COPPER(II) AND IRON(III) COMPLEXES OF N-NITROSO-N-ALKYLHYDROXYLAMINES, AND THE X-RAY CRYSTAL STRUCTURES OF BIS(N-NITROSO-N-ISOPROPYLHYDROXYLAMINATO)COPPER(II) AND TRIS(N-NITROSO-N-PROPYLHYDROXYLAMINATO)IRON(III)

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Abstract—*N*-nitroso-*N*-alkylhydroxylamines have been prepared by hydrolysis of the mixture obtained by reaction of nitric oxide with Grignard reagents, and stabilized as their copper(II) or iron(III) complexes, $Cu(RN_2O_2)_2$ and $Fe(RN_2O_2)_3$, where R is, for example, Me, Et, Pr^{*i*}, Bu^{iso}, Ph, *n*-C₈H₁₇ or *n*-C₁₂H₂₅. The complexes have been characterized by analytical, magnetic and spectroscopic measurements. By single-crystal X-ray methods $Cu(Pr'N_2O_2)_2$ has been found to be *trans*-planar and $Fe(Pr^nN_2O_2)_3$ has a facial octahedral structure; in each complex the N—O bond lengths are equal with no significant variation between the copper and iron complexes.

The action of nitric oxide on alkyl compounds of diamagnetic metal atoms usually yields¹⁻¹⁶ the corresponding *N*-nitroso-*N*-alkylhydroxylamine derivative [eqn (1)]:

$$R - M + 2NO \rightarrow (RN_2O_2)M.$$
(1)

As with cupferron ($\mathbf{R} = \text{phenyl}$) complexes,¹⁷⁻¹⁹ the hydroxylamate ligand is chelated and coordinates through the two oxygen atoms in the X-ray crystallographic structures reported^{8,10,11,13,16-19} to date. Diamagnetic metals in eqn (1) include zinc, 1,2,12 magnesium,2-6 cadmium,² boron,² gallium,⁸ zirconium,^{9,10} aluminium.^{2,7,8} tungsten,^{11,12} copper(I),¹² niobium,^{13,14} tantalum,^{13,14} titanium,^{9,15} rhenium(III)¹⁶ and rhodium(I).¹² For some paramagnetic metal ions, for example, vanadium(IV),¹⁴ and titanium(III),¹⁴ the N-nitroso-Nalkylhydroxylamine derivatives cannot be prepared directly through eqn (1) while the reaction²⁰ of a low-valent cobalt nitrosyl with an alkyl halide afforded the nitrosoalkane complex.

Chemical identification of the products in eqn (1) was first carried out by Sand and Singer.³ They showed that the action of nitric oxide on phen-

ylmagnesium bromide followed by hydrolysis gave the free acid *N*-nitroso-*N*-phenylhydroxylamine (cupferron), identified because its reactions were the same as those of the product²¹ obtained by the action of nitrous acid on *N*-phenylhydroxylamine. The free acid could not be isolated on hydrolysis of the nitric oxide-methylmagnesium iodide reaction mixture, but Sand and Singer³ did obtain a copper(II) complex, Cu(MeN₂O₂)₂, on treatment of the product with copper(II) oxide. There are scattered references to copper(II) complexes of various other *N*nitroso-*N*-alkylhydroxylamines, but little other than their preparation^{1,3,5,9,12} and fungicidal properties²² have been reported.

We present here a convenient route to *N*-nitroso-*N*-alkylhydroxylamine derivatives of copper(II) and iron(III) which is based on the early work of Sand and Singer.³ As far as we know complexes of iron(III) have not been characterized previously.

EXPERIMENTAL

Preparation of the complexes

The ligands were first isolated as the magnesium complexes from the appropriate Grignard reagent.

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For example, magnesium turnings (1.25 g, 0.051 mol) were converted into the methyl Grignard by the slow addition of methyl iodide (7.1 g, 0.05 mol) in dry ether (80 cm^3). When the ethereal solution had been added the contents of the flask were refluxed for 1 h, the flask cooled in ice, evacuated, and nitric oxide admitted. The solution was stirred in nitric oxide until gas uptake ceased (gas burette). The solvent was removed under reduced pressure, and the resulting pale yellow and hygroscopic *N*-nitroso Grignard complex was stored over calcium chloride.

