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Synthesis, Stereochemistry, and Oxygenation of Cobalt(II)–Pyridoxal Model Complexes. A New Family of Chiral Dioxygen Carriers[1]

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A number of representative cobalt(II) complexes of the imines of L-amino acids derived from salicylaldehyde, Co(sal-L-aa), and pyridoxal, Co(pdx-L-aa) (aa = ala, val, phe, his), have been prepared and characterized. The corresponding complexes derived from pyruvate could be obtained only for histidine derivatives. The complexes are high-spin and have five- or six-coordinate structure. Their stereochemical properties were deduced from the circular dichroism spectra and by preparing some representative adducts with donor bases. The Co(sal-L-aa) and Co(pdx-L-aa) complexes can bind molecular oxygen, but while the histidine derivatives react readily in any solvent, the derivatives of amino acids with nonpolar side chains require the presence of additional base molecules. The reactivity of the histidine complexes is determined essentially by the glycine-like mode of binding of the amino acid residue. In fact, the histidine complex derived from pyruvate, in which the amino acid is bound as a substituted histamine, is completely unreactive to dioxygen. Both 1:1 and 2:1 dioxygen adducts are formed by the cobalt–pyridoxal model complexes, but in some cases the presence of bulky, nonpolar side chains on the amino acid residues sterically hinders dimerization of the 1:1 adducts and provides a reversible oxygenation behavior at room temperature. Complementary information on the evolution of the 1:1 and 2:1 dioxygen species during the oxygenation reactions can be obtained by combined ESR and optical/CD measurements. The binuclear μ-peroxo complexes derived from Co(sal-L-his) and Co(pdx-L-his) were also isolated in the solid state and characterized spectrally.

Introduction

The stereochemical properties of a variety of zinc(II) and copper(II) complexes of imines of amino acids have been recently described in a series of papers.[2,3] Particular emphasis was given to the complexes derived from L-histidine, in view of the importance of histidyl residues as metal binding sites in biological systems[4,5] and of the problems associated with chelation of this potentially tridentate ligand to metal ions.[5,6] Metal systems of imines of amino acids have been known for some time as models for the enzymic reactions of amino acids catalyzed by pyridoxal phosphate or pyruvate,[7] though copper(I) complexes of histidine imines have been studied recently also as models for dioxygen binding and activation.[8] This paper reports the synthesis, stereochemistry, and reactivity toward dioxygen of a series of cobalt(II) complexes of the imines of L-amino acids derived from salicylaldehyde, pyridoxal, and pyruvic acid. Although a few cobalt chelates derived from salicylaldehyde[9] or pyridoxal[10] and amino acids with a nonpolar side chain have been reported previously, their reactivity to dioxygen has never been investigated, in spite of the vast literature dealing with the oxygenation of cobalt(II)–imine complexes.[11] A main purpose of the present

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(8) (a) Casella, L.; Silver, M. E.; Ibers, J. A. *Inorg. Chem.* **1984**, *23*, 1409–1418. (b) Casella, L.; Rigoni, L. *J. Chem. Soc., Chem. Commun.* **1985**, 1668–1669.
(9) (a) Carlisle, G. O.; Theriot, L. J. *J. Inorg. Nucl. Chem.* **1973**, *35*, 2093–2096. (b) Percy, G. C. *Ibid.* **1975**, *37*, 2071–2073.
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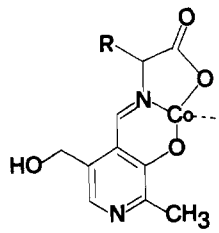
investigation is to relate the reactivity to dioxygen of the complexes derived from histidine to the mode of binding of the amino acid residue, since the understanding of the reactions of simple cobalt(II)–histidine complexes with dioxygen is complicated by the presence of isomers in solution.[5,12,13] The structures of the complexes are summarized by **1–4**;[14] however, the systems of type



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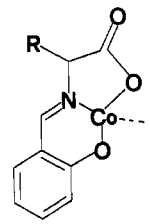

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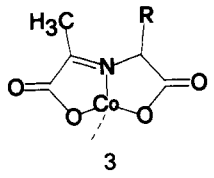

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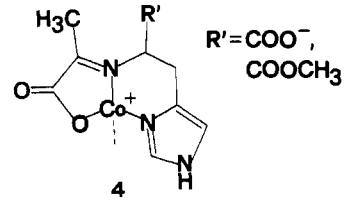

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3 could not be isolated in pure forms, and their spectral properties were studied only qualitatively in solution. The dioxygen adducts of the cobalt(II) complexes presented here may provide an interesting family of chiral reagents for biomimetic oxygenations.

