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Synthesis and Characterization of Some Metal Complexes of a Novel Binucleating Ligand (IV): Quinizarin

PHILIP H. MERRELL
Department of Chemistry, Bowdoin College, Brunswick, Maine 04011, U.S.A.

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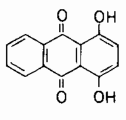
The Mn(II), Co(III), Cu(II), Zn(II) and Ru(II) complexes of the binucleating ligand, quinizarin, have been prepared and characterized by the use of elemental analysis, infrared spectroscopy, electronic spectroscopy, magnetic susceptibility and electron paramagnetic resonance spectroscopy. In addition the magnetic susceptibility versus *temperature is subjected to a line fit for the dicopper complex and the interaction parameter 2J is* -1.6 *cm*$^{-1}$.

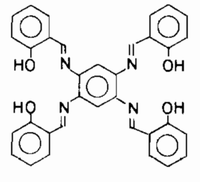
Introduction

The metal complexes of 1,4-dihydroxyanthraquinone (quinizarin, Quin I) have been utilized as dyes for many years because of their deep colors and their insolubility in aqueous media [1].

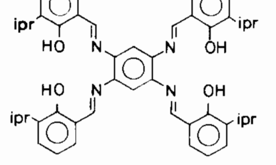
Five compounds have been prepared from this ligand which as a ligand can bind two metal atoms. The dimetal complexes are potentially interesting by virtue of their possible magnetic interactions across an unusual π-electron system [2] and of their unusual electrochemical properties [3]. The magnetic properties of the dicopper complex can be compared to the dicopper complexes in our earlier studies with the TSAB ligands (II, III, and IV) [4–6].



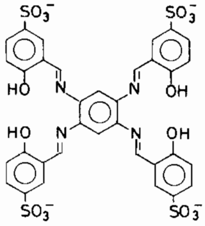
QUIN
I



TSAB
II



iPr-TSAB
III



SO_3^--TSAB
IV

We report here the synthesis and characterization of these compounds and preliminary magnetic studies of the copper complexes.

Experimental

The Quinazarin was obtained from Aldrich Chemical Company and recrystallized from $CHCl_3$. All other compounds were used as received. All analyses were done by N. D. Chasteen at the University of New Hampshire, Durham, N.H.

Quinizarylbisbipyridinedicopper(II) Hexafluorophosphate [Cu₂(Quin)(bipy)₂](PF₆)₂

One gram (5 mmol) of $Cu(OAc)_2\cdot H_2O$ is dissolved in about 50 ml of ethanol. A 0.78 g (5 mmol) sample of bipyridine and 2 g (12.3 mmol) NH_4PF_6 are dissolved in 50 ml EtOH, and the two solutions are poured together. This mixture is then added slowly to a solution of 0.6 g (2.5 mmol) quinizarin dissolved in 50 ml CH_2Cl_2. The final solution turns deep maroon and is heated for several hours and then cooled. A maroon crystalline compound is obtained and recrystallized from CH_3CN. Obtained 1.7 g, 71%. *Anal.*: Calc'd for $Cu_2C_{34}H_{22}N_4O_4(PF_6)_2$: Calcd: C: 42.19; H: 2.28; N: 5.79. Found: C: 42.08; H: 2.57; N: 5.90.

Quinizaryltetrakisbypyridinedimanganese(II) Hexafluorophosphate [Mn₂(Quin)(bipy)₄](PF₆)₂

A 1.2 g (4.9 mmol) sample of $Mn(OAc)_2\cdot 4H_2O$ is dissolved in 50 ml deoxygenated absolute EtOH and kept under dry, O_2-free nitrogen. A solution of 0.5 g (2.1 mmol) Quin in 50 ml CH_2Cl_2 is slowly dripped into the Mn^{2+} solution yielding a deep purple color. A solution is made by adding 1.4 g (9 mmol) bipyridine and 1.5 g (9.2 mmol) NH_4PF_6 into 50 ml of absolute EtOH, and this solution is slowly dropped into the manganese–quinizarin solution and then heated for about an hour (always under a N_2 atmosphere). The deep purple solution is then allowed to cool and a deep blue-purple crystalline compound is obtained and recrystallized from absolute EtOH. Yield 1.0 g (33%). *Anal.*: Calc'd for $Mn_2C_{54}H_{38}N_8O_4(PF_6)_2$. Calcd: C: 51.32; H: 3.00; N: 8.87. Found: C: 51.07; H: 3.12; N: 8.85.

