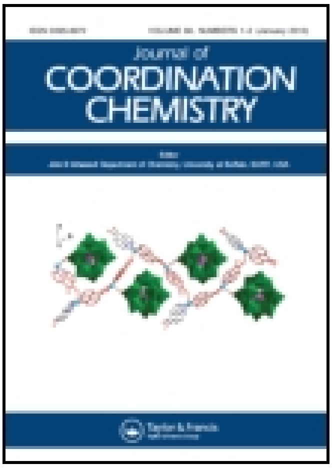


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Bimetallic bis(diphenylphosphino)acetylene bridged copper(I) complexes with 1,10-phenanthroline derivatives: synthesis, crystal structure, and spectroscopic characterization

Atif Fazal[a], Adel Al-Dawsari[b], Bassam El Ali[b], Lahcène Ouahab[c] & Mohammed Fettouhi[b]

[a] Center of Research Excellence in Petroleum Refining and Petrochemicals, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia

[b] Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia

[c] Sciences Chimiques de Rennes, UMR 6226 CNRS, Université de Rennes 1, Rennes, France

Accepted author version posted online: 25 Jun 2014.Published online: 21 Jul 2014.

To cite this article: Atif Fazal, Adel Al-Dawsari, Bassam El Ali, Lahcène Ouahab & Mohammed Fettouhi (2014) Bimetallic bis(diphenylphosphino)acetylene bridged copper(I) complexes with 1,10-phenanthroline derivatives: synthesis, crystal structure, and spectroscopic characterization, Journal of Coordination Chemistry, 67:14, 2357-2364, DOI: 10.1080/00958972.2014.938649

To link to this article: http://dx.doi.org/10.1080/00958972.2014.938649

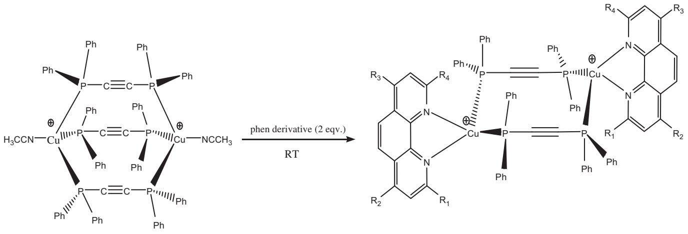
Journal of Coordination Chemistry, 2014
Vol. 67, No. 14, 2357–2364, http://dx.doi.org/10.1080/00958972.2014.938649

Bimetallic bis(diphenylphosphino)acetylene bridged copper(I) complexes with 1,10-phenanthroline derivatives: synthesis, crystal structure, and spectroscopic characterization

ATIF FAZAL†, ADEL AL-DAWSARI‡, BASSAM EL ALI‡, LAHCÈNE OUAHAB§ and MOHAMMED FETTOUHI*‡

†Center of Research Excellence in Petroleum Refining and Petrochemicals, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia
‡Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia
§Sciences Chimiques de Rennes, UMR 6226 CNRS, Université de Rennes 1, Rennes, France

(*Received 3 April 2014; accepted 24 May 2014*)



1. R_1=R_2=R_3=R_4=H

2. R_1=R_3=R_4=H, R_2=Me

3. R_1=R_4=H, R_2=R_3=Me

4. R_2=R_3=H, R_1=R_4=Me

A new series of bimetallic bis(diphenylphosphino)acetylene-bridged copper(I) 1,10-phenanthroline complexes, $[Cu_2(dppa)_2(L)_2](BF_4)_2$; L = 1,10-phenanthroline (**1**); 4-methyl-1,10-phenanthroline (**2**); 4,7-dimethyl-1,10-phenanthroline (**3**); and 2,9-dimethyl-1,10-phenanthroline (**4**), have been prepared and characterized by spectroscopic methods. The X-ray structures of **1** and **4** were determined. The structures consist of centrosymmetric bimetallic 10-membered chair-like dimetallacycles. In **1**, intermolecular C–H···π interactions result in bending of the phenanthroline ligand and sterically induced lengthening of one Cu–P bond. In **1**–**4**, the ^{31}P NMR downfield coordination shift, relative to the free ligand, correlates with the basic strength of the 1,10-phenanthroline ligands.

