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Note

Sugar hydrazone–metal complexes: transition- and non-transition metal complexes of monosaccharide *S*-alkylhydrazonecarbodithioates and dehydro-L-ascorbic acid bis(*S*-alkylhydrazonecarbodithioates)

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Dedicated to Professor Hassan Saad El Khadem on the occasion of his 80th birthday

Abstract

Copper(II), nickel(II) and palladium(II) complexes with *aldehydo*-D-arabinose-, L-arabinose-, D-galactose-, D-glucose- and D-mannose- *S*-methyl- and *S*-benzylhydrazonecarbodithioates were synthesized and characterized by elemental analyses, infrared and UV–Vis. In these complexes the *aldehydo* sugar hydrazone acts as a mononegative NS bidentate ligand. The reaction of Cu(II) chloride, however, proceeded with reduction, and copper(I) complexes were isolated. The hydrazone molecule in these Cu(I) complexes acts as neutral NS bidentate ligand. Dehydro-L-ascorbic acid bis(*S*-methylhydrazinecarbodithioate) and bis(hydrazinecarbothioamide), as well as their corresponding Cu(II), Ni(II), zinc(II) and Pd(II) complexes were prepared and characterized. Electrospray (ES) and field desorption (FD) mass spectra suggest that the Cu(II), Ni(II), and Pd(II) complexes are monomeric (square planar), whereas the Zn(II) are dimeric and pentacoordinate.

Keywords: Aldehydo-monosaccharide *S*-methyl and *S*-benzylhydrazonecarbodithioates; Ni(II), Cu(II), Cu(I) and Pd(II) complexes; dehydro-L-ascorbic acid bis(*S*-methylhydrazonecarbodithioate) and bis(hydrazonecarbothioamide); Ni(II), Cu(II), Pd(II) and Zn(II) complexes

1. Introduction

Condensation of *S*-methyl- and *S*-benzylhydrazinecarbodithioates with aldehydes or ketones affords the corresponding monohydrazones, which can react with transition- and non transition metal(II) salts, giving either cationic or neutral metal(II) bisligand complexes, where the hydrazone molecule acts, respectively, as neutral or mononegative NS bidentate ligands.[1–5] On the other hand, the corresponding bishydrazones derived from α-diketones or α-ketoaldehydes, were found to act as dinegative N_2S_2 ligands, and a series of their Cu(II), Ni(II), Pd(II), Pt(II), and Zn(II) complexes were prepared and characterized.[6–11] It was reported that metal(II) complexes derived from both NS bidentate hydrazones and N_2S_2 tetradentate bishydrazones possess significant antitumor activity as well as low cytotoxicity.[11–14] Most of the neutral metal(II) complexes screened for antitumor activities have been hydrophobic and are soluble in aprotic solvents rather than in water. These findings elicited our interest in introducing a polyhydroxyalkyl chain residue in the monohydrazone ligand, as in **1**, or a dehydro-L-ascorbic acid residue in the bishydrazones as in **2**, aiming to prepare a series of the corresponding hydrophilic metal(II) complexes which can be biologically tested as solutions in water and/or hydroxylic solvents.[11]

The synthesis of a series of *aldehydo*-sugar *S*-alkylhydrazonecarbodithioates (**1**) was previously reported[15] and these were characterized by elemental analyses, electron impact (EI), and fast atomic bombardment

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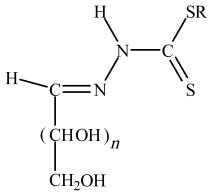
(FAB) mass spectra as well as infrared, ultraviolet, and NMR spectral techniques.[15] Cyclization to the corresponding thiadiazole acyclo C-nucleosides have been also studied.[15,16]

In this paper we describe the synthesis and characterization of some metal(II) complexes derived from **1a**–**1d.** The ligation properties of dehydro-L-ascorbic acid bis(*S*-methylhydrazonecarbodithioate) (**2a**) and bis(hydrazonecarbothioamide) (**2b**) towards transition- and non-transition metals(II) is also discussed.



