Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2020, **30**, 445–448

Mendeleev Communications

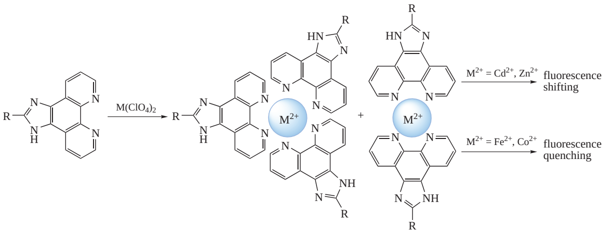
Imidazo[4,5-*f*][1,10]phenanthroline complexes with Fe^{2+}, Cd^{2+}, Co^{2+} and Zn^{2+} ions

Sergey D. Tokarev,*[a,b] Yury V. Fedorov[b] and Olga A. Fedorova[b]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 932 8568; e-mail: tokarevsergeydm@yandex.ru*
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 9280*

DOI: 10.1016/j.mencom.2020.07.013

Reactions of 2-(het)aryl substituted 1*H*-imidazo[4,5-*f*]-[1,10]phenanthrolines with Cd^{2+}, Zn^{2+}, Co^{2+} and Fe^{2+} perchlorates afford complexes of 2:1 and 3:1 ligand/metal ratios. Complexes of ligands with Cd^{2+} and Zn^{2+} are luminescent, while Co^{2+} and Fe^{2+} complexes are highly stable ($K > 10^{21}$), do not luminesce and demonstrate electron transfer from metal to ligand.



Keywords: imidazophenanthrolines, cadmium complexes, zinc complexes, iron complexes, cobalt complexes, optical properties, luminescence, electron transfer.

In the past three decades, organic compounds have attracted much attention as active components in electronic, optical and sensor devices.[1(*a*)–(*d*)] Derivatives of imidazo[4,5-*f*][1,10]phenanthroline, in particular 2-substituted ones, have been employed as photoactive materials, luminescent sensors, OLED components, for nonlinear optical applications.[2(*a*)–(*f*)] They also have biological and medical value due to the ability to penetrate into cells, intercalate into DNA and affect its function.[3(*a*)–(*d*)] 1,10-Phenanthroline complexes with metal cations possess noticeable photo- or electroluminescence,[4(*a*),(*b*)] nonlinear optical properties,[5(*a*),(*b*)] biological activity,[6(*a*)–(*d*)] are able to participate in charge and energy transfer processes[7(*a*),(*b*)] or can form metal-organic framework (MOF) structures.[8(*a*),(*b*)] The Ru^{II} complexes, which are used as photosensitizers of molecular devices,[9] dye-sensitized solar cells,[10(*a*)–(*c*)] photocatalysts[11(*a*),(*b*)] and components of luminescent sensors,[12(*a*),(*b*)] worth highlighting in a separate category. However, examples of systematic information on the structure–property dependence within imidazo[4,5-*f*][1,10]phenanthroline complexes are few and require further development.

Herein, we synthesized ligands **1**–**4** and studied their complexation with Cd^{2+}, Zn^{2+}, Co^{2+} and Fe^{2+} perchlorates (Scheme 1). Our goals were to determine the structure of the complexes, their behavior in solution and to analyze the effect of the substituents in the ligand and the impact of central cation electronic structure on the optical properties of the complexes. Within the series, ligands vary according to the donor ability of the substituent at the 2-position of imidazole ring. Two groups of cations were chosen for complex formation study: Zn^{II} and Cd^{II} possess a stable completely filled d-shell; therefore, d–d transitions in their compounds are impossible. Both the Fe^{2+} and Co^{2+} cations have free d-orbitals; so, electron transfer between ligands and the central cation is possible in their complexes.

Ligands **1**–**4** were prepared[†] as described.[13] The donor ability of the substituent in the imidazole ring increases in the series **1** → **3** ≈ **4** → **2** and, accordingly, the absorption and fluorescence maxima are redshifted.

