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Nitrogenous Chelate Complexes of Transition Metals. IV. Pseudo-Tetrahedral Copper(II) Complexes Containing 2,2'-Biquinolyl[1]

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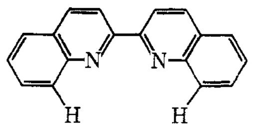
The mono- and bis-2,2'-biquinolyl complexes $Cu(biq)X_2$ ($X = Cl$, Br, and NO_3) and $Cu(biq)_2(ClO_4)_2$ have been prepared. The electronic spectra of these compounds are consistent with a pseudo-tetrahedral arrangement about the copper atoms. The magnetic susceptibilities of these compounds over the temperature range ~80–400°K obey a Curie–Weiss law with θ values in the range 0 to -7°K. The compounds' magnetic moments lie in the range 1.93–2.02 BM and this is comparable with the values of other known pseudo-tetrahedral copper(II) complexes. The brown bis complex readily absorbs water to form a green monohydrate, $Cu(biq)_2(ClO_4)_2 \cdot H_2O$. The possible structure of this compound is discussed.

Introduction

A systematic study of metal chelates of 2,2'-biquinolyl (biq = I) has been recently undertaken by the authors. The investigation was prompted by the steric requirements of this ligand. Models show that in order to function as a planar bidentate chelating agent with transition metal ions, the bonding of only one other atom such as chlorine or bromine is possible in the same plane as the metal and the biquinolyl molecule. Furthermore, bis-chelated metal ions of this ligand cannot adopt a planar arrangement. It was anticipated that this ligand might well force uncommon stereochemical configurations on some transition metal ions. In this regard it is of interest to note that the gold(III) complexes $Au(biq)X_3$ ($X = Cl$, Br) have been recently prepared, and an X-ray structural analysis has demonstrated that these compounds, which are nonelectrolytes in nitrobenzene, possess a five-coordinated monomeric structure.[2]



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The preparation and properties of a series of mono- and bis-chelated copper(II) compounds containing 2,2'-biquinolyl are described here, and spectral evidence suggests a pseudo-tetrahedral structure for a number of compounds. The magnetic susceptibilities of the compounds have been measured over a temperature range.

Experimental Section

Preparation of Compounds. (a) **Mono Complexes.**—A hot solution of the appropriate copper(II) halide or nitrate (2 mmoles) in anhydrous methanol (10 ml) was added to a hot methanol (10 ml)–benzene (10 ml) mixture containing 2 mmoles of 2,2'-biquinolyl. The complexes, which precipitated rapidly, were filtered off, washed with hot benzene followed by methanol, and dried over phosphoric oxide. **Dichloro(2,2'-biquinolyl)copper(II):** *Anal.* Calcd for $C_{18}H_{12}N_2Cl_2Cu$: C, 55.4; H, 3.1; N, 7.2. Found: C, 55.6; H, 3.3; N, 7.0. **Dibromo(2,2'-biquinolyl)-Copper(II):** *Anal.* Calcd for $C_{18}H_{12}N_2Br_2Cu$: C, 45.0; H, 2.5; N, 5.8. Found: C, 45.1; H, 2.5; N, 5.8. This compound has a molecular conductance in 10^{-3} *M* nitrobenzene solution at 25° of 0.3 mho mole^{-1} cm^2. **Dinitrato(2,2'-biquinolyl)copper(II):** *Anal.* Calcd for $C_{18}H_{12}N_4O_6Cu$: C, 48.6; H, 2.7; N, 12.6. Found: C, 48.2; H, 2.8; N, 12.1.

(b) **Bis Complexes.**—Bis(2,2'-biquinolyl)copper(II) perchlorate was readily obtained as reddish brown leaflets by the addition of a hot solution of copper(II) perchlorate hexahydrate (0 74 g) in methanol (20 ml) to a hot methanol (10 ml)–benzene (20 ml) mixture containing 2,2'-biquinolyl (1.0 g). The compound was filtered from the cooled reaction mixture, washed with hot benzene and cold methanol, and dried over phosphoric oxide. *Anal.* Calcd for $C_{36}H_{24}N_4O_8Cl_2Cu$: C, 55.7; H, 3.1; N, 7.2. Found: C, 56.0; H, 3.5; N, 7.2. The anhydrous bis-chelated compound, described above, readily absorbed water on standing in air and formed a green monohydrate. *Anal.* Calcd for $C_{36}H_{26}N_4O_9Cl_2Cu$: C, 54.5; H, 3.3; N, 7.1. Found: C, 54.4; H, 3.5; N, 6.6. This compound reverts to the brown anhydrous compound over phosphoric oxide. The anhydrous compound possesses a molecular conductance in 10^{-3} *M* nitrobenzene solution at 25° of 48 mhos mole^{-1} cm^{-2}.