(**a**)	3	D-*arabino*	CH_3
(**b**)	3	D-*arabino*	CH_3
(**c**)	4	D-*galacto*	CH_3
(**d**)	4	D-*gluco*	CH_3
(**e**)	4	D-*manno*	CH_3
(**f**)	3	D-*arabino*	$CH_2C_6H_5$
(**g**)	3	D-*galacto*	$CH_2C_6H_5$
(**h**)	4	D-*gluco*	$CH_2C_6H_5$
(**i**)	4	D-*manno*	$CH_2C_6H_5$

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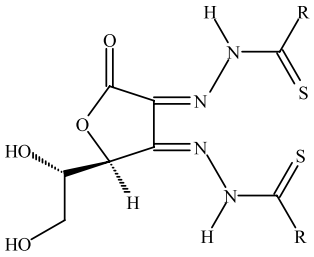
2. Results and discussion

2.1. Metal(II) complexes of aldehydo-sugar *S*-alkylhydrazone carbodithioates

The reaction of **1a**–**1j** with nickel(II) acetate in aqueous methanol afforded green complexes with the general formula $[Ni(L)_2]\cdot H_2O$ (**3a**–**3j**, M = Ni), where L refers to the mononegative hydrazone anion. Similarly, reaction of aqueous K_2PdCl_4 with **1a**–**1j** gave the corresponding $[Pd(L)_2]$ complexes (**3a**–**3j**, M = Pd). Attempts to prepare the monoligand complexes [M(L)Cl] or $[M(L)(CH_3COO)]$ (M = Ni or Pd) were unsuccessful. Copper(II) acetate, on the other hand, also reacts with two equivalents of **1a**–**1c** and **1f**–**1h** to give the bisligand complexes $[Cu(L)_2]$ (**3a**–**3c** and **3f**–**3J**, M = Cu) with no sign of Cu(II) reduction, whereas the reaction of **1d**, **1e**, **1i**, **and 1j** using either 1:1 or 1:2 molar ratios, proceeded with reduction of Cu(II) and eventually gave the corresponding Cu(I) complexes $[Cu(L)\cdot H_2O]$. Moreover, reaction of Cu(II) chloride in ethanol with **1a**–**1i** afforded the corresponding Cu(I) complexes of the general formula [Cu(HL)Cl] irrespective of the molar ratio used. Reduction of Cu(II) with aldehyde aroylhydrazones,[17,18] thiosemicarbazones,[19] *S*-methylhydrazonecarbodithioates,[19] and 1,5 thiocarbohydrazones[20] were previously reported and a tentative reduction mechanism was proposed. It is note worthy that reduction of either Cu(II) acetate or chloride with *aldehydo*-sugar *S*-methylhydrazonecarbodithioates proceeded with concomitant oxidation of the ethanol used as a solvent. This was confirmed by the positive dimedone test for the acetaldehyde produced. The hydrazone ligand remained unaffected, and no oxidative cyclization to the corresponding 2-(alditol-1-yl)-1,3,4-thiadiazoles was observed. The isolated Ni(II), Pd(II), and Cu(II) complexes together with their elemental analyses are listed in Table 1. The elemental analyses of the corresponding Cu(I) complexes are given in Table 2. The bisligand $[Ni(L)_2]\cdot H_2O$ and $[Cu(L)_2]$ complexes obtained were soluble in water, dimethyl sulfoxide, and *N,N*-dimethylformamide, sparingly soluble in methanol and ethanol, and insoluble in aromatic hydrocarbons and halogenated aliphatic solvents. The Pd(II) complexes, on the other hand, showed the same solubility pattern recorded for both Ni(II) and Cu(II) complexes, but had limited solubility in water. The Cu(I) complexes were insoluble in most organic solvents yet revealed limited solubility in Me_2SO.



(**a**) R = SCH_3

(**b**) R = NH_2

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The infrared spectra of the bisligand complexes $[M(L)_2]$ (**3a**–**3j** M=Ni(II), Cu(II), and Pd(II)) as well as the monoligand Cu(I) complexes $[Cu(L)]H_2O$ lacked absorptions caused by ν(N–H) and δ(N–H) vibrations, which appeared in the spectra of the metal-free ligands at approx 3200 and 1640 cm^{-1}, respectively.[15] This confirms the abstraction of the thiolimide proton, and the coordinated hydrazone acts as a mononegative anion. The spectra showed the ν(C=N) absorption at lower frequencies (1570 ± 10 cm^{-1}) relative to those previously reported for the metal-free ligands.[15] As a result of deprotonation of the thiolimide group and coordination of the metal(II) to the thiol sulfur, the thioamide III band [ν(C–N)] in the spectra of the metal(II) complexes appeared at higher energies, whereas the thioamide IV band [ν(C=S)] is shifted to lower frequencies (approx 780 ± 10) relative to those of the corresponding metal-free ligand. The IR spectral data indicated that the hydrazone molecule in the bisligand metal(II) complexes acted as a mononegative NS bidentate ligand (**3**). In contrast to the IR spectra of $M(L)_2$ (M = Ni, Cu, and Pd) and $[Cu(L)]H_2O$ complexes, the spectra of [Cu(HL)Cl] showed both ν(N–H) and δ(N–H) at 3200 and 1640 cm^{-1}, respectively. The ν(C=N) absorption appeared at lower frequencies (approx 1560 cm^{-1}) relative to the corresponding metal-free ligands, implying that the hydrazone molecule in this type of Cu(I) complex also behaved as a neutral NS bidentate ligand.

