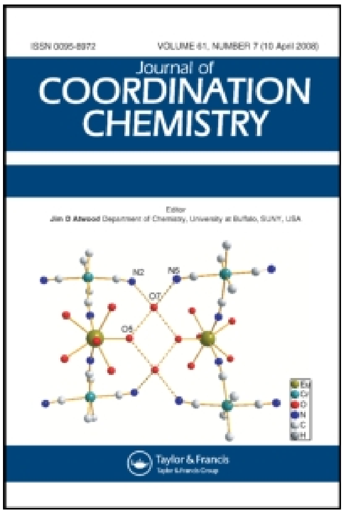

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization and oxygen affinity of Mn(II), Co(II) and Ni(II) complexes of diethylenetriamine Schiff bases

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First published on: 22 September 2010

To cite this Article Emara, Adel A. , Ali, A. M. , Ragab, E. M. and El-Asmy, A. A.(2008) 'Synthesis, characterization and oxygen affinity of Mn(II), Co(II) and Ni(II) complexes of diethylenetriamine Schiff bases', Journal of Coordination Chemistry, 61: 18, 2968 — 2977, First published on: 22 September 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970801993060

URL: http://dx.doi.org/10.1080/00958970801993060

Journal of Coordination Chemistry
Vol. 61, No. 18, 20 September 2008, 2968–2977

Taylor & Francis
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Synthesis, characterization and oxygen affinity of Mn(II), Co(II) and Ni(II) complexes of diethylenetriamine Schiff bases

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(*Received 1 August 2007; revised 12 November 2007; in final form 19 November 2007*)

N,N′-diethyleneamine *bis*(salicylideneimine); H_2DETS and *N,N′*-diethyleneamine *bis*(*o*-hydroxyacetophenoneimine); H_2DETHA have been prepared to produce Mn(II), Co(II) and Ni(II) complexes by the addition of the synthesized Schiff bases to the studied ions under nitrogen. H_2DETS and H_2DETHA are neutral tridentate in the nitrato complexes and binegative pentadentate in the other complexes. A square pyramidal structure was suggested for all complexes based on elemental analysis, molar conductivity, infrared, electronic spectra and magnetic moment measurements. The oxygen absorption properties were studied for the isolated complexes by considering the solubility, oxygen affinity and stability. [Co(DETS)]$\cdot 4H_2O$ has the highest affinity. Different concentrations for the Co(II) complex were studied.

Keywords: Pentadentate Schiff base ligands; Oxygen affinity; Complexes

1. Introduction

Heme or porphinatoiron(II) complexes existing in hemoglobin and myoglobin play an important role in *in vivo* transport and storage of oxygen and can reversibly bind and release oxygen according to the partial pressure of oxygen [1]. Oxygen adsorption-desorption similar to those of natural heme using synthetic porphinatoiron(II), lacunar [2], Schiff bases and macrocyclic complexes of different transition metals have been reported [3, 4]. New complexes having high ability to bind with oxygen [5–7], application as catalysts for oxidation of unsaturated organic compounds [8–10] and inorganic-organic hybrid membranes for oxygen/nitrogen separation with Co(II) complexes [11] are still sought.

The present work deals with synthesis and characterization of H_2DETS and H_2DETHA (Structure 1) and their Mn(II), Co(II) and Ni(II) complexes. The absorption-desorption properties for the complexes were investigated.

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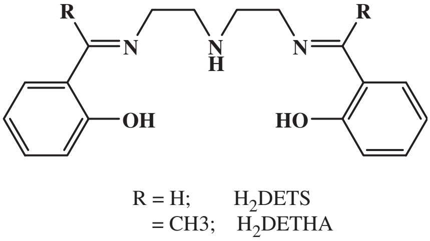
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970801993060



Structure 1. Formula of the ligands.

2. Experimental

2.1. *Materials*

$Mn(OAc)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were purchased from Merck; salicyldehyde, *o*-hydroxyacetophenone and diethylenetriamine from BDH or Merck. Ethyl alcohol (95%), acetone, diethylether, methanol and absolute ethanol were used after purification.

