Electronic Supporting Information for C–H···Cl^- hydrogen bond in solution and the solid-state: $HgCl_2$ complexes with cyclen-based cryptands

Mari Ikeda,*[a] Ajay Kumar Sah,[b] Miki Iwase,[c] Rina Murashige,[c] Jun-ichi Ishi-i,[c,d] Masatoshi Hasegawa,[c,d] Chihiro Kachi-Terajima,[c,d] Ki-Min Park,[e] Shunsuke Kuwahara[c,d] and Yoichi Habata*[c,d]

[a] *Education Centre, Faculty of Engineering, Chiba Institute of Technology, 2-1-1 Shibazono, Narashino, Chiba 275-0023, Japan*

[b] *Department of Chemistry, Birla Institute of Technology and Science, Pilani-333031, Rajasthan, India*

[c] *Department of Chemistry, Faculty of Science, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510*

[d] *Research Centre for Materials with Integrated Properties, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan; E-mail: habata@chem.sci.toho-u.ac.jp; Fax: +81 47 472 4322*

[e] *Research Institue of Natural Science, Gyeongsang National University, Jinju, 52828, S. Korea*

Table of Contents

Synthesis of 2/$HgCl_2$ complex

Compound **2** (0.0151 mmol) in acetonitrile (1 mL) was added to equimolar amounts of $HgCl_2$ in acetonitrile (1 mL). An acetonitrile molecule in the complex did not escape by heating at 100 °C.

Anal. Calcd. for C $(C_{28}H_{42}N_4O_4)_2$ $(CH_3CN)_2(HgCl_2)_3$: C, 38.05; H, 4.79; N, 7.40. Found: C, 38.16; H, 4.68; N, 7.11.