Complexation between compounds **1**–**4** and Fe^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+} ions was studied by optical methods, NMR spectroscopy (except for Co^{II} complexes since they are paramagnetic), and ESI-MS analysis. The ESI-MS spectra of the mixtures of ligand with metal ions Fe^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+} were used to determine the reaction scheme of complexation process.[†] For all cases, mixtures of two complexes with 1:2 and 1:3 metal/ligand ratio were formed (Table 1). According to the reported data, a 1,10-phenanthroline fragment should be the preferred binding site for these cations.[14] The tentative complexation mechanism is outline in Scheme 1.

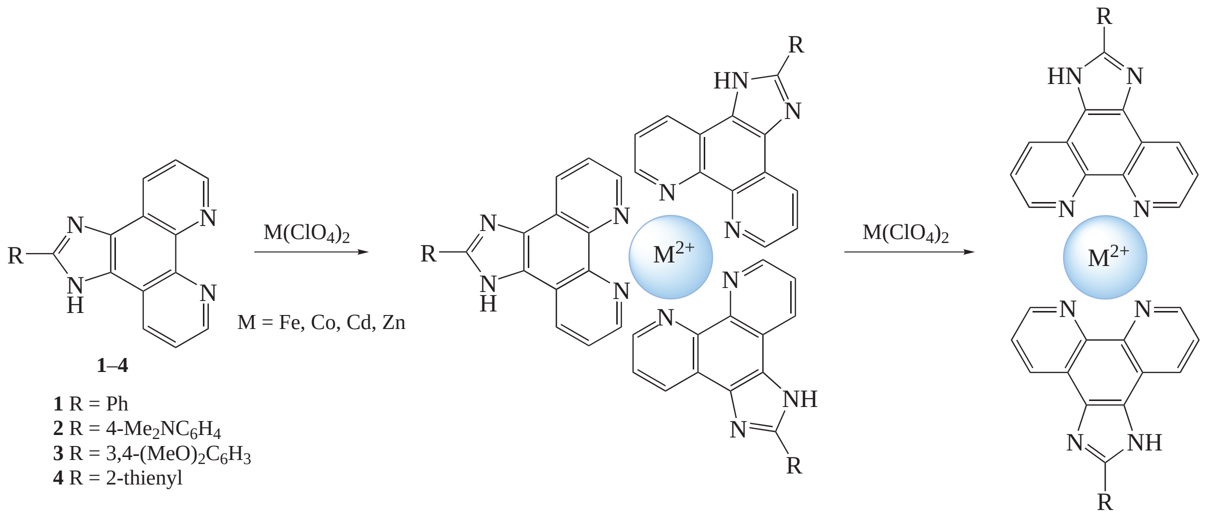
The NMR data (Figure 1) also show formation of complex with 1,10-phenanthroline moiety of ligand and confirms the formation of two types of complexes. When a three-fold excess of Cd^{2+} is added to the ligand, 2:1 (ligand–metal) tetrahedral

Table 1 ESI-MS spectra of reaction mixtures of ligands **1**–**4** and Zn^{2+}, Cd^{2+}, Co^{2+} and Fe^{2+} perchlorates.[a]