2.2. *Synthesis of the Schiff bases*

Precaution was taken to avoid oxygen in the preparation of H_2DETS and H_2DETHA. The apparatus, materials and ethanol were placed in a glove bag flushed with nitrogen gas for 30 min before performing each reaction. Filtration and washing of the products with ethanol and dry diethylether were performed inside the glove bag. Recrystallization after isolation of the ligands was performed. The products were left in a desiccator containing dry $CaCl_2$, filled with nitrogen gas. Structure 1 represents the formulas of the isolated pentadentate ligands.

2.3. *Synthesis of the complexes*

In general, absolute ethanol solution of H_2DETS or H_2DETHA was added dropwise to triethylamine, then the mixture was added dropwise to solutions of Mn(II), Co(II) or Ni(II) salt at room temperature. The reaction mixture was heated for 10 min and left inside the glove bag under nitrogen for 1 h. A sample preparation is: Solution of H_2DETS (2.14 g, 6.87 mmol) in 20 mL absolute ethanol was added dropwise to triethylamine (1.40 g, 6.87 mmol) in 10 mL absolute ethanol. The mixture was added to $Ni(NO_3)_2 \cdot 6H_2O$ (2.00 g, 6.88 mmol) in 20 mL absolute ethanol at room temperature. The reaction mixture was heated for 10 min and left inside the glove bag under nitrogen for 1 h, filtered cold and the product washed several times with diethylether.

2.4. *Measurements*

Carbon, hydrogen and nitrogen content were analyzed at the Microanalytical Center, Cairo University, Egypt. Metal ions were determined by standard methods [12, 13].

FTIR spectra of the ligands and their metal complexes were recorded on a Perkin-Elmer 1430 ratio recording IR Spectrophotometer (4000–200 cm^{-1}) using KBr discs. Electronic spectra were performed using a Jasco V550 Spectrophotometer in DMF (200–800 nm). The ^1H NMR spectrum of H_2DETHA in $CDCl_3$ was recorded on a Bruker WP 200 SY Spectrometer. Magnetic susceptibilities of the complexes were measured at room temperature using a Johnson Matthey, Alfa product, MKI magnetic susceptibility balance. The effective magnetic moments were calculated with diamagnetic corrections using Pascal's constants [14]. Molar conductivity measurements were carried out on a YST model 35 conductance meter (made in the UK). Dissolved oxygen was measured using portable water proof dissolved oxygen water mode HI 9142 (Romania).

3. Results and discussion

3.1. *Schiff-base ligands*

H_2DETS and H_2DETHA were identified by elemental analysis, IR, ^1H NMR and UV spectra. Table 1 lists their physical and analytical data.

The IR bands are consistent with the formation of the Schiff bases. The assignments were aided by comparison with related compounds [15]. The $\nu(NH_2)$ of diethylenetriamine and the $\nu(C{=}O)$ of salicyldehyde or *o*-hydroxyacetophenone disappear and a $\nu(C{=}N)$ appeared at 1614–1632 cm^{-1}.

The ^1H NMR spectrum of H_2DETHA in $CDCl_3$ showed signals for CH_3, CH_2 and phenyl protons at (2.30; 2.33), (3.06; 3.65) and (6.70; 6.87; 7.25; 7.48) ppm, respectively. The phenolic OH appeared at 16.37 ppm which is highly downfield due to strong hydrogen bonding ($O{-}H \cdots N{=}C$).

The absorption spectra of the ligands, in DMF, exhibit bands at 315–318, 307–338 and 360–398 nm corresponding to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ of C=N [16].

3.2. *Characterization of the complexes*

The ligands reacted with hydrated metal salts to yield $[Co(DETS)] \cdot 4H_2O$, Structure 2, $[Ni(DETS)] \cdot 4H_2O$, $[Mn(\mathit{DETHA})] \cdot 4H_2O$ $[Ni(H_2\mathit{DETHA})\text{-}(NO_3)_2] \cdot 3H_2O$ and $[Mn(H_2DETS)(NO_3)_2]$ (table 1).

