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Low-Symmetry Copper(II) Complexes. Spectral Properties of Dihalo[2,6-di(2′-quinolyl)pyridine]copper(II) Complexes

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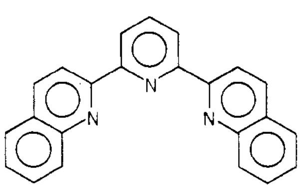
The new compounds $Cu(dqp)Cl_2$ and $Cu(dqp)Br_2$ (dqp = 2,6-di(2′-quinolyl)pyridine) have been synthesized and characterized by electronic and EPR spectroscopy. A C_{2v} five-coordinate structure has been assigned to the complexes. The electronic spectra have been interpreted in terms of crystal field calculations. The complete g anisotropy is resolved for the pure compounds, the corresponding doped zinc complexes, and frozen solutions, but no nuclear hyperfine splitting was resolved. The EPR spectra of solutions of the complexes in dichloromethane and chlorobenzene are novel in that only one line is observed. An upper limit of about 20 × 10^{-4} cm^{-1} is estimated for the electron spin–nuclear spin hyperfine coupling constants.

The syntheses of 2,6-di(2′-quinolyl)pyridine, I (dqp), and its high-spin iron(II) bis chelate have been described[2] as have the preparation and spectroscopic characterization of dqp complexes of ruthenium(II) and osmium(II).[3] The related ligand 2,2′,2″-terpyridine forms a 1:1 complex[4,5] with copper(II) chloride which has five-coordinate distorted trigonal-bipyramidal geometry.[5] It was expected that dqp complexes with copper(II) chloride and bromide give rise to complexes with a related stereochemistry. In view of the current interest in the electronic structure of low-symmetry copper compounds,[4-9] it was important to investigate the spectral (EPR and electronic) properties of the compounds $Cu(dqp)Cl_2$ and $Cu(dqp)Br_2$.



I (dqp)

It was anticipated that $Cu(dqp)X_2$ (X = Cl, Br) complexes would adopt a geometry closely related to the pseudotetrahedral (C_{2v}) geometry found for $Cu(o\text{-phen})Cl_2$.[10] If this is obtained, small values of the copper-63 and -65 electron spin–nuclear spin hyperfine coupling constants in the electron paramagnetic resonance (EPR) spectra would be expected and the dqp compounds would then be somewhat analogous to the "blue" copper proteins. Pseudotetrahedral copper(II) complexes have been suggested as possible models for the "blue" copper proteins. Five-coordinate geometries have also been proposed[11-13] for copper in the "blue" proteins, and studies on a variety of such low-symmetry complexes have been undertaken.

Experimental Section

2,6-Di(2′-quinolyl)pyridine (dqp) was prepared as described by Harris, Patil, and Sinn.[2] Recrystallization from benzene yielded dqp in 60% yield; mp 227–228 °C. All other chemicals were of the best reagent or spectroscopic grades. Carbon, hydrogen, and nitrogen analyses were performed by Chemalytics, Inc., Tempe, Ariz. Copper was determined by EDTA titrations.[14]

The copper complexes were prepared by the method described previously for the related biquinoline compounds.[15] Yields of 91–94% were obtained. Anal. Calcd for $Cu(dqp)Cl_2$: C, 59.05; H, 3.23; N, 8.98; Cu, 13.58. Found: C, 59.67; H, 3.37; N, 8.12; Cu, 13.39. Calcd for $Cu(dqp)Br_2$: C, 49.62; H, 2.72; N, 7.55; Cu, 11.41. Found: C, 50.07; H, 2.69; N, 7.54; Cu, 11.47. Copper-doped zinc complexes

Table I. EPR Data

Compd	Medium	g_1	g_2	g_3	$\langle g\rangle^a$	A_1 (cm^{-1} × 10^4)	A_2 (cm^{-1} × 10^4)	A_3 (cm^{-1} × 10^4)	$\langle A\rangle^b$ (cm^{-1} × 10^4)
Cu(dqp)Cl$_2$	Powder	2.062	2.166	2.239	2.156	15.2	20.0	19.0	18.1
	Zinc complex	2.063	2.167	2.241	2.157	15.2	26.3	17.5	19.7
	Dichloromethane				2.169				19.3
	Chlorobenzene				2.171				15.6
Cu(dqp)Br$_2$	Powder	2.030	2.155	2.230	2.138	14.0	15.7	13.3	14.3
	Dichloromethane				2.190				9.9
	Dichloromethane (77 K)	2.024	2.150	2.225	2.133				
	Chlorobenzene				2.155				11.5
	Chlorobenzene (77 K)	2.028	2.148	2.219	2.132	6.9	7.7	11.1	8.7

