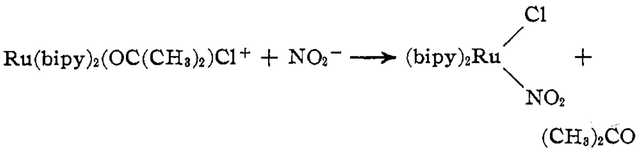
common feature for complexes containing both coordinated nitrite and a good leaving group and being otherwise substitution inert.

In light of the known complexes *trans*-$Ru(das)_2(N_2)Cl^+$ [das = *o*-phenylenebis(dimethylarsine)],[29] $Ru(NH_3)_5N_2{}^{2+}$,[30] and $Ru(NH_3)_5N_2O^{2+}$,[31] it is somewhat surprising that N_2 or N_2O complexes are not formed as products of reaction 3 in acetone. Earlier attempts[8] to coordinate dinitrogen to ruthenium in bipyridine complexes were also unsuccessful. Ruthenium may be considerably less capable of back-bonding to dinitrogen in bipyridine and 1,10-phenanthroline complexes.[10]

In the reaction



$$Ru(bipy)_2(OC(CH_3)_2)Cl^+ + NO_2^- \longrightarrow (bipy)_2Ru\begin{matrix}Cl\\ \\ NO_2\end{matrix} + (CH_3)_2CO$$

nitrite must attack through the nitrogen atom. The product is the pure nitro isomer and under the mild conditions of the reaction the nitrito isomer once formed is stable. By contrast it has been suggested that in the reaction of NO_2^- with $Ru(bipy)_2(OH_2)_2{}^{2+}$ in aqueous solution[32]

$$Ru(bipy)_2(OH_2)_2{}^{2+} + 2NO_2^- \longrightarrow Ru(bipy)_2(NO_2)_2 + 2H_2O$$

a nitrito isomer is formed initially.

Acknowledgments.—Acknowledgments are made to the African-American Institute and to the University of Ife, Ile-Ife, Nigeria, for fellowship support for Mr. Adeyemi, and to the Petroleum Research Fund and the National Science Foundation (Grant No. GY-7311) for support of this research.

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[29] P. G. Douglas, R. D. Feltham, and H. G. Metzger, *J. Amer. Chem. Soc.*, **93**, 84 (1971).

[30] A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

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Synthesis of *cis*-Dihalotetrapyridineruthenium(II) Complexes (Halide = Chloride, Bromide, Iodide) and Verification of Their Cis Stereochemistry

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The syntheses of *cis*-$Ru(py)_4Cl_2$, *cis*-$Ru(py)_4Br_2$ and *cis*-$Ru(py)_4I_2$ are reported. Also reported is the synthesis of *cis*-$Ru(py)_4ox \cdot H_2O$ which is the key intermediate in the synthesis of these complexes. Far-infrared, Raman, and proton nmr spectral data are presented for both the cis and trans isomers of these pyridine–halogen–ruthenium(II) complexes, and this evidence is used to assign the stereochemistry of the geometrical isomers.

In our investigation of the electronic and proton nmr spectral properties of pyridine complexes of Ru(II), we have synthesized both the cis and trans isomers of $Ru(py)_4X_2$ (X^- = Cl^-, Br^-, I^-; py = pyridine). The trans isomers have been previously synthesized.[1–6] We now report the synthesis of the cis isomers and give evidence to support our assignment of the stereochemistry of these geometrical isomers.

Experimental Section

Reagents.—Ruthenium trichloride hydrate ($RuCl_3 \cdot xH_2O$, 38.95% Ru) was used as supplied by Engelhard Industries. Water was doubly distilled, the second distillation being from an alkaline potassium permanganate solution. Argon was bubbled through two chromous solution–zinc amalgam reductors[7] in series to remove any oxygen present. All other chemicals were reagent grade and were used without further purification.

