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Cooperative Metal–Ligand-Induced Properties of Heteroleptic Copper(I) Xanthate/Dithiocarbamate PPh₃ Complexes

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Four new heteroleptic mononuclear complexes, $[Cu(PPh_3)_2L^1]$ (1) { $L^1 = (C_9H_{11}O_2CS_2^-)$, [2-(4-methoxyphenyl)ethyl]xanthate}, [Cu(PPh_3)_2L^2] (2) [$L^2 = (C_6H_7OCS_2^-)$, benzylxanthate], [Cu(PPh_3)_2L^3] (3) [$L^3 = (C_5H_9OCS_2^-)$, (cyclobutylmethyl)xanthate] and [Cu(PPh_3)_2L^4] (4) [$L^4 =$ (NC₁₃H₁₃NCS₂⁻), N-benzyl-N-(4-pyridylmethyl)dithiocarbamate], have been synthesized and characterized by using microanalysis, IR, UV/Vis, ¹H, ¹³C and ³¹P NMR spectroscopy

Introduction

Over more than two decades dithio transition metal complexes have been studied in detail because of their exciting molecular conducting, magnetic and optical properties that provide a myriad of technological applications.^[1–12] Despite their structural simplicity, heteroleptic mono- and dinuclear copper(I) complexes with phosphanes as a coligand have exhibited interesting photoluminescent properties with possible applications as sensors, biological imaging probes, electrochemical devices and as dyes for solar energy conversion.^[13–32] Complexes of the type $[Cu^{I}(dithio)PR_{3}]_{2}$ (R = OMe, Me, Et; dithio = xanthate, dithiocarbamate) have dimeric structures.^[14] Homo- and heteronuclear Cu^I clusters with xanthate, dithiocarbamate and dithiophosphate ligands have also been reported.^[35-37] Copper(I) with a 3d¹⁰ configuration has no low-energy ligand-field transitions and so makes available low-energy charge-transfer excited states, which is an important property for luminescent materials. The coordination sphere of the copper(I) ion can be closely controlled by the use of bidentate sulfur or nitrogen ligands in conjunction with bulky phosphane ligands that reinforce the likelihood of a tetrahedral environment. Furthermore, the incorporation of sterically encumbered phosphane ligands, having strong σ -donor and π -acceptor

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and X-ray crystallography; their photoluminescent behaviour and molecular electrical conductivity have been investigated. Cu^I possesses four-coordinate distorted tetrahedral geometry in all the complexes. All are weakly conducting and exhibit semiconductor behaviour in the studied 303– 363 K temperature range. Complex **4** shows striking luminescent behaviour emitting bluish green light at 480 nm in CH₂Cl₂ solution at room temperature.

properties, in transition metal coordination spheres is important in tuning their physical properties because of the unique energetic stability and reactivity related to the metal–phosphorus bond. Also, this framework provides a rigid environment around copper(I) facilitating the weakening of nonradiative deactivation pathways and also precludes solvent interactions, which promote the quenching of Cu^{I} complexes.

The chemistry and properties of metal dithiocarbamate and xanthate complexes have been extensively reported.^[1] In spite of their synthetic versatility and practical utility, studies on the heteroleptic complexes of Cu^I with xanthate or dithiocarbamate/dithiocarbimate and phosphane ligands are scarce.^[13-21,33] The monoanionic 1,1-dithiocarbamate resembles the dianionic dithiocarbimate ligand that led to the formation of a heteroleptic dinuclear Cu^I phosphane complex with unprecedented bonding behaviour.[34] Although monoanionic xanthate and dithiocarbamate ligands have some common features, they differ significantly in their coordination behaviour owing to the dominant contribution of the resonance structures they exhibit in their complexes (Figure 1). In general, the xanthate and phosphane ligands reduce Cu^{II} to Cu^I, whereas the dithiocarbamates stabilize the +2 oxidation state of copper in their complexes. Influenced by these facts, it was considered worthwhile to



Figure 1. Dominant resonance structures of the dithioligands.

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undertake the synthesis, structural characterization and study of the conducting and photoluminescent properties of four new heteroleptic Cu^{I} complexes containing functionalized xanthate/dithiocarbamate ligands together with PPh₃ as a coligand. The results of these investigations are presented here.

