Polish J. Chem., **78**, 515–520 (2004) **INORGANIC CHEMISTRY**

Synthesis and Characterization of Nickel(II), Cobalt(III) and Iron(III) Complexes of the Schiff Base 1-(2,3-Dihydroxybenzylidene)thiosemicarbazone

by A.H. Al-Kubaisi[*], El-Metwally Nour and M.A-Z Eltayeb

Department of Chemistry, College of Science, University of Qatar,
Doha – P.O. Box 2713, Qatar

(Received September 24th, 2003; revised manuscript December 11th, 2003)

Ni(II), Co(III) and Fe(III) complexes of the Schiff base 1-(2,3-dihydroxybenzylidene)thiosemicarbazone (Hdhbtsc) have been prepared and characterized by elemental analysis, infrared spectra, thermal analysis, molar conductivity and magnetic measurements. The results indicate the formation of 1:2 metal to ligand complexes with empirical formulae $[Ni(Hdhbtsc)_2(Cl)_2]$ and $[M(dhbtsc)_2(Cl)(H_2O)]$, (Hdhbtsc = the Schiff base; dhbtsc = anionic form of the Schiff base; M = Fe^{3+} or Co^{3+}). The three new complexes are six coordinate and octahedral, where the ligands behave as bidentate chelating agents in the neutral form with Ni^{2+} and in the uninegatively charged form with Fe^{3+} or Co^{3+}.

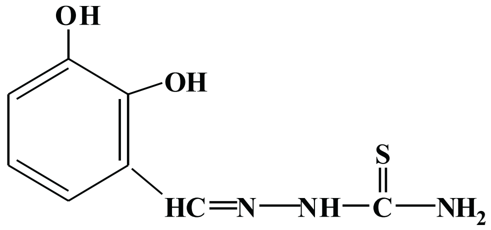
Key words: 1-(2,3-dihydroxybenzylidene)thiosemicarbazone, cobalt(III), iron(III), nickel(II), complexes, infrared, thermal

In recent years, there has been considerable interest in metal complexes of heterocyclic thiosemicarbazones [1–5]. This is due to their antimicrobial activities [6–8]. Moreover, this class of compounds contains the chemicaly active chromophoric group =NN(H)C(S). They are considred as useful models for sulfur containing analogues of purine and pyrimidine bases [1].

It appears that most of the related papers [2–4,9] were focused on divalent metal ions with Schiff bases derived from aldehydes with the hydroxyl either in 2 or in the 3 and 4 positions. The present investigation was undertaken to study the new complexes formed between Ni(II), Co(III) and Fe(III) metal ions and the interesting Schiff base 1-(2,3-dihydroxybenzylidene)thiosemicarbazone (Hdhbtsc), derived from 2,3-dihydroxybenzaldehyde and thiosemicarbazone. Here, we are dealing with a ligand derived from an aldehyde with two hydroxyl groups in the 2 and 3 positions and its complexes with both di- and trivalent metal ions. The results obtained allow us to characterize the new complexes formed and to make assessments of the composition, bonding and geometry of each of these complexes.

---

[*] Author to whom correspondence should be addressed. E-mail address: a_kubaisi@qu.edu.qa



1-(2,3-dihydroxybenzylidene)thiosemicarbazone (Hdhbtsc)