[a] All g values ±0.005; $\langle g\rangle = {}^1/_3(g_1 + g_2 + g_3)$. [b] All A values approximate (see text); $\langle A\rangle = {}^1/_3(A_1 + A_2 + A_3)$.

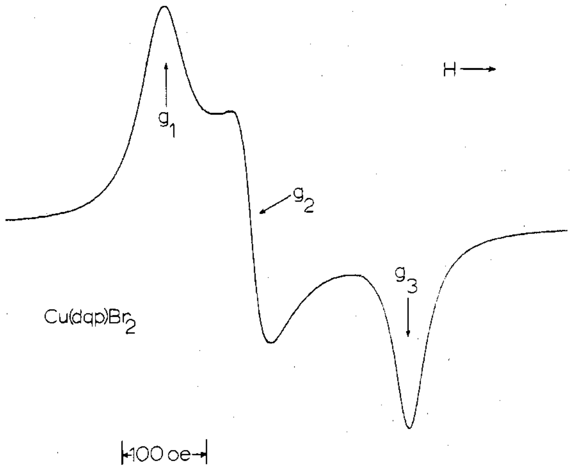


Figure 1. Electron paramagnetic resonance spectrum of a powdered sample of Cu(dqp)Br$_2$ recorded at room temperature; ν = 9.35 GHz.

were also prepared. A hot solution of the appropriate zinc(II) halide containing 5% of the copper(II) halide in anhydrous ethanol (10 mL) was added with stirring to a hot solution of a stoichiometric amount of the ligand dissolved in the minimum amount of anhydrous ethanol. The doped complexes precipitated rapidly, were isolated by filtration, washed with three 20-mL portions of anhydrous ethanol, and vacuum-dried for 25 h over P_2O_5. Yields of 94–97% were obtained.

Mull (transmission) electronic spectra were obtained with a Cary Model 14 recording spectrophotometer using a method described previously.[16] Electron paramagnetic resonance (EPR) spectra were recorded on a Varian E-3 X-band spectrometer. Quartz sample tubes were employed for polycrystalline samples and frozen solutions. Spectra were calibrated with diphenylpicrylhydrazyl (DPPH, g = 2.0036) as a field marker and a solution of oxobis(2,4-pentanedionato)vanadium(IV) in benzene[17] as a field marker and field sweep monitor.

Results

The electronic spectra of mulled solids exhibit a very broad band structure centered at about 1.11 μm^{-1}. The spectrum of Cu(dqp)Cl$_2$ has reasonably well-defined features at about 1.37, 1.20, and 1.03 μm^{-1} while Cu(dqp)Br$_2$ has them at 1.37, 1.19, and 1.08 μm^{-1}.

Typical EPR spectra are shown in Figures 1 and 2 and EPR data are summarized in Table I. It is noted that the g anisotropy is completely resolved in the pure compounds, in the copper-doped zinc complexes, and in frozen-solution samples, but no nuclear hyperfine splitting was resolved. The EPR spectra of solutions at room temperature exhibit only one line. This novel feature has been found in EPR spectra of the pseudotetrahedral complexes Cu(sp)X$_2$ (X = Cl, Br; sp = l-sparteine)[6] and the copper(II)–Schiff base complex derived from pyrrole-2-carboxaldehyde and *tert*-butylamine.[9] The hyperfine coupling constants in Table I were estimated by taking one-third the peak-to-peak width at half-height of the EPR peaks. This procedure provides a reasonable assessment of isotropic nuclear hyperfine coupling constants[6,9] but the application to polycrystalline samples is decidedly tenuous since overlapping lines of finite width (10 G or more), dipolar broadening, and electron exchange, as well as nuclear quadrupole interactions, which may compete with small copper nuclear hyperfine constants, can contribute to the observed peak-to-peak widths. The g values for powdered, doped, and frozen-solution samples are in good agreement with each other while the solution g values are slightly larger than those found for polycrystalline samples. In view of the approximate nature of the evaluation of the hyperfine coupling constants for the solid species, we consider the agreement between the solution and solid-state $\langle A\rangle$ values rather good. The hyperfine coupling data indicate that the pure materials are magnetically dilute, i.e., that the metal ions are well separated, since the line widths of the doped and frozen-solution species do not differ greatly from those found in the pure powdered materials.

