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Synthesis, structural characterization and electrochemical studies of nickel(II), copper(II) and cobalt(III) complexes of some ONS donor ligands derived from thiosemicarbazide and *S*-alkyl/aryl dithiocarbazates

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Abstract Four tridentate ONS ligands, namely 2-hydroxyacetophenonethiosemicarbazone (H_2L^1), the 2-hydroxyacetophenone Schiff base of *S*-methyldithiocarbazate (H_2L^2), the 2-hydroxy-5-nitrobenzaldehyde Schiff base of *S*-methyldithiocarbazate (H_2L^3), and the 2-hydroxy-5-nitrobenzaldehyde Schiff base of *S*-benzyldithiocarbazate (H_2L^4), and their complexes of general formula $[Ni(HL^1)_2]$, [ML] ($M = Ni^{II}$ or Cu^{II}; $L = L^1$, L^2, L^3 and L^4), [Co(HL)(L); $L = L^1$, L^2, L^3 and L^4] and [ML(B)] ($M = Ni^{II}$ or Cu^{II}; $L = L^2$ and L^4; B = py, PPh_3) have been prepared and characterized by physico-chemical techniques. Spectroscopic evidence indicates that the Schiff bases behave as ONS tridentate chelating agents. X-ray crystallographic structure determination of $[NiL^2(PPh_3)]$ and $[CuL^4(py)]$ indicates that these complexes have an approximately square-planar structure with the Schiff bases acting as dinegatively charged ONS tridentate ligands coordinating via the phenoxide oxygen, azomethine nitrogen and thiolate sulfur atoms. The electrochemical properties of the complexes have been studied by cyclic voltammetry.

Introduction

Metal complexes of Schiff bases have been extensively investigated because of their industrial, antifungal, antibacterial, anticancer and herbicidal applications [1]. It is well known that coordination of metals to Schiff base ligands may enhance their biological activities [2, 3]. Many new Schiff bases and their metal complexes reported in the literature have been studied electrochemically, using various electrodes and solvents, with a view to understand the mechanism of their biological activities [4–6]. Tridentate Schiff bases with N, O and S donor atoms are of special interest because of their ability to form stable transition metal complexes with interesting physico-chemical properties. For example, the dimeric nickel(II) complex of the ONS tridentate thiosemicarbazone, 2-hydroxy-5-methyl acetophenone *N*,*N*-dimethylthiosemicarbazone, is known to catalyze reaction 1 below, which is a key reaction of the metalloenzyme, CO dehydrogenase [7]. The nickel(II) complex of 2-hydroxyacetophenonethiosemicarbazone, another ONS chelating agent, also catalyzes the silane alcoholysis reaction 2, which is a related electrophilic activation of small molecules [8].

$$\text{Reaction 1:}\, CO + H_2O + CO_2 + 2H^+ + 2e^+;$$
$$\text{Reaction 2:}\, R_3SiH + R'SiOR + R_3SiOR' + H_2$$

In view of the interesting physico-chemical properties of metal complexes of ONS donor ligands and as part of our study of metal complexes of sulfur–nitrogen chelating agents, we report here the synthesis, spectroscopic, electrochemical and structural characterization of some nickel(II), copper(II) and cobalt(III) complexes of four tridentate ONS ligands derived from thiosemicarbazide and *S*-alkyl/aryl dithioicarbazates (Fig. 1), together with the X-ray crystal and molecular structures of $[NiL^2(PPh_3)]$ and $[CuL^4(py)]$.

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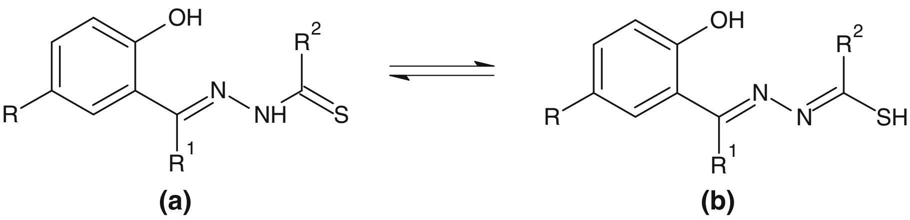

Fig. 1 The thione (**a**) and thiol (**b**) tautomeric forms of the Schiff bases: H_2L^1 (**1**) (R = H, $R^1 = CH_3$, $R^2 = NH_2$, the 2-hydroxyacetophenonethiosemicarbazone); H_2L^2 (**2**) (R = H, $R^1 = CH_3$, $R^2 = SCH_3$,the 2-hydroxyacetophenone Schiff base of *S*-methyldithiocarbazate); H_2L^3 (**3**) ($R = NO_2$, R^1 = H, $R^2 = SCH_3$, the 2-hydroxy-5-nitrobenzaldehyde Schiff base of *S*-methyldithiocarbazate); H_2L^4 (**4**) = the 2-hydroxy-5-nitrobenzaldehyde Schiff base of *S*-benzyldithiocarbazate ($R = NO_2$, R^1 = H, $R^2 = SCH_2C_6H_5$)

Experimental

Materials and methods

S-Methyldithiocarbazate [9] and *S*-benzyldithiocarbazate [10] were prepared according to published procedures. All other chemicals were purchased from Sigma-Aldrich and used without further purification. Electronic spectra were recorded on a Shimadzu UV-300 spectrophotometer. IR spectra were recorded as KBr discs on a Philips SP3100 spectrophotometer. ^{1}H NMR spectra were run in $CDCl_3$ or DMF-d_6 on a Bruker DPX300 FT NMR spectrometer using TMS as internal standard. Microanalyses for C, H and N were performed at the Micronalytical Laboratory of the National University of Singapore. ESI–MS spectra in either dichloromethane or methanol were recorded on a Finnigan LCQ mass spectrometer with a heated capillary temperature of 200 °C, spray voltage 4 kV and capillary voltage 34 V. FAB mass spectra were measured using 3-nitrobenzyl alcohol as a matrix by means of a Finnigan MAT95 mass spectrometer.