To prepare the copper(II) complex, half by weight of the product was suspended in water (100 cm³), cooled, and acidified with dilute sulphuric acid to give the free *N*-nitroso-*N*-methylhydroxylamine which was then extracted into ether (5×20 cm³ portions). Copper(II) oxide in excess was stirred with the combined extract for several hours, and the suspension left to stand overnight. The deep blue liquor was filtered from the copper(II) oxide which was washed with acetone. The ether and acetone solutions were evaporated to dryness, and the solid recrystallized from methylated spirits. The blue crystals were dried in vacuum.

To prepare the iron(III) complex, iron(III) alum in excess was added to a cooled aqueous suspension of the remaining N-nitroso Grignard complex and after stirring for half an hour the iron(III) complex was extracted into chloroform (6×20 -cm³ portions). The extract was dried with calcium chloride, filtered, and taken to dryness. The solid was recrystallized from methylated spirits and the orange crystals dried *in vacuo*.

Complexes of other *N*-nitroso-*N*-substituted hydroxylamines were similarly prepared (Table 1). They were obtained in 20–40% yield based on the mass of magnesium.

The N-methyl derivatives were also prepared from N-methyl hydroxylamine hydrochloride. This was dissolved in water, acidified with hydrochloric acid, cooled to 0°C, and iron(III) alum and sodium nitrite added with stirring. The iron(III) complex was extracted with chloroform as above. The copper(II) complex was prepared by continuous extraction of the N-nitroso-N-methylhydroxylamine into a suspension of the oxide in ether. The N-phenyl-substituted complexes were also prepared from cupferron in aqueous solution. These methods gave 80-90% yields.

Physical measurements

Diffuse-reflectance electronic spectra were recorded using powdered samples with lithium fluoride as reference material on a Beckman Acta MIV spectrophotometer. Relative molecular masses were measured using a calibrated Mechrolab vapour phase osmometer model 301A (solvent chloroform).

Crystallography

Crystals of $Fe(Pr^nN_2O_2)_3$ and $Cu(Pr^iN_2O_2)_2$ suitable for X-ray investigation were obtained from methylated spirits.

Crystal data. $C_9H_{21}N_6O_6Fe(I)$, M = 365.15, orthorhombic, a = 9.059(1), b = 11.492(1), c = 15.988(2) Å, U = 1664.5 Å³, space group $P2_12_12_1$, Z = 4, $D_c = 1.457$ g cm⁻³, F(000) = 764, $\mu(Mo-K_{\alpha}) = 9.4$ cm⁻¹.

 $C_6H_{14}N_4O_4Cu(II), M = 269.74,$ monoclinic, a = 22.789(2), b = 4.865(1), c = 11.400(1) Å, $U = 1106.6 Å^3$, space group C2/c, Z = 4, $D_c = 1.619 \text{ g cm}^{-3}, F(000) = 556, \mu(\text{Mo-}K_{\alpha}) = 19.8 \text{ cm}^{-1}.$

Data collection and processing. Numbers in brackets refer to structure II. Intensity data were collected using graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71069$ Å) on an Enraf-Nonius CAD4 four-circle diffractometer in a ω -2 θ scan mode. 1896 (1253) reflexions were measured [sin $\theta/\lambda \le 0.62$], which reduced to 1875 (1111) unique reflexions with 1537 (926) reflexions having $I \ge 3\sigma(I)$. Following Lp correction, analysis of a standard reflexion showed no significant decay.

Structure analysis and refinement. The heavyatom method was used to solve and develop the structures. In structure II it was noted that (k+l)and (h+l) even were systematically strong and the volume indicated four molecules per unit cell implying that copper is on a centre of symmetry, at $(\frac{1}{4}, \frac{1}{4})$ 0) and related positions. When phased on copper alone the (k+l), l = odd reflexions will have zero calculated F_c s causing two peaks per atom on the F_o map. Correct selection of atom positions overcame this. Full-matrix least-squares refinement was carried out using isotropic thermal parameters and an empirical absorption correction, DIFABS²³ was applied [1768 (1039) reflexions corrected, minimum absorption correction 0.822 (0.851), maximum 1.168 (1.256), average 0.987 (0.989)] prior to refinement with anisotropic thermal parameters. The positions of hydrogen atoms were calculated geometrically and the weighting scheme $w = 1/[\sigma^2(F_o) + 0.05(F_o)^2]$ gave satisfactory agreement analysis. Final R and R_w values are 0.043 (0.025) and 0.056 (0.034). All crystallographic programs used were from the SDP package.²⁴

