



reflux for 1 h. The resulting green precipitate was filtered off, washed several times with EtOH and Et<sub>2</sub>O and dried in vacuo, yield (65%); m.p. 220 °C.

**Nickel(II) complex [Ni(otscb)]<sub>2</sub>, (IV):** To a solution of (H<sub>2</sub>otscb) (0.88 g, 5 mmol) in EtOH (40 mL) was added a solution of Ni (acetate)<sub>2</sub>·4H<sub>2</sub>O (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 filtration, washed thoroughly with EtOH and Et<sub>2</sub>O and dried in vacuo, yield (85%); mp > 300 °C.

**Palladium(II) complex [Pd (otscb)]<sub>2</sub>, (V):** This complex was prepared using Pd (acetate)<sub>2</sub> following the procedure used above, stirring was continued for 5 h at room temperature and the resulting red microcrystals were collected by suction filtration. 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<sub>2</sub>otscb): C, 34.52 (34.50); H, 5.81 (5.74); N, 31.95 (32.16); [Cu(Hotscb)(NO<sub>3</sub>)(H<sub>2</sub>O)]: C, 19.39 (18.92); H, 3.44 (3.47); N, 21.67 (22.06); [Ni(otscb)]<sub>2</sub>: C, 26.44 (25.80); H, 4.30 (4.30); N, 23.73 (24.06); [Pd(otscb)]<sub>2</sub>: 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:** <sup>1</sup>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<sub>4</sub>Si. Infrared spectra were obtained on Nicolet 510P-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<sup>-3</sup> 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<sup>-1</sup>). Cyclic voltammetric

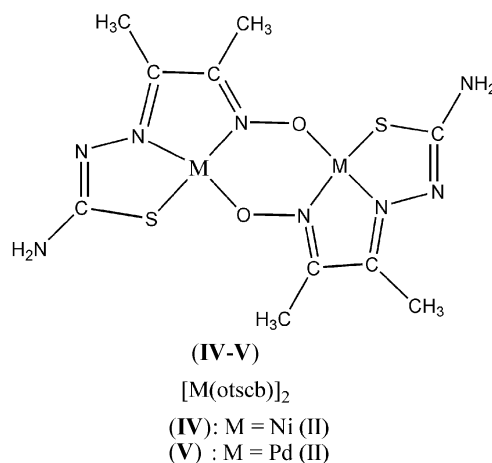
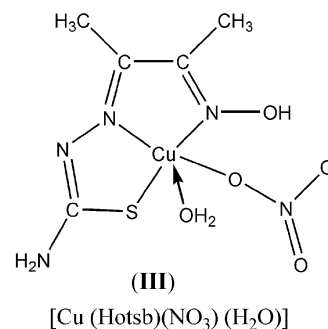
studies were carried out on a potentiostat/wave generator (Oxford Electrodes). Using a platinum working electrode, in conjunction with a Phileps PM 8043 x-y recorder.

## Results and Discussion

The synthesis of 2-oximino-3-thiosemicarbazone-2,3-butanedione (H<sub>2</sub>otscb) (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 <sup>1</sup>H-n.m.r spectrum. In the proposed structure of the (H<sub>2</sub>otscb), 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.

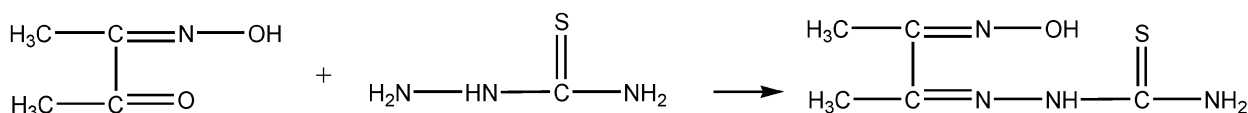
The colours molar conductivities and magnetic susceptibilities of the metal complexes of (H<sub>2</sub>otscb) are shown in Table 1. Brown and Green colours are common to complexes



**Table 1.** Colours, magnetic susceptibilities and molar conductivities of ligand (H<sub>2</sub>otscb) and its complexes

Compound	Colour	$\mu_{\text{eff}}$ BM	$10^{-3}$ M DMSO $\Lambda_{\text{M}}$ ohm <sup>-1</sup> mol <sup>-1</sup>
(H <sub>2</sub> otscb), (II)	White		
[Cu(Hotsb)(NO <sub>3</sub> )(H <sub>2</sub> O)], (III)	Green	1.885	25.0
[Ni(otscb)] <sub>2</sub> , (IV)	Brown	Diamagnetic	7.0
[Pd(otscb)] <sub>2</sub> , (V)	Red	Diamagnetic	4.0