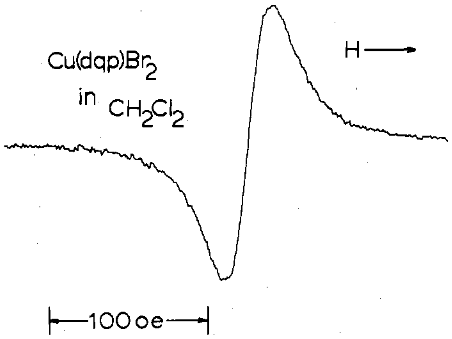


Figure 2. Electron paramagnetic resonance spectrum of Cu(dqp)Br$_2$ in dichloromethane recorded at room temperature; ν = 9.35 GHz.

Discussion

The "d" electronic levels of d^1 and d^9 complexes can be calculated using the explicit crystal field approach described by Companion and Komarynsky.[18] This crystal field method has been developed in several publications[19-21] and only our application to Cu(dqp)X$_2$ compounds is elaborated upon here. The calculations described here employed the coordinate system shown in Figure 3. The three nitrogen donors are in the xz plane and the two chloride ions are in the yz plane. As a consequence of C_{2v} point symmetry[19] only six of the fifteen possible matrix elements[18] need be evaluated. The A_1 d levels are given by

$$\begin{array}{c|cc} A_1 & d_{x^2-y^2} & d_{z^2} \\ \hline d_{x^2-y^2} & H_{11} & H_{13} \\ d_{z^2} & H_{13} & H_{33} \end{array} \qquad (1)$$

where

$$\begin{aligned} H_{11} = {} & -\frac{6}{7}\alpha_2{}^{\mathrm{N}} \cos^2\theta - \frac{2}{7}\alpha_2{}^{\mathrm{Cl}}(3\cos^2\gamma - 1) \\ & + \alpha_4{}^{\mathrm{N}}\left[\frac{1}{21} + \frac{1}{28}\left(\frac{35}{3}\cos^4\theta - 10\cos^2\theta + 1\right)\right. \\ & \left. + \frac{5}{12}\sin^4\theta\right] + \alpha_4{}^{\mathrm{Cl}}\left[\frac{1}{28}\left(\frac{35}{3}\cos^4\gamma - 10\cos^2\gamma\right.\right. \\ & \left.\left. + 1\right) + \frac{5}{12}\sin^4\gamma\right] \end{aligned} \qquad (2)$$

$$\begin{aligned} H_{33} = {} & \frac{6}{7}\alpha^{\mathrm{N}}{}_2 \cos^2\theta + \frac{2}{7}\alpha_2{}^{\mathrm{Cl}}(3\cos^2\gamma - 1) \\ & + \alpha_4{}^{\mathrm{N}}\left[\frac{2}{7} + \frac{3}{14}\left(\frac{35}{3}\cos^4\theta - 10\cos^2\theta + 1\right)\right] \\ & + \frac{3}{14}\alpha_4{}^{\mathrm{Cl}}\left(\frac{35}{3}\cos^4\gamma - 10\cos^2\gamma + 1\right) \end{aligned} \qquad (3)$$

$$\begin{aligned} H_{13} = {} & \frac{-2(3^{1/2})}{7}\alpha_2{}^{\mathrm{N}}\sin^2\theta + \frac{2(3^{1/2})}{7}\alpha_2{}^{\mathrm{Cl}}\sin^2\gamma + \frac{5(3^{1/2})}{42}\alpha_4{}^{\mathrm{N}} \\ & \times \sin^2\theta\,(7\cos^2\theta - 1) - \frac{5(3^{1/2})}{42}\alpha_4{}^{\mathrm{Cl}}\sin^2\gamma(7\cos^2 \\ & \gamma - 1) \end{aligned} \qquad (4)$$