Keywords: Binuclear Cu(I) complexes; Bis(diphenylphosphino)acetylene; 1,10-phenanthroline derivatives; X-ray structure; ^{31}P NMR

---

*Corresponding author. Email: fettouhi@kfupm.edu.sa
This work is dedicated to the parents of Dr. Atif Fazal.

1. Introduction

Despite early examples [1–8], copper(I) mixed-ligand complexes based on diimines and phosphines are still receiving considerable attention for their photophysical [9, 10 and references therein], catalytic [11], and medicinal properties [12]. The synthesis of polynuclear species with this mixed-ligand coordination sphere remains intriguing. Many dinuclear examples based on bridging diphosphinoalkanes have been reported [13, 14]. Special interest was given to bis(diphenylphosphino)acetylene (dppa) [15] as a versatile ligand, since it can coordinate giving a wide range of bimetallic compounds or coordination polymers [16–20], some of them exhibiting interesting luminescence properties [21]. We have shown earlier that the triply-bridged bimetallic $[Cu_2(dppa)_3(CH_3CN)_2]^{2+}$ reacts with a series of 2,2′-bipyridine derivatives to produce bimetallic species. The X-ray structure, the C≡C stretching frequency of dppa and ^{31}P NMR chemical shift were used to elucidate the electronic effect of the 2,2′-bipyridine methyl substitution on bonding in the complexes [22].

We report herein, on the reactivity of $[Cu_2(dppa)_3(CH_3CN)_2]^{2+}$ with a series of ligands including 1,10-phenanthroline and its methyl substituted derivatives: 4-methyl-1,10-phenanthroline; 4,7-dimethyl-1,10-phenanthroline; and 2,9-dimethyl-1,10-phenanthroline. The spectroscopic and X-ray structure characterization of the bimetallic complexes, obtained together with the correlation, with the diimine ligand substitution electronic effects are presented.

2. Experimental

2.1. *General information*

All manipulations were carried out under nitrogen. $[Cu(CH_3CN)_4]BF_4$ and $[Cu_2(dppa)_3(CH_3CN)_2](BF_4)_2$ were prepared as described [16, 23]. Bis(diphenylphosphino)-acetylene, 1,10-phenanthroline; 4-methyl-1,10-phenanthroline; 4,7-dimethyl-1,10-phenanthroline; and 2,9-dimethyl-1,10-phenanthroline were purchased from Aldrich and used as received. Elemental analyses were performed using a Perkin Elmer EA3000 CHNS/O elemental analyzer. UV–vis spectra, in dichloromethane from 600 to 200 nm, were recorded on a Perkin Elmer Lambda EZ 210 spectrometer. Infrared spectra, from 4000 to 400 cm^{-1} with resolution of 4.0 cm^{-1}, were recorded on a Perkin Elmer FTIR 16FPC spectrometer. Raman spectra were collected for solid samples using a Nicolet™ NXR FT-Raman spectrometer equipped with a helium–neon gas laser of frequency 1,5798.250 cm^{-1}, current 0.68A, laser power 0.1 W, and InGaAs detector. ^{31}P NMR spectra were recorded on a JEOL LAMBDA 500 spectrometer. Eighty-five percent of H_3PO_4 was used as an external reference.

2.2. *General procedure for the synthesis of 1–4*

$[Cu_2(dppa)_3(CH_3CN)_2](BF_4)_2$ (0.015 mM) and 1,10-phenanthroline derivatives (0.038 mM) were placed in an oven-dried 100 mL Schlenk flask, in a glove box sealed with a rubber septum, and taken out. Freshly distilled, dried dichloromethane (10 mL) was injected through a septum using a long needle. The mixture was stirred at room temperature for 8 h to result in a clear orange solution. The latter was filtered and the filtrate was concentrated to 5 mL, and then carefully layered with 20 mL of diethyl ether to afford, after a few days, the crystalline products of **1–4**.

