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Studies on Metal Carboxylates.
VI.[1] Mixed Ligand Complexes of Copper(II) Containing Pyridine-2,6-dicarboxylic Acid in its Monoanionic and Dianionic Forms

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Starting from the copper(II) complex of pyridine-2,6-dicarboxylic acid (abbreviated dipicH$_2$) Cu dipic)·2H$_2$O, a series of mixed ligand complexes of the type Cu(dipic)(L)·xH$_2$O (x = 2 for L = 2,2′,2″-terpyridyl or 2,2′-bipyridyl and x = 0 for L = pyridine or α-picoline) have been isolated. The mixed 2,2′,2″-terpyridyl–acetate complexes Cu(terpy)(acetate) X·H$_2$O (X = ClO$_4^-$ or PF$_6^-$) have also been prepared and were found to react with pyridine-2,6-dicarboxylic acid to afford Cu(dipicH)(terpy)ClO$_4$·H$_2$O and Cu(dipicH)(terpy)PF$_6$. The latter derivatives contain this acid molecule in its monoanionic form. The spectral and magnetic properties of the above complexes have been studied and the results are discussed. Where possible comparisons are made with the related silver(II) complexes of these types.

Introduction

Pyridine-2,6-dicarboxylic acid (dipicolinic acid, abbreviated dipicH$_2$) has been found to be an interesting and versatile ligand for several reasons: (1) it can function as a terdentate ligand; (2) the carboxylate group can sometimes bridge two metal atoms;[2] (3) coordination to a metal ion can occur through dianionic (dipic),[3–5] monoanionic (dipicH),[6,7] or neutral (dipicH$_2$) forms of this ligand.[5] Thus a variety of mixed ligand complexes involving the dipicolinic acid molecule or its anions might be anticipated.

Many years ago, Lukes and Jurecek reported complexes of the formula Cu(dipic)(L)$_x$·yH$_2$O (where L = a monodentate nitrogen donor, x = 1 or 3 and y = 0, 1 or 2).[3] Similar complexes involving the vanadyl ion have been prepared with L = mono- or bidentate ligands.[4,8] More recently, we have isolated mixed ligand complexes of silver(II) containing either the dipic or dipicH moieties with 2,2′,2″-terpyridyl.[7] The present work was undertaken to ascertain whether the results for the silver(II) system[7] could be extended to the analogous copper(II) ion. We report here the isolation and characterization of two groups of mixed ligand complexes of copper(II) involving dipic or dipicH. The preparation and characterization of the two acetate derivatives Cu(terpy)(acetate)X·H$_2$O (X = ClO$_4^-$, PF$_6^-$), which we used as synthetic intermediates, is also described.

Experimental

Starting Materials

The ligands used in this study were obtained from the sources given below. Their systematic and trivial names (where appropriate) are listed, together with their common abbreviations: (a) pyridine-2,6-dicarboxylic acid (dipicolinic acid), abbreviated dipicH$_2$, Aldrich Chemical Co.; (b) 2,2′,2″-terpyridyl, abbreviated terpy, G. F. Smith Chemical Co.; (c) pyridine, abbreviated py, Mallinckrodt Chemical Works; (d) α-picoline, abbreviated α-pic, Aldrich Chemical Co.

The α-picoline was distilled over potassium hydroxide prior to use. All other ligands were used as received. Inorganic salts were of reagent quality and were used without further purification.

Preparation of Copper(II) Complexes

(i) Cu(dipic)·2H$_2$O

This complex which has previously been reported by other workers,[3] was used as a starting material in the preparation of complexes (ii)–(v).

Cupric acetate monohydrate (4.005 g, 20.1 mmol) and pyridine-2,6-dicarboxylic acid (3.353 g, 20.1 mmol) were heated to boiling in 175 ml of distilled water. The reaction mixture was cooled to room temperature, the blue crystals filtered off, washed with distilled water (100 ml) and finally air dried; yield, 3.888 g (73%).