$$\begin{aligned} \mathrm{A}_2\!: \quad E_{\mathrm{d}_{xy}} = {} & -\frac{6}{7}\alpha_2{}^{\mathrm{N}}\cos^2\theta - \frac{2}{7}\alpha_2{}^{\mathrm{Cl}}(3\cos^2\gamma - 1) \\ & + \alpha_4{}^{\mathrm{N}}\left[\frac{1}{21} + \frac{1}{28}\left(\frac{35}{3}\cos^4\theta - 10\cos^2\theta + 1\right)\right. \\ & \left. - \frac{5}{12}\sin^4\theta\right] + \alpha_4{}^{\mathrm{Cl}}\left[\frac{1}{28}\left(\frac{35}{3}\cos^4\gamma - 10\cos^2\gamma\right.\right. \\ & \left.\left. + 1\right) - \frac{5}{12}\sin^4\gamma\right] \end{aligned} \qquad (5)$$

$$\begin{aligned} \mathrm{B}_1\!: \quad E_{\mathrm{d}_{xz}} = {} & \alpha_2{}^{\mathrm{N}}\left(3\cos^2\theta + \frac{3}{7}\sin^2\theta\right) + \alpha_2{}^{\mathrm{Cl}}\left[\frac{1}{7}(3\cos^2\gamma\right. \\ & \left. - 1) - \frac{3}{7}\sin^2\gamma\right] + \alpha_4{}^{\mathrm{N}}\left[-\frac{4}{21} - \frac{1}{7}\left(\frac{35}{3}\cos^4\theta\right.\right. \\ & \left.\left. - 10\cos^2\theta + 1\right) + \frac{5}{21}\sin^2\theta(7\cos^2\theta - 1)\right] \\ & + \alpha_4{}^{\mathrm{Cl}}\left[-\frac{1}{7}\left(\frac{35}{3}\cos^4\gamma - 10\cos^2\gamma + 1\right)\right. \\ & \left. - \frac{5}{21}\sin^2\gamma(7\cos^2\gamma - 1)\right] \end{aligned} \qquad (6)$$

$$\begin{aligned} \mathrm{B}_2\!: \quad E_{\mathrm{d}_{yz}} = {} & \frac{3}{7}\alpha_2{}^{\mathrm{N}}(\cos^2\theta - \sin^2\theta) + \alpha_2{}^{\mathrm{Cl}}\left[\frac{1}{7}(3\cos^2\gamma - 1)\right. \\ & \left. + \frac{3}{7}\sin^2\gamma\right] + \alpha_4{}^{\mathrm{N}}\left[-\frac{4}{21} - \frac{1}{7}\left(\frac{35}{3}\cos^4\theta - 10\cos^2\theta + 1\right)\right. \\ & \left. - \frac{5}{21}\sin^2\theta(7\cos^2\theta - 1)\right] + \alpha_4{}^{\mathrm{Cl}}\left[-\frac{1}{7}\left(\frac{35}{3}\cos^4\gamma\right.\right. \\ & \left.\left. - 10\cos^2\gamma + 1\right) + \frac{5}{21}\sin^2\gamma(7\cos^2\gamma - 1)\right] \end{aligned} \qquad (7)$$

In expressions 2–7, which are completely general for any d^1 or d^9 MX_3Y_2 complex with C_{2v} symmetry, the N and Cl superscripts refer to the nitrogen and chlorine donor atoms in Cu(dqp)Cl_2. The α_2 and α_4 values are ligand crystal field parameters. Experience has shown that a realistic approach to the d levels in complexes requires that the α_2/α_4 ratio be fixed at about 1.0. An α_2/α_4 ratio of 0.9 was employed in the present calculations.

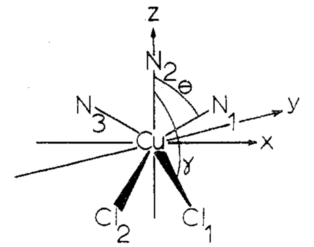


Figure 3. Coordinate system used for crystal field calculations. The three nitrogen atoms lie in the *xz* plane while the chlorine atoms are in the *yz* plane.

