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Complexes of 2,2'-Bi-2-imidazoline with Transition Metal Ions

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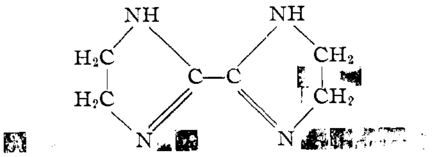
The compound 2,2'-bi-2-imidazoline was prepared and a series of metal chelates with Fe(II), Co(II), Ni(II), and Cu(II) were isolated. The ligand occupies approximately the same position as NH_3 in the spectrochemical series. The free ligand and its metal ion complexes hydrolyze readily in aqueous solution. The hydrolysis product of the ligand was identified to be N,N'-bis(2-aminoethyl)oxamide.

Introduction

The heterocyclic compound 2,2'-bi-2-imidazoline was prepared in a study of bonding in complexes between transition metal ions and ligands having a potential α-diimine structure.



The metal ion complexes of the related bidentate ligands 2-(2-pyridyl)imidazoline and 2-(*o*-hydroxyphenol)imidazoline were studied both by Harkins, *et al.*,[2] and by Lane, *et al.*[3] The latter authors used infrared evidence to conclude that for the two ligands studied, chelation takes place through the unsaturated nitrogen of the imidazoline ring. Approximate formation constants for the Mn(II), Co(II), Cu(II), and Zn(II) complexes of 2-(2-pyridyl)imidazoline were reported by Harkins and Freiser.[4] These are in general of the same order as the corresponding formation constants for the ligand 2,2'-bipyridine,[5] although the ligand 2-(2-pyridyl)-imidazoline has a much higher base strength (pK_a = 8.54 in 50% dioxane at 25°)[4] than 2,2'-bipyridine (pK_a = 4.33 in H_2O at 25°).[5]

This paper presents results of spectroscopic and magnetic measurements on the Fe(II), Co(II), Ni(II), and Cu(II) complexes of 2,2'-bi-2-imidazoline. The hydrolysis of the ligand and its metal ion complexes necessitates the study of complex formation in anhydrous media.

Experimental

Preparation. 2,2'-Bi-2-imidazoline.—The ligand was prepared by a modification of the method of Forssel.[6] In a typical preparation 20 g. of dithiooxamide in 100 ml. of ethanol was treated with 30 ml. of ethyl bromide and heated to 60° for 4 hr. After cooling to room temperature, 75 ml. of ethylenediamine was added during 1 hr. to maintain a steady evolution of ethanethiol. The mixture was heated briefly to 80°, then stirred 45 min. at 0°. The solid was washed with ethanol and air dried to give 17.6 g. (76.5%) of 2,2'-bi-2-imidazoline (I).

Anal. Calcd. for $C_6H_{10}N_4$: C, 52.16; H, 7.29. Found: C, 52.27; H, 7.21.

Hydrolysis of 2,2'-Bi-2-imidazoline to N,N'-Bis-(2-aminoethyl)oxamide Dihydrochloride.—I dissolves slowly in water at room temperature. Drying under vacuum yields a white solid material (II), the infrared spectrum of which shows the typical amide band at 1640 cm.$^{-1}$. The dihydrochloride was prepared by dissolution of II in 0.05 *M* HCl. Addition of 95% ethanol precipitated a white solid (III) which was filtered and dried *in vacuo* at 80°. Elemental analysis of III indicated it to be N,N'-bis(2-aminoethyl)oxamide dihydrochloride.

Anal. Calcd. for $C_6H_{14}N_4O_2{\cdot}2HCl$: C, 29.16; H, 6.53; N, 22.67. Found: C, 29.03; H, 6.57; N, 22.46.

The dihydrochloride of I was prepared by adding excess 1 *M* HCl to a methanol solution of I. The white precipitate was filtered and dried *in vacuo* at room temperature.

Anal. Calcd. for $C_6H_{10}N_4{\cdot}2HCl$: C, 34.13; H, 5.73. Found: C, 34.28; H, 5.93.

Preparation of Metal Complexes of 2,2'-Bi-2-imidazoline. Dichlorobis(2,2'-bi-2-imidazoline)iron(II), $Fe(C_6H_{10}N_4)_2Cl_2$.—Anhydrous $FeCl_2$ was prepared according to the method of Kovacic and Brace.[7] One gram of the ligand was dissolved in 100 ml. of absolute ethanol and a calculated amount of the metal salt was added such that the molar ratio of ligand to metal was approximately 2:1. Red-brown crystals formed on evaporating the red solution under reduced pressure. All work was done in a nitrogen atmosphere to avoid possible air oxidation.

Anal. Calcd. for $Fe(C_6H_{10}N_4)_2Cl_2$: C, 35.8; H, 5.00. Found: C, 35.8; H, 5.03.

