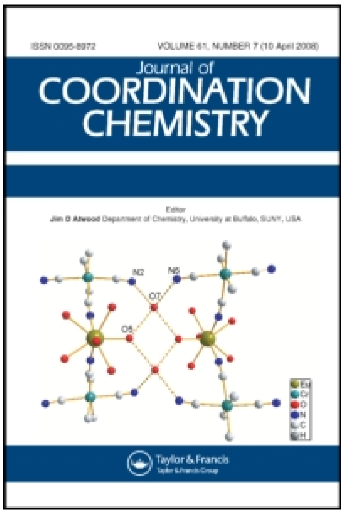


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization and fluorescence spectra of mixed ligand Zn(II), Cd(II) and Hg(II) complexes with 1,10-phenanthroline-5,6-dione ligand

Davar M. Boghaei[a]; Fatemeh Behzadian Asl[a]
[a] Department of Chemistry, Sharif University of Technology, Tehran, Iran

To cite this Article Boghaei, Davar M. and Asl, Fatemeh Behzadian(2007) 'Synthesis, characterization and fluorescence spectra of mixed ligand Zn(II), Cd(II) and Hg(II) complexes with 1,10-phenanthroline-5,6-dione ligand', Journal of Coordination Chemistry, 60: 15, 1629 — 1635

To link to this Article: DOI: 10.1080/00958970601099183

URL: http://dx.doi.org/10.1080/00958970601099183

Journal of Coordination Chemistry
Vol. 60, No. 15, 1 August 2007, 1629–1635

Synthesis, characterization and fluorescence spectra of mixed ligand Zn(II), Cd(II) and Hg(II) complexes with 1,10-phenanthroline-5,6-dione ligand

DAVAR M. BOGHAEI* and FATEMEH BEHZADIAN ASL

Department of Chemistry, Sharif University of Technology,
PO Box 11365-9516, Tehran, Iran

(*Received 8 July 2006; in final form 2 September 2006*)

The novel mixed ligand complexes $[M(bpy)(phen\text{-}dione)](PF_6)_2$ (M = Zn(II), Cd(II) and Hg(II), bpy = 2,2′-bipyridine and phen-dione = 1,10-phenanthroline-5,6-dione) have been synthesized and characterized by elemental analysis, IR, ^1H NMR and electronic absorption spectroscopies. The $\nu(C{=}O)$ of coordinated phen-dione in these complexes are very similar to the free phen-dione ligand showing that phen-dione is not coordinated to metal ion from its C=O sites. Absorption spectra of the complexes show two absorption bands for intraligand transitions. These absorption bands show dependence to the dielectric constant of solvent. These complexes exhibit an intensive fluorescence band around 535 nm in DMF when the excitation wavelength is 260 nm at room temperature. The fluorescence intensity of these complexes is larger than that of the free ligand.

Keywords: Mixed ligand; 1,10-Phenanthroline-5,6-dione; Fluorescence; Zinc(II); Cadmium(II); Mercury(II)

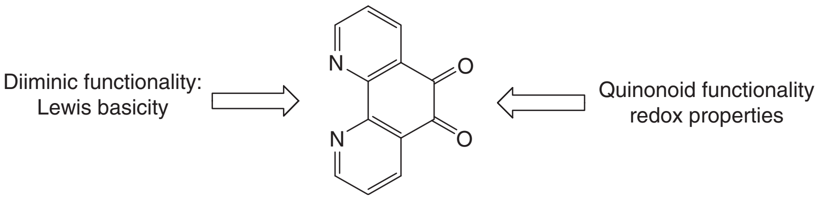
1. Introduction

1,10-Phenanthroline and a number of its derivatives, substituted mainly at the 2,9, the 4,7 or the 5,6 positions, play an important role in complex chemistry because of their unique properties as chelating agents [1–3]. Recently some studies have dealt with the coordination properties of 1,10-phenanthroline-5,6-dione (phen-dione) in connection with its ligating ability towards both early and late transition metals [4, 5]. 1,10-Phenanthroline-5,6-dione (phen-dione) shows a peculiar reactivity due to the presence of two functionalities [4]; it is redox active due to the quinonoid function and it behaves as a Lewis base due to the presence of the diiminic nitrogen atoms (scheme 1). When the phen-dione ligand coordinates through the nitrogen atoms, the entire complex may be used as a "quinine equivalent" in reactions with compounds containing metals in a low oxidation state. On the other hand, oxygen-bound complexes of phen-dione may be used as "bipyridine equivalent" ligands in reactions with Lewis acids [6].