Results and Discussion

Complexes [Cu (PPh₃)₂L] (1–4) were synthesized by treating a methanolic solution of the potassium salt KL (L^1-L^4) of the ligands (Figure 2) with a dichloromethane solution of the precursor [Cu(PPh₃)₂]NO₃ in equimolar ratios at room temperature. All the compounds are air-stable, melt in the 140–160 °C range and are soluble in dichloromethane, chloroform, *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The compounds were characterized by elemental analysis, spectroscopy (IR, NMR, UV/ Vis) and single-crystal X-ray analysis; their photoluminescent behaviour, and solid-phase conductivities were also investigated (Scheme 1).



Figure 2. Structures of the ligands.

$$[Cu(PPh_3)_2]NO_3 + KL \xrightarrow{CH_3OH} [Cu(PPh_3)_2L] + KNO_3$$

Scheme 1. L = [2-(4-methoxyphenyl)ethyl]xanthate (L¹), benzylxanthate (L²), (cyclobutylmethyl)xanthate (L³) and*N*-benzyl-*N*-(4pyridylmethyl)dithiocarbamate (L⁴).

Spectroscopy

In their IR spectra, 1–3 show v(CS₂) and v(C–O) bands near 1090 and 1150 cm⁻¹, respectively, diagnostic of *S*,*S* coordination of the xanthate ligands.^[1] The dithiocarbamate complex 4 exhibits a band at 1388 cm⁻¹ characteristic of a v(C–N) vibration. A perceptible enhancement in the v(C– N) frequency in 4 in comparison with the free dithiocarbamate ligand indicates symmetrical bidentate behaviour of the dithiocarbamate ligand due to a significant contribution of resonance form II (Figure 1). The NMR spectra of all the compounds elucidate their composition, purity and diamagnetic nature. The presence of sharp ¹H NMR resonances in all four compounds correlates well with the corresponding hydrogen atoms. A noticeable upfield shift (δ = 10–12 ppm) in the ¹³C NMR resonances for the CS₂ carbon atom in all the complexes compared to the free ligands, potassium xanthates and potassium dithiocarbamate substantiates M–S bonding in the complexes of Cu^I. The presence of a sharp singlet in the δ = 0.17–0.80 ppm region in the ³¹P NMR spectra of all the compounds reveals the equivalent nature of the PPh₃ ligands bonded to the Cu atom.

Crystal Structures

Single crystals of the complexes were grown by slow concentration of a dichloromethane/ethanol solution of the crude product. The relevant crystallographic data and refinement details are listed in Table S1, and the molecular dimensions are listed in Table 1. The structures are illustrated in Figures 3, 4, 5 and 6.

Table 1. Selected bond lengths and angles for 1, 2, 3 and 4.

Bond lengths [Å]	1 (X = O)	2 (X = O)	3 (X = O)	4 (X = N)
Cu(1)–P(1)	2.2407(13)	2.2357(9)	2.2559(11)	2.262(2)
Cu(1)–P(2)	2.2521(14)	2.2647(8)	2.2755(11)	2.274(2)
Cu(1)–S(11)	2.4263(16)	2.4405(8)	2.4728(12)	2.406(2)
Cu(1)–S(13)	2.3809(15)	2.4157(8)	2.3988(12)	2.417(2)
S(11)-C(12)	1.679(6)	1.686(3)	1.699(4)	1.725(6)
S(13)-C(12)	1.653(7)	1.680(3)	1.689(5)	1.696(6)
X(14)-C(12)	1.329(6)	1.347(4)	1.358(6)	1.354(7)
Bond angles [°]				
P(1)-Cu(1)-P(2)	127.05(5)	118.27(3)	126.22(4)	123.94(6)
P(2)-Cu(1)-S(13)	108.07(5)	102.62(3)	109.17(4)	105.02(6)
P(1)–Cu(1)–S(13)	110.49(6)	123.96(3)	116.31(4)	112.73(7)
P(2)-Cu(1)-S(11)	103.71(6)	108.93(3)	100.18(4)	117.66(6)
S(13)–Cu(1)–S(11)	74.92(6)	74.50(3)	74.57(4)	74.60(6)
P(1)-Cu(1)-S(11)	120.31(5)	120.13(3)	117.93(4)	111.45(7)
S(13)-C(12)-S(11)	122.7(3)	121.66(18)	122.6(3)	117.3(4)
C(12)-S(11)-Cu(1)	80.00(19)	81.12(11)	80.03(15)	83.7(2)
C(12)–S(13)–Cu(1)	81.85(19)	82.01(11)	82.49(15)	84.0(2)



Figure 3. ORTEP diagram for 1 at 30% probability level.

