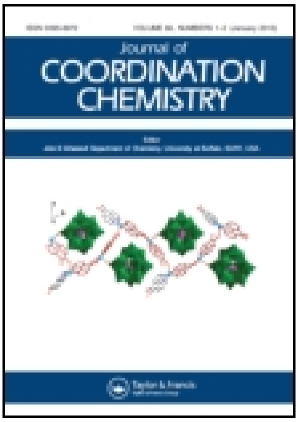
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:47
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Zn(II) and Cd(II)-azido/thiocyanato complexes with thiazolylazo dye and triphenylphosphine: synthesis, characterization and fluorescence

S.S. Chavan [a] , B.A. Yamgar [a] & B.G. Bharate [a]

[a] Department of Chemistry , Shivaji University , Kolhapur , India

Accepted author version posted online: 03 Apr 2013.Published online: 02 May 2013.

To cite this article: S.S. Chavan , B.A. Yamgar & B.G. Bharate (2013) Zn(II) and Cd(II)-azido/thiocyanato complexes with thiazolylazo dye and triphenylphosphine: synthesis, characterization and fluorescence, Journal of Coordination Chemistry, 66:10, 1837-1846, DOI: 10.1080/00958972.2013.791394

To link to this article: http://dx.doi.org/10.1080/00958972.2013.791394

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Journal of Coordination Chemistry, 2013
Vol. 66, No. 10, 1837–1846, http://dx.doi.org/10.1080/00958972.2013.791394

Taylor & Francis
Taylor & Francis Group

Zn(II) and Cd(II)-azido/thiocyanato complexes with thiazolylazo dye and triphenylphosphine: synthesis, characterization and fluorescence

S.S. CHAVAN*, B.A. YAMGAR and B.G. BHARATE

Department of Chemistry, Shivaji University, Kolhapur, India

(*Received 5 October 2012; in final form 4 February 2013*)

[M(**L**)$(PPh_3)_2X_2$] [where M = Zn(II) or Cd(II); **L** = 4-(4′-phenyl, 2′-thiazolylazo)chlorobenzene (**L$_1$**), 4-(4′-phenyl, 2′-thiazolylazo)bromobenzene (**L$_2$**), 4-(4′-phenyl, 2′-thiazolylazo)iodobenzene (**L$_3$**); PPh_3 = triphenylphosphine; X = N_3^- or NCS^-] have been prepared. The complexes were characterized by microanalyses, molar conductance, IR, UV–vis, ^{1}H NMR, ^{31}P NMR, and mass spectral studies. IR spectra reveal that **L$_{1-3}$** coordinate bidentate via azo and thiazole nitrogens. An octahedral geometry is proposed for all the complexes. Thermal behavior indicates that the thiocyanate complexes are more stable than the azide complexes. All the complexes exhibit blue-green emission as a result of fluorescence from the intraligand ($\pi \rightarrow \pi^*$) emission excited state.

Keywords: Thiazolylazo dyes; Zn(II)/Cd(II) complexes; Thermal properties; Fluorescence

1. Introduction

Transition metal complexes with hybrid ligands have been widely explored because they can provide new materials with useful magnetic exchange [1–4], electrical conductivity [5, 6], photoluminescence [7, 8], nonlinear optical property [9, 10], and antimicrobial activity [11, 12]. Arylazo derivatives containing azoimine (–N=N–C=N–) of π-acidic character and *N,N′*-chelating system are an active area of research. The azoimine function stabilizes lower oxidation states of metal ions and tunes the redox and spectroscopic properties of the complex. Such compounds possess properties including molecular aggregation, optical data storage and tautomerization, which define a distinct class of dyestuffs [13, 14]. Thiazolylazo compounds are important because they can form coordination compounds due to several electron rich donor centers with unusual structural and chemical properties. Because of the wide utility of thiazolylazo derivatives acting as polyfunctional ligands, coordination chemistry of thiazolylazo has been intensively investigated [15–18]. Triphenylphosphine is a versatile strong π-accepting ligand, capable to stabilize complexes in low oxidation states. Azide (N_3^-) and thiocyanate (NCS^-) form monomeric, dimeric or polymeric complexes because of versatile coordination modes and ability to mediate strong magnetic coupling.

---

*Corresponding author. Email: sanjaycha2@rediffmail.com

In continuation of our earlier work on structural characterization of transition metal complexes containing thiazolylazo ligands and their luminescence properties [19], we report herein synthesis and characterization of Zn(II) and Cd(II) complexes derived from 4-(4′-phenyl, 2′-thiazolylazo)chlorobenzene (**L$_1$**), 4-(4′-phenyl, 2′-thiazolylazo)bromobenzene (**L$_2$**), and 4-(4′-phenyl, 2′-thiazolylazo)iodobenzene (**L$_3$**) with triphenylphosphine and N_3^- or NCS$^-$as coligands. The complexes were characterized by elemental analyses, molar conductance, spectral (IR, UV–vis, ^{1}H NMR, ^{31}P NMR, ESI-MS) and thermal studies. The fluorescence properties of these complexes are also investigated in dichloromethane solution at room temperature.