---

*Corresponding author. Email: dboghaei@sharif.edu

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970601099183



Scheme 1. Phen-dione functional groups.

Complexes of 1,10-phenanthroline-5,6-dione (phen-dione) are a focus because this ligand is versatile for the assembly of metal organic materials [6], acting as a bis-chelating ligand [7–8], and prepared starting from an already complexed phenanthroline [9]. The diketone functionality can also be easily transformed to other chelating groups such as a diamine or dioxime [10]. Moreover, it is also a versatile organic linker that can form bridges through amine condensation [11] or a combination of coordination and condensation [12].

Complexes composed of transition metals, like copper and ruthenium, and bidentate polypyridine ligand like 1,10-phenanthroline and some of its derivatives have been shown to be useful photophysical and/or chemical probes of DNA of relevance to various biochemical and biomedical applications [13–16].

The ligands or the metal in these complexes can be varied in an easily controlled manner to facilitate individual applications, thus providing understanding of details involved in DNA-binding and cleavage [17, 18]. Clearly, further studies using various phen-dione complexes such as $[M(\text{phen-dione})_3]^{n+}$, $[M(\text{phen-dione})_2\text{tpphz}]^{n+}$ and $[M(\text{phen-dione})_2(LL')]^{n+}$ are needed to evaluate the influence of metal-ion-induced geometry, charge, spin-state, redox potential, etc., on changes in DNA binding and cleavage mechanisms in this important class of complexes as for previous metalloderivatives ($M = Ru^{II}$, Rh^{III}, Co^{III}, Cr^{III}, etc.) of phen or modified phen ligands [13–16]. We now report the preparation, characterization and fluorescence spectra of $[Zn(bpy)(\text{phen-dione})](PF_6)_2$, $[Cd(bpy)(\text{phen-dione})](PF_6)_2$ and $[Hg(bpy)(\text{phen-dione})](PF_6)_2$.

2. Experimental

2.1. *Materials and measurements*

All reagents and solvents were reagent grade, obtained from either Merck or Aldrich and used without further purification. 1,10-Phenanthroline-5,6-dione (phen-dione) was synthesized according to the literature procedure [19].

Elemental analyses were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectra ($4000–400\,cm^{-1}$) were measured on a FT-IR JASCO 460 spectrophotometer with KBr pellets. Electronic spectra were recorded using a CARY 100 Bio VARIAN UV-Vis spectrophotometer. ^{1}H NMR spectra were recorded on a

Bruker FT-NMR 500 (500 MHz) Ultra Shield spectrometer at ambient temperature in DMSO-d_6. Fluorescence measurements were made on a Cary Eclipse Fluorescence spectrophotometer equipped with quartz cuvettes of 1 cm path length.