Characteristic infrared absorption bands include the following (cm^{-1}): 3405(ms) and 3220(ms,br) (ν-

(O–H)); 1683(s) and ∼1615(s,br) (ν_{asym}(COO)); ∼1593(s).

(ii) Cu(dipic)(terpy)·$2H_2O$

To 125 ml of distilled water were added pyridine-2,6-dicarboxylatocopper(II) dihydrate (0.505 g, 1.908 mmol) and 2,2′,2″-terpyridyl (0.450 g, 1.927 mmol). The dark blue–green solution was heated and stirred for 45 min to reduce its volume to 50 ml, cooled to room temperature and the light blue precipitate which had deposited was collected. It was washed with water (25 ml) and benzene (50 ml) and dried *in vacuo* over calcium chloride. During the drying procedure the color of the product changed from light blue to light green, indicating partial dehydration to the more stable dihydrate form; yield, 0.492 g.

The filtrate from this reaction yielded 0.122 g of blue needles when placed in a refrigerator overnight. The needles turned green (as above) after about 10 min of air drying; combined yield, 0.614 g (65%).

The infrared spectrum of this complex includes the following characteristic absorption bands (cm^{-1}): 3515(ms) and 3425(ms) (ν(O–H)); 1652(s) and 1621(s) (ν_{asym}(COO)); 1592(s); 1574(m); 1567(m); 1560(m).

(iii) Cu(dipic)(bipy)·$2H_2O$

A mixture of pyridine-2,6-dicarboxylatocopper(II) dihydrate (0.344 g, 1.300 mmol) and 2,2′-bipyridyl (0.208 g, 1.332 mmol) in 80 ml of distilled water was heated and stirred until the blue solution was concentrated to a volume of 15 ml. The solution was then cooled to room temperature, filtered, and placed in a crystallization dish. The product precipitated first as blue crystals and later as a light blue powder, and was collected after 4.5 hr. The complex was washed with 40 ml of distilled water and air dried. It was then ground and stirred in 75 ml of benzene for 5 min to insure complete removal of 2,2′-bipyridyl. The product was then air dried carefully for several days until a constant weight was attained. Prolonged periods of air drying appear necessary to obtain a stoichiometric complex; yield, 0.258 g (47%).

Characteristic infrared absorption bands include the following (cm^{-1}): 3463(ms) and 3280(mw) (ν(O–H)); 1710(vw,?); 1667(ms), ∼1640(s,sh), 1621(s), and 1607(s) (ν_{asym}(COO)); 1596(s); 1570(ms).

(iv) Cu(dipic)(py)

The formation of this complex was first reported in 1948.[3] Our modification of the original preparation is as follows. Pyridine-2,6-dicarboxylatocopper(II)dihydrate (0.400 g, 1.511 mmol) was added to 125 ml of reagent grade pyridine. The mixture was boiled and stirred till the dark blue solution had a volume of 30 ml and precipitation had started at this point. After cooling the solution to room temperature, the azure blue product was filtered and air dried overnight; yield, 0.270 g (58%).

Infrared absorption bands characteristic of this compound include the following (cm^{-1}): 1672(s), ∼1633 (vs,br), and 1606(ms) (ν_{asym}(COO)); 1593(ms).

(v) Cu(dipic)(α-pic)

This blue product was prepared in a manner analogous to (iv). The filtrate was green rather than blue at the end of this reaction.

Characteristic infrared absorption bands include the following (cm^{-1}): 1672(s) and ∼1624(vs,br) (ν_{asym}(COO)); 1593(ms); 1579(ms).

(vi) Cu(terpy)(acetate)ClO_4·H_2O

Copper(II) acetate monohydrate (0.343 g, 1.718 mmol) and 2,2′,2″-terpyridyl (0.400 g, 1.715 mmol) were added to 75 ml of distilled water. Stirring and heating were carried out for 15 min and the solution was then cooled to room temperature and filtered. An excess of sodium perchlorate (4.2 g, 34.3 mmol) in 20 ml of distilled water was added to the solution and a precipitate formed. The mixture was heated to boiling and the precipitate dissolved to afford a deep blue–green solution. The volume of the solution was reduced to 50 ml and the solution was then allowed to cool to room temperature. The green needles which had deposited were washed with a small volume of water and 60 ml of benzene and air dried; yield, 0.643 g (79%).