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Figure 4. ORTEP diagram for 2 at 30% probability level.



Figure 5. ORTEP diagram for 3 at 30% probability level.



Figure 6. ORTEP diagram for 4 at 30% probability level.

In each complex, the geometry about Cu^{I} is four-coordinate with the Cu atoms bonded to two phosphorus atoms of the PPh₃ moieties together with two sulfur atoms of the bidentate xanthate or dithiocarbamate ligand. For the

xanthate complexes **1**, **2** and **3**, the Cu(1)–S(11) and Cu(1)–S(13) distances differ significantly with the Cu(1)–S(11) bond lengths consistently longer at 2.4263(16), 2.4405(8) and 2.4728(12) Å than the Cu(1)–S(13) bond lengths at 2.3809(15), 2.4157(8) and 2.3988(12) Å.

However, there are no significant differences in the C–S bond lengths. By contrast with this asymmetrical S,S bonding behaviour of the xanthate ligands, in the dithiocarbamate complex **4**, the Cu(1)–S(11) and Cu(1)–S(13) distances are equivalent at 2.410(2) and 2.412(2) Å, thereby indicating symmetrical S,S bidentate behaviour.

In all four complexes, the geometry around the metal atom is distorted tetrahedral as is evident from the angles shown in Table 1. The distortion from ideal geometry occurs primarily as a result of the small S(11)-Cu(1)-S(13)bite angles, which range from 74.50(3) to 75.00(7)°. However, there are significant differences in the remaining angles. The angles in 1 and 3 are similar with P(1)-Cu(1)-P(2) being 127.05(5) and 126.22(4)° and P-Cu(1)-S angles ranging from 103.71(6) to 120.31(5)° and 100.18(4) to 117.93(4)°, respectively. In contrast, in 2 the P(1)-Cu(1)-P(2) angle is much smaller at 118.27(3)°, and this disparity could be due to the disposition of the phenyl rings, as looking along the P···P vector it is apparent that the rings in 2 have a staggered conformation rather than the eclipsed conformation found in 1, 3 and 4. The corresponding angle in 4 is 123.94(6)°.

The angle between the two least-square planes formed by Cu(1), S(11), S(13) and C(12) and by P(1), Cu(1) and P(2) are 84.74(7), 85.09(4), 84.19(5) and 83.67(7)°, respectively, for 1–4, thus indicating that the two planes are approximately perpendicular to each other. The root mean square (r.m.s.) deviations from the planarity of atoms Cu(1), S(11), S(13) and C(12), defining the chelate ring, are 0.044, 0.049, 0.075 and 0.033 Å, respectively.

The Cu-S and Cu-P distances (Table 1) are typical of those found in analogous Cu^I complexes.^[13,20,32] The C(12)-N(14) bond length of 1.354(7) Å in 4 is intermediate between the C–N (1.47 Å) and C=N (1.28 Å) bond lengths, which confirms the significant contribution of resonance form II (Figure 1) of the dithiocarbamate ligand, thereby indicating the partial double-bond character of the C-N bond. The C-S bonds of 1.653(7)-1.699(4) Å in xanthate complexes 1-3 are significantly smaller than that of 1.725(6)and 1.696(6) Å in the dithiocarbamate complex 4, though both are considerably shorter than the C–S single bond (ca. 1.81 Å) due to π delocalization over the CS₂ unit. Although packing diagrams are not shown here, it is obvious that the presence of the bulky triphenylphosphane ligands preclude any possible S...S intermolecular stacking involving the xanthate or dithiocarbamate ligands, a mode of packing often found in their complexes.[34]

Electronic Absorption and Photoluminescent Spectra

The electronic absorption spectra of complexes 1-4 in CH_2Cl_2 solution are given in Figure 7. The free xanthate