Metal (M) ion	m/z $[L_2{\cdot}M]^{2+}$ *vs.* m/z $[L_3{\cdot}M]^{2+}$			
	1	**2**	**3**	**4**
Zn^{2+}	329 $[\mathbf{1}_2{\cdot}Zn]^{2+}$	372 $[\mathbf{2}_2{\cdot}Zn]^{2+}$	389 $[\mathbf{3}_2{\cdot}Zn]^{2+}$	335 $[\mathbf{4}_2{\cdot}Zn]^{2+}$
	478 $[\mathbf{1}_3{\cdot}Zn]^{2+}$	542 $[\mathbf{2}_3{\cdot}Zn]^{2+}$	567 $[\mathbf{3}_3\ Zn]^{2+}$	486 $[\mathbf{4}_3{\cdot}Zn]^{2+}$
Cd^{2+}	352 $[\mathbf{1}_2{\cdot}Cd]^{2+}$	395 $[\mathbf{2}_2{\cdot}Cd]^{2+}$	433 $[\mathbf{3}_2{\cdot}Cd{\cdot}MeCN]^{2+}$	379 $[\mathbf{4}_2{\cdot}Cd{\cdot}MeCN]^{2+}$
	501 $[\mathbf{1}_3{\cdot}Cd]^{2+}$	565 $[\mathbf{2}_3{\cdot}Cd]^{2+}$	591 $[\mathbf{3}_3{\cdot}Cd]^{2+}$	511 $[\mathbf{4}_3{\cdot}Cd]^{2+}$
Co^{2+}	347 $[\mathbf{1}_2{\cdot}Co{\cdot}MeCN]^{2+}$	369 $[\mathbf{2}_2{\cdot}Co]^{2+}$	406 $[\mathbf{3}_2{\cdot}Co{\cdot}MeCN]^{2+}$	351 $[\mathbf{4}_2{\cdot}Co{\cdot}MeCN]^{2+}$
	495 $[\mathbf{1}_3{\cdot}Co{\cdot}MeCN]^{2+}$	538 $[\mathbf{2}_3{\cdot}Co]^{2+}$	564 $[\mathbf{3}_3{\cdot}Co]^{2+}$	501 $[\mathbf{4}_3{\cdot}Co{\cdot}MeCN]^{2+}$
Fe^{2+}	345 $[\mathbf{1}_2{\cdot}Fe]^{2+}$	368 $[\mathbf{2}_2{\cdot}Fe]^{2+}$	405 $[\mathbf{3}_2{\cdot}Fe\ MeCN]^{2+}$	351 $[\mathbf{4}_2{\cdot}Fe{\cdot}MeCN]^{2+}$
	474 $[\mathbf{1}_3{\cdot}Fe]^{2+}$	537 $[\mathbf{2}_3{\cdot}Fe]^{2+}$	563 $[\mathbf{3}_3{\cdot}Fe]^{2+}$	482 $[\mathbf{4}_3{\cdot}Fe]^{2+}$

[a] Initial ligand/cation ratio of 1:1, MeCN.

[†] For details, see Online Supplementary Materials.



Scheme 1

complexes are formed. As a result of pulling the electron density from the ligand to the positively charged central cation, the protons of the phenanthroline moeity are deshielded and their signals are shifted downfield [see Figure 1(*a*)]. When 1/3 equiv. of metal cations is added, mostly 3 : 1 complexes (ligand/metal) with the octahedral configuration are formed. In these complexes, the protons H^2 and H^3 of the phenanthroline moeity also undergo deshielding, however, proton H^1 enters the shielding region of the π-electrons of the pyridine ring of the adjacent ligand, and its signal is upfield shifted [see Figure 1(*c*)]. In either case (3 equiv. or 1/3 equiv. of cadmium(II) perchlorate) we observed only one type of complex in a spectrum.

According to the ESI-MS data, for all the cations and ligands studied, the following complexation scheme may be assumed:

$$3\,L + M^{2+} \underset{}{\overset{K_{31}}{\rightleftarrows}} (L)_3M^{2+} \qquad K_{31} = \frac{[(L)_3M^{2+}]}{[L]^3\,[M^{2+}]}$$

$$2\,L + M^{2+} \underset{}{\overset{K_{21}}{\rightleftarrows}} (L)_2M^{2+} \qquad K_{21} = \frac{[(L)_2M^{2+}]}{[L]^2\,[M^{2+}]}\,,$$

where L – ligands **1**–**4**, M^{2+} – cations Fe^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}.