The infrared spectrum of this compound included the following characteristic absorption bands (cm^{-1}): 3515(mw) and ∼3335(w) (ν(O–H)); 1662(w) (δ(O–H)); 1598(m); 1575(s) and 1564(ms,sh) (ν_{asym}(COO)); ∼1105(vs,br) (ν_3(ClO_4^-)).

(vii) Cu(dipicH)(terpy)ClO_4·H_2O

A mixture of (2,2′,2″-terpyridyl)acetato copper (II) perchlorate monohydrate (0.402 g, 0.849 mmol) and pyridine-2,6-dicarboxylic acid (0.142 g, 0.850 mmol) were dissolved in 50 ml of distilled water and the solution was heated with stirring to near boiling. The reaction mixture was concentrated to 30 ml after 30 min. Precipitation of the complex commenced while the solution was still quite hot. The solution was cooled to room temperature and then placed in a refrigerator for 3 hr. The blue crystalline product was filtered off, washed twice with small portions of distilled water, and air dried; yield, 0.3755 g (76%).

Some characteristic infrared absorption bands for this complex are as follows (cm^{-1}): 3567(m) (ν(O–H)); 1732(m) and 1717(m) (ν(C=O) of (COOH); 1652(m), 1645(m), and 1634(m) (ν_{asym}(COO)); 1594(ms); 1575(ms); ∼1105(vs,br) (ν_3(ClO_4^-)).

This product was also prepared by reacting either Cu(terpy)(Cl)ClO_4[9] or Cu[(terpy)(H_2O)]$(ClO_4)_2$[9] with dipicH_2 in aqueous solution in a similar manner to the above preparation (vii). However, the reaction of Cu(dipic)·$2H_2O$ with 2,2′,2″-terpyridyl and excess $NaClO_4$ in aqueous solution did not give the desired product, Cu(dipicH)(terpy)ClO_4·H_2O, but instead, Cu(dipic)(terpy)·$2H_2O$ was isolated.

(viii) Cu(terpy)(acetate)PF$_6$·H_2O

This complex, which is a greenish color, was prepared in a manner analogous to that of (vi), using excess potassium hexafluorophosphate rather than sodium perchlorate.

Infrared absorption bands which are characteristic of this compound are (cm^{-1}): 3607(m,sharp) and 3315(w) (ν(O–H)); 1662(w) (δ(O–H)); 1598(m); 1574(ms) and 1562(ms) (ν_{asym}(COO)); ∼845(vs,br) ($\nu(PF_6^-)$). An anhydrous complex with this structural formula has been mentioned briefly elsewhere.[10]

(ix) Cu(dipicH)(terpy)PF$_6$

This derivative was prepared in a manner similar to (vii), but using a larger volume (100 ml) of water at the start of the reaction. The copper complex, (2,2′,2″-terpyridyl)acetatocopper(II) hexafluorophosphate monohydrate was reacted with an equimolar amount of pyridine-2,6-dicarboxylic acid to yield shiny blue crystals of the product.

Characteristic infrared absorption bands include the following (cm^{-1}): 1740(ms,br) (ν(C=O) of (COOH); 1683(m) (ν_{asym}(COO) or ν(C=O) of (COOH)?; ∼1612(m,sh); 1602(m) (ν_{asym}(COO)); 1579(m); 1569(mw); ∼845(vs,br) ($\nu(PF_6^-)$).

