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Spectral and structural studies of metal complexes of isatin 3-hexamethyleneiminylthiosemicarbazone prepared electrochemically

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Abstract

Cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and lead(II) complexes of isatin 3-hexamethyleneiminylthiosemicarbazone, $[M(Ishexim)_2]$, as well as a thallium(I) complex, [Tl(Ishexim)], have been prepared by electrochemical synthesis. The crystal structures of $[Zn(Ishexim)_2]$ and $[Pb(Ishexim)_2]$ have been solved, and the metal complexes have been characterized by their ^1H and ^{13}C NMR, IR, UV–Vis and mass spectra. Coordination of the Ishexim anions is via the imine nitrogen and thiolato sulfur atoms with evidence for weak interaction of the amide oxygen with the isatin portion of the ligand.

Keywords: Thiosemicarbazone; Isatin; Crystal structures; Zinc; Lead; Hexamethyleneimine; Metal(II) complexes

1. Introduction

The 3-thiosemicarbazones of isatin have been of interest since 1-methylisatin-3-thiosemicarbazone was found to be active in the treatment of smallpox [1–3] some forty years ago. It has been suggested that thiosemicarbazone drugs may act to inhibit virus growth by binding to copper ions which are constituents of the virus [4]. Therefore, a study of metal complexes for a wide range of thiosemicarbazones has been pursued in numerous studies [5]. Although substitution at N4-position of the thiosemicarbazone moiety (Fig. 1) was found to reduce anti-smallpox activity of isatin thiosemicarbazones [6], two butyl groups attached at the N4-position provides a compound with demonstrated activity against ectromelia (a vaccina virus unaffected by Marboran™) and also against type 2 polio, which is an enterovirus and quite unrelated to the vaccina family [7].

Metal complexes of N4-2-pyridyl- [6], N4-phenyl- [8], N4-ethyl- [9] and N4-dimethylthiosemicarbazones derived from isatin [10] have been studied. More recently, a study of the spectroscopic properties of the copper(II) complexes of eight N4-substituted thiosemicarbazones of isatin was communicated [11]. In this latter communication the crystal structure of the isatin 3-hexamethyleneiminylthiosemicarbazone, HIshexim, was reported, but none of the copper(II) complexes produced crystals of a quality sufficient for structural studies. In this study we report a structural and spectroscopic study of metal complexes of HIshexim prepared by electrochemical oxidation of the various metals.

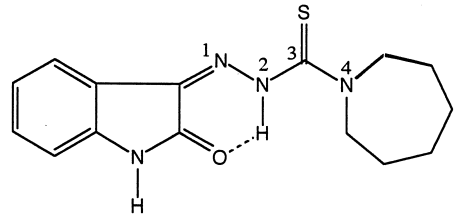

Fig. 1. Representation of HIshexim and numbering for the thiosemicarbazone moiety.

2. Experimental

HIshexim was prepared by reaction of equimolar amounts of 3-hexamethyleneiminylthiosemicarbazide, synthesized following the procedure developed by Holmberg and Psilanderhielm [12] and modified by Scovill [13], with isatin (Aldrich, 98%) at room temperature in absolute ethanol with a catalytic amount of conc. H_2SO_4. The product precipitated as a yellow powder in less than 1 h, and was collected by suction filtration and washed with cold absolute ethanol

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(yield, 76%). Complexes were prepared by electrochemical oxidation of the metals in a solution of HIshexim (0.056 g, 0.19 mmol) in CH_3CN (40 ml) containing 10 mg of tetramethylammonium perchlorate for 1 h at 5 mA and a potential of 10–20 V. A loss of 5.5 mg (Co), 5.5 mg (Ni), 6.1 mg (Zn), 10.5 mg (Cd), 11.8 mg (Cu), 38.1 mg (Tl) and 19.3 mg (Pb) from the anode resulted during the preparation of the complexes. The yields for the complexes and their percentage yield based on metal consumed were as follows: [Co(Ishexim)$_2$], 37 mg, 60%; [Ni(Ishexim)$_2$], 48 mg, 77%; [Cu(Ishexim)$_2$], 17 mg, 28%; [Zn(Ishexim)$_2$], 45 mg, 72%; [Cd(Ishexim)$_2$], 58 mg, 87%; [Tl(Ishexim)], 48 mg, 78%; [Pb(Ishexim)$_2$], 43 mg, 57%. During the reaction the solutions turned from yellow to the color of the various solids, which formed on slow evaporation of the solvent. The initial product, an amorphous dark brown solid, of the electrochemical oxidation of copper analyzes as [Cu(Ishexim)]. Found: C, 49.2; H, 4.7; N, 15.5. Calc.: C, 49.4; H, 4.7; N, 15.4%. This was not characterized further, but crystals formed on slow evaporation of the MeCN solvent analyze as [Cu(Ishexim)$_2$], Table 7.

