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Synthesis and characterization of copper(I) complexes from triphenylphosphine and isatin Schiff bases of semi- and thiosemicarbazide

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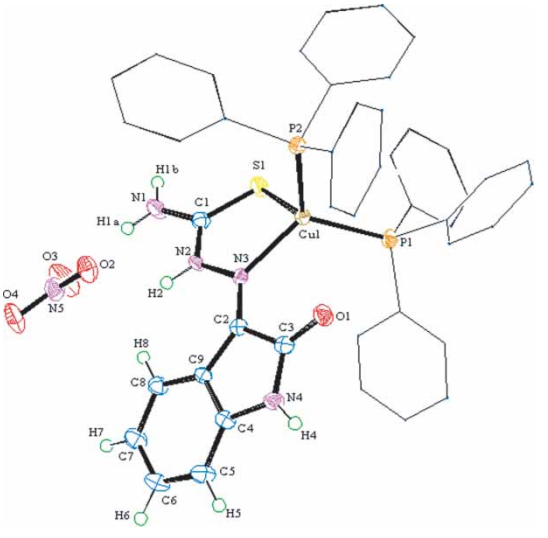
The reaction of isatin-3-thiosemicarbazone (ITC, **1**) or isatin-3-semicarbazone (ISC, **2**) with nitrato bis(triphenylphosphine)copper(I) gave the four coordinate copper(I) complexes $[Cu(PPh_3)_2(ITC)]NO_3$ (**3**) and $[Cu(PPh_3)_2(ISC)]NO_3$ (**4**). The synthesized complexes were characterized by FT-IR, UV–VIS, Raman and elemental analysis. The crystal structure of **3** was investigated by single crystal X-ray diffraction. The ITC coordinates to the copper(I) ion in a bidentate fashion via the N(imine) and S atoms which along with two triphenylphosphine ligands form a tetracoordinate complex. The complex has a distorted tetrahedral coordination environment. Crystal data at 150.0 K: space group $P2_1/c$ with $a = 12.5777(4)$, $b = 15.2062(5)$, $c = 21.9057(7)$ Å, $\beta = 95.628(3)^o$, $Z = 4$, $R_1 = 0.049$.



Keywords: synthesis; spectroscopic characterization; X-ray crystal structure; Cu(I) complex; isatin derivatives

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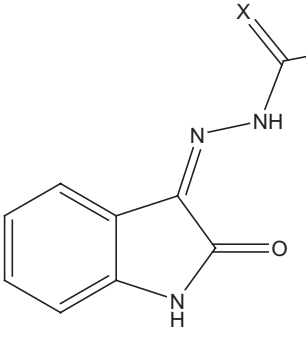
1. Introduction

Isatin was reported to possess a wide range of central nervous system activities (*1*, *2*). Schiff bases of isatin (indolin-2,3-dione) derivatives are reported to show a variety of biological activities such as antibacterial (*3–5*), antifungal (*6–8*), antiviral (*9–11*), anti-HIV (*12–14*), antiprotozoal (*15*, *16*) and anti-helminthic (*17*, *18*) activities. One widely studied class of sulfur and nitrogen donor ligands are the thiosemicarbazides that can bind to metal ions through S and N or both atoms, and similarly, semicarbazides can bind to metal ions through O and N. There is considerable interest in copper(I) complexes because Cu(I) is one of the important ions for many biological reactions in organisms. Copper(I) complexes have also be used as models for biological redox reaction studies (*19*). In our ongoing interest in the coordination chemistry of copper group metals, we have recently reported the reaction of 4-amino-1,2,4-triazin-3(2H)-thione-5-one and triphenylphosphine with copper(I) ions (*20*). In this paper, we report the preparation and characterization of isatin Schiff bases (Scheme 1) along with their copper(I) complexes from the corresponding semi- and thiosemicarbazide derivatives.



X = S **1**
X = O **2**

Scheme 1. The ITC (**1**) and ISC (**2**).

2. Results and discussion

Isatin-3-thiosemicarbazone (ITC, **1**) and isatin-3-semicarbazone (ISC, **2**) were prepared in high yield using a standard method. The carbazones were added to an ethanol suspension of nitrato bis(triphenylphosphine)copper(I) and were heated under nitrogen to yield the complexes $[Cu(PPh_3)_2(ITC)]NO_3$ (**3**) and $[Cu(PPh_3)_2(ISC)]NO_3$ (**4**) (Scheme 2).

$$[Cu(PPh_3)_2NO_3] + ITC/ISC \xrightarrow{Ethanol/\Delta} [Cu(PPh_3)_2(ITC)]NO_3/[Cu(PPh_3)_2(ISC)]NO_3$$

Scheme 2. Synthesis of complexes **3** and**4**.

