

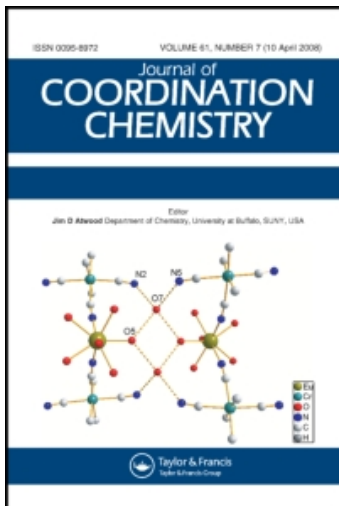
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Syntheses, NMR (^1H , ^{31}P) spectroscopy and crystal structures of complexes of copper(I) halides with isatin-3-thiosemicarbazones

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Syntheses, NMR (^1H , ^{31}P) spectroscopy and crystal structures of complexes of copper(I) halides with isatin-3-thiosemicarbazones

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Isatin-3-thiosemicarbazones (H_2itsc) react with copper(I) bromide or iodide in a 1 : 1 mol ratio in acetonitrile in the presence of two moles of Ph_3P to form tetrahedral monomeric complexes of composition $[\text{CuX}(\eta^1\text{-S-H}_2\text{itsc})(\text{Ph}_3\text{P})_2]$, X = Br (**1**), I (**2**). These complexes, which have been characterized by single-crystal structure determinations, are unlike the iodo-bridged dinuclear complex of copper(I) iodide of pyrrole-2-carbaldehydethiosemicarbazone (Hptsc), namely $[\text{Cu}_2(\mu\text{-I})_2(\eta^1\text{-S-Hptsc})_2(\text{PPh}_3)_2]$ (**3**). In both **1** and **2**, the geometry around Cu is distorted tetrahedral with P–Cu–P bond angles being 121.97(3) (**1**) and 124.09(5) $^\circ$ (**2**). Proton NMR confirms that thiosemicarbazone coordinates to the Cu atom as a neutral ligand, and ^{31}P NMR shows that there is no dissociation of the complexes in solution; coordination shift values suggest that Ph_3P stabilizes the Cu(I) oxidation state.

Keywords: Copper(I); Isatin-3-thiosemicarbazones; Halides; Phosphine; Crystal structures

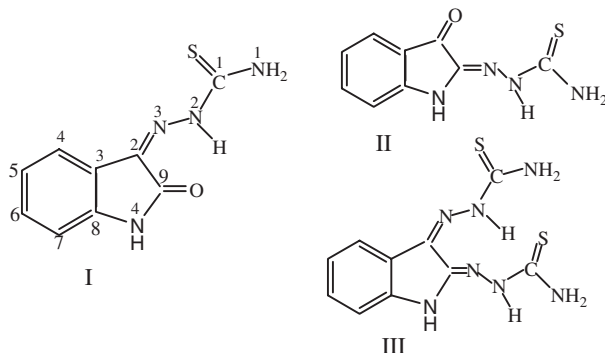
1. Introduction

Isatin diketone, on condensation with a thiosemicarbazide, forms three types of thiosemicarbazones, isatin-3-thiosemicarbazone (I, H_2L), isatin-2-thiosemicarbazone (II, H_2L) and isatin-2,3-bis(thiosemicarbazone) (III, H_2LL), all of which form metal complexes [1–15]. Only a few of these are structurally characterized, namely, $[\text{Ni}(\text{HL})_2] \cdot \text{EtOH}$, $[\text{Ni}(\text{HL})_2] \cdot 2\text{DMF}$ [12], $[\text{TiMe}_2(\text{HL})(\text{DMSO})]$ [13], $[\text{SnMe}_2(\text{L})\{\text{O}(\text{S})\text{PPh}_2\}] \cdot \text{EtOH}$ [14] and $[\text{SnMe}_2(\text{HLL})]$ [14]. Isatin-3-thiosemicarbazone generally coordinates through N, S, O donor atoms and isatin-2, 3-bis-thiosemicarbazone is an

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N,S-chelate. Coordination through O donor atoms is dependent on the nature of the metal and is weak in some cases. Isatin thiosemicarbazones, like other thiosemicarbazones, have several biochemical applications [16–22].