2.2.1. [Cu$_2$(dppa)$_2$(phen)$_2$][BF$_4$]$_2$.

Complex **1**: yellow, yield: 85%. Anal. Calcd for $C_{76}H_{56}B_2Cu_2F_8N_4P_4$: C, 61.70; H, 3.99; N, 3.99. Found: C, 61.75; H, 3.69; N, 3.97. IR (KBr, cm^{-1}) 3418, 2926, 1099, 839, 742, 692, 511, 489. UV–vis (CH_2Cl_2) λ, nm (ε_{molar}, $M^{-1}\,cm^{-1}$) 277.5(4510), 294.5(3340), 360.0(900), 550.0(50), ^{31}P NMR (r.t., DMSO-d$_6$, 202.35 MHz, δ in ppm): −23.80. Raman shift (C≡C cm^{-1}) 2104.

2.2.2. [Cu$_2$(dppa)$_2$(4-Mephen)$_2$][BF$_4$]$_2$.

Complex **2**: yellow, yield: 82%. Anal. Calcd for $C_{78}H_{60}Cu_2N_4P_4B_2F_8$: C, 61.86; H, 4.09; N, 3.79. Found: C, 62.21; H, 4.06; N, 3.91. IR (KBr, cm^{-1}) 3612, 2923, 1512, 1043, 826, 682, 512, 480. UV–vis (CH_2Cl_2) λ, nm (ε_{molar}, $M^{-1}\,cm^{-1}$) 272.0(36,000), 298.0(10,500), ^{31}P NMR (r.t., DMSO-d$_6$, 202.35 MHz, δ in ppm): −24.00. Raman shift (C≡C cm^{-1}) 2109.

2.2.3. [Cu$_2$(dppa)$_2$(4,7-Me$_2$phen)$_2$][BF$_4$]$_2$.

Complex **3**: yellow, yield: 80%. Anal. Calcd for $C_{80}H_{64}B_2Cu_2F_8N_4P_4$: C, 62.89; H, 4.22; N, 3.66. Found: C, 62.72; H, 4.17; N, 3.75. IR (KBr, cm^{-1}) 3042, 2922, 1574, 1432, 1055, 833, 745, 693, 511, 478. UV–vis (CH_2Cl_2) λ, nm (ε, $M^{-1}\,cm^{-1}$): 265.0(25,520), 303.0(4840), 323.0(1000), ^{31}P NMR (r.t., DMSO-d$_6$, 202.35 MHz, δ in ppm): −24.12. Raman shift (C≡C cm^{-1}) 2110.

2.2.4. [Cu$_2$(dppa)$_2$(2,9-Me$_2$phen)$_2$][BF$_4$]$_2$·2CH$_2$Cl$_2$.

Complex **4**: yellow, yield: 85%. Anal. Calcd for $C_{82}H_{68}B_2Cl_4Cu_2F_8N_4P_4$: C, 58.77; H, 4.09; N, 3.34. Found: C, 59.10; H, 4.03; N, 3.62. IR (KBr, cm^{-1}) 3423, 2918, 1620, 1520, 1434, 1059, 862, 742, 694, 512, 485. UV–vis (CH_2Cl_2) λ, nm (ε, $M^{-1}\,cm^{-1}$): 272.0(72,552), 292.0(25,930), 295.5(23,480), 364.0(1610), 383.5(1040), ^{31}P NMR (r.t., DMSO-d$_6$, 202.35 MHz, δ in ppm): −33.51. Raman shift (C≡C cm^{-1}) 2115.

