19)	11210(2)	2241(18)	41(4)
N(6)	-430(2)	10760(2)	1651(17)	46(5)
N(7)	-993(14)	10367(16)	-780(15)	39(4)
N(8)	3040(2)	9830(2)	-1249(18)	50(5)
O(1)	-926(17)	12188(13)	4681(15)	48(4)
O(2)	-2940(2)	11130(2)	4510(19)	66(5)
O(3)	5070(2)	6080(2)	-539(17)	66(5)
O(4)	7070(2)	7150(2)	-221(16)	59(4)
F(1)	-4944(18)	13590(2)	4780(2)	139(8)
F(2)	-3050(2)	14552(17)	5090(3)	172(12)
F(3)	-3740(2)	13062(18)	6445(13)	138(5)
F(4)	9239(17)	4812(16)	-930(2)	143(9)
F(5)	7230(2)	4037(18)	-1491(17)	131(8)
F(6)	7881(16)	3760(10)	340(13)	109(4)
C(1)	6090(2)	7840(2)	2692(17)	33(4)
C(2)	6280(2)	8010(2)	3910(2)	55(6)
C(3)	3950(2)	7550(2)	4690(17)	25(4)
C(4)	3640(2)	7183(19)	3352(19)	29(4)
C(5)	2350(2)	6690(2)	3167(19)	34(5)
C(6)	1570(3)	5590(2)	4000(2)	38(5)
C(7)	570(3)	5090(3)	3560(2)	54(7)
C(8)	-130(3)	5600(3)	2311(18)	63(7)
C(9)	490(2)	6540(3)	1460(2)	56(6)
C(10)	2660(2)	7530(2)	5717(15)	41(5)
C(11)	3140(3)	6800(3)	6910(2)	47(5)
C(12)	1800(3)	6650(3)	7780(2)	72(8)
C(13)	290(3)	7620(2)	7498(19)	50(7)
C(14)	50(2)	8441(18)	6420(2)	51(6)
C(15)	2100(2)	11587(19)	1174(19)	26(4)
C(16)	2530(2)	12470(2)	343(18)	37(4)
C(17)	3910(2)	13130(3)	650(2)	46(6)
C(18)	4340(2)	12780(2)	1870(2)	53(6)
C(19)	3660(3)	11770(2)	2610(2)	48(6)
C(20)	710(2)	10890(2)	700(2)	30(4)
C(21)	550(2)	10720(2)	-400(2)	46(6)
C(22)	-2020(3)	10314(19)	90(2)	51(6)
C(23)	-1630(3)	10460(3)	1330(2)	56(6)
C(24)	1630(2)	10660(2)	-1480(2)	44(6)
C(25)	1340(3)	11580(2)	-2620(2)	42(5)

Table 2. Continued

	x	y	z	*U*(eq)
C(26)	2380(3)	11450(2)	-3565(14)	47(5)
C(27)	3950(3)	10650(3)	-3310(2)	61(7)
C(28)	4250(2)	9800(2)	-2083(18)	45(5)
C(29)	-2300(2)	12150(2)	4712(17)	40(5)
C(30)	-3510(3)	13370(2)	5280(2)	56(6)
C(31)	6570(3)	6170(2)	-491(19)	48(6)
C(32)	7720(3)	4690(3)	-610(2)	58(6)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

polar organic solvents.

Crystal Structure of $[Ag(bpp)(CF_3CO_2)]_2$. The reaction of the bpp ligand with $Ag(CF_3CO_2)$ yielded a cyclodimer, $[Ag(bpp)(CF_3CO_2)]_2$. The structure is depicted in Figures 1 and 2 (packing diagram), and

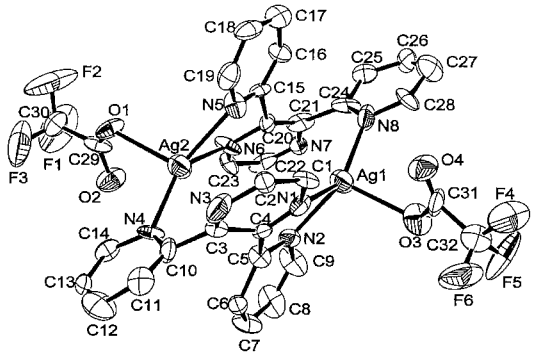


Fig. 1. ORTEP view of $[Ag(bpp)(CF_3CO_2)]_2$ showing refined atoms at the 50% probability level. Hydrogen atoms are omitted for clarity.