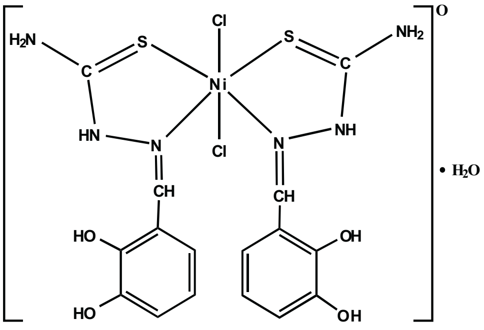
EXPERIMENTAL

The Schiff base 1-(2,3-dihydroxybenzylidene)thiosemicarbazone was prepared as described previously [10]. Complexes of the 1-(2,3-dihydroxybenzylidene)thiosemicarbazone were prepared with chloride salts of cobalt(II), nickel(II) and iron(III). Co(III)-complex was synthesized beginning with Co(II)-chloride after its auto-oxidation in solution by molecular oxygen in the presence of the Schiff base. Hot EtOH solutions containing the (Hdhbtsc) ligand and the metal salt (0.002 mol) in a 2:1 molar ratio were combined (50 mL). The mixture was stirred for 2–3 hrs at room temperature to yield the desired solid chelates. For nickel(II) complex the solution was boiled under reflux for 3 hrs on a water bath to effect precipitation of the solid chelate. The complexes were filtered off, washed several times with EtOH, then with anhydrous Et_2O and dried in vacuum over P_2O_5.

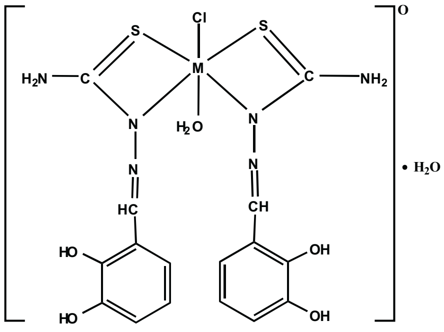
Partial elemental analyses (C, H, N) were performed by Microanalytical Center of Cairo University, while (Cl) was determined using $AgNO_3$ solution. Analysis, $[Ni(Hdhbtsc)_2Cl_2]\cdot H_2O$: C, 33.90 (33.70); H, 3.90 (3.51); N, 15.07 (14.75) and Ni, 9.95% and 10.67% (10.30%); $[Fe(dhbtsc)_2Cl(H_2O)]\cdot H_2O$: C, 34.20 (35.07); H, 2.70 (3.65); N, 14.52 (15.34) and Fe, 10.60% and 10.82% (10.23%); $[Co(dhbtsc)_2Cl(H_2O)]\cdot H_2O$: C, 34.00 (34.88); H, 2.80 (3.63); N, 13.70 (15.06) and Co, 10.39% and 10.40% (10.72%). The calculated values are shown in brackets. Metals were determined gravimetrically (first given value) and by atomic absorption spectroscopy (second given value). The magnetic susceptibilities of the solid complexes were measured with a Johnson Mattey balance at room temperature (298 K). Molar conductivities were measured at 298 K in DMSO (1.0×10^{-3} mol L^{-1}) with CD 8500 laboratory Conductivity Meter. Infrared spectra of the three complexes were recorded on a Nicolet 510P FT-IR spectrometer using KBr and CsI discs. Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were carried out, using a Perkin-Elmer TGA-7 computerized thermal analysis system. The rate of heating of the samples was kept at 5°C min^{-1} under nitrogen flow at 20 mL min^{-1}. $CuSO_4\cdot 5H_2O$ was used as the calibrating standard material.

RESULTS AND DISCUSSION

The Schiff base 1-(2,3-dihydroxybenzylidene)thiosemicarbazone (Hdhbtsc) reacts with $NiCl_2$, $CoCl_2$ and $FeCl_3$ to form the corresponding metal complexes $[Ni(Hdhbtsc)_2(Cl)_2]\cdot H_2O$, $[Co(dhbtsc)_2(Cl)(H_2O)]\cdot H_2O$ and $[Fe(dhbtsc)_2(Cl)(H_2O)]\cdot$ $\cdot H_2O$, (Hdhbtsc = the Schiff base; dhbtsc = anionic form of the Schiff base). The most probable structures of these complexes are shown as (I) and (II).