2. Experimental

2.1. *Materials and methods*

All the chemicals were of analytical reagent grade and of highest purity available. 4-Phenyl, 2-aminothiazole was synthesized by reported procedure [20]. Microanalyses (C, H, N and S) were performed on a Thermo Finnigan FLASH EA-112 CHNS analyzer; molar conductance (Λ_M) was measured on an ELICO (CM-185) conductivity bridge using *ca.* 10^{-3} M solution in dichloromethane. Infrared spectra were recorded on a Perkin–Elmer FT-IR spectrometer as KBr pellets from 4000–400 cm^{-1}. Electronic spectra were recorded in dichloromethane (10^{-4} M) on a Shimadzu UV–vis-NIR-100 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker-300 MHz instrument in $CDCl_3$, using TMS [$(CH_3)_4Si$] as an internal standard. ^{31}P NMR spectra were recorded using a Varian Mercury-300 FT-NMR spectrometer and are referenced to residual chloroform (7.26 ppm) or external H_3PO_4 (0.0 ppm), respectively. ESI mass spectra were recorded in methanol using a Bruker Apex3. Thermal analyses of the complexes were carried out on a Perkin-Elmer thermal analyzer in nitrogen at a heating rate of 10 °C min^{-1}. The fluorescence properties were measured using a JASCO F P-750 fluorescence spectrophotometer at room temperature (298 K) in dichloromethane solution with 1 cm^3 path length quartz cell. Fluorescent life time was measured on a Jobin Yvon IBH time-resolved fluorescence spectrometer.

2.2. *Synthesis of L_{1-3}*

The ligands 4-(4′-phenyl, 2′-thiazolylazo)chlorobenzene (**L$_1$**), 4-(4′-phenyl, 2′-thiazolylazo) bromobenzene (**L$_2$**), and 4-(4′-phenyl, 2′-thiazolylazo)iodobenzene (**L$_3$**) were prepared by diazotization of 4-phenyl, 2-aminothiazole by reported procedure [19] and were characterized by elemental analyses, IR, and UV–Vis spectra.

2.3. *Preparation of azido complexes (1a–3a and 1b–3b)*

To a methanolic solution of metal salt (1 mM, 0.297 g $Zn(NO_3)_2{\cdot}6H_2O$ or 0.308 g $Cd(NO_3)_2{\cdot}4H_2O$), a methanolic solution of **L** (1 mM, 0.299 g **L$_1$**, 0.344 g **L$_2$** or 0.391 g **L$_3$**) was added while stirring. To this, a CH_2Cl_2 solution (5 mL) of triphenylphosphine (2 mM, 0.524 g) was added, followed by addition of NaN_3 (2 mM, 0.130 g) in warm methanol. The resultant mixture was stirred for 3 h at room temperature whereupon the complexes were precipitated, collected by filtration, and washed with ethanol–water (1 : 1) mixture and dried under vacuum over $CaCl_2$.

Complex 1a: Yield 63%; m.p. 247 °C; Elemental analyses (C, H and N, wt.%) Anal. Calcd for $C_{51}H_{40}N_9SP_2ClZn$: C, 62.90; H, 4.14; N, 12.95; found: C, 62.77; H, 4.28; N, 12.82; IR (KBr, cm^{-1}): ν(C=N), 1592; ν(N=N), 1437; ν(PPh_3), 1480, 744, 690; ν(N_3), 2172, 1348; Δ_m (CH_2Cl_2, $\Omega^{-1}\,cm^2\,M^{-1}$): 16.73; UV–vis ($CH_2Cl_2$) λ_{max} (nm) ($\varepsilon \times 10^3$, $M^{-1}\,cm^{-1}$): 292 (21), 338 (13), 463 (5); ^{1}H NMR ($CDCl_3$) (300 MHz): δ (ppm) 6.62–7.74 (m, Ar–H); ^{31}P NMR: δ (ppm) 35.3; ESI MS, *m/z* (%): 997 ($[M+Na]^+$, 24); 999 ($[M+Na+2]^+$, 8); 913 ($[Zn(L_1)(PPh_3)_2]^+$, 100); 391 ($[Zn(L_1)]^+$, 41).

Complex 2a: Yield 62%; m.p. 253 °C; Elemental analyses (C, H and N, wt.%) Anal. Calcd for $C_{51}H_{40}N_9SP_2BrZn$: C, 60.16; H, 3.96; N, 12.38; found: C, 60.34; H, 3.81; N, 12.34; IR (KBr, cm^{-1}): ν(C=N), 1595; ν(N=N), 1440; ν(PPh_3), 1478, 748, 695; ν(N_3), 2173, 1342; Δ_m (CH_2Cl_2, $\Omega^{-1}\,cm^2\,M^{-1}$): 22.31; UV–vis ($CH_2Cl_2$) λ_{max} (nm) ($\varepsilon \times 10^3$, $M^{-1}\,cm^{-1}$): 290 (25), 335 (17), 454 (4); ^{1}H NMR ($CDCl_3$) (300 MHz): δ (ppm) 6.74–7.96 (m, Ar–H); ^{31}P NMR: δ (ppm) 35.2; ESI MS, *m/z* (%): 1041 ($[M+Na]^+$, 21); 1043 ($[M+Na+2]^+$, 20); 957 ($[Zn(L_2)(PPh_3)_2]^+$, 100); 435 ($[Zn(L_2)]^+$, 38).

Complex 3a: Yield 65%; m.p. 254 °C; Elemental analyses (C, H and N, wt.%) Anal. Calcd for $C_{51}H_{40}N_9SP_2IZn$: C, 57.50; H, 3.79; N, 11.84; found: C, 57.63; H, 3.91; N, 11.74; IR (KBr, cm^{-1}): ν(C=N), 1586; ν(N=N), 1434; ν(PPh_3), 1484, 740, 692; ν(N_3), 2173, 1346; Δ_m (CH_2Cl_2, $\Omega^{-1}\,cm^2\,M^{-1}$): 18.32; UV–vis ($CH_2Cl_2$) λ_{max} (nm) ($\varepsilon \times 10^3$, $M^{-1}\,cm^{-1}$): 290 (23), 340 (19), 446 (4); ^{1}H NMR ($CDCl_3$) (300 MHz): δ (ppm) 6.64–7.88 (m, Ar–H); ^{31}P NMR: δ (ppm) 35.2; ESI MS, *m/z* (%): 1089 $[M+Na]^+$, 28); 1005 ($[Zn(L_3)(PPh_3)_2]^+$, 100); 483 ($[Zn(L_3)]^+$, 42).