Elemental analyses were performed with a Carlo Erba 1108 microanalyser. The magnetic susceptibilities were measured with a Digital Measurements system MSB-MKI calibrated with tetrakis(isothiocyanato)cobaltate(II) ion. ^{1}H and ^{13}C NMR spectra were recorded in deuterated $(CD_3)_2SO$ with a Brucker WM-300 spectrometer. Infrared spectra were recorded from 4000–400 cm^{-1} with a Mattson Instruments Cygnus 100 FTIR spectrometer using KBr pellets. UV–Vis spectra were recorded as Nujol mulls adhered to filter paper with a Cary 5E spectrophotometer. Electrospray mass spectral data were obtained with 5×10^{-4} M solutions (MeOH) by flow injection into a Hewlett-Packard 1100 series MSD. The carrier solvent was 50% MeOH in H_2O. Electrospray ionization conditions were as follows: nitrogen drying gas flow, 10.0 l min^{-1}; nebulizer pressure, 40 psig; drying gas temperature, 350°C; capillary voltage, 4 kV. The capillary exit voltage was varied from 0 to 150 V. The ESR spectrum of [Cu(Ishexim)$_2$] was acquired in 3 mm Pyrex tubes with a Brucker EMX spectrometer using a conventional insert Dewar at liquid nitrogen temperature.

Orange prismatic crystals of [Zn(Ishexim)$_2$] and [Pb(Ishexim)$_2$] were mounted on glass fibers and used for data collection on an Enraf-Nonius CAD4 automatic diffractometer. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range $21.25<\theta<45.11°$ for [Zn(Ishexim)$_2$] and $22.945<\theta<45.420°$ for [Pb(Ishexim)$_2$]. Data were collected using the ω-scan technique and corrected for Lorentz and polarization effects [14]. A semi-empirical absorption correction, Ψ-scan, was made for both crystals [15]. The structure was solved by direct methods [16] and subsequent difference Fourier maps, and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement factors [17]. All hydrogen atoms for [Zn(Ishexim)$_2$] were located from difference Fourier maps and refined isotropically and those for [Pb(Ishexim)$_2$] were located in their calculated positions (C–H 0.93–0.97 Å) and refined using a riding model. Atom scattering factors were taken from Ref. [18] and molecular graphics are from ZORTEP [19].

3. Results and discussion

3.1. Structural studies

The crystal data for [Zn(Ishexim)$_2$] and [Pb(Ishexim)$_2$] are shown in Table 1; Table 2 has selected bond distances and Table 3 selected bond angles. Perspective views of [Zn(Ishexim)$_2$] and [Pb(Ishexim)$_2$] are shown in Figs. 2 and 3, respectively. Both compounds are thermochromic; the change for [Pb(Ishexim)$_2$] is an irreversible change from orange to red at ca. 240°C and [Zn(Ishexim)$_2$] is reversible from yellow–orange to deep orange at ca. 100°C.

In [Zn(Ishexim)$_2$] the two Ishexim ligands are coordinated by the imine nitrogen and thiolato sulfur atoms of the thiosemicarbazonato moiety. Additional coordination is by the amide oxygen of the isatin moiety, O11, of one of the ligands, which has a longer bond distance, 2.452(3) Å, than the Zn–S bond distances. However, the oxygen, O21, of the second ligand is at a greater distance from the zinc center, 2.532(3) Å, and is not formally coordinated (i.e. this distance is longer than 1.3 times the sum of the covalent radii, $1.3\times\{1.20(Zn)+0.73(O)\}=2.509$ Å, and is not considered a bond by our X-ray program) as shown in Fig. 2. The geometrical parameter τ, i.e. $\tau=(\beta-\alpha)/60$, where α and β are N12–Zn–N23 and S1–Zn–O11 bond angles, respectively, has a value of 0.2. This suggests that [Zn(Ishexim)$_2$] has a square pyramidal geometry with a 20% distortion towards a trigonal bipyramid. The axial position can be considered to be occupied by S2 with O11, N12, S2 and N22 making up the basal plane. The angles involving S2 range from 122.20(10)° for S2–Zn–N12 to 81.77(9)° for S2–Zn–N22, the latter affected by the rigidity of the thiosemicarbazone moiety.

Intermolecular hydrogen bonding by the NH of the isatin moiety for each ligand (i.e. N11H and N21H in the two ligands) to the oxygens of the isatin moiety on two different molecules, O11A and O21B, yields a molecular chain. As would be expected, the hydrogen bonding distances and angles for N11H···O11A and N21H···O21B are quite similar (Table 4). The rms plane deviations for the two isatin moieties in [Zn(Ishexim)$_2$] are minimal (Table 5) and are at an angle of 101.3(5)° to each other. The thiosemicarbazone moieties, S1–C19–N14–N13–N13–C12 and S2–C29–N24–N23–N22–C22, have greater deviations; their rms plane deviations are 0.0304 and 0.0491 Å, and the two planes are at an angle of 79.65(20)°. The planar portion, N12–S2–N22, of the approximately trigonal bipyramidal arrangement of the donor atoms has a rms plane deviation of 0.0000 and the Zn atom is 0.3642(20) Å from this plane.