The compounds were purified by recrystallization from ethanol and characterized by elemental analysis, Raman and IR spectroscopies. The analytical and spectroscopic data are consistent with the proposed structures. Elemental analysis of **4** revealed that the ratio of triphenylphosphine groups and ISC molecule in $[Cu(PPh_3)_2(ISC)]NO_3$ is 2:1.

The characteristic IR bands for the free ligands are different from those of the related complexes and provide significant indications regarding the bonding sites of ITC and ISC. IR spectral assignments for the ligands and their complexes are listed Section 3. In the IR spectrum of the ISC free

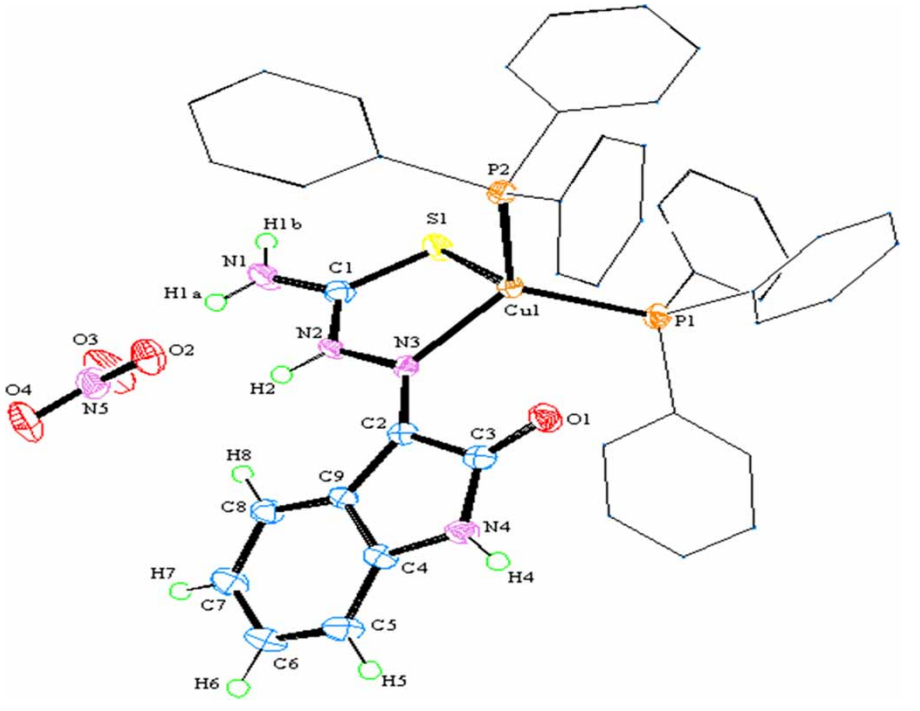


Figure 1. Molecular structure of **3**. Thermal ellipsoids are shown at the 50% probability level.

ligand, the carbonyl stretching frequency appears 56 cm^{-1} higher than that of the coordinated isatin. The imine group shows a strong band at 1624 cm^{-1} in the IR spectrum due to the ISC binding to the metal ion. The Raman spectrum of **4** shows two absorptions at 443 and 314 cm^{-1}, which can be assigned to νCuN and νCuO (*20*). The N–O asymmetric stretching mode (E') of the nitrate anion appears at 1384 cm^{-1} in the IR spectrum.

The numbering scheme 1 shown in Figure 1 is used for the assignment of the signals of the ^{13}C NMR spectra of the free ligands (details are given in Section 3). In the ^{1}H NMR spectra, the aromatic protons appear at 6.9–7.3 ppm while NH and NHCO are observed at lower magnetic field (11.1–11.7 ppm). The signals at 159.9 and 162.6 ppm in the ^{13}C NMR spectrum were assigned to the carbon atoms of the C=N and C=O groups, respectively.

The electronic spectral assignments of the free ligands and the corresponding complexes are given in Section 3. In the spectra of **1** and **2** (free ligands), the bands at 320.9 and 370.6 nm are attributed to $n \rightarrow \pi^*$ transitions of thioamide and carboamide moieties, respectively. The absorptions at 270.8 and 272.5 nm in the spectra of **1** and **2** are assigned to $\pi \rightarrow \pi^*$ transition of ligands which have been shifted in the complexes.