Complex 1b: Yield 64%; m.p. 237 °C; Elemental analyses (C, H and N, wt.%) Anal. Calcd for $C_{51}H_{40}N_9SP_2ClCd$: C, 60.00; H, 3.95; N, 12.35; found: C, 59.58; H, 3.94; N, 12.39; IR (KBr, cm^{-1}): ν(C=N), 1592; ν(N=N), 1437; ν(PPh_3), 1480, 744, 690; ν(N_3), 2172, 1346; Δ_m (CH_2Cl_2, $\Omega^{-1}\,cm^2\,M^{-1}$): 18.70; UV–vis ($CH_2Cl_2$) λ_{max} (nm) ($\varepsilon \times 10^3$, $M^{-1}\,cm^{-1}$): 282 (27), 340 (15), 450 (6); ^{1}H NMR ($CDCl_3$) (300 MHz): δ (ppm) 6.72–7.80 (m, Ar–H); ^{31}P NMR: δ (ppm) 35.3; ESI MS, *m/z* (%): 1044 ($[M+Na]^+$, 24); 1046 ($[M+Na+2]^+$, 7); 960 ($[Cd(L_1)(PPh_3)_2]^+$, 100); 438 ($[Cd(L_1)]^+$, 45).

Complex 2b: Yield 64%; m.p. 243 °C; Elemental analyses (C, H and N, wt.%) Anal. Calcd for $C_{51}H_{40}N_9SP_2BrCd$: C, 57.50; H, 3.79; N, 11.84; found: C, 57.47; H, 3.78; N, 11.87; IR (KBr, cm^{-1}): ν(C=N), 1595; ν(N=N), 1440; ν(PPh_3), 1484, 748, 695; ν(N_3), 2173, 1348; Δ_m (CH_2Cl_2, $\Omega^{-1}\,cm^2\,M^{-1}$): 26.34; UV–vis ($CH_2Cl_2$) λ_{max} (nm) ($\varepsilon \times 10^3$, $M^{-1}\,cm^{-1}$): 292 (31), 342 (14), 448 (5); ^{1}H NMR ($CDCl_3$) (300 MHz): δ (ppm) 6.76–7.94 (m, Ar–H); ^{31}P NMR: δ (ppm) 35.2; ESI MS, *m/z* (%): 1089 ($[M+Na]^+$, 21); 1091 ($[M+Na+2]^+$, 22); 1004 ($[Cd(L_2)(PPh_3)_2]^+$, 100); 483 ($[Cd(L_2)]^+$, 41).

Complex 3b: Yield 65%; m.p. 254 °C; Elemental analyses (C, H and N, wt.%) Anal. Calcd for $C_{51}H_{40}N_9SP_2ICd$: C, 55.07; H, 3.63; N, 11.34; found: C, 54.98; H, 3.62; N, 11.37; IR (KBr, cm^{-1}): ν(C=N), 1586; ν(N=N), 1434; ν(PPh_3), 1482, 740, 692; ν(N_3), 2173, 1342; Δ_m (CH_2Cl_2, $\Omega^{-1}\,cm^2\,M^{-1}$): 18.32; UV–vis ($CH_2Cl_2$) λ_{max} (nm) ($\varepsilon \times 10^3$, $M^{-1}\,cm^{-1}$): 290 (29), 342 (20), 447 (5); ^{1}H NMR ($CDCl_3$) (300 MHz): δ (ppm) 6.70–7.88 (m, Ar–H); ^{31}P NMR: δ (ppm) 35.2; ESI MS, *m/z* (%): 1136 ($[M+Na]^+$, 19); 1052 ($[Cd(L_3)(PPh_3)_2]^+$, 100); 530 ($[Cd(L_3)]^+$, 37).

2.4. *Preparation of thiocyanato complexes (4a–6a and 4b–6b)*

To a methanolic solution of metal salt (1 mM, 0.297 g $Zn(NO_3)_2 \cdot 6H_2O$ or 0.308 g $Cd(NO_3)_2 \cdot 4H_2O$), a methanolic solution of **L** (1 mM, 0.299 g $\mathbf{L_1}$, 0.344 g $\mathbf{L_2}$ or 0.391 g $\mathbf{L_3}$)

was added while stirring. To this, a CH_2Cl_2 solution (5 mL) of triphenylphosphine (2 mM, 0.524 g) was added, followed by addition of NH_4NCS (2 mM, 0.152 g) in warm methanol. The resultant mixture was stirred for 3 h at room temperature whereupon the complexes were precipitated, collected by filtration, and washed with ethanol–water (1 : 1) mixture and dried under vacuum over $CaCl_2$.

