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The Donor Properties of 2,2'-Biquinolyl-N,N'-dioxide.
II. Cobalt(II), Nickel(II) and Copper(II) Complexes

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Complexes of cobalt(II), nickel(II) and copper(II) ions with 2,2'-biquinolyl-N,N'-dioxide have been prepared and characterized. Tris(2,2'-biquinolyl-N,N'-dioxide) complexes were obtained with cobalt(II) and nickel(II) ions while bis(2,2'-biquinolyl-N,N'-dioxide) complexes formed with the copper(II) ion. Electronic and EPR spectra indicated octahedral structures for cobalt(II) and nickel(II) complexes and pseudo-tetrahedral structures for copper(II) complexes.

Introduction

Several complexes of metal ions with the bidentate ligand 2,2'-bipyridyl-N,N'-dioxide have been previously reported. Steric considerations suggest that when this molecule acts as a chelating ligand in metal complexes it must adopt a non-planar conformation. Chelation requires in fact that the plane of one of the pyridine-N-oxide rings is rotated with respect to the other giving rise to a distorted (staggered) conformation. On the other hand, non-planar conformation has been suggested for this ligand in the solid state [1].

Recently, lanthanide(III) and dioxouranium(VI) complexes with 2,2'-biquinolyl-N,N'-dioxide have been prepared and characterized [2]. This molecule has demonstrated to act as a strong donor ligand towards lanthanide(III) cations. However, it is remarkably bulkier than 2,2'-bipyridyl-N,N'-dioxide and is expected to give rise to complexes less rich in ligand molecules and/or to weaken the metal-oxygen bondings.

The synthesis and spectra of cobalt(II), nickel(II) and copper(II) complexes with 2,2'-biquinolyl-N,N'-dioxide are reported in this paper. The spectra of copper(II) complexes with 2,2'-biquinolyl are also considered.

Experimental

Complexes of 2,2'-biquinolyl-N,N'-dioxide(biquO$_2$) and 2,2'-biquinolyl(biqu) with cobalt(II), nickel(II) and copper(II) nitrates, perchlorates and trifluoromethanesulfonates were prepared. Metal trifluoromethanesulfonates were prepared according to previous procedure [3]. The salts were heated at 130 °C for 1 hr. at reduced pressure ($\sim 10^{-2}$ mmHg) and immediately dissolved in the appropriate solvent. The ligand 2,2'-biquinolyl-N,N'-dioxide was prepared following the Nakano procedure [4] and recrystallized from ethanol. Required for $C_{18}H_{12}N_2O_2$ %C = 74.99, %H = 4.20, %N = 9.72; found %C = 74.37, %H = 4.11, %N = 9.58 [2].

Preparation of the Complexes

The complexes of biquO$_2$ with cobalt(II), nickel(II) and copper(II) nitrates, perchlorates and trifluoromethanesulfonates were easily obtained by mixing and stirring 1 mmol of the cation in 10 ml of hot anhydrous ethanol with 3 mmol of the ligand dissolved in the minimum required volume of hot ethanol. Microcrystalline products rapidly formed; they were immediately filtered off, washed with hot ethanol and dried *in vacuo* at room temperature.

Copper(II) complexes with biqu were prepared following a previous procedure [5] from solutions of the cation in anhydrous ethanol and ligand in benzene. The precipitates were rapidly filtered off, washed with a mixture of hot ethanol and benzene (1:5) followed by benzene alone and dried *in vacuo* at room temperature.

Measurements

EPR spectra were recorded on a Bruker ER 200 D instrument equipped with a standard low-temperature apparatus. The field was accurately measured with a Bruker E 35 M gaussmeter and the frequency was checked through the resonance field of DPPH (g = 2.0036). The spectra were run both on solid complexes dissolved in acetone–methanol or methanol–triethylenglicol mixtures, and on samples prepared starting from the reagents in stoichiometric ratio and dissolved in the same mixtures of solvents. A and g values were evaluated directly from the experimental spectra. Other experimental procedures (electrolytic conductivity measurements, thermal analyses, IR and electronic absorption and reflectance spectra) were

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TABLE I. Analytical and Molar Conductivity Data for Cobalt(II), Nickel(II) and Copper(II) Complexes with $biquO_2$ and biqu ($biquO_2$ = 2,2′-biquinolyl-N,N′-dioxide; biqu = 2,2′-biquinolyl). In Parentheses the Calcd. Values.