The observed λ_{max} in the UV–VIS spectra of **3** and **4** appeared at 440 and 408 nm in DMF, respectively. By comparing the frequency of free ligands and the corresponding copper(I) complexes, the electronic transitions of $n \rightarrow \pi^*$ are shifted to a higher value due to the formation of the complexes and coordination to the copper. The conductivities for complexes **3** and **4** were 51.65 and 42.70 $mol^{-1}\,cm^2\,\Omega^{-1}$, respectively, consistent with the presence of a singly charged cationic species.

A single crystal X-ray diffraction study of **3** was also carried out. The molecular structure of $[Cu(PPh_3)_2(ITC)]NO_3$ is depicted in Figure 1. Selected bond lengths and angles are presented in Table 1. The bond lengths of the carbonyl C3–O1 [1.222(2) Å], thiocarbonyl C1–S1 [1.691(2) Å] and imine groups C2–N3 [1.298(3) Å] are typical for double bonds and the two C–N bond distances

Table 1. Selected bond lengths (Å) and angles (°) of compound **3**.

Bond lengths			
Cu1–P1	2.2639(6)	S1–C1	1.691(2)
Cu1–P2	2.2632(6)	N2–C1	1.351(3)
Cu1–S1	2.4156(6)	C3–O1	1.222(2)
Cu1–N3	2.0905(16)	C2–N3	1.298(3)
C1–N1	1.322(3)	N5–O3	1.247(2)
N5–O2	1.268(2)	N5–O4	1.237(2)
Bond angles			
N3–Cu1–S1	81.09(5)	P1–Cu1–N3	119.17(5)
P2–Cu1–S1	108.80(2)	P2–Cu1–N3	120.80(5)
P1–Cu1–P2	113.70(2)	N2–C1–S1	121.54(17)
P1–Cu1–S1	105.67(2)	N1–C1–S1	123.26(19)
O1–C3–N4	127.2(2)	O1–C3–C2	126.9(2)
C1–N2–N3	119.99(18)		

N1–C1 [1.322(3) Å] and N2–C1 [1.352(3) Å] differ significantly from each other but are similar to those reported in the literature for structurally analogous complexes (*21*). These data indicate partial electron delocalization across the S1–C1–N2–N3–Cu1 fragment. The maximum deviation from the S1–C1–N2–N3–Cu1 plane is 0.167 Å for N3. The bond angles about the Cu centre of 81.10°, 108.80°, 119.17° and 113.70° show that the copper atom is located in a distorted tetrahedral environment. In the lattice, individual molecules are joined by intermolecular NH · · · S

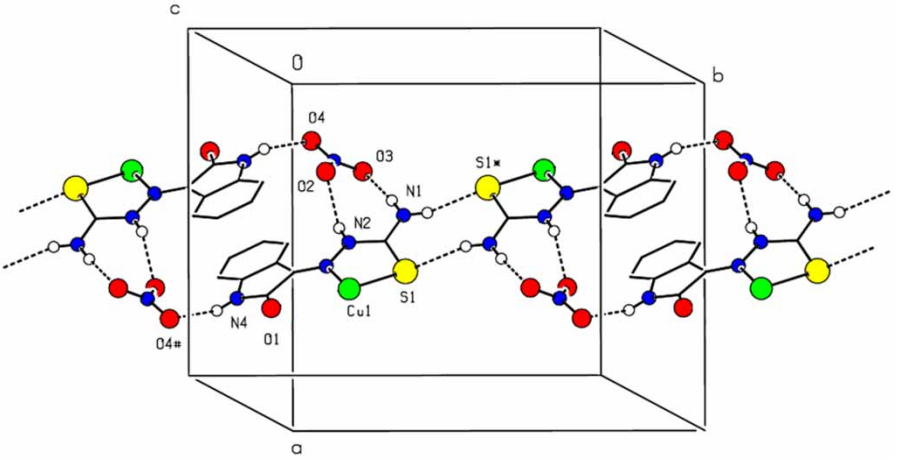


Figure 2. Packing of complex **3**, showing the hydrogen bonded chain formation along the *b*-direction. Only the hydrogen atoms involved in hydrogen bonding are shown. The Ph_3P molecules have been omitted for clarity.

Table 2. Hydrogen-bond dimensions (Å and °) in **3**.

D – H · · · A	D–H	*H* · · · *A*	*D* · · · *A*	D – H · · · A
N1–H1A · · · O3	0.88	2.05	2.924(3)	174
N1–H1B · · · S1[a]	0.88	2.53	3.372(2)	160
N2–H2 · · · O2	0.88	2.10	2.769(2)	132
N4–H4 · · · O4[a]	0.88	2.19	2.984(2)	150

Note: [a]Symmetry operation: 1-*x*, 1-*y*, 1-*z*.

and NH · · · O hydrogen bonds, resulting in a linear, polymeric chain along the *b*-direction as shown in Figure 2 with details in Table 2.