2.2. *Synthesis of [Zn(bpy)(phen-dione)](PF$_6$)$_2$*

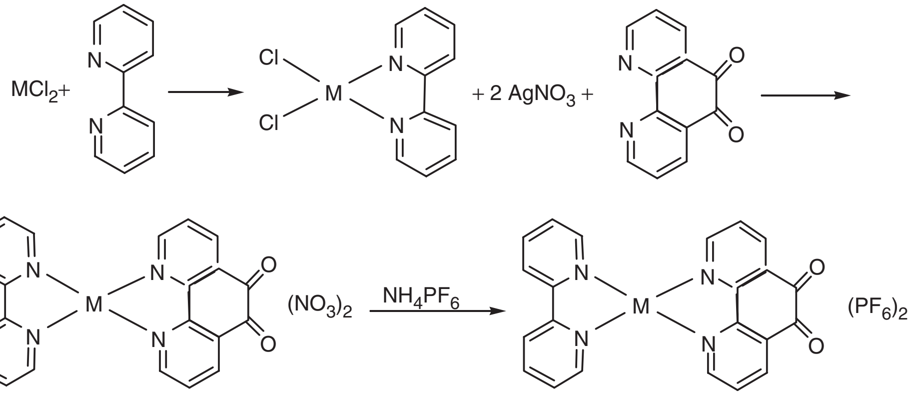
The bpy (0.156 g, 1 mmol) was dissolved in 20 mL ethanol, added drop-wise to a solution of $ZnCl_2$ (0.136 g, 1 mmol) in 30 mL ethanol and stirred and kept at 40°C for 20 h. The white precipitate, [Zn(bpy)Cl_2] which formed was collected by suction filtration and washed with ethanol and ether. This product was dissolved in 50 mL CH_3CN and refluxed for 30 min. To the solution was added $AgNO_3$ (0.340 g, 2 mmol) in 10 mL CH_3CN and stirred at reflux temperature for 30 min. To the solution was then added phen-dione (0.210 g, 1 mmol) in 30 mL CH_3CN and the resulting solution was stirred with heating (40–45°C) for 10 h. The solution was cooled to −5°C overnight and filtered to remove the white precipitate. The solution was evaporated to dryness. The crude product, [Zn(bpy)(phen-dione)]$(NO_3)_2$, was dissolved in water and precipitated from the solution as a hexafluorophosphate salt by addition of NH_4PF_6. The light yellow precipitate was collected, washed with water and ether, and then air dried. The product was recrystallized from CH_3CN. Yield: 0.521 g (72.8%). Elemental analysis: Anal. Calcd for $ZnC_{22}H_{14}N_4O_2P_2F_{12}$: C, 36.59; H, 1.94; N, 7.76; Zn, 9.06%. Found: C, 36.28; H, 1.86; N, 7.71; Zn, 9.01%. ^1H NMR bands of [Zn(bpy) (phen-dione)]$(PF_6)_2$ (DMSO-d_6, ppm): 7.35 (m, 2H), 7.96 (m, 4H), 8.41 (m, 4H), 8.67 (m, 2H), 9.48 (q, 2H).

2.3. *Synthesis of [Cd(bpy)(phen-dione)](PF$_6$)$_2$*

This complex was prepared by following the procedure described for [Zn(bpy)(phen-dione)]$(PF_6)_2$. The light yellow precipitate was collected and recrystallized from CH_3CN. Yield: 0.590 g (76%). Anal. Calcd for $CdC_{22}H_{14}N_4O_2P_2F_{12}$: C, 34.38; H, 1.82; N, 7.31; Cd, 14.58%. Found: C, 34.30; H, 1.85; N, 7.31; Cd, 14.58%. ^1H NMR bands of [Cd(bpy)(phen-dione)]$(PF_6)_2$ (DMSO-d_6, ppm): 7.38 (m, 2H), 7.99 (m, 4H), 8.45 (m, 4H), 8.75 (m, 2H), 9.40 (q, 2H).

2.4. *Synthesis of [Hg(bpy)(phen-dione)](PF$_6$)$_2$*

This complex was prepared by following the procedure described for [Zn(bpy)(phen-dione)]$(PF_6)_2$. The pale yellow precipitate was collected and recrystallized from CH_3CN. Yield: 0620 g (72%). Anal. Calcd for $HgC_{22}H_{14}N_4O_2P_2F_{12}$: C, 30.82; H, 1.63; N, 6.54; Hg, 23.42%. Found: C, 30.85; H, 1.60; N, 6.57;Hg, 23.38%.%. ^1H NMR bands of [Hg(bpy)(phen-dione)]$(PF_6)_2$ (DMSO-d_6, ppm): 7.40 (m, 2H), 7.88 (m, 4H), 8.42 (m, 4H), 8.80 (m, 2H), 9.51 (q, 2H).



Scheme 2. Reaction pathway for the synthesis of the complexes ($M = Zn^{2+}$, Cd^{2+} and Hg^{2+}).

