Articles

Copper(II), Nickel(II) and Palladium(II) Complexes of 2-Oximino-3-thiosemicarbazone-2,3-butanedione

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Received March 18, 2003

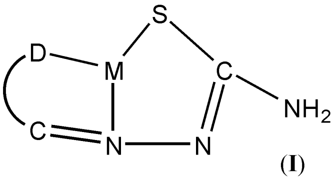
A new tridentate ligand incorporating a monoxime and thiosemi-carbozone moieties has been synthesized. Its copper(II), nickel(II) and palladium(II) complexes have been prepared and characteirzed by physical and spectral methods. Elemental analyses and spectroscopic data of the metal complexes are consistent with the formation of a mononuclear copper(II) complex and binuclear complex with both nickel(II) and palladium(II). In the copper(II) complex the fourth coordination site is occupied by nitrate ion. In the binculear complexes the fourth coordination site is occupied by the deprotonated oxime oxygen of the ligand coordinated to the other metal.

Key Words : 2-Oximino-3-thiosemicarbazone-2,3-butanedione, Copper(II), Nickel(II), Palladium(II), Complexes

Introduction

During the last decade, great attention has been given to the area of multinuclear complexes with extended bridges,[1,2] mainly because of the need to gain insight into the electron transfer pathways in biological systems.[3] Several metal complexes have been synthesized in order to obtain detailed information about the exchange mechanism in these systems since biomolecules with multinuclear metal centres are known to be involved in important biological processes such as catalysis.[4,5] The homomultinuclear copper complexes of macrocyclic or macroacyclic ligands have been reported to undergo redox reactions similar to the active sites in several metalloproteins and has also proved to be efficient catalysts under mild conditions.[6-8] Complexes with mixed oxime and Schiff base ligands coordinated to Co(III) have been reported to show superior electrochemical properties and biological behavior, as vitamin B_{12} mimics, than do the complexes with either oxime or Schiff base ligands alone.[9,10]

The chemistry of transition metal complexes of thiosemicarbazone has been investigated extensively. These studies were largely driven by their biological properties.[11,12] Thiosemicarbazone usually coordinates to a metal ion either by the neutral thione form or by the anionic thiolate form.[11]



(I)

However, incorporation of a third donor site (D) into these thiosemicarbazone ligands linked to the carbonylic carbon *via* one or two intervening atoms usually results in D,N,S tricoordination[11] as shown in (**I**).

Though, the thiosemicarbazone moiety of the free tridentate ligand (I) exists in the thione form,[13] it is known to bind as a dianionic tridentate D,N,S donors.[14]

The present paper describes the syntheses and characterization of the new ligand 2-oximino-3-thiosemicarbazone, 2,3-butanedione (H_2otscb) and its new complexes with Cu(II), Ni(II) and Pd(II). The properties of the complexes were investigated by magnetic, cyclic voltammetry and spectroscopic methods. The study of oxime metal chelates are of special interest owing to their biological activities and semi conducting properties.[15]

Experimental Section

Preparation of ligand and complexes:

Schiff base 2-oximino-3-thiosemicarbazone-2,3-butanedione, (H_2otscb), (II): 2,3-butanedione monoxime (8.1 g, 80 mmol) and thiosemicarbazide (7.3 g, 80 mmol) were mixed in 85% EtOH/H_2O (250 mL). The mixture was boiled under reflux with stirring for 4 h. The solution was reduced to half of its original volume on a water bath and the resulting white solid was collected by suction filteration and washed with cold EtOH. The crude product was recrystallized from EtOH as a white crystalline plates, yield (90%), m.p. 200 °C.

Copper(II) complex [Cu(Hotscb)(NO_3)(H_2O)], (III): A solution of $Cu(NO_3)_2 \cdot 3H_2O$ (1.2 g, 5 mmol) in EtOH (20 mL) was added to a warm solution of (H_2otscb) (0.88 g, 5 mmol) in EtOH (20 mL). The mixture was boiled under

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reflux for 1 h. The resulting green preciptate was filtered off, washed several times with EtOH and Et_2O and dried in vacuo, yield (65%); m.p. 220 °C.