Table 1
Crystal data and structure refinement for metal complexes of isatin 3-hexamethyleneiminylthiosemicarbazone

Empirical formula	$C_{30}H_{34}N_8O_2S_2Zn$	$C_{30}H_{34}N_8O_2S_2Pb$
Color, habit	orange, prism	orange, prism
Formula weight	668.14	809.96
Temperature (K)	293(2)	293(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a (Å)	10.9343(16)	10.4123(8)
b (Å)	14.2567(11)	11.8842(14)
c (Å)	20.334(3)	12.7422(12)
α (°)	90(0)	89.892(9)
β (°)	92.887(11)	78.783(8)
γ (°)	90(0)	81.928(6)
Volume (Å^3)	3165.8(7)	1580.8(3)
Z	4	2
Density (Mg m^{-3})	1.402	1.757
Absorption coefficient (mm^{-1})	2.646	12.340
Crystal size (mm)	0.40×0.10×0.10	0.40×0.35×0.25
Diffractometer	Nonius CAD4	Nonius CAD4
Radiation (λ, Å)	Cu Kα (1.54184)	Cu Kα (1.54184)
θ Range for data collection (°)	3.79–76.00	3.54–75.92
Index ranges	$0 \le h \le 13,\ -17 \le k \le 0,\ -25 \le l \le 25$	$-13 \le h \le 0,\ -14 \le k \le 14,\ -16 \le l \le 15$
Reflections collected	6964	6727
Independent reflections	6615 (R_{int} = 0.0387)	6363 (R_{int} = 0.0504)
Absorption correction	semi-empirical	Ψ-scan
Max./min. transmission	0.978/0.928	0.986/0.738
Refinement method, F^2	full-matrix least-squares	full-matrix least-squares
Data/parameters	6165/525	6363/461
Goodness-of-fit on F^2	0.999	1.057
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0490, wR_2 = 0.1035	R_1 = 0.0442, wR_2 = 0.0767
R indices (all data)	R_1 = 0.1389, wR_2 = 0.1321	R_1 = 0.1768, wR_2 = 0.1000
Largest difference peak/hole (e Å^{-3})	0.361 and −0.347	0.338 and −0.506

Table 2
Selected bond distances (Å) for [Zn(Ishexim)$_2$] and [Pb(Ishexim)$_2$] [a]

	[Zn(Ishexim)$_2$]	[Pb(Ishexim)$_2$]
M–N12	2.074(3)	2.602(4)
M–N22	2.078(3)	2.654(4)
M–S1	2.3631(14)	2.6854(14)
M–S2	2.3618(14)	2.7273(14)
M–O11	2.452(3)	2.829(4)
M–O21	2.532(3)	2.834(4)
S1–C19	1.720(4)	1.727(5)
S2–C29	1.703(4)	1.726(5)
N12–C12	1.308(4)	1.308(6)
N22–C22	1.305(3)	1.300(6)
N12–N13	1.335(4)	1.338(6)
N22–N23	1.338(4)	1.346(5)
N13–C19	1.357(4)	1.360(6)
N23–C29	1.371(5)	1.354(7)
N14–C19	1.343(4)	1.340(6)
N24–C29	1.347(5)	1.343(7)
O11–C11	1.229(4)	1.231(6)
O21–C21	1.226(4)	1.211(7)

[a] Although M–O distances are shown, only O11 is coordinated in [Zn(Ishexim)$_2$] and neither oxygen in [Pb(Ishexim)$_2$].

For [Pb(Ishexim)$_2$] the two oxygens are at a greater distance from the Pb(II) center than either the nitrogen or sulfur donor atoms, suggesting that the oxygens are weakly interacting with the lead center as is indicated in Fig. 3. For [Pb(Ishexim)$_2$], τ = 0.04, suggesting a square pyramidal geometry with only a 4% distortion towards a trigonal bipyramid and the lone pair on the lead atom in the apical position. The geometry of the complex shows that the lone pair on the lead is stereochemically active, and the enormous deviation from the trigonal bipyramidal geometry can be explained as the result of the electrostatic repulsion of this electron pair. The N_2S_2 basal plane has S1–Pb–S2 and N12–Pb–N22 angles of 89.78(5) and 132.65(12)° and there is a deviation by as much as 0.5 Å from the plane of the four donor atoms. Another four coordinate lead-thiosemicarbazone complex [20], [Pb(Ac4M)OAc] (Ac4M = anion of 2-acetylpyridine N(4)-methylthiosemicarbazone), has Pb–N12 and Pb–S1 distances of 2.482(7) and 2.730(3) Å compared to averages of 2.628(4) and 2.7064(14) Å for [Pb(Ishexim)$_2$]. [Pb(Ac4M)OAc] is regarded as derived from a trigonal bipyramid with S1 occupying an axial position and N12 an equatorial position, which helps to account for the differences in bond distances. The N12–Pb–S1 chelate angle in [Pb(Ac4M)OAc] is 69.1(2)°, which is larger than 67.52(9) and 66.35(9)° found for N12–Pb–S1 and N22–Pb–S2 in [Pb(Ishexim)$_2$] consistent with the S1 of the former compound being in an axial position.