In this article we report the complexes of isatin-3-thiosemicarbazone with copper(I) halides, namely $[\text{CuBr}(\eta^1\text{-S-H}_2\text{itsc})(\text{Ph}_3\text{P})_2] \cdot 2\text{CH}_3\text{CN}$ (**1**) and $[\text{CuI}(\eta^1\text{-S-H}_2\text{itsc})(\text{Ph}_3\text{P})_2] \cdot \text{CH}_3\text{CN}$ (**2**), in which the neutral ligand is coordinated through S alone. These are the first examples of structurally characterized complexes of Cu(I)/Cu(II) with isatin thiosemicarbazones.



2. Experimental

Copper(I) bromide and iodide were prepared by the reduction of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ using SO_2 in the presence of NaBr or NaI in water [22]. Isatin-3-thiosemicarbazone was prepared by following the general procedure of Anderson *et al.* [23]. C, H and N analyses were obtained with a Carlo-Erba 1108 instrument. IR spectra were recorded using KBr pellets on a Pye Unicam SP-3-300 or a Nicolet 320 FTIR spectrophotometer in the $4000\text{--}200\text{ cm}^{-1}$ range. ^1H NMR spectra were recorded on a Jeol AL300 FT spectrometer at 300 MHz in CDCl_3 with TMS as internal reference. ^{31}P spectra were recorded at 121.5 MHz, using CDCl_3 with phosphoric acid as external reference.

2.1. Synthesis of 1

To a stirred solution of the ligand (0.038 g, 0.174 mmol) in acetonitrile (15 cm^3) was added a solution of copper(I) bromide (0.025 g, 0.174 mmol) in the same solvent (15 cm^3). The mixture was stirred for 4 h at room temperature. Solid Ph_3P (0.092 g, 0.348 mmol) was then added and stirring continued for 1 h. The clear orange solution that formed was filtered and set aside for crystallization. The orange crystals obtained were filtered off, washed and dried (yield 65%; m.p. $217\text{--}219^\circ\text{C}$). The complex is only very slightly soluble in CHCl_3 and CH_2Cl_2 , but is soluble in DMSO and hot acetonitrile. Anal. Calcd for $\text{C}_{45}\text{H}_{38}\text{BrN}_4\text{OP}_2\text{SCu}$ (%): C, 60.84; H, 4.28; N, 6.30. Found: C, 60.59; H, 4.36; N, 6.27. ^1H NMR (CDCl_3 , δ ppm): 7.61 sb ($^1\text{NH}_2$), 7.56 dd ($\text{C}^{4,7}\text{H}$), 7.21 d (C^5H), 7.3 s (C^6H), 7.64 dd ($\text{C}^{6,8}\text{H}$), 7.46 m ($\text{C}^{3,5}\text{H}$), 7.26–7.40 m (Ph_3P). ^{31}P NMR (CDCl_3 , δ ppm): 24.02 (PPh₃).

2.2. Synthesis of 2

To a stirred solution of the ligand (0.028 g, 0.131 mmol) in acetonitrile (15 cm³) was added a solution of copper(I) iodide (0.025 g, 0.13 mmol) in the same solvent (15 cm³). The mixture was stirred for 4 h at room temperature and then solid Ph₃P (0.068 g, 0.262 mmol) was added. The same procedure was followed as above to obtain orange crystals (yield 68%; m.p. 192–195°C). Anal. Calcd C₄₇H₄₁IN₅OP₂SCu(%): C, 57.81; H, 4.20; N, 7.18. Found: C, 57.44; H, 4.25; N, 7.22. ¹H NMR (CDCl₃, δ ppm): 7.68 sb (¹NH₂), 12.67 s (N²H), 7.59 dd (C^{4,7}H), 6.92 d (C⁵H), 7.15 s (C⁶H), 7.26–7.37 m (Ph + Ph₃P). ³¹P NMR (CDCl₃, δ ppm): 24.17 (PPh₃).

2.3. Crystallography

An orange prismatic crystal of **1** was mounted on a glass fiber. Crystal data were collected on an Enraf Nonius CAD4 automatic diffractometer equipped with a graphite monochromator and Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Unit cell dimensions and intensity data were measured at 223 K. The structure was solved by direct methods and refined by full-matrix least-squares based on F^2 with anisotropic thermal parameters for nonhydrogen atoms using XCAD-49 (data reduction) and SHELXL (absorption correction, structure solution refinement and molecular graphics) [24]. H-atoms were included in structure factor calculations in idealized positions.