(I)
$[Ni(Hdhbtsc)_2(Cl)_2] \cdot H_2O$



(II)
$[M(dhbtsc)_2(Cl)(H_2O)] \cdot H_2O$
M = Co(III) or Fe(III)

The conclusions, concerning the compositions and structures of these three new complexes, are based on elemental analysis data, which agree quite well with the 1:2 (metal to ligand) stoichiometry and from molar conductivity, magnetic measurements, infrared spectra and thermal analysis. Molar conductivity measurements for each of the complexes under study are in the *ca.* 10–20 Ω^{-1} cm^{-2} mol^{-1} range indicating non-electrolytic behaviour [9,11] and that the complexes are non-ionic. Moreover, the magnetic measurements are consistent with the structures proposed. As expected for octahedral structure, $[Ni(Hdhbtsc)_2(Cl)_2]$ and $[Fe(dhbtsc)_2(Cl)(H_2O)]$ are paramagnetic (μ_{eff} (B.M.) = 3.00 and 5.70) with two and five unpaired electrons, respectively, while the third complex $[Co(dhbtsc)_2(Cl)(H_2O)]$ is a diamagnetic.

The infrared spectra of the Schiff base and the metal complexes and their band assignments are given in Table 1. The free Schiff base has a strong band at 1538 cm^{-1}, assigned to ν(C=N). This band appears in the spectra of Fe(III) and Co(III) complexes at around the same frequency, but is shifted by 125 cm^{-1} to lower frequency in the spectrum of Ni(II) complex. This clearly indicates that the Schiff base coordinates to Ni(II) *via* the azomethine nitrogen, which is not the case in Fe(III) and Co(III) complexes. The decrease of the ν(C=N) from 1538 to 1413 cm^{-1} upon coordination to Ni(II) is normal, it could be related to the increase of the reduced mass value of the C=N bond beside the expected π-back donation from the filled t_{2g} d-orbitals of Ni(II) to the half empty π^*-orbital of C=N decreasing the C=N bond strength and hence its bond vibration wavenumber value compared with that of the free ligand. The spectral regions (1000–600) cm^{-1} in the spectra of the three complexes are almost identical, but they differ from that of the free ligand. In this region, the ν(C=S) in the free ligand is observed at 980 cm^{-1}, shifted to lower wavenumber value at around 870 cm^{-1} in the spectra of the three complexes. This indicates that the S-atom of C=S is involved in the coordination to Ni(II), Fe(III) and Co(III) in a similar way. The shift of ν(C=S) to lower value upon coordination is well known [3]. We conclude here, that the ligand coordinates to Ni(II) as a bidentate neutral ligand without deprotonation through both the S of C=S and the N of C=N, while it coordinates to Fe(III) and Co(III) as a bidentate uninegatively charged ligand form through the S of C=S and the N of the deprotonated NH group (structures I and II). The formation of the latter Fe–N and Co–N bonds in a four membered ring systems is similar to that recently reported [12]

Table 1. Infrared spectra (cm^{-1}) and band assignment of the Schiff base (Hdhbtsc) and its complexes $[Ni(Hdhbtsc)_2(Cl)_2]\cdot H_2O$, $[Fe(dhbtsc)_2(Cl)(H_2O)]\cdot H_2O$ and $[Co(dhbtsc)_2(Cl)(H_2O)]\cdot H_2O$.