All the Schiff bases were washed with ethanol or methanol after filtration and dried in a vacuum desiccator over anhydrous silica gel.

Preparation of H_2L^1 (**1**)

Thiosemicarbazide (1.22 g) was dissolved in a 1:1 mixture of boiling absolute ethanol (10 mL) and dicholoromethane (10 mL). The resulting colorless solution turned yellow when a solution of 2-hydroxyacetophenone (1.2 mL) in hot methanol (24 mL) was added. After the addition of a few drops of 10 % HCl, the reaction mixture was heated under reflux for 3 h to obtain a yellow solution which was left to cool to room temperature. The resulting white precipitate was filtered off. Yield (1.78 g, 64 %) m.p. 173–175 °C; Anal. Calc. for $C_9H_{11}N_3OS.2H_2O$: C, 51.7; H, 5.3; N, 20.1. Found: C, 51.6; H, 5.0; N, 20.5 %. ^{1}H NMR δ 2.20 (3H, s, –CCH_3), 6.80–7.00 (br, 2H, NH_2), 8.50 (s, ArH), 8.30 (s, ArH),7.80 (s, ArH),7.20 (s, ArH), 8.70 (s,1H, NH), 10.65 (1H, s, OH); ^{13}C NMR (DMSO-d_6), δ 181.22 (CS), 157.42 (C–OH), 153.21 (CN), 130.82, 120.96, 120.12, 117.13, 110.84 (ArC), 17.50 (CH_3). ESI–MS: m/z = 210.0 ($[M + H]^+$).

Preparation of H_2L^2 (**2**) and H_2L^3 (**3**)

H_2L^2 was prepared by the method of Akbar Ali et al. [11]. Yield (0.98 g, 47 %) m.p. 169–171 °C, lit. 171–172 °C [11]; Anal. Calc. for $C_{10}H_{12}N_2OS_2$: C, 50.0; H, 5.0; N, 11.7. Found C, 50.1; H, 4.7; N, 11.7 %. ^{1}H NMR δ 11.40 (1H, s, OH), 10.0 (1H, s, NH), 6.95 (m, ArH), 7.34 (m, ArH), 2.41 (3H, s, CH_3), 2.67 (3H, s,SCH_3), 7.50 (d, ArH), 7.00 (d, ArH); ^{13}C NMR: δ 13.09 (CH_3), 17.99 (SCH_3), 199.31 (CS), 153.00 (C=N), 158.48 (C–OH), 132.26, 128.34, 118.34 (ArC); ESI–MS: m/z : 240.9 $[M + H]^+$.

H_2L^3 was prepared by the method of Akbar Ali et al. [12]. Yield (2.50 g, 77 %); M.p. 181–183 °C, lit. 185 °C [12]; Anal. Calc. for $C_9H_9N_3O_3S_2$: C, 39.8; H, 3.3; N, 15.5. Found C, 40.2; H, 3.2; N, 15.5 %. ^{1}H NMR δ 13.43 (1H, s, OH), 12.04 (1H, s, NH), 8.74 (s, CH=N), 8.68 (d, ArH), 8.20 (dd, ArH), 7.20 (1H, d, ArH), 2.64 (3H, s, SCH_3); ^{13}C NMR: δ 17.39 (SCH_3), 199.78 (CS), 142.66, 127.70, 126.63, 121.02, 117.83 (ArC), 117.51 (ArC); ESI–MS: m/z = 270.1, $[M + H]^+$.

Preparation of H_2L^4 (**4**)

To a boiling solution of 2-hydroxy-5-nitrobenzaldehyde (0.33 g, 1 mmol) in absolute ethanol (25 mL), a hot solution of *S*-benzyldithiocarbazate (0.41 g, 1 mmol) in the same solvent (25 mL) was added, giving a pale yellow solution. After the addition of a few drops of glacial acetic acid to the mixture, it was heated under reflux for 3 h. The volume of the reaction mixture was then reduced to half of its original by heating on a water bath, when yellow crystals were obtained. Yield (0.14 g, 41 %); m.p. 196–198 °C; Anal. Calc. for $C_{15}H_{11}N_3O_3S_2$: C, 51.9; H, 3.8; N, 12.6. Found: C, 51.5; H, 3.5; N, 12.1 %. ^{1}H NMR δ 13.49 (s, OH), 12.08 (s, NH), 8.76 (s, ArH), 8.65 (d, ArH), 8.20 (dd, ArH), 8.02 (1H, s, CH=N), 7.50 (d, ArH), 7.27–7.39 (m, ArH), 7.20 (d, ArH), 4.70 (s, SCH_2–). ^{13}C

