The similarity of the $[Ni(i\text{-mns})_3]^{2-}$ chelate with the nickel(IV) dichalcogenocarbamates leads to the question concerning analogies in the photosensitivity of both systems.[19,20] Solutions of $[Ni(i\text{-mns})_3]^{2-}$ are found to be fairly stable. The absorptivity of the first band (16.1×10^3 cm^{-1}) decreases only to about 4% in the dark and to about 30% at laboratory light within 3 weeks (acetonic solution; $c = 10^{-3}$ M). However, treatment of this solution with strong visible light (1000-W projection lamp) results in the disappearance of the intense green color leaving the red-brown Ni(II) species. After removal of the light source, the green color reappears. Repeated color changes of the solution with visible light have a clear discernible effect upon the intensity of the green color. Though there are analogies to the photobleaching of the $[Ni(S_2CNR_2)_3]^+$ complexes, the fatigue of the photochromism of the *i*-mns system is faster than that of the former.[20] The mechanism of the photochromic behavior of the latter is not known up to now.

Registry No. $(n\text{-}Bu_4N)_2[Ni(i\text{-mns})_2]$, 65701-74-8; $(Ph_4As)_2[Ni(i\text{-mns})_2]$, 65701-75-9; $(Ph_4As)_2[Ni(i\text{-mns})_3]$, 65701-73-7; $(Ph_4As)_3[Co(i\text{-mns})_3]$, 27902-48-3.

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Contribution from the Institute of Geochemistry and Analytical Chemistry, Moscow State University, Moscow, USSR

Electron Spin Resonance Spectra of Copper(II) Bipyridyl Complexes

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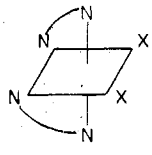
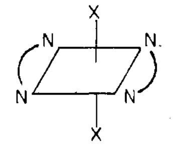
Complexes of copper(II) with 2,2′-bipyridyl (bpy) have been studied by the ESR method.[1-4] The ESR spectral parameters of the mono (I), bis (II), and tris (III) complexes have been reported and are summarized in Table I. Bis(bipyridyl)copper(II) can exist as the cis or trans isomer. There are conflicting reports in the literature with respect to the stability of the bis(bipyridyl)copper(II) species.[1-10] The ESR spectral parameters for transition-metal complexes depend on the nature of the ligands and their geometric arrangements,[11] and for a variety of complexes the ESR parameters of cis and trans isomers are different.[9,11]



cis



trans

During the investigation of ethanol–water solutions (40%, 60%) containing copper(II) bipyridyl complexes with a bipyridyl:copper ratio of 2.0, Noack and Gordon[1] simultaneously observed two different spectra, $g_\parallel = 2.285 \pm 0.010$, $A_\parallel = (165.4 \pm 2.0) \times 10^{-4}$ cm^{-1} and $g_\parallel = 2.227 \pm 0.010$, $A_\parallel = (128.9 \pm 2.0) \times 10^{-4}$ cm^{-1}, which were ascribed to the trans isomer and the cis isomer as is noted in Table I.

Later, Walker and Siegel[2] repeated some of the latter experiments with the pure ^{63}Cu isotope and concluded that the two series of lines observed by Noack and Gordon were due to the complexes of $Cu(bpy)^{2+}$ and $Cu(bpy)_3{}^{2+}$, which resulted from disproportionation of $Cu(bpy)_2{}^{2+}$. The authors suggested that under such conditions the spectrum with $g_\parallel = 2.227$ and $A_\parallel = 128.9 \times 10^{-4}$ cm^{-1}, previously assigned to the cis isomer of bis(bipyridyl)copper(II), was absent. According to Walker and Siegel, the predominant geometric isomer of $Cu(bpy)_2{}^{2+}$ in the range of its coexistence with mono- and tris(bipyridyl) complexes must have spectral parameters similar to, although not fully identical with, those of $Cu(bpy)_3{}^{2+}$.

In frozen methanol–chloroform solutions Rehorek and Thomas[3] observed the ESR signal for the copper(II) bipyridyl complex and reported the appropriate ESR parameters. Despite the suggestion of Walker and Siegel,[2] the authors[3] considered the existence of bis(bipyridyl)copper(II) as a real fact although they did not observe the cis spectrum II (Table I). In 1971, McKenzie[9] suggested that the two spectra observed by Noack and Gordon could be due to bis(bipyridyl)copper(II) complexes containing different numbers of solvent molecules.