2.3. *X-ray structure analysis*

Single crystals were mounted on an APEXII Bruker-AXS diffractometer of the Center de Diffractométrie, Université de Rennes 1, France (**1**), or Bruker Smart Apex diffractometer (**4**) equipped with a CCD camera and a graphite-monochromated MoKα radiation source ($\lambda = 0.71073$ Å). An empirical absorption correction was applied using SADABS [24]. All structures were solved by direct methods and subsequent Fourier difference techniques, and refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations using the SHELXTL package [25]. All hydrogens were included at calculated positions using a riding model. In **4**, the BF_4^- presents an orientation disorder. Crystal data and details of data collection, and structure refinements are given in table 1. Bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Synthesis of the complexes*

The four bis-chelate doubly-bridged bimetallics were obtained by the reaction of one equivalent of the precursor [Cu$_2$(dppa)$_3$(CH$_3$CN)$_2$](BF$_4$)$_2$ with two equivalents of a series

Table 1. Crystal data and structure refinements for **1** and **4**.

Empirical formula	$C_{76}H_{56}B_2Cu_2F_8N_4P_4$	$C_{82}H_{68}B_2Cl_4Cu_2F_8N_4P_4$
Formula weight	1449.83	1675.78
Temperature (K)	296	293
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\text{-}1$
a (Å)	13.0674(12)	11.4880(8)
b (Å)	12.3143(12)	12.8148(9)
c (Å)	21.4167(12)	15.3951(10)
α (°)	90	105.2420(10)
β (°)	91.3213(10)	101.3620(10)
γ (°)	90	108.0280(10)
Volume (Å^3)	3445.4(5)	1981.3(2)
Z	2	1
Calculated density (g cm^{-3})	1.398	1.404
Absorption coefficient (mm^{-1})	0.779	0.818
F (0 0 0)	1480	856
θ range for data collection (°)	3.53–27.50	1.44–28.35
Index range	$-16 \le h \le 16$ $-15 \le k \le 15$ $-27 \le l \le 27$	$-15 \le h \le 15$ $-17 \le k \le 17$ $-20 \le l \le 20$
Reflections/unique [R(int)]	38337/7813 [0.0930]	27146/9815 [0.0295]
Data/restraints/parameters	7813/0/433	9815/0/471
GOF on F^2	1.019	1.042
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0506, 0.1216	0.0636, 0.1835
R_1, wR_2 (all data)	0.1291, 0.1466	0.0913, 0.2036

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **4**.

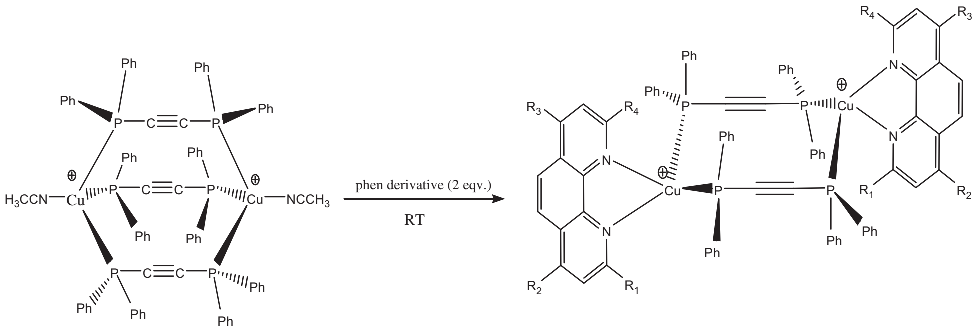
Complex **1**		Complex **4**	
Cu1–N1	2.073(3)	Cu1–N1	2.076(3)
Cu1–N2	2.053(3)	Cu1–N2	2.068(3)
Cu1–P1	2.2976(9)	Cu1–P1	2.2182(9)
Cu1–P2	2.2091(9)	Cu1–P2	2.2794(9)
C13–C26^{i}	1.204(5)	C1–C2	1.184(5)
P1–C13	1.764(4)	C1–P1^{ii}	1.779(3)
P2–C26	1.766(4)	P2–C2	1.771(3)
N2–Cu1–N1	81.88(11)	N2–Cu1–N1	81.68(11)
N2–Cu1–P2	134.37(8)	N2–Cu1–P1	120.40(8)
N1–Cu1–P2	117.28(8)	N1–Cu1–P1	122.19(8)
N2–Cu1–P1	98.99(8)	N2–Cu1–P2	99.97(8)
N1–Cu1–P1	100.44(8)	N1–Cu1–P2	107.31(8)
P2–Cu1–P1	115.62(3)	P1–Cu1–P2	118.15(3)
C13–C26^{i}–P2^{i}	172.6(3)	C1–C2–P2	170.1(3)
C26^{i}–C13–P1	176.0(3)	C2–C1–P1^{ii}	165.1(3)

