Inorganica Chimica Acta 363 (2010) 1897-1901



Contents lists available at ScienceDirect

Inorganica Chimica Acta



journal homepage: www.elsevier.com/locate/ica

Note

Synthesis, characterization and luminescent properties of heteroligand copper(I) complexes with *N*-thiophosphorylated thioureas RNHC(S)NHP(S)(O*i*Pr)₂ (R = *i*Pr, *t*Bu, Ph, 2,6-Me₂C₆H₃, 2,4,6-Me₃C₆H₂) and phosphines (PPh₃, Ph₂P(C₅H₄FeC₅H₄)PPh₂)

Damir A. Safin^{a,*}, Maria G. Babashkina^a, Michael Bolte^b, Axel Klein^{a,*}

^a Institut f
ür Anorganische Chemie, Universit
ät zu K
öln, Greinstrasse 6, D-50939 K
öln, Germany
^b Institut f
ür Anorganische Chemie J.-W.-Goethe-Universit
ät, Frankfurt/Main, Germany

ARTICLE INFO

Article history: Received 30 September 2009 Received in revised form 13 December 2009 Accepted 21 February 2010 Available online 24 February 2010

Keywords: Copper(I) Crystal structure Thiourea Phosphine NMR spectroscopy Luminescence

1. Introduction

ABSTRACT

Reaction of the potassium salts of RNHC(S)NHP(S)(OiPr)₂ (R = iPr, **HL**¹; *t*Bu, **HL**^{II}; Ph, **HL**^{III}; 2,6-Me₂C₆H₃, **HL**^{IV}; 2,4,6-Me₃C₆H₂, **HL**^V) with [Cu(PPh₃)₃I] or a mixture of CuI and Ph₂P(C₅H₄FeC₅H₄)PPh₂ in aqueous EtOH/CH₂Cl₂ leads to mononuclear [Cu(PPh₃)₂L^{II}] (1), [Cu(PPh₃)₂L^V] (2), [Cu{Ph₂P(C₅H₄FeC₅H₄)PPh₂]L^{II}] (3), [Cu{Ph₂P(C₅H₄FeC₅H₄)PPh₂]L^{II}] (4), [Cu{Ph₂P(C₅H₄FeC₅H₄)PPh₂]L^{III}] (5), [Cu{Ph₂P(C₅H₄FeC₅H₄)PPh₂]-L^{IV}] (6) and [Cu{Ph₂P(C₅H₄FeC₅H₄)PPh₂]L^V] (7) complexes. The structures of these complexes were investigated by ¹H, ³¹P{¹H} NMR spectroscopy and elemental analysis. The crystal structures of 1, 2 and 4 were determined by single crystal X-ray diffraction. The complexes **3–7** exhibit emission in the solid state at ambient temperature that might be explained by the presence of the ferrocene-diyl unit in the chelate phosphine.

© 2010 Elsevier B.V. All rights reserved.

In preceding papers, we have described heteroligand Cu(I) complexes with a number of *N*-thiophosphorylated thioureas and thioamides RC(S)NHP(S)(OiPr)₂ (R = morpholin-*N*-yl, piperidin-*N*-yl [1]; α -naphthylNH [2]; NH₂ [1,3]; pyridin-2-ylNH, pyridin-3-ylNH, H₂N-6-Py-2-NH [4]; Ph, Et₂N [5–7]; (EtO)₂P(O)CH₂C₆H₄-4-NH [8]; MeNH, *i*PrNH, *t*BuNH, Me₂N, PhNH, 2,6-Me₂C₆H₃NH, 2,4,6-Me₃C₆H₂NH [9,10]), and triphenylphosphine or Ph₂P(CH₂)_n*PPh*₂ (n = 1–3) phosphines. Reaction of alkaline salts of the tetrakis-thiourea, containing a cyclam fragment, with [Cu(PPh₃)₃] leads to the tetranuclear Cu(I) complex [{Cu(PPh₃)₂]₄(cyclam)] [11].

Furthermore, we have described two Cu(I) complexes [Cu(PPh₃) {RC(S)NP(S)(OiPr)₂}] (R = H₂N-6-Py-2-NH [4], (EtO)₂P(O)CH₂C₆H₄-4-NH [8]) (Chart 1), containing one triphenylphosphine ligand. From this preliminary work it can be supposed, that the coordination of two molecules of PPh₃ to the Cu(I) atom is feasible in cases where, in the crystal, hydrogen bonded dimers are formed through the hydrogen atom of the NH group and the sulfur atom of the C=S fragment, or in cases where no hydrogen bonded dimers can be

* Corresponding authors.

formed (usually due to missing NH-functions). In contrast to this, formation of dimers through the thiophosphoryl O atoms goes along with the binding of only one PPh₃ ligand.