Complex 4a: Yield 62%; m.p. 272 °C; Elemental analyses (C, H and N, wt.%) Anal. Calcd for $C_{53}H_{40}N_5S_3P_2ClZn$: C, 63.28; H, 4.01; N, 6.96; found: C, 63.17; H, 3.89; N, 6.81; IR (KBr, cm^{-1}): *v*(C=N), 1592; *v*(N=N), 1437; *v*(PPh_3), 1480, 744, 690; *v*(NCS), 2096, 756, 486; Δ_m (CH_2Cl_2, $\Omega^{-1}\,cm^2\,M^{-1}$): 19.92; UV–vis ($CH_2Cl_2$) λ_{max} (nm) ($\varepsilon \times 10^3$, $M^{-1}\,cm^{-1}$): 286 (26), 342 (17), 462 (4); ^{1}H NMR (CH_2Cl_2) (300 MHz): δ (ppm) 6.65–7.93 (m, Ar–H); ^{31}P NMR: δ (ppm) 35.2; ESI MS, *m/z* (%): 1029 ([M + Na]$^+$, 15); 1031 ([M + Na + 2]$^+$, 5); 913 ([Zn(L_1)(PPh_3)$_2$]$^+$, 100); 391([Zn(L_1)]$^+$, 35).

Complex 5a: Yield 64%; m.p. 258 °C; Elemental analyses (C, H and N, wt.%) Anal. Calcd for $C_{53}H_{40}N_5S_3P_2BrZn$: C, 60.60; H, 3.84; N, 6.67; found: C, 60.75; H, 3.69; N, 6.54; IR (KBr, cm^{-1}): *v*(C=N), 1595; *v*(N=N), 1440; *v*(PPh_3), 1484, 748, 695; *v*(NCS), 2096, 754, 488; Δ_m (CH_2Cl_2, $\Omega^{-1}\,cm^2\,M^{-1}$): 21.51; UV–vis ($CH_2Cl_2$) λ_{max} (nm) ($\varepsilon \times 10^3$, $M^{-1}\,cm^{-1}$): 284 (24), 335 (14), 452 (4); ^{1}H NMR ($CDCl_3$) (300 MHz): δ (ppm) 6.77–7.82 (m, Ar–H); ^{31}P NMR: δ (ppm) 35.3; ESI MS, *m/z* (%): 1073([M + Na]$^+$, 17); 1075 ([M + Na + 2]$^+$, 17); 957 ([Zn(L_2)(PPh_3)$_2$]$^+$, 100); 435 ([Zn(L_2)]$^+$, 45).

Complex 6a: Yield 62%; m.p. 264 °C; Elemental analyses (C, H and N, wt.%) Anal. Calcd for $C_{53}H_{40}N_5S_3P_2IZn$: C, 58.01; H, 3.67; N, 6.38; found: C, 58.13; H, 3.54; N, 6.53; IR (KBr, cm^{-1}): *v*(C=N), 1586; *v*(N=N), 1434; *v*(PPh_3), 1482, 740, 692; *v*(NCS), 2095, 750 484; Δ_m (CH_2Cl_2, $\Omega^{-1}\,cm^2\,M^{-1}$): 15.93; UV–vis ($CH_2Cl_2$) λ_{max} (nm) ($\varepsilon \times 10^3$, $M^{-1}\,cm^{-1}$): 288 (27), 346 (12), 450 (3); ^{1}H NMR ($CDCl_3$) (300 MHz): δ (ppm) 6.65–7.96 (m, Ar–H); ^{31}P NMR: δ (ppm) 35.4; ESI MS, *m/z* (%): 1121 ([M + Na]$^+$, 12); 1005 ([Zn (L_3)(PPh_3)$_2$]$^+$, 100); 483 ([Zn(L_3)]$^+$, 32).

Complex 4b: Yield 61%; m.p. 272 °C; Elemental analyses (C, H and N, wt.%) Anal. Calcd for $C_{53}H_{40}N_5S_3P_2ClCd$: C, 60.46; H, 3.83; N, 6.65; found: C, 60.44; H, 3.82; N, 6.67; IR (KBr, cm^{-1}): *v*(C=N), 1592; *v*(N=N), 1437; *v*(PPh_3), 1480, 744, 690; *v*(NCS), 2096, 755, 490; Δ_m (CH_2Cl_2, $\Omega^{-1}\,cm^2\,M^{-1}$): 18.90; UV–vis ($CH_2Cl_2$) λ_{max} (nm) ($\varepsilon \times 10^3$, $M^{-1}\,cm^{-1}$): 286 (29), 348 (16), 450 (6); ^{1}H NMR ($CDCl_3$) (300 MHz): δ (ppm) 6.82–7.86 (m, Ar–H); ^{31}P NMR: δ (ppm) 35.2; ESI MS, *m/z* (%): 1076 ([M + Na]$^+$, 24); 1078 {M + Na + 2]$^+$, 8); 960 ([Cd(L_1)(PPh_3)$_2$]$^+$, 100); 438 ([Cd(L_1)]$^+$, 45).

Complex 5b: Yield 64%; m.p. 248 °C; Elemental analyses (C, H and N, wt.%) Anal. Calcd for $C_{53}H_{40}N_5S_3P_2BrCd$: C, 58.01; H, 3.67; N, 6.38; found: C, 57.99; H, 3.67; N, 6.48; IR (KBr, cm^{-1}): *v*(C=N), 1595; *v*(N=N), 1440; *v*(PPh_3), 1484, 748, 695; *v*(NCS), 2096, 752, 488; Δ_m (CH_2Cl_2, $\Omega^{-1}\,cm^2\,M^{-1}$): 22.12; UV–vis ($CH_2Cl_2$) λ_{max} (nm) ($\varepsilon \times 10^3$, $M^{-1}\,cm^{-1}$): 296 (25), 335 (18), 448 (6); ^{1}H NMR ($CDCl_3$) (300 MHz): δ (ppm) 6.72–7.94 (m, Ar–H); ^{31}P NMR: δ (ppm) 35.2; ESI MS, *m/z* (%): 1121([M + Na]$^+$, 21); 1123 ([M + Na + 2]$^+$, 21); 1005 ([Cd(L_2)(PPh_3)$_2$]$^+$, 100); 483 ([Cd(L_2)]$^+$, 39).