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ligands (L¹–L³) display two strong absorptions near 225 nm ($\varepsilon = 92000-122000 \text{ M}^{-1} \text{ cm}^{-1}$) and 305 nm ($\varepsilon = 59000-76000 \text{ M}^{-1} \text{ cm}^{-1}$), dithiocarbamate at 258 nm ($\varepsilon = 105000 \text{ M}^{-1} \text{ cm}^{-1}$) and 295 nm ($75000 \text{ M}^{-1} \text{ cm}^{-1}$) and PPh₃ at 262 nm^[43] arising from intraligand (IL) charge-transfer transitions (Figures S2–S5). The features of the absorption bands of all the heteroleptic Cu^I complexes are virtually alike, encompassing strong absorptions near 240 nm ($\varepsilon = 16000-25000 \text{ M}^{-1} \text{ cm}^{-1}$) and 267 nm ($\varepsilon = 14000-25000 \text{ M}^{-1} \text{ cm}^{-1}$) and showing considerable redshifts that can be assigned to metal-perturbed π – π^* intraligand charge-



Figure 7. Electronic absorption spectra for 1–4 in CH₂Cl₂.



Figure 8. (a) Emission spectra for 1–3. (b) Excitation and emission ($\lambda_{\text{emis}} = 480 \text{ nm}$) spectra for 4 in CH₂Cl₂.

transfer transitions. The lowest excited state at 325 nm ($\varepsilon = 8000-10000 \text{ M}^{-1} \text{ cm}^{-1}$) present in **2** and **4** may be ascribed to an IL charge-transfer transition with some admixture of a metal-to-ligand charge-transfer transition (MLCT).

Upon excitation at 250 nm in CH₂Cl₂ solution at room temperature, the xanthate complexes 1, 2 and 3 give rise to a medium broad emission band and a shoulder emission band at about 300 and 350 nm, respectively, arising from intraligand $\pi - \pi^*$ charge-transfer transitions (Figure 8a). The excitation spectrum for the emission (λ_{em}^{max}) in a CH₂Cl₂ solution of **4** is shown in Figure 8b. Unlike the xanthate complexes, 4 shows an unstructured emission at 480 nm upon excitation at 300 nm, emitting bluish green light with a pronounced Stokes shift of 180 nm, which emanates from the π - π * IL states in the perturbed coordination environment about the metal atom (Figure 8). The remarkable luminescent behaviour of 4 seems to arise, because the presence of the pyridine substituent on the dithiocarbamate enhances conjugation. An additional factor may be that only minimal changes are found in the structure of the complex in the excited state compared to the ground state, because the geometry around the metal atom is fixed by the sterically demanding PPh₃ ligands.

Pressed-Pellet Conductivity

The pressed-pellet conductivity of all the complexes was measured with a Keithley 236 source measure unit using the conventional two-probe technique. Complexes 1–4 are weakly conducting with σ_{rt} values of the order 10^{-13} S cm⁻¹. Their lower conductivities may be attributed to the lack of S···S intermolecular stacking (vide supra in the crystallography section), which is prevented by the bulky PPh₃ ligands. A plot of log σ vs. T^{-1} in the 303–363 K range with band gaps of 0.81, 0.75, 0.77 and 0.71 eV for 1–4, respectively, shows their semiconducting behaviour (Figure 9). An increase in σ values at higher temperature is due to the thermal activation of electrons.



Figure 9. Pressed-pellet conductivity for 1-4.

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Conclusions

Four new mononuclear heteroleptic CuI complexes containing xanthate/dithiocarbamate and PPh₃ ligands have been synthesized and fully characterized by spectroscopic and X-ray crystallographic techniques. It is worth mentioning that all the bis(phosphane) complexes 1-4 involving the bulky PPh₃ ligand are mononuclear in comparison to those of the analogous monophosphane dimeric complexes formed with less bulky phosphane ligands such as [(Cu^Idithio) PR_3]₂ (R = OMe, Me, Et; dithio = xanthate, dithiocarbamate).^[14] The xanthate complexes 1, 2 and 3, despite variation in functionalities, are weakly luminescent in the UV region, whereas the dithiocarbamate complex 4 strikingly emits observable bluish green light in the visible region. The interesting photoluminescent behaviour of this complex probably stems from the presence of a pyridine substituent on the dithiocarbamate moiety with a lone pair of electrons on the nitrogen atom, which causes greater conjugation in the molecule. This widens the scope for the synthesis and study of luminescent properties of heteroleptic dithio complexes with enhanced delocalization in the molecule. All the complexes are weakly conducting because of the absence of any significant S…S intermolecular contacts, no doubt because any stacking is inhibited by the bulky PPh₃ molecules. It is worth mentioning that in contrast to the dinuclear dithiocarbimate CuI-PPh3 complex,[34] the Cu^I dithiocarbamate PPh₃ complex is mononuclear, though both ligands are quite similar.