Experimental Section

Physical Measurements. Elemental analyses were from the microanalytical laboratory of the University of Milano. Infrared spectra were recorded on a Nicolet MX-1E FT-IR instrument; a standard resolution of 2.0 cm^{-1} was used in the measurements. Electronic spectra were recorded on Perkin-Elmer Lambda-5 and on Beckman DK-2A spectrophotometers equipped with a reflectance attachment. Circular dichroism spectra were recorded on a Jobin-Yvonne Mark III dichrograph, calibrated with a solution of isoandrosteron in dioxane. The optical and CD spectra of air-sensitive solutions were obtained in 1-cm and 1-mm quartz cells fitted with Schlenk connections. ESR spectra were obtained at X-band frequencies on a Varian E-109 instrument from samples contained in 3-mm quartz tubes fitted with Schlenk connections. Magnetic susceptibilities of solid samples were measured at 295 K by the Faraday technique on a Cahn 1000 electrobalance. Tetrakis(thiocyanato)mercury cobaltate was used as a susceptibility standard, and diamagnetic corrections were estimated with use of the appropriate Pascal constants.[15] Manometric measurements of oxygen uptake were performed as described previously.[8a]

Reagents and Preparations.[14] All reagents were of the highest grade commercially available and were used as received. Pyruvic acid was distilled under vacuum prior to use. Pyridine (Carlo Erba Spectral grade, permanganate resistant) was distilled from potassium hydroxide under reduced pressure before use. Dimethylformamide was refluxed under vacuum over barium oxide to remove dimethylamine, stored over calcium hydride, and distilled under reduced pressure before use. Diethyl ether was dried over magnesium sulfate. The syntheses of all cobalt(II) complexes were performed under an atmosphere of purified, dry nitrogen with use of Schlenk glassware.

The complexes Co(sal-L-ala), Co(sal-L-val), and Co(sal-L-phe) were prepared according to the following procedure. Equimolar amounts of salicylaldehyde and the amino acid (5 mmol) were refluxed for about 2 h in ethanol–water (3:1 v/v, 50 mL) under nitrogen. After cooling, solid cobalt(II) acetate tetrahydrate (5 mmol) was added to the solution. The mixture was stirred for a few hours, and then it was concentrated under vacuum at room temperature to about half of the volume. The precipitate of the cobalt(II) complex was collected by filtration, washed with a small amount of degassed ethanol–water, and dried under vacuum. The compound Co(sal-L-his) was prepared similarly but with immediate addition of the cobalt(II) salt to the solution of salicylaldehyde and L-histidine. The product obtained under these conditions is a dihydrate and has a light brown color; crystallization of this material from hot methanol or refluxing of the reaction mixture afforded a hemihydrate, red-violet form of the compound.

The complexes Co(Hpdx-L-ala)Cl and Co(Hpdx-L-his)Cl were prepared by adding solid cobalt(II) acetate tetrahydrate (3 mmol) to a degassed solution of pyridoxal hydrochloride (3 mmol) and the amino acid (3 mmol) in water–methanol (1:1 v/v, 50 mL). The solution was evaporated under vacuum to a small volume, and degassed ethanol was added to the residue. The precipitate thus formed was collected by filtration, washed with little amounts of degassed water–ethanol, and dried under vacuum. When the same procedure was followed, the neutral derivatives of L-valine and L-phenylalanine, Co(pdx-L-val) and Co(pdx-L-phe), precipitated on concentrating the reaction mixture, apparently because of their lower solubility; these precipitates were filtered, washed with small amounts of water–methanol, and dried under vacuum. To prepare the neutral complexes Co(pdx-L-ala) and Co(pdx-L-his) solid cobalt(II) acetate tetrahydrate (3 mmol) was added to a degassed solution of free pyridoxal (3 mmol) and the amino acid (3 mmol) in water–ethanol (1:3 v/v, 40 mL). The solution was concentrated to a small volume until precipitation of the product occurred. The precipitate was filtered and dried under vacuum.

The complex Co(pyv-L-his) was prepared from equimolar amounts of pyruvic acid, L-histidine, and cobalt(II) chloride hexahydrate (5 mmol) in degassed water (40 mL). After the addition of a degassed solution of sodium hydroxide (10 mmol), the solution was concentrated to a small volume. The product was precipitated by adding degassed methanol, and then it was filtered, washed with small amounts of degassed water–methanol, and dried under vacuum. To obtain Co(pyv-L-hisOMe)Cl, a ligand solution was prepared from L-histidine methyl ester dihydrochloride (5 mmol), pyruvic acid (5 mmol), and methanolic ~1 N sodium hydroxide (10 mmol) in methanol (30 mL). After degassing, solid cobalt(II) chloride hexahydrate (5 mmol) and degassed methanolic sodium hydroxide (slightly less than 5 mmol) were added. The mixture was allowed to react for ~2 h under stirring, then it was evaporated to dryness under vacuum. The residue was treated with degassed ethanol–toluene (4:1 v/v, 50 mL), and the precipitate of sodium chloride was filtered off. The filtrate was concentrated to less than half of the volume under vacuum, and the product was precipitated by the addition of degassed diethyl ether. After filtration, the product was dried under vacuum. The complex Co(pyc-L-his)ClO_4 was obtained by addition of solid cobalt(II) perchlorate hexahydrate (5 mmol) to a degassed solution of 2-formylpyridine (5 mmol) and L-histidine (5 mmol) in methanol (25 mL). The precipitate of the product, which deposited slowly from the solution, was filtered, washed with a small amount of methanol, and dried under vacuum.

The pyridine adducts Co(sal-L-ala)·2py, Co(sal-L-val)·2py, Co(sal-L-his)·py, and Co(pyv-L-hisOMe)Cl·py were obtained by slow evaporation under vacuum, almost to dryness, of solutions of the complexes in carefully degassed pyridine and dropwise addition of dry, degassed diethyl ether to the cold residues. The light brown precipitates thus formed were collected by filtration and dried under vacuum. The adduct Co(sal-L-ala)·dab was obtained by reacting Co(sal-L-ala) with a tenfold molar excess of phenylenediamine in degassed ethanol; the product was then precipitated by addition of degassed diethyl ether [IR: ν(NH) at 3322, 3265, 3218 and 3166 cm^{-1} (Nujol mull)].