Instruments and Techniques.—Proton nmr spectra were obtained on the Varian T-60 spectrometer. Far-infrared spectra were obtained with the Beckman IR-11 spectrophotometer (350–70 cm^{-1}) using Nujol mulls between polyethylene plates and with the Perkin-Elmer 457 spectrophotometer (600–250 cm^{-1}) using CsI pellets. Raman spectra were obtained with the Spex Industries Ramalog laser-Raman system, using a Spectra Physics He–Ne laser (exciting wavelength 6328 Å). The spectra were obtained from solid samples in capillary tubes.

Preparation of *cis*-Dichlorotetrapyridineruthenium(II).—The preparation of *cis*-$Ru(py)_4Cl_2$ involved three steps: (1) synthesis of a form[8–10] of potassium tris(oxalato)ruthenate(III) hydrate, (2) synthesis of *cis*-$Ru(py)_4ox \cdot H_2O$ (ox = $C_2O_4{}^{2-}$),[11] and (3) synthesis of *cis*-$Ru(py)_4Cl_2$.

Step 1.—$RuCl_3 \cdot xH_2O$ (1.0 g) and potassium oxalate monohydrate (2.7 g) were dissolved in 30 ml of water. Absolute ethanol (5 ml) was added and the solution was refluxed for 4 hr. Ethanol was quickly added to the resulting hot, brown solution until a brown oil formed and sank to the bottom of the beaker. The cloudy yellow supernate was decanted and the oil was cooled in a refrigerator for 5 min to give a brown solid (2.0 g). The infrared spectrum indicated this solid to be $K_3Ru(ox)_3 \cdot xH_2O$.[8]

Step 2.—The substance $K_3Ru(ox)_3 \cdot xH_2O$ (2.0 g) was dissolved in 20 ml of water, and 6 ml of pyridine was added to this solution. The mixture was then refluxed for 1 hr. During this time, the solution exhibited a color change from an initial dark brown to a

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[4] J. Lewis, F. E. Mabbs, and R. A. Walton, *J. Chem. Soc. A*, 1366 (1967).

[5] J. D. Gilbert, D. Rose and G. Wilkinson, *ibid.*, 2765 (1970).

[6] Barry Loescher, private communication, University of Toronto.

[7] R. G. Gaunder, Ph.D. Thesis, Stanford University, 1969, p 8.

[8] The composition of potassium tris(oxalato)ruthenate(III) hydrate varies with the method and conditions of synthesis.[9] The method given is an adaptation of an already existing method.[10]

[9] W. P. Griffith, "The Chemistry of the Rarer Platinum Metals," Interscience, New York, N. Y., 1967, pp 158–159.

[10] C. Creutz, Ph.D. Thesis, Stanford University, 1970, pp 23–24.

[11] *cis*-Oxalatotetrapyridineruthenium(II) has also been synthesized from the hexapyridineruthenium(II) cation.[6]

final deep green. This dark green solution was then reduced by zinc amalgam in an argon atmosphere. After several hours the green solution became red-orange. This orange solution was suction filtered to remove zinc amalgam, and the filtrate was added to a beaker containing 100 ml of ethanol. (The solution was not air sensitive at this point and no special precautions were taken to eliminate oxygen.) The potassium oxalate monohydrate and any potassium chloride in the solution were precipitated by the ethanol, but the ruthenium species remained in solution. Suction filtration removed the white crystalline solids and produced an orange filtrate. More ethanol was added to the filtrate, and the above process was repeated until addition of ethanol produced no precipitate. The final filtrate was rotoevaporated to dryness. Upon evaporation of the solvent, a viscous yellow-brown oil was formed. It proved exceedingly difficult to transform the oil to a crystalline solid. The greatest success was achieved when the oil was dissolved in a minimal amount of methanol. The methanol solution was then cooled in a Dry Ice–acetone bath, and ether was added until a yellow solid began to form. At this point the solution was kept in the bath for 3–6 hr. Crystals formed during this time. The solution was then warmed to room temperature and filtered by suction to give an orange solid (0.67 g, 33% overall yield). Often, upon warming, the solid reverted to the oil, and the cooling process had to be repeated several times in order to obtain a substance which remained solid at room temperature. Recrystallization was also effected using the above cooling technique and solvents. The solid was washed with ether and dried under vacuum over anhydrous calcium sulfate. *Anal.* Calcd for *cis*-$Ru(C_5H_5N)_4(C_2O_4)\cdot H_2O$: C, 50.47; N, 10.70; H, 4.24. Found: C, 50.43; N, 10.57; H, 4.42.