**Figure 1.** Structures of [Cu(Hotsb)(NO<sub>3</sub>)(H<sub>2</sub>O)] and [M(otscb)]<sub>2</sub>, (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.<sup>16</sup> 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 nitrate ligand by the solvent molecules.<sup>17</sup> 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  $\mu_{\text{eff}} = 1.885$  BM for [Cu(Hotscb)(NO<sub>3</sub>)(H<sub>2</sub>O)] showed that it is paramagnetic and confirmed the +2 oxidation state of copper.

The <sup>1</sup>H-n.m.r. data for [H<sub>2</sub>otscb] and its Ni(II) and Pd(II) complexes in DMSO have been analysed. For the free ligand, the two CH<sub>3</sub> protons gave two singlets at  $\delta$  2.00 p.p.m, and  $\delta$  2.25 p.p.m. The OH, NH and NH<sub>2</sub> protons appeared as singlets at  $\delta$  11.61,  $\delta$  10.26 and  $\delta$  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<sub>2</sub> 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 characteristic absorption assignable to C=O function was found, confirming the formation of the Schiff base ligand. The shift of the imine  $\nu$ (C=N) band of the oxime thiosemicarbazones from 1595  $\text{cm}^{-1}$  to 1527-1572  $\text{cm}^{-1}$  for the metal complexes indicates coordination of the imine nitrogen.<sup>18-20</sup> On loss of -NH proton in thiosemicarbazone moiety in the complexes, an additional  $\nu$ (C=N) absorption is found at higher energy than  $\nu$ (C=N) of the uncomplexed thiosemicarbazone.<sup>21</sup> In this study all synthesized complexes have shown this band at 1627-1633  $\text{cm}^{-1}$ . The spectra of the uncoordinated thiosemicarbazones show the thioamide IV band, which possesses a considerable contribution from  $\nu$ (CS), in the 838  $\text{cm}^{-1}$  region. This band shifts to a lower frequency (55-100  $\text{cm}^{-1}$ ) on coordination of the anionic form of the thiosemicarbazones

in agreement with previous studies of the thiosemicarbazone complexes.<sup>22,23</sup> Stretching vibrations of NO in the oxime moiety in (H<sub>2</sub>otscb) were seen as medium-strong bands at 1366  $\text{cm}^{-1}$ .<sup>24</sup> The  $\nu$ (N-O) stretching 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 stretching vibrations for dinuclear complexes indicates that the oxime groups are oxygen coordinated too. Two oxime groups, which are derived from two different (H<sub>2</sub>otscb) anions, are coordinated to two nickel (II) or palladium (II) ions to form six membered ring bridge.<sup>25</sup> The  $\nu$ (MS) bands have been assigned in the 350  $\text{cm}^{-1}$  region confirming the coordination of the sulphur atoms.<sup>26</sup> Bands in the 470-502  $\text{cm}^{-1}$  region are assigned to  $\nu$ (MN) vibrations, supporting the coordination of the ligands as tridentate NNS chelating agents.<sup>23</sup> The isolated dinuclear complexes (IV-V) show extra bands at 420  $\text{cm}^{-1}$  which may be due to  $\nu$ (MO) in these complexes and suggesting the coordination of the oxygen atoms.<sup>27</sup> Absorption due to the nitrate ligand in mononuclear copper (II) complex (III) were found at 1405 and 1311  $\text{cm}^{-1}$ .<sup>28</sup>

The infrared data confirms the existence 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 donor groups of (H<sub>2</sub>otscb) and to the nitrate 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 weak absorption in the visible range are observed. The former may be attributed to the charge-transfer transition and is thought to be d- $\pi$  oximate in character.<sup>29</sup> The latter may be attributed to the d-d transitions. The band at 380 nm in the nitrate complex (III) is absent in the spectra of (IV-V) complexes and is attributable to (nitrate O  $\rightarrow$  Cu(II)) ligand to metal charge transfer transition.<sup>14b</sup> The d-d band of complex (III) is similar to those shown by five coordinate Cu(II) complexes.<sup>27,30-31</sup> 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 ( $\text{cm}^{-1}$ )