The metal–ligand bonds of [Pb(Ishexim)$_2$] are about 0.3 Å longer than the analogous bonds of [Zn(Ishexim)$_2$], as

Table 3
Selected bond angles (°) for [Zn(Ishexim)$_2$] and [Pb(Ishexim)$_2$] [a]

	[Zn(Ishexim)$_2$]	[Pb(Ishexim)$_2$]
N12–M–N22	145.35(12)	132.65(12)
N12–M–S2	122.20(10)	84.57(9)
N12–M–S1	81.63(9)	67.52(9)
N12–M–O11	75.38(11)	63.50(12)
N12–M–O21	77.62(10)	141.75(13)
N22–M–S2	81.77(9)	66.35(9)
N22–M–S1	120.31(9)	75.52(9)
N22–M–O11	79.27(11)	127.99(12)
N22–M–O21	74.44(10)	62.81(12)
S2–M–S1	102.01(6)	89.78(5)
S2–M–O11	92.45(8)	67.79(9)
S2–M–O21	155.69(7)	127.47(8)
S1–M–O11	156.87(7)	127.28(9)
S1–M–O21	94.35(8)	89.85(11)
O11–M–O21	78.44(10)	141.97(14)
C19–S1–M	95.23(14)	103.50(17)
C29–S2–M	95.05(14)	102.93(17)
C11–O11–M	103.5(3)	108.7(3)
C21–O21–M	101.7(2)	110.7(3)
C12–N12–M	118.6(2)	117.8(3)
C22–N22–M	119.1(2)	119.4(3
N13–N12–M	123.1(2)	124.4(3)
N23–N22–M	122.2(2)	124.4(3)
C12–N12–N13	118.2(3)	116.1(4)
N12–N13–C19	113.4(3)	113.7(4)
N13–C19–N14	114.3(3)	114.5(4)
N13–C19–S1	126.0(3)	126.8(4)
N14–C19–S1	119.6(3)	118.7(4)
C22–N22–N23	118.5(3)	116.2(4)
N22–N23–C29	113.3(3)	114.0(4)
N23–C29–N24	113.5(4)	114.2(5)
N23–C29–S2	126.1(3)	126.4(4)
N24–C29–S2	120.4(3)	119.4(4)
O11–C11–N11	127.5(4)	125.8(5)
O11–C11–C12	126.5(4)	127.4(5)
O21–C21–N21	126.6(4)	126.4(5)
O21–C21–C22	127.2(4)	128.4(5)

[a] Although angles for the oxygens with the metals are shown, only O11 is coordinated in [Zn(Ishexim)$_2$] and neither oxygen in [Pb(Ishexim)$_2$].

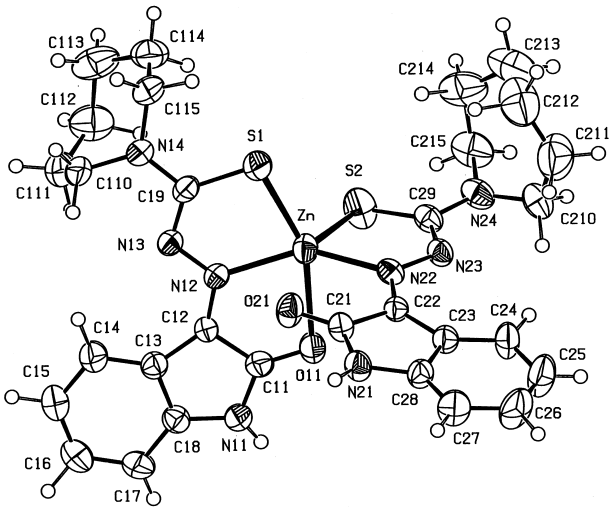

Fig. 2. Ortep diagram of [Zn(Ishexim)$_2$] at 50% probability.

would be expected based on the larger ionic radius of Pb, and the bond distances to nitrogen and to sulfur are not very different for [Pb(Ishexim)$_2$]. Differences in the bonding to the metal center between the two ligands of a complex are much greater for [Pb(Ishexim)$_2$] than for [Zn(Ishexim)$_2$]; the Pb–N and Pb–S bond distances differ by about 0.05 and 0.04 Å, respectively, but Zn–N and Zn–S by only 0.004 and 0.001 Å, respectively.