An orange prismatic crystal of **2** was mounted on a glass fiber. Crystal data were collected at 193(1) K using a Rigaku MSC Mercury CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71071 \text{ \AA}$). The structure was solved by Patterson methods and expanded using Fourier techniques [24]. Nonhydrogen atoms were refined anisotropically. Crystallographic data are summarized in table 1.

Table 1. Crystal data for **1** and **2**.

	1	2
Empirical formula	C ₄₉ H ₄₄ BrCuN ₆ OP ₂ S	C ₄₇ H ₄₁ CuN ₅ OP ₂ SI
<i>M</i>	970.35	976.33
Temperature (K)	223(3)	193
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Unit cell dimensions		
<i>a</i> (Å)	12.5058(12)	11.623(1)
<i>b</i> (Å)	12.9855(12)	13.632(1)
<i>c</i> (Å)	16.8013(17)	16.261(2)
α (°)	100.804(9)	67.93(1)
β (°)	102.810(8)	70.26(1)
γ (°)	112.897(8)	69.09(1)
<i>V</i> (Å ³)	2334.3(4)	2167.8(5)
<i>Z</i>	2	2
<i>D</i> _{calc} (Mg m ⁻³)	1.381	1.496
Absorption coefficient (mm ⁻¹)	1.480	1.380
<i>F</i> (000)	996	988
Crystal size (mm ³)	0.30 × 0.20 × 0.15	0.30 × 0.20 × 0.20
2 θ range (°) for data collection	3.11–28.01	6.1–55.0
Reflections collected	12 768	21 287
Independent reflections	11 247 (<i>R</i> _{int} = 0.0439)	9410 (<i>R</i> _{int} = 0.055)
Goodness-of-fit on <i>F</i> ²	1.005	1.00
<i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] (<i>R</i> , ω <i>R</i>)	0.0470, 0.0891	0.063, 0.115

3. Results and discussion

When copper(I) halides were reacted with H₂itsc in the absence of Ph₃P, orange, insoluble products were formed. The addition of one mol equivalent of Ph₃P did not form a clear solution, but addition of a further mol equivalent of Ph₃P did. Slow evaporation of the solutions gave orange crystals of [CuX(η^1 -S-H₂itsc)(Ph₃P)₂], X = Br (**1**), I (**2**).

3.1. Crystal structures

The atom numbering schemes for **1** and **2** are shown in figures 1 and 2, respectively, and selected bond lengths and angles are given in table 2. In both complexes the geometry around copper is a distorted tetrahedron. Isatin-3-thiosemicarbazone acts as a neutral, monodentate ligand coordinating through S alone. Other coordination sites of the tetrahedron are occupied by two P atoms from two Ph₃P ligands and a halide ion. Cu–S bond distances, 2.3566(10) and 2.399(2) Å in **1** and **2**, respectively, are close to those [2.379(3), 2.402(3) Å] in [CuBr(PPh₃)₂(L)] and [CuI(PPh₃)₂(L)] [25], but somewhat shorter than the distance [2.331(4) Å] in the iodo-bridged dimer, [Cu₂(μ -I)₂(η^1 -S-H₂itsc)₂(PPh₃)₂] (H₂itsc = pyrrole-2-carbaldehyde thiosemicarbazone) [22]. This difference may be attributed to the number of Ph₃P ligands involved. In complexes in which isatin-3-thiosemicarbazone acts as an anionic ligand, M–S distances are considerably longer: 2.456(2) Å in [SnMe₂(HL){O(S)PPh₂}]·EtOH (HL = anion of isatin-3-thiosemicarbazone) [14] and 2.900(4) Å in [TlMe₂(HL)(DMSO)] [13]. Furthermore, C–S distances, 1.689(3) Å in **1** and 1.676(5) Å in **2**, are shorter than the C–S distances in related species: 1.741(6) in [SnMe₂(HL){O(S)PPh₂}]·EtOH [14],