Compound	$\nu$ (OH)	$\nu$ (NH)	$\nu$ (C=N) imine or oxime	$\nu$ (N-O)	$\nu$ (CS)	$\nu$ (MN)	$\nu$ (MO)	$\nu$ (MS)	Others
(H <sub>2</sub> otscb), (II)	3411	3233 3144	1594	1366	838				
[Cu(Hotscb)(NO <sub>3</sub> )(H <sub>2</sub> O)], (III)	3411	3288 3133	1572	1377	778	470	–	350	1633; C=N New 1405; NO <sub>3</sub> <sup>-</sup> 1311; NO <sub>3</sub> <sup>-</sup>
[Ni(otscb)] <sub>2</sub> , (IV)	–	3288 3133	1572	1333	783	502	420	350	1627; C=N New
[Pd(otscb)] <sub>2</sub> , (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				Cyclic Voltammetric data		TG data*		Other fragments	
	$\lambda_{\max}$ , nm ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )				E <sub>pc</sub> V	E <sub>pa</sub> V	Decom. Temp. range C°		CH <sub>3</sub> C=N-O	NH <sub>2</sub> CSN
	d-d	O → M(II)	S-M(II)	n → $\pi^*$			H <sub>2</sub> O	NO <sub>3</sub>		
[Cu(Hotscb)(NO <sub>3</sub> )(H <sub>2</sub> O)], (III)	603 (373)	380 (555)	–	306 (16250)	0.47 -0.05	0.75 0.275	118-130 <u>5.66</u> (5.68)	225-245 <u>20.3</u> (19.55)	270-295 <u>18</u> (17.98)	–
[Ni(otscb)] <sub>2</sub> , (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 <u>33</u> (31)
[Pd(otscb)] <sub>2</sub> , (V)	480 (506)	–	340 (4891)	302 (11950)	–	–	–	–	–	287-380 <u>28</u> (27.7)

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

suggests distorted square pyramidal geometry.<sup>32</sup> The bands near 340 nm for complexes (IV-V) are due to S( $\sigma$ ,  $\pi$ ) → M(II) charge transfer bands.<sup>13</sup>

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<sub>3</sub>)(H<sub>2</sub>O)] (III) (5 °C min<sup>-1</sup> 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<sub>3</sub>-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)]<sub>2</sub> (5 °C min<sup>-1</sup>, 0.424 mg) shows the first weight loss endotherm between 287-380 °C which may be attributed to the release of two NH<sub>2</sub> CSN fragments<sup>33</sup> (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.<sup>34</sup>

The electrochemical properties of the complexes in organic media were investigated by cyclic voltammetry. The data are summarised 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<sub>4</sub>N)PF<sub>6</sub>] exhibited two irreversible couples. The couple Cu(III/II) showed two waves at E<sub>pa</sub> = 0.75 V and E<sub>pc</sub> = 0.47 V. The couple Cu(II/I) waves appear at E<sub>pa</sub> = 0.275 V and E<sub>pc</sub> = -0.05 V. The  $\Delta E_p$  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<sub>pa</sub> = 0.87 V and E<sub>pc</sub> = 0.62 V. The second couple waves appear at E<sub>pa</sub> = 0.375 V and E<sub>pc</sub> = -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<sub>pa</sub> = -0.25 and E<sub>pc</sub> = -0.75 V. The second couple shows its waves at E<sub>pa</sub> = -1.06 and E<sub>pc</sub> = -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.