Intermolecular hydrogen bonding by the NH of the isatin moiety occurs for each ligand (i.e. N11H and N21H in the two ligands). N11H is bifurcated between an oxygen of the isatin moiety on another molecule, O11C, and a thiolato sulfur of the thiosemicarbazone of the second ligand in the same molecule, S2C. N21H hydrogen bonds to hydrazinic nitrogen of another molecule, N13D. The hydrogen bonding interactions are weaker for [Pb(Ishexim)$_2$] than for [Zn(Ishexim)$_2$], Table 4. The rms plane deviations for the two isatin moieties in [Pb(Ishexim)$_2$] are greater than for [Zn(Ishexim)$_2$], but the amide oxygen is included in the former, but not the latter (Table 5). The angle between the two isatin planes is 89.45(11)° for [Pb(Ishexim)$_2$] compared to 101.3(5)° for [Zn(Ishexim)$_2$]. The thiosemicarbazone moieties, S1–C19–N14–N13–N13–C12 and S2–C29–N24–N23–N22–C22, have rms plane deviations of 0.0292 and 0.0678 Å, and the two planes are at an angle of 116.68(52)°.

Table 6 shows a comparison of the bond distances and angles of HIshexim [11] with the average of the two ligands in [Zn(Ishexim)$_2$] and [Pb(Ishexim)$_2$]. Since formation of the monoanionic ligands causes C19–S1 to convert from a formal double bond to a single bond, changes in its bond distance would be expected to be greatest among the various ligand bonds. The change from 1.672(4) Å for HIshexim to 1.711(4) and 1.726(6) Å for [Zn(Ishexim)$_2$] and [Pb(Ishexim)$_2$], respectively, is not, however, to the bond distance usually associated with a C–S single bond. For example, [Pd(6MAchexim)Cl] and [Pt(6MAchexim)Cl], where 6MAchexim is the monoanion of 6-methyl-2-acetylpyridine 3-hexamethyleneiminylthiosemicarbazone, have C–S bond distances of 1.769(4) and 1.782(10) Å [21]. However, in both [Zn(Ishexim)$_2$] and [Pb(Ishexim)$_2$] there is not a significant change in the imine bond, C12–N12, even though N12 is coordinated in both complexes. Even the

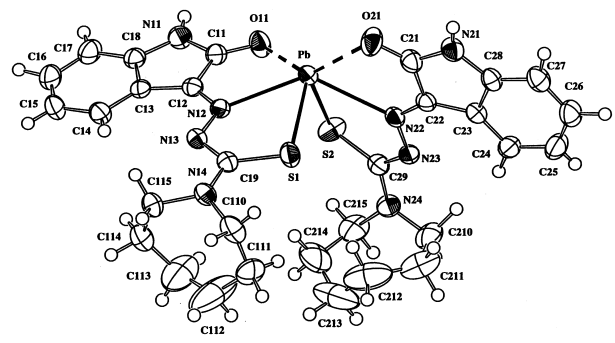

Fig. 3. Ortep diagram of [Pb(Ishexim)$_2$] at 50% probability.

Table 4
Hydrogen bonding (Å, °) for [Zn(Ishexim)$_2$] and [Pb(Ishexim)$_2$]

Compound	Donor	Acceptor [a]	D–H	H···A	D···A	∠D–H···A
[Zn(Ishexim)$_2$]	N11	O11A	0.81(4)	2.11(4)	2.887(5)	163(4)
	N21	O21B	0.85(4)	2.05(4)	2.887(4)	166(4)
[Pb(Ishexim)$_2$]	N11	O11C	0.86	2.44	2.968(6)	120.5
	N11	S2C	0.86	2.96	3.758(5)	155.8
	N21	N13D	0.71(9)	2.79(9)	3.329(7)	150(9)

[a] Symmetry transformation used to generate equivalent atoms: A, $-x+1$, $-y$, $-z$; B, $-x+2$, $-y$, $-z$; C, $-x+1$, $-y+1$, $-z+1$; D, $-x+1$, $-y+1$, $-z+2$.

Table 5
Root mean squared plane deviations (Å) and angles (°) between planes

[Zn(Ishexim)$_2$] [a]			[Pb(Ishexim)$_2$] [b]		
Plane	Rms deviation	∠ with previous plane	Plane	Rms deviation	∠ with previous plane
A	0.0077		F	0.0292	
B	0.0304	7.32(0.16)	G	0.0287	4.51(0.24)
C	0.0000	77.27(0.06)	H	0.0172	89.45(0.11)
D	0.0491	2.48(0.14)	I	0.0678	22.72(0.17)
E	0.0054	14.25(0.17)			

[a] Plane A C11–C12–C13–C14–C15–C16–C17–C18–N11; plane B S1–C19–N14–N13–N12–C12; plane C N12–S2–N22; plane D S2–C29–N24–N23–N22–C22; plane E C21–C22–C23–C24–C25–C26–C27–C28–N21.
[b] Plane F S1–C19–N14–N13–N12–C12; plane G O11–C11–N11–C12–C13–C14–C15–C16–C17–C18; plane H O21–C21–N21–C32–C33–C34–C35–C36–C37–C38; plane I S2–C29–N24–N23–N22–C22.