Table 1 Crystallographic data for the compounds

Compound	$[NiL^2(PPh_3)].0.5CH_2Cl_2$	$[(Cu\ L^4(py)]$
Empirical formula	$C_{28.5}H_{26}ClN_2NiOPS_2$	$C_{20}H_{16}CuN_4O_3S_2$
Formula weight	601.76	488.03
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a (Å)	8.8073(4)	8.5974(16)
b (Å)	12.5239(6)	9.9938(19)
c (Å)	13.8526(7)	11.962(2)
α (°)	78.5440 (10)	101.621(3)
β (°)	71.4910 (10)	99.527(3)
γ (°)	70.125(10)	97.147(3)
Volume (Å^3, Z)	1355.56(11), 2	980.6(3), 2
Density (calculated) (Mg/m^3)	1.474	1.653
Absorption coefficient (mm^{-1})	1.053	1.358
F(000)	622	498
Crystal size (mm^3)	0.60 × 0.46 × 0.38	0.46 × 0.20 × 0.12
Theta range for data collection (°)	1.56–27.500	1.77–27.49
Reflections collected	17,7480	12,593
Independent reflections	6222 [*R*(int) = 0.0247]	4479 [*R*(int) = 0.0272]
Maximum and minimum transmission	0.7456 and 0.6519	0.8540 and 0.5738
Data/restraints/ parameters	6222/15/339	4479/0/271
Goodness-of-fit on F^2	1.042	1.148
Final *R* indices [$I > 2$sigma(I)], *R*1, w*R*2	0.0421, 0.1145	0.0416, 0.1018
R indices (all data); *R*1,w*R*2	0.0446, 0.1164	0.0447, 0.1037
Largest diff. peak and hole (e Å^{-3})	1.456 and −1.233	0.640 and −0.309

NMR: δ 38.82 (SCH_2), 117.51 (ArC), 198.01 (CS), 120.98–142.96 (m, ArC). ES–MS: m/z = 346.2 $[M + H]^+$.

Preparation of NiL and CuL

The complexes ML^x (M = Ni(II), Cu(II); $x = 1$–4) were prepared by mixing a boiling solution of the appropriate Schiff base (1 mmol) in a 1:1 mixture of absolute ethanol (25 mL) and dichloromethane (25 mL) with a hot solution of the metal(II) acetate (1 mmol) in methanol (ca. 50 mL) and heating the mixture on a water bath for ca. 5 min. The resulting precipitates was filtered off, washed with cold ethanol and dried in vacuo.

$[Ni(HL^1)_2]$ (5); Yield (0.1 g, 19 %); ^1H NMR δ 2.39 (s, CH_3), 4.68(s, 2H, NH_2), 6.91–7.61 (m, ArH), 11.06 (s, OH); Anal. Calc. for $C_{18}H_{18}N_6O_2S_2Ni$; C, 45.7; H, 3.4; N, 16.8. Found: C, 45.6; H, 4.6; N, 16.5 %. FAB–MS: 475.1 (52 %) $[M]^+$.

$[NiL^2]$ (6); Yield (0.3717 g, 48 %); Anal. Calc. for $C_{10}H_{10}N_2OS_2Ni$: C, 40.4; H, 3.3; N, 9.4. Found: C, 40.3; H, 4.0; N, 9.5 %. ESI–MS: m/z = 534.8, $[(NiL^2)_2 - Ni + 3H]^+$.

$[NiL^3]$ (7); Yield (0.46 g, 86 %); ^1H NMR δ 2.37 (s, SCH_3), 6.32 (CH=N), 8.03–8.65 (m, Ar–H); Anal. Calc. for $C_9H_7N_3O_3S_2Ni$: C, 33.0; H, 2.2; N, 12.8. Found: C, 32.1; H, 2.4; N, 12.5 %. FAB–MS: m/z: 597.2(44 %) $[(NiL^3)_2\text{–}Ni]^+$.

$[NiL^4].H_2O$ (8); Yield (0.59 g, 86 %); ^1H NMR: δ 8.57–9.15 (m, 3H, $O_2N\text{–}Ar\text{–}\underline{H}$), 7.06–7.58 (6H, Ar–H, N=C–H), 4.35–4.78 (d, 2H, CH_2); Anal. Calc for $C_{15}H_{11}N_3O_3S_2Ni{\cdot}H_2O$: C, 43.4; H, 2.9; N, 10.1. Found: C, 42.7; H, 3.1; N, 10.0 %. FAB–MS: m/z = 402.9(100 %), $[NiL^4]^+$; 806.0(7 %) $[(NiL^4)_2]^+$.

$CuL^1{\cdot}H_2O$ (9); Yield (0.055 g, 10 %); Anal. Calc. for $C_9H_9N_3OSCu{\cdot}H_2O$:C, 37.2; H, 3.8; N, 14.6. Found: C, 37.2; H, 3.4; N, 14.3 %; μ_{eff} (BM) = 0.54; ESI–MS: m/z = 544.7(25 %) $[(Cu\ L^1)_2 + H]^+$.

CuL^2 (**10**); Yield (0.45 g, 92 %); Anal. Calc. for $C_{10}H_{10}N_2OS_2Cu$: C, 39.8; H, 3.3; N, 9.3 .

Found: C, 40.0; H, 3.3; N, 9.2 %.; μ_{eff} (BM) = 0.59.

CuL^3 (**11**); Yield (0.05 g, 27 %); Anal. Calc. for $C_9H_7N_3O_3S_2Cu$: C, 32.5; H, 2.1; N, 12.6.; Found: C, 32.4; H, 2.2; N, 12.3 %; μ_{eff} (BM) = 0.56; FAB–MS: m/z = 331.8 $[CuL^3]^+$, m/z = 663.8 $[(CuL^3)_2]^+$.

CuL^4 (**12**);Yield (0.08 g, 20 %); Anal. Calc. for $C_{15}H_{11}N_3O_3S_2Cu$: C, 44.1; H, 2.7; N, 10.3. Found: C, 44.4; H, 3.1; N, 10.0 %.; μ_{eff} (BM) = 0.57; FAB–MS: m/z = 407.8 (CuL^4) (100 %); m/z = 817.8, $[(CuL^4)_2]^+$ (18 %).