3. Experimental

3.1. *Materials and techniques*

All chemicals and solvents were purchased from Merck. The carbazones and nitrato bis(triphenylphosphine)copper(I) were prepared according to literature procedures (*22*, *23*). Melting points were determined using a Bamstead Electrotermal 9200 instrument. UV–VIS spectra were recorded with a Shimadzu UV–VIS spectrophotometer 2550 in DMF. IR spectra were recorded on a Shimadzu FT-IR 8400 spectrophotometer with samples prepared as KBr discs. Elemental analyses (CHN) were performed using a Thermo Finnigan Flash 1112EA elemental analyzer. The Raman spectra were measured using a Nicolet Fourier-transform spectrometer (model 910). ^{1}H and ^{13}C NMR spectra were recorded at 25 °C with Bruker BRX 100 AVANCE and Bruker BRX-300 AVANCE spectrometer, respectively. The conductivities were measured using a Metrohm Herisau Model 691 conductivity meter in DMF.

3.1.1. *X-ray crystallography*

X-ray data were collected on an Oxford Diffraction Gemini Ultra diffractometer (MoKα radiation, graphite monochromator) at 150 K. Data integration, scaling and empirical absorption correction were carried out using the CrysAlis Pro program package (*24*). The structure was solved using direct methods and refined by full-matrix-least squares against F^2. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at idealized positions and refined using the riding model. All calculations were carried out using the program Olex2 (*25*). Important crystallographic data and refinement details are summarized in Table 3.

3.2. *Synthesis of the ligand (1, 2)*

3.2.1. *Isatin-3-thiosemicarbazone (1)*

The free ligand was prepared essentially as described (*22*) by heating a mixture of isatin (1.47 g, 0.01 mol) and thiosemicarbazide (0.91 g, 0.01 mol) in ethanol (10 ml) under reflux for 1 h. Yellow solid, yield: 76.5% (1.7 g); mp: 238–240 °C; IR (ν_{max}/cm^{-1}): 3421, 3302 (NH_2), 3238 (NH_2), 3143 (NH), 3053 (CH(Ph)), 1682 (C=O), 1612 (C=N), 1604 (NH_2), 1497, 1464, 1063, 852 (C=S); ^{1}H NMR (d_6-DMSO): δ 6.6–7.6 (m, 4H, Ar), 8.6–9.0 (d, 2H, NH_2), 11.1 (s, 1H, NH), 12.4 (s, 1H, NHCO) ppm; ^{13}C NMR (d_6-DMSO): 110.9 (C^7), 119.8 (C^8), 120.8 (C^6), 122.2 (C^9), 131.1 (C^5), 131.9 (C^2), 142.2 (C^4), 162.5 (C^3), 178.5 (C^1) ppm; UV–VIS (DMF, λ_{max} (nm)/ε): 320.9/21309, 270.8/21071 ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$); Anal. Calcd. for $C_9H_8N_4OS$: C 56.04; H 3.32; N 23.06. Found: C 55.83; H 3.76; N 22.47%.

3.2.2. *Isatin-3-semicarbazone (2)*

A mixture of isatin (1.47 g, 0.01 mol) and semicarbazide hydrochloride (1.12 g, 0.01 mol) was dissolved in ethanol (10 ml), stirred and heated in a water bath (60–70 °C) for 30 min. After cooling the mixture, a yellow solid was obtained which was filtered off and dried. Yellow solid, yield: 73.8% (1.51 g); mp: 260–262 °C; IR (ν_{max}/cm^{-1}): 3470, 3305 (NH_2), 3236 (NH_2), 3136

(NH), 3001 (CH), 1713 (C=O, sem), 1657 (C=O), 1624 (C=N), 1576 (NH_2), 1468, 1384, 1169, 790; ^{1}H NMR (d_6-DMSO): δ 6.9–7.3 (m, 4H, Ar), 7.4–7.6 (d, 2H, NH_2), 11.1 (s, 1H, NH), 11.7 (s, 1H, NHCO) ppm; ^{13}C NMR (d_6-DMSO): 110.7 (C^7), 120.1 (C^8), 120.2 (C^6), 122.1 (C^9), 130.2 (C^5), 130.9 (C^2), 141.3 (C^4), 159.9 (C^1), 162.6 (C^3) ppm; UV–VIS (DMF, λ_{max} (nm)/ε): 370.6/20333, 272.5/10727 ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$); Anal. Calcd. for $C_9H_8N_4O_2$: C 52.94; H 3.95; N 27.44. Found: C 53.75; H 4.06; N 26.37%.

