Comparison between the Bis(2-thiopyridine *N*-oxide) Derivatives of Cu^{II} and Ni^{I}: an Electron Spin Resonance Study†

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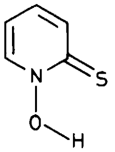
The e.s.r. spectra for dilute solutions of Cu^{II} and Ni^{I} in bis(2-thiopyridine *N*-oxide)nickel(II) have been studied at 77 K. The latter, formed by exposure to ionizing radiation, was also prepared by electron addition to the Ni^{II} complex in CD_3OD and 2-methyltetrahydrofuran. The spectra are typical of $3d^9$ complexes with a $d_{x^2-y^2}$ semi-occupied molecular orbital. Analysis of the ^{61}Ni and ^{63}Cu hyperfine coupling constants gave spin densities of 59 and 87% on copper and nickel respectively. The reduced delocalisation for the Ni^{I} complex is discussed in terms of the smaller positive charge and consequent weaker bonding. This is also thought to be responsible for the low stability of the Ni^{I} complex, which changed irreversibly on annealing to *ca.* 140 K. Analysis of the *g*-tensor components shows that the d_{xz} and d_{yz} levels are split, as expected because of the low symmetry, and are higher in energy than the in-plane d_{xy} orbital. Unfortunately, attempts to detect the Ni^{III} complex after radiolysis were not successful.

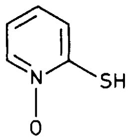
Since the preparation[1] of 1-hydroxy-2-pyridinethione (**1**) or its tautomer 2-mercaptopyridine *N*-oxide (**2**), with the former considered to be the dominant form,[2] there has been only limited study of this substance and its ability to form metal ion complexes. The first report of the preparation of such complexes was a study of their bactericidal and fungicidal properties,[3] little attention being paid to their chemical properties. Robinson[4] reported the preparation of first-row transition-metal ion complexes and measured their molecular weights, molar conductivities, magnetic susceptibilities, electronic spectra, and a few bands of their i.r. spectra. In a report[5] of the lanthanide complexes of this ligand the important bands from the i.r. spectra of the complexed ligand for the chromium(III) solid were reassigned. More recently an e.s.r. study of the amine adducts to the bis(2-thiopyridine *N*-oxide)copper(II) has been communicated.[6]

Apart from our general interest in the potentialities of this ligand, we wished to examine the possibility of converting the diamagnetic Ni^{II} complex into the paramagnetic Ni^{III} and Ni^{I} complexes using ionizing radiation, and hence, in particular, to compare the magnetic properties of the Ni^{I} complex with those of the isoelectronic Cu^{II}.

We have shown over the past few years that ionizing radiation provides an effective route to electron-gain and -loss species, which, if formed from a diamagnetic precursor, are paramagnetic and hence are generally suitable for e.s.r. study.[7] Since this is one of the most powerful tools for investigating the magnetic properties of paramagnetic centres, the combination of techniques can give considerable insight into the structure of centres which are often not accessible by other routes. In particular, novel transition-metal complexes are readily prepared by this technique, which has the unique advantage that the paramagnetic centres can be prepared directly as dilute solutions in diamagnetic host lattices, which is a required situation for e.s.r. studies. Examples of such studies include the preparation of $[Fe(CN)_x(NO)]^{3-}$ complexes,[8] various paramagnetic $[M(CO)_xX]^{y-}$(X = halogen) complexes,[9-11] and various paramagnetic cyclopentadienyl derivatives.[12,13]

Our study of electron-gain and -loss by $[Ni(CN)_4]^{3-}$ ions is particularly relevant to the present work.[14] In this study, both gain and loss centres were detected by e.s.r. spectroscopy. These were identified only from chemical expectation and the forms of the *g*-tensor components. Characterisation is much more precise if metal hyperfine coupling can be detected, but ^{61}Ni has such low abundance (1.25%) and such a low magnetic moment (0.746 B.M.) that it is usually impossible to pick up features from ^{61}Ni in natural abundance. Hence, in order to facilitate identification and comparison with the Cu^{II} derivative, we have used samples 44% enriched in ^{61}Ni in the present study.