Preparation of Co(L)(HL)

The complexes $[Co(L^x)(HL^x)]$ ($x = 1$–4) were prepared by the following general method. $Co(NO_3)_2{\cdot}6H_2O$ (1 mmol) was dissolved in a 1:1 mixture of methanol (6 mL) and 2,2-dimethoxypropane (6 mL) and mixed with a solution of the appropriate ligand (2 mmol) in hot acetonitrile (20 mL). The mixture was heated on a water bath for ca. 5 min then allowed to cool to room temperature. The resulting precipitate was filtered off, washed with methanol and dried in a desiccator over anhydrous silica gel.

$[Co(HL^1)(L^1)]$ (13); Yield (0.18 g, 86 %); ^1H NMR δ 1.56 (s, CH_3), 7.26 (m, ArH), 12.3 (s, NH). Anal. Calc. for $C_{18}H_{20}N_6S_2O_2Co.5H_2O$: C, 37.9; H, 4.1; N, 14.8. Found: C, 38.2; H, 3.5; N, 14.9 %. FAB–MS: m/z = 474.9 $[M]^+$.

$[Co(HL^2)(L^{2)}]$ (14); Yield (0.4902 g, 62 %); ^1H NMR δ 7.84 (1H, d, ArH), 7.16 (1H, tr, ArH), 6.97 (2H, m, ArH),

Table 2 Selected IR and UV–Vis absorption bands

Compound	IR assignments (cm^{-1})				UV–Vis bands (nm)	
	νO–H/ν(N–H)	ν(C=N)	ν(N–N)	ν(CSS)	Solvent	λ_{max} (log ε/mol^{-1}dm^{3}cm^{-1})
1	3391br	1618s	1106m	906m	DMSO	331(4.21), 302 (4.48)
2	3429br	1596s	1055m	954m	DMF	399(4.18), 294(3.30)
3	3428br	1606s	1062m	948s	DMF	469(4.17), 389 (3.5)
4	3511br	1602s	1053m	943m	DMF	471(4.26), 398 (3.69)
5	–	1595m	1102m	923m	Nujol	379, 268
6	–	1602m	1003m	945m	Nujol	370, 269
7	–	1603m	1102s	942m	Nujol	301, 384
8	–	1601m	1097s	949m	DMF	407(4.10), ca.380 sh
9	–	1598m	1155s	937m	DMF	580(3.53), 386(3.53), 354 (3.51)
10	–	1607m	1104s	947m	DMSO	610(3.20), 421(3.21), 413(4.21)
11	–	1608s	1104m	945m	Nujol	408, ca.354sh
12	–	1603m	1103m	930m	DMSO	632(3.14),466(4.25),401(3.46)
13	3290br	1595m	1041s	962m	Nujol	408, 350
14	3406br	1597m	1009s	945m	DMF	416(4.17), 351(3.88)
15	3490br	1558m	1029m	945m	DMF	415 (4.00), 289 (3.39)
16	3465br	1596s	1010s	951m	DMF	414(4.10), 361(3.85)
17	–	1561m	1003s	960m	DMSO	363(4.265), 277 (4.37)
18	–	1570s	1010s	950m	DMSO	632(3.26), 394(4.24), 302(4.22)

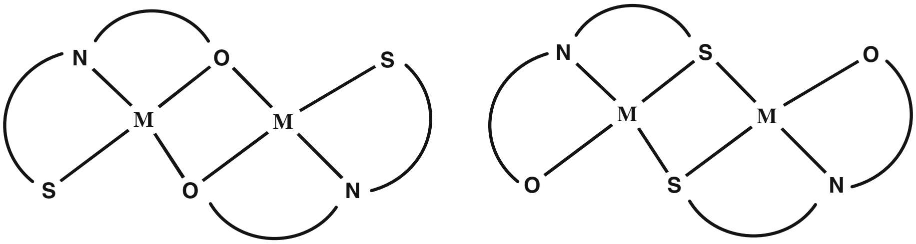

Fig. 2 Possible phenolic oxygen- and thiolate sulfur bridging in the 1:1 ML complexes

2.43 (3H, s, N=C–CH$_3$), 2.67 (3H, s, SCH$_3$). Anal. Calc. for C$_{20}$H$_{21}$N$_4$O$_2$S$_4$Co: C, 44.8; H, 3.9; N, 10.4. Found: C, 44.9; H, 3.8; N, 10.4 %. ESI–MS m/z: 536.9 (20 %), [M + H]$^+$.

[Co(HL^3)(L^3)] (15); Yield (0.055 g, 10 %); ^{1}H NMR δ 2.62 (s, SCH$_3$), 6.56–6.59 (HC=N), 7.84–8.96 (m, Ar–H). Anal. Calc. for C$_{18}$H$_{15}$N$_6$O$_6$S$_4$Co: C, 36.1; H, 2.5; N, 14.0. Found: C, 36.0; H, 2.5; N, 9.5. ESI–MS: m/z = 598.8(20 %), [M + H]$^+$.

[Co(HL^4)(L)] (16); Yield (0.17 g, 14 %); ^{1}H NMR δ 8.1 (s, Ar–H), 8.4 (m, ArH), 8.6 (s, ArH), 7.9 (m, 5H, ArH), 7.2 (s, N=C–H), 5.16 (s, CH$_2$S); Anal. Calc for C$_{30}$H$_{24}$N$_6$O$_6$S$_4$Co : C, 47.9; H, 3.2; N, 11.2; Found: C, 48.3; H, 3.3; N, 11.3 %. ESI–MS: 750.9 (20 %), [M + H]$^+$.

