Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Synthesis and characterization of tris(2-pyridylthio)methanido Zn complex with a Zn–C bond and DFT calculation of its one-electron oxidized product

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Experimental

General Procedures. All chemicals were purchased from Aldrich, Nacalai Tesque and Wako Pure Chemical. All reagents and solvents were used without further purification. Tris(pyridylthio)methane (tptmH) was prepared as described in the literature.[1] NMR spectra were recorded on JEOL Lambda 300 and 400 spectrometers at room temperature. Infrared spectra were recorded using KBr discs on a JASCO FTIR 420 spectrophotometer in the range of 4000—400 cm^{-1}. Electrochemical measurements were performed with a BAS CV-50W voltammetric analyzer. Cyclic voltammograms were measured at 20 ºC using platinum disk working (ϕ = 1.6 mm), Ag/Ag$^+$ reference and platinum wire counter electrodes. n-Bu$_4$NPF$_6$ (0.1 M) was used as supporting electrolyte and dichloromethane was used as solvent. Potentials were referred to an internal Fc/Fc$^+$ couple, of which the redox potential was standardized as 0.400 V *vs.* SHE. Elemental analyses were performed by the Analytical Research Service Centre at Osaka City University on FISONS Instrument EA108 or Perkin Elmer 240C elemental analyzers. Electrospray ionization mass spectrometry was performed on an Applied Biosystem Mariner time-of-flight mass spectrometer.

Synthesis of [ZnCl(tptm)] (1-Cl). Tris(pyridylthio)methane (tptmH, 0.20 mmol, 69 mg) and K$_2$CO$_3$ (0.10 mmol, 14 mg) were added to a solution of ZnCl$_2$ (0.20 mmol, 27 mg) in acetonitrile (40 mL), and the resulting mixture was refluxed for 17 h at 80 ºC. After insoluble white solids were filtered off, the filtrate was concentrated on a rotary evaporator to ca. 10 mL. The concentrated filtrate was kept in a refrigerator to give a yellow solid (27 mg, 0.060 mmol, 30%). Single crystals suitable for X-ray diffraction analysis were obtained from a yellow solution of the complex in dichloromethane by slow diffusion of cyclohexane layered on the solution. Anal. Calcd for C$_{16}$H$_{12}$ClN$_3$S$_3$Zn: C, 43.35; H, 2.73; N, 9.48, Found: C, 43.29; H, 2.65; N, 9.38%. ^{1}H

NMR ($CDCl_3$): δ9.46 (d, 3H, 6-py), 7.57 (t, 3H, 4-py), 7.11—7.06 (m, 6H, 3-py, 5-py). IR (KBr; cm^{-1}): 1589(s), 1558(s), 1453(s), 1414(s), 1281(s), 1159(w), 1131(m), 1092(w), 1046(s), 1004(s), 877(w), 762(m), 723(s), 638(s), 614(m), 490(w), 408(w).

Synthesis of [ZnBr(tptm)] (1-Br). The bromo complex was prepared in a similar manner as the chloro complex using a solution of $ZnBr_2$ (0.20 mmol, 45.0 mg). A small amount of single crystals of [$ZnBr_2$(tptmH)] (**2-Br**) produced during trial of recrystallization to obtain suitable single crystals for X-ray diffraction analysis from a solution of the complex in acetonitrile by slow diffusion of diethylether layered on the solution. **1-Br**: Anal. Calcd for $C_{16}H_{12}BrN_3S_3Zn$: C, 39.40; H, 2.48; N, 8.61, Found: C, 39.97; H, 2.45; N, 8.57%. ^1H NMR ($CDCl_3$): δ9.51 (d, 3H, 6-py), 7.57 (t, 3H, 4-py), 7.11–7.07 (m, 6H, 3-py, 5-py). IR (KBr; cm^{-1}): 1589(s), 1557(s), 1453(s), 1414(s), 1281(s), 1158(w), 1131(m), 1092(w), 1047(s), 1002(s), 876(w), 761(m), 724(s), 638(s), 621(w), 489(w), 408(w).