Quinizaryltetrakisbipyridinedicobalt(III) Hexafluorophosphate $[Co_2(Quin)(bipy)_4](PF_6)_4$

Under dry, O_2-free N_2, 1.25 g (5 mm) $Co(OAc)_2 \cdot 4H_2O$ is dissolved in 50 ml CH_3CN forming the pale pink solution. To this a mixture of 1.56 g (10 mmol) bipyridine and 0.6 g (2.5 mmol) quinizarin dissolved in CH_2Cl_2 is slowly added turning the solution a deep maroon. The solution is refluxed for an hour and 1.64 g (10.0 mmol) NH_4PF_6 is added and the solution refluxed another hour. Air is bubbled through the solution and a deep blue crystalline compound forms after reducing the volume considerably. This compound is recrystallized from acetone–ethanol mixture. Obtained 0.5 g (15%). *Anal.*: Calcd for $Co_2C_{54}H_{38}N_8O_4(PF_6)_4$, C: 41.5; H: 2.43; N: 7.18. Found, C: 40.40; H: 2.58; N: 7.17.

Quinizaryltetrakisbipyridinediruthenium(II) Hexafluorophosphate $[Ru_2(Quin)(bipy)_4](PF_6)_2$

Under N_2 a 0.6 g (1.2 mmol) sample of $Ru(bipy)_2Cl_2$ is dissolved in 100 ml deoxygenated EtOH forming a deep maroon solution. A 0.15 g (0.6 mmol) sample of quinizarine is dissolved in 50 ml of $CHCl_3$ and slowly added to the Ru^{2+} solution. A 0.1 g (2.6 mmol) sample of LiOMe is added slowly in solid form. The resultant mixture is refluxed for two hours under N_2 and then excess NH_4PF_6 [1 g (6.2 mmol)] is added and the solution cooled. A deep blue compound is filtered from solution and recrystallized from acetone and dried *in vacuo*. Obtained 0.9 g (55%). *Anal.*: Calcd for $Ru_2C_{54}H_{38}N_8O_4(PF_6)_2$, C: 47.86; H: 2.81; N: 8.27. Found, C: 47.61; H: 2.95; N: 8.20.

Diquinizarylcopper(II) $Cu(HQuin)_2$

A 0.41 g (2.1 mmol) sample of $Cu(OAc)_2 \cdot 4H_2O$ is dissolved in 50 ml of absolute EtOH and is slowly dripped into a solution of 1.0 g (4.2 mmol) of quinizarine in 50 ml $CHCl_3$. The deep maroon slurry is refluxed for four hours and slowly turns brown. The mixture was allowed to cool and a deep brown crystalline material is filtered, washed with $CHCl_3$ and dried. Yield 0.9 g (79%). *Anal.*: Calcd for $CuC_{28}H_{14}O_8$, C: 62.05; H: 2.59. Found, C: 61.1; H: 2.68.

Results and Discussion

Several bimetallic complexes of quinizarin (Quin, I) have been prepared and characterized by elemental analysis, infrared spectroscopy, electronic spectroscopy, electron paramagnetic resonance, and some magnetic measurements. The bimetallic complexes prepared are Mn(II), Cu(II), Zn(II), Co(III), and Ru(II) and a monometallic Cu(II) complex. Attempts at preparing the Fe(II) and Ni(II) have failed to yield good elemental analyses. Quin is utilized as a bidentate ligand by each metal atom bonding to two oxygen atoms and forming a six-membered ring with a negative charge dispersed over a π system. The ligand acts as two acac ligands back to back with a totally conjugated backbone. The remaining coördination sphere of each metal atoms is completed by 2,2′-bipyridine and excess positive charge is balanced by PF_6^-. These compounds are in general deeply-colored, crystalline compounds which are soluble in a variety of polar organic solvents.

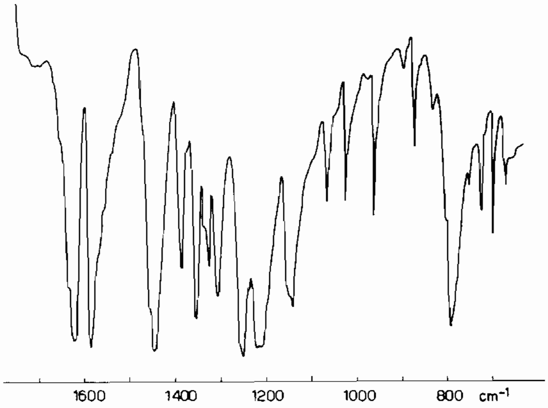


Figure 1. Infrared spectrum of 1,4-dihydroxyanthraquinone (Quinizarin) KBr pellet.

Syntheses

The basic synthetic procedure is to add the quinizarin dissolved in a non-polar organic solvent to a solution of the metal acetate. A solution of 2,2′-bipyridine (bipy) is then added to fill out the normal coordination sphere, and finally excess NH_4PF_6 is added to balance the cation charge with a large anion that will allow crystallization. The acetate salt of the metals used to deprotonate the quinizarin except in the case of the ruthenium complex in which the starting complex is $Ru(bipy)_2Cl_2$ where LiOMe is utilized as the deprotonating agent.