Preparation of [ML(py)] and (NiL^2(PPh$_3$)]

[NiL^2 (py)] and [CuL^4 (py)] were obtained by dissolving [ML^x] (M = Ni or Cu) (0.05 g; 0.12 mmol) in hot pyridine (10 mL) and letting the solution evaporate slowly at room temperature over a period of 3 days. The crystals that formed were filtered off, washed with cold ethanol and dried in a desiccator over anhydrous silica gel.

[NiL^2 (PPh$_3$)] was obtained by dissolving [NiL^2] (0.07 g; 0.25 mmol) in hot acetonitrile (100 mL) and adding triphenylphosphine (0.13 g; 0.5 mmol) to the solution. The complex crystallized out of the solution as diffraction quality crystals which were filtered off, washed with cold ethanol and dried in a desiccator over anhydrous silica gel.

[NiL^2(PPh$_3$)]0.0.5CH$_2$Cl$_2$ (**17**); Yield: 0.06 g; 40 %; Anal. Found: C, 58.3; H, 4.4; N, 4.9. Calc. for C$_{28.5}$H$_{26}$ClN$_2$NiOPS$_2$: C, 58.8; H, 4.5; N, 4.8 %. Diamagnetic.

[CuL^4 (py)] (**18**); Yield, 0.29 g; 50 %. Anal. Found: C, 49.2; H, 3.2; N, 11.8; S, 12.5; Calc. for C$_{20}$H$_{16}$CuN$_4$O$_3$S$_2$: C, 50.0; H, 3.3; N, 11.5; S, 13.1 %. μ(BM) = 1.73.

X-Ray crystallography

The diffraction data were obtained with a Bruker Smart CCD Diffractometer using graphite monochromated Mo K_α

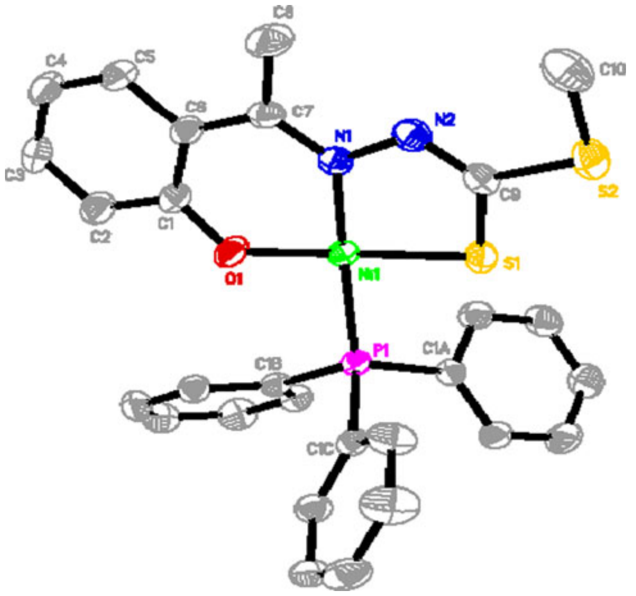

Fig. 3 ORTEP plot of [Ni $L^2(PPh_3)$]. Thermal ellipsoids are drawn at 30 % probability level

Table 3 Selected bond lengths (Å) and bond angles (°) of [$NiL^2(PPh_3)$] and [CuL^4(py)]

Bond	[NiL^2 (PPh_3)]	[CuL^4 (py)]
M(1)–O(1)	1.8247(17)	1.9186(18)
M(1)–S(1)	2.1451(7)	2.2802(8)
M(1)–N(1)	1.9019(19)	1.963(2)
M(1)–N(4/3)/P1	2.2177(2)	2.041(2)
N(1)–C(7)	1.314(3)	1.296(3)
N(1)–N(2)	1.413(3)	1.401(3)
C(8/9)–N(2)	1.278(3)	1.294(3)
C(8/9)–S(1)	1.734(3)	1.782(3)
C(8/9)–S(2)	1.749(3)	1.749(3)
Bond angles (°)		
O(1)–M(1)–N(1)	94.39(8)	91.62(8)
N(1)–M(1)–S(1)	88.03(6)	84.97(6)
O(1)-Ni(1)-N(3/4)/P1	89.28(6)	88.11(8)
N(1)–M(1)–N(3/4)/P1	172.01(6)	172.92(8)
N(3/4)/P1–M(1)–S(1)	88.62(7)	95.10(7)
O(1)–M(1)–S(1)	176.57(6)	176.28(6)

radiation (0.71073 Å) and operating in the $\omega - 2\theta$ mode within the range $2° < 2\theta < 55°$. An empirical absorption correction (ψ scans) and data reduction [13] were performed within the WINGX [14] suite programs. The structures were solved by direct methods with SHELXS86 and refined by full-matrix least-squares analysis with SHELXL97 [15]. Non-hydrogen atoms were refined with anisotropic thermal parameters, whereas H-atoms were included at estimated positions. Drawings of all molecules were produced with ORTEP3 [16] and PLATON [17]. A summary of the crystal data, structure solution and refinement parameters is given in Table 1. Crystallographic data in CIF format have been deposited at the Cambridge Crystallographic Data Centre. CCDC numbers 871667 and 871666 contain the supplementary crystallographic data for [$NiL^2(PPh_3)$] and [CuL^4(py)], respectively. These data are available free of charge from the Director, Cambridge Crystallographic Data Centre, 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).