The elemental analyses of the cobalt(II) complexes are collected in Table I.[16]

For the observation of the CD features of cobalt(II) complexes of pyruvate Schiff bases of nonpolar L-amino acids, solutions of cobalt(II) perchlorate hexahydrate (1 mmol), pyruvic acid (1 mmol), the amino

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(13) See for instance: (a) Bagger, S.; Gibson, K. *Acta Chem. Scand.* **1972**, *26*, 3788–3796. (b) Ritsma, J. H. *J. Inorg. Nucl. Chem.* **1976**, *38*, 907–915. (c) Woods, M.; Weil, J. A.; Kinnaird, J. K. *Inorg. Chem.* **1972**, *11*, 1713–1715. (d) Stadtherr, L. G.; Prados, R.; Martin, R. B. *Ibid.* **1973**, *12*, 1814–1818. (e) Salama, S.; Spiro, T. G. *J. Am. Chem. Soc.* **1978**, *100*, 1105–1111. (f) Kitagawa, S.; Yoshikawa, K.; Morishima, I. *J. Phys. Chem.* **1978**, *82*, 89–97. (g) Eaton, D. R.; Weegar, J. D. *Inorg. Chim. Acta* **1984**, *93*, 73–83.

(14) Abbreviations: *N*-salicylideneamino acidato dianion = sal-aa; *N*-pyridoxylideneamino acidato dianion = pdx-aa; ring protonated form of *N*-pyridoxylideneamino acidato dianion = Hpdx-aa; *N*-pyruvilideneamino acidato dianion = pyv-aa; *N*-(2-pyridylmethylidene)amino acidato anion = pyc-aa; condensed amino acidato anion = aa; alaninate anion = ala; valinate anion = val; phenylalaninate anion = phe; histidinate anion = his; pyridoxamine = pdm; pyruvate anion = pyv; phenylglyoxylic acid anion = phg; histidine methyl ester = hisOMe; pyridine = py; imidazole = im; 1,2-diaminobenzene = dab; phenyl = Ph.

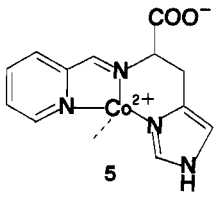
(15) Mabbs, F. E.; Machin, D. J. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1974; Chapter 1.

(16) Supplementary material.

acid (1 mmol), and sodium hydroxide (2 mmol) in water (10 mL) were prepared under nitrogen. Solutions containing the cobalt(II) complexes of *N*-pyridoxylidene-L-amino acids were obtained by adding solid cobalt(II) acetate tetrahydrate (0.1 mmol) to degassed solutions of pyridoxal hydrochloride (0.1 mmol), the amino acid (0.1 mmol), and methanolic 0.1 M sodium hydroxide (0.3 mmol) in methanol (final volume 20 mL). Solutions containing the cobalt(II) complexes of the ketimines formed between pyridoxamine and α-keto acids were prepared similarly from pyridoxamine dihydrochloride, the α-keto acid, cobalt(II) acetate tetrahydrate, and methanolic sodium hydroxide in methanol.

Results

Synthesis and Characterization. The cobalt(II) complexes of several imines of L-amino acids were synthesized by metal template condensation. A few representative amino acids were selected for each group of complexes, but the complete series could be obtained only for derivatives of pyridoxal (**1**) and salicylaldehyde (**2**). While the histidine derivatives **4** were obtained easily, all attempts to synthesize pyruvate complexes of type **3** yielded impure materials. This is partly due to the low chemical stability of metal systems containing two fused five-membered chelate rings,[3c] but the effect seems particularly pronounced for cobalt(II), since pyruvate complexes of type **3** could be isolated under the same conditions in the case of zinc(II)[2a] and copper(II).[3a] This is confirmed by the finding that although it was possible to obtain the 2-formylpyridine derivative **5**, the material isolated is optically



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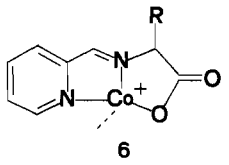
inactive, while the corresponding zinc(II) and copper(II) complexes were much more optically stable.[3c] As expected, systems of the type **6**, which carry a positive charge, are very unstable, and as



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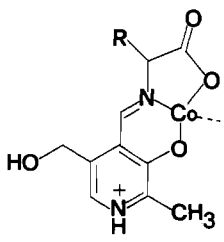
for the analogous zinc(II) and copper(II) systems,[3c] the corresponding complexes could not be isolated. The complex pattern of reactions undergone by the ligands in these systems deserves an appropriate separate investigation.