Table 1
Melting points and elemental analyses of Ni(II), Cu(II), and Pd(II) complexes derived from *aldehydo*-sugar *S*-alkylhydrazonecarbodithioates

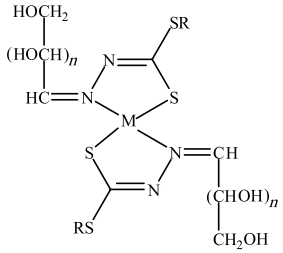
Compound	M	Yield (%)	Mp (°C) (decomp)	Found (Calcd) (%)			
				C	H	N	M
3a	Ni	85	> 300	30.0 (29.7)	4.9 (4.6)	9.9 (9.9)	10.4 (10.4)
3b	Ni	85	210–212	30.0 (29.7)	5.0 (4.6)	9.9 (9.9)	10.5 (10.4)
3c	Ni	82	200–203	30.9 (30.7)	4.9 (4.8)	8.6 (9.0)	9.7 (9.4)
3d	Ni	80	190–193	31.2 (30.7)	4.8 (4.8)	8.8 (9.0)	9.8 (9.4)
3e	Ni	75	200–202	31.1 (30.7)	5.1 (4.8)	9.2 (9.0)	9.6 (9.4)
3f [a]	Ni	76	> 300	42.1 (42.5)	5.2 (4.9)	7.5 (7.6)	8.5 (8.0)
3g [a]	Ni	76	180–183	42.4 (42.5)	4.8 (4.9)	7.9 (7.6)	8.2 (8.0)
3h [a]	Ni	70	180–183	42.1 (42.3)	5.0 (5.1)	7.3 (7.0)	7.8 (7.4)
3i [a]	Ni	60	175–178	42.2 (42.3)	4.5 (5.1)	7.3 (7.0)	8.0 (7.4)
3j [a]	Ni	65	> 300	41.8 (42.3)	4.7 (5.1)	6.8 (7.0)	8.0 (7.4)
3a	Cu	85	175–178	29.6 (29.5)	4.7 (4.6)	10.0 (9.8)	11.3 (11.1)
3b	Cu	85	172–175	29.5 (29.5)	5.0 (4.6)	9.9 (9.8)	10.9 (11.1)
3c	Cu	85	170–173	30.8 (30.5)	5.2 (4.8)	9.3 (8.9)	10.1 (10.1)
3a	Pd	50	210–212	27.0 (27.4)	5.0 (4.3)	10.0 (9.1)	16.9 (17.4)
3b	Pd	45	215–216	27.1 (27.4)	4.5 (4.3)	9.5 (9.1)	17.6 (17.4)
3c	Pd	50	225–230	29.0 (28.6)	4.9 (4.5)	8.6 (8.3)	15.3 (15.8)
3d	Pd	40	250–255	28.3 (28.6)	4.2 (4.5)	8.4 (8.3)	15.4 (15.8)
3e	Pd	55	260–262	28.7(28.6)	4.3 (4.5)	8.3 (8.3)	16.3 (15.8)
3f	Pd	50	195–200	40.4 (40.8)	4.3 (4.5)	7.4 (7.3)	13.5 (13.9)
3g	Pd	45	200–205	40.3 (40.8)	5.0 (4.5)	7.6 (7.3)	13.6 (13.9)
3h	Pd	55	170–173	41.0 (40.8)	4.8 (4.6)	6.8 (6.8)	13.2 (12.9)
3i	Pd	50	185–190	41.2 (40.8)	5.0 (4.6)	7.1 (6.8)	12.6 (12.9)
3j	Pd	50	190–193	40.6 (40.8)	4.3 (4.6)	7.2 (6.8)	12.5 (12.9)

[a] Isolated as monohydrates.