Bis(2,2'-bi-2-biimidazoline)cobalt(II) Nitrate $[Co(C_6H_{10}N_4)_2(NO_3)_2]$.—Approximately 1 g. of ligand was dissolved in 100 ml. of ethanol to which a calculated amount of $Co(NO_3)_2{\cdot}6H_2O$ was added such that the molar ratio of ligand to metal was approximately 2:1. Orange crystals formed on standing at 0° overnight and were filtered and recrystallized once from ethanol. The crystals originally contained two molecules of water per metal ion. This water was removed either by recrystallization from ethanol or by drying *in vacuo* at 80° for several hours.

Anal. Calcd. for $Co(C_6H_{10}N_4)_2(NO_3)_2{\cdot}2H_2O$: C, 29.1; H, 4.88. Found: C, 29.2; H, 5.02. Calcd. for $Co(C_6H_{10}N_4)_2(NO_3)_2$: C, 31.4; H, 4.39. Found: C, 31.5; H, 4.57.

Tris(2,2'-bi-2-biimidazoline)cobalt(II) Nitrate $[Co(C_6H_{10}N_4)_3(NO_3)_2]$.—Orange-brown crystals of the tris compound were prepared as above by holding the metal to ligand molar ratio at 1:3.

Anal. Calcd. for $Co(C_6H_{10}N_4)_3(NO_3)_2$: C, 36.2; H, 5.08. Found: C, 36.5; H, 5.22.

Bis(2,2'-bi-2-biimidazoline)nickel(II) Nitrate $[Ni(C_6H_{10}N_4)_2(NO_3)_2]$.—Green crystals were prepared as the Co(II) system by starting with $Ni(NO_3)_2{\cdot}6H_2O$. Nickel was analyzed gravimetrically by dimethylgloxime after destroying the organic portion of the complex with concentrated HNO_3. The original blue-green crystals contained two molecules of water per nickel.

Anal. Calcd. for $Ni(C_6H_{10}N_4)_2(NO_3)_2{\cdot}2H_2O$: C, 29.1; H, 4.88. Found: C, 29.0; H, 4.88. Calcd. for $Ni(C_6H_{10}N_4)_2$-

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(1) Taken in part from the Ph.D. thesis of J.C.W., June 1964.

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$(NO_3)_2$: C, 31.4; H, 4.39; Ni, 12.8. Found: C, 31.0; H, 4.36; Ni, 12.9.

Bis(2,2′-bi-2-biimidazoline)nickel(II) Chloride $[Ni(C_6H_{10}N_4)_2Cl_2]$.—Green crystals were prepared similarly to the nitrate starting with $NiCl_2 \cdot 6H_2O$. An infrared spectrum showed that the crystals first formed from the ethanol solution contained water which was later removed by drying at 80° *in vacuo*.

Anal. Calcd. for $Ni(C_6H_{10}N_4)Cl_2$: Ni, 14.5. Found: Ni, 14.5.

Bis(2,2′-bi-2-biimidazoline)copper(II) Nitrate $[Cu(C_6H_{10}N_4)_2(NO_3)_2]$.—The green crystals were prepared similarly to the Co(II) complex. Copper was determined gravimetrically as copper salicylaldoximate after destroying the organic material in the complex with concentrated HNO_3.

Anal. Calcd. for $Cu(C_6H_{10}N_4)_2(NO_3)_2$: C, 31.0; H, 4.35; Cu, 13.9. Found: C, 31.0; H, 4.34; Cu, 13.7.

Preparation of Deuterated Species.—2,2′-Bi-2-imidazoline-N,N′-d_2 and 2,2′-bi-2-imidazoline-N,N′-$d_2 \cdot 2DCl$ were prepared from the corresponding undeuterated compounds by exchanging with methanol-O-*d*. The latter was made by exchanging absolute methanol with D_2O (99.8%, Bio-Rad Labs). By examining the N–H and N–D stretching bands in the infrared spectrum of the crystallized ligands it was estimated that deuteration was approximately 90% complete. No appreciable change occurred in the C–H stretching bands, indicating no significant C–D exchange.

Magnetic measurements on the solid complexes were made at room temperature with a Gouy balance calibrated with $Hg[Co(CNS)_4]$. The molar susceptibilities (μ_{eff}) were corrected for the diamagnetic contributions of the anions and the ligands as follows: NO_3^-, 18.9×10^{-6}; Cl^-, 23.4×10^{-6}, 2,2′-bi-2-imidazoline, 104×10^{-6}, all in c.g.s. units.

Infrared spectra were obtained on a Perkin-Elmer Model 237 Infracord using Nujol or Fluorolube mulls. A spectrum of the ligand was obtained in chloroform solution.