Experimental Section

Materials and Reagents: All reactions were performed in air at ambient temperature. The solvents dichloromethane, diethyl ether, methanol and carbon disulfide were purchased from commercial sources and – where necessary – were purified by standard procedures prior to their use. The starting compound $[Cu(PPh_3)_2]NO_3$ was obtained by using a literature method.^[39] Potassium salts of the anionic ligands [2-(4-methoxyphenyl)ethyl]xanthate (L¹), benz-ylxanthate (L²), (cyclobutylmethyl)xanthate (L³), *N*-benzyl-*N*-(4-pyridylmethyl)dithiocarbamate (L⁴) were synthesized by treating the appropriate alcohol or secondary amine with KOH and CS₂ according to a previously reported procedure,^[38] and characterized by elemental analysis, IR, ¹H and ¹³C NMR spectra.

Physical Measurements: The melting points of the complexes were determined in open capillaries with a Gallenkamp apparatus and are uncorrected. Elemental analyses (C, H, N and S) were performed with a CE-440 CHN analyzer. IR spectra were recorded as KBr discs with a Varian 3100 FTIR instrument; ¹H, ¹³C{¹H} and ³¹P NMR spectra in CDCl₃ were recorded with a JEOL AL300 FTNMR spectrometer. Chemical shifts are quoted in parts per million with TMS as an internal standard for ¹H and ¹³C, and PCl₃ as an external standard ($\delta = 220$ ppm) for ³¹P NMR spectra. The electronic absorption and emission spectra of the ligands in methanol and the complexes in CH₂Cl₂ solution were collected at room temperature with Shimadzu UV-1700 Pharma Spec UV/Vis and Varian Cary Eclipse Fluorescence spectrophotometers, respectively.

[Cu(PPh₃)₂L¹] (1): A solution of Cu(PPh₃)₂NO₃ (0.665 g, 1 mmol) in CH_2Cl_2 (5 mL) was added gradually to a stirred solution of KL¹ (0.227 g, 1 mmol) in methanol (25 mL). A yellowish brown solid was formed within a short time, and the reaction mixture was stirred for 1 h. The solid was collected by filtration and washed with methanol followed by diethyl ether. The product thus obtained was recrystallized from a dichloromethane/ethanol mixture, yielding block-shaped crystals. Yield 0.676 g, 82%; m.p. 135 °C. C46H41CuOP2S2 (824.40): calcd. C 68.51, H 4.83, S 8.31; found C 68.13, H 4.69, S 7.79. IR (KBr): $\tilde{v} = 1154 (v_{C-O}), 1094 (v_{C-S}) \text{ cm}^{-1}$. ¹H NMR (300.40 MHz, CDCl₃): $\delta = 7.75-6.81$ (m, 34 H, Ar-H), 4.51 (t, J = 7.2 Hz, 2 H, OCH₂), 3.00 (t, J = 14.7 Hz, 2 H, CH₂Ar), 3.78 (s, 3 H, OCH₃) ppm. ¹³C NMR (75.45 MHz, CDCl₃): δ = 226.88 (CS₂), 55.25 (OCH₃), 73.66 (OCH₂), 34.08 (CH₂Ar), 158.18, 113.84, 128.57, 129.43 (C₆H₅), 131.51, 129.93, 128.57, 128.34 (CPPh₃) ppm. ³¹P NMR (121.50 MHz, CDCl₃): δ = 0.753 ppm.