Magnetic Measurements.—Magnetic susceptibility measurements were made by the Gouy method using $HgCo(SCN)_4$ as the calibrant.[3] The data are summarized in Table I. The results were fitted to a Curie–Weiss law: $\chi_M^{cor} = C/(T + \theta)$. The magnetic moments have been corrected for the small observed θ values and the diamagnetic corrections (Δ) that were used were calculated from Pascal's constants. No correction was made for temperature-independent paramagnetism.

Spectrophotometric Measurements.—Infrared spectra were obtained with a Perkin-Elmer Infracord spectrometer using Nujol and hexachlorobutadiene mulls on sodium chloride plates. Near-infrared and visible spectra were obtained with a Carl Zeiss PMQ11 spectrophotometer equipped with matched 1-cm silica cells. The diffuse reflectance spectra were measured using the Carl Zeiss RA3 reflectance attachment and magnesium oxide as the reference.

Analyses.—The carbon, hydrogen, and nitrogen analyses were carried out in the microanalytical laboratory under the direction of Dr. E. Challen.

Results and Discussion

The mono complexes $Cu(biq)X_2$ ($X = Cl$, Br, and NO_3) were readily obtained by allowing the appropriate copper(II) salt to react with the ligand in methanol–benzene mixtures. The chloro complex has been described previously.[4] Attempts to isolate thiocyanato

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(1) Part III of this series: C. M. Harris and E. D. McKenzie, *J. Inorg. Nucl. Chem.*, in press.

(2) R. J. Charlton, C. M. Harris, H. Patil, and N. C. Stephenson, *Inorg. Nucl. Chem. Letters*, **2**, 409 (1966).

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(4) J. G. Breckenridge, R. W. J. Lewis, and L. A. Quick, *Can. J. Res.*, **17B**, 258 (1939).

TABLE I

THE ELECTRONIC SPECTRA AND MAGNETIC DATA OF 2,2′-BIQUINOLYL COMPLEXES OF COPPER(II)

Compound	Medium	Electronic spectrum, cm^{-1} (ϵ)					Magnetic data[a]	
							μ_{eff}, BM	θ, °K
$Cu(biq)(NO_3)_2$	Solid	27,000	22,200 sh		11,760	10,800	1.94	−7
$Cu(biq)Cl_2$	Solid		21,200 sh		10,500	<9,000	1.99	−5
$Cu(biq)Br_2$	Solid	27,000	22,200	16,700	11,760	10,000	2.02	0
	Nitrobenzene		21,500 (2200)	17,540 (730)	11,110 (210)	9,090 (210)		
$Cu(biq)_2(ClO_4)_2$	Solid	26,300	22,800 sh	19,600	13,300	9,500	1.93	−3
	Nitrobenzene		23,600 (1190)	19,230 (950)	13,300 (170)	9,300 (90)		
$Cu(biq)_2(ClO_4)_2 \cdot H_2O$	Solid				11,800	10,000	1.93	−8

[a] The mean values of the effective magnetic moments are given. The detailed magnetic results over the temperature range 80–400°K have been deposited as Document No. 9393 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

or iodo complexes were unsuccessful due to reduction to copper(I). The bromo compound, dibromo(2,2′-biquinolyl)copper(II), is essentially a nonconductor in nitrobenzene solution (see Experimental Section). Infrared measurements on dinitrato(2,2′-biquinolyl)-copper(II) indicate that the nitrate groups are coordinated. Using the assignments of Addison and Logan[5] the following values (cm^{-1}) were observed: ν_1 NO_2 symmetric stretch, 1265; ν_2 NO stretch, 1010; ν_4 NO_2 asymmetric stretch, ~1500; ν_6 out-of-plane rock, 810.