Synthesis of [$ZnBr_2$(tptmH)] (2-Br). The tptmH bromo complex **2-Br** was separately prepared. Solutions of $ZnBr_2$ (46 mg, 0.20 mmol) and tptmH (65 mg, 0.19 mmol) in acetonitrile (10 mL each) were mixed together. The resulting solution was kept in a refrigerator to give a white solid, which was collected by filtration (79 mg, 0.14 mmol, 73%). Anal. Calcd for **2-Br•CH_3CN** ($C_{18}H_{16}Br_2N_4S_3Zn$): C, 35.46; H, 2.64; N, 9.19, Found: C, 35.31; H, 2.51; N, 8.86%. ^1H NMR ($CDCl_3$): δ9.4 (br, 2H, py), 8.2—7.4 (br, 8H, py), 7.2 (br, 2H, py), 6.66 (s, 1H, CH).

Synthesis of [$ZnCl_2$(tptmH)] (2-Cl). The tptmH chloro complex **2-Cl** was prepared in a similar manner as the corresponding bromo complex using solutions of $ZnCl_2$ (32 mg, 0.23 mmol) and tptmH (80 mg, 0.23 mmol) in acetonitrile (5 mL each). The resulting a white solid was collected by filtration (88 mg, 0.18 mmol, 78%). Anal. Calcd for **2-Cl** ($C_{18}H_{16}Cl_2N_4S_3Zn$): C, 40.05; H, 2.73; N, 8.76, Found: C, 39.80; H, 2.97; N, 8.71%. ^1H NMR ($CDCl_3$): δ9.3 (br, 3H, py), 8.2—7.5 (br, 9H, py), 6.66 (s, 1H, CH).

Chemical oxidation of [ZnCl(tptm)] (1-Cl). The chloro complex **1-Cl** was oxidized in acetonitrile by excess cerium ammonium nitrate. After removal of the solvent, the residue was extracted with CD_2Cl_2. Although the ^1H NMR spectrum of the extract showed that the reaction gave a complicated mixture, the electrospray mass spectrum clearly showed that the mixture contains 2,2’-dopyridyldisulfide as the protonated form and the sodium adduct.

