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**HOTEL VISTANA, KUANTAN, PAHANG**

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# IRON AND COBALT MONONITROSYLS WITH SCHIFF BASE CO-LIGANDS

HADARIAH BAHRON

Fakulti Sains Gunaan, Universiti Teknologi MARA  
Seksyen 17, 40200 Shah Alam

## ABSTRACT

The ligand *N*-4-methoxybenzylsalicylideneimine (MeObsal) is reacted with  $Fe^{2+}$  and  $Co^{2+}$  ions separately. Both the systems are then reacted with nitric oxide (NO) to form two different complexes which are bis(*N*-4-methoxybenzylsalicylideneiminato)nitrosyliron,  $[Fe(MeObsal)_2NO]$ ; and bis(*N*-4-methoxybenzylsalicylideneiminato)nitrosylcobalt,  $[Co(MeObsal)_2NO]$ . Both the complexes are microanalysed and subjected to infrared spectroscopy investigation and magnetic measurement. From the infrared investigation,  $[Fe(MeObsal)_2NO]$  is found to exhibit an NO stretching frequency,  $\nu_{NO}$ , at  $1777\text{ cm}^{-1}$  whereas  $[Co(MeObsal)_2NO]$  shows  $\nu_{NO}$  at  $1640\text{ cm}^{-1}$ . These values suggest that the iron nitrosyl complex contains linear Fe-N-O bond and the cobalt nitrosyl complex contains bent Co-N-O bond. The room temperature effective magnetic moment of  $[Fe(MeObsal)_2NO]$  is measured to be 3.97 B.M. indicative of the presence of 3 unpaired electrons. The value shows that  $[Fe(MeObsal)_2NO]$  is a high spin  $\{Fe(NO)\}^7$  system. However, the complex  $[Co(MeObsal)_2NO]$  gives an effective magnetic moment of 0.91 B.M. indicating that there are no unpaired electrons present in this complex. It can be concluded that  $[Co(MeObsal)_2NO]$  is a low spin  $\{Co(NO)\}^8$ .

## INTRODUCTION

Nitric oxide, NO, is the simplest thermally stable odd-electron molecule known, and consequently, its electronic structure and reaction chemistry have been extensively studied. Many studies have been carried out to understand the modes of bonding of NO molecule, which exhibits greater coordination versatility compared with that of many other simple molecules such as carbon monoxide and dinitrogen.

Because of the lability of coordinated NO in redox processes and its versatility as a ligand, upon complexation with transition metal centres,<sup>1</sup> various modes of bonding are found in nitrosyl complexes. In many cases, the MNO bond angle is linear (close to  $180^\circ$ ), but in other cases, the MNO bond is strongly bent ( $120^\circ$ - $130^\circ$ ). However, in between the two extreme cases, compounds with partially bent MNO groups have been reported. The geometry of the MNO group can also be fluxional in solution. It is difficult to predict beforehand the preferred geometry of the whole range of complexes.<sup>2</sup>

As early as 1934, it was recognised that nitric oxide could lose or gain one electron<sup>3</sup> in its bonding interaction with a transition metal to give complexes of  $NO^+$  and  $NO^-$  i.e. complexes in which NO serves as a three-electron donor or one-electron donor,<sup>4</sup> respectively. It has hence been designated that linear MNO bonds contain  $NO^+$  whereas bent MNO bonds contain  $NO^-$ . However, this designation is found rigid and unsuitable in cases where extensive electron delocalization between metal and nitrosyl group occurs. This dichotomy has been partially overcome by using the  $\{MNO\}^n$  notation,<sup>5</sup> in which *n* is the number of *d*-type electron on the metal when the nitrosyl is formally considered to be  $NO^+$ . This system avoids any partition of the electrons to one fragment or another.