(**1**)


(**2**)

Experimental

The complex bis(2-thiopyridine *N*-oxide)nickel(II) was prepared as previously described,[6] and its identity was established by i.r. spectroscopic analysis. Traces of Cu^{II} were readily incorporated into the crystalline product, the Cu^{II} being uniformly distributed as established by the narrow e.s.r. features (Figure 1).

Dilute solutions in CD_3OD (used in preference to CH_3OH because of the greatly reduced span of signals from trapped solvent radicals) and 2-methyltetrahydrofuran (mthf) were degassed and frozen as small beads prior to irradiation at 77 K. Samples were irradiated in a ^{60}Co Vickrad γ-ray source for up to 2 h at a dose rate of *ca.* 1 Mrad h^{-1}. E.s.r. spectra were measured at 77 K with a Varian E109 spectrometer calibrated with a Hewlett-Packard 5246L frequency counter and a Bruker B-H12E field probe, which were standardized with a sample of diphenylpicrylhydrazyl (dpph). Samples were annealed above 77 K after decanting the liquid nitrogen from the insert Dewar flask. They were recooled to 77 K whenever significant changes in the spectra were detected.

Results and Discussion

The Copper(II) *Complex.*—The 77 K *X*-band powder e.s.r. spectrum for this complex in the lattice of the Ni^{II} complex is

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† *Non-S.I. units employed*: B.M. = 9.274×10^{-24} J T^{-1}, rad = 10^{-2} J kg^{-1}, G = 10^{-4} T.

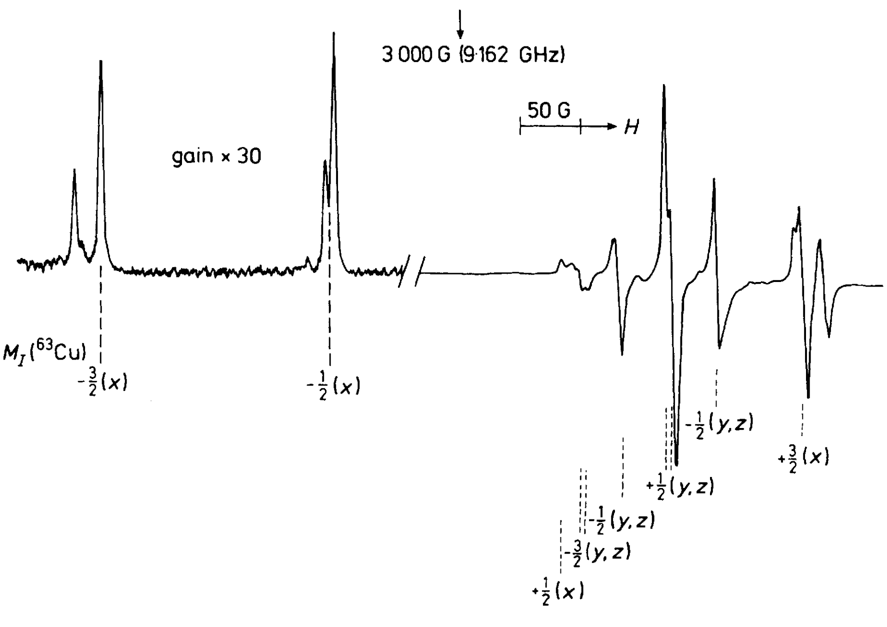

Figure 1. First-derivative *X*-band e.s.r. spectrum for bis(2-thiopyridine *N*-oxide)copper(II) in the Ni^{II} complex at 77 K

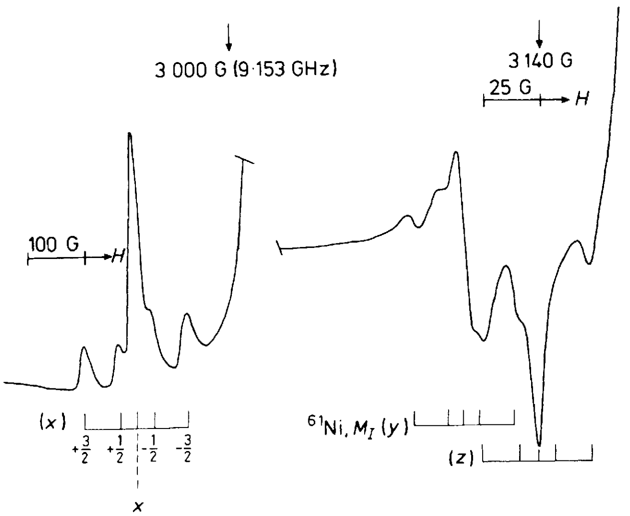

Figure 2. First-derivative *X*-band e.s.r. spectrum for a dilute solution of bis(2-thiopyridine *N*-oxide)nickel(II) in mthf at 77 K after exposure to ^{60}Co γ-rays, showing features assigned to the Ni^I complex