The addition of Fe^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+} salts to solutions of ligands **1**–**4** leads to changes in the absorption and fluorescence spectra as a result of complexation and redistribution of electron density in the ligands. In case of ligand **1** and Zn^{II}, complex formation results in the appearance of prominent maxima in the absorption spectra at 278 and 300 nm [Figure 2(*a*)]. We calculated the stability constants of complexes with Cd^{2+}, Zn^{2+} cations based on changes in the absorption spectra during spectrophotometric titration (for details, see Online Supplementary Materials) and the proposed complexation scheme using the SpecFit32 program[15] (Table 2).

Fluorescence spectra of ligands **1**–**4** show more pronounce changes upon the addition of Cd^{2+}, Zn^{2+} than changes observed in absorption spectra (see Figure 2). Emission of the complexes is less intense and significantly shifted to the longer wavelengths (up to 130 nm for ligand **3**) compared to free ligand band.

The main mechanism of excitation of the Zn^{II} and Cd^{II} complexes is the intraligand transitions (π–π* transitions) since they have a filled d^{10} electronic configuration. Thus, the role of Cd^{2+}, Zn^{2+} cations in complexes consists mainly in the stabilization of ligand molecules.[16] As a result, emission occurs from an excited state of ligand-centred position.[17]

The nature of the substituent at the 2-position of imidazole ring in ligands affects the characteristics of Zn^{II} and Cd^{II} complexes. For either 3 : 1 or 2 : 1 complexes (ligand–metal), their stability

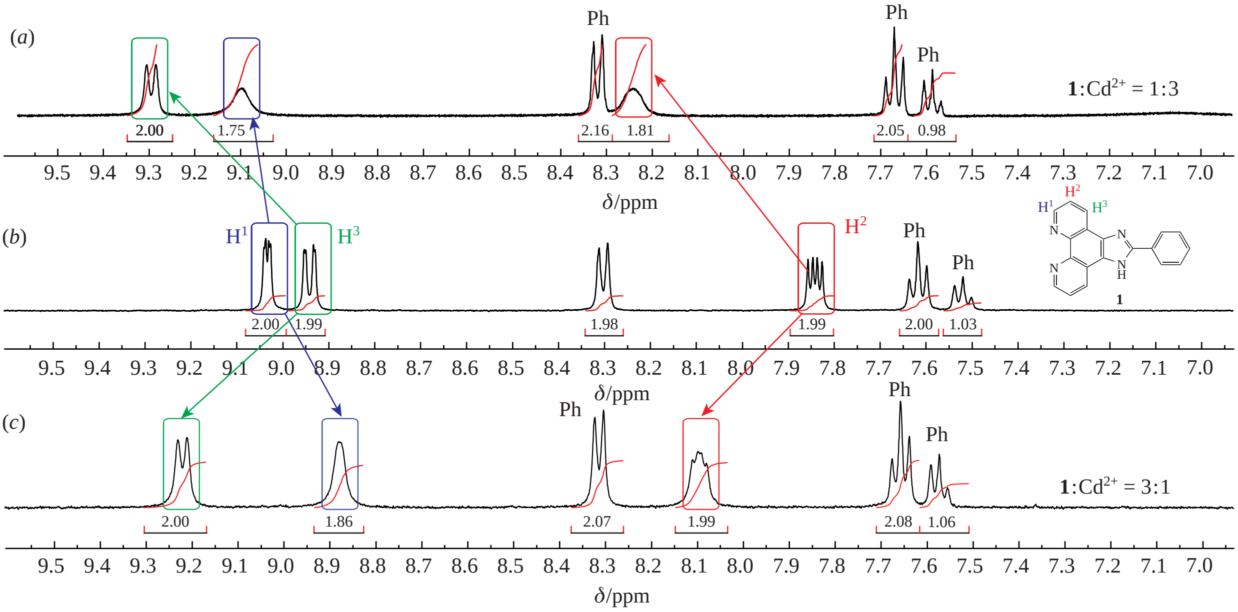


Figure 1 ^{1}H NMR spectral changes of ligand **1** protons upon complexation: (*a*) with **1**/Cd(ClO$_4$)$_2$ ratio 1 : 3; (*b*) free ligand **1**; (*c*) with **1**/Cd(ClO$_4$)$_2$ ratio 3 : 1.