Physical Measurements

Infrared spectra and magnetic moments were determined as reported previously.[7] Electronic absorption spectra were recorded as nujol mulls or as solution spectra in distilled water or spectral grade nitromethane (0.5–$5.1 \times 10^{-3} M$) using a Cary 14 spectrophotometer. Conductance measurements were carried out in distilled water or spectral grade nitromethane at concentrations $\sim 5 \times 10^{-4} M$, using a Model RC 16B2 conductivity bridge from Industrial Instruments Inc. It was necessary to heat some of the solutions for the electronic spectral and conductance measurements to ensure complete dissolution of the complexes (see Tables II and III); the solutions were then cooled to room temperature prior to the measurements.

Analytical Procedures

Copper was determined volumetrically by the standard iodine-sodium thiosulfate titration method. It was necessary to destroy the organic matter in the complexes by careful thermal decomposition before the determination could be carried out. Copper was not determined for the perchlorate complexes as thermal decomposition is accompanied by an explosion. All other analyses were performed by Dr. C.S. Yeh of the microanalytical laboratory of this department.

Results and Discussion

Analytical data for all the complexes in this paper are presented in Table I. Two series of copper(II) mixed-ligand complexes containing either dipic or dipicH were prepared. When Cu(dipic)·$2H_2O$ is reacted with 2,2′,2″-terpyridyl, 2,2′-bipyridyl, pyridine, or α-picoline, in the correct proportions, complexes of the type Cu(dipic)(L)·xH_2O are isolated (x = 2 for L = terpy or bipy and x = 0 for L = py or α-pic). It is noteworthy that the complexes with pyridine and α-picoline each contain only one equivalent of the bases, even though the reactions were carried out in a large excess of base. The interesting compounds Cu (terpy)(acetate)X·H_2O (X = ClO_4^-, PF_6^-) were prepared for use as starting materials and their physical properties were also studied. When these latter derivatives are reacted with dipicolinic acid (1 to 1 mole proportions) in aqueous solution, the ionic derivatives Cu(dipicH)(terpy)ClO_4·H_2O and Cu(dipicH)(terpy) PF_6 are formed. Unsuccessful attempts were made to prepare mixed-ligand complexes of the type Cu(pic) (terpy)X (pic = the monoanion of pyridine-2-carboxylic acid, X = a simple monoanion). The analogous silver (II) complex Ag(pic)(terpy)$(S_2O_8)_{1/2}$·$2H_2O$ has been prepared.[7]

An examination of some of the physical properties of the present series of compounds is now presented.

Infrared Spectra

Infrared spectral data for important regions is presented in the Experimental. Those complexes which contain the dipic dianion *1–5* (numbers are those given to the complexes in Table I) exhibit strong ν_{asym} (COO) stretches, some of which occur at rather high energies (1650–1680 cm^{-1}). The structure of Cu (dipic)·$2H_2O$,[2] complex *1*, revealed the presence of different types of carboxylate groups. In addition to a «normal» carboxylate group covalently bonded (through one of its oxygen atoms) to one copper ion, the other carboxylate group serves as a bridging ligand between two copper ions, through use of *one* of its oxygen atoms. The large energy difference for the two ν_{asym}(COO) stretches in Cu(dipic)·$2H_2O$, i.e., 1683(s) and 1615(s,br) cm^{-1}, probably reflects this structural inequivalence of the two carboxylate groups.

The complexes containing an acetate group, *6* and *8*, both have two ν_{asym}(COO) stretches at ∼1575(ms) and 1562(ms) cm^{-1}, at much lower energies than in complexes *1–5*, but in the frequency range (1610–1520 cm^{-1}) usually encountered for metal acetates.[11]

TABLE I. Analytical data and magnetic properties for the copper (II) complexes.