The IR bands of the complexes and their assignments are listed in table 2. The $\nu(OH)$ and $\delta(OH)$ of the ligands disappear in the spectra of $[Co(DETS)] \cdot 4H_2O$, $[Ni(DETS)] \cdot 4H_2O$ and $[Mn(\mathit{DETHA})] \cdot 4H_2O$, but are more or less unchanged in $[Ni(H_2\mathit{DETHA})(NO_3)_2] \cdot 3H_2O$ and $[Mn(H_2DETS)(NO_3)_2]$. The shift of $\nu(NH)$ to lower wavenumbers in all complexes support chelation. The new broad band centered at 3423–3441 cm^{-1} is assigned to $\nu(H_2O)$ of the hydrated water. The $\nu(C{=}N)$ is shifted to 1590–1602 cm^{-1} supporting coordination to the metal varying in the order: Co(II) > Ni(II) > Mn(II). Evidence for the metal bonding to O and N is the appearance of weak bands in the low frequency region at 475–433 and 350–305 cm^{-1} assigned to $\nu(M{-}O)$ and $\nu(M{-}N)$, respectively [17]. The absence of bands at *ca* 1620, 850 and 550 cm^{-1} indicate water is not coordinated. In $[Ni(H_2DETHA)(NO_3)_2] \cdot 3H_2O$ and $[Mn(H_2DETS)(NO_3)_2]$, Structure 3, there are bands due to the NO vibrations

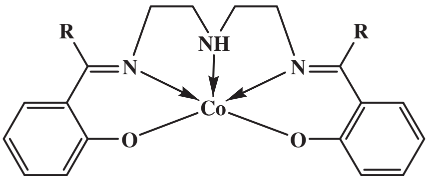
Table 1. Physical and analytical data of the ligands and their complexes.

						Elemental analysis % found (Calcd)			
Compound	Formula	M.F.	Color	Yield (%)	M.p. (°C)	C	H	N	M
H_2DETHA	$C_{20}H_{25}N_3O_2$	339.44	Golden yellow	92	105	71.05 (70.77)	7.37 (7.42)	12.23 (12.38)	–
H_2DETS*	$C_{18}H_{21}N_3O_2$	311.38	Reddish brown	85	–	–	–	–	–
[Ni(H_2DETHA)$(NO_3)_2$] · $3H_2O$	$C_{20}H_{31}N_5O_{11}Ni$	576.18	Pale orange	87	235	41.84 (41.69)	5.68 (5.42)	12.12 (12.16)	10.23 (10.19)
[Ni(DETS)] · $4H_2O$	$C_{18}H_{27}N_3O_6Ni$	440.12	Orange	77	250	49.64 (49.12)	5.97 (6.13)	9.63 (9.55)	13.63 (13.34)
[Co(DETS)] · $4H_2O$	$C_{18}H_{27}N_3O_6Co$	440.30	Pale brown	83	290	49.17 (49.10)	6.03 (6.13)	9.38 (9.54)	13.10 (13.39)
[Mn(H_2DETS)$(NO_3)_2$]	$C_{18}H_{21}N_5O_8Mn$	456.41	Dark green	76	>300	48.68 (47.38)	5.05 (4.60)	–	12.03 (12.04)
[Mn(DETHA)] · $4H_2O$	$C_{20}H_{31}N_3O_6Mn$	464.11	Dark green	74	>300	51.54 (51.72)	6.39 (6.68)	9.52 (9.06)	11.25 (11.64)

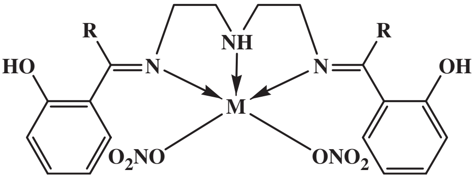
*Oily product.