The reaction of hydrated copper(II) perchlorate with excess 2,2′-biquinolyl in methanol yields brown bis-(2,2′-biquinolyl)copper(II) perchlorate which functions as a di-univalent electrolyte in nitrobenzene (see Experimental Section). The presence of a broad absorption band in the infrared region at 1075 cm^{-1} is taken to infer that this compound possesses predominantly ionic perchlorate groups in the solid state.[6,7] A similar, sharp absorption was also observed in nitrobenzene (1100 cm^{-1}) and acetone (1080 cm^{-1}) solution. The close similarity of the electronic spectra of the compound in nitrobenzene solution and in reflectance (Table I), together with the above observations, is believed to provide good evidence that in this compound there exists the four-coordinated $[Cu(biq)_2]^{2+}$ ion. This brown complex slowly absorbs water from the atmosphere to form the green monohydrate $Cu(biq)_2(ClO_4)_2 \cdot H_2O$. Although it would appear that the green compound might well be a five-coordinated monoaquo complex, infrared measurements reveal that the broad absorption present in the anhydrous compound at 1075 cm^{-1} is split in the hydrate with the appearance of two bands at 1100 and 1060 cm^{-1}. Whether this is due to coordination of perchlorate or to some other effect such as hydrogen bonding is not known. The reflectance spectrum of the green hydrate is different from that of the anhydrous compound in that the intense absorptions above 19,000 cm^{-1} are absent. The compound possesses absorptions at 10,000 and 11,800 cm^{-1} (see Table I).

Attempts to isolate five-coordinated complexes of the type $[Cu(biq)_2X]ClO_4$ (X = Cl, Br) similar to the extensive series reported by Harris, Lockyer, and Waterman[8] containing 1,10-phenanthroline and 2,2′-bipyridyl were unsuccessful. However, the formation of this type of ion in dilute nitrobenzene solution is indicated by the conductometric titration of 10^{-3} *M* nitrobenzene solutions of bis(2,2′-biquinolyl)copper(II) perchlorate with tetraethylammonium bromide and triphenylmethylarsonium chloride. End points corresponding to the addition of 1 and 2 equiv of halide ion were observed as expected for the reactions

$$Cu(biq)_2^{2+} + X^- \rightleftharpoons Cu(biq)_2X^+$$

$$Cu(biq)_2X^+ + X^- \rightleftharpoons Cu(biq)X_2 + biq$$

The results for the chloride titration are illustrated in Figure 1.

The preparation of the five-coordinated compounds $[Cu(biq)_2L](ClO_4)_2$ (where L = NH_3 or pyridine) was attempted by exposing bis(2,2′-biquinolyl)copper(II) perchlorate to pyridine or ammonia vapor. A ready reaction occurred and the compounds $Cu(C_5H_5N)_4(ClO_4)_2$ and $Cu(NH_3)_4(ClO_4)_2$ were formed with elimination of 2,2′-biquinolyl. The biquinolyl was removed by washing with benzene and the resulting compounds were characterized by analyses. Similarly, the mono compounds $Cu(biq)X_2$ (X = Cl, Br) were also found to react with pyridine vapor to form bis(pyridine)-copper(II) halide.

Electronic Spectra.—The spectra (Figures 2 and 3) of the 2,2′-biquinolyl complexes are summarized in Table I and are quite different from those usually associated with bivalent copper in square or tetragonal arrangements. The brown bis(2,2′-biquinolyl)copper-(II) perchlorate can be safely inferred to contain four-coordinated copper(II) since no evidence of perchlorato coordination has been found in this compound. The spectrum of the compound in nitrobenzene solution is characterized by two broad ligand-field bands at 9300 cm^{-1} (ϵ 90) and 13,300 cm^{-1} (ϵ 170). The spectra of the mono 2,2′-biquinolyl complexes are also characterized by two absorptions in the region ~9000–12,000 cm^{-1}, and these compounds are also believed to contain a pseudo-tetrahedral arrangement. Absorptions

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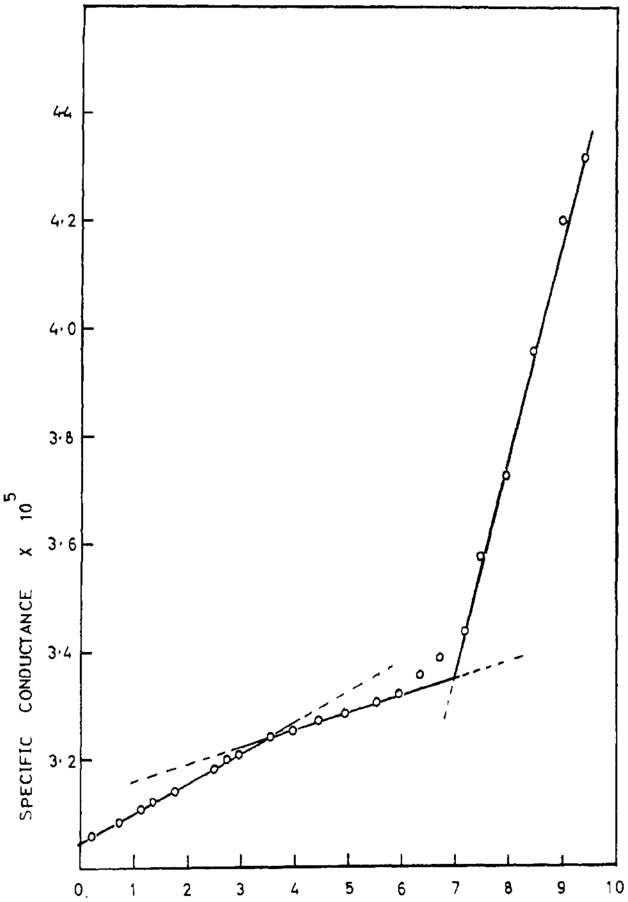

