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Mononitrosyl derivatives of iron and cobalt complexes of quadridentate ligands from 2-hydroxy-1-naphthaldehyde and ethylenediamine, *o*-phenylenediamine, and 4-methyl-*o*-phenylenediamine

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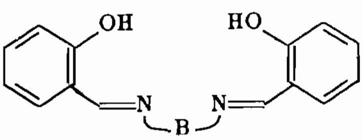
Abstract

The quadridentate Schiff bases prepared by condensation of 2-hydroxy-1-naphthaldehyde and ethylenediamine (naphth-enH_2), *o*-phenylenediamine (naphth-phH_2), and 4-methyl-*o*-phenylenediamine (naphth-mphH_2) form with cobalt(II) acetate and iron(II) perchlorate in methanol under nitric oxide the tetragonal pyramidal mononitrosyls [M(NO)(naphth-en)], [M(NO)(naphth-ph)] and [M(NO)(naphth-mph)], where M = Co or Fe. The iron complexes have temperature-independent magnetic moments corresponding to the presence of three unpaired electrons ($S=\frac{3}{2}$). The cobalt complexes are diamagnetic and the low field ^{15}N NMR shifts (*c.* 740 ppm with respect to $MeNO_2$) of the ^{15}NO-labelled complexes in solution show that they contain bent Co–N–O groups.

Introduction

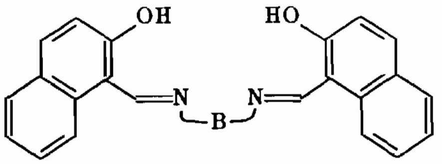
Transitions between the $S=\frac{3}{2}$ and $S=\frac{1}{2}$ spin states in [Fe(NO)(salen)] [1, 2] and [Fe(NO)(salphen)] [3–5] were detected by magnetic susceptibility measurements and confirmed by Mössbauer spectroscopy. The formulae of the quadridentate ligands salenH_2 and salphenH_2 are indicated in Scheme 1. The transition temperature T_c for [Fe(NO)(salen)] is 175 K, and the Mössbauer spectrum of each isomer can be observed in this region. As the temperature is lowered the spectrum of the $S=\frac{3}{2}$ state is progressively replaced by that of the $S=\frac{1}{2}$ state, with the reverse on heating. Thus the transition is slow on the Mössbauer effect time-scale. Spin pairing in [Fe(NO)(salen)] is also accompanied by a decrease in metal–ligand bond distances and the Fe–N–O bond angle [6]. The spin state transition in [Fe(NO)(salphen)] is centred at $T_c \approx 181$ K, but the transition is rapid on the Mössbauer time-scale since averaged spectra are observed in the region of T_c rather than a superposition of the spectra of the individual isomers [4]. Structural studies have been unsuccessful because of poor quality crystals. New iron mononitrosyls with quadridentrate co-ligands (Scheme 2) derived from 2-hydroxy-1-naphthaldehyde and ethylenediamine (naphth-enH_2), *o*-phenylenediamine (naphth-phH_2), and 4-methyl-*o*-phenylenediamine (naphth-mphH_2) have been prepared in a search for further examples of spin-state transitions. The corresponding cobalt mononitrosyls have also been characterised, and labelled with ^{15}NO for ^{15}N NMR investigations since it has been found that the position of the ^{15}N NMR resonance can be used to determine whether the Co–N–O bond is linear or bent [7].



salenH_2, B = CH_2CH_2

salphenH_2, B = o-C_6H_4

Scheme 1.



naphth–enH_2, B = CH_2CH_2

naphth–phH_2, B = o-C_6H_4

naphth–mphH_2, B = 4-Me-o-C_6H_4

Scheme 2.

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Experimental

Preparation of ligands

The ligands were prepared by the slow addition of the diamine in 1:2 molar ratio to a boiling ethanolic solution of 2-hydroxy-1-naphthaldehyde.

Preparation of metal complexes

The metal complexes were prepared in nitrogen from deoxygenated solvents. To prepare [Co(naphth-en)] cobalt(II) acetate tetrahydrate (0.25 g) was added to naphth-enH_2 (0.36 g) in ethanol (25 cm^3). The reaction mixture was heated to boiling and stirred for about 1 h. The red compound which separated was filtered off rapidly in air, washed with ethanol, and dried *in vacuo*.