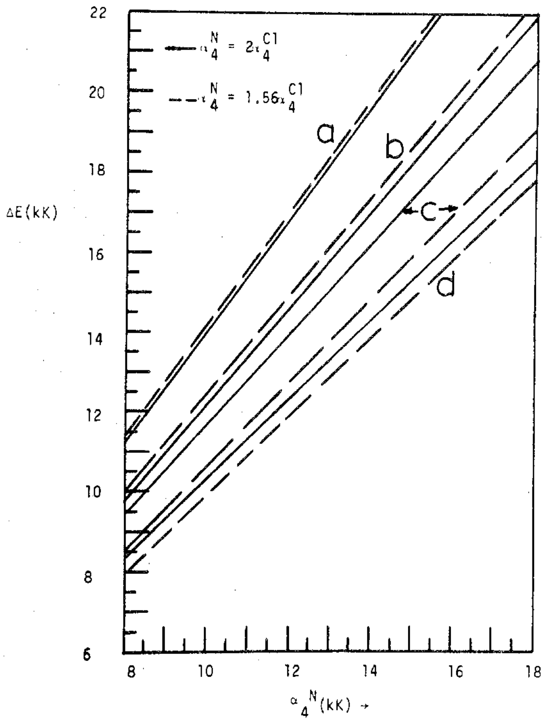


Figure 4. Calculated electronic transition energies as a function of the α_4 crystal field parameter for nitrogen. *a*, *b*, *c*, and *d* refer to the $d_{x^2-y^2} \leftarrow d_{xy}$, $d_{x^2-y^2} \leftarrow d_{xz}$, $d_{x^2-y^2} \leftarrow d_{yz}$, and $d_{x^2-y^2} \leftarrow d_{z^2}$ excitations, respectively. 1 kK = 0.1 μm^{-1}.

The electronic transitions calculated for Cu(dqp)Cl_2 are shown in Figure 4 as a function of the α_4 parameter for nitrogen and chloride ligands.[22] The N–Cu–N and Cl–Cu–Cl bond angles were assumed to be 80 and 116°, respectively, based on the structures of Cu(1-sp)Cl_2[23] and Zn(1,10-phen)Cl_2.[24] For an $\alpha_4{}^{N}$ value of 0.98 μm^{-1} the calculated transition energies are 1.37, 1.19, 1.14, and 1.01 μm^{-1} which compare fairly well with the experimental values of 1.37, 1.20, and 1.03 μm^{-1} for the spectrum of Cu(dqp)Cl_2. Since the bond angles have been assumed, the agreement between the experimental and calculated results may be somewhat fortuitous. However, the assumed structure is a reasonable one and we have no good reason to doubt the general validity of the results.

The crystal field "d" energy level sequence is $x^2 - y^2 > z^2 > yz > xz > xy$ with the unpaired electron residing in the $d_{x^2-y^2}$ orbital. Since both $d_{x^2-y^2}$ and d_{z^2} belong to the a_1 irreducible representation of the C_{2v} point group, the levels are mixed and the energy level sequence given above only reflects the dominant parentage of the level. The $x^2 - y^2$ level consists of about 60% $d_{x^2-y^2}$ and 40% d_{z^2} character irrespective of the α_4 values employed in the crystal field calculations. This is of consequence in the discussion of *g* values which follows.

Within the crystal field approximation the wave functions of the "d" levels may be given by

$$\phi_{a_1}{}^{gs} = a d_{x^2-y^2} + b d_{z^2} + c p_z + d s \tag{8}$$

$$\phi_{a_1} = e d_{x^2-y^2} + f d_{z^2} + g p_z + h s \tag{9}$$

$$\phi_{b_1} = j d_{yz} + k p_y \tag{10}$$

$$\phi_{b_1} = l d_{xz} + m p_x \tag{11}$$

$$\phi_{a_2} = n d_{xy} \tag{12}$$

where a, b, c, d, e, f, g, h, j, k, l, m, and n are orbital coefficients and the metal d, s, and p orbitals are all included since d–s and d–p "mixing" is allowed by the symmetry of the complexes. The expressions for the g values obtained by standard procedures[25] are

$$g_x = 2.0023 - \frac{2\lambda(aj + 3^{1/2}bj - ck)^2}{E_{x^2-y^2} \leftarrow E_{yz}} \tag{13}$$