Complex	% C	% H	% N	% M	Λ_M[a]
$Co(biquO_2)_3(ClO_4)_2$	58.65(57.77)	3.11(3.23)	7.18(7.49)	5.63(5.25)	185
$Co(biquO_2)_3(CF_3SO_3)_2$	54.83(55.04)	3.00(2.97)	6.35(6.88)	5.19(4.82)	177
$Ni(biquO_2)_3(ClO_4)_2$	58.04(57.78)	3.40(3.23)	7.21(7.49)	5.54(5.23)	194
$Ni(biquO_2)_3(CF_3SO_3)_2$	54.37(55.05)	2.84(2.97)	6.50(6.88)	5.02(4.81)	172
$Ni(biquO_2)_3(NO_3)_2$	60.78(61.91)	3.51(3.46)	10.92(10.70)	5.91(5.60)	183
$Cu(biquO_2)_2(ClO_4)_2$	50.34(51.53)	3.06(2.88)	6.29(6.68)	7.80(7.57)	174
$Cu(biquO_2)_2(CF_3SO_3)_2 \cdot 2H_2O$	47.53(46.84)	3.14(2.90)	5.48(5.75)	6.07(6.52)	169
$Cu(biquO_2)_2(NO_3)_2$	56.16(56.58)	3.31(3.17)	10.74(11.00)	8.60(8.32)	180
$Cu(biqu)_2(CF_3SO_3)_2 \cdot 2H_2O$	48.62(50.15)	3.27(3.10)	5.75(6.16)	7.45(6.98)	163

[a] In solution of a mixture of acetonitrile and chloroform (3:1) at 25 ± 0.1 °C; c = 0.8–1.0 × 10^{-3} *M*.

TABLE II. Infrared Frequencies (cm^{-1}) for Divalent Metal Ions Complexes with $biquO_2$.

Complex	Assignment			
	$\nu(NO)$	$\nu(M-O)$[b]	Anion modes	
$biquO_2$	1212s, 1200sh			
$Ni(biquO_2)_3(CF_3SO_3)_2$	1197sbr	380w, 364mbr	1280s, 1033s, 640s[a]	$\nu_4(E)$, $\nu_1(A_1)$ and $\nu_3(A_1)$ modes of SO_3 group having C_{3v} symmetry.
$Cu(biquO_2)_2(CF_3SO_3)_2 \cdot 2H_2O$	1195sbr	402m, 395m	1275sbr, 1032s, 640s[a]	
$Co(biquO_2)_3(CF_3SO_3)_2$	1195sbr	360sbr	1280s, 1035s, 640s[a]	
$Co(biquO_2)_3(ClO_4)_2$	1197sbr	365m, 345w	1090vs, 624s	ν_3 and ν_4 modes of ClO_4 group having T_d symmetry with deviation for copper complex.
$Ni(biquO_2)_3(ClO_4)_2$	1198m, 1190s	380w, 362m	1090vs, 622s	
$Cu(biquO_2)_2(ClO_4)_2$	1202m, 1192s	400m, 395m	1110w, 1088s (ν_3), 1050sh, 623sbr (ν_4)	
$Ni(biquO_2)_3(NO_3)_2$	1200m, 1194s	380w, 363m	1388vs, 835m	ν_3 and ν_2 modes of NO_3 group having D_{3h} symmetry with deviation for copper complex.
$Cu(biquO_2)_2(NO_3)_2$	1203w, 1194s	400m, 395m	1470w, 1370s (ν_3), 1290w, 1020w, 835m (ν_2)	

[a] $\nu_2(A_1)$, $\nu_5(E)$ and $\nu_6(E)$ bands are masked by ligand absorptions in the regions 750, 525 and 350 cm^{-1}. [b] A $\nu(M-N)$ mode is observed at 292, 295 and 320 cm^{-1} in the spectra of the complexes $M(biqu)(NO_3)_2$ where M = Co, Ni and Cu respectively. Mono(bipy) complexes show this band at lower frequencies [13].

the same as previously described [2]. Solutions of the complexes in mixtures of acetonitrile and chloroform (3:1) or acetone and methanol (1:1) were used for these measurements.