## References

1. *Magnetostructural Correlations in Exchange Coupled System*; Willett, R. D.; Gatteschi, D.; Kahn, O., Eds.; Reidel: Dordrecht, Holland, 1985.
2. *Molecular Magnetic Material*, NATO. ASI Series; Gatteschi, D.; Kahn, O.; Miller, J. S.; Palacio, F., Eds.; Kluwer: Dordrecht, 1991.
3. Zhuang, Z. J.; Okawa, H.; Matsumoto, N.; Sakiyama, H.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1991**, 497.
4. Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, 27, 89.
5. Vigato, P. A.; Fenton, D. E. *Coord. Chem. Rev.* **1990**, 106, 25.
6. Liao, Z.; Liu, W.; Jiang, Y.; Shi, J.; Lin, C. J. *Inorg. Chem.* **1994**, 55, 165.
7. Güner, S.; Karaböcek, S. J. *Biochem. Mol. Toxicol.* **1998**, 12, 53.
8. Karaböcek, S.; Güner, S.; Karaböcek, N. *Transition Met. Chem.* **1998**, 23, 159.
9. Costa, G.; Mestroni, G.; de Savorgnari, E. *Inorg. Chem. Acta* **1969**, 3, 323.
10. Serbest, K.; Deđirmenciođlu, I.; Karaböcek, S.; Güner, S. *Transition Met. Chem.* **2001**, 26, 232.
11. Basuli, F.; Peng, S. M.; Bhattacharya, S. *Inorg. Chim.* **1997**, 36, 5645.
12. (a) Campbell, M. J. M. *Coord. Chem. Rev.* **1975**, 15, 279. (b) West, D. X.; Liberta, A. E.; Padhye, S. B.; Chikate, R. C.; Sonawane, P. B.; Kumbhar, A. S.; Yerande, R. G. *Coord. Chem. Rev.* **1993**, 123, 49.
13. Chattopadhyay, D.; Mazamdar, S. K.; Banerjee, T.; Ghost, S.; Mak, T. *Acta Crystallogr.* **1988**, C44, 1025.
14. (a) De Bolfo, A.; Smith, T. D.; Boas, J. F.; Pilbrow, J. R. *Aust. J. Chem.* **1976**, 29, 2583. (b) West, D. X.; Yang, Y. H.; Klein, T. L.; Goldberg, K. I.; Liberta, A. E.; Valdes Martinez, J.; Joscano, R. A. *Polyhedron* **1995**, 14, 1681.
15. (a) Brown, D. G. *Prog. Inorg. Chem.* **1973**, 18, 17. (b) Thomas, T. W.; Underhill, A. E. *Chem. Soc. Rev.* **1972**, 1, 99. (c) Underhill, A. E.; Watkins, D. W.; Petrig, R. *Inorg. Nucl. Chem. Lett.* **1973**, 9, 1269.
16. Swearingen, J. K.; West, D. X. *Transition Met. Chem.* **2001**, 26, 252.
17. Geary, W. J. *Coord. Chem. Rev.* **1971**, 7, 81.
18. Sousa, P.; Garcia-Vazquez, J. A.; Masaquer, J. A. *Transition Met.*

- Chem.* **1984**, 9, 318.
19. Agrawal, S. K.; Tulfani, D. R.; Gupta, R.; Hajela, S. K. *Inorg. Chim. Acta* **1987**, 129, 257.
20. Saha, N.; Sinha, S. *Indian J. Chem.* **1990**, 29A, 292.
21. West, D. X.; Swearingen, J. K.; Valdes-Martinez, J.; Hernandez-Ortega, S.; El-Sawaf, A. K.; Van Meurs, F.; Castineiras, A.; Garcia, I.; Bermejo, E. *Polyhedron* **1999**, 18, 2919.
22. West, D. X.; Beraldo, H.; Nassar, A. A.; El-Saied, F. A.; Ayad, M. I. *Transition Met. Chem.* **1999**, 24, 421.
23. West, D. X.; Salberg, M. M.; Bain, G. A.; Liberta, A. E. *Transition Met. Chem.* **1997**, 22, 180.
24. Blinc, R.; Hadzi, D. *J. Chem. Soc. A* **1958**, 4536.
25. Song, Y.; Chen, X. T.; Zheng, C. G.; Zhu, D. R.; You, X. Z. *Transition Metal Chem.* **2001**, 26, 247.
26. De Voto, G.; Massaccesi, M.; Pinna, R.; Ponticelli, G. *Spectrochim. Acta* **1982**, 38A, 725.
27. Bindu, P.; Kurup, M. R. P.; Satyackeerty, T. R. *Polyhedron* **1999**, 18, 321.
28. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5<sup>th</sup> Ed.; Wiley: New York, 1997; Part B, p 87.
29. Blinc, R.; Hadzi, D. *J. Chem. Soc. A* **1958**, 4536.
30. Garia, T. J.; Lezama, L.; Pizarro, J. L.; Instausti, M.; Arriotuo, M. I.; Rojo, T. *Polyhedron* **1999**, 18, 3703.
31. Goodgame, D. M. L.; Rayner Cenham, G. W. *J. Chem. Soc. A* **1971**, 1923.
32. Ruiz, R.; Sanz, J.; Cervera, B.; Lloret, F.; Julve, M.; Bois, C.; Faus, J.; Munoz, M. C. *J. Chem. Soc., Dalton Trans.* **1993**, 1623.
33. Zayed, M. A.; Nour El-Dein, F. A. *Thermochim. Acta* **1987**, 114, 53.
34. Steger, H. F. *J. Inor. Nucl. Chem.* **1972**, 34, 175.
-