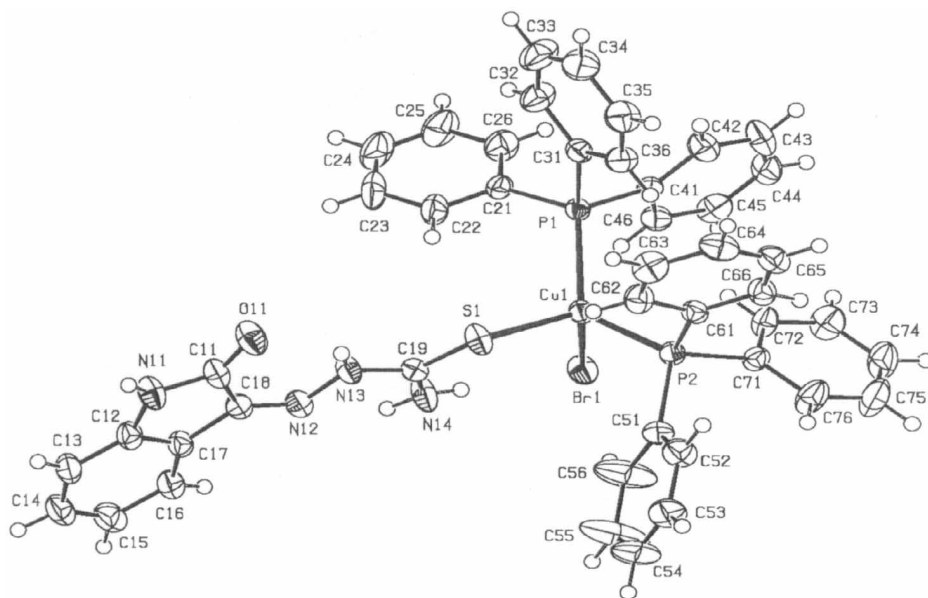


Figure 1. The structure of complex **1** showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity.

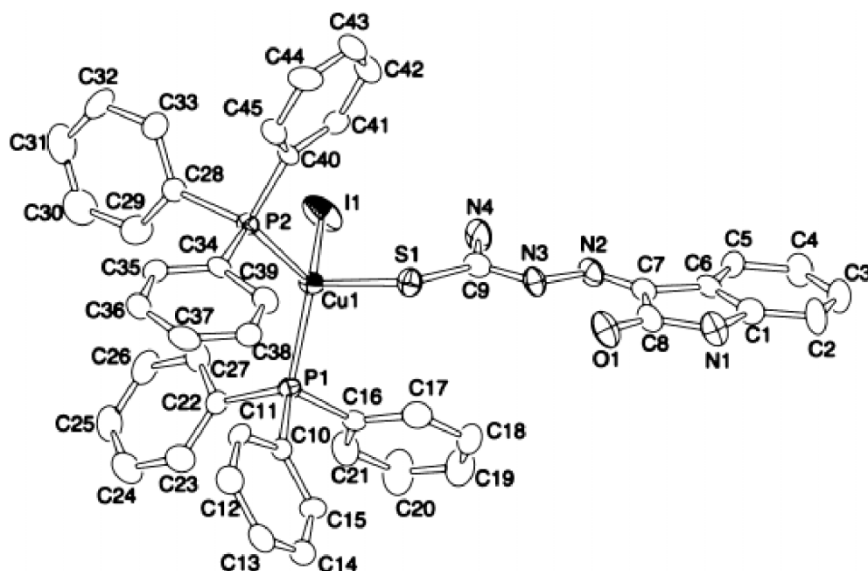


Figure 2. The structure of complex **2** showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity.