Table 2. Characteristic IR bands (cm^{-1}) of the Schiff bases and their Co(II), Mn(II) and Ni(II) complexes.

Ligands and complexes	$\nu(H_2O)$	ν(O–H)	ν(N–H)	N(=C–H)	$\nu(CH_3)$	ν(C=N)	ν(C–O)	δ(OH) in plane	ν(M–O)	ν(M–N)
H_2DETS	–	3410 m	3200 br	3056 br	2846 s	1632 sh	1278 sh	1338 m	–	–
H_2DETHA	–	3414 br	3250 w	3058 br	2914 br	1614 sh	1242 m	1326 m	–	–
$[Co(DETS)] \cdot 4H_2O$	3441 br	–	3100 br	–	–	1602 m	1202 w	–	475 w	323 w
$[Mn(HDETS)(NO_3)] \cdot 3H_2O$	3408 br	3408 br	3230 sh	3040 br	2924 br	1600 sh	1204 m	1340 m	–	306 vw
$[Mn(DETHA)] \cdot 4H_2O$	3424 br	–	3150 sh	3063 m	2926 m	1590 s	1236 sh	–	446 sh	375 br
$[Ni(H_2DETHA)(NO_3)_2] \cdot 3H_2O$	3474 br	3425	3128 sh	3040 br	2866 m	1586 m	1240 m	1338 m	–	345 br
$[Ni(DETS)] \cdot 4H_2O$	3423 br	–	3180 sh	3052 br	2938 m	1600 br	1199 m	–	433 br	305 vw



Structure 2. Square pyramid structure of [Co(DETS)] · 4H2O.



Structure 3. Square pyramid structure of the nitrato complexes [M=Ni(II) or Mn(II)].

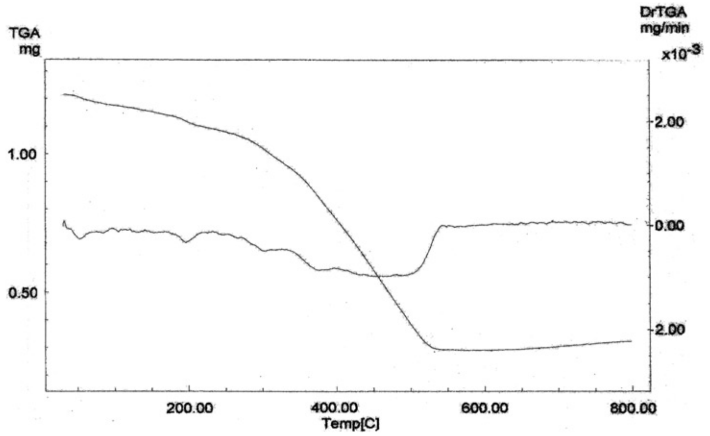


Figure 1. TGA and D TGA curves of [Mn(DETHA)] · $4H_2O$.

at 1420 (ν_5), 1030 (ν_1) and 898 (ν_2) cm^{-1} with difference between ν_5 and $\nu_1 = 390\,cm^{-1}$ supporting monodentate nitrate [18]. The above data clearly suggest that the ligands are dibasic pentadentate in [Co(DETS)] · $4H_2O$, [Ni(DETS)] · $4H_2O$ and [Mn(*DETHA*)] · $4H_2O$ and neutral tridentate in [Ni(H_2DETHA)(NO_3)$_2$] · $3H_2O$ and [Mn(H_2DETS)(NO_3)$_2$]. The IR spectra of H_2DETS and its Co(II) complex are provided in Supplemental Material.

The TG of [Mn(*DETHA*)] · $4H_2O$ (figure 1) showed five overlapped decomposition steps beginning from 45 to 412°C with evolution of $4H_2O + 2CH_3 + (CH_2–CH_2)_2NH$ [Found 39.6 (Calcd 37.3%)]. The other step at 413–542°C corresponds to evolution of $C_{14}H_8$ [Found 35.3 (Calcd 37.9%)] leaving MnO_2N_2 as a residue at 800°C [Found 24.4 (Calcd 24.6%)].