The Nujol mull electronic spectra of solid Ni(II) complexes showed an intense band at approx 430 nm, originating from a metal to ligand charge-transfer transition (LMCT) in addition to a broad unresolved absorption centered at 650 nm due to different metal to ligand charge transfer transitions (MLCT). The recorded spectra are typical of square planar Ni(II) complexes.[21] The diamagnetism of the solid Ni(II)

Table 2
Melting points and elemental analyses of Cu(I) complexes, $[Cu(L)]\cdot H_2O$ and [Cu(HL)Cl], derived from *aldehydo*-sugar *S*-alkylhydrazonecarbodithioates

Sugar residue	*n*	R	Yield (%)	Mp (°C) (decomp)	Found (Calcd) (%)			
					C	H	N	M
(i) $[Cu(L)]\cdot H_2O$								
D-*gluco*	4	CH_3	58	200–202	26.0 (26.3)	4.7 (4.7)	7.3 (7.7)	17.0 (17.4)
D-*manno*	4	CH_3	52	> 250	26.2 (26.3)	5.2 (4.7)	7.5 (7.7)	17.3 (17.4)
(ii) [Cu(HL)Cl]								
D-*arabino*	3	CH_3	67	> 250	23.4 (23.8)	4.2 (4.0)	8.1 (7.9)	17.6 (18.0)
L-*arabino*	3	CH_3	60	> 250	23.3 (23.8)	3.9 (4.0)	7.6 (7.9)	17.8 (18.0)
D-*galacto*	4	CH_3	60	> 250	25.4 (25.0)	4.0 (4.2)	7.1 (7.3)	16.5 (16.6)
D-*gluco*	4	CH_3	65	> 250	25.3 (25.0)	3.9 (4.2)	7.0 (7.3)	16.4 (16.6)
D-*manno*	4	CH_3	63	> 250	25.3 (25.0)	4.0 (4.2)	7.2 (7.3)	16.5 (16.6)
D-*arabino*	3	$CH_2C_6H_5$	63	> 250	36.5 (36.4)	4.0 (4.2)	6.2 (6.5)	14.3 (14.8)
L-*arabino*	3	$CH_2C_6H_5$	60	> 250	36.2 (36.4)	3.8 (4.2)	6.4 (6.5)	14.9 (14.8)
D-*galacto*	4	$CH_2C_6H_5$	60	> 250	36.3 (36.6)	4.2 (4.4)	6.3 (6.1)	13.5 (13.8)
D-*gluco*	4	$CH_2C_6H_5$	60	> 250	36.2 (36.6)	4.0 (4.4)	6.3 (6.1)	13.5 (13.8)
D-*manno*	4	$CH_2C_6H_5$	60	> 250	36.4 (36.6)	4.6 (4.4)	6.2 (6.1)	13.6 (13.8)



(**a**)	3	D-*arabino*	CH_3
(**b**)	3	L-*arabino*	CH_3
(**c**)	4	D-*galacto*	CH_3
(**d**)	4	D-*gluco*	CH_3
(**e**)	4	D-*manno*	CH_3
(**f**)	3	D-*arabino*	$CH_2C_6H_5$
(**g**)	3	D-*galacto*	$CH_2C_6H_5$
(**h**)	4	D-*gluco*	$CH_2C_6H_5$
(**i**)	4	D-*manno*	$CH_2C_6H_5$