Results and discussion

Compounds containing the thioamide functional group may exhibit thione–thiol tautomerism, and therefore, the present Schiff bases (Fig. 1) can exist either as the thione (Fig. 1a) or as the thiol (Fig. 1b) tautomeric forms, or as a mixture of both. The absence of a ν(SH) band at ca. 2,570 cm^{-1} in their IR spectra indicates that the thiol form is not present in the solid state. Their ^1H NMR spectra in DMSO-d_6 also do not exhibit any signal due to the SH proton at ca. 4.00 ppm, again suggesting that, even in a polar solvent like DMSO, the thiol tautomer is not present. However, in the presence of metal(II) acetate salts, they convert to the thiol tautomeric form, deprotonate and coordinate as doubly negatively charged tridentate ligands yielding 1:1 metal–ligand copper(II) and nickel(II) complexes and 1:2 metal–ligand cobalt(III) complexes. The IR spectral data together with assignments are shown in Table 2. The IR spectra of the free ligands exhibits a broad band in the range of 3,400–3,200 cm^{-1} whose envelope includes both the ν(O–H) and ν(N–H) bands. These bands are not present in the IR spectra of the nickel(II) and copper(II) complexes indicating that the ligands are coordinated to these metals in their doubly deprotonated forms. However, in the IR spectra of the cobalt(III) complexes a broad band in the range 3,200–3,500 cm^{-1} is observed, which may be attributed to the ν(O–H) of the monodeprotonated ligand.

The IR spectra of the complexes also indicate that bonding of the ligands to the metal occurs via the azomethine nitrogen atom since the ν(CN) and ν(NN) bands of the free ligands is shifted in the spectra of the complexes (Table 2). The presence of a ν(M–O) band at ca. 740 cm^{-1} in the spectra of the complexes supports coordination of the ligands via the phenolic oxygen [7].

The reactions of cobalt(II) nitrate in methanol with these Schiff bases do not give cobalt(II) complexes, but rather cobalt(III) complexes of general formula, [Co(HL)(L)] (HL = monodeprotonated form of the ligand and L = doubly deprotonated form of the ligand). These

Table 4 Comparison of selected bond distances in square-planar copper(II) and nickel(II) complexes

Complex[a]	M–S	M–$N_{azomethine}$	M–N_{py}/P	M–O	Ref.
[NiL^2(py)]	2.157	1.872	1.930	1.825	[11]
[NiL^2(PPh$_3$)]	2.1451	1.9019	2.2177	2.041	This work
[Ni(hapNMe tsc)(PPh$_3$)]	2.1260	1.878	2.1923	1.857	[29]
[Ni(atmtssA)]$_2$	2.129	1.855	–	1.851	[8]
[Ni(acacsme)(py)]	2.157	1.872	1.930	1.825	[30]
[Ni(sal$_4$Ph)(NH$_3$)]	2.166	1.844	1.921	1.858	[31]
[CuL^4(py)]	2.2802	1.963	2.041	1.9186	This work
[Cu(ttacsme)(py)]	2.239	1.9584	2.239	1.9316	[32]
[Cu(SMPD)(Im)]	2.251	1.944	2.029	1.95	[33]
[Cu(PNSB)(NO$_3$)]$_2$	2.2254	1.939	1.95	1.949	[33]
[Cu(mpsme)Cl]	2.227	1.952	–	2.060	[34]

[a] hapNMetsc = doubly deprotonated form of the 2-hydroxyacetophenone-^{4}*N*-methylthiosemicarbazone; atmttsA = doubly deprotonated form of the 2-hydroxy-5-methylacetophenone thiosemicarbazone; acacsme = dianionic form of the 2,4-pentanedione Schiff base of *S*-methyldithiocarbazate; sal$_4$Ph = doubly deprotonated form of the salicylaldehyde ^{4}*N*-phenylthiosemicarbazone; ttacsme = doubly deprotonated form of the thenoyltrifluoroacetone Schiff base of *S*-benzyldithiocarbazate; SMPD = deprotonated form of 2-pyridinecarboxaldehyde-*N*-oxide Schiff base of *S*-methyldithiocarbazate; ImH = imidazole); PNSB = deprotonated form of the 2-pyridinecarboxaldehyde Schiff base of *S*-benzyldithiocarbazate); mpsme = monodeprotonated form of the methylpyruvate Schiff base of *S*-methyldithiocarbazate

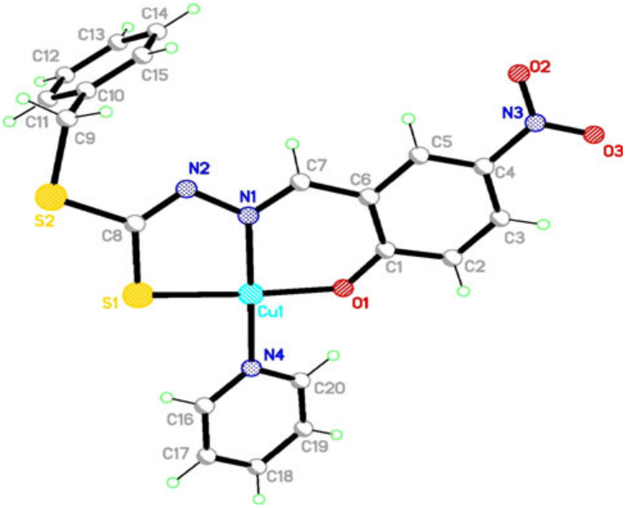

Fig. 4 ORTEP diagram of the molecular structure of [CuL^4(py)]. Thermal ellipsoids are drawn at 30 % probability level

complexes are diamagnetic, indicating that they are not cobalt(II) but low-spin cobalt(III). It seems that, while reacting with the ligands, the cobalt(II) is readily oxidized. Similar rapid oxidation of cobalt(II) in the presence of dithiocarbazate ligands to yield cobalt(III) complexes has been previously observed [18, 19].