Treatment of the light brown dihydrate Co(sal-L-his) in hot alcohol affords a red-violet, hemihydrate modification of the compound. This material is probably polymeric and is completely insoluble in solvents like alcohol or water, but it can be dissolved in basic solvents like pyridine or dimethylformamide; these solutions display spectra practically identical with those of the dihydrate modification. Treatment of the other Co(sal-L-aa) complexes in similar conditions did not afford a different modification of the compounds. A few pyridoxal derivatives were prepared with either the pyridine ring protonated **7**, or non-



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protonated **1**, since these forms may exhibit different reactivity. Rather surprisingly the synthesis of the derivatives of L-valine and L-phenylalanine performed under the conditions expected to lead to the positively charged complexes Co(Hpdx-L-val)Cl and Co(Hpdx-L-phe)Cl yielded the neutral species Co(pdx-L-val) and Co(pdx-L-phe), respectively, probably because of the much lower solubility of the latter systems. The complexes of type Co(pdx-L-aa) can be easily distinguished from those of type Co(Hpdx-L-aa)Cl for their different colors in the solid state, since the former are brown while the latter tend to be green (Table II). Solutions of both groups of complexes in oxygen-free, polar solvents have light pink-orange to yellow colors and exhibit negligible electrical conductivity.

The spectral and magnetic properties of the cobalt(II) complexes in the solid state are summarized in Table II; complete infrared data have been made available in supplementary Table III. The infrared spectra are clearly indicative of the imine structure of the ligands in the complexes. Since these spectra are similar to those of the zinc(II) and copper(II) complexes described previously,[2,3] the same arguments can be applied for the assignments of the main IR bands. The spectra of all the pyridoxal derivatives display broad and featureless absorptions at about 2600–2700 cm^{-1}; these may be due to strong intermolecular hydrogen bonding and, at least in the case of the ring-protonated complexes Co(Hpdx-L-ala)Cl and Co(Hpdx-L-his)Cl to the pyridine "ammonium bands".[17] The room-temperature magnetic moments of most of the cobalt(II) complexes indicate a high-spin d^7 configuration, with μ_{eff} values (4.3–4.8 μ_B) somewhat lower than those normally found for octahedral complexes.[18] In a few cases the values of μ_{eff} occur in the range 3.2–3.8 μ_B, intermediate between those expected for high-spin and low-spin complexes. These low μ_{eff} values may arise from the presence of spin equilibria[19] or magnetic exchange interactions,[20] but such phenomena can be studied by magnetic measurements at low temperatures that are currently not available to us; however, no ESR signal could be detected in the powder or frozen, oxygen-free solution spectra of the complexes down to −150 °C. In general the diffuse-reflectance electronic spectra of the cobalt(II) complexes show two main ligand field bands, often with multicomponent structure, between 450 and 560 nm and above 1000 nm, while somewhat weaker absorptions can be detected in several cases between 650 and 750 nm. The spectra of the chloride-containing complexes Co(Hpdx-L-ala)Cl and Co(pyv-L-hisOMe)Cl exhibit the most intense ligand field band in the range 620–660 nm, while that of the red-violet Co(sal-L-his) compound displays several resolved bands that suggest the presence of a mixture of species with different coordination geometry.

Electronic and CD Spectral Behavior in Solution. The relevant electronic and CD spectral data below 800 nm of the cobalt(II) complexes derived from salicylaldehyde or pyridoxal in oxygen-free methanolic solutions are collected in Table IV; representative spectra are given in Figures 1–3.[16] In general, the visible absorption spectra feature weak ligand field bands near and above 500 nm, often appearing as shoulders on the intense near-UV absorptions, while two or three CD bands are well resolved in the region corresponding to weak electronic absorption (450–800 nm). These CD extrema occur between 460 and 485 nm (band I), 490 and 550 nm (band II), and 600 and 680 nm (band III). Additional electronic and CD absorptions occur near 420–430 nm, at energies that seem too high for ligand field transitions. The visible CD bands show often multicomponent structure, and that above 600 nm is usually rather broad, resembling those observed in the CD spectra of simple Co(II)–carboxylic acid systems.[21] The near-UV electronic spectra of the complexes are dominated by moderately intense bands near 360 nm (salicylidene derivatives) and 380 nm (pyridoxylidene derivatives) that, by analogy with the related

(17) See for instance: Nakanishi, K. *Infrared Absorption Spectroscopy*; Holden-Day: San Francisco, 1962; Chapter 2.
(18) Banci, L.; Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *Struct. Bonding (Berlin)* **1982**, *52*, 37–86.
(19) (a) Kennedy, B. J.; Fallon, G. D.; Gatehouse, B. M. K. C.; Murray, K. S. *Inorg. Chem.* **1984**, *23*, 580–588. (b) Zarembowitch, J.; Kahn, O. *Ibid.* **1984**, *23*, 589–593.
(20) (a) Bencini, A.; Benelli, C.; Gatteschi, D. *Inorg. Chem.* **1983**, *22*, 470–473. (b) Drew, M. G. B.; Esho, F. S.; Lavery, A.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1984**, 545–556.
(21) Katzin, L. I. *Inorg. Chem.* **1973**, *12*, 649–655.