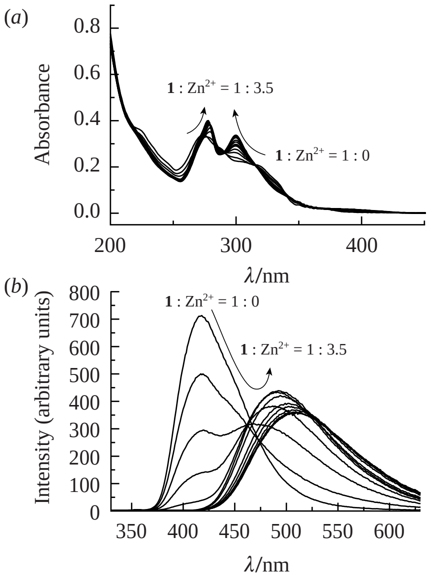


Figure 2 Electronic (*a*) absorption and (*b*) emission spectra of a MeCN solution of ligand **1** at various concentrations of zinc(II) perchlorate. The initial concentration of the ligand $C_1 = 1\times10^{-5}$ M, the concentration of salt varies in the range of 0–3.5×10^{-5} M.

decreases in the sequence **2** > **1** > **4** > **3** (for Zn^{2+}) and **1** ≈ **2** ≈ **4** > **3** (for Cd^{2+}). Ligand **3** is the poorest metal binder probably due to the *–I*-effect of the methoxy groups which slightly reduce the electron density on the phenanthroline nitrogen atoms, although the differences are not so large approaching the measurement errors. More donor substituent in the ligand causes the larger red shift of the emission maximum as well as the larger quench of luminescence intensity upon complexation up to virtually zero in case of complexes with ligand **2** (for details, see Online Supplementary Materials).

When Co^{2+} or Fe^{2+} is added to solutions of ligands, the absorption bands shift in the near UV region and their intensity increases until 0.33 equiv. of the cation is reached, after which the changes cease [Figure 3(*a*), for details, see Online Supplementary Materials]. A further increase in the metal cation concentration up to 20 equiv. leads to insignificant changes in the absorption spectra. This indicates the strong coordination of Co^{2+} and Fe^{2+} cations with ligands with the predominant formation of very stable 3 : 1 complexes (ligand/metal). In the NMR spectra of 3 : 1 and 1 : 3 mixtures [**2**/$Fe(ClO_4)_2$], we also revealed only one type of complexes. Based on these data, it was not possible to calculate the stability constants of the complexes because of their very high values.

The interaction of ligands **1–4** with Co^{2+} and Fe^{2+} cations differs from the case of Cd^{2+} and Zn^{2+} in fluorescence spectra. Complexation with Co^{2+} and Fe^{2+} leads to complete quenching of fluorescence when adding 0.33 equiv. of metal [see Figure 3(*b*)].

Table 2 Stability constant logarithms[a] for complexes of Cd^{2+} and Zn^{2+} ions with ligands **1**–**4**.

Ligand, ion	lg(K_{31})	lg(K_{21})
1, Zn^{2+}	18.0 ± 0.4	11.6 ± 0.2
1, Cd^{2+}	18.8 ± 0.6	12.1 ± 0.5
2, Zn^{2+}	20.0 ± 0.5	13.2 ± 0.5
2, Cd^{2+}	18.5 ± 0.7	12.8 ± 0.7
3, Zn^{2+}	16.0 ± 0.7	10.5 ± 0.8
3, Cd^{2+}	16.9 ± 0.3	10.5 ± 0.7
4, Zn^{2+}	16.9 ± 0.4	11.8 ± 0.2
4, Cd^{2+}	18.9 ± 0.5	12.6 ± 0.3

[a] K_{31} for 3 : 1 ligand/M^{2+} ratio, K_{21} for the 2 : 1 one.