Figure 1.—Conductometric titration of 5.5×10^{-4} *M* $Cu(biq)_2(ClO_4)_2$ with 6.4×10^{-3} *M* $(C_6H_5)_3CH_3AsCl$ in nitrobenzene; 1 mole of Cl^- = 3.5 ml.

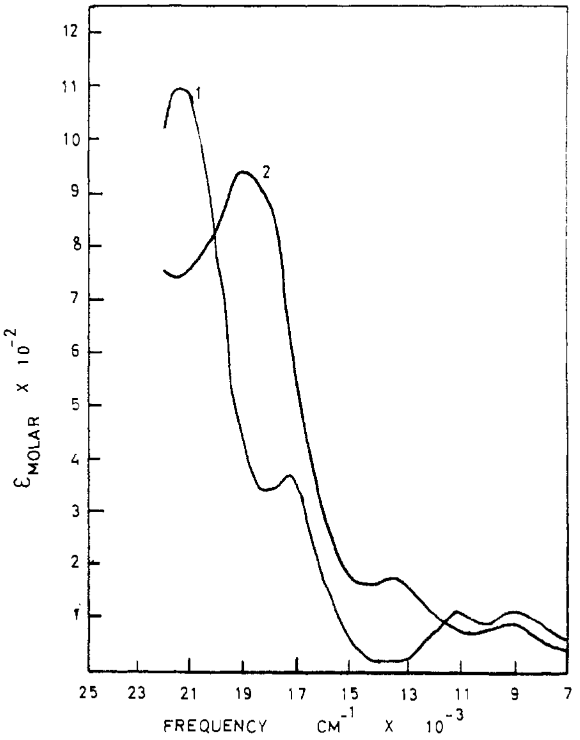

Figure 2.—Absorption spectra in nitrobenzene; 1, $Cu(biq)Br_2$ plotted as ε/2; 2, $Cu(biq)_2(ClO_4)_2$.

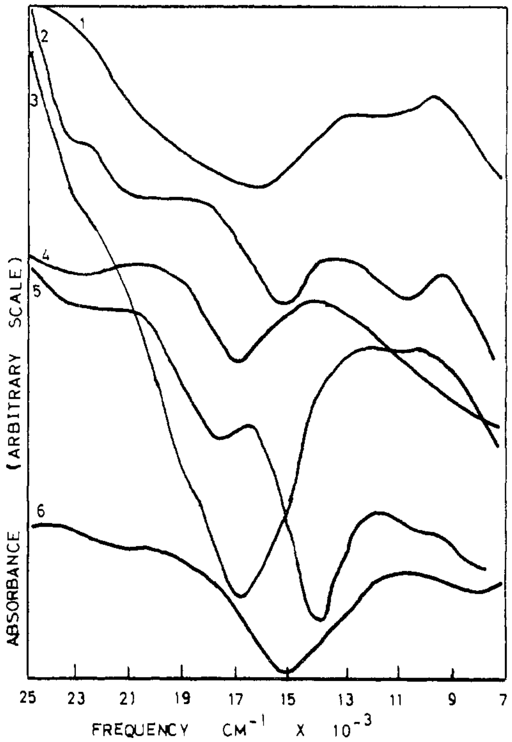

Figure 3.—Reflectance spectra: 1, $Cu(biq)_2(ClO_4)_2 \cdot H_2O$; 2, $Cu(biq)_2(ClO_4)_2$; 3, $Cu(biq)(NO_3)_2$; 4, $Cu(bipy)Br_2$; 5, $Cu(biq)Br_2$; 6, $Cu(biq)Cl_2$.

above 16,000 cm^{-1} are also present in the spectra of these compounds and the values of the molar extinction coefficients, where measurable, are of the order of 10^3. These absorptions are undoubtedly due to charge-transfer phenomena.