Table II. Magnetic Data,[a] Low-Energy Electronic Bands,[b,c] and Selected Infrared Data[d] for Cobalt(II) Complexes of Imines of Amino Acids in the Solid State[e]

compd	color	μ_{eff}, μ_B	vis–near-IR λ_{max}, nm	IR $\bar{\nu}$, cm^{-1} [mode]
Co(sal-L-ala)·$2H_2O$	light brown	4.50	450 sh, 530, 1130	3585 m, 3285 s [ν(OH)]; 1643 s [ν(C=N)]; 1600 w, 1542 s [ν(ring)]; 1560 sh [ν_{as}(COO)]; 1416 w [ν_s(COO)]; 1300 m [ν(O–Ph)]
Co(sal-L-val)·$1.5H_2O$	light brown	4.35	450 sh, 525, 550 sh, 700, 1030	3315 s [ν(OH)]; 1630 sh, 1619 s [ν(C=N)]; 1600 m, 1535 s, 1523 m [ν(ring)]; 1576 s [ν_{as}(COO)]; 1444 m [ν_s(COO)]; 1304 m [ν(O–Ph)]
Co(sal-L-phe)·$0.5H_2O$	orange	3.60	500, 675, 850 sh, 1100	3485 w, 3422 w [ν(OH)]; 1645 s [ν(C=N)]; 1611 s [ν_{as}(COO)]; 1581 w, 1550 sh, 1495 vw [ν(ring)]; 1419 [ν_s(COO)]; 1282 [ν(O–Ph)]
Co(sal-L-his)·$2H_2O$	light brown	5.06	520, 675 sh, 1200	3270 s br [ν(OH), ν(NH)]; 3147 w [im ν(CH)]; 1636 s [ν(C=N)]; 1599 s, 1540 sh [ν(ring)]; 1561 [ν_{as}(COO)]; 1420 sh [ν_s(COO)]; 1294 m [ν(O–Ph)]
Co(sal-L-his)·$0.5H_2O$	red violet	4.62	450 sh, 550, 690, 900, 1300, 1700	3140 w, 3070 w [ν(CH)]; 1665 s, 1646 s, 1637 s, 1597 s, 1569 m, 1555 m [ν(C=N), ν_{as}(COO), ν(ring)]; 1432 s [ν_s(COO)]; 1328 m [ν(O–Ph)]
Co(pdx-L-ala)·$2H_2O$	brown	4.34	530 sh, 700 sh, 1200	3400 s, br [ν(OH)]; 1625 s [ν(C=N)]; 1575 s, br, 1506 m [ν_{as}(COO), ν(ring)]; 1419 s [ν_s(COO)]; 1307 m [ν(O–Ph)]
Co(pdx-L-val)·H_2O	light brown	3.79	450, 560 sh, 1000, 1200 sh	3370 s, br, 3250 s, br [ν(OH)]; 1629 s [ν(C=N)]; 1577 s, br, 1506 s [ν_{as}(COO), ν(ring)]; 1420 sh [ν_s(COO)]; 1311 m [ν(O-Ph)]
Co(pdx-L-phe)	brown	3.56	460, 560 sh, 950, 1100 sh	3250 s, br [ν(OH)]; 1625 s [ν(C=N)]; 1585 s, br, 1504 s [ν_{as}(COO), ν(ring)]; 1420 sh [ν_s(COO)]; 1305 m [ν(O-Ph)]
Co(pdx-L-his)·$2H_2O$	light brown	4.81	450, 550 sh, 1070 sh, 1350	3230 s, br [ν(OH), ν(NH)]; 3147 m [im ν(CH)]; 1610 s, br, 1506 m [ν(C=N), ν_{as}(COO), ν(ring)]; 1420 s [ν_s(COO)]; 1307 m [ν(O-Ph)]
Co(Hpdx-L-ala)Cl·H_2O	green brown	4.05	450 sh,550 sh, 625, 1250	3350 s, br [ν(OH)]; 1628 s [ν(C=N)]; 1590 sh, br, 1508 m [ν_{as}(COO), ν(ring)]; 1420 s [ν_s(COO)]; 1308 m [ν(O-Ph)]
Co(Hpdx-L-his)Cl·$2H_2O$	green brown	4.57	450 sh, 540 sh, 1050 sh, 1350	3250 s, br [ν(OH), ν(NH)]; 3140 sh [im ν(CH)]; 1623 s [ν(C=N)]; 1600 s, br, 1506 m [ν_{as}(COO), ν(ring)]; 1435 s [ν_s(COO)]; 1307 m [ν(O-Ph)]
Co(pyv-L-his)·$1.5H_2O$	light brown	4.73	450 sh, 520 sh, 750, 850 sh, 1370	3250 sh, br [ν(OH)]; 3142 m [im ν(CH)]; 1627 s [ν(C=N)]; 1590 s, br [ν_{as}(COO)]; 1499 w [ν(ring)]; 1430 sh [ν_s(COO)]
Co(pyv-L-hisOMe)Cl·$1.5H_2O$	light blue	4.76	490, 660, 1030, 1260, 1550	3250 s, br [ν(OH)]; 3150 sh [im ν(CH)]; 1737 s [ν(C=O)]; 1631 s [ν(C=N)]; 1580 sh, 1500 w [ν(ring)]
Co(pyc-L-his)ClO_4	brown	3.21	520, 650 sh, 950 sh	3173 m, 3141 m, 3031 w [ν(CH)]; 1639 s [ν(C=N)]; 1596 s, 1583 m, 1568 w, 1517 m [ν_{as}(COO), ν(ring)]; 1430 sh [ν_s(COO)]; 1090 s, br, 620 s [$\nu(ClO_4)$]