Ultraviolet and visible spectra were obtained on a Beckman DU spectrophotometer.

Potentiometric titrations were made by using a Metrohm E-388 pH meter with a combination electrode (20-01-20x). Because of reasonably slow hydrolysis of the ligand, only approximate protonation constants could be obtained. A weighed amount (55.4 mg.) of ligand was dissolved in 100 ml. of 0.00992 *M* HCl and titrated with 0.1168 *M* NaOH. The extent of hydrolysis occurring during titration was estimated to be 10% by neutralizing the final solution, evaporating to dryness at room temperature under reduced pressure, and examining the infrared spectrum of the residue.

Results and Discussion

Magnetic measurements of the solid complexes are shown in Table I. The complexes all appear to be of the spin-free octahedral type. The absorption bands of the Co(II), Ni(II), and Cu(II) complexes are shown in Table II. The Laporte-forbidden transition bands of the Fe(II) complex were obscured by an intense absorption band from the ultraviolet. The free ligand has an absorption band at 39,200 cm.$^{-1}$ with ϵ_{max} 6470. Each of the complexes exhibits an intense absorption band beginning at about 21,000 cm.$^{-1}$ and extending into the ultraviolet, peaking at approximately 37,000 cm.$^{-1}$ with ϵ_{max} 1.6×10^4.

Identifying the two bands in the tris ligand Ni(II) spectrum as $(^3A_{2g} \rightarrow {}^3T_{2g}) = 10{,}500$ cm.$^{-1}$ and $(^3T_{2g} \rightarrow {}^3T_{1g}(F)) = 17{,}500$ cm.$^{-1}$, one can calculate Dq as 1050 cm.$^{-1}$. This value is significantly less than the 1270 cm.$^{-1}$ found for a series of α-diimine complexes of Ni(II).[8] In this latter series of ligands related to 2,2′-bipyridine, the red Fe(II) chromophore is well known.

TABLE I

MOLAR SUSCEPTIBILITIES AND EFFECTIVE MOMENTS OF SOLID COMPLEXES

L = 2,2′-Bi-2-imidazoline

Formula	Molar susceptibility of complex $\chi_m \times 10^6$ c.g.s.	μ_{eff}, B.M.
FeL_2Cl_2	10,800	5.2
$CoL_2(NO_3)_2$	9,580	4.8
$NiL_2(NO_3)_2$	4,300	3.3
$CoL_3(NO_3)_2$	10,600	5.1
$NiL_3(NO_3)_2$	4,130	3.3

TABLE II

ABSORPTION BANDS OF Co(II), Ni(II), AND Cu(II) COMPLEXES IN METHANOL

L = 2,2′-Bi-2-imidazoline; anion, NO_3^-; 25°

Complex	λ_{max}, cm.$^{-1}$	ϵ_{max}
$[CoL_2]^{2+}$	9,100; 21,740	4.9; 29.6
$[CoL_3]^{2+}$	9,530; 20,640	8.9; 40.3
$[NiL_2]^{2+}$	10,200; 16,680	10.6; 8.4
$[NiL_3]^{2+}$	10,540; 17,500	10.3; 18.2
$[CuL_2]^{2+}$	15,500	60.8

Because of the low Dq value and the absence of the Fe(II) chromophore one may suppose that chelation in the case of 2,2′-bi-2-imidazoline is not of the α-diimine type.

In order to evaluate the effect of bonding on the N–H vibrational spectra the ligand was deuterated as described in the Experimental section and an attempt was made to identify the N–H contribution to the infrared spectra both at 2600–3250 and at 1400–1700 cm.$^{-1}$. The infrared spectrum of the free solid ligand shows a band at 3150 cm.$^{-1}$ which shifted to 2330 cm.$^{-1}$ on deuteration and can be identified as the N–H stretch. In chloroform solution this band appeared at 3450 cm.$^{-1}$. This latter shift suggests intermolecular association of the ligand in the solid state.[2,9] Note also that there is no evidence of intramolecular N–H–N bonding from these data.