[Cu(PPh₃)₂L²] (2): The light yellow complex **2** was synthesized and isolated by adopting the same method as described for **1** and using KL² (0.171 g, 1 mmol). Yield 0.663 g, 86%; m.p. 160 °C. C₄₄H₃₇CuOP₂S₂ (771.34): calcd. C 67.32, H 5.25, S 8.56; found C 67.02, H 5.33, S 8.23. IR (KBr): $\tilde{v} = 1148 (v_{C-O})$, 1093 (v_{C-S}) cm⁻¹. ¹H NMR (300.40 MHz, CDCl₃): $\delta = 7.37-7.16$ (m, 35 H, ArH), 5.29 (s, 2 H, CH₂O) ppm. ¹³C NMR (75.45 MHz, CDCl₃): $\delta = 226.66$ (CS₂), 74.41 (OCH₂), 141.21, 136.16, 133.67, 129.46, (C₆H₅), 128.37, 128.31, 128.22, 127.86 (CPPh₃) ppm. ³¹P NMR (121.50 MHz, CDCl₃): $\delta = 0.803$ ppm.

[Cu(PPh₃)₂L³] (3): The pale yellow complex **3** was prepared and isolated by adopting the same method as described for **1** and using **KL**³ (0.161 g, 1 mmol). Yield 0.636 g, 85%; m.p. 160 °C. C₄₂H₃₉CuOP₂S₂ (749.33): calcd. C 69.11, H 5.17, S 8.02; found C 68.84, H 5.09, S 7.76. IR (KBr): $\tilde{v} = 1141 (v_{C-O})$, 1092 (v_{C-S}) cm⁻¹. ¹H NMR (300.40 MHz, CDCl₃): $\delta = 7.33-7.16$ (m, 30 H, PPh₃), 2.76–1.54 (m, 6 H, C₆H₇), 3.95 (s, 1 H, C₆H₇), 4.35 (d, J = 6.6 Hz, 2 H, OCH₂) ppm. ¹³C NMR (75.45 MHz, CDCl₃): $\delta = 227.41$ (CS₂), 34.08–18.50 (C₄H₇), 59.71 (OCH₂), 133.65, 129.41, 129.57, 128.32 (CPPh₃) ppm. ³¹P NMR (121.50 MHz, CDCl₃): $\delta = 0.778$ ppm.

[Cu(PPh₃)₂L⁴] (4): A solution of Cu(PPh₃)₂NO₃ (0.665 g, 1 mmol) in CH₂Cl₂ (5 mL) was added dropwise to a stirred solution of KL⁴ (0.31 g, 1 mmol) in methanol (15 mL). The reaction mixture was stirred overnight, and the solvent was removed to obtain a light yellow solid. Yield 0.852 g, 87%; m.p. 140–142 °C. C₅₀H₄₃CuN₂P₂S₂ (861.52): calcd. C 69.71, H 5.03, N 3.25, S 7.44; found C 69.28, H 4.92, N 3.15, S 6.90. IR (KBr): $\tilde{v} = 1388$ (v_{C-N}), 1091 (v_{C-S}) cm⁻¹. ¹H NMR (300.40 MHz, CDCl₃): $\delta = 8.51$ (m, 2 H, C₅H₄N), 7.37–7.11 (s, 30 H, C₆H₅), 5.29 (s, CH₂NC₅H₄) ppm. ¹³C NMR (75.45 MHz, CDCl₃): $\delta = 216.7$ (CS₂), 153.8, 149.3 (NC₅H₄), 138.6, 137.0, 134.4, 129.0, 128.8, 128.7, 128.5, 128.4, 128.3, 127.8, 122.2 (C₅H₄N, C₅H₅), 58.0 (CH₂C₆H₅N), 54.0 (CH₂Ar) ppm. ³¹P (121.50 MHz, CDCl₃): $\delta = 0.17$ ppm.

Structure Determination: Single-crystal X-ray data, space group, unit-cell dimensions and intensity data for 1, 2, 3 and 4 were collected with an Oxford Diffraction X-calibur CCD diffractometer at 150 K (1–3) and 293 K (4) using Mo- K_a radiation (for 1, 3, 4) and Cu- K_a radiation (for 2). Data reduction for 1–4 was carried out by the CrysAlis program.^[40] The structures were solved by direct methods using SHELXS-97^[41] and refined on F^2 by full-matrix least-squares technique using SHELXL-97.^[41] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were geometrically fixed with thermal parameters equivalent to 1.2 times that of the atom to which they are bonded. Two water molecules were located in 1 and refined with 0.25 occupancy, but their hydro-