When the deep orange solution of quinizarin is added to the metal ion, deeply colored solutions are formed indicating that a reaction has occurred. The compounds fall out of solution on cooling as very small crystalline solids which are recrystallized using various solvents and are dried *in vacuo*. At least one complex contained small amounts of water before drying which was probably obtained from the water of hydration of the metal acetates. The compounds are all deeply colored browns and purples in the solid

TABLE I. Electronic Spectra of Quin and Its Metal Complexes.

Compound	Color	Solvent	λ_{max} in kK (ϵ)
Quin	orange	$CHCl_3$	19.0 (sh); 20.8 (4830; 21.3 (sh); 21.8 (sh); 36.4 (14,800); 40.7 (46,600)
$[Cu_2(Quin)(bipy)_2](PF_6)_2$	maroon	CH_3CN	17.8 (2220); 18.87 (1880); 20.1 (sh); 32.26 (8315)
$[Zn_2(Quin)(bipy)_2](PF_6)_2$	red	CH_3CN	17.7 (4900); 19.3 (5940); 20.7 (6690); 31.2 (sh); 33.0 (40, 100); 36.1 (65, 400); 40.3 (78,800)
$[Co_2(Quin)(bipy)_4](PF_6)_4$	deep blue	MeOH	16.89 (5400); 18.32 (5600); 19.61 (sh); 29.15 (16,200)
$[Ru_2(Quin)(bipy)_4](PF_6)_2$	deep blue	CH_3CN	16.72 (25,600); 17.4 (sh); 23.15 (11,600); 24.39 (sh) 27.4 (12,650); 29.19 (sh); 34.8 (105,400); 40.8 (81,300)
$[Mn_2(Quin)_2(bipy)_4](PF_6)_2$	purple	CH_3CN	16.9 (sh); 17.5 (6200); 18.8 (6100); 20.0 (sh); 35.3 (25,000); 39.2 (21,200)

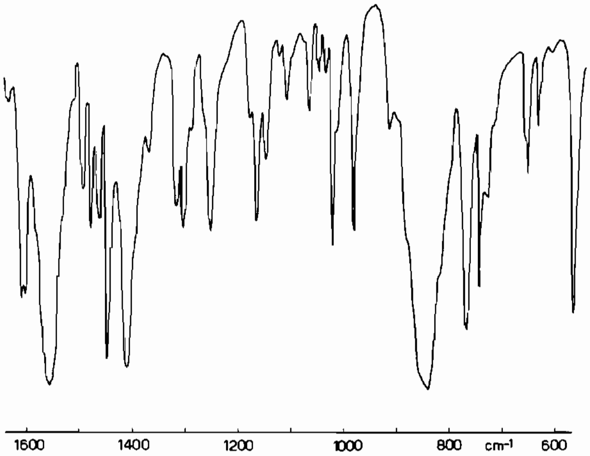


Figure 2. Infrared spectrum of $[Mn_2(Quin)(bipy)_4](PF_6)_2$ (KBr pellet).

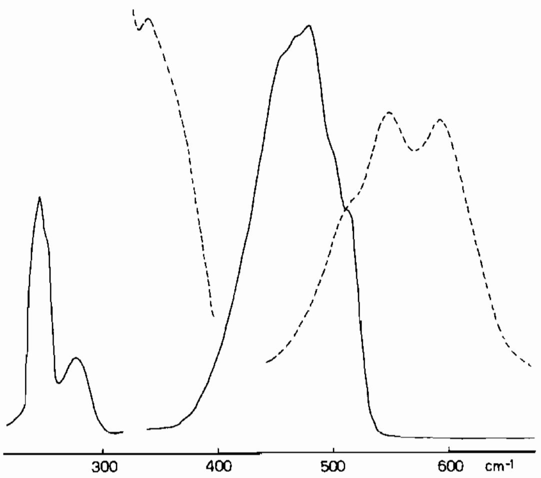


Figure 3. Solution electronic spectra of quin, ——, and $Co_2(Quin)(bipy)_4(PF_6)_4$, ----.

state and after recrystallization are obtained in 30–70% yields.

Infrared Spectra

The infrared spectra of the parent ligand, quinizarin, and a typical metal complex are shown in Fig. 1 and 2 respectively. As is characteristic of most aromatic compounds, the infrared spectra show many strong, sharp bands especially in the region from 1300 to 1600 cm^{-1}. The parent ligand has two strong bands at 1625 and 1585 cm^{-1} while the bimetallic complexes have a close, sharp doublet centered around 1600 cm^{-1} and a strong broader band around 1560 cm^{-1}. The upper band may be attributed to metal bonded C=O while the lower band is probably aromatic ring breating. There are five strong sharp bands between 1300–1500 cm^{-1} which are present in all the metal complexes and are indicative of the presence of the ligand and bipyridine. Quinizarin has a strong broad band around 800 cm^{-1} which is shifted to 850 cm^{-1} in all the metal complexes.