The N–H stretching frequencies of the groups —NH_2^+— and =NH^+— have been studied by several persons. In salts of pyridine, indolene, and Schiffs' bases the group —C=NH^+— absorbs at 2325 to 2500 cm.$^{-1}$ but not apparently between 1560 and 1620 cm.$^{-1}$.[10] On the other hand, Heacock and Marion[11] analyzed the spectra of the hydrochlorides of 17 secondary amines and concluded that the group —NH_2^+— is characterized by a NH_2 deformation band between 1560 and 1620 cm.$^{-1}$. It is interesting that the spectrum of 2,2′-bi-2-imidazolinium dihydrochloride more nearly resembles that of the latter model whereas imidazolium hydrochloride resembles the former. The 1565 cm.$^{-1}$ band of the protonated 2,2′-bi-2-imidazoline shifted to a doublet at 1490 and 1520 cm.$^{-1}$ on deuteration. The strong band at 1587 cm.$^{-1}$ for protonated imidazole remains in the spectrum of the deuterated

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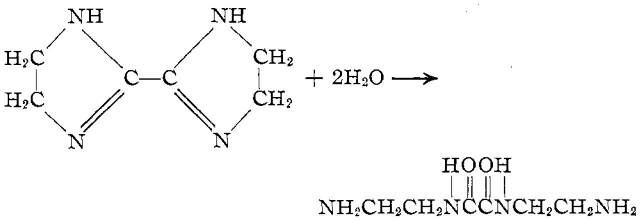
compound.[12] Admittedly the infrared evidence is not at all definitive in these regions of the spectrum, but the nature of the bonding site on the ligand can at least be held open for the moment. It is interesting that the closely related ligand, 2,2′-biimidazole, also exhibits anomalous chelating ability.[13]

Hydrolysis of 2,2′-Bi-2-imidazoline.—The ligand hydrolyzed in aqueous solution according to the following equation to give N,N′-bis(2-aminoethyl)oxamide.



$NH_2CH_2CH_2\overset{H}{N}\overset{O}{C}\overset{O}{C}\overset{H}{N}CH_2CH_2NH_2$

The hydrolysis product appears to be dibasic with $pK_{a_1} = 8.30$ and $pK_{a_2} = 9.54$ at 25° in a 1.0 M KNO_3 solution. A rapid titration of the original ligand gave approximate constants pK_{a_1} and pK_{a_2} of 3.8 and 7.7, respectively.

All of the metal ion complexes appeared to hydrolyze, the original complexes not being recoverable after dissolution in water. Apparently the rate of hydrolysis was quite slow, judging from the 15,600 cm.$^{-1}$ band in the Cu(II) complex spectrum which shifted gradually to about 16,000 cm.$^{-1}$ over a 2-day period. During this time the solution changed from blue-green to pale violet in color. Although insufficient quantities of complex were isolated for elemental analysis, an infrared spectrum of the blue solid obtained after hydrolysis shows that the compound is likely a complex of N,N′-bis(2-aminoethyl)oxamide.

Woodburn and O'Gee[14] reported that 2,2′-bi-2-imidazoline was soluble in water to give a basic solution and yielded ethylenediamine and oxalic acid after refluxing several hours with 10% NaOH. The rapid hydrolysis of biimidazoline in hot water to ethylenediamine and oxalic acid was reported by Reggel, Henry, and Wender.[15] No intermediate species were reported. It was found in the present work that the ligand hydrolyzed in either hot (100°) or cold water, but the hydrolysis product was N,N′-bis(2-aminoethyl)oxamide. No ethylenediamine or oxalate ion was detected unless a more drastic condition was used, such as refluxing with 10% NaOH. The composition and characteristics of the possible metal ion complexes of this intermediate as well as the further hydrolysis to ethylenediamine complexes await further studies.

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Concerning the Synthesis of Dithio-α-diketone Complexes of Transition Metals from Thiophosphates of 1,2-Dithiols

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The synthesis of transition metal complexes of dithio-α-diketones of composition $M(S_2C_2R_2)_n$ ($n = 2, 3$) from metal salts, acyloins, and P_4S_{10} is described. The reaction of benzoin with P_4S_{10} is shown to produce a mixture of isomeric thiophosphates of stilbenedithiol. Evidence is presented for the latter as the main organic solvolysis product. Small amounts of the acid $(C_6H_5)_2C_2S_2PS_2H$ are formed during the partial hydrolysis of the thioester mixture. The stable nickel chelate $((C_6H_5)_2C_2S_2PS_2)_2Ni$ is described. The reaction of the thioesters with $Fe(CO)_5$ affords the complex $(C_6H_5)_2C_2S_2Fe_2(CO)_6$.

Introduction

Recently,[3,4] a general method of preparation of transition metal complexes of dithio-α-diketones $M(S_2C_2R_2)_n$ ($n = 2$ or 3) has been developed which utilizes the easily accessible acyloins and P_4S_{10} for the synthesis of the novel bidentate sulfur-containing ligands. In the present paper details of this reaction are reported.

General Description of the Method

In the preferred procedure the acyloin is first heated with a 3- to 6-fold molar excess of P_4S_{10} in an inert organic solvent (*e.g.*, xylene or dioxane). The thiolation of the acyloin is exothermic and accompanied by the evolution of H_2S; most of the P_4S_{10} dissolves during

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