Complex 6b: Yield 63%; m.p. 252 °C; Elemental analyses (C, H and N, wt.%) Anal. Calcd for $C_{53}H_{40}N_5S_3P_2ICd$: C, 55.63; H, 3.52; N, 6.12; found: C, 55.61; H, 3.52; N, 6.14; IR (KBr, cm^{-1}): *v*(C=N), 1586; *v*(N=N), 1434; *v*(PPh_3), 1482, 740, 692; *v*(NCS), 2095, 750, 486; Δ_m (CH_2Cl_2, $\Omega^{-1}\,cm^2\,M^{-1}$): 17.20; UV–vis ($CH_2Cl_2$) λ_{max} (nm) ($\varepsilon \times 10^3$, $M^{-1}\,cm^{-1}$): 288 (30), 342 (21), 446 (5); ^{1}H NMR ($CDCl_3$) (300 MHz): δ (ppm) 6.68–7.88 (m, Ar–H); ^{31}P NMR: δ (ppm) 35.3; ESI MS, *m/z* (%): 1167([M + Na]$^+$, 14); 1051 ([Cd (L_3)(PPh_3)$_2$]$^+$, 100); 529 ([Cd(L_3)]$^+$, 31).

3. Results and discussion

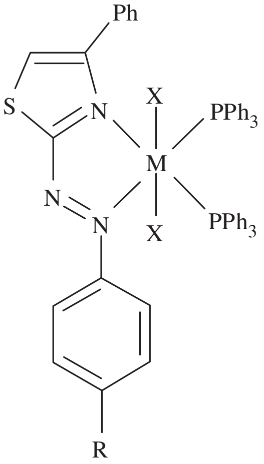
Reaction of thiazolylazo ligands $\mathbf{L_{1-3}}$ with Zn(II) or Cd(II) in presence of triphenylphosphine and NaN_3 or NH_4NCS in 1 : 1 : 2 : 2 M ratio yields $[M(\mathbf{L})(PPh_3)_2(N_3)_2]$ (**1a**–**3a** and **1b**–**3b**) and $[M(\mathbf{L})(PPh_3)_2(NCS)_2]$ (**4a**–**6a** and **4b**–**6b**); where M = Zn(II), Cd(II); **L** = 4-(4′-phenyl, 2′-thiazolylazo)chlorobenzene ($\mathbf{L_1}$), 4-(4′-phenyl, 2′-thiazolylazo)bromobenzene ($\mathbf{L_2}$), 4-(4′-phenyl, 2′-thiazolylazo)iodobenzene ($\mathbf{L_3}$); and PPh_3 = triphenylphosphine (figure 1). The air stable, moisture insensitive complexes are soluble in chloroform, dichloromethane, acetonitrile, etc. The elemental analyses support the assigned composition of the complexes.

3.1. *Molar conductivity*

The solubility of the complexes in CH_2Cl_2 permitted calculation of molar conductivity of 10^{-3} M solutions at 25 °C and, by comparison, the electrolytic nature of each complex. The molar conductance of the complexes are 16.73–26.34 $\Omega^{-1}\,cm^2\,M^{-1}$ indicating that, although some dissociation of these complexes seems to occur in the solvent, the conductance value supports the non-electrolytic nature of the complexes [21]. This is further supported by the general formula of the complexes from elemental analyses and IR spectra.

3.2. *Spectral studies*

The structure of the complexes is also supported by IR spectra and comparison of IR spectrum of $\mathbf{L_{1-3}}$ with those of metal complexes. A medium strong band at 1624–1630 cm^{-1} in the free $\mathbf{L_{1-3}}$ is assigned to ν(C=N) of thiazole nitrogen, shifted to lower frequencies by 32–34 cm^{-1} in spectra of all complexes, suggesting involvement of thiazole nitrogen in coordination [22]. Another band at 1466–1472 cm^{-1} in spectra of $\mathbf{L_{1-3}}$, assigned to υ(N=N) shifts to lower frequency (1434–1440 cm^{-1}) in the complexes providing evidence for coordination of azo nitrogen [23]. This was also confirmed by a new band at



R= Cl, Br, I; M= Zn(II), Cd(II);

X= N_3^- (**1a-3a** and **1b-3b**); NCS^-(**4a-6a** and **4b-6b**)

Figure 1. Proposed structures of the complexes.

436–442 cm^{-1} due to ν(M–N) [24]. A band observed at ~746 cm^{-1} in spectra of free $\mathbf{L_{1-3}}$ remains unaltered in the spectra of all complexes, indicating non-involvement of thiazole sulfur in coordination. IR spectra of **1a**–**6a** and **1b**–**6b** exhibit the expected bands due to PPh_3 at 1481, 744 and 692 cm^{-1}. The azido complexes (**1a**–**3a** and **1b**–**3b**) exhibit $\nu_{as}(N_3)$ of the azide at ~2172 cm^{-1} and a band at ~1345 cm^{-1} attributed to $\nu_s(N_3)$ corresponding to terminally coordinated azide in the complexes [25]. In thiocyanato complexes (**4a**–**6a** and **4b**–**6b**), a very strong and sharp band at ~2095 cm^{-1}, a medium band at ~752 cm^{-1} and a weak band at ~487 cm^{-1} are assigned to υ(CN), υ(CS) and δ(NCS) of NCS, respectively. The intensity and position of these bands indicate monodentate coordination through nitrogen [26].