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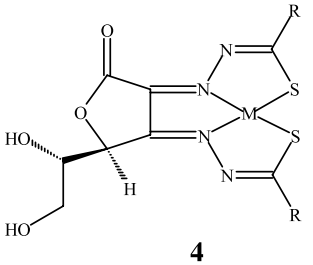
complexes confirmed this assignment. However, in methanol or Me_2SO, these Ni(II) complexes were found to be paramagnetic. The measured magnetic moments, using the Evans method,[22] ($\mu_{eff} = 2.8–3.0\ \mu_\beta$), are within the range reported for high-spin octahedral Ni(II) complexes. This behavior suggests that, in coordinating solvents, the central Ni(II) in solid square-planar complexes $[Ni(L)_2]$ can expand its coordination number, giving a solvated octahedral species $[Ni(L)_2(Solv)_2]$.[23] The UV–Vis electronic absorption spectra recorded for the Ni(II) complexes in methanol or Me_2SO (Table 3), showed a series of bands within the range 270–340 nm due to the different inter-ligand (L–L*) transition of the coordinated mononegative hydrazone anion. The spectra also showed an intense absorption due to ligand to metal charge-transfer transition (LMCT) (approx 430 nm), in addition to absorptions from d–d transitions at 540–560, 640–650, 880–900 nm, respectively due to $^3A_{2g}$-$^3T_{1g}$(p), $^3A_{2g}$-$^3T_{2g}$(F), and $^3A_{2g}$-$^3T_{2g}$ transitions in an idealized octahedral environment.[23] The spectra of the Pd(II) complexes in solution and in solid state suggest a square planar environment around the central metal ion. This is in agreement with the diamagnetic behavior of these complexes. The Cu(I) complexes $[Cu(L)]\cdot H_2O$ and [Cu(L)Cl] are also diamagnetic and their electronic absorption spectra did not show any absorption due to d–d transitions. The Cu(II) complexes, on the other hand, are paramagnetic and showed magnetic moments ($\mu = 1.80 \pm 0.02\ \mu_\beta$), within the range reported for magnetically diluted Cu(II) complexes.[24] Their solution electronic spectra in methanol are diagnostic of distorted octahedral species $[Cu(L)_2(MeOH)_2]$.[24]

2.2. Metal (II) complexes with dehydro-L-ascorbic acid bis(*S*-methyl hydrazonecarbodithioate) (2a) and bis(hydrazonecarbothioamide) (2b)

Reaction of an aqueous solution of dehydro-L-ascorbic acid with two equivalents of *S*-methylhydrazinecarbodithioate or hydrazinecarbothioamide afforded the corresponding bishydrazones **2a** and **2b**. The FAB mass spectra of **2a** and **2b** showed their molecular ion peaks at $m/z = 382$ and 320, respectively. The IR spectrum of **2**a displayed absorptions due to ν(OH), ν(NH), lactone ν(C=O), ν(C=N), ν(C=S), and $\nu(CSSCH_3)$. In addition, the spectrum of **2b** showed absorptions due to $\nu_{asym}(NH_2)$ and $\nu_{sym}(NH_2)$ vibrations of the thiosemicarbazide residue. The ^{1}H NMR spectra of **2a** and **2b** displayed signals due to NH, NH_2, CH=N, and the alditolyl chain H and OH protons. As with other bis(*S*-methylhydrazonecarbodithioate) Schiff bases derived from unsymmetrical α-ketoaldehydes or α-diketones, the ^{1}H NMR spectrum of **1a** showed two SCH_3 signals at 2.61 and 2.70 ppm.[25]

The reactions of **2a** and **2b** with Cu(II), Ni(II), or Zn(II) acetate in methanol afforded the monoligand complexes (**4a** and **4b**, M = Ni, Cu and Zn), as shown in Table 4. Similarly, the reaction of aqueous K_2PdCl_4 with **1a** and **1b** gave the corresponding Pd(II) complexes (**4a** and **4b**, M = Pd).

The IR spectra of the metal(II) complexes prepared lacked absorptions for ν(N–H) and δ(N–H), which appeared in the spectra of the metal-free ligands at approx 3200 and 1640 cm^{-1}, respectively. This indicated the deprotonation of the two thiolimide residues of the bishydrazone upon complex formation. The lactone absorbtion, ν(C=O), in the spectra of **4a** and **4b** (M = Ni, Cu, Pd, and Zn) appeared at almost the same position as in the uncoordinated bishydrazone. The ν(C=N) absorption is shifted from approx 1600 cm^{-1} in the spectra of **2a** and **2b** to lower frequencies at (approx 1550 cm^{-1}) in the spectra of the corresponding metal(II) complexes, implying the coordination of the imine nitrogens. The thioamide III band, which is mainly due to ν(C–N), is shifted to higher frequencies whereas the thioamide IV [ν(C–S)] band appeared at much lower frequencies relative to that of the corresponding metal-free ligand.[26–28] It is thus apparent from the stoichiometry, and IR spectral data of these metal(II) complexes that both **2a** and **2b** act as dinegative N_2S_2 tetradentate ligands.