To verify (or falsify) this rule, we have embarked on a systematic study on heteroligand Cu(I) complexes, using one HL ligand and triphenylphosphine (PPh₃) or alternatively the chelate phosphine $Ph_2P(C_5H_4FeC_5H_4)PPh_2$ providing a rather large P–Cu–P bite angle.

On the other hand a number of heteroligand Cu(I) complexes, containing both aryl-substituted pnictines and cyclic thioureas or pyridine thiolates, were also described [12–14]. Combination of these two types of ligands might lead to interesting and unusual photophysical and electrochemical properties [15].

2. Results and discussion

The *N*-thiophosphorylated thioureas HL^{I-V} were prepared as described previously [10]. The complexes **1** and **2** were also prepared according to previously described methods (Scheme 1) [10]. Reaction of the potassium salts of HL^{I-V} with a mixture of CuI and $Ph_2P(C_5H_4FeC_5H_4)PPh_2$ in aqueous EtOH/CH₂Cl₂ leads to the complexes **3–7** (Scheme 2).

The complexes **1** and **2** are colorless powders, soluble in acetone, benzene, CH_2Cl_2 , DMSO, DMF and insoluble in *n*-hexane.

E-mail addresses: damir.safin@ksu.ru (D.A. Safin), axel.klein@uni-koeln.de (A. Klein).

^{0020-1693/\$ -} see front matter \circledcirc 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2010.02.028





 $R = iPr(3), tBu(4), Ph(5), 2,6-Me_2C_6H_3(6), 2,4,6-Me_3C_6H_2(7)$

Scheme 2.

The complexes **3–7** are yellow or orange powders, slightly soluble in acetone, DMSO, DMF, poorly soluble in benzene, CH_2Cl_2 , and insoluble in *n*-hexane. ¹H, ³¹P{¹H} NMR data indicated that in all complexes the deprotonated ligands **L**^{I–V} are 1,5-*S*,*S*'-coordinating.

In the ³¹P{¹H} NMR spectra of the complexes, the resonances in the range 56.2–58.3 ppm correspond to the phosphorus atoms of the thiophosphoryl group [16]. The signals of $Ph_2P(C_5H_4-FeC_5H_4)PPh_2$ in the spectra of the complexes **3–7** exhibit chemical shifts from –17.9 to –17.4 ppm and observed in the area typical for the coordinated bisphosphines.

The ¹H NMR spectra of the complexes **3–7** contain only signals which correspond to the proposed structures. The spectra contain a

set of signals for the iPrO protons: a singlet, triplet or two doublets for the CH₃ protons at 0.95–1.23 ppm and a doublet of septets or broad singlet for the CH protons at 4.36–4.65 ppm. In the spectrum of **3** there are signals for the *i*PrN protons: a doublet for the CH₃ protons at 0.99 ppm and a doublet of septets for the CH protons at 3.95 ppm. The signal for the *t*Bu and Me protons in the spectra of **4** and **6**, and **7** are found at 1.21 and 2.06–2.22 ppm, respectively. The signals for the phenyl, aryl and NH protons in the spectra of 3-7 are at 6.89–7.77 ppm. The ¹H NMR spectra contain the signals for the C_5H_4 protons at 4.17–4.33 ppm. Signals of the NH group proton in the spectra of **3** and **4** are at 5.62–5.78 ppm. A rather high ${}^{4}J_{P,H}$ coupling constant (7.5-9.1 Hz) for the NH proton in 3 and 4 is explained by the so-called W-criterion for the PNCNH chain [16]. The contribution of the observed splitting to the presence of ${}^{4}J_{P,H}$ spinspin coupling was unambiguously confirmed by recording ¹H NMR spectra with ³¹P decoupling.

Crystals of **1**, **2** and **4** were obtained by slow evaporation of the solvent from their dichloromethane–*n*-hexane mixtures, v/v 1:5 (Table 1). The molecular structures of **1**, **2** and **4** are shown in Figs. 1–3, respectively. Selected bond lengths and bond angles are given in Table 2.