Electronic spectra for all the complexes were recorded in dichloromethane (10^{-4} M) from 200 to 900 nm. The complexes exhibit two bands at 284–292 and 335–346 nm for **1a**–**6a,** and 282–296 nm and 335–348 nm for **1b**–**6b**, due to intra-ligand π–π^* and n–π^* transitions, respectively. Another intense absorption at 446–463 (**1a**–**6a**) and 446–450 (**1b**–**6b**) nm may be assigned to metal to ligand charge transfer transition.

The ^{1}H NMR spectra of all the complexes were recorded in $CDCl_3$. ^{1}H NMR spectra of **1a**–**6a** and **1b**–**6b** show resonances of phenyl protons of PPh_3 overlap to some extent with those of phenyl hydrogens of $\mathbf{L_{1-3}}$ (Supplementary material). The broad multiplet at δ 6.62–7.96 ppm in **1a**–**6a** and δ 6.68–7.94 ppm in **1b**–**6b** is assigned to phenyl protons of PPh_3 together with ring protons of $\mathbf{L_{1-3}}$. Comparison with resonances observed in complexes with free $\mathbf{L_{1-3}}$ indicates downfield shift of ring protons by 0.1–0.2 ppm in the complexes.

The ^{31}P NMR spectra of all complexes in $CDCl_3$ show a resonance at ~35.2 ppm consistent with octahedral geometry around metal ion, and presence of two equivalent *cis* phosphine moieties in the complexes [27].

3.3. *Thermal analysis*

To examine thermal stability, thermogravimetric (TG) and differential thermal analyses (DTA) were carried out for **1a**–**6a** to 1000 °C under nitrogen. The thermal analysis data are presented in table 1.

Thermal decomposition of the azide complexes (**1a**, **2a,** and **3a**) involves three decomposition stages. The complexes show no mass loss to 155, 152, and 158 °C, respectively, revealing the absence of water or solvent in the complexes. The first decomposition stage takes place at 155–270, 152–274 and 158–268 °C with DTA peaks at 230 °C (**1a**), 217 °C (**2a**), and 214 °C (**3a**), respectively, corresponding to mass loss of 9.23, 7.65, and 8.74% of azide (Calcd% = 8.62, 8.24, and 7.88). The second step occurs at 270–384, 274–386, and 268–384 °C accompanied by a mass loss of 29.47, 32.10, and 35.06% for **1a**, **2a,** and **3a**, respectively, corresponding to decomposition of **L** (Calcd% = 30.76, 33.78 and 36.70). The DTA curve gives peaks at 336 for **1a**, 342 for **2a,** and 340 °C for **3a**. The third step takes place at 384–840, 386–835 and 384–836 °C for **1a**, **2a,** and **3a**, respectively, corresponding to mass loss of 52.92, 52.54 and 50.85% attributed to decomposition of triphenylphosphine (Calcd% = 53.78, 51.53 and 49.16) leaving ZnO as a residue.

The thiocyanato complexes **4a**, **5a**, and **6a** show similar behavior; once again absence of water or solvent is indicated by no mass loss to 168, 167, or 171 °C for **4a**, **5a,** and **6a**, respectively. The first stage corresponding to mass loss of 10.40, 10.54, and 11.63% may be attributed to decomposition of thiocyanate (Calcd% = 11.53, 11.04 and 10.57) at 168–276, 167–278, and 171–282 °C with exothermic peak at 250 °C for **4a**, 248 °C for **5a,**

Table 1. Thermal behavior of the Zn(II) complexes.

	Thermogravimetry (TG)			Mass loss (%)		
Compound	Stage	Temp. range (°C)	DTA peak (°C)	Found	Calcd	Decomposition product loss
1a	I	155–270	230	9.23	8.62	$2N_3$
	II	270–384	336	29.47	30.76	$C_{15}H_{10}N_3SCl$
	III	384–840	814	52.92	53.78	$2C_{18}H_{15}P$
2a	I	152–274	217	7.65	8.24	$2N_3$
	II	274–386	342	32.10	33.78	$C_{15}H_{10}N_3SBr$
	III	386–835	812	52.54	51.53	$2C_{18}H_{15}P$
3a	I	158–268	214	8.74	7.88	$2N_3$
	II	268–384	340	35.06	36.70	$C_{15}H_{10}N_3SI$
	III	384–836	812	50.85	49.16	$2C_{18}H_{15}P$
4a	I	168–276	250	10.40	11.53	2NCS
	II	276–388	348	28.34	29.78	$C_{15}H_{10}N_3SCl$
	III	388–882	810	50.76	52.07	$2C_{18}H_{15}P$
5a	I	167–278	248	10.54	11.04	2NCS
	II	278–384	344	33.64	32.75	$C_{15}H_{10}N_3SBr$
	III	384–875	824	48.27	49.87	$2C_{18}H_{15}P$
6a	I	171–282	242	11.63	10.57	2NCS
	II	282–388	340	32.94	31.37	$C_{15}H_{10}N_3SI$
	III	388–885	820	48.07	53.98	$2C_{18}H_{15}P$

and 242 °C for **6a**. The second stage occurs at 276–388, 278–384, and 282–388 °C, accompanied by mass loss of 28.34, 33.64, and 32.94%, respectively, attributed to decomposition of **L** (Calcd% = 29.78, 32.75, and 31.37%) with DTA peak at 348 °C for **4a**, 344 °C for **5a,** and 340 °C for **6a**. In the third stage (388–882, 384–875, and 388–885 °C) mass losses of 50.76, 48.27, and 48.07% in **1a**, **2a,** and **3a** correspond to decomposition of triphenylphosphine leaving anhydrous ZnO (Calcd% = 52.07, 49.87, and 53.98).