3. Results and discussion

Complexes were synthesized in good yield according to the following reaction (scheme 2):

Under these conditions, the phen-dione preferentially binds to M^{II} through the nitrogen instead of the carbonyl groups. The different bite angles of the *oxy*-*versus* *azo*-sites may dictate the current metals preference for the *azo*-site. Similar studies of Cu^{2+}, Co^{3+}, Co^{2+}, $Ru^{2+}$and Ni^{2+} complexes with phen-dione also show that the phen-dione coordinates through their nitrogen atoms [20–24]. Previous studies show that the bond angle formed by two nitrogen atoms of the phen-dione ligand and metal ions was around 79°, slightly smaller than that formed by two nitrogen atoms of the bpy ligand [25–27].

The ^1H NMR spectral data for the ligand and complexes show signals at 7.2–9.6 ppm. These signals arise from the hydrogen atoms of phen-dione and bpy. The relative intensities of these signals are in accord with the proposed structure.

The IR spectrum of phen-dione has a band at $1675\,cm^{-1}$ ascribable to a stretching frequency of the C=O band on the ligand [28]. This band does not shift much in the corresponding complexes, which is reasonable since the C=O moieties are far removed from the site of coordination of this ligand with the metal ion [19, 28]. The IR spectrum of the complexes had a band around $1690\,cm^{-1}$ assigned to the ν(C=O) band of an *o*-quinoid group of the phen-dione ligand. This ν(C=O) band is close to that of the mono phen-dione metal complexes, $[Ru(bpy)_2(phen\text{-}dione)](ClO_4)_2$ ($1702\,cm^{-1}$) [25] and $[Ru(terpy)(phen\text{-}dione)Cl](PF_6)$ ($1696\,cm^{-1}$) [26]. It is also reported that higher wavenumber shifts of the ν(C=O) band are observed in complexes formed by phen-dione (N,N′-coordination) and the tetra chlorides of group 4 metals (Ti, Zr and Hf) [28].

In complexes where the phen-dione ligands coordinated metal ions via C=O moieties such as $Ti(O,O'\text{-}phen\text{-}dione)_3$, $V(O,O'\text{-}phen\text{-}dione)_3$, $V(O,O'\text{-}phen\text{-}dione)_3(TiCl_4)_3$ and $Ti(O,O'\text{-}phen\text{-}dione)_3(TiCp_2)_3$ the ν(C=O) was shifted about $200\text{–}300\,cm^{-1}$ to lower wave number [6, 29, 30]. The strong absorption band at $843\,cm^{-1}$ is assigned to ν(P–F) and demonstrates the existence of PF_6^- as a counter ion [31]. The IR spectral data of the phen-dione ligand and its complexes are given in table 1.

Table 1. IR[a] data for free phen-dione and [M(bpy)(phen-dione)](PF_6)$_2$.

Compound	ν(C=O) (cm^{-1})	ν(P–F) (cm^{-1})
Phen-dione	1675	–
[Zn(bpy)(phen-dione)](PF_6)$_2$	1688	843
[Cd(bpy)(phen-dione)](PF_6)$_2$	1695	841
[Hg(bpy)(phen-dione)](PF_6)$_2$	1692	843

[a] IR data (KBr pellets) in cm^{-1}; strong absorptions.