In the structures of **1**, **2** and **4** the Cu(I) cation is in a P_2S_2 tetrahedral environment formed by two sulfur atoms of the corresponding deprotonated N-thiophosphoryl thiourea ligand and two phosphorus atoms of two PPh₃ (Figs. 1 and 2) or one $Ph_2P(C_5H_4FeC_5H_4)PPh_2$ (Fig. 3). The asymmetric unit of **2** contains two independent molecules forming a centrosymmetric dimer through intermolecular hydrogen bonds (Fig. 4). They are formed by the hydrogen atom of the NH group and the sulfur atom of the C=S group of a further molecule. The hydrogen bond parameters are following: $N(2)-H(2)\cdots S(2A)$, N(2)-H(2) 0.83(2) Å, $H(2) \cdots S(2A) 2.77(2) \text{ Å, } N(2) \cdots S(2A) 3.5713(17) \text{ Å, } \angle N(2) - H(2) \cdots$ $S(2A) = 162.5(18)^{\circ}; N(2A) - H(2A) - S(2), N(2A) - H(2A) = 0.86(3) \text{ Å},$ $H(2A) \cdots S(2) = 2.56(3) \text{ Å}, \quad N(2A) \cdots S(2) = 3.3821(18) \text{ Å}, \quad \angle N(2A) - (AA) = -(AA) - (AA) H(2A) \cdot \cdot \cdot S(2)$ 160(2)°. The six-membered CuSPNCS metallocycles have the conformation of a distorted boat. The fragments NC(S)NP are almost planar, only the sulfur of the thiophosphoryl group is significantly deviated from the average planes of these fragments. This deviation of the phosphoryl sulfur is common for complexes of *N*-thiophosphorylated thioureas and thioamides [16].

The luminescent properties of **3–7** were investigated in the solid state at room temperature. Previously, we found that the complexes **1** and **2** show no emission under the same conditions [10a].



Fig. 1. Thermal ellipsoid representation of the complex 1 (hydrogen atoms were omitted for clarity). Ellipsoids are drawn at the 30% probability level.

Table 1		
Crystal data, data collection	and refinement de	etails for 1 , 2 and 4 .

	1	2	4
Empirical formula	$C_{47}H_{54}CuN_2O_2P_3S_2$	$C_{52}H_{56}CuN_2O_2P_3S_2$	$C_{45}H_{52}CuFeN_2O_2P_3S_2$
Formula weight	899.49	961.56	929.31
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	ΡĪ	ΡĪ
a (Å)	13.0066(8)	11.4710(4)	10.9625(9)
b (Å)	21.6122(13)	17.0614(6)	12.5534(10)
c (Å)	17.6985(11)	26.1059(9)	17.7400(13)
α (°)	90	74.242(3)	74.108(6)
β(°)	111.093(1)	89.937(3)	73.336(6)
γ(°)	90	86.435(3)	78.173(6)
V (Å ³)	4641.7(5)	4907.0(3)	2228.1(3)
Ζ	4	4	2
D_{calc} (g cm ⁻³)	1.287	1.302	1.385
T (K)	293(2)	173(2)	173(2)
$F(0\ 0\ 0)$	1888	2016	968
μ (mm ⁻¹)	0.703	0.669	1.043
Reflections collected	38 749	83 997	16 027
Unique reflections	10 826	14 443	4764
Observed reflections	8635 (<i>R</i> _{int} = 0.024)	18 331 (<i>R</i> _{int} = 0.0562)	$8100 \ (R_{\rm int} = 0.0701)$
R indices (all	$R_1 = 0.0320$,	$R_1 = 0.0428$,	$R_1 = 0.0896$,
data)	$wR_2 = 0.0885$	$wR_2 = 0.0743$	$wR_2 = 0.0781$

The complexes **3** and **4** show a blue emission band at 464–467 nm, while the complexes **5–7** show cyan emission at 481–487 nm (Table 3). Very similar emission maxima were recently reported for similar mononuclear complexes containing various chelate phosphine ligands $Ph_2P(CH_2)_nPPh_2$ (n = 1–3) [10a]. Also, in this study all complexes containing the monodentate PPh_3 ligand failed to



Fig. 2. Thermal ellipsoid representation of the complex 2 (hydrogen atoms were omitted for clarity). Ellipsoids are drawn at the 30% probability level.



Fig. 3. Thermal ellipsoid representation of the complex 4 (hydrogen atoms were omitted for clarity). Ellipsoids are drawn at the 30% probability level.