Note: Symmetry code: i = 2 − x, 2 − y, −z; ii = −x, −y, 2 − z.

of chelating ligands, 1,10-phenanthroline, 4-methyl-1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline, and 2,9-dimethyl-1,10-phenanthroline, with elimination of one dppa and two acetonitrile molecules (scheme 1).

3.2. *X-ray structures of 1 and 4*

The single crystal X-ray structures of **1** and **4** were determined. They are shown in figures 1 and 2, respectively.



1. $R_1=R_2=R_3=R_4=H$

2. $R_1=R_3=R_4=H, R_2=Me$

3. $R_1=R_4=H, R_2=R_3=Me$

4. $R_2=R_3=H, R_1=R_4=Me$

Scheme 1. Synthesis of bimetallics **1**–**4**.

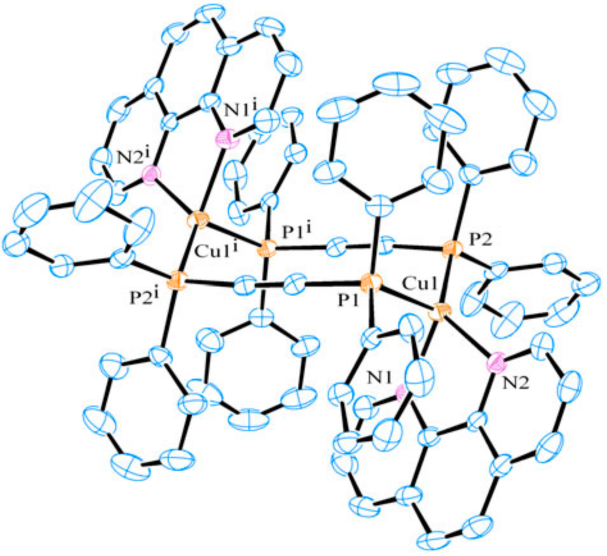


Figure 1. Molecular structure of **1**. The BF_4^- and hydrogens have been omitted for clarity. Symmetry code: $i=-x+2, -y+2, -z$.

Compound **1** crystallizes in the monoclinic *P2₁/c* space group. It consists of a centrosymmetric bimetallic 10-memberedchair-like dimetallacycles. Each Cu(I) is bonded to two nitrogens of a phenanthroline chelating ligand and two phosphorus atoms each belonging to a bridging dppa molecule. The $[CuN_2P_2]$ coordination sphere geometry is distorted tetrahedral. The N–Cu–N bite angle is 81.88(11)°, while the P–Cu–N and P–Cu–P bond angles