Table 6
A comparison of HIshexim bond distances (Å) and angles (°) with the average of the two ligands in [Zn(Ishexim)$_2$] and [Pb(Ishexim)$_2$]

	HIshexim	[Zn(Ishexim)$_2$]	[Pb(Ishexim)$_2$]
C12–N12	1.305(5)	1.306(4)	1.304(6)
N12–N13	1.362(6)	1.337(4)	1.342(6)
N13–C19	1.375(4)	1.364(5)	1.357(7)
C13–S1	1.672(4)	1.711(4)	1.726(6)
C19–N14	1.339(6)	1.345(5)	1.342(7)
C11–O11	1.236(7)	1.228(4)	1.221(7)
C12–N12–N13	115.4(4)	118.4(3)	116.2(4)
N12–N13–C19	119.8(4)	113.4(3)	113.8(4)
N13–C19–N14	114.6(4)	113.9(4)	114.4(5)
N13–C19–S1	121.5(4)	126.0(3)	126.6(4)
N14–C19–S1	123.9(3)	120.0(3)	119.0(4)
N11–C11–O11	127.7(4)	127.0(4)	126.1(5)
C12–C11–O11	126.3(4)	126.8(4)	127.9(5)

weakly interacting amide oxygens cause a greater change in C11–O11 in the complexes. However, the N12–N13–C19 bond angle is much smaller at about 113.6° for the complexes compared to 119.8(4)° for HIshexim, and C12–N12–N13 is also different in the complexes. Both N–C–S bonds undergo significant changes in the complexes, but C12–C11–O11 is not changed by more than three times the combination of the estimated standard deviations of the angles.

3.2. Spectral studies

The colors, partial elemental analyses and magnetic susceptibilities of the seven complexes formed electrochemically from HIshexm are listed in Table 7. All but [Tl(Ishexim)] have two ligands per metal center and the yellow and orange colors are in part due to the original color of the ligand, the formation of a conjugated thiosemicarbazone moiety on loss of N3H and L → M charge transfer bands.

The assignments for N11*H* and N13*H* in the ^{1}H NMR spectrum of HIshexim were previously reported as 11.258 and 13.504 ppm [11]. Assignments for the resonances that undergo change in the diamagnetic metal complexes formed from HIshexim are listed in Table 8. Loss of the N13H hydrogen on coordination results in the absence of a resonance above 13 ppm in the spectra of the metal complexes and N1*H* ranges from 10.673 ppm in [Tl(Ishexim)] to 11.018 ppm in [Cd(Ishexim)$_2$]. The difference between the ^{1}H NMR spectrum of HIshexim and its metal complexes involves the protons of the hexamethyleneiminyl ring. Listed in Table 7 are the hydrogens attached to the α-carbon atoms of the ring, which are different owing to restricted rotation about the C–N bond connecting the ring to the thioamide carbon. This bond distance is more consistent with a double bond than a single bond. In HIshexim the distance of this bond is 1.339(6) Å [11], and its distance in [Zn(Ishexim)$_2$] and [Pb(Ishexim)$_2$] averages 1.345(5) and 1.342(7) Å, respectively. In the complexes these resonances are downfield from their position in the spectrum of HIshexim. There are differences in the complexes between the hydrogens attached to the two β-carbons and γ-carbons, which is probably due to the different environment for the two ligands in a complex.

In the ^{13}C spectrum of isatin [22] the amide carbon, C11, is assigned at 159.4 ppm and the ketonic carbon, C12, at

Table 7
Colors, partial elemental analyses and magnetic susceptibilities of the metal complexes of HIshexim

Compound	Color	Found (calc.)			μ_{eff} (BM)
		C (%)	H (%)	N (%)	
[Co(Ishexim)$_2$]	brown	54.4 (54.4)	4.9 (5.1)	16.8 (16.9)	4.1
[Ni(Ishexim)$_2$]	dark brown	54.5 (54.5)	5.0 (5.1)	17.0 (16.9)	3.4
[Cu(Ishexim)$_2$]	dark brown	54.1 (54.1)	5.2 (5.1)	17.2 (16.8)	1.9
[Zn(Ishexim)$_2$]	yellow–orange	54.5 (53.9)	5.0 (5.1)	17.0 (16.8)	0
[Cd(Ishexim)$_2$]	yellow–orange	49.8 (50.3)	4.6 (4.7)	15.4 (15.6)	0
[Tl(Ishexim)]	orange	35.3 (35.6)	3.3 (3.3)	11.0 (11.0)	0
[Pb(Ishexim)$_2$]	orange	44.0 (44.4)	4.2 (4.2)	13.7 (13.8)	0