(**a**) R = SCH_3
(**b**) R = NH_2

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The UV–Vis absorption spectra of the Zn(II) complexes **4a** and **4b** were dominated by the spectra of the highly conjugated dinegative anion of **2a** or **2b**. The spectra show absorption bands that extended from 270 to 480 nm, in agreement with the behavior highly conjugated systems.[6] In principle, Zn(II) favors either tetrahedral or square pyramidal coordination. With rigid, highly conjugated N_2S_2 tetradentate ligands such as **2a** or **2b,** which can impose square planar coordination around the central Zn(II), tetrahedral coordination

Table 3
UV–Vis spectra of Ni(II), Cu(II), and Pd(II) complexes derived from *aldehydo*-sugar *S*-alkylhydrazonecarbodithioate in methanol

Compound	M	λ_{max} nm (log ε)		
		L–L*	LMCT	d–d
3a	Ni	275 (4.6), 320 sh	430 (3.6)	588 (1.5), 650 sh, 888 (1.5)
3b	Ni	275 (4.6), 315 sh	430 (3.6)	575 (1.6), 650 sh, 880 (1.5)
3c	Ni	275 (4.8). 320 sh	435 (3.7)	665 (1.8), 880 sh
3d	Ni	275 (4.5), 310 sh	435 (3.6)	590 (1.5), 880 (1.8)
3e	Ni	273 (4.5), 340 (4.0)	430 (3.6)	520 sh, 645 sh
3a	Ni	278 (4.6), 340 (4.0)	435 (3.9)	650 sh, 880 (1.7)
3b	Ni	275 (4.3), 330 sh	430 (3.8)	650 (1.4), 875 (1.6)
3c	Ni	275 (4.5), 325 sh	435 (3.5)	650 (1.4), 875 (1.5)
3d	Ni	275 (4.6), 330 sh	435 (3.8)	565 sh, 650 (1.6), 890 (1.4)
3e	Ni	275 (4.4)	435 (3.5)	650 (1.5), 885 (1.5)
3a	Cu	270 (4.5), 310 sh	430 (3.5)	770 (2.1), 890 (2.0)
3b	Cu	275 (4.3), 340 sh	430 (3.2)	740 (2.2), 900 (2.0)
3c	Cu	270 (4.5)		
3a	Pd	270 (4.5), 325 sh	400 (2.5)	
3b	Pd	270 (4.6)	420 (2.1)	
3c	Pd	280 (4.5), 340 sh	435 (2.0)	
3d	Pd	280 (4.5), 340 sh	435 (2.0)	
3e	Pd	270 (4.5)	435 (2.0)	
3a	Pd	270 (4.0), 340 sh	430 (2.0)	
3b	Pd	280 (4.3)	425 (2.3)	
3c	Pd	270 (4.5)	435 (2.5)	
3d	Pd	270 (4.4)	435 (2.3)	
3e	Pd	290 (4.6), 350 sh	440 (3.5)	

is energetically unfavored, yet square pyramidal coordination can be achieved either through dimerization or via additional coordination with a neutral monodentate ligand.[6,7 29] The FD and ES mass spectra of the Zn(II) complexes (**4a** and **4b**, M = Zn) showed the molecular ion [M^+], as the base peaks, at $m/z = 890$ and 767, respectively, corresponding to the dimeric species $[\{Zn(L')\}_2]^+$ where L′ refers to the bishydrazone dianion. Similar dimeric structures, where Zn(II) is in a square pyramidal environment were previously proposed for Zn(II) complexes derived from α-ketoaldehyde or α-diketone bis-*S*-alkylhydrazonecarbodithioates as well as bis(thiosemicarbazones).[7,29] The dimeric structure of these complexes was confirmed by X-ray structural analyses or Zn K-edge XANES studies.[29] Apart from the Zn(II) complexes (**4a** and **4b**, M = Zn), the corresponding Ni(II), Cu(II), and Pd(II) complexes exist as monomeric species [ML′]. This is evident from the FD and ES mass spectra of these complexes, which showed the monomeric molecular ion peaks $[ML']^+$ rather than dimeric or cluster ions of higher nuclearity.