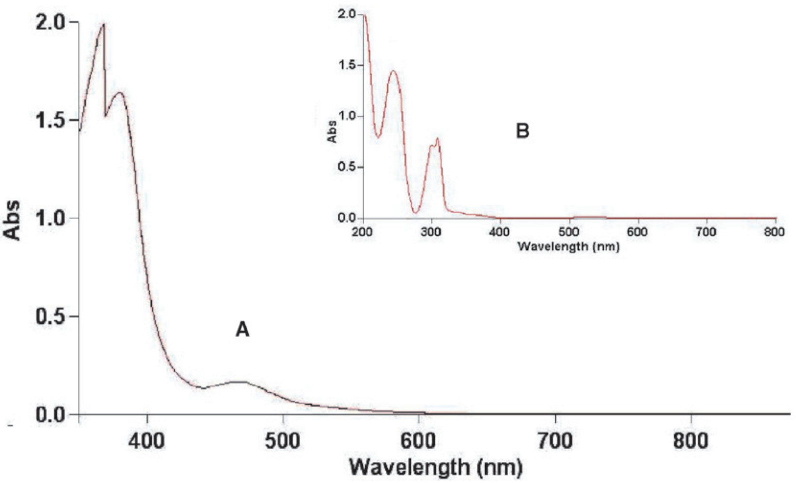


Figure 1. Electronic spectra of (A) [Zn(bpy)(phen-dione)](PF_6) (1×10^{-4} M) in acetonitrile, (B) [Zn(bpy)(phen-dione)](PF_6) (1×10^{-6} M) in acetonitrile.

Electronic spectra of these complexes were taken in acetonitrile. Figure 1 shows the UV-Vis spectrum of [Zn(bpy)(phen-dione)](PF_6)$_2$ in acetonitrile. Electronic spectra of the complexes show two absorption bands in the UV region and three absorption bands in the visible region.

Absorption bands centered at 234, 313 and 367 nm are assigned to ligand-centered $\pi \rightarrow \pi^*$ transitions. However, given that there are different metal ions involved, the similar absorption bands and intensities in all three complexes spectra imply a similar origin and one that does not involve metal orbitals. The intense absorption bands centered at approximately 380 and 478 nm are intraligand transitions. These absorption bands are assigned to $n \rightarrow \pi^*$ of the carbonyl group of phen-dione because these band are shifted toward shorter wavelengths (blue shift) in high dielectric solvents while a red shift was observed for the $\pi \rightarrow \pi^*$ transitions in high dielectric solvents [32]. Electronic spectral data for the three complexes in acetonitrile are given in table 2.

The fluorescence emission spectra of the complexes were taken in DMF with excitation wavelength of 260 nm at room temperature. The fluorescence emission spectrum of [Zn(bpy)(phen-dione)](PF_6)$_2$ is depicted in figure 2. [Cd(bpy)(phen-dione)](PF_6)$_2$ and [Hg(bpy)(phen-dione)](PF_6)$_2$ complexes exhibit very similar fluorescence spectra. The peaks around 535 nm for all complexes may be attributed to the intraligand emission ($\pi \rightarrow \pi^*$) from the phen-dione ligand [33, 34]. The free phen-dione molecule displays a weak luminescence at ca 543.9 nm.

Table 2. UV-Vis[a] data for [M(bpy)(phen-dione)](PF_6)$_2$.

Complex	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
[Zn(bpy)(phen-dione)](PF_6)$_2$	241(5.61), 313(5.28), 367(3.59)	380(3.48), 473(1.41)
Cd(bpy)(phen-dione)](PF_6)$_2$	240(5.63), 312(5.21), 363(3.56)	378(3.42), 475(1.39)
Hg(bpy)(phen-dione)](PF_6)$_2$	242(5.58), 311(5.16), 366 (3.55)	379(3.44), 476(1.40)

[a] λ in the nm (log ε); in acetonitrile solution.

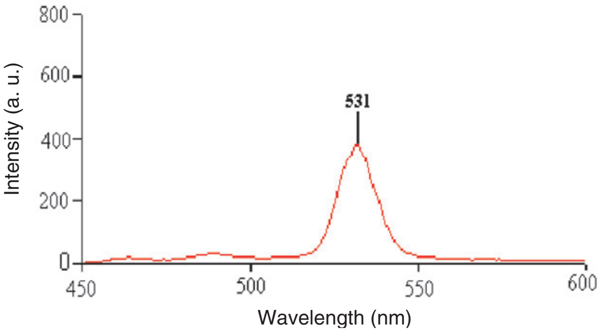


Figure 2. Fluorescence spectrum of [Zn(bpy)(phen-dione)](PF_6)$_2$ with Ex = 260 nm at room temperature in DMF.