Complex No.	Complex	%C Calcd.	%C Found	%H Calcd.	%H Found	%N Calcd.	%N Found	%Cl or F Calcd.	%Cl or F Found	%Cu Calcd.	%Cu Found	μ_{eff} (B.M.), 298° K
1	Cu(dipic) $2H_2O$	31.76	31.76	2.67	2.73	5.29	5.05	–	–	–	–	–
2	Cu(dipic) (terpy)·$2H_2O$	53.06	52.77	3.64	3.62	11.25	11.31	–	–	12.76	12.47	1.98
3	Cu(dipic) (bipy)·$2H_2O$	48.51	48.52	3.59	3.65	9.98	9.81	–	–	15.10	15.48	–
4	Cu(dipic)(py)	46.83	47.09	2.62	2.87	9.10	9.07	–	–	20.65	20.53	–
5	Cu(dipic) (α-pic)	48.52	48.45	3.13	3.14	8.71	8.51	–	–	19.75	19.51	1.84
6	Cu(terpy) (acetate) $ClO_4·H_2O$	43.14	42.89	3.41	3.22	–	–	7.49	7.61	–	–	1.94
7	Cu(dipicH) (terpy) $ClO_4·H_2O$	45.53	45.68	2.95	3.14	–	–	6.11	6.00	–	–	1.93
8	Cu(terpy) (acetate) $PF_6·H_2O$	39.35	39.43	3.11	3.20	–	–	21.97	22.10	12.25	11.79	1.89
9	Cu(dipicH) (terpy)PF_6	43.47	43.33	2.49	2.30	9.22	9.26	18.75	18.55	10.45	10.29	1.94

Structural work on $[(Cu(terpy)(acetate))_2](PF_6)_2$[10] has shown it to be a weakly bonded dimeric unit with a unique structural feature, i.e., one oxygen atom of the chelating acetate groups bridges two different copper ions. It is possible that one or both of the acetate complexes (*6* and *8*) reported here might have similar structural features. However, the fact that *6* and *8* are hydrated, whereas $[(Cu(terpy)(acetate))_2]$ $(PF_6)_2$ is not, opens up other structural possibilities for these complexes.

The complexes Cu(dipicH)(terpy)$ClO_4·H_2O$ (*7*) and Cu(dipicH)(terpy)PF_6 (*9*) exhibit bands assigned to ν(C=O) of COOH as follows: 1732(m) and 1717(m) cm^{-1} for *7*; 1740(ms,br) cm^{-1} for *9*. This observation eliminates the possibility of a structural formula such as Cu(dipic)(terpy)·$HClO_4·H_2O$. The presence of ν(C=O) of COOH as well as the absence of bands characteristic of the terpyridinium cation[12] rules out another alternative, namely Cu(dipic) $(terpyH^+)ClO_4·H_2O$. The infrared spectra of Cu (dipicH)(terpy)$ClO_4·H_2O$ and Cu(dipicH)(terpy) PF_6 differ appreciably in the region 1800–1500 cm^{-1} (see Experimental), although their formulae are closely related. These differences are attributed, at least in part, to the hydration differences of the two. The presence of a molecule of water in complex *7* offers the possibility of strong hydrogen bonding to the COO and COOH groups and this can greatly affect the stretching frequencies associated with these groups. Since compound *9* is anhydrous, this particular possibility for hydrogen bonding does not exist.

Electronic Absorption Spectra and Magnetic Studies

Electronic spectral data for the copper(II) complexes in the region 8500–20,000 cm^{-1} are presented in Table II. The position of ν_{max} for the high energy ligand-field band envelope of these complexes shows a relatively small range (12,300–15,700 cm^{-1}). Molar extinction coefficients for the solution spectra range from 46 to 127 for the above ligand-field bands, values which are normal for copper(II) complexes.

In Cu(dipic)·$2H_2O$ the copper ion is in a tetragonally distorted octahedral environment.[2] Coordination occurs through the dipic dianion (three donor sites), two water molecules, and an oxygen atom from a bridging carboxylate group on another Cu(dipic)·$2H_2O$ unit. The ligand-field maxima are at 12,300 and 12,900 cm^{-1} in the mull spectrum of this complex. The six-coordinate complex Cu(dipic)(terpy)·$2H_2O$ has a ν_{max} of 14,900 cm^{-1} (mull) fo its d $\leftrightarrow$ d transitions. This shift of ν_{max} to higher energy on conversion of Cu(dipic)·$2H_2O$ to the terpy derivative is consistent with the replacement of three oxygen atoms by the stronger ligand-field terpy ligand. Since Cu(dipic) (bipy)·$2H_2O$ has nearly identical spectra in the solid state and aqueous solution (see Table II), it is assumed to have a coordination number of six, with a water molecule occupying the sixth position. The ν_{max} for this compound occurs at 13,750 cm^{-1} (mull). This is consistent with the shift to lower energy expected in going from the terpy to the bipy complex, as a terpy nitrogen is replaced by a much weaker water molecule.