Nickel(II) complex [Ni(otscb)]$_2$, (IV): To a solution of (H_2otscb) (0.88 g, 5 mmol) in EtoH (40 mL) was added a solution of Ni (acetate)$_2$·$4H_2O$ (1.22 g, 5 mmol) in EtOH (20 mL). The mixture was boiled under reflux with stirring. After a few minutes brown microcrystals deposited, the reflux was continued for Ca 2 h. The brown precipitate was collected by filteration, washed thoroughly with EtOH and Et_2O and dried in vacuo, yield (85%); mp > 300 °C.

Palladium(II) complex [Pd (otscb)]$_2$, (V): This complex was prepared using Pd (acetate)$_2$ following the procedure used above, stirring was continued for 5 h at room temperature and the resulting red microcrystals were collected by suction filteration. Yield (85%) m.p. 270 °C.

The ligand and the three complexes were characterized by their elemental and thermal analysis, electronic and infrared spectra and magnetic and cyclic voltammetry measurements.

Analysis, (H_2otscb): C, 34.52 (34.50); H, 5.81 (5.74); N, 31.95 (32.16); [Cu(Hotscb)(NO_3)(H_2O)]: C, 19.39 (18.92); H, 3.44 (3.47); N, 21.67 (22.06); [Ni(otscb)]$_2$: C, 26.44 (25.80); H, 4.30 (4.30); N, 23.73 (24.06); [Pd(otscb)]$_2$; C, 21.89 (21.44); H, 2.76 (2.87); N, 19.14 (19.94). The calculated values are shown in parentheses.

Physical and spectral measurements: ^{1}H-n.m.r spectra were recorded on a Varian spectrometer using DMSO as solvent. Chemical shifts (δ) are reported in p.p.m relative to Me_4Si. Infrared spectra were obtained on Nicolet 51OP-FT-IR spectrometer with samples prepared as KBr pellets. Solution (DMSO solution in 1 cm cells) electronic spectra were recorded with Lambda 25 UV-vis spectrometer. Magnetic susceptibility measurement (Table 1) were carried out at room temperature (298 K) using Johnson Matthey susceptibility balance and calculations were made using computed values of Pascal constants for diamagnetic corrections. Molar conductivities (10^{-3} M in DMSO) were measured with CMD 8500 Laboratory Conductivity Meter (Table 1). Thermogravimetric data were obtained on Perkin-Elmer TGA7 unit (heating rate 5 °C, min^{-1}). Cyclic voltammetric studies were carried out on a potentiostate/wave generator (Oxford Electrodes). Using a platinum working electrode, in conjunction with a Phileps PM 8043 x-y recorder.

Table 1. Colours, magnetic susceptibilities and molar conductivities of ligand (H_2otscb) and its complexes

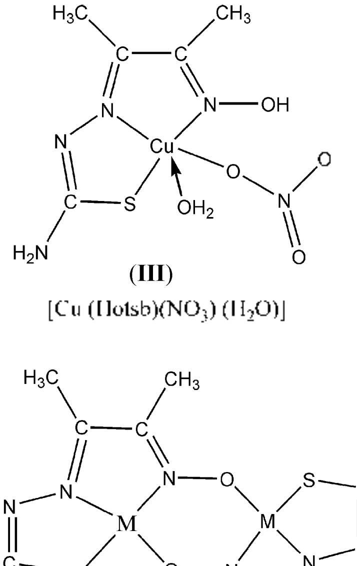
Compound	Colour	μ_{eff} BM	10^{-3} M DMSO Λ_M ohm^{-1} mol^{-1}
(H_2otscb), **(II)**	White		
[Cu(Hotscb)(NO_3)(H_2O)], **(III)**	Green	1.885	25.0
[Ni(otscb)]$_2$, **(IV)**	Brown	Diamagnetic	7.0
[Pd(otscb)]$_2$, **(V)**	Red	Diamagnetic	4.0

Results and Discussion

The synthesis of 2-oximino-3-thiosemicarbazone-2,3-butanedione (H_2otscb) (**II**) was accomplished in good yield (85%) by reacting 2,3-butanedione monoxime with thiosemicarbazide in aqueous EtOH at 100 °C after recrystallization from EtOH (Scheme 1).