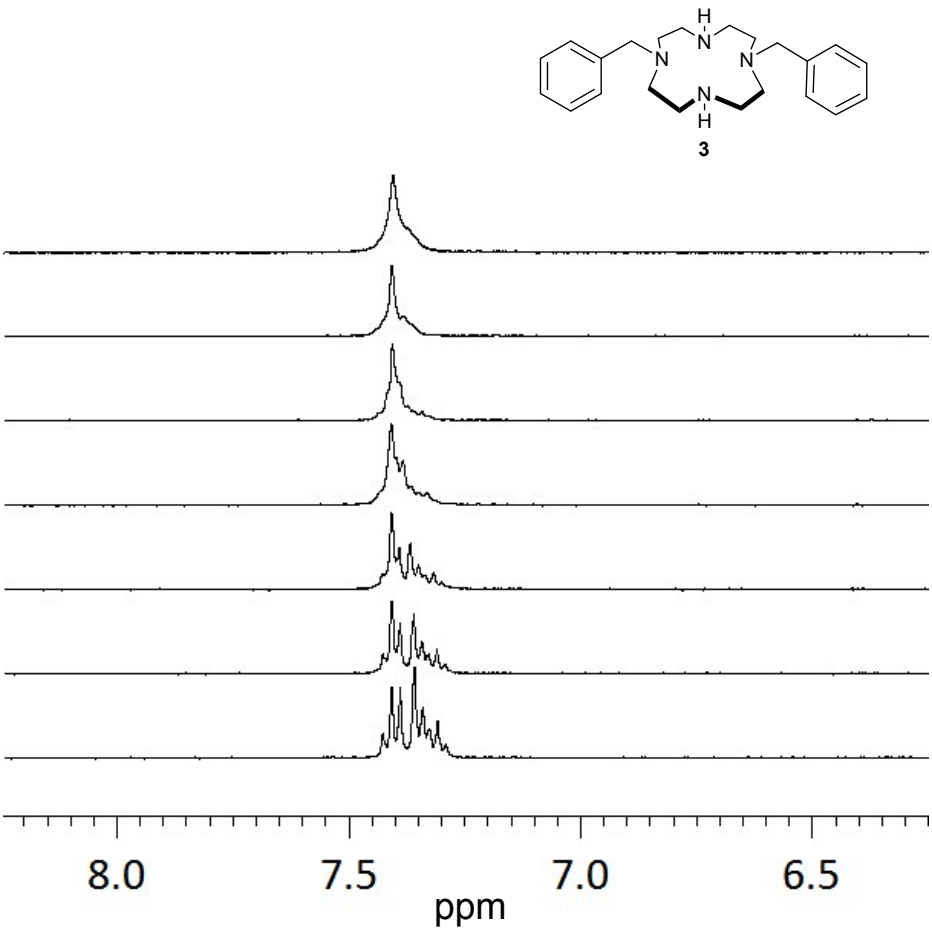

Fig. S1. $HgCl_2$-induced ^1H NMR spectral changes (aromatic region; δ 8.25–6.25) of 3 in CD_2Cl_2/CD_3OD. From bottom to top, $[HgCl_2]/[3]$ = 0, 0.2, 0.4, 0.6, 0.8, 1.0, and 2.0.

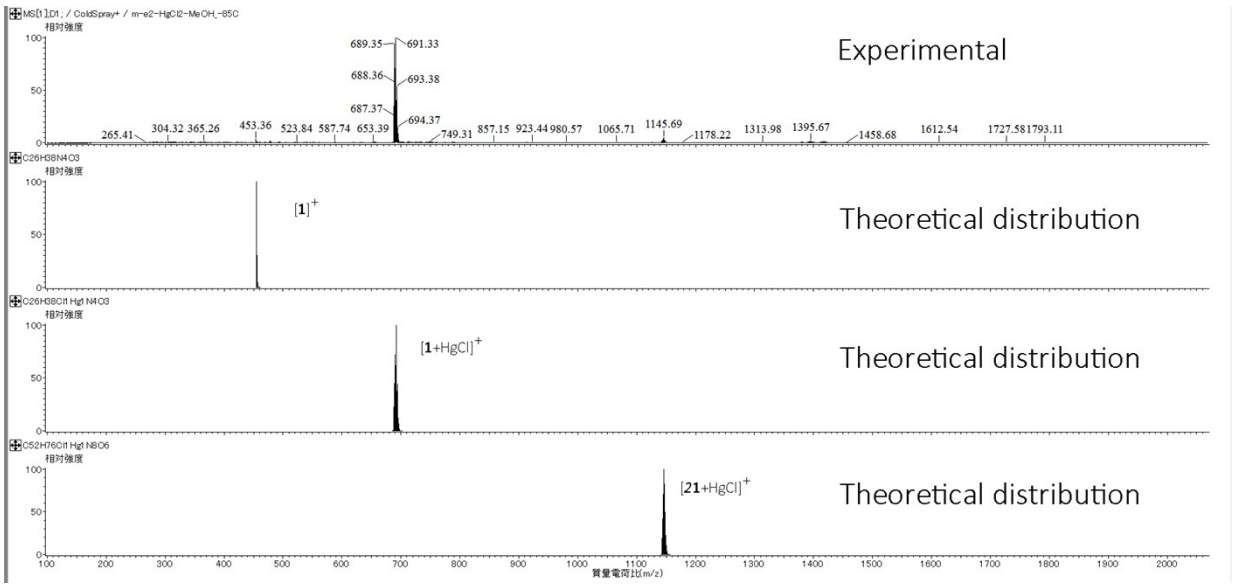

Fig. S2. CSI-MS of 1/$HgCl_2$ complex at –85 °C in MeOH. Experimental data (top) and theoretical distributions.