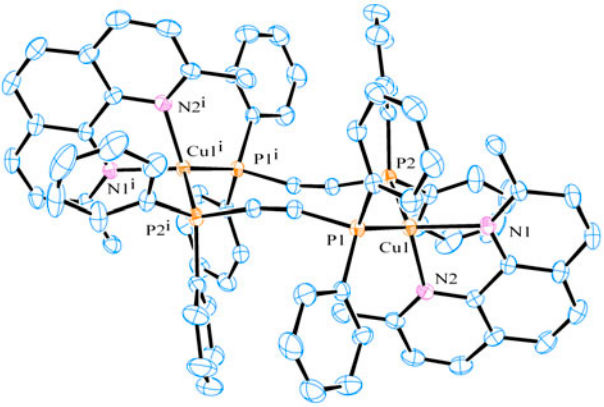


Figure 2. Molecular structure of **4**. The BF_4^- anion, the solvent molecule and hydrogens have been omitted for clarity. Symmetry code: i = −*x*, −*y*, −*z* + 2.

are 98.99(8)° and 115.62(3)°, respectively. The Cu–N and Cu–P bond distances are 2.053 (3)–2.073(3) Å and 2.2091(9)–2.2976(9) Å, respectively. These geometrical values are similar to those reported [16, 22]. The phenanthroline mean plane is tilted relatively to the [CuN_1N_2] plane with an angle of 13.3(2)°, probably due to an intermolecular C–H···π interaction taking place between phenanthroline and a phosphine phenyl ring belonging to an adjacent molecule. Such a bending towards one of the phosphines likely induces, sterically, the lengthening of the Cu–P_1 bond (2.2976(9) Å) compared to Cu–P_2 (2.2091(9) Å).

Compound **4** crystallizes in the triclinic *P-1* space group. The structure is similar to that of **1** with a distorted tetrahedral geometry at the metal center and C–N and Cu–P bond distances in the ranges 2.068(3)–2.076(3) Å and 2.2182(9)–2.2794(9) Å, respectively. The N–Cu–N and P–Cu–P bond angles are 81.68(11)° and 118.15(3)°, respectively. In this case, the dihedral angle between the phenanthroline mean plane and the [CuN_1N_2] plane is 2.9 (1)° compared to 13.3(2)° in **1**. The chair conformation of the bimetallic 10-membered dimetallacycle is twisted in **4** and the bridging dppa deviates pronouncedly from linearity, and the C2–C1–P1 bond angle being 165.1(3)°. One BF_4^- interacts, through CH···F hydrogen bonding interactions, with one 2,9-dimethyl-phenanthroline bound to one metal center and the phenyl group of a phosphine ligand bound to the second metal. This interaction results in a squeezing effect, likely the origin of the dppa bridge deviation from linearity.

3.3. *Spectroscopic characterization*

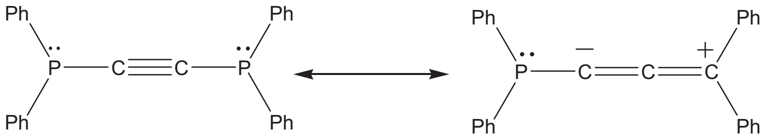
UV–visible spectra of free phenanthroline derivatives in dichloromethane are characterized by intense bands below 300 nm due to π–π* transitions [26]. The spectra of **1**, **3,** and **4** reveal, in addition to the ligand-centered transitions bands, broad bands in the 320–384 nm region, likely due to metal-to-ligand charge-transfer transitions [27, 28].

Insight into metal phosphorus bonding, using C≡C vibrational frequencies, was reported by Carty *et al.* [27]. The C≡C stretch is infrared inactive for free dppa, and its symmetrically bonded bimetallics; however, it is readily identified in Raman spectra as a very strong band. The Raman shift values for the dppa triple bond stretch and ^{31}P NMR chemical shifts are summarized in table 3. For free dppa, $\upsilon_{(C\equiv C)}$ is 2095 cm^{-1} and δ ^{31}P is −35.63 ppm and

Table 3. Dppa triple bond stretch Raman shift and ^{31}P NMR shifts for free dppa and **1–4**.