cm^{-1}				
Hdhbtsc	Complexes			Assignments
	Ni(II)	Fe(III)	Co(III)	
–	3428 m	3440 w	3442 w	$\nu(H_2O)$; uncoordinated
–	–	3381 w	3386 w	$\nu(H_2O)$; coordinated
3356 vs	3310 s	–	–	
3297 s	3286 w	3298 m	3299 m	
3256 vs	–	3240 w	3231 vw	ν(N–H)
3167 s	3177 s	3166 m	3166 s	
–	3051 m	3096 w	3041 w	ν(C–H); aromatic
	2964 w, 2881 mw	3005 w, 2930 w, 2860 w	2958 wm, 2871 w	ν(C–H); aliphatic
1614 s	1610 vs	1610 vs	1618 vs	
1595 shoul.	1570 s	1585 shoul.	–	ν(C=C); aromatic
1538 s	–	1551 m	1548 m	ν(C=N); Hdhbtsc, Fe(III) and Co(III) complexes
1471 m	1458 mw	1446 sm	1454 s	$\delta(NH_2)$
–	1413 s	–	–	ν (C=N); Ni(II) complex
1344 s	1328 m	1340 m	1342 m	δ(CH), aliphatic
–	–	1311 m	1315 m	
1277 s	1274 m	1260 m	1255 m	ν(C–O), ν(C–N),
1250 w	–	–	–	ν(N–N),
–	1217 m	1211 m	1210 ms	
1197 m	1173 mw	–	–	OH-deformation. Phenolic
1157 mw	–	1164 m	1163 m	
1103 mw	1091 mw	1095 w	1075 w	
1062 w	1041 wm	1060 w	1052 w	δ_w(CH); –CH=N–
980 sm	–	–	–	ν (C=S); Hdhbtsc
940 w	954 w	952 w	949 w	$\delta_r(NH_2)$
–	868 w	874 m	866 m	ν_{as}(C=S); complexes
824 m	–	–	–	
786 mw	781 m	787 m	783 m	δ(CH); aromatic, O.P.
733 mw	740 mw	736 m	736 m	δ_w(NH)
692 w	685 w	681 w	682 w	
–	643 w	601 w	605 w	ν_s(C=S); complexes
586 m	581 w	576 w	575 w	Out of plane ring bends
550 shoul.	–	–	–	+ other deformations
490 shoul.	476 m	470 m	477 wm	
419 mw	–	–	–	
–	–	455 wm	447 wm	ν(M(III)-O); O of H_2O
–	448 wm	–	–	ν(Ni–N)
–	350 w	346 w	349 wm	ν(M–S); complexes
–	–	322 w	302 w	ν(M(III)-N); N of deprotonated NH
–	–	270 w	251 wm	ν(M(III)-Cl)
–	246 wm	–	–	ν(Ni–Cl)

a – s: strong; m: medium; v: very; w: weak; shoul.: shoulder

b – ν_s: symmetric bond vibration, ν_{as}: asymmetric bond vibration; δ: bend; δ_r: rock; $\delta_{o.p.}$: out of plane; δ_w: wag on a related compound based on X-ray structural data. The ν(O–H) of H_2O in the three complexes are observed at 3428 for Ni(II), 3440 and 3381 for Fe(III) and at 3442 and 3386 cm^{-1} for Co(III) complexes. These bands do not exist in the spectrum of free ligand. These two $\nu(H_2O)$ vibrations in the spectrum of each of Fe(III) and Co(III) complexes correspond to only one $\nu(H_2O)$ vibration in the spectrum of Ni(II) complex and support the existence of one and two H_2O molecules in the Ni(II) and M(III) complexes, respectively, (structures I and II). The 3428, 3440 and 3342 cm^{-1} bands observed in the spectra of Ni(II), Fe(III) and Co(III) complexes, respectively, are typical for ν(O–H) of uncoordinated H_2O molecule, water of crystallization, in the three complexes, while the observed extra band in the spectra of Fe(III) and Co(III) complexes only at 3381 and 3386 cm^{-1}, respectively, is characteristic for ν(O–H) of coordinated H_2O [13] in agreement with the complex structures shown in I and II. The infrared bands related to the different ν(N–H) and ν(C–H) vibrations are well resolved and occur in a larger number compared with those of the free ligand. This supports the existence of a number of two ligands in each complex (Table 1).

Several new bands appeared in the far infrared spectra of the formed complexes, Table 1. These bands were assigned to the different metal–ligand vibrations. The ν(M–S) in the three complexes is observed as expected at around 350 cm^{-1}, supporting the existence of M–S=C unit in these complexes. The ν(Ni–N) and ν(Ni–Cl) are observed at 448 and 246 cm^{-1}, respectively. The ν(Fe–O) and ν(Fe–N) bond vibrations are observed at 455 and 322 cm^{-1}, respectively. The corresponding values for Co(III) complex appear at 474 and 302 cm^{-1}. The ν(Fe–Cl) and ν(Co–Cl) bands appear at 270 and 251 cm^{-1}, respectively. All of these assignments for metal–ligand vibrations are in agreement with those known for related compounds [2,9–13].