Selected bond lengths and angles are given in Table 2. Fractional atomic coordinates, anisotropic temperature factor coefficients and F_o/F_c values

Complex ^a	M.p. (°C)	RMM ^{bc}	Analysis (%) ^b				Reflectance ^e spectrum absorption ^f	
			С	Н	N	μ_{eff}^{d} (BM)	maxima (cm ⁻¹)	
$\overline{\text{Cu(MeN}_2\text{O}_2)_2}$	196	212 ⁴				1.93 ⁱ		
	196 ^g	(214)						
$Cu(EtN_2O_2)_2^{j}$	113	261 [*] (241)				1.93		
$Cu(Pr'N_2O_2)_2$	131	274 ^h	27.9	5.6	20.6	1.87 ⁱ	15,600	17,900
·	133 ^g	(270)	(26.7)	(5.2)	(20.8)			
$Cu(Bu''N_2O_2)_2$	73		32.5	6.0	18.8		16,000	(17,900)
			(32.3)	(6.1)	(18.8)			
$Cu(Bu^{iso}N_2O_2)_2$	79		32.4	6.7	18.6		16,000	17,900
	80–83 ^k		(32.3)	(6.1)	(18.8)			
$Cu(Bu^{sec}N_2O_2)_2^{j}$	115	297 ^h	32.3	6.1	18.5		15,900	(17,900)
	122 ^g	(296)	(32.3)	(6.1)	(18.8)			
$Cu(Bu'N_2O_2)_2$	152		32.6	6.0	18.6		16,000	(18,900)
			(32.3)	(6.1)	(18.8)			
$Cu(n-C_8H_{17}N_2O_2)_2$	106	410	46.4	8.1	13.5	2.02^{j}	16,000	17,900
		(434)	(46.9)	(8.4)	(13.7)			
$Cu(n-C_{12}H_{25}N_2O_2)_2$	99		55.7	10.0	10.6	1.97	16,000	17,900
			(55.2)	(9.7)	(10.7)			
$Cu(allylN_2O_2)_2$	73		27.3	3.7	21.0		15,700	17,700
			(27.1)	(3.8)	(21.1)			
$Cu(PhN_2O_2)_2$	197					2.02		
$Fc(McN_2O_2)_3^{j}$	150	297	12.9	3.2	29.6	6.00		
		(281)	(12.8)	(3.2)	(29.9)			
$Fe(EtN_2O_2)_3$	85	350	23.1	5.0	25.0	5.94		
		(323)	(22.3)	(4.7)	(26.0)			
$Fe(Pr'N_2O_2)_3$	61		29.7	5.8	22.7	5.81		
			(29.6)	(5.8)	(23.0)			
$Fe(Bu^{sec}N_2O_2)_3$	64		34.3	6.6	19.0			
			(35.4)	(6.7)	(20.6)			
$Fe(n-C_{12}H_{25}N_2O_2)_3$	42	760	58.8	10.2	11.5	6.03		
		(744)	(58.2)	(10.3)	(11.3)			
$Fe(PhN_2O_2)_2$	141	510	46.5	3.1	17.2	5.96		
		(470)	(46.3)	(4.2)	(18.0)			

Table 1. Analytical, spectroscopic and related data

^{*a*}Cu(II) complexes of cyclohexyl⁵ and trimethylsilylmethyl¹² also known. Complexes are new except Cu, R = Me, Pr^{i} , Bu^{iso} , Bu^{sec} , Ph; Fe, R = Ph.

^bCalculated values in parentheses.

^c Vapour pressure osmometry (CHCl₃).

^d At room temperature, 1 BM = 9.274×10^{-24} A m².

^e Also a shoulder near $13,200 \text{ cm}^{-1}$.

^fParentheses indicate ill-defined maximum.

^g Reference 22.

^h Parent ions observed in mass spectra.

'The Me derivative⁹ has $\theta = 8^{\circ}$, the *n*-C₈H₁₇ derivative has $\theta = 10^{\circ}$, and the Pr' derivative obeys the Curie law [μ_{eff} (90 K) = 1.88 BM] with $1/\chi = C(T+\theta)$.