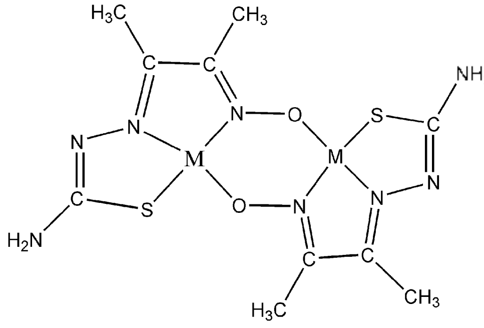
The structure proposed for this ligand is consistent with data obtained from elemental analysis data and ^{1}H-n.m.r spectrum. In the proposed structure of the (H_2otscb), three sites are available for the complexation of metal ions in mononuclear copper complex (**III**) as depicted in Figure 1. Additional site arising from oxime oxygen atom is involved in complexation of metal ions in dinuclear nickel and palladium complexes (**IV-V**) shown in Figure 1.

The colours molar conductivities and magnetic susceptibilities of the metal complexes of (H_2otscb) are shown in Table 1. Brown and Green colours are common to complexes



(**III**)

[Cu (Hotsb)(NO_3) (H_2O)]



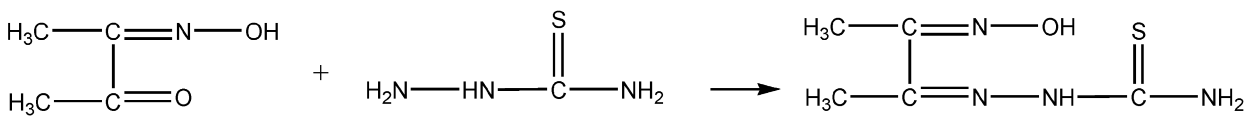
(**IV-V**)

[M(otscb)]$_2$

(**IV**): M = Ni (II)

(**V**) : M = Pd (II)

Figure 1. Structures of [Cu(Hotscb)(NO_3)(H_2O)] and [M(otscb)]$_2$, (M=Ni(II)), Pd(II)) complexes.



Scheme 1

involving thiosemicarbazone coordination due to the sulphur-to-metal charge transfer bands, which dominate their visible spectra.[16] The low values of molar conductance (10^{-3} M in DMSO) for the Ni(II) and Pd(II) complexes indicate a non-electrolyte behavior which is consistent with the proposed dimeric structure. For the Cu(II) complex, however, the presence of a small number of ions may be attributed to replacement of the nitrato ligand by the solvent molecules.[17] The magnetic susceptibilities values obtained for Ni(II) and Pd(II) complexes are consistent with diamagnetic structures given to the complex (low spin d^8). However the value μ_{eff} = 1.885 BM for [Cu(Hotscb)(NO_3)(H_2O)] showed that it is paramagnetic and confirmed the +2 oxidation state of copper.

The ^{1}H-n.m.r. data for [H_2otscb] and its Ni(II) and Pd(II) complexes in DMSO have been analysed. For the free ligand, the two CH_3 protons gave two singlets at δ 2.00 p.p.m, and δ 2.25 p.p.m. The OH, NH and NH_2 protons appeared as singlets at δ 11.61, δ 10.26 and δ 7.9 p.p.m respectively. For the complexes the resonance arising from the oxime hydroxyl proton and NH proton disappeared whereas that arising from NH_2 protons are shifted upfield. The absence of any OH and NH protons signals indicate involvement in complexation with nickel and palladium metal ions.