shown in Figure 1. Weak satellite lines whose intensity increased with power are assigned to neighbouring proton 'spin-flip' transitions,[15] and weak features between the main *x*, *y* components are assigned to forbidden electron–nuclear transitions enhanced by nuclear quadrupole interactions. The appearance of *x*–*y* splitting on some features and not on others is also explicable in terms of differing quadrupole shifts for the *x* and *y* components.

The 61-*Nickel*(I) *Complex*.—Initial spectra obtained from the crystalline complex, and from solutions in CD_3OD and mthf were similar, the best resolution being shown by the mthf system (Figure 2). The central ($g = 2$) signal from solvent radicals has been omitted. This is much less extensive for the CD_3OD system and we are sure that there are no extra components from the Ni^I complex.

Table 1. Experimental e.s.r. parameters for Cu^{II} and Ni^I complexes

Metal ion		g_x	g_y	g_z	A_x/G	A_y/G	A_z/G
Cu^{II}		2.150	2.041	2.039	194[b]	36.5	36.5
	a	2.153	2.066	2.027			
	c	2.145	2.042	2.042	190	43	43
Ni^I	*d*	2.257	2.086	2.0655	61	15	15.8
	e	2.253	2.086	2.071			
	f	2.214	2.1005	2.1005	65	14	14
	g	2.225	2.107	2.099			

[a] Pure compound; ref. 8. [b] ^{63}Cu, ^{65}Cu, 207 G. [c] Solution in $MeNO_2$. [d] In mthf. [e] In CD_3OD. [f] Second species in mthf. [g] Second species in CD_3OD.

We are confident of our identification of this species as a Ni^I centre for three major reasons. (*i*) It is now well established that the only significant reaction experienced by dilute solutes in these solvents is reaction with electrons. (*ii*) The e.s.r. parameters are those expected for d^9 complexes with a $d_{x^2-y^2}$ semi-occupied molecular orbital (s.o.m.o.). (*iii*) As we show below, the results compare very well with those for the Cu^{II} complex.

We conclude that the primary product is a Ni^I complex having a square-planar co-ordination (O_2S_2) comparable with that for the Ni^{II} and Cu^{II} complexes. This, however, is not the most stable co-ordination, since, on annealing, quite drastic changes in the e.s.r. spectra were observed (Table 1). Unfortunately, although the modified *g* values were clearly obtained from the non-magnetic nickel isotopes, the hyperfine features for ^{61}Ni were so poorly defined that we have been unable to make any firm identification of this secondary Ni^I species. We note that the hyperfine features are asymmetrically placed with respect to the non-magnetic components, indicating a descent in symmetry such that the *g*- and *A*-tensors no longer share common axes. This may imply a relaxation away from the original 'square-planar' configuration, or the breaking of one or more metal–ligand bonds. In the absence of better spectra we confine our attention to the primary species.

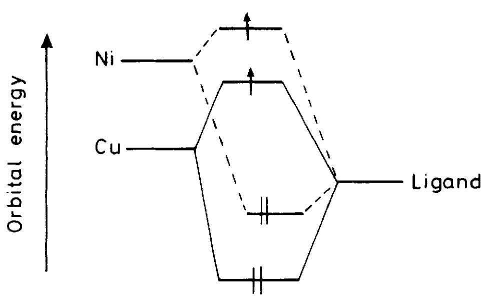

Figure 3. Qualitative energy-level diagrams designed to show the increase in localisation of the s.o.m.o. on the metal on going from copper to nickel

Comparison between the $\mathrm{Cu^{II}}$ *and* $\mathrm{Ni^{I}}$ *Complexes.*—(*i*) *The* g*-tensor components.* The most notable difference is the greatly enhanced g shifts for the $\mathrm{Ni^{I}}$ complex (Table 1). This is opposite to the trend expected, since the spin–orbit coupling constant for $\mathrm{Cu^{2+}}$ (830 $\mathrm{cm^{-1}}$) is greater than that for $\mathrm{Ni^{+}}$ (603 $\mathrm{cm^{-1}}$).