¹Non-conducting in acetone at 25°C.

^k Reference 5.

			(i) Fe(1	$Pr^n N_2 O_2)_3$			
Atom 1	Atom 2	Di	stance	Aton	n 1	Atom 2	Distance
Fe	0	2.0	01(10)	0		N	1.313(11)
Ν	Ν	1.2	66(10)	Ν		С	1.468(6)
С	С	1.4	98(16)				
	Ato	m 1	Atom 2	Atom 3	A	ngle	
	0	(11)	Fe	O(12)	7	6.2(2)	
	O	(11)	Fe	O(32)	9	1.7(2)	
	O	(11)	Fe	O(22)	16	2.4(2)	
	O	(11)	N(11)	N(12)	12	2.8(4)	
	O	(11)	N(11)	C(11)	11	8.3(4)	
	N	(22)	N(21)	C(21)	12	0.3(5)	
			(ii) Cu	$(\mathbf{Pr'N}_2\mathbf{O}_2)_2$			
Atom 1	Atom 2	Di	stance	Aton	n 1	Atom 2	Distance
Cu	0	1.9	906(4)	0		N	1.316(4)
Ν	Ν	1.	273(3)	N		С	1.473(3)
С	С	1.	514(4)				
	Ato	m 1	Atom 2	Atom 3	A	ngle	
	0	(1)	Cu	O(1′)	18	0.0(1)	
	O	(1)	Cu	O(2)	8	1.99(6)	
	Cu	1	O(1)	N(1)	10	8.6(1)	
	Cı	1	O(2)	N(2)	11	3.4(1)	
	O	(1)	N(12)	N(2)	12	2.5(2)	
	N	(2)	N(1)	C(1)	11	9.7(2)	

Table 2. Selected bond distances (Å) and angles (°)

have been deposted as supplementary data with the Editor.*

RESULTS AND DISCUSSION

The three methods of preparation of the copper(II) and iron(III) complexes are outlined in Schemes 1–3.

The N-methyl-substituted copper(II) and iron(III) complexes whether prepared by Scheme 1 or 2 had identical melting points and IR and mass spectra. The same is true for the N-phenyl derivatives from Schemes 1 and 3. The constitution of the complexes is therefore clearly established although the structure of the N-nitroso Grignard intermediate remains uncertain. Although alkylmagnesium bromides and iodides are monomeric in ether at low concentration (less than about 3×10^{-2} mol dm⁻³), 25,26 at concentrations used in preparative studies they are mostly dimeric and exist either as III or IV. 26



It is possible that the action of nitric oxide on III or IV in ether would initially yield species I or II, respectively, but in either case hydrolysis will give RN(NO)OH and complex formation with, e.g. Cu^{2+} will give $[Rn(NO)O]_2Cu$. Since neither the active species in the Grignard reagent nor the initial

^{*} Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.



$$RNH_{2}OH^{+} + NaNO_{2} \xrightarrow{H^{+}} N \xrightarrow{R} OH \xrightarrow{Cu^{2^{+}} \text{ or }} metal \text{ complexes}$$

Scheme 2.

 $\underset{\text{cupferron}}{\text{NH}_4[\text{PhN}_2\text{O}_2]} \xrightarrow{M^{n+}} M(\text{PhN}_2\text{O}_2)_n \begin{cases} M = \text{Cu}, \ n = 2\\ M = \text{Fe}, \ n = 3 \end{cases}$

Scheme 3.

magnesium complex produced is known, the simplest schematic formulation that is stoichiometrically correct is given below:

$$Mg + RX \longrightarrow RMgX \xrightarrow{NO} R - N - O - MgX$$
$$\downarrow N = O$$
I

Molecular structures

The molecular structure and the atom-numbering scheme for $Cu(Pr^iN_2O_2)_2$ are shown in Fig. 1. The molecule excluding the alkyl substituents is planar, and the ligands are *trans* as in the *N*-phenyl analogue.¹⁷ The Cu—O bond distances are equal

(Table 2) within experimental error but the small bite of the ligand leads to angles significantly below 90° subtended at the metal atom (O(1)—Cu—O(2) = 81.99°). The nearest neighbours axially to the copper(II) ion are N(2) atoms at 3.2 Å, which is much greater than the sum of the radii of Cu²⁺ and nitrogen (*ca* 2.3 Å). Thus there is no intermolecular interaction and the copper(II) ions are in essentially planar coordination.