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

1			
Cu(1)–Br(1)	2.5459(6)	C(19)–N(14)	1.311(4)
Cu(1)–P(1)	2.2967(9)	C(19)–N(13)	1.351(4)
Cu(1)–P(2)	2.2852(9)	N(13)–N(12)	1.362(3)
Cu(1)–S(1)	2.3566(10)	N(12)–C(18)	1.288(4)
S(1)–C(19)	1.689(3)		
P(2)–Cu(1)–Br(1)	105.32(3)	Cu(1)–S(1)–C(19)	113.30(12)
P(2)–Cu(1)–P(1)	121.97(3)	S(1)–C(19)–N(14)	125.5(3)
P(1)–Cu(1)–S(1)	110.19(4)	S(1)–C(19)–N(13)	117.6(2)
S(1)–Cu(1)–Br(1)	109.22(3)	N(14)–C(19)–N(13)	117.0(3)
P(2)–Cu(1)–S(1)	105.16(3)	C(19)–N(13)–N(12)	119.5(3)
P(1)–Cu(1)–Br(1)	104.48(3)	N(13)–N(12)–C(18)	116.0(3)
2			
Cu(1)–I(1)	2.692(1)	C(9)–N(4)	1.321(9)
Cu(1)–P(1)	2.296(2)	C(9)–N(3)	1.355(9)
Cu(1)–P(2)	2.278(2)	N(3)–N(2)	1.355(6)
Cu(1)–S(1)	2.399(2)	N(2)–C(7)	1.283(9)
S(1)–C(9)	1.676(5)		
P(2)–Cu(1)–I(1)	105.87(6)	Cu(1)–S(1)–C(9)	115.5(2)
P(2)–Cu(1)–P(1)	124.09(5)	S(1)–C(9)–N(4)	124.6(6)
P(1)–Cu(1)–S(1)	108.61(7)	S(1)–C(9)–N(3)	117.3(5)
S(1)–Cu(1)–I(1)	112.13(4)	N(4)–C(9)–N(3)	118.0(5)
P(2)–Cu(1)–S(1)	98.87(6)	C(9)–N(3)–N(2)	121.2(5)
P(1)–Cu(1)–I(1)	107.09(5)	N(3)–N(2)–C(7)	118.2(5)

1.705(14) in [TlMe₂(HL)(DMSO)] [13], 1.712(4), 1.723(8) Å in [Ni(HL)₂]·EtOH and [Ni(HL)₂]·2DMF (HL = isatin-3-thiosemicarbazone) [18]. The free ligand has a C–S bond length of 1.663(4) Å [14], and this supports the view that the ligand coordinates to Cu in the thione form.

Cu–P bond lengths, 2.2852(9), 2.2967(9) Å in **1** and 2.296(2), 2.278(2) Å in **2**, are similar to Cu–P distances in analogous complexes [22, 25]. The Cu–Br bond length, 2.5459(6) Å in **1**, is close to that in [CuBr(PPh₃)₂(L)], 2.536(2) Å. These are less than sum of the ionic radii of Cu and Br, 2.73 Å [26]. Similarly, the Cu–I bond distance, 2.692 Å, in **2** is close that in [CuI(PPh₃)₂(L)], 2.661(2) Å, but smaller than the bridging Cu–I bond distance, 2.707(2) Å, in [Cu₂(μ-I)₂(η¹-S-Hptsc)₂(PPh₃)₂]. All Cu–I distances are less than the sum of the ionic radii of Cu and I, 2.97 Å [26]. Angles around Cu range from 104.48(3) to 121.97(3)° in **1** and 98.87(6) to 124.09(5)° in **2**, indicating some distortion of the tetrahedron. This distortion is greater in **2** than in **1**. The P1–Cu–P2 angle is 121.97(3)° in **1** and 124.09(5)° in **2** and this may be attributed to steric interactions between Ph₃P ligands. Cu–S–C angles of 113.30(12) and 115.5(2)° in **1** and **2**, respectively, are larger than in cases when the ligand chelates [92.1(2)–100.7(5)°] [13, 14].

3.2. NMR spectroscopy

Proton NMR of **2** shows a characteristic imino N²H signal at low field, δ 12.67 ppm, similar to that for the free ligand at δ 12.46 ppm [14], and indicates that the imino hydrogen is not deprotonated when the ligand coordinates through S. N¹H₂ protons of free H₂itsc show two broad peaks at δ 8.84(s) and 8.49(s) ppm in DMSO-*d*₆ [14], which shift to higher field at δ 7.68(sb) ppm in **2**. This is in accord with the behavior of thiosemicarbazones in the coordinated form although the magnitude of the shift is small, considering that H₂itsc in **2** is not deprotonated [20, 21]. The same behavior is expected for **1**. The ³¹P NMR signal for free Ph₃P appears at –7.17 ppm and this is shifted downfield to δ 24.02 ppm in **1** and δ 24.17 ppm in **2**. This shows that PPh₃ is not dissociated in CDCl₃ [27].

Supplementary material

Supplementary data are available from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>) on request, quoting the deposition numbers CCDC 252075 for **1** and 251683 for **2**.

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