In our study of the interaction between components of the copper(II)-catalyzed oxidation of hydroquinone (H_2Q) with hydrogen peroxide in the presence of bipyridyl in borate buffers, we observed a complex with $g_\parallel = 2.222 \pm 0.005$ and $A_\parallel = (129 \pm 3) \times 10^{-4}$ cm^{-1} (II_1) as is shown in Figure 1a and 1b and Table I. In the pH range of 7.0–8.2, and in the presence of all of the reaction components, with an ~20-fold excess of bipyridyl, only the complex II_1 is observed. It is necessary to note in this context that complex II_1 could be observed only by using precooled reagents at approximately 5 °C.

The ESR spectral parameters we observed in the catalytic system containing mixed bipyridylcopper(II) complexes, within the limits of experimental error, are the same as those reported by Noack and Gordon for the *cis*-bis(bipyridyl)copper(II) species. In this connection the existence of the *cis*-bis(bipyridyl)copper(II) complex is interesting, in that it appears to play an important role in the general mechanism for the catalytic oxidation[12] of hydroquinone with H_2O_2 in the presence of such activators as pyridine and 2,2′-bipyridyl. A number of our other experimental results which will be published in detail elsewhere permit us to suggest that H_2O_2 and H_2Q also enter the coordination sphere of the bis(bipyridyl)copper(II) species during the catalytic process.

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Table I. ESR Parameters of Copper Bipyridyl Complexes

Complex no.	Proposed compn of complex	$g_{\parallel}$	$10^4 A_{\parallel}$, cm^{-1}	Conditions of formn	Ref
I_0	$Cu(bpy)(OH_2)_4$	2.315 ± 0.008	165.4 ± 2	40% ethanol-60% water, $C_{bpy}/C_{Cu} = 1$	1
I_0	$^{63}Cu(bpy)(OH_2)_4$	2.308 ± 0.004	166 ± 2	40% ethanol-60% water, $C_{bpy}/C_{Cu} = 1$	2
I_0	$Cu(bpy)(OH_2)_4$	2.305 ± 0.005	164 ± 3	40% ethanol-60% water, $C_{bpy}/C_{Cu} = 2$	This work
I_1	$Cu(bpy)X_{4-n}Y_n$	2.295 ± 0.005	174 ± 3	Borate buffer, pH 8.5, $C_{bpy}/C_{Cu} = 2$	This work
II_0	*cis*-$Cu(bpy)_2(OH_2)_2$	2.227 ± 0.010	128.9 ± 2	40% ethanol-60% water, $C_{bpy}/C_{Cu} = 2$	1
II_0	*cis*-$Cu(bpy)_2(OH_2)_2$	2.222 ± 0.003	118 ± 3	40% ethanol-60% water, pH 2.2, $C_{bpy}/C_{Cu} = 4$	This work
II_1	*cis*-$Cu(bpy)_2H_2O_2 \cdot H_2Q$	2.222 ± 0.003	129 ± 3	Borate buffers, pH 7.0-8.2, $C_{bpy}/C_{Cu} = 20$ in presence of H_2O_2 and hydroquinone (H_2Q)	This work
II_2	*cis*-$Cu(bpy)_2X_{2-n}Y_n$	2.222 ± 0.003	118 ± 3	Borate buffer, pH 8.5, $C_{bpy}/C_{Cu} = 4$	This work
II_3	*trans*-$Cu(bpy)_2(OH_2)_2$	2.285 ± 0.010	165.4 ± 2	40% ethanol-60% water, $C_{bpy}/C_{Cu} = 2$	1
II_3	*trans*-$Cu(bpy)_2(CH_3OH)_2$	2.281 ± 0.005	160 ± 3	Methanol-chloroform soln	3
III_0	$Cu(bpy)_3^{2+}$	2.271 ± 0.008	160.5 ± 2	40% ethanol-60% water, $C_{bpy}/C_{Cu} = 3$	1
III_0	$Cu(bpy)_3^{2+}$	2.266 ± 0.004	161 ± 2	40% ethanol-60% water, $C_{bpy}/C_{Cu} = 3$	2
III_0	$Cu(bpy)_3^{2+}$	2.260 ± 0.005	165 ± 3	40% ethanol-60% water, pH 2.2, $C_{bpy}/C_{Cu} = 20$	This work