The electronic spectra of the nickel(II) complexes (Table 2) exhibit a *d–d* band at around 696 nm. A band at ca. 400 nm is attributed to the S → Ni ligand-to-metal charge transfer (LMCT) transition. Similar LMCT bands have also been observed in the electronic spectra of other square-planar nickel(II) complexes of related sulfur–nitrogen ligands [20]. The electronic spectra of the copper(II) complexes in DMF display a *d–d* band as a shoulder at ca. 580 nm and intra-ligand bands in the regions 303–354 and 253–260 nm. A very strong band at ca. 420 nm in the electronic spectra of the copper(II) complexes is attributed to a S → Cu^{II} LMCT transition. Similar LMCT bands have also been observed in copper(II) complexes of the related Schiff bases derived from dithiocarbazates [21, 22] and thiosemicarbazones [23].

The diamagnetism of Ni(HL^1)$_2$, NiL^2 and NiL^4 is consistent with a four-coordinate square-planar structure. In contrast, NiL^3 exhibits a room-temperature magnetic moment of 2.54 B.M. indicating that it does not have a four-coordinate geometry. It probably has a trimeric or a polymeric structure involving oxygen and/or thiolate sulfur bridges between the nickel(II) centres. Unfortunately, in spite of repeated attempts, crystals of this complex suitable for X-ray diffraction analysis could not be obtained. However, its electrospray mass spectrum, although it does not show any ion attributable to an intact trimer or tetramer, exhibits a peak at m/z = 948, with a relative abundance of 100 % which may be assigned to the $[\mathrm{Ni_2L^3_3} + \mathrm{Na} + 2\mathrm{H}]^+$ ion, suggesting the presence of a tetramer.

The room-temperature magnetic moments of the CuL complexes are less than that expected for a 3d^9 metal ion in a magnetically dilute environment. Since these complexes contain dinegatively charged ONS tridentate ligands (as unambiguously proven by X-ray crystallography in the cases of [NiL^2(PPh$_3$)] and [CuL^4(py)] (see below) and the metal-to-ligand ratio in these complexes is 1:1, they must dimerize so that each metal(II) centre adopts at least a four-coordinate configuration. A phenolic oxygen-bridged

Table 5 Cyclic voltammetric data# for oxidation of the metal complexes in DMSO solution using 3-mm glassy carbon electrode and scan rate of 100 mV s^{-1}

Complex	E_{pa} (mV)	E_{pc} (mV)	ΔE_p (mV)	I_{pa} (μA)	I_{pc} (μA)	I_{pc}/I_{pa}	Remarks
6	956	*A*	–	17.1	*A*	–	Irreversible
7	747	*A*	–	4.6	*A*	–	Irreversible
8	174	150	24	0.8	0.5	0.62	Quasi-reversible
9	499	200	200	1.0	0.9	0.90	Quasi-reversible
10	852	*A*	–	8.7	*A*	–	Irreversible
11	496	263	233	2.5	1.3	0.52	Quasi-reversible
13	813	*A*	–	27.1	*A*	–	Irreversible
16	251	*A*	–	2.0	*A*	–	Irreversible

A indicates that no cathodic peak was observed in the reverse scan

Table 6 Cyclic voltammetric data# for reduction of the metal complexes in DMSO solution using 3-mm glassy carbon electrode and scan rate of 100 mV s^{-1}

Complex	E_{pc} (mV)	E_{pa} (mV)	ΔE_p (mV)	I_{pc} (μA)	I_{pa} (μA)	I_{pa}/I_{pc}	Remarks
5	−546	*B*	–	6.9	*B*	–	Irreversible
6	−608	−686	79	10.4	6.4	0.62	Quasi-reversible
7	−689	*B*	–	11.6	*B*	–	Irreversible
8	−601	−706	105	14.3	3.9	0.27	Quasi-reversible
12	−631	−740	109	12.4	4.3	0.35	Quasi-reversible
13	−409	*B*	–	5.7	*B*	–	Irreversible
15	−748	*B*	–	26	*B*	–	Irreversible

B indicates that no anodic peak was observed in the reverse scan

dimeric structure (Fig. 2) is very likely since iminothiolate sulfur atoms tend not to form bridges with another metal if a phenolic oxygen atom is also available for bridging [8, 24–26].

Bridging of the two nickel(II) and copper(II) centres in the proposed dimers by the phenolate oxygen is further supported by the presence of a medium intensity IR band at 720 cm^{-1} in the spectrum of the ML complexes, attributable to the M–O–M bridging vibration [27, 28]. This band is absent in the IR spectra of the free ligands as well as those of [ML(B)] (M = Ni(II) or Cu(II); L = L^2 or L^4; B = py or PPh_3), for which X-ray crystallographic structure determination has unequivocally established a monomeric, approximately square-planar structure.

The room-temperature magnetic moments of the complexes [CuL(py)] are in the range 0.54–0.59 B.M., lower than that required for a $3d^9$ configuration in a magnetically dilute environment. The ν(NH) band of the free ligand at 3,195 cm^{-1} is absent in the IR spectra of the complexes suggesting deprotonation of this ligand followed by coordination to the copper(II). The ν(C=N) band at 1,593 cm^{-1} is very little affected on coordination.