The spectrum of a nitromethane solution of dibromo-(2,2′-bipyridyl)copper(II) exhibits a broad ligand-field absorption at 14,290 cm^{-1} (ε 210) as well as a charge-transfer band at 20,200 (ε 620).[9] This compound is expected to possess a structure containing a planar arrangement of bromine and nitrogen atoms. It possesses a very similar spectrum (Figure 3) to those of the bis(pyridine)copper(II) complexes $Cu(C_5H_5N)_2X_2$ (X = Cl, Br, and NCS) whose crystal spectra[10] possess bands at about 14,000 cm^{-1} and whose tetragonal structures have been established by X-rays.[11-13] These compounds also have absorption bands in the region 20,000–25,000 cm^{-1} which Ferguson[10] has assigned to electronic charge-transfer transitions.

The complexes of copper(II) with N-isopropyl and N-*sec*-butylsalicylideneamines have been established by X-ray measurements to possess a pseudo-tetrahedral structure in contrast with the N-*n*-alkyl complexes, which are planar.[14] Sacconi and Ciampolini[14] examined the electronic spectra of a number of these compounds. They found that the planar complexes have a single broad band in the range 14,000–16,000 cm^{-1}, whereas

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the pseudo-tetrahedral complexes have bands at 8700–10,000 and 12,800–13,800 cm^{-1}, which they assigned on the basis of their frequencies and relatively low intensities to crystal-field transitions of the copper(II) ion in a pseudo-tetrahedral environment. The spectra of the above biquinolyl complexes are similar to those of these known pseudo-tetrahedral complexes.

Magnetism.—The magnetic data for the copper(II) 2,2′-biquinolyl complexes are presented in Table I. The measurements were performed over a temperature range of ~80–400°K and the compounds obey the Curie–Weiss law with small values of θ in the range 0 to −8°. The moments of the compounds lie in the range 1.9–2.0 BM and are comparable with those reported for other pseudo-tetrahedral copper(II) compounds.[15–19] Although a room-temperature moment of ~2.2 BM has been predicted for copper(II) in a tetrahedral environment,[20] distortions can appreciably lower it if the low-symmetry ligand fields produced are large compared to spin–orbit coupling. In related complexes there is some evidence for a correlation between the magnitude of the moment and distortions from planar toward tetrahedral symmetry. For example, the $CuCl_4^{2-}$ ion is planar in the compound $[Pt(NH_3)_4][CuCl_4]$ and μ = 1.77 BM compared with the value of 2.0 BM in Cs_2CuCl_4, where the ion is present in the form of a flattened tetrahedron.[21] Similarly, Sacconi, Ciampolini, and Campigli[14] have commented on the fact that the magnetic moments (1.90–1.92 BM) of the distorted tetrahedral N-*sec*-alkylsalicylaldiminocopper(II) complexes are slightly higher than those (1.85–1.86 BM) of the N-*n*-alkyl-substituted planar compounds. The moments in the biquinolyl series $Cu(biq)X_2$ ($X = NO_3$, Cl, Br) steadily increase from 1.93 to 2.02 BM and the highest moment is associated with the dibromo complex, which is expected to show the greatest deviation from a planar arrangement of the two nitrogen and two halogen atoms.

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Rare Earth Chelates of 1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyl-4,6-octanedione[1,2]

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Fifteen chelates of the ligand 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione, H(fod), with trivalent rare earth metal ions have been synthesized and investigated. The tris chelates are more volatile than any other known lanthanide compounds. The complexes have been characterized by their elemental analyses, infrared and nuclear magnetic resonance spectra, melting points, molecular weights, and Karl Fischer titrations. All of the complexes [except that of Sc(III), which is anhydrous] are isolated as monohydrates which can be easily dehydrated *in vacuo* over P_4O_{10}. The complexes have been studied by gas chromatography and thermogravimetric analysis. The results indicate an increase in volatility with a decrease in the radius of the central metal ion.

Introduction

Of the many rare earth chelates of β-diketones that have been described[4–7] the tris complexes generally have the most promising properties necessary for gas chromatographic elution, *i.e.*, thermal and solvolytic stability and volatility. However, the prevalence of hydration in compounds of this type seems to produce undesirable effects on the thermal stability in many cases[8–10] and attempts to elute neodymium(III) trifluoroacetylacetonate dihydrate, $Nd(tfa)_3 \cdot 2H_2O$, were unsuccessful.[11] Recently, however, Eisentraut and Sievers have used a sterically crowded ligand to preclude the formation of hydrated complexes,[12] a possibility that was suggested by Brown, Steinbach, and Wagner.[13]

It has been well demonstrated that the incorporation of fluorocarbon moieties in the ligand enhances the

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(2) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(3) Author to whom correspondence should be addressed at the Aerospace Research Laboratories.

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