[a] Measured at room temperature. [b] Diffuse reflectance spectra recorded in the range 400–2000 nm. [c] Spectra recorded as Nujol mulls. [d] Weak water overtone bands near 1900 nm are often resolved in the spectra. [e] Shoulder = sh, broad = br, strong = s, medium = m, and weak = w.

zinc(II)[2a,b,22] and copper(II)[3a,d,23] chelates, can be assigned to the imine $\pi \rightarrow \pi^*$ transitions. These bands invariably display Cotton effects of negative sign in the CD spectra. The intense absorption bands occurring at higher energy are associated with benzene or pyridine ring $\pi \rightarrow \pi^*$ transitions. The imine absorption bands are often flanked by prominent shoulders at 320–330 nm, but these correspond to relatively weak CD activity. The CD spectrum of Co(pdx-L-val) exhibits an intriguing two-signed curve, resembling an exciton couplet,[24] in the range spanned by the imine absorption band (330–400 nm) (Figure 3).[16] The CD couplet seems present, but is poorly defined for the low resolution, in the solid-state mull spectrum of the compound and may therefore arise from some kind of molecular association that is not affected by dissolution in methanol. In fact, the couplet is replaced by a single negative imine CD band in the CD spectrum of Co(pdx-L-val) recorded in oxygen-free pyridine (Figure 3, Table V)[16] and in that of the complex formed in situ from a 1:1:1 mixture of pyridoxal-L-valine–cobalt(II) in neutral, oxygen-free methanolic solution (Figure 3, Table VI).[16] A similar behavior is exhibited by Co(pdx-L-phe), although the positive component of the imine CD band in methanol has a much lower intensity. The CD spectrum of Co(pdx-L-his) displays very weak activity within the imine band in methanol, but its behavior in pyridine is quite normal (Figure 2).[16] Note that the CD spectral features of Co(pdx-L-val), Co(pdx-L-phe), and Co(pdx-L-his) were reproduced in repeated preparations of the complexes.

The near-UV electronic spectra of the pyridoxal complexes recorded in pyridine (Table V)[16] or DMF solutions show often prominent bands near 350 nm, of intensity comparable with that of the imine band. But the CD extrema occur invariably near 380 nm. In the visible region, the pyridine and DMF CD spectra of the complexes derived from amino acids with nonpolar side chain show appreciable variations with respect to those in methanol solution. By contrast, those of the histidine complexes show little solvent dependence. Pyridine solutions of the compound Co(pdx-L-ala) exhibit very low CD activity and those of Co(Hpdx-L-ala)Cl are virtually optically inactive. Moreover while for Co(pdx-L-ala) the magnitude of the CD bands in methanol is comparable with that of the pyridoxal–L-alanine–cobalt(II) (1:1:1) system prepared in situ (Table VI)[16] the intensity of the CD spectrum of Co(Hpdx-L-ala)Cl in methanol is 1 order of magnitude lower. This compound has thus probably undergone at least a partial racemization during preparation.

In order to determine the number of base molecules that can occupy the available coordination positions of the cobalt(II) complexes we prepared a few representative pyridine adducts of

(22) (a) Matsushima, Y.; Martell, A. E. *J. Am. Chem. Soc.* **1967**, *89*, 1322–1330. (b) *Ibid.* **1967**, *89*, 1331–1335.
(23) (a) Weinstein, G. N.; O'Connor, M. J.; Holm, R. H. *Inorg. Chem.* **1970**, *9*, 2104–2112. (b) Wagner, M. R.; Walker, F. A. *Ibid.* **1983**, *22*, 3021–3028.
(24) Mason, S. F. *Molecular Optical Activity and the Chiral Discriminations*; Cambridge University: Cambridge, U.K., 1982; Chapter 3.

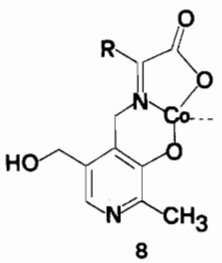
Table IV. Electronic and Circular Dichroism Spectra of Cobalt(II) Complexes of Imines of Amino Acids in Methanol Solution[a]