Results and Discussion

Analytical and molar conductivity data are collected in Table I.

IR Spectra

The IR spectra of the complexes with biqu show, in comparison with the free ligand, those spectral changes that have been normally associated for similar ligands with N-coordination.

The IR spectrum of $biquO_2$ has been recently reported [2]. In the range 1340–1120 cm^{-1}, where the NO stretching mode is expected, the spectrum shows with respect to the spectrum of biqu new and asymmetric bands at 1333 and 1212 cm^{-1}. The band at 1333 cm^{-1} has been assigned to an activated vibration due to the distortion that 2,2′-biquinolyl undergoes upon dioxidation while the band at 1212 cm^{-1} has been tentatively assigned to the NO stretching mode. Similarly, the strong absorption at 813 cm^{-1} has been assigned to the NO bending mode. The splitting or asymmetry of these bands agrees with a non-symmetrical conformation. Like $bipyO_2$, this molecule would exist in fact in the solid state in a non-coplanar conformation.

In the spectra of the present complexes the band at 1333 cm^{-1} shifts at 1355–1350 cm^{-1} while the band at 1212 cm^{-1} splits and shifts globally to lower frequencies as a result of oxygen–metal coordination (Table II). The barycentre of this band lies between

1195 and 1190 cm^{-1}, thus representing a small shift, considerably smaller than the 30–40 cm^{-1} shifts observed for the corresponding $bipyO_2$ complexes [1]. Since $biquO_2$ is remarkably bulkier than $bipyO_2$ it is reasonable to expect that for the $biquO_2$ complexes the metal-oxygen bond becomes weaker by steric interactions not only between the metal and the bulky ligand but also by ligand–ligand repulsion. This trend is similar to that observed for the complexes of d-transition metal ions with pyridine- and quinoline-N-oxides [6]. No shift or shift to higher frequencies of the NO stretching mode was observed for the complexes with quinoline-N-oxides. A reasonable explanation for this result is connected with a lowering for the quinoline-N-oxides of the π-system energy and a more pronounced metal-to-ligand back-donation to replace the electron density on the oxygen atoms lost by σ-donation.

The NO bending mode is slightly affected upon complexation and appears generally as a doublet between 820 and 810 cm^{-1}. This effect is the same as that occurring for the NO stretching and for some skeletal and CH modes, and is largely due to the ligand *trans–cis* rearrangement that is necessary for chelation. A staggered conformation becomes, however, the only possible in this case as suggested by steric considerations.

In the CsBr region the spectra of the complexes with $biquO_2$ show a new band between 410 and 340 cm^{-1}. This band can be assigned to a metal-oxygen stretching vibration. This assignment is supported by the observation that the frequency of this band depends on the metal ion following the series $Cu^{2+} > Ni^{2+} > Co^{2+} > UO_2{}^{2+} > Ln^{3+}$ [2]. The splitting of this band is consistent with non-regular geometries. The frequency values measured for these complexes are lower than those reported for the $bipyO_2$ complexes [1], as expected from the greater steric hindrance of $biquO_2$.

UV Spectra

The UV spectrum of $biquO_2$ in $CHCl_3$ consists of π–π^* transition bands at 258 and 300 nm, both showing shoulders at higher and lower frequencies [2]. The shoulder at 345 nm may be associated with n–π^* transition.

It has been found that $bipyO_2$ in the solid state exists in the *trans*-form and assumes a configuration that is close to that of the *cis*-form in the metal chelates. Chelation of $bipyO_2$ may thus be expressed in terms of molecular *trans–cis* rearrangement. The same behaviour seems to characterize the complexes of $biquO_2$ with metal ions [2]. The band at 258 nm shifts on the whole to higher frequencies while the band at 300 nm suffers large splitting and shifts globally to lower frequencies. The overall UV evidence suggests that the free ligand has a configuration that is close to the *trans*-form in the solid state and assumes a configuration that is close to the *cis*-form in the metal chelates, but involving non-coplanarity of the two quinoline rings.