$$g_y = 2.0023 - \frac{2\lambda(al + 3^{1/2}bl + cm)^2}{E_{x^2-y^2} \leftarrow E_{xz}} \tag{14}$$

$$g_z = 2.0023 - \frac{8\lambda a^2 n^2}{E_{x^2-y^2} \leftarrow E_{xy}} \tag{15}$$

where the transition energies are indicated in the denominators, λ is the spin–orbit coupling constant ($\lambda = -828$ cm^{-1} for the free Cu(II) ion), and the orbital coefficients are those in eq 8–12. It is apparent that metal s orbital mixing into the ground state has no effect on the g values while d–p mixing makes a noticeable contribution to the g anisotropy. Equations 13–15 can be rearranged in order to obtain orbital reduction factors

$$k_{x^2} = \frac{\Delta g_x(E_{x^2-y^2} \leftarrow E_{yz})}{2\lambda} = \frac{0.166(10300)}{1656} = 1.032 \tag{16}$$

$$k_{y^2} = \frac{\Delta g_y(E_{x^2-y^2} \leftarrow E_{xz})}{2\lambda} = \frac{0.060(12000)}{1656} = 0.435 \tag{17}$$

$$k_{z^2} = \frac{\Delta g_z(E_{x^2-y^2} \leftarrow E_{xy})}{8\lambda} = \frac{0.237(13700)}{6624} = 0.490 \tag{18}$$

if g_1, g_2, and g_3 for Cu(dqp)Cl$_2$ (Table I) are identified with g_z, g_x, and g_y, respectively, and the appropriate transition energies are chosen. (Considering the uncertainties in the electronic band assignments we do not attach any special significance to $k_x{}^2$ being slightly greater than 1.0.) In noncentrosymmetric complexes the orbital reduction factor is a measure of metal–ligand covalency as well as d–p orbital mixing.[26] Comparison of eq 13–15 with eq 16–18 shows that there are more variables than experimental parameters and that interpretation of the orbital reduction factors is somewhat intractable. Since $k_{y^2} \approx k_{z^2}$, the omission of ligand orbitals from the calculations of the g values is probably not fully justified. Molecular orbital calculations seem warranted before a detailed analysis of metal–ligand covalency and orbital reduction factors is attempted.

Inspection of the EPR literature (summarized in ref 11) shows that the "blue" copper proteins have isotropic nuclear hyperfine coupling constants in the range (19–36) × 10^{-4} cm^{-1}. This range of values was necessarily estimated from the anisotropic data. The present work shows that the EPR data for the "blue" copper proteins is also consistent with a five-coordinate geometry about the metal ion. Previous "blue" copper protein model system studies[27–29] have tended to favor a pseudotetrahedral four-coordinate geometry for the copper ion. It is noted that five-coordinate copper(II) complexes[7,30,31] exhibit smaller hyperfine coupling constants than planar species and show a variation with detailed geometry as pseudotetrahedral species do.

The origin of the small nuclear hyperfine coupling constants in pseudotetrahedral copper(II) complexes has been largely attributed to 4p orbital mixing into the ground state.[32–35] As noted in eq 8, the ground state in complexes with C_{2v} symmetry contains some metal 4s character. The isotropic parts of nuclear hyperfine constants of centrosymmetric copper(II) complexes arise from core polarization and are predominantly negative. The admixture of 4s character into the ground state in noncentrosymmetric complexes provides a positive contribution[36] to the hyperfine splitting and reduces the observed hyperfine coupling constant. Yokoi[37] has commented on this problem and has pointed out the need for additional calculations of spin-polarization of all of the metal s electrons associated with the exchange interaction with the metal 4p orbital mixed into the ground state. Thus, quantitatively sorting out the various contributions to the observed hyperfine coupling constants is not readily accomplished at the present time.

In summary, the Cu(dqp)X$_2$ complexes have been assigned a five-coordinate geometry. Crystal field calculations yield an energy level sequence for the complexes and provide a reasonable description of the electronic spectra of the complexes. The EPR spectra show that the complexes are magnetically dilute. g Anisotropy is completely resolved, but no nuclear hyperfine splitting was observed in the solid state nor, more notably, in solution. The lack of resolved nuclear hyperfine structure in the EPR spectra can be quantitatively interpreted in terms of 4s and 4p orbital admixture into the ground states of the complexes.