The infrared absorption bands are most useful for determining the ligand's mode of coordination. These absorptions are given and assigned in Table 2. No characterestic absorption assignable to C=O function was found, confirming the formation of the Schif base ligand. The shift of the imine ν(C=N) band of the oxime thiosemicarbazones from 1595 cm^{-1} to 1527-1572 cm^{-1} for the metal complexes indicates coordination of the imine nitrogen.[18-20] On loss of -NH proton in thiosemicarbazone moiety in the complexes, an additional ν(C=N) absorption is found at higher energy than ν(C=N) of the uncomplexed thiosemicarbazone.[21] In this study all synthesized complexes have shown this band at 1627-1633 cm^{-1}. The spectra of the uncoordinated thiosemicarbazones show the thioamide IV band, which possesses a considerable contribution from ν(CS), in the 838 cm^{-1} region. This band shifts to a lower frequency (55-100 cm^{-1}) on coordination of the anionic form of the thiosemicarbazones in agreement with previous studies of the thiosemicarbazone complexes.[22,23] Streching vibrations of NO in the oxime moiety in (H_2otscb) were seen as medium-strong bands at 1366 cm^{-1}.[24] The ν(N-O) streching vibrations for the dinuclear metal complexes (**IV-V**) shift to lower frequency and for the mononuclear complex to higher frequency suggesting that the oxime groups are nitrogen coordinated. The absence of O-H streching vibrations for dinuclear complexes indicates that the oxime groups are oxygen coordinated too. Two oxime groups, which are derived from two different (H_2otscb) anions, are coordinated to two nickel (II) or palladium (II) ions to form six membered ring bridge.[25] The ν(MS) bands have been assigned in the 350 cm^{-1} region confirming the coordination of the sulphur atoms.[26] Bands in the 470-502 cm^{-1} region are assigned to ν(MN) vibrations, supporting the coordination of the ligands as tridentate NNS chelating agents.[23] The isolated dinuclear complexes (**IV-V**) show extra bands at 420 cm^{-1} which may be due to ν(MO) in these complexes and suggesting the coordination of the oxygen atoms.[27] Absorption due to the nitrato ligand in momonuclear copper (II) complex (**III**) were found at 1405 and 1311 cm^{-1}.[28]

The infrared data confirms the existance of an unusual structural feature which consists of pair of metal ions (nickel or palladium) bridged by two oxime groups in a planar six membered ring conformation, Figure 1. All the infrared data support coordination of copper (II) ions to NNS doner groups of (H_2otscb) and to the nitrato monoligand and are consistent with the proposed structure for the mononuclear complex (Fig. 1).

The electronic absorption data (DMSO solution) are given in Table 3. Strong absorption in the uv range and a week absorption in the visible range are observed. The former may be attributed to the charge-transfer transition and is thought to be d-Π oximate in character.[29] The latter may be attributed to the d-d transitions. The band at 380 nm in the nitrato complex (**III**) is absent in the spectra of (**IV-V**) complexes and is attributable to (nitrato O → Cu(II)) ligand to metal charge transfer transition.[14b] The d-d band of complex (**III**) is similar to those shown by five coodinate Cu(II) complexes.[27,30-31] In all complexes, d-d transitions were observed at *ca* 480-603 nm. The energy of the d-d transition of complex (**III**)

Table 2. Infrared spectra and assignments of 2-oximino-3-thiosemicarbazone-2,3-butanedione (Hotscb) and its metal ion complexes (cm^{-1})

Compound	ν(OH)	ν(NH)	ν(C=N) imine or oxime	ν(N-O)	ν(CS)	ν(MN)	ν(MO)	ν(MS)	Others
(H_2otscb), (**II**)	3411	3233 3144	1594	1366	838				
[Cu(Hotscb)(NO_3)(H_2O)], (**III**)	3411	3288 3133	1572	1377	778	470	–	350	1633; C=N New 1405; NO_3^- 1311; NO_3^-
[Ni(otscb)]$_2$, (**IV**)	–	3288 3133	1572	1333	783	502	420	350	1627; C=N New
[Pd(otscb)]$_2$, (**V**)	–	3277	1527	1322	738	489	422	350	1627; C=N New