The UV spectrum of biqu is characterized by a π–π^* band at 262 nm and another band below 300 nm, which in benzene shows peaks at 314, 327 and 340 nm. Upon complexation this band shifts to lower frequencies, as a result of N-coordination.

Cobalt(II) and Nickel(II) Complexes with $biquO_2$

Tris(2,2'-biquinolyl-N,N'-dioxide) complexes were obtained with cobalt(II) and nickel(II) ions independently of the counter ion. All complexes are red-brown and soluble in methanol, acetone, acetonitrile and chloroform, where they act as 1:2 electrolytes. The IR spectra indicate that nitrate, perchlorate and trifluoromethanesulfonate groups are all ionic, the spectra showing none of the band splitting which results from anion coordination (Table II). Ionic nitrate group has D_{3h} symmetry and three IR active vibrations. If coordination occurs through one or two oxygen atoms the symmetry is lowered to C_{2v} in both instances and all six normal modes of vibration become IR active. Similarly, perchlorate ion has T_d symmetry and two IR active vibrations. Coordination through one or two oxygen atoms causes the symmetry to be lowered to C_{3v} or C_{2v} respectively while the IR active vibrations become six or nine. The $-SO_3$ group has C_{3v} symmetry and six IR active vibrations which become nine by coordination through one oxygen atom. These results suggest the present complexes to be $[M(biquO_2)_3]X_2$ where M = Co^{2+}, Ni^{2+} and X = NO_3, ClO_4, CF_3SO_3.

The absorption spectra obtained from the complexes dissolved in mixtures of chloroform and acetonitrile or acetone and methanol are similar to the reflectance spectra and appear to be independent of the anion present.

The reflectance spectra of the nickel(II) complexes consist of bands at 7407 and 11765 cm^{-1}, which in solution shift to higher frequencies (Table III and Fig. 1). A further band appears at 12903 cm^{-1} while the band at 7407 cm^{-1} exhibits a shoulder at lower frequencies. The spectra resemble those usually observed for weak field nickel(II) complexes in distorted octahedral geometry. The asymmetric band at 7407 cm^{-1} can thus be assigned to the ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ν_1 transition, split because of distortion of the crystal field, and the band at 11765 cm^{-1} to the ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, ν_2 transition. The band at 12903 cm^{-1} may be assigned to the transition to the ${}^1E_g$ level in weak octahedral field [7].

In Table III are also reported the frequency values of the ν_3 transition which should lie around 22000 cm^{-1}. The spectra show in the range 23000–17000 cm^{-1} four peaks or shoulders, three of which also appear in the spectra of the cobalt(II) and copper(II) complexes but which are effectively absent in the

TABLE III. Electronic Spectra of Complexes of d–transition Metal Ions with $biquO_2$ ($biquO_2$ = 2,2′-biquinolyl-N,N′-dioxide). Frequency Values in cm^{-1}.

Complex	Reflectance	Solution[a]	Assignment	10Dq[g]	B[g]
$Co(biquO_2)_3X_2$	7194	7194(13.6)	$^4T_{1g} \rightarrow {}^4T_{2g}$	7298[b]	629[c]
($X = ClO_4, CF_3SO_3$)	14388	14492(2.1)	$^4T_{1g} \rightarrow {}^4A_{2g}$		
	16393	16529(42.7)	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$		
	17921	17857(190)			
	19471	19231(305)			
	20618	20833(391)			
$Ni(biquO_2)_3X_2$	7000	7000(sh)			
($X = NO_3, ClO_4, CF_3SO_3$)	7407	7462(7.5)	$^3A_{2g} \rightarrow {}^3T_{2g}$	7462[d]	765[e]
	11765	11834(8.1)	$^3A_{2g} \rightarrow {}^3T_{1g}$		
	12903	12987(9.4)	$^3A_{2g} \rightarrow {}^1E_g$		
	17540	17699(115)			
	18600	19047(283)			
	20000	20408(325)			
	21978	22026(348)	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$[f]		
$Cu(biquO_2)_2(NO_3)_2$	7937	8771(14.5)			
	9615sh				
	11764	12987(71.8)			
	17391	17544(185)			
	18621	18587(310)			
	20000	20202(391)			
$Cu(biquO_2)_2X_2 \cdot nH_2O$	8196	9259(19.5)			
($X = ClO_4, CF_3SO_3$)	11236	13158(67.3)			
	13333sh				
	17301	17391(163)			
	18587	18518(281)			
	20000	20202(397)			