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Registry No. Cu(dqp)Cl$_2$, 62416-00-6; Cu(dqp)Br$_2$, 62415-99-0.

References and Notes

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Intramolecular Hydration of Nitriles Coordinated to Cobalt(III). Formation of Five- and Six-Membered Chelated Amides

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Treatment of *cis*-$[Co(en)_2(NH_2CH_2CN)X]^{2+}$ ions (X = Cl, Br) with Hg^{2+} results in the formation of both $[Co(en)_2(glyNH_2)]^{3+}$ and $[Co(en)_2(NH_2CH_2CONH)]^{2+}$ with the product ratio depending on the leaving group; similar treatment of *cis*-$[Co(en)_2(NH_2CH_2CH_2CN)Br]^{2+}$ forms *cis*-$[Co(en)_2(NH_2CH_2CH_2CN)(OH_2)]^{3+}$ initially and $[Co(en)_2(\beta\text{-alaNH}_2)]^{3+}$ finally. Oxidation of *cis*-$[Co(en)_2(NH_2CH_2CN)Br]^{2+}$ with HOCl gives the *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$ ion ($pK_a = 5.60$), and ^{18}O-tracer studies establish that the Hg^{2+}-catalyzed formation of $[Co(en)_2(glyNH_2)]^{3+}$ from *cis*-$[Co(en)_2(NH_2CH_2CN)(^{18}OH_2)]^{3+}$ occurs with retention of the oxygen label. Rate data for the spontaneous hydration of *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$ agree with the rate expression $k_{obsd} = k_1K_a/(K_a + [H^+])$ with $k_1 = 1.15 \times 10^{-2}\ s^{-1}$ ($\Delta H^{\ddagger} = 10.7$ kcal mol^{-1}; $\Delta S^{\ddagger} = -31$ cal deg^{-1} mol^{-1}) and $pK_a = 5.6$ at 25 °C, $\mu = 1.0$ ($NaClO_4$). The rate law for the Hg^{2+}-catalyzed reactions of *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$ and *cis*-$[Co(en)_2(NH_2CH_2CH_2CN)(OH_2)]^{3+}$ takes the form $k_{obsd} = k_{Hg^{2+}}[Hg^{2+}]/[H^+]$ with $k_{Hg^{2+}} = 0.48$ and $6.5 \times 10^{-5}\ s^{-1}$, respectively. Catalysis by Ag^+ is more complex with the rate data for *cis*-$[Co(en)_2(NH_2CH_2CN)(OH_2)]^{3+}$ agreeing with the expression $k_{obsd} = (k_1'[Ag^+] + k_2'[Ag^+]^2)/[H^+](1 + K_{Ag^+}[Ag^+])$, with $k_1' = 0.8 \times 10^{-3}\ s^{-1}$, $k_2' = 8 \times 10^{-3}\ M^{-1}\ s^{-1}$, and $K_{Ag^+} = 1.3$ M. Catalysis by Zn^{2+}, Hg_2^{2+}, Cd^{2+}, and HPO_4^{2-} is also observed. Full retention of optical configuration obtains in all the reactions.

Introduction

The ability of coordinated water, hydroxide, and amide to act as nucleophiles in intramolecular reactions centered about cobalt(III) has been demonstrated in many instances recently.[1-6] In addition, several examples of the metal-promoted (or -catalyzed) hydration of nitriles to amides have been reported but these studies have involved the solvolysis of the directly coordinated $M\text{-}NCR^{n+}$ moiety.[7-12] This paper reports on the Co(III)-promoted intramolecular hydration of aminoacetonitrile and aminopropionitrile in which the –CN group is not directly bound to the metal center. It reports in detail and extends results given in an earlier communication[13] and subsequently amplified by Nolan and Hay.[14] A following paper will deal with the reaction in neutral and alkaline solutions in which amidine complexes are produced.[25]