The brown iron(II) complex [Fe(naphth-en)] separated when iron(II) perchlorate (0.36 g) was added to a solution of naphth-enH_2 (0.36 g) in methanol (25 cm^3). Sodium acetate (0.16 g) was also added to the reaction mixture which was stirred for about 4 h. The product was filtered off and washed with methanol (10 cm^3) under nitrogen, and then dried *in vacuo*. Solutions of this complex soon oxidise in air.

Preparation of cobalt mononitrosyls

The mononitrosyls [Co(NO)(naphth-en)], [Co(NO)(naphth-ph)] and [Co(NO)(naphth-mph)] were prepared in approximately 65% yield by the addition of cobalt(II) acetate tetrahydrate to a solution of the ligand in methanol under an atmosphere of nitric oxide. The apparatus was connected to a gas burette and it was found that one mole of NO was absorbed per mole of cobalt acetate. The preparation of [Co(NO)(naphth-en)] is typical. To naphth-enH_2 (0.36 g) in methanol (20 cm^3) was added cobalt(II) acetate tetrahydrate (0.25 g) under nitric oxide. The reaction mixture was stirred for 3 h by which time the uptake of NO had ceased. The dark brown precipitate was filtered off, washed with methanol (10 cm^3), and dried *in vacuo*. The complexes were labelled with ^{15}NO as before [7].

Preparation of iron mononitrosyls

The mononitrosyls [Fe(NO)(naphth-en)], [Fe(NO)(naphth-ph)] and [Fe(NO)(naphth-mph)] were similarly prepared in approximately 80% yield from iron(II) perchlorate and the ligand and sodium acetate in methanol with the absorption of one mole of NO per mole of iron(II) perchlorate. In the preparation of [Fe(NO)(naphth-en)] iron(II) perchlorate (0.36 g) and anhydrous sodium acetate (0.16 g) were added to naphth-enH_2 (0.36 g) in methanol (20 cm^3) under an atmosphere of nitric oxide. The reactants were stirred for 4 h and the blackish brown precipitate obtained was filtered off under nitrogen and dried *in vacuo*.

Physical measurements

Magnetic measurements were made from room to liquid nitrogen temperature by the Gouy method. Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer and at liquid nitrogen temperature with a cell VLT-1 from the Research and Industrial Instruments Company. ^{15}N and ^{59}Co NMR spectra were measured on a 400 MHz spectrometer at the University of Warwick.

Results and discussion

Iron complexes

The source of iron(II) in previous preparations was the acetate and to prepare the nitrosyls nitric oxide was allowed to react with the preformed iron(II) complex suspended in ethanol [1]. The more convenient method of mixing the acetate with the ligand under nitric oxide gave, from various solvents, light brown products without NO absorptions thought to be oxo-bridged iron(III) species. However, the iron mononitrosyls [Fe(NO)(naphth-en)], Fe(NO)-(naphth-ph)] and Fe(NO)(naphth-mph)] have been prepared (see 'Experimental') by the latter method from iron(II) perchlorate in methanol, as used recently by Bult *et al.* [5] for the preparation of [Fe(NO)(salphen)].

The magnetic moments of the iron nitrosyls at room temperature (Table 1) are *c.* 4.0 BM close to the spin-only values for 3 unpaired electrons (3.87 BM). Thus these are further examples of $S=\frac{3}{2}$ iron mononitrosyls. However, the moments decrease little with temperature over the range available so the behaviour is analogous to that of [Fe(NO)(5-Mesalen)] [1] rather than [Fe(NO)(salen)] or [Fe(NO)(salphen)]. Consistent with the essentially temperature-invariant magnetic moment, the infrared spectrum of [Fe(NO)(naphth-ph)] showed no change except sharpening of bands when the sample was cooled to liquid nitrogen temperature. When spin pairing occurs the NO stretching frequency is markedly affected [1, 3, 5]. Except for the NO absorptions the infrared spectra of the corresponding iron and cobalt nitrosyl complexes are closely similar. The NO stretching vibrations [ν(NO), Table 2] of [Fe(NO)(naphth-ph)] and [Fe(NO)(naphth-mph)] are easily assigned. The spectrum of Fe(NO)(naphth-en) shows very broad absorption in the region 1570–1660 cm^{-1} which overlaps the bands at 1610 and 1600 cm^{-1}; consequently, the shoulder at 1630