3.3. *Synthesis of the Cu complexes*

3.3.1. *(ITC)bis(triphenylphosphine)copper(I) nitrate (3)*

An ethanol solution (35 ml) of ITC (0.22 g, 1 mmol) was added to an ethanol suspension (30 ml) of nitrato bis(triphenylphosphine)copper(I) (0.65 g, 1 mmol) and was stirred for 3 h at 50°C under nitrogen. A red solution was immediately obtained. Single crystals were obtained after a few days. Dark red crystals, yield: 68% (0.59 g); mp: 224°C; IR (ν_{max}/cm^{-1}): 3390, 3250 (NH_2), 3110 (NH), 3055 (CH(Ph)), 1730 (C=O), 1679 (C=N),1614 (NH_2), 1560, 1515, 1469, 1429 (CC(Ph)),1386 (NO_3),1334 (CC(Ph)), 1311 (NO_3), 746 (C=S); ^{1}H NMR (D_2O): δ 7–7.7 (m, 4H, Ar) ppm; Conductivity (DMF, mol^{-1} cm^2 Ω^{-1}): 51.65, $C = 0.001$ mol l^{-1}; Raman (Raman shift, cm^{-1}): 3110 (NH), 1664, 1558, 1450, 1331, 1251, 1056, 958, 745 (C=S), 618, 511; UV–VIS (DMF, λ_{max} (nm)/ε): 440/9783, 366/14693, 263/32888 ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$); Anal. Calcd. for $C_{45}H_{38}CuN_5O_4P_2S$: C 62.17; H 4.29; N 8.06. Found: C 62.19; H 4.46; N 7.63%.

3.3.2. *(ISC)bis(triphenylphosphine)copper(I) nitrate (4)*

An ethanol solution (150 ml) of ISC (0.2 g, 1 mmol) was added to an ethanol suspension (30 ml) of nitrato bis(triphenylphosphine)copper(I) (0.65 g, 1 mmol) and was stirred for 3 h at 50 °C under nitrogen. A red solution was immediately obtained. The product was obtained after a few days

Table 3. Crystallographic and refinement data for compound **3**.

Compound	**3**
Empirical formula	$C_{45}H_{38}Cu\ N_5O_4P_2S$
Formula weight	870.34
Temperature	150.0
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 12.5777(4)$, $b = 15.2062(5)$, $c = 21.9057(7)$ Å, $\beta = 95.628(3)°$
Volume	4169.5(2) Å^3
Z	4
Density (calculated)	1.386 mg/m^3
Absorption coefficient	0.700 mm^{-1}
$F(000)$	1800
Crystal size	0.14 × 0.09 × 0.02 mm^3
Theta range for data collection	2.92–29.51
Index ranges	$-17 \le h \le 15$, $-19 \le k \le 17$, $-28 \le l \le 22$
Reflections collected	22,809
Independent reflections	9794 [$R_{(int)} = 0.0490$]
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9794/0/523
Goodness-of-fit on F^2	0.810
Final R indices [$I > 2$sigma(I)]	$R_1 = 0.0402$, $wR_2 = 0.0624$
R indices (all data)	$R_1 = 0.0842$, $wR_2 = 0.0674$
Largest diff. peak and hole	0.360 and −0.401e Å^{-3}

on leaving the mixture at room temperature. Orange solid, yield: 85% (0.725 g); mp: 233°C; IR (ν_{max}/cm^{-1}): 3394, 3256 (NH_2), 3112 (NH), 1747 (C=O, sem), 1718 (C=O), 1622 (C=N), 1514, 1461 (CC(Ph)), 1384 (NO_3), 1161; ^{1}H NMR (D_2O): δ 6.9–7.2 (m, 4H, Ar); Conductivity (DMF, $mol^{-1}\,cm^2\,\Omega^{-1}$): 42.70, $C = 0.001\,mol\,l^{-1}$; Raman (Raman shift, cm^{-1}): 443 (Cu−N), 314 (Cu−O); UV–VIS (DMF, λ_{max} (nm)/ε): 408/12840, 262/57727 ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$); Anal. Calcd for $C_{45}H_{38}CuN_5O_5P_2$: C 60.77; H 4.65; N 7.87. Found: C 59.94; H 4.24; N 6.69%.

4. Supplementary material

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-768932 for $[Cu(PPh_3)_2(ITC)]NO_3$ (**3**). Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; Email: ordeposit@ccdc.cam.ac.uk).

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