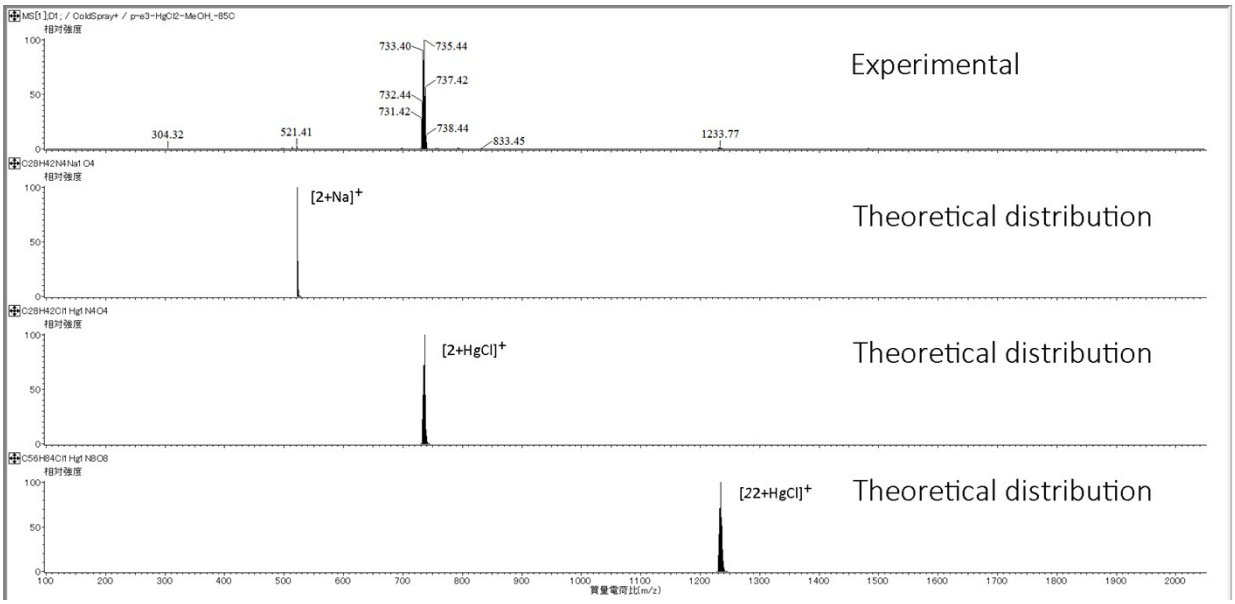

Fig. S3. CSI-MS of 2/$HgCl_2$ complex at –85 °C in MeOH. Experimental data (top) and theoretical distributions.

Table S1. Condition of TGA measurement

Sample weight: 13.70 mg

Nitrogen flow rate: 200 mL/min

Rate of temperature increase: 5 °C/min

The range of temperature: r.t. – 800 °C

Table S2. Selected bond distances (Å) in the 2/$HgCl_2$ complex.

O2···H29c	2.705	Cl1···C15	3.656	Hg1···N1	2.503
O3···H29c	2.426	Cl1···H18	2.716	Hg1···N2	2.310
N5···H2	2.191	Cl1···C18	3.647	Hg1···N3	2.497
Cl1···H15	2.734	Hg1···Cl1	2.392	Hg1···N4	2.371

Table S3. Crystal data and structure refinement for the 2/$HgCl_2$ complex.

Empirical formula	$C_{60}H_{90}Cl_6Hg_3N_{10}O_8$
M	1893.89
T/K	150
Crystal system	Orthorhombic
Space group	Pccn
a/Å	43.064(2)
b/Å	9.2965(4)
c/Å	17.5771(8)
α/°	90 °
β/°	90 °
γ/°	90 °
U/Å^3	7036.9(6)
Z	4
Dc/g cm^{-3}	1.788
μ/mm^{-1}	6.814
No. reflns used [> 2σ(*I*)]	6245 [R(int) = 0.1234]
R_1, wR_2 [I>2σ(*I*)]	0.0787, 0.2036
R_1, wR_2 [all data]	0.0969, 0.2148
Completeness to theta =	25.0 ° 99.9 %
Data / restraints / parameters	6245 / 82 / 394
GOF	1.115

Synthesis of 2/$ZnCl_2$ complex

Compound **2** (0.0151 mmol) in acetonitrile (1 mL) was added to $ZnCl_2$ (0.023 mmol) in acetonitrile (1 mL). Acetonitrile molecules in the complex did not escape by heating at 100 °C.