TABLE 1. Variation of magnetic moments (μ_{eff}) and magnetic susceptibilities (χ_A) of iron mononitrosyls with temperature

Fe(NO)(naphth-en)								
T (K)	293	261	229	197	165	133	101	87
$\chi_A \times 10^6$	7721	7665	8606	9953	11640	14300	18640	21190
μ_{eff} (BM)	4.03	4.00	3.97	3.96	3.92	3.90	3.88	3.84
Fe(NO)(naphth-ph)								
T (K)	293	261	229	197	165	133	101	87
$\chi_A \times 10^6$	6883	7736	8683	10060	11990	14770	18990	21660
μ_{eff} (BM)	4.02	4.02	3.98	3.98	3.98	3.96	3.91	3.88
Fe(NO)(naphth-mph)								
T (K)	293	261	229	197	165	133	101	
$\chi_A \times 10^6$	7189	7979	9057	10280	12190	14820	18430	
μ_{eff} (BM)	4.10	4.08	4.07	4.02	4.01	3.96	3.86	

TABLE 2. Analyses and NO stretching frequencies

Compound	Colour	Analyses (%)[a]			ν(NO)
		C	H	N	
Co(naphth-en)	reddish brown	66.8(67.8)	4.3(4.2)	7.6(6.6)	
Fe(naphth-en)	brown	68.1(68.3)	4.2(4.3)	6.2(6.6)	
Co(NO)(naphth-en)	dark brown	62.6(63.3)	4.1(3.95)	9.2(9.2)	1640s; ~1600s[b]
Co(NO)(naphth-ph)	reddish brown	66.1(66.8)	3.6(3.6)	8.2(8.35)	1628s; ~1590s[b]
Co(NO)(naphth-mph)	brownish black	67.8(67.3)	4.2(3.9)	8.2(8.1)	1645s; ~1600s[b]
Fe(NO)(naphth-en)	dark brown	62.8(63.7)	4.0(4.0)	8.8(9.3)	1710w, br; 1630sh[c]
Fe(NO)(naphth-ph)	brown	65.65(67.2)	3.8(3.6)	8.15(8.4)	1770s, vb
Fe(NO)(naphth-mph)	brown	67.1(67.7)	4.1(3.9)	8.1(8.2)	1755s
naphth-enH_2	lemon yellow	77.1(78.3)	5.4(5.4)	8.0(7.6)	
naphth-phH_2	yellowish orange	79.3(80.8)	4.55(4.8)	6.4(6.7)	
naphth-mphH_2	orange	79.0(80.9)	5.1(5.1)	6.5(6.5)	

[a] Calculated values are in parentheses. [b] ^{15}NO derivative; wave number uncertain because of overlap with ligand absorption. [c] Overlap with ligand absorption.

cm^{-1} has been tentatively assigned to ν(NO). A band at 1710 cm^{-1} seems too weak to be due to this vibration.

Cobalt complexes

The mononitrosyl cobalt complexes are further examples of the class of pyramidal complexes with apical NO ligands typified by [Co(NO)(salen)], which contains a bent Co–N–O group (Co–N̂–O = 127.0°) [8]. The NO stretching frequencies are close to that for Co(NO)(salen) (1624 cm^{-1}) [9], but infrared evidence does not clearly distinguish between linear and bent Co–N–O groups. However, ^{15}N resonances were detected in the 725–755 ppm region for the ^{15}NO labelled nitrosyls (Table 3) where the highly de-shielded ^{15}N nuclei of bent Co–N–O groups have been shown to resonate [7]. The ^{59}Co NMR signals are typical of cobalt(III) complexes. Thus, these mononitrosyls contain bent Co(III)–(N=O)$^-$ groups.

TABLE 3. ^{15}N and ^{59}Co NMR parameters of cobalt mononitrosyl complexes

Compound[a]	$\delta(^{15}N)$[b]	$\delta(^{59}Co)$[b]
Co(NO)(naphth-en)	725.7	8178
Co(NO)(naphth-ph)	752.1	8315
Co(NO)(naphth-mph)	748.4	8372

[a] Dissolved in deutero-dimethyl sulphoxide. [b] $\delta(^{15}N)$ relative to neat nitromethane and $\delta(^{59}Co)$ relative to aqueous $K_3[Co(CN)_6]$.

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