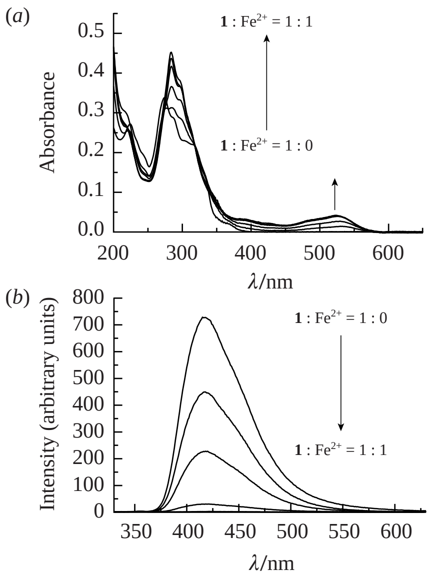


Figure 3 Electronic (*a*) absorption and (*b*) emission spectra of a solution of ligand **1** at various concentrations of $Fe(ClO_4)_2$ in MeCN. The initial concentration of the ligand $C_1 = 1\times10^{-5}$ M, the concentration of $Fe(ClO_4)_2$ in the range of 0–1×10^{-5} M.

In the octahedral complexes of transition metals, the electric field of the ligands splits five degenerate metal d-orbitals into two groups (t_2 and e) with an energy difference Δ.[18] For iron and cobalt cations, the splitting energy is small; therefore, the lowest excited state of their complexes is of d–d nature[17] (Figure 4). Such states are not emitting, since direct d–d transitions are forbidden. As a result, ligand fluorescence quenches during complex formation. The absorption bands in the UV region of complexes with ligands **1**–**4** and Co^{2+} and Fe^{2+} cations correspond to the π–π* transitions. Excited states resulting from these π–π* transitions then relax to the lowest excited states of non-radiating d–d nature. Wide low-intensity maxima at 530 nm (Fe^{2+} complexes) and 390 nm (Co^{2+}) should be attributed to metal-to-ligand charge transfer (MLCT).[19(*a*),(*b*)] The position and intensity of these bands do not depend on the substituent in the ligand. That indicates the localization of the MLCT excited state mainly on the invariant imidazophenanthroline moiety of the ligands.

In summary, complexation of ligands **1**– **4** with Cd^{2+}, Zn^{2+} cations affords mixtures of 3 : 1 and 2 : 1 complexes which exhibit luminescence and are not capable of intramolecular charge transfer. In the case of Fe^{+2} and Co^{+2}, very stable complexes are formed predominantly with a 3 : 1 composition showing electron transfer from metal to ligand. In our previous study[14] we found an opposite electron transfer from ligand to metall in some copper(II) complexes of ligands **1**–**4**. Thus, it appears that 2-substituted imidazophenanthroline derivatives are not only universal, strongly bonding chelating agents for a wide range of metal cations, but also can act either as donor, neutral or acceptor ligands, depending on the researcher's needs.

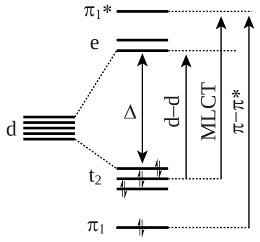


Figure 4 A model of the electronic structure of octahedral homoleptic complexes of d^6-metals MX_6 involving d, π and π* orbitals, arrows indicate electronic transitions.

This work was supported by the Russian Foundation for Basic Research (grant no. 18-33-00715). The use of equipment from Center of collective facilities of A. N. Nesmeyanov Institute of Organoelement Compounds is gratefully acknowledged.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.07.013.