The fluorescence intensity of these complexes is larger than that of the free ligand, probably due to rigidity enhancement of coordinated ligand in these complexes in comparison to the free ligand. On the other hand, the fluorescent intensity enhancement may be due to coordination of ligand to M(II) (M = Zn, Cd and Hg) reducing the non-radiative decay of the intraligand excited state [34, 35].

The present work describes the reactivity of group XII metals with a phen-dione ligand. Elemental analysis, IR, electronic, ^{1}H NMR, and spectral data are in good agreement with previous studies [25–27]. The spectroscopic data for these complexes clearly suggests that the phen-dione ligand is coordinated to metal ions from its C=N moieties. The UV-Vis spectra show two intraligand transitions (($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$)). The presence of the free C=O moiety in these complexes has prompted us to study the synthesis of polynuclear complexes and the study of their spectroelectrochemical properties.

Acknowledgement

We are grateful to the Sharif University of Technology for financial support.

References

[1] P. Lenaerts, A. Torms, J. Mullens, J.D. Haen, C. Görller-Waleand, K. Binnemans, K. Driesen. *Chem. Mater.*, **17**, 5194 (2005).
[2] P.G. Sammes, G. Yahioglu. *Chem. Soc. Rev.*, **23**, 327 (1994).

[3] M. Yamada, Y. Tanaka, Y. Yoshimoto, S. Kuroda, I. Shimao. *Bull. Chem. Soc. Jpn*, **65**, 1006 (1992).

[4] F. Calderazzo, F. Marchetti, G. Pampaloni, V. Passarelli. *J. Chem. Soc., Dalton Trans.*, 4389 (1999).

[5] P.L. Hill, L.Y. Lee, T.R. Ypunkin, S.D. Orth, L. McElwee-White. *Inorg. Chem.*, **36**, 5655 (1997).

[6] F. Calderazzoz, G. Pampaloni, V. Passarelli. *Inorg. Chim. Acta*, **330**, 136 (2002).

[7] K. Binnemans, P. Lenaerts, K. Driesen, C. Görller-Walrand. *J. Mater. Chem.*, **14** (2004).

[8] A.Y. Girgis, Y.S. Sohn, A.L. Balch. *Inorg. Chem.*, **14**, 2327 (1975).

[9] R.D. Gillard, R.E.E. Hill, R. Maskill. *J. Chem. Soc.*, 1447 (1970).

[10] S. Bodige, F.M. MacDonnell. *Tetrahed. Lett.*, **38**, 8159 (1997).

[11] M.J. Kim, R. Konduri, H.W. Ye, F.M. MacDonnell, F. Rajeshwar. *Inorg. Chem.*, **41**, 2471 (2002).

[12] K. Wärnmark, J.A. Thomas, O. Heyke, J.M. Lehn. *J. Chem. Soc., Chem. Commun.*, 701 (1996).

[13] D.S. Sigman, A. Mazumder, D.M. Perrin. *Chem. Rev.*, **93**, 2295 (1993).

[14] A. Sigl, H. Sigl (Eds). *Metal Ions in Biological System, Probing of Nucleic Acids by Metal Ion Complexes of Small Molecules*, Vol. 33, Marcell Dekker, New York (1996).

[15] D.R. McMillin, K.M. McNett. *Chem. Rev.*, **98**, 1201 (1998).

[16] K.E. Erkkila, D.T. Odom, J.K. Barton. *Chem. Rev.*, **99**, 2777 (1999).

[17] K. Naing, M. Takashani, M. Taniguchi, A. Yamagishi. *Inorg. Chem.*, **34**, 350 (1995).

[18] P.G. Sammes, G. Yahioglu. *Chem. Soc. Rev.*, 327 (1994).

[19] M. Yamada, Y. Tanaka, Y. Yoshimoto. *Bull. Chem. Soc. Jpn*, **65**, 1006 (1992).

[20] Y. Yamada, H. Sakurai, Y. Miyashita, K. Fujisawa, K. Okamoto. *Polyhedron*, **21**, 2143 (2002).