Fig. 4. Hydrogen bonded dimer of **2** (hydrogen atoms except NH were omitted for clarity).

emit under these conditions, with the exception of the complex $[Cu(PPh_3)_2(MeNHC(S)NP(S)(OiPr)_2)]$ which shows an emission band at 429 nm [10a]. The emission around 450-510 nm is typical of Cu–P containing chromophores with either ³MLCT $(d-\sigma^*)$ or ³ILCT (σ - a_{π}) excited states [17]. On the other hand, quite similar emissions have been observed for Zn(II) complexes of N-phosphorylated thioamides and thioureas RC(S)NHP(O)(OiPr)₂. Combining the results from the previous study and the here presented data we can conclude, that very probably the emission arises from excited states with a phosphine contribution. The emission of the ferrocene-diyl derivatives 3-7 shows a bathochromic shift compared to the PPh₃ derivative with R = MeNH. The failure of the complexes 1 (R = iPrNH) and 2 (R = tBuNH) to show emission compared to the R = MeNH derivative and the ferrocenyl-diyl derivatives is a strong argument for the assumption that ³ILCT (σ - a_{π}) excited states are mainly responsible for the emission. While the ferrocene-diyl derivatives provide sterically favorable (orientation of the Cp group towards the P–Cu bond) and electronically stabilized π^{\uparrow} contributions, most of the PPh₃ derivatives fail to do so. For the exceptional case with R = MeNH the low steric bulk of the Me-substituents allows an optimum orientation of the PPh₃ ligand for an efficient stabilization of such a ³ILCT (σ -a_{π}) excited state, while bulkier substituents R = iPr or tBu fail to do so. This is also in line with

Table 2	
Selected bond lengths (Å) and bo	ond angles (°) for 1 , 2 and 4 .

	1	2 ^a		4
		Molecule A	Molecule B	-
C=S	1.742(2)	1.7388(17)	1.7310(18)	1.741(4)
P=S	1.9752(6)	1.9825(6)	1.9849(6)	1.9812(14)
P–N	1.5995(14)	1.6004(14)	1.5881(15)	1.613(4)
P-O	1.5874(12),	1.5827(13),	1.5859(13),	1.583(3)
	1.5896(15)	1.5908(13)	1.5921(13)	
C-N(P)	1.313(2)	1.315(2)	1.315(2)	1.308(5)
C-N	1.349(2)	1.356(2)	1.354(2)	1.355(5)
Cu-S(C)	2.3013(5)	2.2946(5)	2.2888(5)	2.2919(11)
Cu-S(P)	2.3534(5)	2.3736(5)	2.3545(5)	2.3370(11)
Cu–P	2.2991(5),	2.2775(5),	2.2850(5),	2.2626(12),
	2.3200(5)	2.3444(5)	2.3028(5)	2.2937(11)
S-C-N	113.47(13)	114.20(13)	115.19(14)	113.1(3)
S-C-N(P)	128.40(13)	128.75(13)	129.22(13)	128.5(3)
N-C-N	118.09(14)	117.05(15)	115.59(16)	118.5(4)
C-N-P	128.99(12)	130.24(13)	134.51(13)	125.2(3)
N-P-S	121.45(6)	122.12(6)	121.48(6)	120.83(13)
S-Cu-S	107.43(2)	107.985(17)	110.930(17)	108.06(4)
P-Cu-P	111.01(2)	115.763(17)	113.757(17)	111.49(4)
P-Cu-S(C)	106.78(2),	108.478(19),	110.498(19),	109.95(4),
	109.50(2)	120.778(18)	113.905(19)	117.05(4)
P-Cu-S(P)	103.14(2),	93.498(18),	98.407(18),	100.61(4),
	118.74(2)	108.468(18)	108.656(18)	108.32(4)
Cu-S-C	109.29(6)	109.80(6)	108.36(6)	106.62(14)
Cu-S-P	99.78(2)	100.86(2)	100.34(2)	97.84(5)

^a Data for two independent molecules **A** and **B**.

Table 3

Photophysical data for complexes 3-7 (the excitation wavelength was 346 nm).