The infrared spectrum supports this formulation and the proton nmr spectrum definitively indicates a cis arrangement of the four pyridine ligands (see Table I). In view of the recent paper reporting the crystal structure of μ-oxalato-bis(tetrapyridineruthenium(II)) fluoroborate,[12] a possible formulation of the complex might be μ-oxalato-bis(tetrapyridineruthenium(II)) oxalate dihydrate [*cis*-$\{(Ru(py)_4)_2ox\}ox\cdot 2H_2O$]. However, ion-exchange experiments indicate the species to be neutral and thus support the monomer formulation.

TABLE I

PROTON NMR SPECTRA (δ, PPM) FOR $Ru(py)_4X_2$ COMPLEXES[a,b]

	Protons			
Complex	2, 6	2′, 6′	4	3, 5
Trans X = Cl	8.60 d	...	7.61 t	7.05 t
Trans X = Br	8.74 d	...	7.63 t	7.06 t
Trans X = I	9.01 d	...	7.63 t	7.01 t
Cis X = Cl	8.68 d	8.35 d	7.63 q	7.12 q
Cis X = Br	8.89 d	8.40 d	7.66 q	7.13 q
Cis X = I	9.08 d	8.42 d	7.63 q	7.11 q
Cis X = $^1/_2$ ox	8.50 d	8.16 d	7.63 t	7.16 q
Pyridine	8.66 d	...	7.70 t	7.29 t

[a] Solvent was $CDCl_3$ + 1% TMS (internal standard). Solutions were saturated with exception of pyridine which was 10% pyridine by volume; many of the solutions were easily oxidized by air and thus solution preparation and transfer were done under an argon atmosphere. [b] δ values are the mean middle position of a group of peaks associated with a given type of proton; although there is much fine structure, the groups of resonances approximate to first-order doublet (d), triplet (t), or quartet (q) patterns.

Step 3.—*cis*-$Ru(py)_4ox\cdot H_2O$ (0.67 g) was dissolved in 10 ml of water to give a deep orange solution. This solution was warmed gently and stirred vigorously on a heat-stir plate. To the warm solution, concentrated hydrochloric acid was added in 1-ml amounts. The temperature was gradually increased and concentrated hydrochloric acid was added until a solid began to precipitate. After 5–10 min, the solution was filtered by suction to obtain a yellow-orange solid (0.50 g, 27% overall yield). The solid was washed with water, ethanol, and ether and dried under vacuum over anhydrous calcium sulfate. (Note: if the solution was heated too long or too strongly, a green solution was produced and the complex was lost.) *Anal.* Calcd for *cis*-$Ru(C_5H_5N)_4Cl_2$: C, 49.19; Cl, 14.52; N, 11.47; H, 4.13. Found: C, 48.29; Cl, 14.41; N, 11.32; H, 4.21.

Preparation of *cis*-Dibromotetrapyridineruthenium(II) and *cis*-Diiodotetrapyridineruthenium(II).—The same procedure as with the chloro complex was used except that in step 3 the appropriate hydrogen halide solution was used. *cis*-$Ru(py)_4Br_2$ was obtained as a red-brown solid. *Anal.* Calcd for *cis*-$Ru(C_5H_5N)_4Br_2$: C, 41.61; H, 3.49; N, 9.71; Br, 27.68. Found: C, 41.35; H, 3.57; N, 10.00; Br, 27.70.

cis-$Ru(py)_4I_2$ was obtained as a yellow-brown solid. *Anal.* Calcd for *cis*-$Ru(C_5H_5N)_4I_2$: C, 35.78; H, 3.00; N, 8.35; I, 37.81. Found: C, 35.23; H, 2.99; N, 8.39; I, 37.60.