[a] In a mixture of acetonitrile and chloroform (3:1). Molar extinction coefficient in parentheses. [b] Obtained from the relationship: $10Dq = \nu_2 - \nu_1$. [c] Obtained from the relationship: $B = (\nu_2 + \nu_3 - 3\nu_1)/15$. [d] Taken directly from the first spin-allowed transition band. [e] Obtained from the relationship: $(\nu_2 + \nu_3 - 30Dq)/15$, assuming that the position of the ν_3 transition is real. [f] Tentative assignment. [g] From the solution spectra.

spectra of the lanthanide(III) and dioxouranium(VI) complexes with the same ligand [2]. By comparison of the spectra of the nickel complexes with those of the cobalt and copper complexes, the band at 21978 cm^{-1} is tentatively assigned to the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, ν_3, transition in O_h symmetry and the other absorptions to charge-transfers. The extinction coefficient values measured for this transition are obviously affected by the stronger absorptions in this region.

The reflectance spectra of the cobalt(II) complexes show bands of relative low intensity at 7194 and 16393 cm^{-1}. These spectra are characteristic of cobalt(II) ions in a weak octahedral field. Octahedral complexes show normally two bands in the ranges 6000–10000 and 17000–22000 cm^{-1} associated with the ν_1 and ν_3 transitions, respectively. A third band is sometimes observed between 12000 and 15000 cm^{-1} and assigned to the ν_2 transition [7]. The band at 7194 cm^{-1} can thus be assigned to the $^4T_{1g} \rightarrow {}^4T_{2g}$, ν_1, transition and the band at 16393 cm^{-1} to the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$, ν_3, transition. The transition to the $^4A_{2g}$ level, ν_2 transition, may be observed around 14500 cm^{-1}.

The Dq values measured for the present complexes with both cations are considerably smaller than those reported for the $bipyO_2$ complexes [8, 9], although a more metal to ligand back-donation should raise them. On the other hand, binding three molecules of $biquO_2$ is certainly more difficult than binding three molecules of the less bulky $bipyO_2$ ligand.

Copper(II) Complexes

Only bis(2,2′-biquinolyl-N,N′-dioxide) complexes formed with the copper(II) ion even with excess of ligand. All complexes are red and soluble in methanol, acetone, acetonitrile and chloroform. Molar conductivity values are almost the same as those found for equimolar solutions of the nickel and cobalt complexes and indicate 1:2 electrolytic behaviour. These data are inconclusive about the environment of the copper(II) ion because of possible anion-solvent interchanges. Not even IR data provide