The molar conductance values, in DMF, are 9–22 $Ohm^{-1}cm^2mol^{-1}$ (table 3) indicating that all complexes are non-electrolytes [19] and nitrate is coordinated.

The electronic spectrum of [Co(DETS)] · $4H_2O$, in DMF, exhibits bands at 600, 412 and 370 nm in agreement with low spin Co(II) square pyramid complexes [20]. This geometry (Structure 2) is expected to have lower intensity than other geometries

Table 3. Electronic spectral bands, magnetic moments and molar conductivity values of the complexes.

Complex	d–d transition, nm	Magnetic moment (BM)	Molar conductivity[a]
[Ni(H_2*DETHA*)(NO_3)$_2$] · $3H_2O$	569	0.0	18
[Ni(DETS)] · $4H_2O$	578	0.0	9
[Co(DETS)] · $4H_2O$	600, 412, 370	2.43	22
[Mn(H_2DETS)(NO_3)$_2$]	470	1.73	13
[Mn(*DETHA*)] · $4H_2O$	449	–	15

[a] Values measured in DMF solution ($Ohm^{-1} cm^2 mol^{-1}$).

for Co(II) complexes. Its magnetic moment value is 2.43 BM in the range reported for a square pyramidal structure [5].

Electronic spectra of [Mn(H_2DETS)(NO_3)$_2$] and [Mn(DETHA] · $4H_2O$ in DMF, exhibit very weak bands at 470 and 449 nm, respectively [21] (table 3). It is impossible to identify the type of transitions in square pyramid complexes. The spectra of the present complexes are different from those of octahedral and tetrahedral complexes. The magnetic moment of [Mn(H_2DETS)(NO_3)$_2$] is 1.73 BM confirming the presence of one unpaired electron in a square-planar or square pyramid structure.

The Ni(II) complexes exhibit one band due to $^1E \leftarrow {}^1A_1$ in agreement with square pyramidal structure [22]. Their diamagnetic behavior is consistent with the proposed geometry [23].

3.3. *Oxygen absorption and desorption processes*

[Co(DETS)] · $4H_2O$, [Ni(DETS)] · $4H_2O$ and [Mn(DETHA)] · $4H_2O$ were tested as carriers for oxygen with respect to: (i) solubility which is important in the total oxygen capacity of solutions, (ii) oxygen affinity (absorption and desorption processes) and (iii) stability. Although the solubility of the Ni(II) and Mn(II) complexes is significant in both DMF and chloroform, the oxygen affinity of these ions is less than the Co(II) complex. This may be due to Co(II) being easily oxidized [24]. The Co(II) complex showed significant absorption and desorption of O_2. Its color turned red on absorption of oxygen at –10°C in both DMF and chloroform and brown on desorption at 60–80°C. The solubility, oxygen affinity and stability of the complexes in DMF and chloroform are discussed in detail.

3.3.1. Solubility. Before studying the efficiency of these complexes as oxygen carriers, it is important to know maximum solubility, an important parameter for capacity to carry oxygen. Polar (DMF, THF and pyridine) and non polar (nitrobenzene, dichloroethane and chloroform) solvents were tested; DMF and chloroform are more efficient than the other solvents. DMF replaced NO_3^- in the metal complexes giving efficient absorption and desorption. It is a good medium at low temperature for binding oxygen to the complex and to replace oxygen in desorption at elevated temperature. The data indicate that [Co(DETS)] · $4H_2O$ is highly soluble and the trend of solubility decreases in the order: Co(II) > Ni(II) > Mn(II).

Table 4. Oxygen absorption capacity of Co(II), Ni(II) and Mn(II) oxygen carriers in 100 mL DMF and chloroform from −5°C (absorption) to 100°C (desorption).