Anal. Calcd. for C $(C_{28}H_{42}N_4O_4)_2$ $(CH_3CN)_3$ $(ZnCl_2)_3$: C, 48.95; H, 6.16. Found: C, 48.85; H, 6.34.

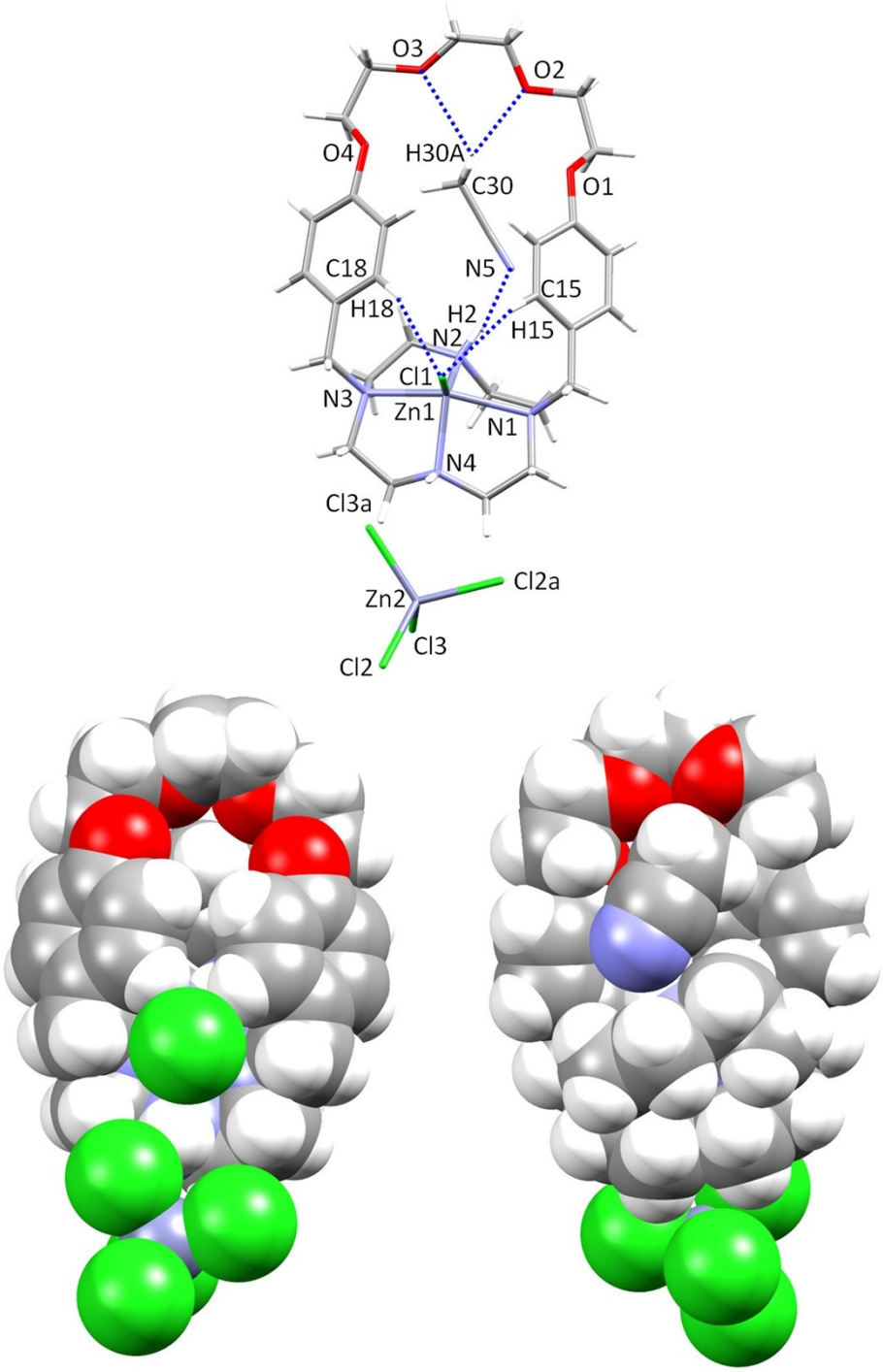

Fig. S4. Tube representation (top) and space-filling representations [foreside (bottom left) and back side (bottom right)] of the 2/$ZnCl_2$ complex. Crystal solvents (CH_3CN and H_2O) were omitted to clarify.

We obtained X-ray structure of **2**/$ZnCl_2$ complex which has Zn as a congener. The X-ray structure of **2**/$ZnCl_2$ is similar with that of the structure of **2**/$HgCl_2$. The Zn–*tert*-N (N1 and N3) and the Zn–*sec*-N (N2 and N4) distances are 2.288–2.215 Å and 2.071–2.078 Å, respectively. The Cl1–Zn1 distance is 2.257 Å. These distances are comparable to those of the $ZnCl_2$ complexes with cyclens.[1-9] In this system, Cl1 makes hydrogen bonds with the aromatic hydrogens (H15 and H18) of the side-arms, and the H15···Cl1, H15, C15···Cl1, H18···Cl1, and C18···Cl1 distances are 2.652, 3.546, 2.675, and 3.580 Å, respectively. The C–(H)···Cl^- distances determined in this system are also comparable with typical CH···Cl^- hydrogen bonds in the solid state.