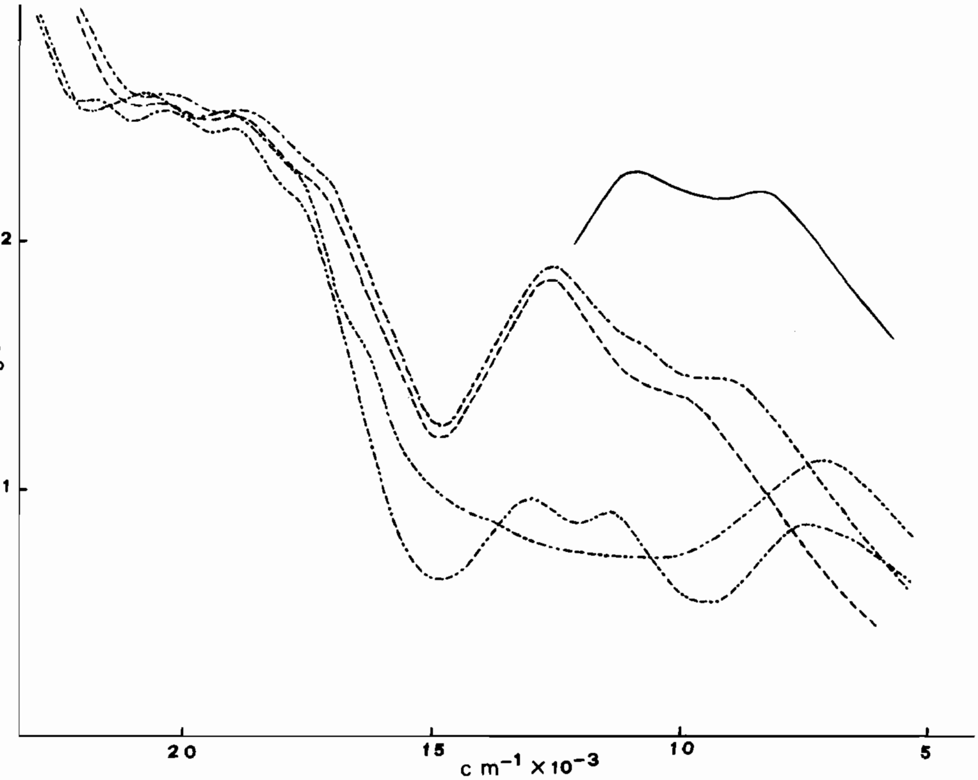

Fig. 1. Absorption spectra: (— — · ·) $Ni(biquO_2)_3(ClO_4)_2$; (— · ·) $Co(biquO_2)_3(CF_3SO_3)_2$; (— · — ·) $Cu(biquO_2)_2(NO_3)_2$; (— — —) $Cu(biquO_2)_2ClO_4)_2$. (———) Reflectance spectrum of $Cu(biquO_2)_2(ClO_4)_2$. Absorption spectra in acetonitrile–chloroform mixture solutions (3:1).

any definitive conclusion, because of the splitting or broadness that undergo some anion bands which suggest deviation from regular T_d (perchlorate) and D_{3h} (nitrate) symmetries. Although it is probable that these effects arise from solid state phenomena, however, axial interactions between anions and the copper(II) ion, perhaps of the long-distance type, cannot at this stage be reasonably excluded.

More reliable information can be drawn from electronic and EPR spectra. The reflectance spectra of the $biquO_2$ complexes consist of two bands in the range 13,000–7,000 cm^{-1}. Small differences in the position and relative intensity of the bands may be observed on changing the anion. The spectra are different from that reported for the octahedral tris(2,2'-bipyridyl-N,N'-dioxide)copper(II) perchlorate which exhibits a unique band at 12,300 cm^{-1} [8], but are similar to those reported for complexes for which pseudo-tetrahedral arrangements have been proposed [10]. In the solid state these complexes may thus be reasonably described in terms of pseudo-tetrahedral arrangements around the copper(II) ion. In acetonitrile solution both bands shift to higher frequencies while the intensity of the band at lower frequency decreases with respect to the higher-frequency one. These spectral features may represent apical cation-solvent interactions. Elongated rhombic octahedral structures have been found recently for some bis(2,2'-bipyridyl)copper(II) complexes [11]. Spectra of the present complexes are reported in Table III and Fig. 1.

Spin hamiltonian parameters of the EPR spectra concerning the mono- and bis(biquinolyl-N,N'-dioxide)copper(II) complexes in methanol–acetone mixture solutions are reported in Table IV. In Fig. 2 the frozen solution EPR spectra of $Cu(biquO_2)_2^{2+}$ is depicted. EPR data of the mono(2,2'-biquinolyl) and mono(2,2'-bipyridyl)copper(II) complexes are also reported in Table IV. All spectra show $g_{\parallel} > g_{\perp} > 2.04$. This result is indicative of a $d_{x^2-y^2}$ or d_{xy} ground state. Thus, square planar, square pyramidal or tetragonally-distorted octahedral stereochemistry is involved in these complexes [12].