References

1 (*a*) P. A. Panchenko, A. S. Polyakova, Yu. V. Fedorov and O. A. Fedorova, *Mendeleev Commun.*, 2019, **29**, 155; (*b*) S. D. Tokarev, Yu. A. Sotnikova, A. V. Anisimov, Yu. V. Fedorov, G. Jonusauskas, D. A. Lypenko, V. V. Malov, A. R. Tameev, E. I. Mal'tsev and O. A. Fedorova, *Mendeleev Commun.*, 2019, **29**, 567; (*c*) A. G. Starikov, A. A. Tsaturyan, A. A. Starikova, E. A. Gusakov and V. I. Minkin, *Russ. Chem. Bull., Int. Ed.*, 2018, **67**, 1182 (*Izv. Akad. Nauk, Ser. Khim.*, 2018, 1182); (*d*) A. G. Starikov, A. A. Starikova, M. G. Chegerev and V. I. Minkin, *Russ. Chem. Bull., Int. Ed.*, 2019, **68**, 725 (*Izv. Akad. Nauk, Ser. Khim.*, 2019, 725).

2 (*a*) R.-Y. Wang, W.-L. Jia, H. Aziz, G. Vamvounis, S. Wang, N.-X. Hu and J. A. Coggan, *Adv. Funct. Mater.*, 2005, **15**, 1483; (*b*) S. Xiao, T. Yi, Y. Zhou, Q. Zhao, F. Li and C. Huang, *Tetrahedron*, 2006, **62**, 10072; (*c*) J.-F. Lee, Y.-C. Chen, J.-T. Lin, C.-C. Wu, C.-Y. Chen, C.-A. Dai, C.-Y. Chao, H.-L. Chen and W.-B. Liau, *Tetrahedron*, 2011, **67**, 1696; (*d*) Y. J. Bing, L. M. Leung and G. Menglian, *Tetrahedron Lett.*, 2004, **45**, 6361; (*e*) J. Peng, J. Sun, P. Gong, P. Xue, Z. Zhang, G. Zhang and R. Lu, *Chem. – Asian J.*, 2015, **10**, 1717; (*f*) J. Jayabharathi, V. Thanikachalam and M. V. Perumal, *Spectrochim. Acta, Part A*, 2012, **95**, 614.

3 (*a*) J.-Z. Wu, G. Yang, S. Chen, L.-N. Ji, J.-Y. Zhou and Y. Xu, *Inorg. Chim. Acta.*, 1998, **283**, 17; (*b*) N. Zhen, Q. Yang, K. Zheng, Z. Han, F. Sun, W. Mei and Y. Yu, *Int. J. Biochem. Cell Biol.*, 2016, **79**, 158; (*c*) S. Liao, Z. Zhang, Q. Wu, X. Wang and W. Mei, *Bioorg. Med. Chem.*, 2014, **22**, 6503; (*d*) N. Zhen, Q. Yang, Q. Wu, X. Zhu, Y. Wang, F. Sun and Y. Yu, *Cancer Chemother. Pharmacol.*, 2016, **77**, 169.

4 (*a*) Z.-Q. Bian, K.-Z. Wang and L.-P. Jin, *Polyhedron*, 2002, **21**, 313; (*b*) Q.-Q. Liu, J. Geng, X.-X. Wang, K.-H. Gu, W. Huang and Y.-X. Zheng, *Polyhedron*, 2013, **59**, 52.

5 (*a*) Y. Wang, Y. Zhang, D. Zhu, K. Ma, H. Ni and G. Tang, *Spectrochim. Acta, Part A*, 2015, **147**, 31; (*b*) Y. Wei, Y. Yu and K. Wu, *Cryst. Growth Des.*, 2007, **7**, 2262.

6 (*a*) S.-Y. Niu, S.-S. Zhang, L. Wang and X.-M. Li, *J. Electroanal. Chem.*, 2006, **597**, 111; (*b*) Q.-L. Zhang, J.-G. Liu, J. Liu, G.-Q. Xue, H. Li, J.-Z. Liu, H. Zhou, L.-H. Qu and L.-N. Ji, *J. Inorg. Biochem.*, 2001, **85**, 291; (*c*) Q.-L. Zhang, J.-G. Liu, H. Chao, G.-Q. Xue and L.-N. Ji, *J. Inorg. Biochem.*, 2001, **83**, 49; (*d*) M. Shilpa, J. N. L. Latha, A. G. Devi, A. Nagarjuna, Y. P. Kumar, P. Nagababu and S. Satyanarayana, *J. Inclusion Phenom. Macrocycl. Chem.*, 2011, **70**, 187.