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gen atoms could not be located. In **3**, some atoms in the cyclobutyl ring showed high thermal motion, and disordered models were investigated. One model was chosen in which one atom was disordered over two sites with occupation factors x and 1 - x with x refining to 0.54(2). Four solvent water molecules were located in **4** and refined with reduced occupancies. The hydrogen atoms could not be located. Diagrams for all complexes were prepared using ORTEP.^[42] CCDC-803645 (for **1**), -870133 (for **2**), -803643 (for **3**) and -881935 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

Crystal Data for 1: $C_{46}H_{42}CuO_{2.50}P_2S_2$, formula mass 824.40, triclinic space group $P\overline{1}$, a = 12.3315(14), b = 13.0377(11), c = 15.0501(16) Å, a = 92.123(8), $\beta = 92.225(9)$, $\gamma = 115.574(10)^\circ$, V = 2177.1(4) Å³, Z = 2, $d_{calcd.} = 1.258$ g cm⁻³, F(000) = 858, reflections collected 11173, independent reflections 6720, final indices $[I > 2\sigma(I)]$ $R_1 = 0.0640$, $wR_2 = 0.1639$, R indices (all data) $R_1 = 0.1064$, $wR_2 = 0.1833$, GOF 1.038.

Crystal Data for 2: $C_{44}H_{37}CuOP_2S_2$, formula mass 771.34, monoclinic space group $P2_1/c$, a = 10.9581(3), b = 19.8423(4), c = 17.7195(5) Å, $\beta = 106.248(3)^\circ$, V = 3698.97(16) Å³, Z = 4, $d_{caled.} = 1.385$ gcm⁻³, F(000) = 1600, reflections collected 15346, independent reflections 5226, final indices $[I > 2\sigma(I)] R_1 = 0.0449$, $wR_2 = 0.1222$, R indices (all data) $R_1 = 0.0540$, $wR_2 = 0.1327$, GOF 0.978.

Crystal Data for 3: C₄₂H₃₉CuOP₂S₂, formula mass 749.33, triclinic space group $P\overline{1}$, a = 10.3928(15), b = 13.1640(15), c = 14.4155(17)Å, a = 92.082(9), $\beta = 105.993(12)$, $\gamma = 100.309(11)^\circ$, V = 1857.6(4)Å³, Z = 2, $d_{calcd.} = 1.340$ g cm⁻³, F(000) = 780.0, reflections collected 16764, independent reflections 5102, final indices [$I > 2\sigma(I)$] $R_1 = 0.0598$, $wR_2 = 0.1786$, R indices (all data) $R_1 = 0.0637$, $wR_2 = 0.1835$, GOF 1.056.

Crystal Data for 4: $C_{50}H_{47}CuO_2N_2P_2S_2$, formula mass 897.50, triclinic space group $P\bar{1}$, a = 12.6418(12), b = 13.0045(513), c = 16.5164(718) Å, a = 109.887(10), $\beta = 92.126(8)$, $\gamma = 114.519(10)^\circ$, V = 2272.1(4) Å³, Z = 2, $d_{calcd.} = 1.312$ gcm⁻³, F(000) = 936, reflections collected 19914, independent reflections 10024, final indices $[I > 2\sigma(I)]$ $R_1 = 0.0894$, $wR_2 = 0.1843$, R indices (all data) $R_1 = 0.2021$, $wR_2 = 0.2177$, GOF 1.007.

Supporting Information (see footnote on the first page of this article): UV/Vis spectra of ligands and crystallographic data and structure refinement parameters.

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Heteroleptic Copper(I) Xanthate/Dithiocarbamate PPh3 Complexes

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FULL PAPER

Heteroleptic Cu^I dithiocarbamate/xanthate PPh₃ complexes are synthesized and structurally characterized. Their conductivity and photoluminescence are investigated. The dithiocarbamate complex bearing the pyridine substituent exhibited bluish green light in the visible region. The semiconductor behaviour of the complexes was ascribed to the lack of intermolecular S···S contacts in the solid state.



Heteroleptic Cu(I) Complexes

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Cooperative Metal–Ligand-Induced Properties of Heteroleptic Copper(I) Xanthate/Dithiocarbamate PPh₃ Complexes

Keywords: Xanthate / S ligands / Phosphane ligands / Copper / Photoluminescence / Semiconductivity