Experimental Section

Analytical reagents were used for kinetic measurements without further purification. Aminoacetonitrile hydrogen sulfate was obtained from Adams Chemical Co. or prepared locally.[16,17] Aminoacetonitrile hydrochloride was used in later preparations and was prepared as for the hydrogen sulfate salt using 35% HCl instead of H_2SO_4 and without heating. Anal. Calcd for $C_2N_2H_5Cl$: C, 25.96; H, 5.46; N, 30.28; Cl, 38.31. Found: C, 26.3; H, 5.4; N, 30.2; Cl, 38.3. Aminopropionitrile was purchased from Frinton Laboratories or prepared directly from acrylonitrile.[18] β-Alanine amide hydrobromide was prepared locally from dimedone β-alanine ethyl ester and ammonia.[19] Oxygen-18-enriched water (1.5 atom %) was purchased from Bio-Rad Laboratories. Bio-Rad analytical Dowex 50W-X2 (200–400 mesh) and Sephadex C-25 ion-exchange resins (H^+ form) were used in the analysis of reaction products.

Visible spectra were recorded using a Cary 14 or 118C spectrophotometer. Infrared measurements were made with a Perkin-Elmer 457 spectrophotometer. Optical rotatory power was measured with a Perkin-Elmer P22 spectropolarimeter in a 1-dm tube (±0.002°). ^1H NMR spectra were recorded using Varian HA-100 and JEOLCO Minimar MH-100 spectrometers, with complex concentrations between 0.1 and 0.3 M in deuterated solvents (D_2O, $Me_2SO\text{-}d_6$) with NaTPS or external TMS as references and at 34 or 25 °C, respectively. Atomic absorption determinations for Co were carried out using Varian-Techtron AA4 and AA1000 spectrometers. Determinations of pH were made using a Radiometer TTT 1c pH meter, a pH A 630T scale expander, a G202C glass electrode, and a calomel electrode protected with a NH_4NO_3 (1.6 M)–$NaNO_3$ (0.2 M) salt bridge. The meter was calibrated with 0.05 M potassium hydrogen phthalate (pH 4.01 (25 °C), 4.03 (37 °C), 4.06 (50 °C)) or 0.01 M borax (pH 9.18 (25 °C), 9.09 (37 °C), 9.01 (50 °C)).

Preparation of Complexes. *cis*-$[Co(en)_2Br(NH_2CH_2CN)]Br_2$ was prepared[20] by triturating *trans*-$[Co(en)_2Br_2]Br$ (4.19 g, 0.01 mol), aminoacetonitrile hydrogen sulfate (or aminoacetonitrile hydrochloride) (0.01 mol), and diethylamine (1.03 mL, 0.01 mol), as a paste in methanol. Further, diethylamine (1.03 mL) was slowly added with grinding over 30 min by which time the mixture had turned purple. After alternate grinding and standing for a further 1 h the product was filtered from methanol and air-dried. The product was recrystallized following dissolution in the minimum volume of 0.1 M HBr at ~50 °C and cooling in an ice bath, by the addition of solid NaBr (yield ~40–70%). In some preparations the crude product was purified by dissolution in a large volume of dilute HBr (~0.01 M) and adsorption and elution (1 M NaBr) from Dowex 50W-X2 ion-exchange resin. The purple 2+ band was collected, the volume of the solution was reduced on a rotary evaporator (less than 50 °C) until crystallization of the complex commenced, and then the mixture was cooled in an ice bath. The bromide salt was collected, washed with ethanol, and air-dried (yield ca. 40%). Anal. Calcd for $CoC_6H_{20}N_6Br_3$: Co, 12.41; C, 15.17; H, 4.24; N, 17.70; Br, 50.48. Found (for both methods): Co, 12.6 (12.6); C, 15.2 (15.1); H, 4.3 (4.3); N, 17.4 (17.6); Br, 50.3 (50.5); ϵ_{545} 84 in 0.5 M $HClO_4$–0.5 M $NaClO_4$ at 25.0 °C. *cis*-$[Co(en)_2Br(NH_2CH_2CN)](ClO_4)_2$ was prepared from the above bromide salt by slurrying 4.93 g (0.01 mol) with water (15 mL containing 5 drops of glacial acetic acid), adding silver acetate (3.34 g, 0.02 mol) and shaking rapidly with some glass beads for several minutes. The precipitated AgBr was removed on a Hyflow-supercel filter and washed with 5 mL of dilute $HClO_4$, and