Table S4. Selected bond distances (Å) in the 2/$ZnCl_2$ complex.

O2···H30A	2.550	Cl1···C15	3.546	Zn1···N1	2.288
O3···H30A	2.818	Cl1···H18	2.675	Zn1···N2	2.071
N2···H5	2.237	Cl1···C18	3.580	Zn1···N3	2.215
Cl1···H15	2.652	Zn1···Cl1	2.257	Zn1···N4	2.078

Table S5. Crystal data and structure refinement for the 2/$ZnCl_2$ complex.

Empirical formula	$C_{62}H_{96}Cl_6Zn_3N_{11}O_{9.5}$
M	1556.31
T/K	150 K
Crystal system	Orthorhombic
Space group	Pcca
a/Å	46.221(2)
b/Å	8.9997(4)
c/Å	17.4129(8)
α/°	90 °
β/°	90 °
γ/°	90 °
U/Å^3	7243.4(6)
Z	4
Dc/g cm^{-3}	1.427
μ/mm^{-1}	1.267
No. reflns used [> 2σ(*I*)]	5890 [R(int) = 0.0634]
R_1, wR_2 [I>2σ(*I*)]	0.0757, 0.1835
R_1, wR_2 [all data]	0.0952, 0.2000
Completeness to theta =	24.30 ° 99.8%
Data / restraints / parameters	5890 / 57 / 434
GOF 1.221	

The structure of **2**/$ZnCl_2$ complex in solution was confirmed by CSI-MS and ^{1}H NMR. Both data clearly suggest that **2** forms a 1:1complex with $ZnCl_2$. The structure of **2**/$ZnCl_2$ complex is similar with that of **2**/$HgCl_2$ complex in the solution.