TABLE II. Electronic spectra maxima (8500–20,000 cm^{-1})[a] for the copper (II) complexes.

Complex	Nujol Mull	H_2O	CH_3NO_2
Cu(dipic)·$2H_2O$	12,300, 12,900[b]	–	–
Cu(dipic)(terpy)·$2H_2O$	14,900	15,300(77)[c]	–
Cu(dipic)(bipy)·$2H_2O$	13,750	13,800(46)	–
Cu(dipic)(py)	15,100	–	–
Cu(dipic)(α-pic)	13,900	–	–
Cu(terpy)(acetate)ClO_4·H_2O	15,200	14,750(95)	15,600(123)
Cu(dipicH)(terpy)ClO_4·H_2O	15,100	15,400(90)	~14,500(127)[d]
Cu(terpy)(acetate)PF_6·H_2O	15,300	14,800(98)	15,600(120)
Cu(dipicH)(terpy)PF_6	15,700	15,400(85)	~14,500(111)[d]

[a] Certain of the complexes had a weak, ill-defined absorption in the region ~9,000–11,000 cm^{-1}. For a discussion of this feature see text. [b] Absorption maxima are given in cm^{-1}. [c] Values in parentheses refer to the molar extinction coefficients. [d] Heating of the solution was necessary to completely dissolve the complex. Measurements were made immediately after the solution cooled to room temperature.

All the [Cu(dipic(H))(terpy)] species (*2*, *7* and *9*) exhibit similar electronic spectra in water, indicating the formation of a common species. This was previously observed for the analogous silver(II) derivatives.[7] Since the complexes with the dipicH ligand (*7* and *9*) probably ionize to the dipic form in aqueous solution (see the section on conductivity measurements), this suggests that [Cu(dipic)(terpy)] is the common species in water. Also, the similarity of the mull spectra of *7* and *9* (dipicH–terpy complexes) to that of *2* (dipic–terpy complex) make it likely that all three complexes are six-coordinate.

The complexes Cu(dipic)(py) (*4*) and Cu(dipic) (α-pic) (*5*) would be four-coordinate if they existed as monomers. However, the presence of bridging carboxylate groups could, of course, increase the coordination number, a possibility for which there is some support from the electronic spectra. The position of ν_{max} is lower than that found for other [CuN_2O_2] chromophores which are known to be planar,[13,14] a feature which is in keeping with an increase in coordination number. The significant lowering of ν_{max} for the α-picoline relative to the pyridine derivative is tentatively attributed to steric hindrance of the methyl group weakening the Cu–N bond in the α-picoline complex.

The electronic spectra of the complexes *2*, *3*, *7* and *9* also exhibit a weak absorption with poorly defined maxima in the region 9,000 to 11,000 cm^{-1}. The ε_{max} values for this low energy absorption in aqueous solutions of the complexes are between 0.5 and 0.75 of the value for the band at 13,800–15,400 cm^{-1} (Table II). This band occurs only for chromophores of the type [Cu(dipic(H))(L)], where L = terpy or bipy. There is presumably a common structural feature for these derivatives, lacking in the other complexes, which is responsible for these low energy absorptions. It is possible that the 9,000–11,000 cm^{-1} band for the copper (II) derivatives corresponds to the lowest energy band found for the analogous silver(II) species (13,100–15,200 cm^{-1}).[7] This is plausible since a significant increase in the energy of analogous $d \leftrightarrow d$ transitions is expected in going from the first to the second transition series. Until detailed information on the molecular structures of these species is available, further speculation is not justified at present.