Carrier	Carrier conc. ($\times 10^{-2}$ M)	Solvent	Cycle number	Oxygen conc. ($\times 10^{-3}$ M)	Oxygen capacity ($\times 10^{-4}$ g)	Carrier loading (%)	Average carrier loading (%)
[Co(DETS)] · $4H_2O$	15	DMF	1	15	4.69	12.5	11.08
			2	14.5	4.53	12.08	
			3	12.7	3.97	10.58	
			4	11	3.44	9.17	
[Co(DETS)] · $4H_2O$	10	Chloroform	1	7.7	2.41	6.42	6
			2	8	2.5	6.66	
			3	6.4	2	5.33	
			4	6.7	2.09	5.57	
[Ni(DETS)] · $4H_2O$	11	DMF	1	5.3	1.66	4.43	3.75
			2	4.8	1.5	4	
			3	4.3	1.34	3.57	
			4	3.6	1.13	3.01	
[Ni(DETS)] · $4H_2O$	10	Chloroform	1	4.1	1.28	3.41	3.21
			2	3.4	1.06	2.83	
			3	3.6	1.13	3.01	
			4	4.3	1.34	3.57	
[Mn(*DETHA*)] · $4H_2O$	9	DMF	1	5.3	1.66	4.43	4.11
			2	4.8	1.5	4	
			3	5.5	1.72	4.59	
			4	4.2	1.31	3.49	
[Mn(*DETHA*)] · $4H_2O$	8	Chloroform	1	5	1.56	4.16	3.60
			2	4.2	1.31	3.49	
			3	3.8	1.19	3.17	
			4	4.3	1.34	3.57	

3.3.2. Oxygen affinity. The oxygen affinity of complexes in DMF and $CHCl_3$ at −5 to 100°C, is presented in table 4. The vacant axial site in the complexes is suitable for carrying oxygen. Comparing the data of the three complexes, $[Co(DETS)] \cdot 4H_2O$ has greater affinity, as studied by repeating the absorption and desorption several times. The first four cycles undertaken within 4 h increase the carrier loading. Ten additional cycles of absorption and desorption were conducted during 16 h, after which the complex solution did not show any change in color. The additional cycles took longer than the first four cycles.

In table 4, the oxygen concentration is the amount of dissolved oxygen (D.O.) which indicates the molar ratio of the complex carrier: the oxygen carried in the complex. The oxygen capacity is the weight of oxygen carried by the complex. The percentage of carrier loading is calculated by:

$$\text{Carrier loading \%} = \frac{[\mathrm{O_2}\ \text{carried}]}{[\text{Oxygenated carrier complex}]} \times 100$$

The average carrier loading gives indication about the carrier affinity for oxygen. The affinity is described empirically, as there is no mechanistic oxygen complexation information, such as whether the oxygen binding species is 2 : 1 or 1 : 1 (carrier complex:oxygen) [25–27]. $[Co(DETS)] \cdot 4H_2O$ in DMF has greater oxygen affinity than in $CHCl_3$. Table 4 lists the oxygen absorption and desorption capacities of the Ni(II) and Mn(II) complexes in DMF and $CHCl_3$ at −5 to 100°C. The oxygen capacity and percentage carrier loading of Ni(II) and Mn(II) are lower than for Co(II).

3.3.3. Stability. The effect of different concentrations of $[Co(DETS)] \cdot 4H_2O$ on the oxygen affinity from −5°C (absorption) to 100°C (desorption) was studied. The data showed that absorption of oxygen decreases with decrease of concentration of the carrier complex.

4. Conclusion

Mn(II), Co(II) and Ni(II) complexes of pentadentate Schiff bases were prepared under nitrogen, identified and examined as oxygen carriers. The absorption and desorption behavior of these complexes clearly reveal that, the Co(II) complex is a better oxygen carrier than Ni(II) and Mn(II). Thus, $[Co(DETS)] \cdot 4H_2O$ can be used as a catalyst in the oxidation of organic and petrochemicals.

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