Analyses.—All analyses were performed by the Stanford University Microanalytical Laboratory.

Results and Discussion

The assignment of the cis configuration to the $Ru(py)_4X_2$ ($X^- = Cl^-, Br^-, I^-$) complexes reported in this paper and the trans configuration to previously synthesized $Ru(py)_4X_2$ complexes is made on the basis of far-infrared, Raman, and proton nmr spectral results.

Infrared Spectra.—The use of infrared data to assign the configurations of geometrical isomers is fraught with problems.[13] The first difficulty is to assign the vibrations of interest (Ru–py and Ru–X stretches in this case) to specific bands in the observed spectra. For the system at hand, the best that can be done is to assign tentatively the Ru–Cl, Ru–Br, and some Ru–py stretching frequencies (Table II). These assignments were made by comparing the far-infrared spectra given in Table II and by utilizing accumulations of data on metal–halogen and metal–pyridine stretching frequencies.[14,15] Comparing the predictions (Table III) for infrared-active stretching modes with the results as shown in Table II, we find that our assignments are supported by the far-infrared data, at least for the chloro isomers. *trans*-$Ru(py)_4Cl_2$ has only one Ru–Cl stretching mode (338 cm^{-1}) active in the infrared spectrum while *cis*-$Ru(py)_4Cl_2$ has two (325, 313 cm^{-1}). Since the methods of synthesis for the bromo and iodo complexes are similar to those of the corresponding chloro complexes, we assume the bromo and iodo complexes will have the same configurations as the corresponding chloro complexes, even though this is not necessarily indicated by the infrared data.

TABLE II

FAR INFRARED SPECTRA (CM^{-1}) FOR $Ru(py)_4X_2$[a]

X = Cl		X = Br		X = I	
Trans	Cis	Trans	Cis	Trans	Cis
468 s	478 m	467 s	474 m	467 m	470 m
402 m	414 vw	404 w	468 m	408 w	299 m[c]
338 s[b]	325 m[b]	315 vw	420 vw	296 s[c]	281 m[c]
298 s[c]	313 w[b]	297 s[c]	411 vw	209 vw	184 w
237 s	298 m[c]	213 m	308 m[c]	142 m	110 vw
215 m	282 vw[c]	184 s[b]	290 m[c]		
165 s	256 s	170 m[b]	175 s[b]		
	238 s	127 w	168 s[b]		
	193 m		115 m		

[a] Samples run as CsI pellets and Nujol mulls; calibration by means of water vapor [L. R. Blaine, E. K. Plyler, and W. S. Benedict, *J. Res. Nat. Bur. Stand., Sect. A*, **66**, 223 (1962)]; maximum error ±3 cm^{-1}. Key: s, strong; m, medium; w, weak; v, very. [b] Tentative Ru–X stretching modes. [c] Tentative Ru–py stretching modes.

Raman Spectra.—Further support for our assignment

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[12] P. T. Cheng, B. R. Loescher, and S. C. Nyburg, *Inorg. Chem.*, **10**, 1275 (1971).

[13] A. Finch, P. N. Gates, K. Radcliffe, F. N. Dickson, and F. F. Bentley, "Chemical Applications of Far Infrared Spectroscopy," Academic Press, New York, N. Y., 1970, pp 121–129, 170.

[14] R. J. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

[15] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley-Interscience, New York, N. Y., 1970, pp 212–219.