Compound	pK_a (Phen)	$\upsilon_{C\equiv C}$ (cm^{-1})	δ^{31}P (ppm)
DPPA	–	2095	−35.63
1	4.84[a]	2104	−23.80
2	–	2109	−24.00
3	5.95[b]	2110	−24.12
4	6.17[c]	2115	−33.51

[a] [29].
[b] [31].
[c] [30].



Scheme 2. Two resonance forms of DPPA.

upon coordination, $\upsilon_{(C\equiv C)}$ increases by 9–20 cm^{-1} in this series of complexes and the ^{31}P NMR resonance is shifted downfield by 2.12–11.83 ppm. The ^{31}P NMR shift is consistent with phosphine σ donation to the metal ion inducing an increase in the contribution of the acetylenic resonance form of dppa in the complexes (scheme 2), hence explaining the C≡C bond strengthening upon coordination. In **1–4**, the ^{31}P NMR downfield shift correlates with the basic strength of the phenanthroline ligand (table 2). The maximum downfield NMR shift of 11.83 ppm is observed for 1,10-phenanthroline ($pK_a = 4.84$ [29]) in **1**. This shift is mitigated by the increase of the metal back-bonding induced by the higher σ donation strength of the methyl-substituted phenanthroline ligands and reaching a minimum of 2.12 ppm for the 2,9-dimethyl-1,10-phenanthroline ($pK_a = 6.17$ [30]) in **4**.

4. Conclusion

Reaction of the triply-bridged bimetallic $[Cu_2(dppa)_3(CH_3CN)_2]^{2+}$ with a series of chelating 1,10-phenanthroline derivatives leads to formation of the bis-chelate doubly-bridged bimetallic products. In this series of complexes, the ^{31}P NMR downfield coordination shift relative to the free ligand correlates with the basic strength of the 1,10-phenanthroline ligand.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center with CCDC numbers 942349 and 942388 for **1** and **4**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336 033; or Email: deposit@ccdc.cam.ac.uk.

Acknowledgements

The authors acknowledge the support of King Fahd University of Petroleum & Minerals (KFUPM), Dhahran, Saudi Arabia, and express their appreciation to the support from the Ministry of Higher Education, Saudi Arabia, in establishment of the Center of Research Excellence in Petroleum Refining and Petrochemicals at KFUPM.