There are two associated factors which are likely to be responsible: an increase in the spin density, and a weakening of the metal–ligand bonds, on going from copper to nickel. These are a direct consequence of the increase in electronegativity for copper, as can be judged from a consideration of the simple scheme in Figure 3. We have estimated the metal spin densities from our analysis of the hyperfine coupling parameters (see below). Using these values and equation (1) we have made

$$\Delta E_i = n_i \lambda k/\Delta g_i \qquad (1)$$

estimates of the $3d$ orbital separations from the g-tensor components (Table 2). (The parameter k is the orbital reduction factor, equated to the spin density on the metal, λ is the spin–orbit coupling constant, the values of n_i are given by the magic pentagon, and ΔE_i is the energy separation between the s.o.m.o. and the orbital with which it couples.)

The results show that the d_{xz} and d_{yz} orbitals are above the d_{xy} orbital in energy, as is usually the case, although the splitting is only *ca.* 963 $\mathrm{cm^{-1}}$ for the copper complex. This proximity can be understood in terms of a significant degree of in-plane π bonding for d_{xy} and the in-plane $2p$(O) and $3p$(S) orbitals of the ligands.

There is a significant decrease in the orbital separations on going from $\mathrm{Cu^{II}}$ to $\mathrm{Ni^{I}}$. This reflects the expected decrease in bond strengths predicted in Figure 3. There is a relatively larger splitting between the x and y components for the $\mathrm{Ni^{I}}$ complex. Such a splitting is expected for these complexes because they do not have strict axial symmetry. The increase for the nickel complex is again thought to be a reflection of the weaker bonding, giving a greater differentiation between bonding to sulphur and to oxygen.

(*ii*) *The hyperfine coupling constants.* Before these can be processed to give estimates of spin densities on the metal atoms, they have to be corrected for orbital magnetic contributions to the coupling. This is readily done using the experimental g-tensor components and equations (2) and (3).[16]

$$A_{\parallel} = A_{\mathrm{iso}} + 2B(1 - \tfrac{7}{4}\Delta g_{\parallel} - \tfrac{3}{4}\Delta g_{\perp}) \qquad (2)$$

$$A_{\perp} = A_{\mathrm{iso}} - B(1 + \tfrac{11}{4}\Delta g_{\perp}) \qquad (3)$$

Table 2. $3d$ Orbital splitting parameters ($\mathrm{cm^{-1}}$)

Metal ion	$\Delta[(x^2 - y^2) - xy]$	$\Delta[(x^2 - y^2) - xz, yz]$
$\mathrm{Cu^{II}}$	15 405	14 442
$\mathrm{Ni^{I}}$	14 321	12 092

Table 3. Derived hyperfine coupling parameters and orbital populations for $\mathrm{Cu^{II}}$ and $\mathrm{Ni^{I}}$ complexes

Metal ion	A_{iso}/MHz	$2B$/MHz	$3d_{x^2-y^2}$ population (%)
$\mathrm{Cu^{II}}$ [a]	289	416.8	59 [b]
$\mathrm{Ni^{I}}$ [a]	110.3	164.2	87 [c]

[a] Using like signs for A-tensor components. [b] Using atomic value $2B^{\circ} = 705.6$ MHz. [c] Using $2B^{\circ} = 189$ MHz.

To facilitate the calculations of spin densities, we have averaged the x and y parameters to obtain effective perpendicular data. The results of these calculations are given in Table 3. They confirm the prediction of Figure 3 that the extent of delocalisation of the s.o.m.o. onto the ligands should be greater for copper than for nickel. We have used like-signs for the A-tensor components since, in both cases, the results using opposite signs seemed to us to be unacceptable.

We conclude that the e.s.r. parameters for these complexes can be used to illustrate and quantify the general trends predicted (Figure 3). It would be most interesting to obtain e.s.r. data for the $\mathrm{Ni^{III}}$ complex which should have been formed on irradiation. Unfortunately, no such complex was detected. Central features characteristic of organic radicals were obtained, and it is possible that electron loss occurred primarily from the ligands rather than the metal.

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