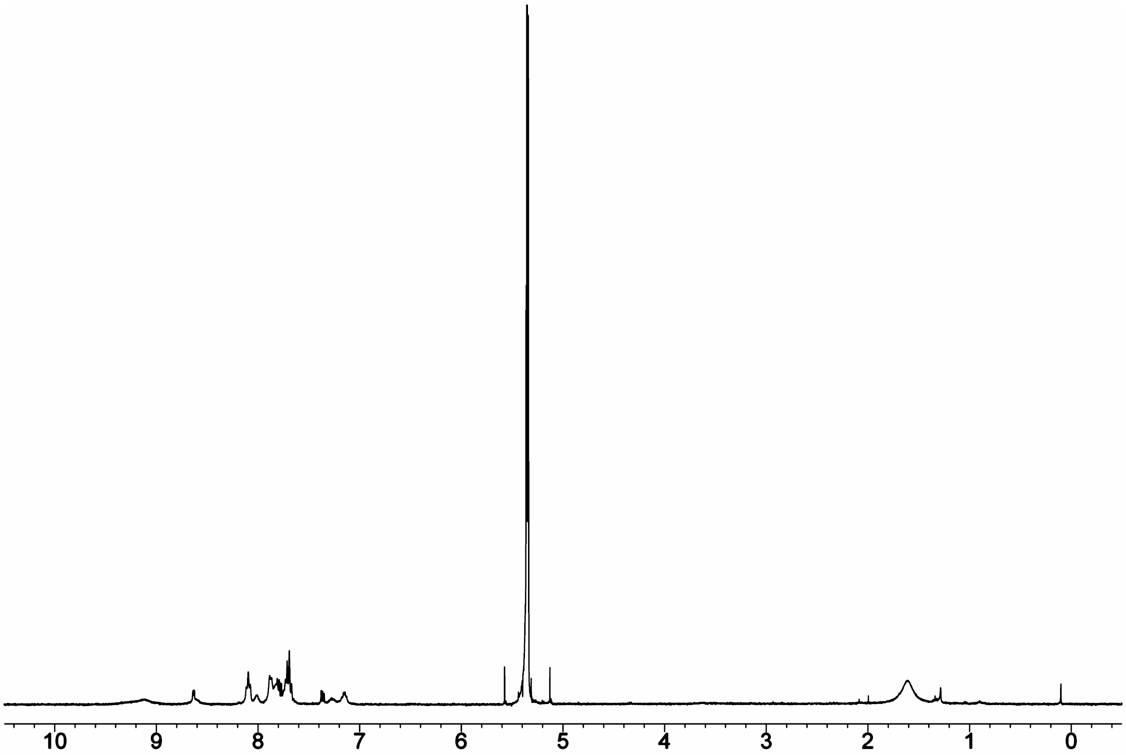

Fig. S1. ^{1}H NMR spectrum (CD_2Cl_2) of the products obtained by oxidative decomposition reaction of [ZnCl(tptm)] **1-Cl**.

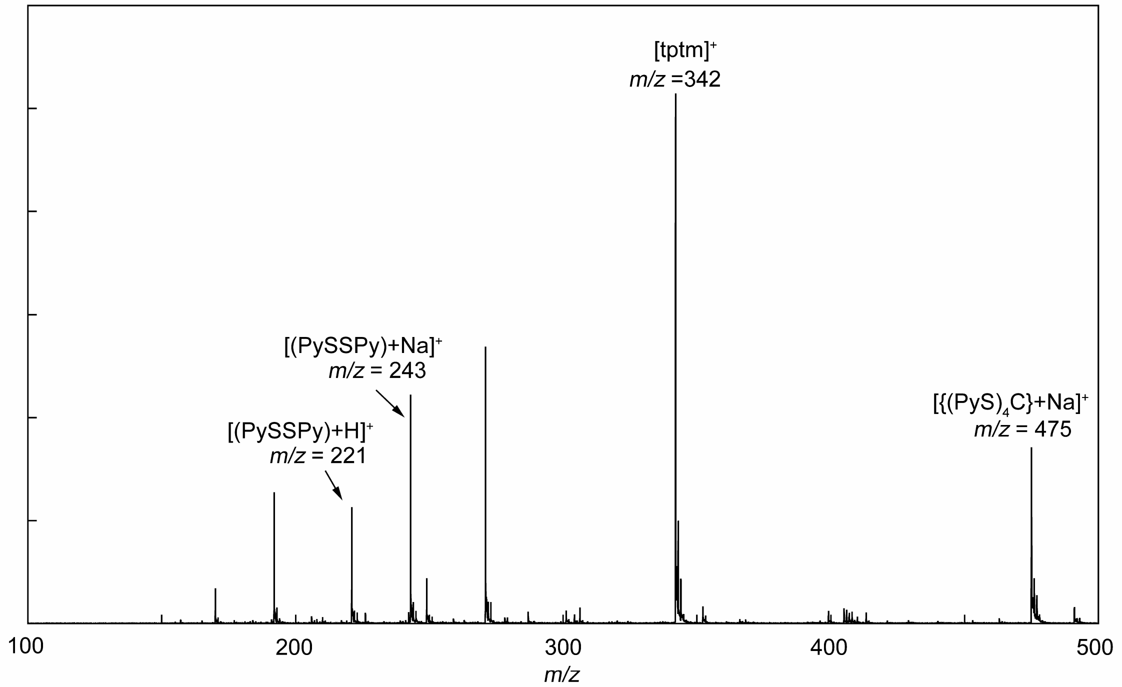

Fig. S2. Electrospray ionization mass spectrum of the products obtained by oxidative decomposition reaction of [ZnCl(tptm)] **1-Cl**.