It has been found that the EPR data of $Cu(biqu)^{2+}$ differ from those of $Cu(bipy)^{2+}$ for a higher $g_{\parallel}$ value and a lower $A_{\parallel}$ splitting constant. This might suggest that, in the presence of a similar set of donor atoms, a less covalent situation is present in the in-plane bond of the former complex. The frequency values of the Cu–N stretching mode are higher than those found for the corresponding complexes with bipy [13]: this may be connected with a stronger metal-

TABLE IV. EPR Data for Copper(II) Complexes with biqu and $biquO_2$ (biqu = 2,2'-biquinolyl; $biquO_2$ = 2,2'-biquinolyl-N,N'-dioxide).

Species	$g_\parallel$ (±0.002)	$A_\parallel$ (±2)	$g_\perp$ (±0.005)	$A_\perp$ (±5)	$A_\parallel^N$ (±2)	$A_\perp^N$ (±2)	Reference
$Cu(biqu)^{2+}$	2.335	157	2.072	12	13	–	This work
$Cu(bipy)^{2+}$	2.308	166	2.068	7	14	10	16
$Cu(biquO_2)^{2+}$	2.435	105	2.081	9	–	–	This work
$Cu(biquO_2)_2{}^{2+}$	2.380	113	2.069	11	–	–	This work

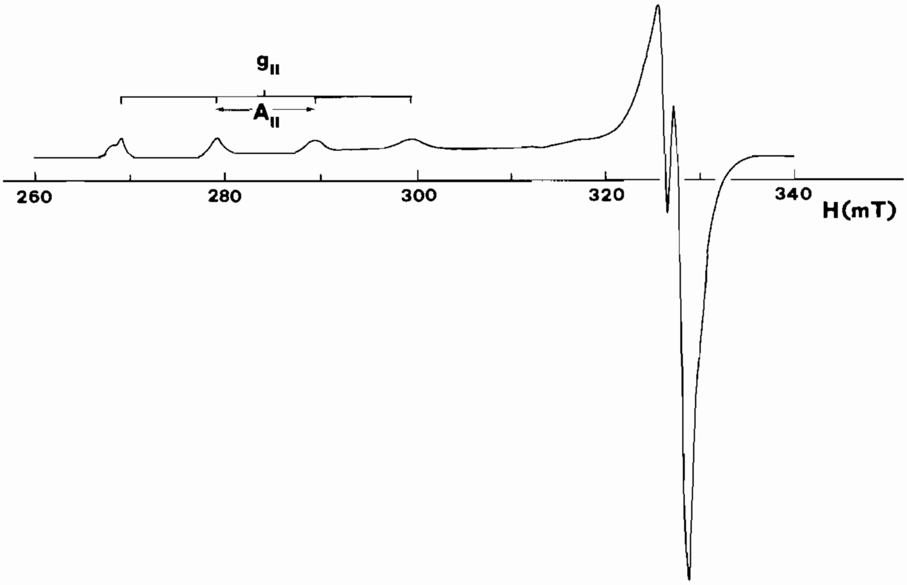

Fig. 2. EPR spectrum of $Cu(biquO_2)_2(ClO_4)_2$ at liquid nitrogen temperature in acetone–methanol mixture solution.

nitrogen bonding. On the other hand, a tetrahedral distortion could also account for the EPR results [14]. The electronic spectra of the mono- and bis(2,2'-biquinolyl)copper(II) complexes have been previously studied and interpreted in terms of pseudo-tetrahedral environments around the copper-(II) ion [5]. Most likely, the geometrical factor predominates. Any attempt of run spectra in solutions where the copper(II)/biqu ratios are more than two failed, probably due to the instability of the bis(biqu) complexes at low temperatures.

A and g values undergo a dramatic change in the case of the mono- and bis-complexes of copper(II) ion with $biquO_2$ in comparison with the complexes with the N-donor ligands biqu and bipy. This trend can be principally ascribed to two factors. The first concerns the substitution of nitrogen atoms with oxygens in the coordination sphere of the copper(II) ion. This substitution is responsible of a change in the bonding situation towards a greater ionicity [15]. The second factor is geometrical, since it is very difficult to think of a $biquO_2$ coordination to metal ions in a planar conformation. The very low values of the copper(II) ion splitting constants are in fact indicative of an environment involving one or two molecules of $biquO_2$ with a pronounced tetrahedral distortion.

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