The atom-numbering scheme and the molecular structure of $Fe(Pr^{T}N_2O_2)_3$ are presented in Fig. 2. The six O atoms form a distorted octahedron around the iron(III) ion, and the Fe—O distances (Table 2) are the same (2.00 Å) as in the phenyl derivative.¹⁸ The ligands are in a facial arrangement. As in the copper(II) complex, the ligands



Fig. 1. Atom-numbering scheme, structure, and stereoscopic view of Cu(Pr'N₂O₂)₂.



Fig. 2. Atom-numbering scheme, structure, and stereoscopic view of Fe(Pr"N₂O₂)₃.

subtend small angles at the metal ion (76.2°) . The ligand dimensions are the same in the two complexes within the stated standard deviations. The N—O bond lengths in the copper(II) and iron(III) complexes are almost equal [Cu, 1.316(4) Å; and Fe, 1.313(11) Å]. Those for Cu(II) are much better refined than any ^{8,10,11,13,16-19} previously reported. On reviewing the available structures of N-nitroso-N-nitroso-N-arylhydroxylaminato N-alkylor complexes we find no compelling evidence, as judged by the reported standard deviations in the N-O bond lengths, to support the claim¹⁰ that significantly different N-O bond lengths occur within a single ligand in any given complex. Our values are intermediate between those expected¹⁰ for single (ca 1.37 Å) and double (ca 1.23 Å) bonds. Our N-N bond lengths are short¹⁰ and invariant with clear evidence for significant double-bond character. The C-N bond distances are normal for single bonds (Table 2).

Magnetic measurements

The effective magnetic moments (μ_{eff}) of the copper(II) complexes (Table 1) are a little above the spin-only value (1.73 BM) as expected for planar or tetragonally-distorted, six-coordinate complexes; and the moments of Cu(Pr'N₂O₂)₂ and Cu(n-C₈H₁₇N₂O₂)₂ are almost independent of temperature (Table 1) as expected for monomeric complexes. The iron(III) complexes are high-spin (for the $t_{2g}^3 e_g^2$ configuration moments close to the spin-only value of 5.92 BM are expected); thus the *N*-nitroso-*N*-alkylhydroxylamines are weak field ligands.

Electronic spectroscopic measurements on the copper(II) complexes

The electronic spectra of copper(II) complexes have been extensively reviewed.^{27,28} Potentially π bonding ligands such as acetylacetonate (acac) and its derivatives appear to favour square planar CuO₄ geometry. The electronic spectra of this chromophore, recorded by diffuse reflectance from powdered samples or by polarized measurements from single crystals, exhibit three or four bands in the visible region with no absorption maxima below 10,000 cm⁻¹. The polarized spectrum of Cu(3- ϕ acac)₂ is typical with maxima at 15,400, 16,900, 19,000 and 20,600 cm⁻¹, while in other cases, e.g. CaCuSi₄O₁₀ and Cu(3-Meacac)₂, the spectrum is shifted to lower energy by 2500–1000 cm⁻¹.

These complexes have T (a corrected ratio of the in-plane bond lengths to axial contacts) in the range 0.56–0.66. Semi-coordination need not be considered. If the in-plane bond lengths are about 2 Å then the close contacts in the axial directions are at least 2.8–3 Å for true square planar CuO₄ chromophores. The bond lengths in the solid state are not temperature-dependent.

The diffuse-reflectance spectra of powdered samples of our blue/violet copper(II) complexes (Table 1) are all very similar. A broad envelope centred near 16,700 cm⁻¹ has two ill-resolved maxima near 15,600 and 17,800 cm⁻¹, with a low-energy shoulder at about 13,200 cm⁻¹. The complex $Cu(Pr^iN_2O_2)_2$ is square planar with T (uncorrected) = 0.59 as determined by the in-plane Cu-O distances and the closest contacts to Cu from N(2) above and below the plane at 3.205 Å. The spectra show that all of the copper(II) complexes reported here are square planar and confirm the established structure-spectral correlations for such chromophores. It would appear that the olefinic function in $Cu(allylN_2O_2)_2$ does not interact with the copper(II) atom.

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