To investigate the detailed properties of the copper(II) complex corresponding to spectrum II_0 which Noack and Gordon reported was due to the cis isomer of $Cu(bpy)_2^{2+}$, we have studied the ESR spectra of copper(II)-bipyridyl mixtures in the presence of borate buffers and 60% water-40% ethanol solvent mixtures. For the experiments reported here, the bipyridyl-copper(II) solutions were prepared from precooled (~+5 °C) copper(II) and bipyridyl solutions.

The ESR spectra of copper(II) in borate buffer solution (pH 8.5) in the presence of various amounts of bipyridyl are shown in Figure 1c and 1d. At a copper:bpy ratio of 2, the spectrum observed has $g_{\parallel} = 2.295$ and $A_{\parallel} = 174 \times 10^{-4}$ cm^{-1}. Consistent with previous reports in the literature,[1,2] this corresponds to the spectrum of the mono(bipyridyl)copper(II) species. The small differences in parameters reported here are most probably associated with the substitution by borate anions for water molecules in the first coordination sphere of the bis copper(II) complex.

Increasing the bipyridyl concentration gives rise to the appearance of the spectrum with $g_{\parallel} = 2.222$ and $A_{\parallel} = 118 \times 10^{-4}$ cm^{-1} which is termed II_2. At the copper:bpy ratio from 2 to 4, the spectra represent a superposition of the spectra of mono(bipyridyl)copper(II) and complex II_2 as is shown in Table I. At the copper:bpy ratio of 4, complex II_2 is dominant in solution as is shown in Figure 1d.

Spectral parameters for this complex are close to those reported for the *cis*-bis(bipyridyl)copper(II) complex. The value for $A_{\parallel}$ is somewhat smaller than that reported by Noack and Gordon and appears to depend on the replacement of one or two molecules of water by borate anion.

To reproduce the Noack and Gordon experiments[1] we obtained the ESR spectra of copper(II) in a 40/60% ethanol-water mixture. Unfortunately, the authors did not indicate the pH value but our experiments were carried out at pH 2.2. As can be seen from Figure 2, depending upon the copper:bpy ratio, complexes with $g_{\parallel} = 2.305$, $A_{\parallel} = 164 \times 10^{-4}$ cm^{-1} (I_0), $g_{\parallel} = 2.222$, $A_{\parallel} = 118 \times 10^{-4}$ cm^{-1} (II_0), and $g_{\parallel} = 2.260$, $A_{\parallel} = 165 \times 10^{-5}$ cm^{-1} (III_0) are formed in the solutions. The first spectrum (I_0) corresponds to mono(bipyridyl)copper(II). The parameters of the second spectrum (II_0) are close to those of