References

[1] A. Dairiki, T. Tsukuda, K. Matsumoto, T. Tsubomura. *Polyhedron*, **28**, 2730 (2009).
[2] J.L. Chen, P. Song, J. Liao, H.R. Wen, R. Hong, Z.N. Chen, Y. Chi. *Inorg. Chem. Commun.*, **13**, 1057 (2010).
[3] D.R. McMillin, K.M. McNett. *Chem. Rev.*, **98**, 1201 (1998).
[4] N. Armaroli. *Chem. Soc. Rev.*, **30**, 113 (2001).
[5] D.V. Scaltrito, D.W. Thompson, J.A. O'Callaghan, G.J. Meyer. *Coord. Chem. Rev.*, **208**, 243 (2000).
[6] S.B. Harkins, J.C. Peters. *J. Am. Chem. Soc.*, **127**, 2030 (2005).
[7] S.M. Kuang, D.G. Cuttell, D.R. McMillin, P.E. Fanwick, R.A. Walton. *Inorg. Chem.*, **41**, 3313 (2002).
[8] D.G. Cuttell, S.M. Kuang, P.E. Fanwick, D.R. McMillin, R.A. Walton. *J. Am. Chem. Soc.*, **124**, 6 (2002).
[9] A. Kaeser, M. Mohankumar, J. Mohanraj, F. Monti, M. Holler, J.-J. Cid, O. Moudam, I. Nierengarten, L. Karmazin-Brelot, C. Duhayon, B. Delavaux-Nicot, N. Armaroli, J.-F. Nierengarten. *Inorg. Chem.*, **52**, 12140 (2013).
[10] R.D. Costa, D. Tordera, E. Ortí, H.J. Bolink, J. Schönle, S. Graber, C.E. Housecroft, E.C. Constable, J.A. Zampese. *J. Mater. Chem.*, **21**, 16108 (2011).
[11] A. Fazal, S. Al-Fayez, L.H. Abdel-Rahman, Z.S. Seddigi, A. Al-Arfaj, B. Ali, M.A. Dastageer, M.A. Gondal, M. Fettouhi. *Polyhedron*, **28**, 4072 (2009).
[12] C. Santini, M. Pellei, V. Gandin, M. Porchia, F. Tisato, C. Marzano. *Chem. Rev.*, **114**, 815 (2014).
[13] C. Femoni, S. Muzzioli, A. Palazzi, S. Stagni, S. Zacchini, F. Monti, G. Accorsi, M. Bolognesi, N. Armaroli, M. Massi, G. Valenti, M. Marcacciod. *J. Chem. Soc., Dalton Trans.*, 997 (2013).
[14] X.-L. Li, X.-L. Xin, Y.-B. Ai, M. Tan, H. Lu, B.-X. Du. *Inorg. Chim. Acta*, **401**, 58 (2013).
[15] A.J. Carty, A. Efraty. *Chem. Commun.*, 1559 (1968).
[16] Y.C. Liu, C.I. Li, W.Y. Yeh, G.H. Lee, S.M. Peng. *Inorg. Chim. Acta*, **359**, 2361 (2006).
[17] K.-S. Shin, K.-I. Son, J.I. Kim, C.S. Hong, M. Suh, D.-Y. Noh. *J. Chem. Soc., Dalton Trans.*, 1767 (2009).
[18] Y.C. Liu, W.-Y. Yeh, G.-H. Lee, T.-S. Kuo. *Inorg. Chim. Acta*, **362**, 3595 (2009).
[19] Y. Yamamoto, S. Sawa, Y. Funada, T. Morimoto, M. Falkenström, H. Miyasaka, S. Shishido, T. Ozeki, K. Koike, O. Ishitani. *J. Am. Chem. Soc.*, **130**, 14659 (2008).
[20] G. Peli, S. Rizzato, S. Cassese, L. Garlaschelli, M. Manassero. *CrystEngCommun.* **7**, 575 (2005).
[21] H. Liu, M.J. Calhorda, M.G.B. Drew, V. Félix, J. Novosad, L.F. Veiros, F.F. de Bianig, P. Zanello. *J. Chem. Soc., Dalton Trans.*, 4365 (2002).
[22] A. Fazal, B. El Ali, L. Ouahab, M. Fettouhi. *Polyhedron*, **49**, 7 (2013).
[23] G.J. Kubas. *Inorg. Synth.*, **19**, 90 (1979).
[24] G.M. Sheldrick. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Gottingen, Germany (1996).
[25] G.M. Sheldrick, *SHELXTL V5.1 Software*, Bruker AXS, Inc., Madison, WI (1997).
[26] Y. Sun, S. Zhang, G. Li, Y. Xie, D. Zhao. *Transition Met. Chem.*, **28**, 772 (2003).
[27] A.J. Carty, A. Efraty. *Can. J. Chem.*, **47**, 2573 (1969).
[28] Y. Suenaga, Y. Umehata, T. Minematsu, M. Maekawa. *Sci. Technol.*, **21**, 35 (2009).
[29] L.A.O. Ortiz-Frade, L.R. Ruiz-Ramírez, I. González, A.M. Marín-Becerra, M. Alcarazo, J.G.A. Alvarado-Rodriguez, R.M. Moreno-Esparza. *Inorg. Chem.*, **42**, 1825 (2003).
[30] A.A. Schilt, G.F. Smith. *J. Phys. Chem.*, **60**, 1546 (1956).
[31] L. Gasque, G. Medina, L.R. Ruiz-Ramírez, R.M. Moreno-Esparza. *Inorg. Chim. Acta*, **288**, 106 (1999).