7 (*a*) H.-J. Park, K. Kim and Y.-K. Chung, *Inorg. Chim. Acta.*, 2014, **410**, 214; (*b*) R. Liu, M.-M. Huang, X.-X. Yao, H.-H. Li, F.-L. Yang and X.-L. Li, *Inorg. Chim. Acta.*, 2015, **434**, 172.

8 (*a*) C. Zhong, H. Huang, A. He and H. Zhang, *Dyes Pigm.*, 2008, **77**, 578; (*b*) H.-Y. Sun, C.-B. Liu, Y. Cong, M.-H. Yu, H.-Y. Bai and G.-B. Che, *Inorg. Chem. Commun.*, 2013, **35**, 130.

9 V. Balzani, G. Bergamini, F. Marchioni and P. Ceroni, *Coord. Chem. Rev.*, 2006, **250**, 1254.

10 (*a*) C.-Y. Chen, M. Wang, J.-Y. Li, N. Pootrakulchote, L. Alibabaei, C.-H. Ngoc-le, J.-D. Decoppet, J.-H. Tsai, C. Grätzel, C.-G. Wu, S. M. Zakeeruddin and M. Grätzel, *ACS Nano*, 2009, **3**, 3103; (*b*) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595; (*c*) J. Schindler, K. Stephan, M. Wächtler, J. Guthmuller, S. Rau and B. Dietzek, *ChemPhysChem*, 2015, **16**, 1061.

11 (*a*) S. Tschierlei, M. Karnahl, M. Presselt, B. Dietzek, J. Guthmuller, L. González, M. Schmitt, S. Rau and J. Popp, *Angew. Chem., Int. Ed.*, 2010, **49**, 3981; (*b*) E. S. Andreiadis, M. Chavarot-Kerlidou, M. Fontecave and V. Artero, *Photochem. Photobiol.*, 2011, **87**, 946.

12 (*a*) S. Ji, W. Wu, W. Wu, P. Song, K. Han, Z. Wang, S. Liu, H. Guo and J. Zhao, *J. Mater. Chem.*, 2010, **20**, 1953; (*b*) S. Monro, J. Scott, A. Chouai, R. Lincoln, R. Zong, R. P. Thummel and S. McFarland, *Inorg. Chem.*, 2010, **49**, 2889.

13 E. A. Steck and A. R. Day, *J. Am. Chem. Soc.*, 1943, **65**, 452.

14 O. A. Fedorova, N. E. Shepel, S. D. Tokarev, E. V. Lukovskaya, Y. A. Sotnikova, A. A. Moiseeva and Y. V. Fedorov, *New J. Chem.*, 2019, **43**, 2817.

15 H. Gampp, M. Maeder, C. J. Meyer and A. D. Zuberbühler, *Talanta*, 1985, **32**, 257.

16 A. Barbieri, G. Accorsi and N. Armaroli, *Chem. Commun.*, 2008, 2185.

17 S. L. Zheng and X. M. Chen, *Aust. J. Chem.*, 2004, **57**, 703.

18 J. N. Demas and B. A. DeGraff, *Anal. Chem.*, 1991, **63**, 829A.

19 (*a*) Z. Yang, C. Yan, Y. Chen, C. Zhu, C. Zhang, X. Dong and W. He, *Dalton Trans.*, 2011, **40**, 2173; (*b*) X. W. Huang, W. T. Zhu, J. C. Zhang and G. J. Su, *Monatsh. Chem.*, 2012, **143**, 101.

Received: 17th February 2020; Com. 20/6136