3.4. *Fluorescence spectral studies*

The fluorescence properties of Zn(II) and Cd(II) complexes were investigated in dichloromethane solution at room temperature (figures 2 and 3), and fluorescence emission data are presented in table 2. The Zn(II) complexes (**1a**–**6a**) show emission with maximum wavelength at 426–438 nm (λ_{ex} = 342–348 nm), with lifetime of the fluorescence of 2.53–2.57 ns. However, Cd(II) complexes (**1b**–**6b**) show intense broad emission at 428–436 nm (λ_{ex} = 344–350 nm), with lifetime of 2.56–2.63 ns. Compared to **L_{1-3}**, all the complexes show strong fluorescence in dichloromethane, enhanced by > 128 nm. No emissions originating from the metal-centered excited states are observed for Zn(II) and Cd(II) complexes, since they are difficult to oxidize or reduce. The emission observed in these complexes is attributed to the fluorescence from the intraligand ($\pi \rightarrow \pi^*$) emission excited state. The slight red-shifts of Zn(II) and Cd(II) complexes in comparison to their respective ligands **L_{1-3}**, probably result from formation of mononuclear complexes effectively increasing the ligand conformational rigidity and thus, reducing non-radiative energy loss [28, 29].

The fluorescence quantum yields (ϕ) of the complexes were determined using quinine sulfate as a reference with known ϕ_R of 0.52. The area of emission spectrum was integrated using the software available in the instrument and quantum yield was calculated according to the following equation

$$\phi_S = A_S/A_R \times (\mathrm{Abs})_R/(\mathrm{Abs})_S \times \phi_R$$

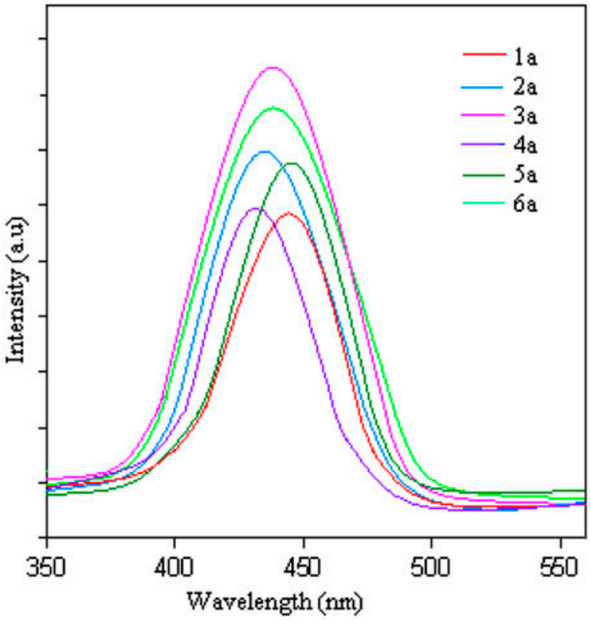


Figure 2. Emission spectra of Zn(II) complexes (**1a**–**6a**).

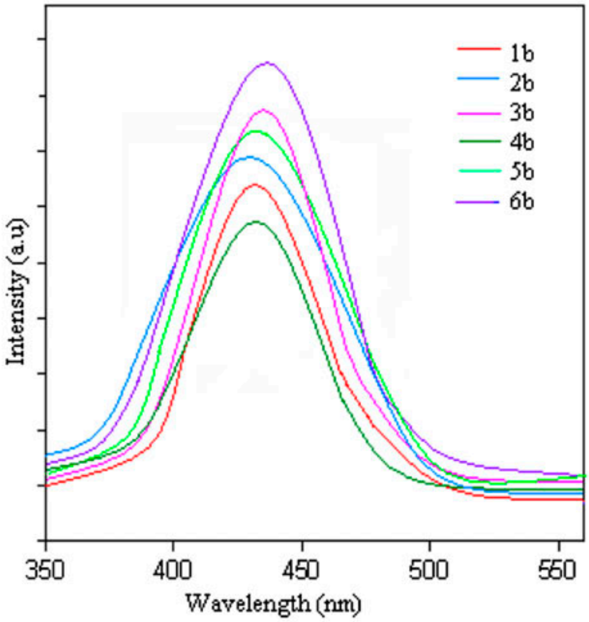


Figure 3. Emission spectra of Cd(II) complexes (**1b**–**6b**).

Table 2. Photophysical data of Zn(II) and Cd(II) complexes.

Compound	Excitation (nm)	Emission (nm)	Quantum yield (ϕ)
1a	342	438	0.015
2a	348	426	0.017
3a	345	431	0.014
4a	342	426	0.030
5a	345	438	0.014
6a	346	431	0.020
1b	345	430	0.019
2b	348	428	0.034
3b	346	436	0.049
4b	348	431	0.047
5b	344	432	0.030
6b	350	434	0.034

Here ϕ_S and ϕ_R are the fluorescence quantm yields of the sample and reference, respectively. A_S and A_R are the area under the fluorescence spectra of the sample and reference respectively. $(\mathrm{Abs})_S$ and $(\mathrm{Abs})_R$ are the respective optical densities of the sample and the reference solution at the wavelength of excitation. The fluorescence quantum yields of all the complexes are 0.014–0.030 for **1a**–**6a** and 0.019–0.049 for **1b**–**6b**. Higher quantum yields observed for **1b**–**6b** compared to **1a**–**6a** might be due to ligands coordinated to Cd (II) better than Zn(II). These results are in agreement with those reported in the literature [30].