[21] S. Ghumaan, B. Sarkar, S. Patra, J.V. Slageren, J. Fiedler, W. Kaim, G.K. Lahiri. *Inorg. Chem.*, **44**, 3210 (2005).

[22] Y. Lei, C. Shi, F.C. Anson. *Inorg. Chem.*, **35**, 3044 (1996).

[23] F.M. Macdonnell, M.J. Kim, S. Bodige. *Coord. Chem. Rev.*, **185**, 535 (1999).

[24] K. Larsson, L. Ohrstrom. *Inorg. Chem. Acta*, **357**, 657 (2004).

[25] K. Yokoyama, A. Wakabayashi, K. Noguchi, N. Nakamura, H. Ohno. *Inorg. Chim. Acta*, **359**, 807 (2005).

[26] T. Fujihara, R. Okamura, T. Wada, K. Tanaka. *J. Chem. Soc., Dalton Trans.*, 3221 (2003).

[27] C.A. Goss, H.D. Abruna. *Inorg. Chem.*, **24**, 4263 (1985).

[28] F. Calderazzo, G. Pampaloni, V. Passarelli. *J. Chem. Soc., Dalton Trans.*, 4389 (1999).

[29] F. Calderazzo, U. Englert, G. Pamploni, U. Köllet, G. Tripepi. *J. Organomet. Chem.*, **501**, 201 (1997).

[30] J.Q. Chambers. In *Electrochemistry of Quinones in the Chemistry of Quinonid Compounds*, S. Patai (Ed.), Wily, New York (1974).

[31] K. Nakamato. *Infrared and Raman Spectra of Inorganic and Coordination Compounds Part II: Application in Coordination, Organometallic and Bioinorganic Chemistry*, 5th Edn, Wiley-Intersience, New York (1997).

[32] R.S. Drago. *Physical Methods for Chemists*, p. 118, Saunders College Publishing, New York (1992).

[33] D.M. Boghaei, F. Behzadian-Asl. *J. Coord. Chem.* (in press).

[34] Q. Ye, X.-B. Chen, Y.-M. Song, X.-S. Wang, J. Zhang, R.-G. Xiong, H.-K. Fun, X.-Z. You. *Inorg. Chem. Acta*, **358**, 1258 (2005).

[35] (a) H.-K. Fun, S.S.S. Raj, R.-G. Xiong, J.-L. Zuo, Z. Yu, X.-Z. You. *J. Chem. Soc., Dalton*, **19**, 4183 (2000); (b) R.-G. Xiong, J.-L. Zuo, X.-Z. You, B.F. Abrahams, Z.-P. Bai, C.-M. Che, H.-K. Fun. *Chem. Commun.*, 2061 (2000); (c) Z.-F. Chen, R.-G. Xiong, J. Zhang, J.-l. Zuo, C.-M. Che, H.-K. Fun. *J. Chem. Soc., Dalton Trans.*, 4011 (2000); (d) Z.-F. Chen, R.-G. Xiong, J. Zhang, X.-T. Chen, Z. Xue, X.-Z. You. *Inorg. Chem.*, **40**, 4075 (2001); (e) C.-G. Zheng, Y.-L. Xie, R.-G. Xiong, X.-Z. You. *Inorg. Chem. Commun.*, **4**, 405 (2001); (f) J. Zhang, R.-G. Xiong, Z.-F. Chen, X.-Z. You, G.-H. Lee, S.-M. Peng. *Chem. Lett.*, 676 (2001); (g) Y.-X. Li, Y.-H. Li, X.-R. Zeng, R.-G. Xiong, X.-Z. You, H.-K. Fun. *Inorg. Chem. Commun.*, **6**, 1144 (2003); (h) J. Zhang, Y.-R. Xie, Q. Ye, R.-G. Xiong, Z.-L. Xue, X.-Z. You. *Eur. J. Inorg. Chem.*, 2575 (2003); (i) X. Xue, X.-S. Wang, L.-Z. Wang, R.-G. Xiong, B.-F. Abrahams, X.-Z. You, Z.-L. Xue, C.-M. Che. *Inorg. Chem.*, **41**, 6544 (2002).