Infrared spectroscopy has been an accepted method for characterising metal nitrosyl complexes.<sup>6</sup> Coordinated NO groups absorb in the range of  $1045$  to  $1940\text{ cm}^{-1}$ , the majority being in the range of  $1626$  to  $1938\text{ cm}^{-1}$  which are recognised as containing  $NO^+$  species (linear MNO). The complexes which exhibit  $\nu_{NO}$  values in the range of  $1000$  to  $1200\text{ cm}^{-1}$  are considered to contain  $NO^-$  (bent MNO). Symons et al.<sup>7</sup> later suggested that  $NO^+$  ion showing an absorption band around  $1650\text{ cm}^{-1}$  and  $NO^-$  around  $1900\text{ cm}^{-1}$ . Many consequent studies have further redefined these values and the ranges of  $2000$ - $1600\text{ cm}^{-1}$  and  $1720$ - $1525\text{ cm}^{-1}$  have now been quoted for linear and bent MNO respectively.<sup>8</sup>

The value of effective magnetic moment,  $\mu_{\text{eff}}$ , of any coordination compound can be measured using a Gouy balance. This measurement can be used to investigate the magnetic behaviour of the complex and to find out the number of unpaired electrons, if any, in the metal center. The crystal field splitting diagram of the *d* orbitals of a metal in a square planar and in a metal schiff base mononitrosyl is illustrated in Figure 1. The



magnitude of  $\Delta$  determines the arrangement of electrons in the orbitals which can give rise to either high spin or low spin complexes.

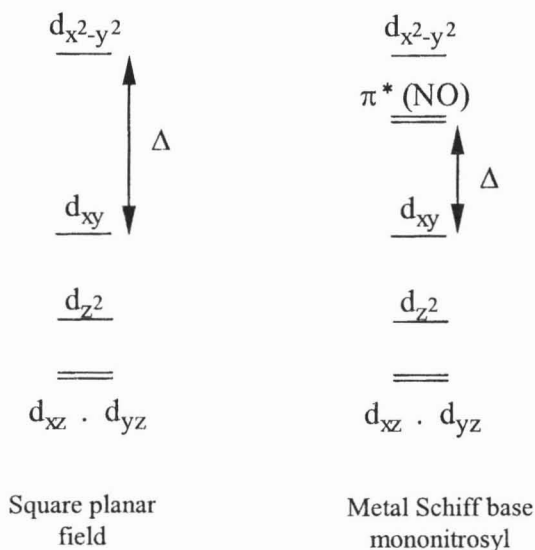


Figure 1 : Qualitative crystal field splitting diagrams of the  $d$  orbitals of a metal in a square planar field and a mononitrosyl Schiff base complex.

## EXPERIMENTAL

### *Preparation of the ligand N-4-methoxybenzylsalicylideneimine - (MeObsal)*

Equimolar ethanolic solutions (20 cm<sup>3</sup>) of salicylaldehyde (5.00 g, 40.94 mmol) and 4-methoxybenzylamine (6.27 g, 40.94 mmol) were mixed and heated under reflux for one hour. The bright yellow crystals obtained on cooling were filtered off, washed with cold ethanol and dried. Yield, 7.91 g (80%).

### *Preparation of the complex bis(N-4-methoxybenzylsalicylideneiminato)nitrosyliron - [Fe(MeObsal)<sub>2</sub>NO]*

As iron(II) is sensitive to aerial oxidation, the preparation was carried out fully in a full-glass nitrogen line, followed by a nitric oxide (NO) line. All manipulations were done under the environment of nitrogen gas, vacuum or NO gas.

The ligand (1.33 g, 5.51 mmol) and anhydrous sodium acetate (0.45 g, 5.51 mmol) were added to methanol (20 mL) and the solution was deoxygenated by the freeze-pump-thaw method before iron(II) perchlorate hexahydrate (1.00 g, 2.75 mmol) was added against a stream of nitrogen. The yellow colour of the solution immediately turned bright red but no solid was formed. The reaction mixture was stirred for 5 hours before NO gas was admitted and gas uptake started after stirring for about 1 minute. The colour darkened and some red solid appeared. When the reaction was complete (NO = 56 mL, 762.5 mmHg, 25°C, 2.51 mmol), the NO gas was replaced by nitrogen. The molar ratio of iron to NO was approximately 1:1. The flask was left overnight in a freezer to obtain more solid. The dark red product was filtered off, washed with cold methanol and dried under vacuum. It was air stable. Yield, 1.23 g (82%).