compd	UV–vis λ_{max}, nm (ϵ)[b]	CD λ_{max}, nm ($\Delta\epsilon$)[b]
Co(sal-L-ala)	520 sh (28), 485 (35), 356 (4700), 320 sh (2000), 290 sh (1600), 262 (7100)	670 (br, +0.01), 600 sh (−0.01), 570 sh (−0.05), 540 (−0.08), 505 sh (−0.05), 460 (+0.07), 420 sh (−0.25), 365 (−1.26), 310 (br, +0.45), 276 (−1.90)
Co(sal-L-val)	525 sh (30), 490 (34), 356 (5400), 320 sh (2400), 265 (8800)	655 (br, +0.03), 625 sh (+0.02), 570 sh (−0.07), 540 (−0.09), 520 sh (−0.08), 490 sh (+0.01), 460 (+0.11), 425 sh (−0.35), 362 (−2.40), 310 (+0.45), 275 (−2.30)
Co(sal-L-phe)	520 sh (18), 490 (20), 355 (3100), 325 sh (3000), 256 (10000), 240 sh (11100)	670 (br, +0.01), 600 sh (−0.01), 570 sh (−0.05), 538 (−0.08), 500 sh (−0.05), 460 (+0.05), 425 sh (−0.34), 360 (−4.60), 320 sh (−1.92), 268 (−7.21)[c]
Co(sal-L-his)[d]	660 sh (5), 525 sh (44), 480 sh (48), 354 (3300), 320 sh (2100), 250 sh (7500)	655 (br, +0.13), 542 (−0.58), 500 sh (−0.15), 465 (+0.09), 420 sh (−0.75), 372 (−2.94), 335 (br, +0.25), 276 (−3.50), 250 sh (+0.50), 232 (+4.50)
Co(pdx-L-ala)	660 sh (10), 550 sh (60), 430 sh (1300), 382 (3300), 330 sh (1800), 260 sh (6000)	550 (−0.03), 475 (+0.01), 380 (−0.22), 250 sh (−0.90)
Co(pdx-L-val)	620 sh (50), 570 sh (85), 430 sh (1400), 379 (6000), 330 sh (2500), 290 sh (3400)	635 (−0.16), 550 sh (−0.15), 500 (−0.35), 432 (+0.65), 392 (+2.23), 360 (−2.08), 310 (−1.84), 255 sh (−2.20)
Co(pdx-L-phe)	620 sh (50), 560 sh (100), 430 sh (1400), 377 (6200), 330 sh (3000), 290 sh (2800)	605 (−0.29), 490 (−0.59), 432 (+0.26), 414 (−0.09), 401 (+0.20), 368 (−7.49), 330 sh (−2.00), 287 (−0.46), 270 (+0.37), 250 (−2.59)
Co(pdx-L-his)	640 sh (10), 550 sh (55), 440 sh (500), 377 (3000), 330 sh (1800), 270 sh (5200)	615 (br, +0.13), 542 (−0.41), 520 sh (−0.25), 432 (−1.06), 390 sh (−0.43), 360 sh (−0.07), 328 (+0.10), 305 (−0.13), 280 sh (+0.40) 235 (+4.35)
Co(Hpdx-L-ala)Cl	660 sh (20), 550 sh (100), 430 sh (1100), 376 (2900), 325 (2850), 260 sh (8000)	570 (−0.002), 480 (+0.001), 380 (−0.01)
Co(Hpdx-L-his)Cl	550 sh (90), 430 sh (1100), 376 (3500), 325 sh (2000), 285 sh (2800), 260 sh (5400)	605 (+0.21), 530 (−0.42), 432 (−0.87), 370 (−1.00), 310 (−0.81), 250 (+3.43)
Co(pyv-L-his)	540 sh (15), 503 (21), 477 (22), 320 sh (300)	540 (+0.08), 510 (+0.11), 485 sh (+0.07), 452 (−0.05), 390 (−0.03), 330 (+0.08), 240 (−5.56)
Co(pyv-L-hisOMe)Cl	530 sh (17), 500 (22), 480 sh (21), 310 sh (300), 270 sh (520)	640 (br, +0.02), 530 (−0.01), 490 sh (+0.02), 450 (+0.05), 300 (+0.02), 240 sh (−0.86)

[a] All the spectra were recorded under nitrogen. [b] Shoulder = sh, broad = br. [c] Most intense peak of fine structure. [d] Dihydrate form.

the salicylaldehyde complexes. The pyridoxal complexes gave no pyridine adducts in the solid state, probably because in this state the polar groups on the pyridoxal residues can compete effectively with the donor molecules for the metal sites. An adduct with the potentially chelating phenylenediamine ligand, Co(sal-L-ala)·dab, was also obtained. In general, the CD spectra of the pyridine adducts recorded in methanol solution show extensive base dissociation, while that of Co(sal-L-ala)·dab appears unaffected by further addition of dab (Figure 1). Interestingly, the visible CD spectrum of Co(sal-L-ala) in the presence of excess imidazole (Figure 1) is very similar to those of the histidine complexes.

Included in Table VI[16] are also spectral data for ternary systems of pyridoxamine–α-keto acid–cobalt(II) (1:1:1) in neutral, oxygen-free methanolic solutions; the representative α-keto acids employed were pyruvic and phenylglyoxylic acids.[14] These ternary systems were studied to gain an appreciation of the spectral features associated with the ketimine species of type **8**, i.e. the



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products resulting from the possible transamination of the aldimine species of type **1**. The ketimine complexes **8** are characterized by an absorption band near 300 nm,[22,25,26] but the spectra change with time (much more rapidly for the system Co–pdm–pyv than for Co–pdm–phg), due to the formation of the aldimine complex **1**. The initial spectrum and that obtained after about 20 h for the Co–pdm–pyv system in neutral, oxygen-free methanolic solution are displayed in Figure 4.[16] By contrast, the spectra of the cobalt(II)–aldimine complexes are stable on the same time scale provided the solutions are kept under an inert atmosphere.

The CD spectra of Co(pyv-L-his) and Co(pyv-L-hisOMe)Cl in methanol solution are slightly different from each other (Table II, Figure 5[16]) and remain practically unchanged in pyridine (Table V),[16] but both are dominated by Cotton effects of positive sign in the visible region and are negative near 250 nm, where CD absorptions associated with the imine group for this type of complexes occur.[2a,3a] These spectra display a rough mirror-image relationship with those of the systems of pyruvic acid–L-amino acid–cobalt(II) (1:1:1) in neutral, oxygen-free aqueous solutions (Figure 5, Table VI),[16] that should provide at least a qualitative description of the chiroptical properties of complexes of type **3**. This behavior parallels that more nicely displayed by the corresponding copper(II) systems, for which the whole series of pure complexes could be prepared. A pyridine adduct of Co(pyv-L-hisOMe)Cl has been isolated in the solid state.