Complex	Emission maximum (nm)	Complex	Emission maximum (nm)
3 4 5	464 467 481	6 7	485 487

the observation that for the above mentioned derivatives with $Ph_2P(CH_2)_nPPh_2$ (n = 1–3) ligands emission is observed for most of the derivatives with the very flexible diphosphine ligand dppp n = 3, while the dppm (n = 1) and dppe (n = 2) fail to show emission. We are aware substantiated conclusions cannot be drawn from the present data. To this end more sophisticated measurements (e.g. at low temperature, in solution, determination of lifetimes) are necessary. Such investigations are currently underway.

3. Experimental

N-Thiophosphorylated thioureas **HL**^{I-V} were prepared according to previously described methods [10]. The complexes **1** and **2** were prepared according the previously described methods [10].

3.1. Synthesis of 3-7

A suspension of HL^{I-v} (0.149, 0.156, 0.166, 0.180 or 0.187 g, respectively; 0.5 mmol) in aqueous ethanol (35 mL) was mixed with an ethanol solution of potassium hydroxide (0.031 g, 0.55 mmol). A mixture of CuI (0.095 g, 0.5 mmol) and Ph₂P(C₅H₄FeC₅H₄)PPh₂ (0.277 g, 0.5 mmol) in CH₂Cl₂ (25 mL) was refluxed for 0.5 h and then added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred for an hour and the resulting precipitate of KI was filtered off. The filtrate was concentrated until crystallization began. Isolated crystals were obtained from a CH₂Cl₂–*n*-hexane mixture 5:1 (v/v).

3. Yield: 0.430 g (94%). Mp 103–104 °C. ¹H NMR: δ 0.99 (d, ³*J*_{H,H} = 6.2 Hz, 6H, CH₃, *i*PrN), 1.21 (t, ³*J*_{H,H} = 6.0 Hz, 12H, CH₃, *i*PrO), 3.95 (d. sept, ³*J*_{H,H} = 6.0 Hz, ³*J*_{HCNH} = 7.6 Hz, 1H, NCH), 4.19 (br. s,

4H, C₅H₄), 4.29 (br. s, 4H, C₅H₄), 4.64 (d. sept, ${}^{3}J_{H,H}$ = 6.1 Hz, ${}^{3}J_{P,H}$ = 10.5 Hz, 2H, OCH), 5.62 (t, ${}^{3}J_{HCNH}$ = ${}^{4}J_{P,H}$ = 7.5 Hz, 1H, NH), 7.24–7.68 (m, overlapped with the solvent signal, Ph) ppm. ${}^{31}P{}^{1}H$ NMR: δ –17.6 (br. s, 2P, PPh₂), 57.8 (s, 1P, NPS) ppm. Calc. for C₄₄H₅₀CuFeN₂O₂P₃S₂ (915.33): C, 57.74; H, 5.51; N, 3.06. Found: C, 57.65; H, 5.58; N, 3.02%.

4. Yield: 0.376 g (81%). Mp 117–118 °C. ¹H NMR: δ 1.21 (s, 9H, CH₃, *t*Bu), 1.23 (s, 12H, CH₃, *i*Pr), 4.17 (br. s, 4H, C₅H₄), 4.28 (br. s, 4H, C₅H₄), 4.65 (d. sept, ³J_{H,H} = 6.2 Hz, ³J_{P,H} = 10.4 Hz, 2H, OCH), 5.78 (d, ⁴J_{P,H} = 9.1 Hz, 1H, NH), 7.23–7.70 (m, overlapped with the solvent signal, Ph) ppm. ³¹P{¹H} NMR: δ –17.5 (br. s, 2P, PPh₂), 56.9 (s, 1 P, NPS) ppm. Calc. for C₄₄H₅₂CuFeN₂O₂P₃S₂ (929.35): C, 58.16; H, 5.64; N, 3.01. Found: C, 58.24; H, 5.71; N, 2.97%.

5. Yield: 0.408 g (86%). Mp 146–147 °C. ¹H NMR: δ 1.20 (d, ³J_{H,H} = 6.1 Hz, 6H, CH₃, *i*Pr), 1.23 (d, ³J_{H,H} = 6.2 Hz, 6H, CH₃, *i*Pr), 4.24 (br. s, 8H, C₅H₄), 4.63 (br. s, 2H, OCH), 6.91–7.77 (m, overlapped with the solvent signal, Ph + NH) ppm. ³¹P{¹H} NMR: δ –17.4 (br. s, 2 P, PPh₂), 58.3 (s, 1 P, NPS) ppm. Calc. for C₄₇H₄₈Cu-FeN₂O₂P₃S₂ (949.34): C, 59.46; H, 5.10; N, 2.95. Found: C, 59.38; H, 5.14; N, 3.02.