### *Preparation of the complex bis(N-4-methoxybenzylsalicylideneiminato)nitrosylcobalt - [Co(MeObsal)<sub>2</sub>NO]*

A solution of the ligand (1.00 g, 3.88 mmol) in methanol (20 mL) was allowed to react with cobalt(II) acetate tetrahydrate (0.48 g, 1.94 mmol) in a nitric oxide atmosphere. When the reaction was complete, 1.06 moles of NO was taken up per mole of cobalt(II) (NO = 50 mL, 20°C, 762 mmHg, 2.06 mmol). The black solid formed was filtered off, washed with methanol and air dried. Yield, 0.96 g (80%).

## RESULTS AND DISCUSSION

### Microanalyses of the ligand and complexes

The compounds synthesized were subjected to elemental analysis for C, H and N and the results are given in Table 1 below:

Table 1 : Results of C, H and N analyses of the ligand and coordination compounds synthesised.

	Percentage of C		Percentage of H		Percentage of N	
	Calc. (%)	Exp. (%)	Calc. (%)	Exp. (%)	Calc. (%)	Exp. (%)
Ligand MeObsal	74.67	74.66	6.27	6.25	5.81	5.76
Complex Fe(MeObsal) <sub>2</sub> NO	63.62	65.82	4.98	5.26	7.41	7.57
Complex Co(MeObsal) <sub>2</sub> NO	63.27	63.25	4.96	4.86	7.27	7.27

The results of the microanalyses above indicate that the compounds synthesized were of high purity.

### Proton NMR of the ligand N-4-methoxybenzylsalicylideneimine - (MeObsal)

The co-ligand N-4-methoxybenzylsalicylideneimine (MeObsal) is a bidentate Schiff base which has the structure below:

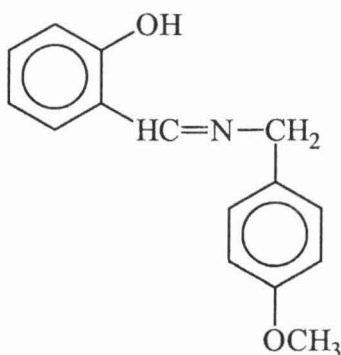


Figure 2 : The structure of the ligand N-4-methoxybenzylsalicylideneimine - (MeObsal)

Table 2 : Proton NMR data of N-4-methoxybenzylsalicylideneimine

Residue	No. of H	$\delta_H$ (ppm)
Phenyl rings	8	6.60-7.40 (multiplet)
CH	1	8.46 (singlet)
CH <sub>2</sub>	2	4.80 (singlet)
CH <sub>3</sub>	3	3.86 (singlet)

The proton NMR above showed that the ligand had indeed been formed in the synthesis. The OH signal of the Schiff base was not observed as the solvent used was deuterated methanol for reasons of solubility limitations. The proton and the deuterium of OH and OD of the ligand and the solvent respectively would exchange resulting in the absence of the OH signal, expected in the region of 10.00 to 13.00 ppm.<sup>9</sup>

### Infrared spectroscopy of the iron and cobalt complexes

The infrared spectra were recorded on a Perkin Elmer System 2000 Fourier Transformed Infrared (FTIR) from the range of 4000 – 400 cm<sup>-1</sup>. Samples were made up in KBr discs using a presser. Spectroscopic grade potassium bromide was pre-dried in a 400°C oven overnight and allowed to cool in a desiccator before used.

The NO stretching frequency,  $\nu_{\text{NO}}$ , for  $[\text{Fe}(\text{MeObsal})_2\text{NO}]$  was assigned at  $1777\text{ cm}^{-1}$  and for  $[\text{Co}(\text{MeObsal})_2\text{NO}]$  was at  $1640\text{ cm}^{-1}$ . These results indicate that the Fe-N-O bond is linear whereas the Co-N-O bond is bent.

#### Magnetic susceptibility measurements of the iron and cobalt complexes

Temperature variable magnetic measurements were carried out using a Gouy Balance supplied by Newport Instrument Ltd., the temperature ranging from room temperature to liquid nitrogen temperature. The field strength,  $H$ , was controlled by varying the current supply to the electromagnet using an ammeter, which was able to make precise reproduction of a particular field.