Table 8
^{1}H and ^{13}C NMR spectral assignments (ppm) for HIshexim and its metal complexes

Compound	N1*H*	C*H*$_2$ [a]	C*H*$_2$ [b]	*C*=S	*C*=N	*C*=O
HIshexim	11.258	4.073	3.814	178.5	134.8	162.9
[Zn(Ishexim)$_2$]	10.864	4.081	4.023	184.3	131.1	166.7
[Cd(Ishexim)$_2$]	11.018	4.129	4.090	184.2	130.4	167.4
[Tl(Ishexim)]	10.673	4.136	4.084	189.6	135.2	168.7
[Pb(Ishexim)$_2$]	10.856	4.118	3.917	185.6	129.4	168.1

[a] Furthest downfield signal for the hydrogens attached to an α-C of the hexamethyliminyl ring.
[b] Upfield signal for the hydrogens attached to an α-C of the hexamethyliminyl ring.

Table 9
Infrared and electronic spectra (cm^{-1}) for HIshexim and its metal complexes

Compound	ν(CO)	ν(CN)	ν(CS)	Intraligand	CT, d→d
Hishexim	1690s	1584m	868m	39970, 35780, 27820	
[Co(Ishexim)$_2$]	1665s	1569w	750m	38600, 34590	23340, 16810, 8300
[Ni(Ishexim)$_2$]	1665s	1567m	748m	37370, 34290	24830, 21710, 20520, 17520, 14540, 10910
[Cu(Ishexim)$_2$]	1700s	1543s	753m	38360, 34590, 27700	25020, 22310, 16640
[Zn(Ishexim)$_2$]	1682m	1570m	747m	39070, 37280, 33990	27280, 22320
[Cd(Ishexim)$_2$]	1667s	1565m	747m	38950, 37100, 34170	26680, 22310
[Tl(Ishexim)]	1680m	1540m	743m	[a]	
[Pb(Ishexim)$_2$]	1671m	1548m	745m	41770, 38950, 34980	25310, 20940

[a] Not recorded.

184.4 ppm. In the the eight isatin N(4)-substituted thiosemicarbazones [11], the ketonic (now azomethine) carbon signal is at significantly higher field (i.e. 131.5–134.8 ppm), the exact position being dependent on the nature of the substituent of the thiosemicarbazone moiety. Its resonance in the spectrum of HIshexim is 134.8 ppm and C11 is at 162.9 ppm and C19 at 178.5 ppm, Table 8. In the spectra of the complexes the thioamide and amide carbons, C19 and C11, respectively, are found downfield from their position in the spectrum of HIshexim, suggesting coordination by the thiolato sulfur and amide oxygen. In the spectra of the complexes the imine carbon, C12, is found upfield indicating coordination of the imine nitrogen. The lone exception is [Tl(Ishexim)] which shows C12 essentially unshifted, but has a significantly larger shift of C19 and a larger shift of C11. Like the ^{1}H NMR spectra the complexes have more peaks for the carbons of the hexamethyleneiminyl ring than does HIshexim.

The IR bands, Table 9, assigned to ν(CO), ν(CN) and ν(CS) generally undergo shifts from their positions in the spectrum of HIshexim to lower energy on coordination to the metal ions. These shifts indicate coordination of the amide oxygen, imine nitrogen and thiolato sulfur atoms for most of the complexes. In the spectrum of [Cu(Ishexim)$_2$], ν(CO) is found at higher energy than in the spectrum of HIshexim, suggesting that the oxygen is not strongly coordinated in this complex. The shifts in these bands for [Tl(Ishexim)], which are generally comparable to those of the remaining complexes with divalent metal ions, suggest that the thiolato sulfur atom may be bridging to adjacent Tl centers rather than the amide oxygen.

The UV–Vis spectra of HIshexim and the complexes are included in Table 9. The highest energy $\pi \rightarrow \pi^*$ band is at lower energy in the spectrum of [Zn(Ishexim)$_2$] and higher energy for [Pb(Ishexim)$_2$] compared to HIshexim. The $\pi \rightarrow \pi^*$ band at 35780 cm^{-1} in the spectrum of HIshexim is

Table 10
Positive ion mass spectral data for the metal complexes of HIshexim

Compound	Positive ion mass fragments (m/z values and relative intensities)
[Co(Ishexim)$_2$]	M+1 (662, 12 and 661, 31), M−301 (361, 6.5 and 360, 31, Ishexim [a])
[Ni(Ishexim)$_2$]	M−301 (360, 47, Ishexim)
[Cu(Ishexim)$_2$]	M+1 (667, 100), M−301 (364, 16, Ishexim), M−364 (303, 14, Ishexim, Cu)
[Zn(Ishexim)$_2$]	M+1 (667, 47), M−16 (651, 38, O), M−32 (635, 18, S), M−301 (366, 22, 365, 100, Ishexim), M−366 (301, 24, Ishexim, Zn)
[Cd(Ishexim)$_2$]	M−301 (413, 1.5, Ishexim)
[Tl(Ishexim)]	M+1 (507, 7), M−16 (491, 14, O), M−301 (205, 6, Ishexim)
[Pb(Ishexim)$_2$]	M+1 (811, 66), M−301 (509, 21, Ishexim), M−507 (303, 27, Ishexim, Pb)