Electronic Spectra

The band positions (λ_{max}) and the extinction coefficients (ϵ) in the electronic spectra of the free ligand, Quin, and the dicobalt complex are shown in Figure 3 and given for all the compounds in Table I. In general the extinction coefficients range from 5,000 to 20,000 showing the deep colors. Due to these strong charge transfer bands which occur in all of the metal complexes, absorptions due to the much

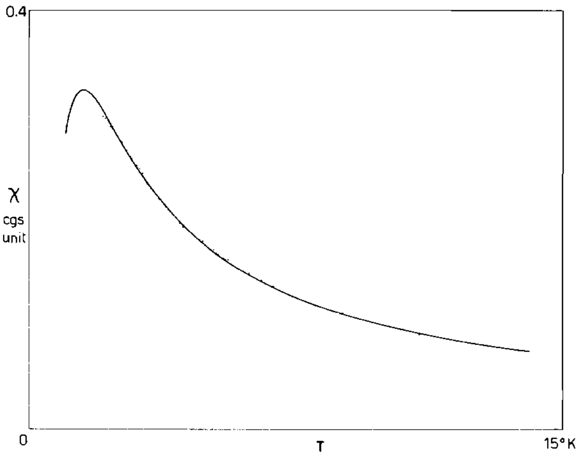


Figure 4. Magnetic susceptibility *vs.* temperature of $Cu_2(Quin)(bipy)_2(PF_6)_2$. Experimental, ...; theoretical fit, ———.

weaker d–d transitions of the metal ions were not observed (the extinction coefficients are not corrected for overlapping bands and as such are reported as larger values than they actually are).

The spectrum of the orange Quin shows a broad multiple band with shoulders on each side of a band that has in maximum at 20,800 cm^{-1} (4830). The shoulders lie at 19,000; 20,100; 21,300; and 21,800 cm^{-1}. Two much stronger bands lie in the UV at 36,400 cm^{-1} (14,800) and 40,700 (46,600). The metal complexes all show a broad multiplet similar to the ligand but it is shifted to lower energy. Each of the metal complexes show at least three bands in the visible region with the Ru(II) and Mn(II) complexes having four bands. The Co(III), Cu(II), and Zn(II) complexes have three bands the first between 16,000 and 17,000 cm^{-1}; the second between 18,500 and 19,500 cm^{-1}; and the third between 19,600 and 20,700 cm^{-1}. These bands have extinction coefficients on the order of 5000 and are responsible for the deep colors that these compounds exhibit. The spectra are run in CH_3CN and they are soluble to at least 10^{-4} molar.

There are two large ligand–ligand bands in the UV in the metal complexes which appear almost invariantly at 36,000 cm^{-1} and 40,000 cm^{-1} with very high extinction coefficients on the order of 50,000–100,000.

Magnetic Susceptibility

The Co(III), Ru(II), and Zn(II) complexes are diamagnetic and show no magnetic moment. The room temperature magnetic moment for the copper and the dicopper complexes were 1.96 and 1.97 B.M. (per copper atom) respectively.

Figure 4 shows a plot of the magnetic susceptibility *vs.* temperature for the dicopper complex and the theoretical curve for a line fit using the Van Vleck equation [7]. The complex is only slightly antiferromagnetic with a 2J value of -1.6 cm^{-1}. The interaction of the two Cu atoms is much weaker than the coupling of the copper atoms in the TSAB (II, III, and IV) series reported earlier [4, 6]. The π-system in Quin is quite different than that in TSAB. In the Quin complex the copper atoms are between two π-systems while in the TSAB there is only one π-system. It is not unlikely that the interaction parameter shows almost non-existent coupling in the Cu_2 Quin complex because of the possible nodal plane between the two Cu atoms in several M.O. configurations. Also, the filled p-orbitals on the oxygen atoms lower the effect of the conjugation of the ligand and thus weaken the interactions. In TSAB, the sp^2 hybridization and half-filled p-orbitals of the nitrogens continue the conjugation.

Conclusions

Several bimetallic transition metal complexes of the ligand quinizarin have been synthesized and have been characterized by elemental analysis, infrared spectroscopy, UV–visible spectroscopy, and magnetic properties. The compounds are deeply colored dye-like complexes which are soluble in CH_3CN but totally insoluble in water. The dicopper complex shows very weak magnetic interaction with a 2J value of -1.6 cm^{-1}.

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