TABLE III

SYMMETRY PREDICTIONS FOR VIBRATIONAL MODE ACTIVITY[13,14]

Complex	Point group	Vibrations	Normal mode desc	Active modes Ir	Active modes Raman
trans-$Ru(py)_4X_2$	D_{4h}	Ru–py str	$A_{1g} + B_{1g} + E_u$	1 (E_u)	2 ($A_{1g} + B_{1g}$)
		Ru–X str	$A_{1g} + A_{2u}$	1 (A_{2u})	1 (A_{1g})
cis-$Ru(py)_4X_2$	C_{2v}	Ru–py str	2 $A_1 + B_1 + B_2$	4 (2 $A_1 + B_1 + B_2$)	4 (2 $A_1 + B_1 + B_2$)
		Ru–X str	$A_1 + B_1$	2 ($A_1 + B_1$)	2 ($A_1 + B_1$)

of stereochemistry comes from the Raman spectra which could be obtained only for the chloro complexes due to laser decomposition of the bromo and iodo complexes. The *trans*-$Ru(py)_4Cl_2$ complex (D_{4h}) has a center of symmetry which in effect prevents any infrared-active mode from being Raman active and *vice versa*.[16–18] For the cis isomer (C_{2v}), however, all stretching modes are both infrared and Raman active. As can be seen by comparing Tables II and IV, there is a one-to-one correspondence between the bands in the Raman and the far-infrared spectra for the cis isomer over the region covered by both instruments (with the exception of the weak 282-cm^{-1} infrared band not seen in the Raman). The trans isomer has no infrared and Raman coincidences.

TABLE IV

RAMAN SPECTRA FOR $Ru(py)_4Cl_2$ (CM^{-1})[a]

Trans	260, 203, 90
Cis	328, 312, 301, 253, 236, 193

[a] Calibration *via* liquid carbon tetrachloride bands; maximum error ±5 cm^{-1}; region covered was from 350 cm^{-1} to as near the exciting line as possible.

Nmr Spectra.—The proton nmr spectra of the complexes allow a definitive assignment of the cis and trans configurations. A study of the proton nmr of pyridine complexes of Ru(II), Ru(III), and Ir(III)[19] has shown that the chemical shift of protons 2 and 6 is a function of the geometrical relationship between the pyridine ligand to which they belong and the other ligands of the complex. For the *trans*-$Ru(py)_4Cl_2$ complex, all the pyridine ligands are equivalent (that is, the pyridine molecules are interchanged by operations of the symmetry group to which the complex belongs). Thus, all the 2 and 6 protons have the same chemical shift, and only one set of signals is expected. The *cis*-$Ru(py)_4Cl_2$ complex on the other hand has two types of pyridine ligands. One type consists of the two mutually trans pyridines, while the other consists of the two pyridine ligands trans to Cl^- ligands. Thus, the cis isomer should have two sets of 2- and 6-proton signals, and these two sets should correspond to equivalent numbers of protons. The proton nmr spectra for *trans*- and *cis*-$Ru(py)_4Cl_2$ are given in Figures 1 and 2. The general shape of the spectrum is the same for the bromo and iodo complexes although the exact values for the chemical shifts (Table I) vary with the halogen. The shifts in resonance positions with change in halogen, stereochemistry, and number of pyridine ligands are being studied further.[19] As is evident from Figures 1 and 2 and Table I, the complexes re-