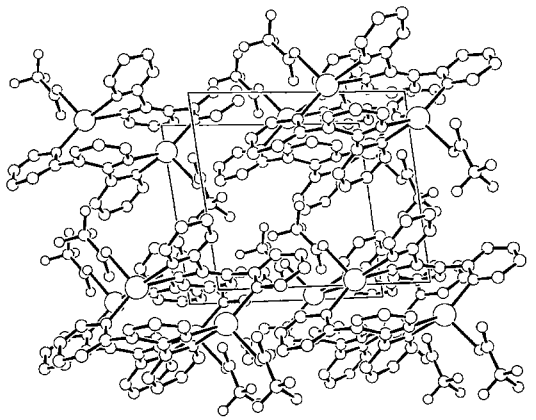


Fig. 2. Packing diagram of $[Ag(bpp)(CF_3CO_2)]_2$.

Table 3. Bond lengths [Å] and angles [deg] for $[Ag(bpp)(CF_3CO_2)]_2$

Ag(1)-N(8)	2.26(2)	Ag(1)-N(2)	2.312(18)
Ag(1)-N(1)	2.316(19)	Ag(1)-O(3)	2.382(17)
Ag(2)-N(4)	2.218(16)	Ag(2)-O(1)	2.378(13)
Ag(2)-N(5)	2.402(18)	Ag(2)-N(6)	2.429(18)
N(1)-C(4)	1.28(3)	N(1)-C(1)	1.43(2)
N(2)-C(9)	1.35(3)	N(2)-C(5)	1.52(3)
N(3)-C(3)	1.19(3)	N(3)-C(2)	1.41(3)
N(4)-C(14)	1.37(2)	N(4)-C(10)	1.40(3)
N(5)-C(15)	1.17(3)	N(5)-C(19)	1.35(3)
N(6)-C(23)	1.20(3)	N(6)-C(20)	1.39(2)
N(7)-C(22)	1.25(3)	N(7)-C(21)	1.52(2)
N(8)-C(24)	1.28(3)	N(8)-C(28)	1.33(2)
O(1)-C(29)	1.18(2)	O(2)-C(29)	1.27(2)
O(3)-C(31)	1.30(3)	O(4)-C(31)	1.19(3)
F(1)-C(30)	1.30(3)	F(2)-C(30)	1.27(3)
F(3)-C(30)	1.25(3)	F(4)-C(32)	1.35(3)
F(5)-C(32)	1.34(3)	F(6)-C(32)	1.23(2)
C(1)-C(2)	1.35(3)	C(3)-C(10)	1.51(3)
C(3)-C(4)	1.56(2)	C(4)-C(5)	1.33(3)
C(5)-C(6)	1.53(3)	C(6)-C(7)	1.22(3)
C(7)-C(8)	1.44(3)	C(8)-C(9)	1.36(3)
C(10)-C(11)	1.37(3)	C(11)-C(12)	1.46(3)
C(12)-C(13)	1.39(4)	C(13)-C(14)	1.28(3)
C(15)-C(16)	1.23(3)	C(15)-C(20)	1.62(3)
C(16)-C(17)	1.53(3)	C(17)-C(18)	1.33(3)
C(18)-C(19)	1.37(3)	C(20)-C(21)	1.22(3)
C(21)-C(24)	1.44(3)	C(22)-C(23)	1.40(3)
C(24)-C(25)	1.37(3)	C(25)-C(26)	1.31(3)
C(26)-C(27)	1.38(3)	C(27)-C(28)	1.43(3)
C(29)-C(30)	1.53(3)	C(31)-C(32)	1.53(3)
N(8)-Ag(1)-N(2)	131.3(7)	N(8)-Ag(1)-N(1)	141.2(6)
N(2)-Ag(1)-N(1)	72.5(6)	N(8)-Ag(1)-O(3)	99.6(6)
N(2)-Ag(1)-O(3)	107.5(6)	N(1)-Ag(1)-O(3)	100.0(6)
N(4)-Ag(2)-O(1)	101.2(6)	N(4)-Ag(2)-N(5)	135.1(6)
O(1)-Ag(2)-N(5)	107.3(6)	N(4)-Ag(2)-N(6)	139.1(6)
O(1)-Ag(2)-N(6)	99.1(6)	N(5)-Ag(2)-N(6)	69.1(6)
C(4)-N(1)-C(1)	122.3(18)	C(4)-N(1)-Ag(1)	113.9(14)
C(1)-N(1)-Ag(1)	120.8(14)	C(9)-N(2)-C(5)	121.4(18)
C(9)-N(2)-Ag(1)	124.8(14)	C(5)-N(2)-Ag(1)	110.9(13)
C(3)-N(3)-C(2)	119(2)	C(14)-N(4)-C(10)	113.5(16)
C(14)-N(4)-Ag(2)	122.3(13)	C(10)-N(4)-Ag(2)	121.0(11)
C(15)-N(5)-C(19)	115(2)	C(15)-N(5)-Ag(2)	120.8(13)
C(19)-N(5)-Ag(2)	121.3(15)	C(23)-N(6)-C(20)	115(2)
C(23)-N(6)-Ag(2)	127.3(16)	C(20)-N(6)-Ag(2)	112.5(14)
C(22)-N(7)-C(21)	114.8(18)	C(24)-N(8)-C(28)	122(2)
C(24)-N(8)-Ag(1)	120.8(14)	C(28)-N(8)-Ag(1)	116.2(16)
C(29)-O(1)-Ag(2)	111.7(13)	C(31)-O(3)-Ag(1)	106.4(12)