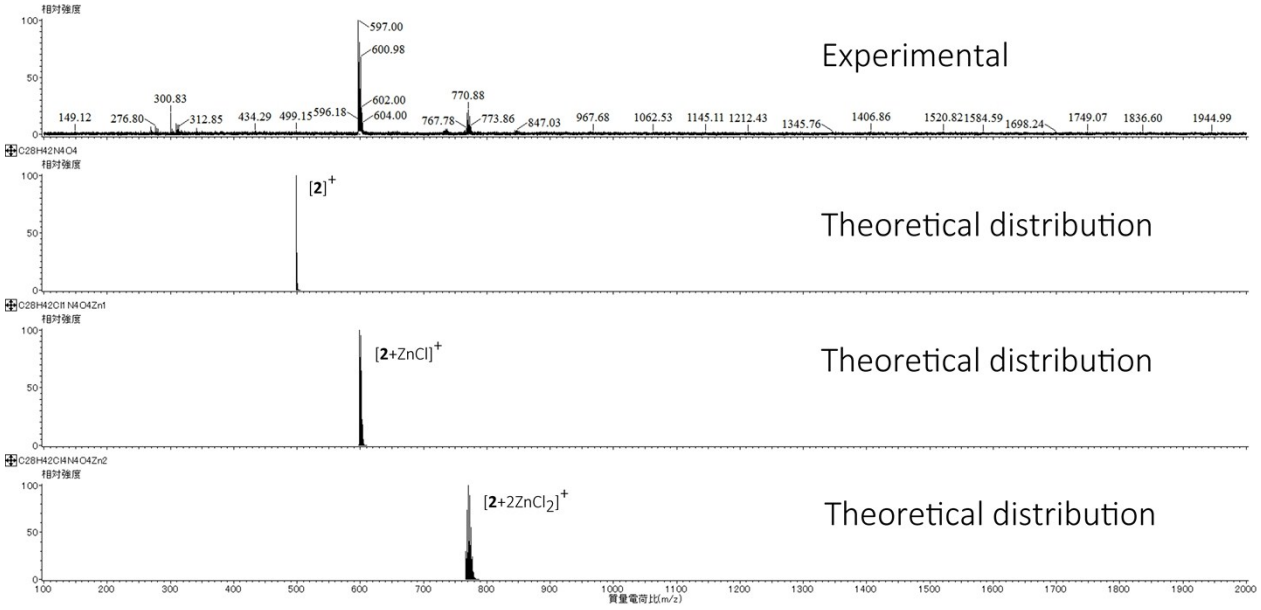

Fig. S5. CSI-MS of 2/$ZnCl_2$ complex at 25 ^{o}C in MeOH. Experimental data (top) and theoretical distributions.