The Ni(II) complexes **4a** and **4b** (M = Ni) are diamagnetic both in the solid state and in Me_2SO

Table 4
Elemental analyses of Zn(II), Ni(II), Cu(II), and Pd(II) complexes derived from dehydro-L-ascorbic acid *S*-alkylhydrazonecarbodithioate and hydrazonecarbothioamide

Complex	M	Mp (°C)	Found (Calcd) (%)			
			C	H	N	M
4a	Zn	> 300	26.4 (26.9)	2.9 (2.7)	12.5 (12.6)	15.2 (14.7)
4b	Zn	> 300	25.2 (25.0)	2.5 (2.6)	21.5 (12.9)	17.5 (17.1)
4a	Ni	> 300	27.3 (27.35)	2.4 (2.75)	12.5 (12.8)	13.1 (13.4)
4b	Ni	210–212	25.8 (25.4)	3.1 (2.7)	21.8 (22.8)	15.3 (15.8)
4a	Cu	> 300	26.4 (26.0)	3.2 (3.0)	12.5 (12.1)	14.3 (13.8)
4b	Cu	215–218	24.9 (25.2)	3.01(2.6)	21.6 (22.0)	16.9 (16.7)
4a	Pd	> 300	25.0 (24.7)	2.8 (2.5)	11.1 (11.5)	21.5 (21.9)

solutions, indicating a square planar arrangement around the Ni(II) ion. The UV–Vis spectra of Ni(II) complexes (**4a** and **4b**, M = Ni) (Table 3), showed a series of bands between 260 and 490 nm originating from the different interligand (L–L*) transitions. The extended conjugation, as well as the p-π interaction within the tricyclic NiS_2N_2 chromophore, decreases the energy difference between the unfilled ligand π* orbitals (LUMO) and the filled Ni(II) d-orbitals, and the intense bands at 560, 590, and 654 nm can be related to the different MLCT [d(M)-π*(L)] transitions rather than d–d transitions. The LMCT band(s) expected to appear at 400–430 nm in the spectra of Ni(II) complexes are, most probably, hidden under the absorptions of L–L* transitions. The Pd(II) complexes **4a** and **4b** (M = Pd) showed the MLCT bands at lower energies relative to those recorded for the corresponding Ni(II) complexes, and square planar structure can be adopted for these complexes. The room temperature magnetic moments of the Cu(II) complexes (**4a** and **4b**, M = Cu) are within the range reported for monomeric Cu(II) complexes.[24] The electronic absorption spectra of these complexes suggested a square planar structure.

3. Experimental

3.1. General methods

Melting points (mp) (uncorrected) were determined using a Mel-Temp I apparatus. Elemental microanalyses (C, H, N) were performed at the Microanalytical Lab of Cairo University, Cairo, Egypt. IR spectra were recorded on Unicam SP-1025 or Perkin–Elmer 1430 data-system spectrophotometers. UV–Vis absorption spectra were acquired as Nujol mulls or MeOH solutions with Cary 17 or Perkin–Elmer Lamda 4B spectrophotometers. NMR (^{1}H and ^{13}C) spectra were obtained with a Bruker WM 400 (400 MHz) instrument at Phillips University, Marburg, Germany. EI mass spectra were obtained with a Dupont 21–419 spectrometer, and electron spray (ES) mass spectra were performed with a Hewlett–Packard 1100 MSD spectrometer for methanol or acetonitrile solutions. Magnetic susceptibilities of the solid metal complexes were measured at rt using a Faraday type of magnetometer with a computer controlled Cahn D-200 microbalance. Magnetic moments of solutions were measured using the Evans method.[22]

3.2. *aldehydo*-Sugar *S*-methyl- (1a–1e) and *S*-benzylhydrazonecarbodithioates (1f–1j)

These compounds were prepared as previously described.[15]

3.3. Bis(*aldehydo*-sugar-*S*-methyl- and *S*-benzylhydrazonatecarbodithioate) metal(II) complexes (3a–3j, M = Ni, Cu and Pd)

To a suspension of the appropriate *aldehydo*-sugar *S*-methyl- (**1a–1e**) or *S*-benzylhydrazonecarbodithioate (**1f–1j**) (2.0 mmol) in MeOH (10 mL), a soln of Cu(II) or Ni(II) acetate (0.01 mmol) in MeOH (30 mL) was added dropwise with stirring. The mixture was boiled under reflux for 30 min, and then left at room temperature for 24 h. The separated product was filtered, off washed with Et_2O and then dried. An aqueous soln of K_2PdCl_4 was used instead the of metal(II) acetate to obtain the corresponding Pd(II) complexes. The prepared Ni(II), Cu(II), and Pd(II) complexes, their % yield, mp, and elemental analyses are listed in Table 1.