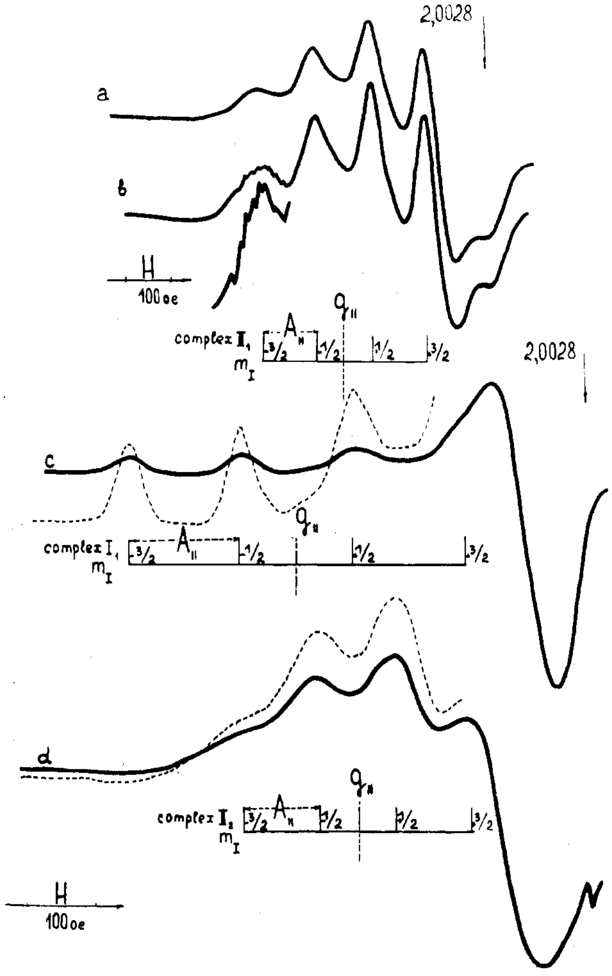

Figure 1. ESR spectra of copper(II) complexes in borate buffer solutions: (a, b) $C_{Cu} = 2.5 \times 10^{-4}$ M, $C_{bpy} = 4 \times 10^{-3}$ M, $C_{H_2Q} = 2 \times 10^{-3}$ M, $C_{H_2O_2} = 1$ M, pH 7.5; (b) solution prepared in D_2O; (c) $C_{Cu} = 5 \times 10^{-4}$ M, $C_{bpy} = 1 \times 10^{-3}$ M, pH 8.5; (d) $C_{Cu} = 5 \times 10^{-4}$ M, $C_{bpy} = 2 \times 10^{-3}$ M, pH 8.5.

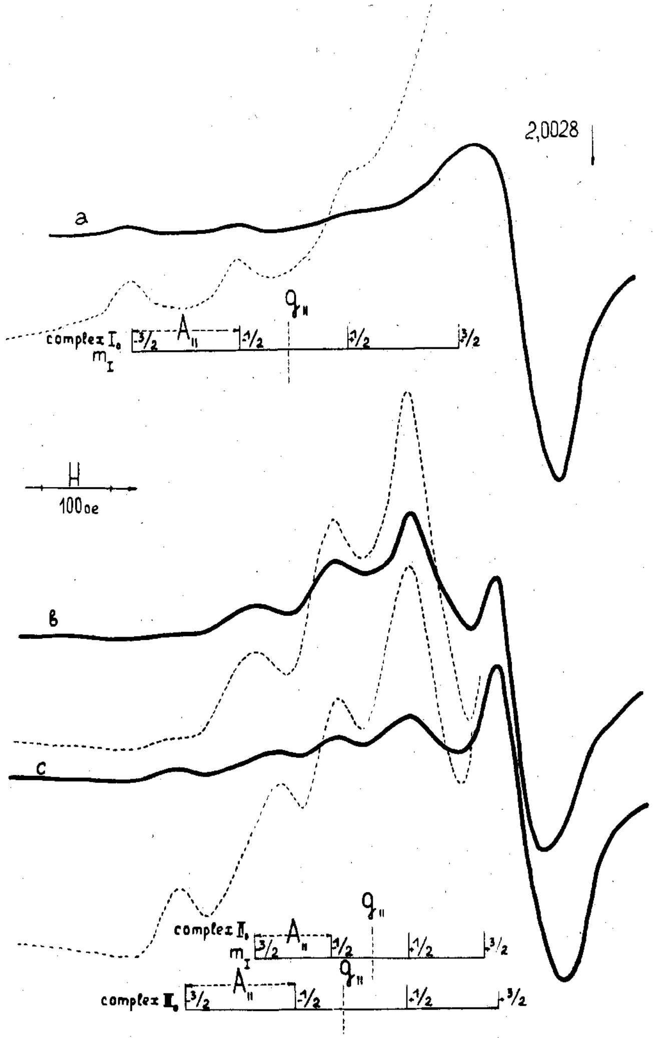

Figure 2. ESR spectra of copper(II) bipyridyl complexes in 60% water–40% ethanol mixtures with $C_{Cu} = 5 \times 10^{-4}$ M, pH 2.2: (a) $C_{bpy} = 1 \times 10^{-3}$ M; (b) $C_{bpy} = 4 \times 10^{-3}$ M; (c) $C_{bpy} = 11 \times 10^{-3}$ M.

the spectrum of the cis isomer of bis(bipyridyl)copper(II) reported by Noack and Gordon.