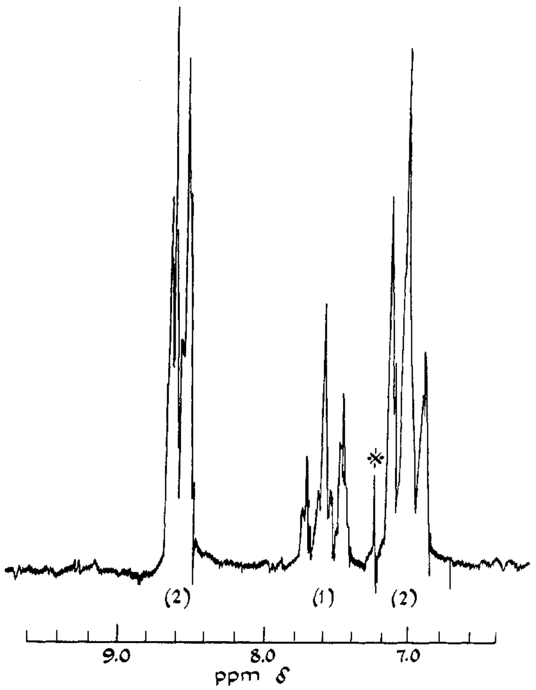

Figure 1.—Nmr spectrum of *trans*-$Ru(py)_4Cl_2$ in $CDCl_3$ at 60 MHz; the numbers in parentheses denote relative areas and the asterisk indicates the $CHCl_3$ signal.

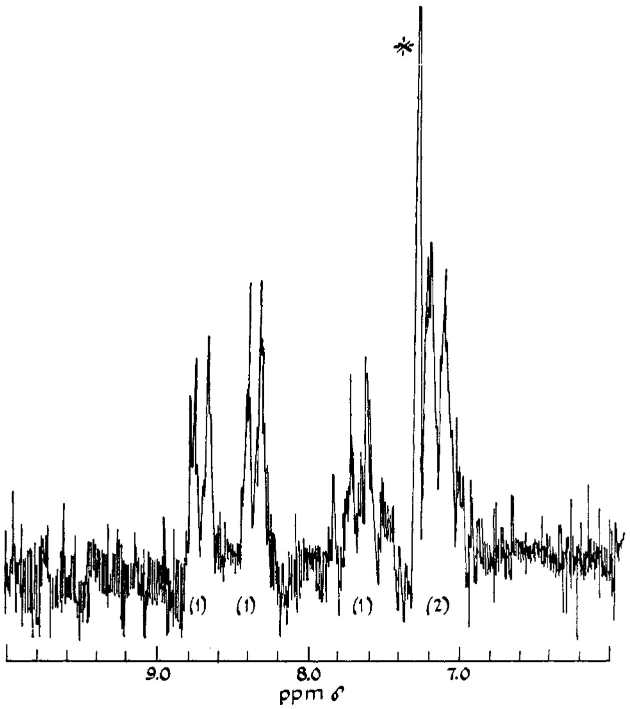

Figure 2.—Nmr spectrum of *cis*-$Ru(py)_4Cl_2$ in $CDCl_3$ at 60 MHz; the numbers in parentheses denote relative areas and the asterisk indicates the $CHCl_3$ signal—this signal obscures the fourth member of the quartet which can be seen using 1,1,2,2-tetrachloroethane as a solvent.

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(16) This "mutual exclusion" rule is only approximately valid for *trans*-$Ru(py)_4Cl_2$, since the pyridine rings probably have a propeller-like orientation about the Ru metal center which removes the center of symmetry.[17,18]

(17) D. R. Russell, *Chem. Commun.*, 63 (1967).

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ported in this paper have proton nmr corresponding to a cis configuration while the previously reported complexes[1-5] have proton nmr indicative of the trans stereochemistry.

Conclusion

In view of the work done with *cis*-[Ir(py)$_4$Cl$_2$]Cl,[20-22] the hexapyridine complexes,[6,12,23-25] the [Ru(py)$_4$bipy]$^{2+}$ (bipy = 2,2′-bipyridine) complex,[26] and the [(Ru(py)$_4$)$_2$ox](BF$_4$)$_2$ complex,[12] it is not surprising that a relatively stable *cis*-Ru(py)$_4$X$_2$ (X$^-$ = Cl$^-$, Br$^-$, I$^-$) series can be rather easily prepared. However, as has been suggested by other workers,[12,27] the cis isomer does seem to be less stable than the trans. Indications of this come from the following observations. The cis isomer, upon recrystallization from hot pyridine, is converted largely to the trans form. A solution of the cis isomer in methylene chloride when exposed to air turns green. The proton nmr shows a merging of the two sets of 2- and 6-proton resonances to form a single doublet. Upon reduction of the green solution, the trans isomer is formed.