6. Yield: 0.352 g (72%). Mp 132–133 °C. ¹H NMR: δ 0.95 (t, ${}^{3}J_{\text{H,H}}$ = 6.2 Hz, 6H, CH₃, *i*Pr), 1.04 (t, ${}^{3}J_{\text{H,H}}$ = 6.0 Hz, 6H, CH₃, *i*Pr), 2.06 (s, 6H, CH₃, Me), 4.18 (br. s, 4H, C₅H₄), 4.30 (br. s, 4H, C₅H₄), 4.36 (d. sept, ${}^{3}J_{\text{H,H}}$ = 6.1 Hz, ${}^{3}J_{\text{P,H}}$ = 10.6 Hz, 2H, OCH), 6.89–7.74 (m, overlapped with the solvent signal, Ph + C₆H₃ + NH) ppm. ³¹P{¹H} NMR: δ –17.9 (br. s, 2 P, PPh₂), 56.2 (s, 1 P, NPS) ppm. Calc. for C₄₉H₅₂CuFeN₂O₂P₃S₂ (977.40): C, 60.21; H, 5.36; N, 2.87. Found: C, 60.32; H, 5.30; N, 2.83.

7. Yield: 0.387 g (78%). Mp 168–169 °C. ¹H NMR: δ 0.97 (t, ${}^{3}J_{\text{H,H}}$ = 6.1 Hz, 6H, CH₃, *i*Pr), 1.06 (t, ${}^{3}J_{\text{H,H}}$ = 6.2 Hz, 6H, CH₃, *i*Pr), 2.17 (s, 3H, CH₃, Me), 2.22 (s, 6H, CH₃, Me), 4.17 (br. s, 4H, C₅H₄), 4.33 (br. s, 4H, C₅H₄), 4.39 (d. sept, ${}^{3}J_{\text{H,H}}$ = 6.0 Hz, ${}^{3}J_{\text{P,H}}$ = 10.3 Hz, 2H, OCH), 6.70–7.72 (m, overlapped with the solvent signal, Ph + C₆H₂ + NH) ppm. ³¹P{¹H} NMR: δ –17.7 (br. s, 2P, PPh₂), 56.3 (s, 1P, NPS) ppm. Calc. for C₅₀H₅₄CuFeN₂O₂P₃S₂ (991.43): C, 60.57; H, 5.49; N, 2.83. Found: C, 60.69; H, 5.44; N, 2.89.

3.2. Physical measurements

NMR spectra were obtained on a Bruker Avance 300 MHz spectrometer at 25 °C. ¹H and ³¹P{¹H} NMR spectra in CDCl₃ were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to SiMe₄ (¹H) and 85% H₃PO₄ (³¹P{¹H}). Fluorescence measurements were carried out on finely ground solid samples on a Spex FluoroMax-3 spectrofluorometer at room temperature. Elemental analyses were performed on a CHNS HEKAtech EuroEA 3000 analyzer.

3.3. Crystal structure determination and refinement

The X-ray diffraction data for the crystal of **1** were collected on a Bruker Smart Apex II diffractometer. Data were corrected for absorption using the SADABS program [18]. The structure was solved by direct method using the SHELXS97 program [19] and refined by the full matrix least-squares using SHELXL97 [19]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located on difference map and refined isotropically.

The X-ray diffraction data for the crystals of **2** and **4** were collected on a STOE IPDS-II diffractometer. The images were indexed, integrated and scaled using the X-Area package [20]. Data were corrected for absorption using the PLATON program [21]. The structures were solved by direct methods using the SHELXS program [19] and all non-hydrogen atoms were refined anisotropically using SHELXL97 [19]. Hydrogen atoms were revealed from $\Delta\rho$ maps and refined using a riding model. All figures were generated using the program MERCURY [22].

4. Conclusions

Reaction of $[Cu(PPh_3)_3I]$ or a mixture of CuI and $Ph_2P(C_5H_4FeC_5H_4)PPh_2$ with the potassium salts of HL^{I-V} has allowed us to obtain mononuclear 1–7 complexes. The complex 2 forms a dimer in the crystal by the NH function and the thiocarbonyl S atom of the chelate backbone.

Furthermore, the complexes **3–7** exhibit emission in the solid state at ambient temperature, which together with previous results provides some evidence that the emission of such complexes originates from ³ILCT states and require optimum sterical and electronical availability of the aromatic substituents on the phosphorus atom.