We also propose that complex II_1, with $A_{\parallel} = 129 \times 10^{-4}$ cm^{-1} observed in solutions containing Cu(II), bpy, H_2Q, H_2O_2, and borate buffer, is the mixed-ligand complex containing bipridyl, H_2O_2, and H_2Q. Replacement of H_2O_2 and H_2Q into the first coordination sphere of Cu(II) appears to increase the $A_{\parallel}$ value which can be seen by comparison with that of [$Cu(bpy)_2(H_2O)_2^{2+}$]. The perpendicular region of the spectra of complexes II_1 and II_2 is different as well. For example, an additional absorption overlapping with the perpendicular region lines is readily detected in the spectrum of complexes II_1 as is noted in Figure 1a and 1b.

In connection with the attempt to determine the composition and structure of bipyridylcopper(II) complexes produced under catalytic reaction conditions, an experiment using D_2O instead of ordinary water was carried out with all other experimental conditions identical. The copper(II) ESR spectrum in D_2O has the same parameters as observed in H_2O as can be seen in Figure 1b. Since the lines are sharper in D_2O, superhyperfine structure (SHFS) arising from interactions with the ^{14}N nuclei is observed in the parallel region of the Cu(II) ESR spectrum.

It is difficult to determine the exact number of SHFS lines arising from the ^{14}N splitting of both the ^{63}Cu and ^{65}Cu isotopes. From an analysis of the spectrum, however, it is apparent that the number of SHFS lines is greater than five. Hence, it is obvious that the spectrum in question can not be that of the mono(bipyridyl)copper(II) species. Moreover, $g_{\parallel}$ and $A_{\parallel}$ for this spectrum differ markedly from $g_{\parallel}$ and $A_{\parallel}$ observed for the tris(bipyridyl)copper(II) complex. Thus, these data give additional indirect evidence for the assignment of the spectrum in question to the *cis*-$Cu(bpy)_2(H_2O)_2^{2+}$ species.[3,9]

The difficulties associated with detection of the complex with $g_{\parallel} = 2.222$ and $A_{\parallel} = 118 \times 10^{-4}$ cm^{-1} suggest the necessity to use precooled copper(II) and bpy solutions. As noted above, Noack and Gordon[1] considered the complex with $g_{\parallel} = 2.227$ and $A_{\parallel} = 128.9 \times 10^{-4}$ cm^{-1} to be the cis isomer of $Cu(bpy)_2(H_2O)_2^{2+}$. From our point of view there are good reasons for this assignment.

Registry No. I_0, 22941-48-6; II_0, 21087-94-5; II_1, 65930-65-6; III_0, 17168-72-8.

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Free Radicals Produced by the γ Irradiation of Thiazyl Fluoride in Sulfur Hexafluoride

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The γ irradiation of solid solutions of inorganic molecules in sulfur hexafluoride has proved to be a fruitful source of free radicals for study by EPR spectroscopy. In addition to being a tumbling matrix at temperatures as low as 100 K, SF_6 is also a source of fluorine atoms upon irradiation.[2] Thus, isotropic EPR spectra of paramagnetic fluorides can be readily generated provided the acceptor molecule is soluble in sulfur hexafluoride. FSO_2 from SO_2, PF_4 from PF_3, ClF_4 from ClF_3, and ClF_6 from ClF_5 are but a few examples of the successful application of this technique.[2,3] In this paper we report the spectra of radicals generated by the γ irradiation of thiazyl fluoride (NSF) in SF_6.

An examination of the EPR spectrum at 110 K of a γ-irradiated solid solution of NSF in SF_6 reveals the presence of a number of lines not detectable in the irradiated pure host. Closer inspection shows that the extra resonances are associated with two distinct centers, both of which show isotropic hyperfine interactions with a single ^{14}N ($I = 1$) nucleus and further interactions with two ^{19}F ($I = 1/2$) nuclei (Table I). The species with two equivalent fluorine nuclei was produced alone by the γ irradiation of solid solutions of $ClNSF_2$ or $BrNSF_2$ in SF_6 and by the codeposition of Na, $ClNSF_2$, and SF_6 on a rotating cryostat.[4] We identify the latter species with the radical NSF_2, having a terminal nitrogen atom and two equivalent fluorines, since it is an expected primary product

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