Whatever the form of and reason for the instability of the cis isomer with respect to the trans, it seems clear that the success of this work depended on the use of the oxalate ligand. The oxalate group forces the complex to adapt a cis configuration and can be replaced under conditions which leave the configuration of pyridine ligands unaltered.

Acknowledgment.—The use of the Shell Research and Development Co. Beckman IR-11 spectrophotometer, an NSF fellowship (1968–1972) for D. W. R., and financial support through NSF Grant GP5322X are gratefully acknowledged.

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[20] M. Delepine and M. Lareze, *C. R. Acad. Sci.*, **257**, 3772 (1963).

[21] Actually, the cis configuration had not been definitively established since the assignment was based only on the far-infrared comparison of the two forms of [Ir(py)$_4$Cl$_2$]Cl.[14] However, proton nmr results[19] do indicate the far-infrared assignments to be correct.

[22] A recent Mössbauer study indicates that Fe(py)$_4$Cl$_2$ may have the cis configuration: P. B. Merrithew, P. G. Rasmussen, and D. H. Vincent, *Inorg. Chem.*, **10**, 1401 (1971).

[23] D. W. Herlocker and M. R. Rosenthal, *Inorg. Chim. Acta*, **4**, 501 (1970).

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N,N,N‴,N‴-Diglycylethylenediaminetetraacetic Acid. A New Cobalt(II) Oxygen Carrier[1,2]

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The formation, stability, and properties of a new cobalt(II) chelate oxygen carrier, formed from Co(II) and diglycylethylenediaminetetraacetic acid, H$_4$L, are described. One mole of oxygen is absorbed per 2 mol of metal chelate, CoL^{2-}, to form the oxygen complex. Potentiometric data indicate that two hydrogen ions are released per ligand upon oxygenation, indicating ionization of the amide hydrogens, with formation of a complex having the composition Co$_2$O$_2$(H$_{-2}$L)$_2{}^{8-}$. Ligand protonation constants, the formation constant of the 1:1 unoxygenated complex, and the formation constant of the oxygenated chelate are reported. Facile equilibrium with molecular oxygen, rapid pH equilibrium, and relative slowness of an irreversible reaction to a cobalt(III) complex of the ligand make this oxygen carrier a convenient model system for further study of the nature of oxygen complexes of cobalt(II) peptides in solution.

Introduction

Cobalt(II) complexes of dipeptides have been known to absorb oxygen for some time.[3-7] Recently Nakon and Martell[8] have elucidated the nature of the solution species of the glycylglycinatocobalt(II) system, showing that the chelate having a 1:1 molar ratio of ligand to metal ion forms a binuclear complex in which the amide group of the ligand undergoes proton dissociation on oxygenation and in which there are μ-peroxo and μ-hydroxo bridges between two Co^{3+} ions. The chelate having a 2:1 molar ratio of ligand to metal ion forms a μ-peroxo bridge between two Co^{3+} ions but does not form a μ-hydroxo bridge on oxygenation, and only one ligand per metal ion undergoes amide proton dissociation. Because of a relatively rapid irreversible side reaction to form a cobalt(III)–glycylglycine species, oxygen equilibrium data have not been obtained. The purpose of this paper is to describe a new oxygen-carrying chelate compound formed from Co(II) ion and a new ligand, *N,N,N‴,N‴*-diglycylethylenediaminetetraacetic acid, H$_4$L, I. In the absence of oxygen this ligand forms the normal chelate compounds CoHL$^-$ (II) and CoL^{2-} (III), described previously.[9] In the

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[2] This work was supported by a fellowship granted to R. S. N. by the Petroleum Research Fund, administered by the American Chemical Society.

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