Crystal structures of [$NiL^2(PPh_3)$] and [CuL^4(py)]

Crystals of [NiL^2(py)] and [CuL^4(py)], suitable for X-ray analysis, were obtained by dissolving the ML complexes in a minimum amount of anhydrous pyridine at room temperature and letting the solution evaporate slowly over a period of 48 h. Crystals of [$NiL^2(PPh_3)$] were obtained during the preparation of the complex.

The X-ray crystal and molecular structure of [$NiL^2(PPh_3)$] is shown in Fig. 3, and bond lengths and angles are compiled in Table 3. The nickel(II) centre in this complex is four-coordinate, with the ligand coordinated in a dinegatively charged tridentate mode via the thiolate sulfur, the azomethane nitrogen atom and the phenolate oxygen atom. The fourth coordination position is occupied by the phosphorus atom of the triphenylphosphine ligand. The Ni–S, $Ni–N_{azomethine}$ and Ni–O bond distances (Table 3) of the complex are comparable and agree well with those observed in other related four-coordinate, approximately square-planar nickel(II) complexes of ONS ligands [8, 29–31]. The Ni–P bond length [2.2177(2)Å] in [$NiL^2(PPh_3)$] also agrees well with that of the related [Ni(hapNMetsc)PPh_3] (hapNMetsc = doubly deprotonated form of the 2-hydroxyacetophenone ^4N-methylthiosemicarbazone), whose structure has been reported by Ülküseven et al. [29]. For the purpose of comparison, bond lengths of some four-coordinate, approximately square-planar nickel(II) complexes of tridentate ONS ligands, for which X-ray structures are known, are compiled in Table 4. The data show that the Ni-donor atom distances in all these complexes are similar.

The crystal structure of [CuL^4(py)] is depicted in Fig. 4, and selected bond angles and lengths are given in Table 3.

The structure, like the [NiL^2(py)] complex [11], is also a four-coordinate monomeric complex in which the Schiff base is coordinated to the copper(II) as a dinegatively charged tridentate ligand via the phenoxyl oxygen, the azomethine nitrogen and the thiolate sulfur atoms, similar to that observed in the nickel(II) complex described above. The fourth coordination position is occupied by the pyridine nitrogen atom. The Cu–S, $Cu–N_{azomethine}$ and $Cu–N_{py}$ bond lengths, 2.2802(8), 1.963(2) and 2.041(2)Å, respectively, compare well with those reported for other four-coordinate, approximately square-planar copper(II) complexes whose structures have been determined by X-ray diffraction (see Table 4). Based on the data in Table 4, the present copper complex has the strongest Cu–O bond and weakest Cu–S bond. Similar to that observed in the nickel(II) complexes described above, the Cu–$N_{pyridine}$ bond distance (2.041(2)Å] in this complex is also longer than the Cu–$N_{azomethine}$ bond [(1.963(2)Å].

The stereochemistry around the copper atom may be considered as distorted square-planar, the distortion being more pronounced in this compound than in the corresponding nickel(II) complex. Thus, the angles N(1)–M(1)–S(1) [84.97(6)°] and N(4)–M(1)–S(1) [95.10(7)°] deviate by ca. 3° and 5°, respectively, from these required for an ideal square-planar geometry. The five- and six-membered chelate rings (S1–Cu1–N1–N2–C8) and (Cu1–O1–C1–C6–C7–N1), respectively, are approximately planar. The angle between the pyridine ring and the plane containing the chelate rings is 172.92(8)°.

An interesting aspect of the bond distances in all these complexes is that the M–$N_{pyridine}$ bonds are slightly longer than the M–$N_{azomethine}$ bonds. Since the pyridine nitrogen atom is thought to be more basic than the azomethine nitrogen atom, it might have been expected that the M–N_{py} bonds would be shorter than the M–$N_{azomethine}$ bonds. However, it has been pointed out by Curtis [35] that, in the case of nickel(II) complexes, the Ni–N distances not only depend on the nature of the nitrogen donor atoms, but also depend on the number of atoms in the chelate rings incorporating the Ni–N bonds.

Electrochemical studies

The electrochemical properties of the complexes were investigated and cyclic voltammetric data are summarized in Tables 5 and 6.

The general reaction involved in the oxidation process (Table 5) is assigned to one-electron oxidation of the metal centre, while the reduction (Table 6) also involves a one-electron metal-centred process. The observed cyclic voltammograms are characterized by either irreversibility or quasi-reversibility as seen by wide separation of anodic and cathodic peaks, as well as the absence, or marked reduction in the peak height, of the reverse scan. Moreover, there are no apparent trends observed in the electrochemical behavior of the three metals studied with respect to any ligand.

Conclusion

The 2-hydroxyacetophenone and 5-nitro-2-hydroxybenzaldehyde Schiff bases of *S*-methyl- and *S*-benzyldithiocarbazate behave as dinegatively charged ONS tridentate ligands yielding 1:1 metal–ligand nickel(II) and copper(II) complexes which are thought to be phenolic oxygen-bridged and di-, tri- or tetrameric in nature. The related 2-hydroxyacetophenonethiosemicarbazone, however, forms a bis-ligand nickel(II) complex but a mono-ligand copper(II) complex. In methanolic solution, the cobalt(II) centre is rapidly oxidized in the presence of these Schiff bases to give spin-paired bis-ligand six-coordinate cobalt(III) complexes. All the complexes studied here undergo one-electron oxidation–reduction reactions which are either irreversible or quasi-reversible.

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