4. Conclusion

Some Zn(II) and Cd(II) complexes (**1a**–**6a** and **1b**–**6b**) of thiazolylazo dye with triphenylphosphine and N_3^- or NCS^- as coligands have been synthesized and characterized. IR spectra reveal that the thiazolylazo is coordinated bidentate via azo nitrogen and thiazole nitrogen. TGA/DTA reveals that the thiocyanate complexes are thermally more stable than the azide complexes. All the complexes exhibit blue-green emission as a result of fluorescence from the intraligand ($\pi \rightarrow \pi^*$) emission excited state.

References

[1] R.C. Mayura, P. Sharma, D. Sutradhar. *Synth. React. Inorg. Met. Org. Chem.*, **33**, 669 (2003).

[2] J.S. Miller, M. Drillon (Eds.), *Magnetism, Molecules to Materials IV*, pp. 1–60, Wiley-VCH, Weinheim (2003).

[3] Y.T. Li, C.W. Yan, C.Y. Zhu, H.S. Guan. *Synth. React. Inorg. Met. Org. Chem.*, **34**, 1165 (2004).

[4] O. Kahn. *Molecular Magnetism*, VCH, New York, NY (1993).

[5] D.M. Vriezema, J. Hoogboom, K. Velonia, K. Takazawa, P.C.M. Christianen, J.C. Mann, A.E. Rowan, R.J. M. Nolte. *Angew. Chem. Int. Ed.*, **42**, 772 (2003).

[6] Y. Aydogdo, F. Yakuphanoglu, A. Aydogdu, E. Tas, A. Cukurovali. *Mater. Lett.*, **57**, 3755 (2003).

[7] S.H. Rehman, D. Bose, H. Chowdhury, G. Mostafa, H.K. Fun, B.K. Ghosh. *Polyhedron*, **24**, 1837 (2005).

[8] B. Ramchandran, A. Samanta. *Chem. Commun.*, **11**, 1037 (1997).

[9] H.Y. Bie, J.H. Yu, J.Q. Xu, J. Lu, Y. Li, X.B. Cui, X. Zhang, Y.H. Sun, L.Y. Pan. *J. Mol. Struct.*, **660**, 107 (2003).

[10] M.M.M. Raposo, A.M.R.C. Sousa, G. Kirsch, P. Cardoso, M. Belsley, E. de Matos Gomes, A.M.C. Fonseca. *Org. Lett.*, **8**, 3681 (2006).

[11] X.Y. Xu, T.T. Xu, J. Gao, M.Y. Wang, S.R. Niu, S.S. Ni, G.X. Xu. *Synth. React. Inorg. Met. Org. Chem.*, **36**, 677 (2006).

[12] I.M.A. Awad. *Phosphorus Sulfur Silicon*, **114**, 17 (1996).

[13] W.M. Fabian, L. Antonov, D. Nedeltcheva, F.S. Kamounad, P.J. Taylor. *J. Phys. Chem.*, **108**, 7603 (1997).

[14] X. Chen, J. Zhang, H. Zhang, Z. Jiang, G. Shi, Y. Li, Y. Song. *Dyes Pigm.*, **77**, 223 (2008).

[15] G. Zhang, S. Wang, J.S. Ma, G. Yang. *Inorg. Chim. Acta*, **384**, 97 (2012).

[16] F. Karipcin, E. Kabalcilar, S. Ilican, Y. Caglar, M. Caglar. *Spectrochim. Acta, Part A*, **73**, 174 (2009).

[17] F. Karipcin, B. Dede, S. Percin-Ozkorucuklu, E. Kabalcilar. *Dyes Pigm.*, **84**, 14 (2010).

[18] M.M. Omar, G.G. Mohamad. *Spectrochim. Acta, Part A*, **61**, 929 (2005).

[19] B.A. Yamgar, V.A. Sawant, S.K. Sawant, S.S. Chavan. *J. Coord. Chem.*, **62**, 2367 (2009).

[20] B. Dash, M.K. Rout. *J. Indian Chem. Soc.*, **32**, 663 (1955).

[21] R.G. Goel, N.K. Jha. *Can. J. Chem.*, **59**, 3267 (1981).

[22] U.S. Ray, D. Banerjee, C. Sinha. *J. Proc. Indian Acad. Sci.*, **115**, 169 (2003).

[23] D. Banerjee, U.S. Ray, S. Jasimuddin, J.C. Liou, T.H. Lu, C. Sinha. *Polyhedron*, **25**, 1299 (2006).

[24] M. Gaber, I.A. Mansour, Y.S.Y. El-Sayed. *Spectrochim. Acta, Part A*, **68**, 305 (2007).

[25] B.G. Chand, U.S. Ray, G. Moustfa, J. Cheng, T.H. Lu, C. Sinha. *Inorg. Chim. Acta*, **358**, 1927 (2005).

[26] N. Mondal, M.K. Saha, S. Mitra, V. Gramlich. *J. Chem. Soc., Dalton Trans.*, 3218 (2000).

[27] M. Moszner, E. Kwaskowska-Che, J.J. Ziołkowski. *Inorg. Chim. Acta*, **357**, 2483 (2004).

[28] Y. Bai, W.L. Shang, D.B. Dang, H. Gao, X.F. Niu, Y.F. Guan. *Inorg. Chem. Commun.*, **11**, 1470 (2008).

[29] J.M. Shi, H.L. Yin, C.J. Wu, F.L. Liu, W. Xu. *Polyhedron*, **22**, 493 (2003).

[30] S. Roy, S. Konar, A. Jana, S. Jana, A. Patra, S. Chatterjee, J.A. Golen, A.L. Rheingold, S.S. Mandal, S.K. Kar. *Polyhedron*, **33**, 82 (2012).