Acknowledgments

This work was supported by the Russian Science Support Foundation. M.G.B. and D.A.S. thank DAAD for the scholarships (Forschungsstipendien 2008/2009).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.02.028.

CCDC 690254, 749403 and 749290 contain the supplementary crystallographic data **1**, **2** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

 F.D. Sokolov, M.G. Babashkina, D.A. Safin, A.I. Rakhmatullin, F. Fayon, N.G. Zabirov, M. Bolte, V.V. Brusko, J. Galezowska, H. Kozlowski, Dalton Trans. (2007) 4693.

- [2] M.G. Babashkina, D.A. Safin, Ł. Szyrwiel, M. Kubiak, F.D. Sokolov, Y.V. Starikov, H. Kozlowski, Z. Anorg. Allg. Chem. 635 (2009) 554.
- [3] R.C. Luckay, X. Sheng, C.E. Strasser, H.G. Raubenheimer, D.A. Safin, M.G. Babashkina, A. Klein, Dalton Trans. (2009) 4646.
- [4] D.A. Safin, M.G. Babashkina, M. Bolte, F.D. Sokolov, V.V. Brusko, Inorg. Chim. Acta 362 (2009) 1895.
- [5] N.G. Zabirov, A.Yu. Verat, F.D. Sokolov, M.G. Babashkina, D.B. Krivolapov, V.V. Brusko, Mendeleev Commun. 13 (2003) 163.
- [6] A.Y. Verat, F.D. Sokolov, N.G. Zabirov, M.G. Babashkina, D.B. Krivolapov, V.V. Brusko, I.A. Litvinov, Inorg. Chim. Acta 359 (2006) 475.
- [7] M.G. Babashkina, A.I. Rakhmatullin, D.A. Safin, F. Fayon, F.D. Sokolov, A. Klein, D.B. Krivolapov, T. Pape, F.E. Hahn, in preparation.
- [8] D.A. Safin, M.G. Babashkina, T.R. Gimadiev, M. Bolte, M.V. Pinus, D.B. Krivolapov, I.A. Litvinov, Polyhedron 27 (2008) 2978.
- [9] F.D. Sokolov, M.G. Babashkina, F. Fayon, A.I. Rakhmatullin, D.A. Safin, T. Pape, F.E. Hahn, J. Organomet. Chem. 694 (2009) 167.
- [10] (a) M.G. Babashkina, D.A. Safin, M. Bolte, A. Klein, CrystEngComm 12 (2010) 134;
- (b) M.G. Babashkina, Ph.D. Thesis, Kazan State University, Kazan, Russian Federation, 2006.
- [11] D.A. Safin, M.G. Babashkina, F.D. Sokolov, N.G. Zabirov, J. Galezowska, H. Kozlowski, Polyhedron 26 (2007) 1113.
- [12] A. Kaltzoglou, P.J. Cox, P. Aslanidis, Inorg. Chim. Acta 358 (2005) 3048.
- [13] P. Aslanidis, P.J. Cox, S. Divanidis, A.C. Tsipis, Inorg. Chem. 41 (2002) 6875.
- [14] T.S. Lobana, R. Sharma, R. Sharma, S. Mehra, A. Castineiras, P. Turner, Inorg. Chem. 44 (2005) 1914.
- [15] V.W.-W. Yam, K.K.-W. Lo, C.-R. Wang, K.-K. Cheung, J. Phys. Chem. A 101 (1997) 4666.
- [16] F.D. Sokolov, V.V. Brusko, N.G. Zabirov, R.A. Cherkasov, Curr. Org. Chem. 10 (2006) 27.
- [17] A. Vogler, H. Kunkely, Coord. Chem. Rev. 230 (2002) 243.
- [18] G.M. Sheldrick, sADABS, Program for Empirical X-ray Absorption Correction, Bruker-Nonius, 1990–2004.
- [19] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
- [20] Stoe & Cie, X-AREA. Area-Detector Control and Integration Software, Stoe & Cie, Darmstadt, Germany, 2001.
- [21] A.L. Spek, J. Appl. Crystallogr., Sect. A A36 (2003) 7.
- [22] I.J. Bruno, J.C. Cole, P.R. Edgington, M. Kessler, C.F. Macrae, P. McCabe, J. Pearson, R. Taylor, Acta Crystallogr., Sect. B 58 (2002) 389.