Room temperature magnetic moments for several of the copper(II) chelates are listed in Table I. The values, which are not corrected for temperature independent paramagnetism,[15] fall in the range normally observed for magnetically dilute copper(II) complexes. These results suggest that magnetic exchange is not significant at room temperature. It was previously observed that the weakly bonded dimeric complex [(Cu(terpy)(acetate))$_2$](PF_6)$_2$ showed no significant metal-metal interaction at room temperature.[10]

Conductivity Studies in Water and Nitromethane

Results of the conductivity studies are presented in Table III. As expected, Cu(dipic)(terpy)·$2H_2O$ is non-conducting in aqueous solution, implying that the copper(II) is six-coordinate, and complementing the electronic spectral results.

The compounds, Cu(dipicH)(terpy)ClO_4·H_2O and Cu(dipicH)(terpy)PF_6 have molar conductivities of 99 and 94 mho mole^{-1} cm^2, respectively, in nitromethane solution, values which indicate they are uni–univalent electrolytes in this solvent.[16] In aqueous solution, at the same concentrations, the molar conductivities for these compounds are greatly increased to 382 (ClO_4^-) and 369(PF_6^-). This is probably caused by a further ionization, Cu(dipicH)(terpy)$^+ \underset{H_2O}{\rightleftharpoons}$ Cu(dipic)(terpy) + H_3O^+, with the equilibrium shifted far to the right. The conductivity data parallels the electronic spectral results which show that the complexes containing the [Cu(dipic(H))(terpy)] moieties have similar aqueous solution spectra.

TABLE III. Molar conductivities for the copper (II) complexes.

Complex	H_2O			CH_3NO_2		
	Λ_M(mho mole^{-1} cm^2)	conc ($\times 10^{-4}M$)	T,° C	Λ_M(mho mole^{-1} cm^2)	conc ($\times 10^{-4}M$)	T,° C
Cu(dipic)(terpy)·$2H_2O$	4	5.55	25	–	–	–
Cu(terpy)(acetate)ClO_4·H_2O	161	5.16	25	99	5.16	24
Cu(dipicH)(terpy)ClO_4·H_2O	382	5.10	25	99	5.10[a]	24
Cu(terpy)(acetate)PF_6·H_2O	164	5.48[a]	25	101	5.48	24
Cu(dipicH)(terpy)PF_6	369	5.40	25	94	5.40[a]	24

[a] Heating of the solution was necessary to completely dissolve the complex. Measurements were made immediately after the solutions cooled to room temperature.

The derivatives, Cu(terpy)(acetate)PF_6·H_2O and Cu(terpy)(acetate)ClO_4·H_2O behave as uni-univalent electrolytes in nitromethane with molar conductivities of 99 and 101 mho mole^{-1} cm^2, respectively. In this solvent the acetate groups are coordinated. At the same concentrations in aqueous solution, the molar conductivities are 161 (ClO_4^-) and 164 (PF_6^-), indicating behavior as di–univalent electrolytes. This could be represented by the following equilibrium in which the acetate group is now ionic, Cu(terpy) (acetate) $ClO_4 \overset{H_2O}{\rightleftharpoons}$ Cu(terpy)$(H_2O)^{+2}$ + acetate$^-$ + ClO_4^-.

Concluding Remarks

In the present study we have established the existence of several mixed ligand complexes of copper(II) which are apparently analogs of the related silver(II) derivatives[7,17] of the types Ag(dipic) (L)·xH_2O (L = terpy or bipy) and Ag(dipicH) (terpy)$^+$. Attempts to synthesize copper(II) derivatives containing the Cu $(dipicH_2)^{2+}$ moiety were unsuccessful. To date the only complexes which have been found to contain the neutral terdentate ligand molecule dipicH_2 are the parent copper(II) and silver(II) carboxylates of the type M(dipic) (dipicH_2)·xH_2O.[5,18,19]

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