Thermal analysis (TG and DTG) were carried out for the three complexes $[Ni(Hdhbtsc)_2(Cl)_2]\cdot H_2O$, $[Fe(dhbtsc)_2(Cl)(H_2O]\cdot H_2O$ and $[Co(dhbtsc)_2(Cl)(H_2O)]\cdot\cdot H_2O$ under a N_2 flow. The thermogram of $[Ni(Hdhbtsc)_2(Cl)_2]\cdot H_2O$ shows the first degradation step at a maximum of 181°C and is accompanied by a weight loss of 3.0% and corresponds to the loss of one molecule of H_2O in agreement with the theoretically calculated weight loss of 3.16%. The second stage of decomposition occurs at 268°C due to the loss of two $H_2NC(NH)S$ fragments. The calculated weight loss for this step is 26.3% very close to the found value of 27.0%. The next two stages of decomposition occur at 387 and 500°C with broad structures. The total weight loss accompanying these two steps was 43.5% and may be attributed to the loss of two $Ph(OH)_2CH$ fragments. This is very close to the theoretical weight loss of 42.8%. The weight found for the residue after decomposition corresponds to about 22% due to the formation of $NiCl_2$ close to the calculated weight loss of 22.7%. The formation of the above mentioned fragments as thermal decomposition products are similar to those reported in other related systems [2,14]. Fe(III) and Co(III) thermograms are similar and different from that of Ni(II) complex due to their different molecular composition and structure.

In the complex $[Co(dhbtsc)_2(Cl)(H_2O)]\cdot H_2O$, the first weight loss occurs at 255.6°C related to the loss of $2H_2O$ molecules (Found, 6.90%; Calc., 6.54%). The loss of two H_2O molecules (one coordinated and the second water of crystallization) at one temperature of 255.6°C could be related to the expected strong hydrogen bonding involving the two H_2O molecules. The second degradation step occurs at 377 and 453°C and corresponds to the loss of two $H_2NC(N)S$ and two PhCH fragments (Found, 59.0%; Calc., 58.9%). The found weight for the residue after decomposition corresponds to 15.0% due to the formation of Co_2O_3 as the final product, in good agreement with the theoretically calculated value of 15.08%.

REFERENCES

1. Ali M.A., Mirza A.H., Rahman M.N.H. and Butcher R.J., *Polyhedron*, **20**, 2431 (2001).
2. Mostafa S.I., El-Asmy A.A. and El-Shahawi M.S., *Trans. Met. Chem.*, **25**, 470 (2000).
3. Offiong O.E. and Martelli S., *Trans. Met. Chem.*, **22**, 263 (1977).
4. West D.X., Salberg M.M., Bain G.A. and Liberta A.E., *Trans. Met. Chem.*, **22**, 180 (1997).
5. Ortner K. and Abram U., *Inorg. Chim. Acta*, **1**, 251 (1998).
6. West D.X., Padhye S.B., Sonawane P.B. and Chikate R.C., *Asian J. Chem. Rev.*, **1**, 125 (1990).
7. Subsezynki W.K., Antholine W.E., Hyde J.S. and Petering D.H., *J. Am. Chem. Soc.*, **109**, 46 (1987).
8. Liberta A.E. and West D.X., *BioMetals*, **5**, 125 (1992).
9. Zhu X., Wang C., Lu Z. and Dang Y., *Trans. Met. Chem.*, **22**, 9 (1997).
10. Al-Kubaisi A.H., *International J. Chem.*, **12**, 213 (2002).
11. Geary W.J., *Coord. Chem. Rev.*, **7**, 81 (1971).
12. Basuli F., Ruf M., Pierpont C.G. and Bhattacharya S., *Inorg. Chem.*, **37**, 6113 (1998).
13. Nakamoto K., *Infrared and Raman Spectra of Inorganic and Coordinaton Compounds*, Wiley, NY 1978.
14. Zayed M.A. and Nour El-Dien F.A., *Thermochim. Acta*, **114**, 53 (1987).