3.4. Dehydro-L-ascorbic acid bis(*S*-methylhydrazonecarbodithioate) (2a)

A soln of *S*-methylhydrazinecarbodithioate (0.02 mol) in MeOH (20 mL) was treated with a soln of dehydro-L-ascorbic acid (0.01 mol) in water (20 mL) and the mixture was heated under reflux for 30 min. The red product that separated was filtered off, washed with Et_2O and dried; yield 75%; mp 214–216 °C; λ_{max}(MeOH): 223, 290, and 363 nm; IR ν_{max}(KBr): 3360 (OH), 1780 (COO), 1606, 1554 (C=N), 1320 (thioamide III band), 1178, 1156, 1080, 1042 and 920 (HNCSSR) and 830 cm^{-1} (thioamide IV band); ^{1}H NMR (Me_2SO-d_6): δ 13.15 (s, 1 H, exchangeable NH), 5.60 (s, 1 H, H-4), 5.30 (s, 1 H, H-5), 4.50 (d, 1 H, exchangable OH), 4.15–3.85 (m, 2 H, CH_2) and 2.71, 2.61 ppm (2 s, 6 H, 2 SCH_3); ^{13}C NMR (Me_2SO-d_6): δ 203.64, 174.67 (2 C=S), 1630, 159.10 (2 C=N), 129.35 (C=O), 78.03 (C-4), 69.53, 61.34 (C-6), 17.81, 16.64 ppm (2 SCH_3); FD mass spectra: *m*/*z* 382; Anal. Calcd for $C_{10}H_{14}N_4O_4S_4$: C, 31.4; H, 3.7; N, 14.7. Found: C, 30.9; H, 4.0; N, 14.5.

3.5. Dehydro-L-ascorbic acid bis(hydrazonecarbothioamide) (2b)

A soln of thiosemicarbazide (0.02 mol) in MeOH (40 mL) was added to a soln of dehydro-L-ascorbic acid (0.01 mol) in water (10 mL). The mixture was heated under reflux for 30 min. The product formed was filtered off and crystallized from MeOH–water to give **2b** as orange crystals; yield 80%; mp 230–232 °C; λ_{max}(MeOH): 234, 260, and 405 nm; IR: 3342 (OH), 3228 (NH), 1790 (COO), 1597, 1545 (C=N), 1300 (thioamide III band), 1172, 1109, 1071, 1070 (HN(CS)NH_2, and 820 cm^{-1} (thioamide VI band); ^{1}H NMR (Me_2SO-d_6): δ (ppm), 12.15 (s, exchangeable NH), 855 (s, 2 H, exchangeable), 5.55 (s, 1 H, H-4), 5.20

(1 H, H-5), 5.0–4.55 (m, 2 H, exchangeable 2 OH) and 4.15–3.80 (m, 2 H, H-6); FD mass spectra: *m/z* 320; Anal. Calcd for $C_8H_{12}N_6O_4S_2$: C, 30.0; H, 3.8; N, 26.3. Found: C, 30.4; H, 4.1; N, 26.7.

3.6. Dehydro-L-ascorbic acid bis(*S*-methylhydrazonatocarbodithioate) metal(II) complexes (4a, M = Ni, Cu, Zn and Pd)

A soln of the Cu(II), Ni(II), or Zn(II) acetate (1.0 mmol) in MeOH (20 mL) was added dropwise with stirring to a suspension of **2a** (1.0 mmol) in MeOH (20 mL). The turbid reaction mixture was treated with two drops of AcOH then heated under reflux for 30 min. The clear soln obtained was concentrated to one half its volume and then kept at ambient temperature for 24 h. The isolated complex was filtered off, washed with Et_2O, and then dried. The corresponding Pd(II) complex was similarly prepared using K_2PdCl_4. Yield, mp, and elemental analyses of the prepared complexes are listed in Table 4.

3.7. Dehydro-L-ascorbic acid bis(hydrazonatocarbothioamide) metal(II) complexes (4b, M = Ni, Cu, Zn, and Pd)

Metal(II) complexes derived from from **2b** (M = Ni, Cu, Zn, and Pd) were prepared as previously described for **4a** meta(II) complexes. The prepared metal(II) complexes are included in Table 4.

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