Table 3. Continued

C(2)-C(1)-N(1)	114.7(16)	C(1)-C(2)-N(3)	125.4(18)
N(3)-C(3)-C(10)	119.6(19)	N(3)-C(3)-C(4)	121.0(19)
C(10)-C(3)-C(4)	119.4(15)	N(1)-C(4)-C(5)	123.0(19)
N(1)-C(4)-C(3)	116.9(16)	C(5)-C(4)-C(3)	120.0(18)
C(4)-C(5)-N(2)	114.7(19)	C(4)-C(5)-C(6)	131(2)
N(2)-C(5)-C(6)	113.1(16)	C(7)-C(6)-C(5)	120(2)
C(6)-C(7)-C(8)	125(2)	C(9)-C(8)-C(7)	120.7(18)
C(8)-C(9)-N(2)	119(2)	C(11)-C(10)-N(4)	124.6(17)
C(11)-C(10)-C(3)	118.1(19)	N(4)-C(10)-C(3)	116.7(16)
C(10)-C(11)-C(12)	114(2)	C(13)-C(12)-C(11)	117(2)
C(14)-C(13)-C(12)	121(2)	C(13)-C(14)-N(4)	126.5(19)
N(5)-C(15)-C(16)	130.9(19)	N(5)-C(15)-C(20)	115.6(18)
C(16)-C(15)-C(20)	113.4(18)	C(15)-C(16)-C(17)	118.2(18)
C(18)-C(17)-C(16)	113(2)	C(17)-C(18)-C(19)	117.4(19)
N(5)-C(19)-C(18)	125(2)	C(21)-C(20)-N(6)	123.9(19)
C(21)-C(20)-C(15)	124.4(19)	N(6)-C(20)-C(15)	110.8(16)
C(20)-C(21)-C(24)	132.6(18)	C(20)-C(21)-N(7)	119(2)
C(24)-C(21)-N(7)	107.9(18)	N(7)-C(22)-C(23)	119.5(18)
N(6)-C(23)-C(22)	127(2)	N(8)-C(24)-C(25)	119(2)
N(8)-C(24)-C(21)	114.2(19)	C(25)-C(24)-C(21)	125(2)
C(26)-C(25)-C(24)	122(2)	C(25)-C(26)-C(27)	118.6(19)
C(26)-C(27)-C(28)	117(2)	N(8)-C(28)-C(27)	119(2)
O(1)-C(29)-O(2)	130(2)	O(1)-C(29)-C(30)	117.0(17)
O(2)-C(29)-C(30)	112.3(17)	F(3)-C(30)-F(2)	108(2)
F(3)-C(30)-F(1)	104(2)	F(2)-C(30)-F(1)	110(2)
F(3)-C(30)-C(29)	113.4(18)	F(2)-C(30)-C(29)	111.2(19)
F(1)-C(30)-C(29)	110.5(17)	O(4)-C(31)-O(3)	129(2)
O(4)-C(31)-C(32)	121(2)	O(3)-C(31)-C(32)	109.7(19)
F(6)-C(32)-F(4)	105(2)	F(6)-C(32)-F(5)	103(2)
F(4)-C(32)-F(5)	107(2)	F(6)-C(32)-C(31)	116(2)
F(4)-C(32)-C(31)	112.1(19)	F(5)-C(32)-C(31)	112.1(18)