The sample was prepared by packing the solid tightly into a flat-based Pyrex glass tube of uniform bore which had been calibrated for its diamagnetism at various field strength throughout the range of temperatures.

It was found that the effective magnetic moment,  $\mu_{\text{eff}}$ , of  $\text{Fe}(\text{MeObsal})_2\text{NO}$  did not differ much in the range of temperatures investigated. At 291 K and 85 K, the values of  $\mu_{\text{eff}}$  were 3.97 and 3.90 B.M., respectively, which indicated the presence of 3 unpaired electrons. Hence it can be deduced that the system was high spin  $\{\text{Fe}(\text{NO})\}^7$ . The crystal field splitting diagram of such system is illustrated in Figure 3-a. Even though there is a slight lowering of the value of  $\mu_{\text{eff}}$ , there is no indication that a spin crossover from a high spin (Figure 3-a) to low spin (Figure 3-b) would occur above liquid nitrogen temperature.

The room temperature effective magnetic moment of the complex  $\text{Co}(\text{MeObsal})_2\text{NO}$  was measured to be 0.91 B.M. indicating that the system was low spin  $\{\text{Co}(\text{NO})\}^8$ . There were no unpaired electrons in the system as illustrated in Figure 3-d. It was therefore unnecessary to measure  $\mu_{\text{eff}}$  at a lower temperature.

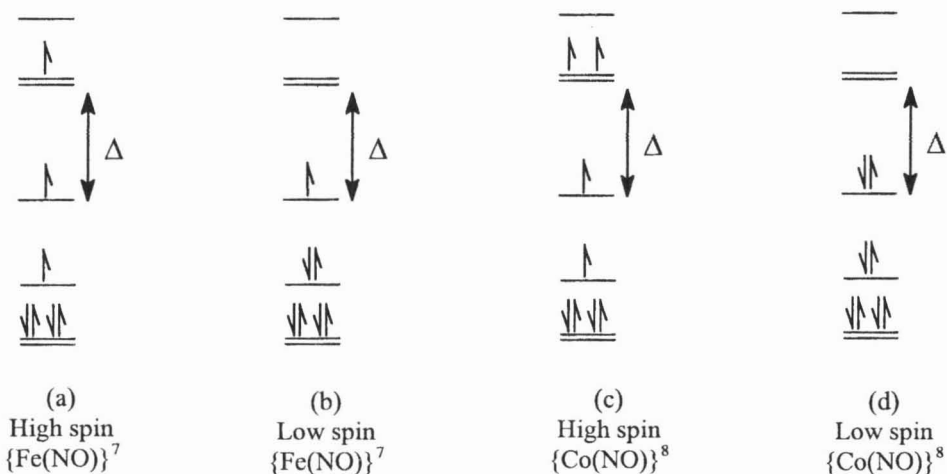


Figure 3 : High spin and low spin arrangements of electrons in  $\{\text{Fe}(\text{NO})\}^7$  and  $\{\text{Co}(\text{NO})\}^8$  – metal Schiff base mononitrosyl systems.

### CONCLUSION

This study has revealed a few interesting findings on the mode of bonding of nitrosyl ligand with Fe and Co centers in the presence of a same co-ligand. It also appears that these different metal centers give rise to different magnetic behaviours when they form complexes with the same ligands. Table 3 below summarises the finding:

Table 3 : Difference of mode of bonding of NO and the magnetism of Fe and Co centers when forming a complex with the same ligands.

	Fe center	Co center
NO stretching frequency, $\nu_{\text{NO}}$	1777 $\text{cm}^{-1}$	1640 $\text{cm}^{-1}$
M-N-O bond	Linear	Bent
Effective magnetic moment, $\mu_{\text{eff}}$	3.97 B.M.	0.91 B.M.
Magnetism	Paramagnetic 3 unpaired electrons High spin {Fe(NO)} <sup>7</sup>	Diamagnetic No unpaired electrons Low spin {Co(NO)} <sup>8</sup>

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