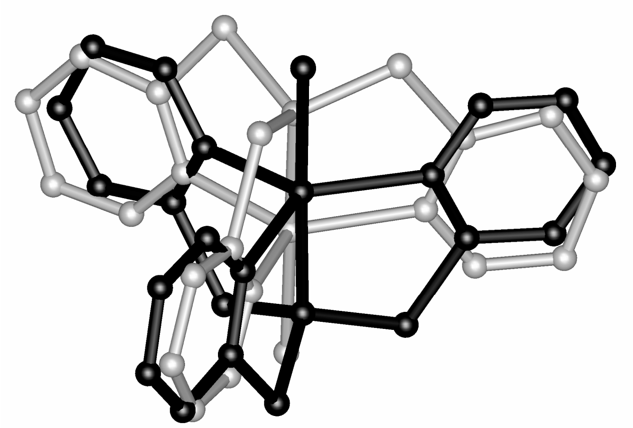

Fig. S3. Disordered structure of **2-Cl** obtained by X-ray analysis. The black and gray colored molecules represent the two disordered components in the asymmetric unit with 0.8 and 0.2 occupancies, respectively.

Table S1. Mulliken atomic spin densities

1	C	0.552105
2	S	0.111015
3	S	0.111284
4	S	0.111223
5	C	0.003024
6	C	0.003045
7	C	0.002971
8	N	0.014408
9	N	0.014331
10	N	0.014397
11	C	-0.006167
12	C	-0.006148
13	C	-0.006169
14	C	0.013827
15	C	0.013763
16	C	0.013852
17	C	-0.006628
18	C	-0.006605
19	C	-0.006637
20	C	0.012694
21	C	0.012652
22	C	0.012728
23	H	0.001066
24	H	0.001068
25	H	-0.000513
26	H	-0.000510
27	H	-0.000514
28	H	0.000172
29	H	0.000172
30	H	0.000172
31	H	-0.000031
32	H	-0.000028
33	H	-0.000034
34	Cl	0.000401
35	Zn	0.018544
36	H	0.001069

Table S2. Molecular coordinates of the oxidized complex, $[ZnCl(tptm)]^+$, optimized by the density functional calculation.

	Atomic Number	Atomic Type	x	y	z
1	6	0	-0.002006	-0.004815	-1.791599
2	16	0	-1.625067	0.621308	-2.061586
3	16	0	1.351746	1.087267	-2.063170
4	16	0	0.265988	-1.724433	-2.056280
5	6	0	-2.558229	-0.197285	-0.770845
6	6	0	1.105385	2.310789	-0.778673
7	6	0	1.447167	-2.119221	-0.769401
8	7	0	-1.969734	-0.447335	0.415037
9	7	0	0.594573	1.930264	0.408420
10	7	0	1.374398	-1.480438	0.414469
11	6	0	-2.712443	-1.016118	1.390251
12	6	0	0.477111	2.859403	1.382321
13	6	0	2.243651	-1.834321	1.386675
14	6	0	-4.052925	-1.338312	1.219277
15	6	0	0.869299	4.180685	1.207856
16	6	0	3.193280	-2.833707	1.214747
17	6	0	-4.657479	-1.067691	-0.007656
18	6	0	1.404300	4.565450	-0.020901
19	6	0	3.255982	-3.497047	-0.010048
20	6	0	-3.897355	-0.494359	-1.024642
21	6	0	1.518889	3.617953	-1.035849
22	6	0	2.373914	-3.130247	-1.024083
23	1	0	0.078953	2.499551	2.325362
24	1	0	2.135376	-1.303466	2.326709
25	1	0	-4.605208	-1.787549	2.037004
26	1	0	0.759130	4.885415	2.024391
27	1	0	3.862962	-3.083384	2.030045
28	1	0	-5.702256	-1.308811	-0.178372
29	1	0	1.719482	5.589879	-0.194253
30	1	0	3.987486	-4.280831	-0.181597
31	1	0	-4.323676	-0.289390	-2.000744
32	1	0	1.910877	3.881562	-2.012253

33	1	0	2.405390	-3.605423	-1.998651
34	17	0	0.002135	0.009608	3.147824
35	30	0	0.000200	0.001733	0.893477
36	1	0	-2.199378	-1.183517	2.331547

Reference

1 I. Kinoshita, L. J.. Wright, S. Kubo, K. Kimura, A. Sakata, T. Yano, R. Miyamoto, T. Nishioka, K. Isobe, *Dalton Trans.*, 2003, 1993-2003.