selected bond lengths and angles are collected in Table 3. Each bpp ligand connects two tetrahedral silver(I) ions both in a monodentate fashion to one Ag atom (Ag(2)-N(4)=2.22(2) Å; Ag(1)-N(8)=2.26(2) Å) and in a bidentate fashion to the second Ag site (Ag(1)-N(1)=2.32(2) Å; Ag(1)-N(2)=2.31(3) Å; Ag(2)-N(5)=2.40(2) Å; Ag(2)-N(6)=2.43(2) Å). The bridged tridentate fashion creates a large cycle consisting of an alternating arrangement of the bpp and silver atom. Such a tridentate bonding mode seems to be reasonable for tetrahedral geometric metals. The bonding mode is similar to that of bipypz in [CuBr(bipypz)] (bipypz=bis(2,3-(2-pyridyl)pyrazine).[21] The pyridine ring of the monodentate site (N(4), C(10), C(11), C(12), C(13), and C(14)) is not coplanar with the pyrazine ring (N(1), C(1), C(2), N(3), C(3), and C(4)); in fact, the monodentate ring is twisted by 55.7(6)° with respect to the pyrazine plane. Within the bidentate group, the dihedral angle between the pyrazine ring and the pyridine ring (N(2), C(5), C(6), C(7), C(8), and C(9)) is 34.9(9)°. The small bite angles of the bpp (N(1)-Ag(1)-N(2) =72.3(6)°; N(5)-Ag(2)-N(6)=69.4(6)°) deviate the tetrahedral geometry of the silver(I) center. The trifluoroacetato anion is bonded to each silver(I) ion as a fourth ligand in a monodentate (2.44(2), 2.49(2) Å). The packing diagram indicates that the crystal is consisted of discrete cyclodimeric molecules.

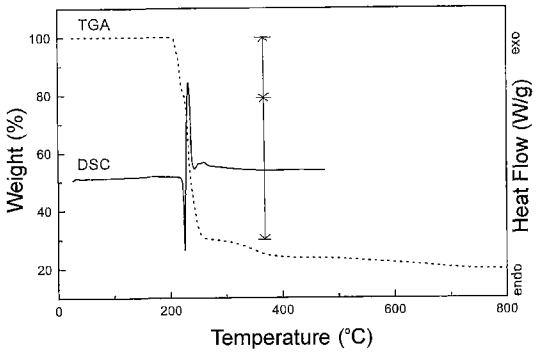


Fig. 3. Overlay of TGA and DSC traces of [Ag(bpp)$(CF_3CO_2)]_2$, each recorded at a heating rate of 10°C min^{-1}.

Thermal Properties. The TGA (thermogravimetric analysis) and DSC (differential scanning calorimeter) traces of $[Ag(bpp)(CF_3CO_2)]_2$ are depicted in Figure 3. The TGA curve shows that the compound is stable up to 212°C. Two steps weight loss at 212-230°C: a weight loss corresponding to the CF_3CO_2 group (eq 1), and followed by the dissociation of the bpp (eq 2).

$$[Ag(bpp)(CF_3CO_2)]_2 \rightarrow [Ag(bpp)]_2+2CF_3CO_2 \quad (1)$$

$$[Ag(bpp)]_2 \rightarrow 2Ag \text{ or } Ag_2O+2bpp \quad (2)$$

The thermal stability of the compound may be in part attributed to the interligand face-to-face interaction (ca. 3.7-4.0 Å) within the cyclic dimer. The IR bands of the sample are consistent with the functional groups of the structure. In particular, $\nu(CF_3CO_2)$ band strongly appears at 1686 cm^{-1}, which is explicable for the monodentate bonding mode.

In conclusion, the bpp ligand is bonded to the Ag(I) metal center in a bridged tridentate mode, resulting in a discrete cyclodimeric molecule. The specific geometry of the central metal ion is an important factor for tuning the bonding mode and the conformation around the inter-annular C-C bond. Our results along with thermal analyses may be applied to design and construct rationally the elaborate structures that exhibit desirable properties.

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Supporting Information Available: X-ray crystallographic files of $[Ag(bpp)(CF_3CO_2)]_2$ are available from OSJ.

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