Table 3. Electronic spectra, cyclic voltammetric and TG data for complexes

Compound	U.V. visible data λ_{max}, nm (ε, M^{-1} cm^{-1})				Cyclic Voltammetric data		TG data* Decom. Temp. range C°		Other fragments	
	d-d	O → M(II)	S-M(II)	n → π^*	Ep_c V	Ep_a V	H_2O	NO_3	$CH_3C=NO$	NH_2CSN
[Cu(Hotscb)(NO_3)(H_2O)], (**III**)	603 (373)	380 (555)	–	306 (16250)	0.47 -0.05	0.75 0.275	118-130 5.66(5.68)	225-245 20.3(19.55)	270-295 18(17.98)	–
[Ni(otscb)]$_2$,(**IV**)	490 (625)	–	344 (9000)	303 (15050)	0.62 -0.125 -0.75 -1.185	0.87 0.375 -0.25 -1.06	–	–	–	342-380 33(31)
[Pd(otscb)]$_2$,(**V**)	480 (506)	–	340 (4891)	302 (11950)	–	–	–	–	–	287-380 28(27.7)

*Under line data represent a % of found weight loss and (Calcd).

sugests distorted square pyrimidal geometry.[32] The bands near 340 nm for complexes (**IV-V**) are due to S(σ. π) → M(II) charge transfer bands.[13]

The thermal behavior of the reported complexes was investigated using T.G. technique and the resulting data are given in Table 3. The T.G. curve of [Cu(Hotscb)(NO_3)(H_2O)] (**III**) (5 °C min^{-1} 0.780 mg) shows a weight loss of 5.66% occurs over the temperature 118-130 °C. The weight loss agrees well with that calculated value for the loss of one molecule of water (5.68%). Between 225-245 °C, a further loss in weight 20.3% was found which agrees reasonably with the theoretical value for complete loss of a nitrate group (19.55%). A third weight loss of 18% was found between 270-295 °C which may corresponds to release of CH_3–C=N–O fragment (17.98%). Thermograms of Ni(II) and Pd(II) complexes (**IV-V**) are very similar and shows higher thermal stability than Cu(II) complex (**III**). The thermogram of [Ni(otscb)]$_2$ (5 °C min^{-1}, 0.424 mg) shows the first weight loss endotherm between 287-380 °C which may be attributed to the release of two NH_2 CSN fragments[33] (found 28%, calcd 27.7%). The last step for the degradation of all complexes under investigation may be due to the formation of mixed metal oxide and sulphate.[34]

The electrochemical properties of the complexes in organic media were investigated by cyclic voltammetry. The data are summerised in Table 3. The I-E profiles of the mono- and dinuclear complexes are different and their cyclic voltammograms are shown in Figure 2. The voltammogram of Cu(II) complex in DMSO [0.1 M (n-Bu_4N)PF_6] exhibited two irreversible couples. The couple Cu(III/II) showed two waves at E_{pa} = 0.75 V and E_{pc} = 0.47 V. The couple Cu(II/I) waves appear at E_{pa} = 0.275 V and E_{pc} = -0.05 V. The ΔE_p for the two couples show that the two processes are irreversible. The binuclear Ni(II) complex showed two successive couples. The waves of the first couple appear at E_{pa} = 0.87 V and E_{pc} = 0.62 V. The second couple waves appear at E_{pa} = 0.375 V and E_{pc} = -0.125 V. These successive couples corresponding to the oxidation of the two Ni(II) ions forming Ni(III). The oxidation of the first Ni(II) ions make the oxidation of the second Ni(II) ion more difficult and appear at higher potential. Two other successive couples appeared in the voltammogram of Ni(II) complex. The wave of the first couple appear at E_{pa} = -0.25 and E_{pc} = -0.75 V. The secnd couple shows its waves at E_{pa} = -1.06 and E_{pc} = -1.185 V. These couples are due to the Ni(II/I) of the two Ni(II) ions in the binuclear complex. The voltammogram of binuclear Pd(II) complex (not shown) exhibited similar behaviour to that shown by Ni(II) complex, but the peaks are not very well defined.

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