[a] Species suggested to be lost.

at higher energy in the spectra of the complexes, suggesting it likely arises from one of the functional groups that is coordinating rather than the aromatic ring. In the spectrum of HIshexim the band at 27820 cm^{-1} is very broad and likely involves n→π* transitions for the C=O, C=N and C=S functions. The two lowest energy bands in the spectra of the complexes are assigned to L→M charge transfer transitions with the lowest energy band probably associated with the thiolato sulfur donor.

The positive ion mass spectra of the complexes, Table 10, show a cluster of ions with significant intensity centered at *m/z* for their molecular ions, $(M+1)^+$, with the exception of [Ni(Ishexim)$_2$] and [Cd(Ishexim)$_2$]. The other significant cluster of peaks in their spectra occurs at $(M-302)^+$, due to loss of an Ishexim ligand. The loss of this ligand appears to be a one-step process because there is little indication of its partial decompostion (i.e. ions between M−1 and M−302) except for [Zn(Ishexim)$_2$] which shows $(M-16)^+$ and $(M-32)^+$ fragments due to loss of oxygen and either sulfur or oxygens from both ligands. [Tl(Ishexim)] also shows a $(M-16)^+$ fragment. [Cu(Ishexim)$_2$], [Zn(Ishexim)$_2$] and [Pb(Ishexim)$_2$] all show a signficant peak at *m/z* 301, suggesting loss of the metal as well as one of the Ishexim ligands.

[Cd(Ishexim)$_2$], based on its various spectral properties, is expected to have a similar stereochemistry to that of [Zn(Ishexim)$_2$]. [Tl(Ishexim)] is probably four coordinate with the thiolato sulfur serving as the bridging donor atom based on its large downfield shift of *C*(S) in its ^{13}C NMR spectrum and the large decrease in energy of ν(CS) on coordination. The IR spectrum of [Cu(Ishexim)$_2$] shows that ν(CO) is shifted to higher energy compared to HIshexim, suggesting that the amide oxygens of the two ligands are not coordinated. Consistent with CuN_2S_2 coordination is the d→d composite band at 16640 cm^{-1} [23], and its EPR parameters of $g_\parallel = 2.190$, $g_\perp = 2.059$, $g_{av} = 2.103$ and $A_\parallel = 162$ G for the solid at liquid nitrogen temperature. The *g*-values are considerably higher than those of a CuN_2S_2 center such as [Cu(Buhexim)] (Buhexim = dianion of 2,3-butanedione bis{3-hexamethyleniminylthiosemicarbazone}), which has $g_\parallel = 2.104$, $g_\perp = 2.030$, $g_{av} = 2.055$. Therefore, the parameters for [Cu(Ishexim)$_2$] suggest that the carbonyl oxygens interact more strongly with the copper center at the lower temperature. Copper(II) complexes with N_2S_2 coordination generally have $g_\parallel = 2.145$ [24]. The resolution of the $g_\parallel$ feature is presumably due to the bulkiness of the ligand; at room temperature we are unable to assign $g_\parallel$.

For [Co(Ishexim)$_2$] assignment of the bands at 8300 and 16810 cm^{-1} to $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, respectively, allows calculation [25] of $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ as 17600 cm^{-1}, $B = 633$ cm^{-1}, $\beta = 0.65$ and $D_q = 930$ cm^{-1}, which are reasonable parameters for approximately octahedral $CoO_2N_2S_2$ coordination. In contrast, assignment of 10910 cm^{-1} to $^3A_{2g} \rightarrow {}^3T_{2g}$ and either 14540 or 17520 cm^{-1} as $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ for [Ni(Ishexim)$_2$] does not give reasonable values for *B*, β and D_q for an octahedral $NiO_2N_2S_2$ center. This suggests, based on $\nu(CO) = 1665$ cm^{-1}, indicating oxygen coordination, and $\mu = 3.4$ BM, that [Ni(Ishexim)$_2$] is six coordinate and more tetragonally distorted than [Co(Ishexim)$_2$] [26,27].

Supplementary data

Crystallographic data for $C_{30}H_{34}N_8O_2S_2Zn$, [Zn(Isheixm)$_2$], CCDC 134850, and $C_{30}H_{34}N_8O_2S_2Pb$, [Pb(Isheixm)$_2$], CCDC 134851 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1003/m. Copies of available material can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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