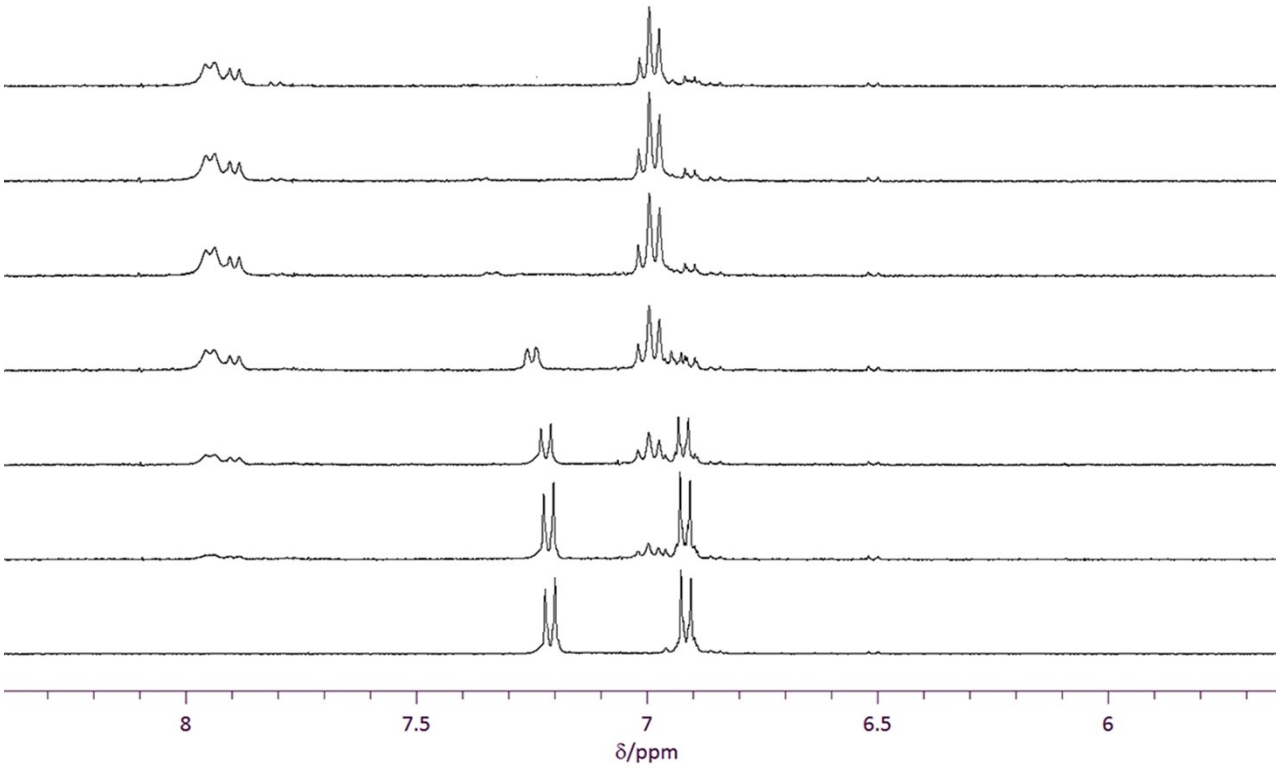

Fig. S6. $ZnCl_2$-induced ^{1}H NMR spectral changes (aromatic region; δ 8.4–5.7) of 2 in CD_2Cl_2/CD_3OD. From bottom to top, [$ZnCl_2$]/[2] = 0, 0.2, 0.4, 0.6, 0.8, 1.0, and 2.0.

References

1. S. Amatori, G. Ambrosi, M. Fanelli, M. Formica, V. Fusi, L. Giorgi, E. Macedi, M. Micheloni, P. Paoli, R. Pontellini, P. Rossi and M. A. Varrese, *Chemistry – A Eur. J.*, 2012, **18**, 4274-4284.
2. S. Aoki, Y. Tomiyama, Y. Kageyama, Y. Yamada, M. Shiro and E. Kimura, *Chemistry – An Asian J.*, 2009, **4**, 561-573.
3. C. Bazzicalupi, A. Bencini, E. Berni, C. Giorgi, S. Maoggi and B. Valtancoli, *Dalton Trans.*, 2003, 3574-3580.
4. M. Bhuyan, E. Katayev, S. Stadlbauer, H. Nonaka, A. Ojida, I. Hamachi and B. König, *Eur. J. Org. Chem.*, 2011, **2011**, 2807-2817.
5. G. Gasser, M. J. Belousoff, A. M. Bond, Z. Kosowski and L. Spiccia, *Inorg. Chem.*, 2007, **46**, 1665-1674.
6. T. J. Hubin, N. W. Alcock, M. D. Morton and D. H. Busch, *Inorg. Chim. Acta*, 2003, **348**, 33-40.
7. K. Kobayashi, M. Shionoya, E. Kimura, K. Tsuboyama and S. Tsuboyama, *Anal. Sci.*, 1995, **11**, 1029-1030.
8. V. S. Stafford, K. Suntharalingam, A. Shivalingam, A. J. P. White, D. J. Mann and R. Vilar, *Dalton Transactions*, 2015, **44**, 3686-3700.
9. H.-R. Xu, K. Li, M.-Q. Wang, B.-L. Wang, X. Wang and X.-Q. Yu, *Org. Chem. Front.*, 2014, **1**, 1276-1279.