Oxygenation. The histidine complexes derived from salicylaldehyde or pyridoxal are rather air-sensitive in the solid state and undergo easy oxygenation reactions in solution. Figure 6 displays the spectral changes undergone by a dilute solution of Co(sal-L-his) in methanol upon exposure to air; the reaction with pure oxygen is obviously much faster. The changes in the CD spectra are dramatic, the overall remarkable increase of optical activity indicating the chiral center on the amino acid residue is unaffected in the reaction. The amount of dioxygen absorbed after 8 h corresponds to ca. 0.3 mol of O_2 (±10%) per cobalt and after 24 h to ~0.5 mol of O_2 per cobalt.[27] Following the reaction by ESR spectroscopy, it is possible to detect the signal typical for 1:1 adducts near $g = 2.0$[11a] (Figure 6b). This signal completely disappears on bubbling nitrogen through the solution at room temperature, while the electronic and CD spectra remain practically unchanged even on refluxing the oxygenated solution under a stream of nitrogen. The oxygenation of Co(sal-L-his) in dry,

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(27) The measurements of dioxygen absorbed by the cobalt(II) complexes were carried out in separate experiments at 15 °C and at concentrations (~10^{-2} M) much higher than those used to follow the spectral changes (~10^{-3} M) so that the readings could be compatible with the size of the gas burette (5 cm^3).[8a] In these conditions the cobalt(II) complexes were largely undissolved, particularly the histidine complexes in methanol, and the readings of dioxygen absorbed became therefore reliable only at long reaction times.

nonprotic solvents like pyridine or DMF[28] reproduces the spectral behavior observed in methanol. Since pure dioxygen (1 atm) was used in these experiments, the growth of CD activity and the disappearance of the ESR signal were faster than those shown in Figure 6, the reaction being virtually complete within 3–4 h. Also in these cases the amount of dioxygen absorbed corresponded to ~0.5 mol of O_2 per cobalt.[27] The oxygenated pyridine or DMF solutions undergo partially reversible absorption and CD spectral changes when kept at reflux under a stream of nitrogen. The products isolated from the oxygenation of Co(sal-L-his) in either methanol or pyridine are substantially diamagnetic and their analytical data are in agreement with the incorporation of one oxygen atom into the original cobalt(II) complex.[29] Therefore we formulate them as binuclear μ-peroxo complexes, $[Co(sal\text{-}L\text{-}his)L]_2O_2$, where L is equal to H_2O or pyridine. These products apparently release hydrogen peroxide upon acid treatment, but titrations with the iodometric[30] or iron(II)–phenanthroline[31] methods gave only 60–70% of the expected amount under the best conditions, probably because, as for other peroxo complexes derived from polyamine ligands,[32] some decomposition of hydrogen peroxide occurs under the conditions required to cleave the peroxo complexes. The oxygenation behavior of Co(pdx-L-his) in methanol, pyridine, or DMF[28] solutions parallels that observed for Co(sal-L-his), but the reactions occur at somewhat slower rate, judging from the slower increase of CD activity associated with the oxygenated species and the evolution of the ESR signal near $g = 2.0$ (Figure 7).[16] The product isolated from the oxygenation of Co(pdx-L-his) in methanol agrees with the formulation $[Co(pdx\text{-}L\text{-}his)(H_2O)_2]_2O_2$.[33] The oxygenation of solutions of Co(Hpdx-L-his)Cl produces spectral changes that are identical with those observed for the corresponding Co(pdx-L-his) systems but generally occur at rates that are significantly lower.

The complexes of type Co(sal-L-aa) derived from amino acids with a nonpolar side chain are reasonably air-stable in the solid state, while the corresponding Co(pdx-L-aa) complexes are slowly affected by moisture. When methanolic solutions of these Co(sal-L-aa) or Co(pdx-L-aa) complexes are kept in contact with air, only the CD spectra undergo some slow changes, but no buildup of dioxygen complexes of type $Co–O_2$ occurs, since the solutions remain ESR silent down to −150 °C. When solutions of these complexes in dry pyridine[28] are exposed to dioxygen (1 atm), well-resolved ESR signals appear near $g = 2.0$ due to the $Co–O_2$ species, but the electronic and CD spectra are little affected within a few hours of the oxygenation. This behavior is exemplified by the spectra recorded during the oxygenation of Co(sal-L-val), Figure 8, and Co(pdx-L-val), Figure 9.[16] Although the measurements of dioxygen uptake carried out for Co(sal-L-val) and Co(pdx-L-val) show that the amount of dioxygen absorbed by these solutions must be low, 0.1–0.2 mol of O_2 per cobalt after 3–4 h,[27] the oxygenations are fully reversed by bubbling nitrogen through the solutions at room temperature. On longer reaction times the ESR signals progressively decrease in intensity and eventually disappear, and the absorption and CD spectra undergo changes that cannot be reversed by bubbling nitrogen through the solutions. The oxygenations of Co(sal-L-aa) and Co(pdx-L-aa) complexes in dry DMF[28] produce ESR signals for the $Co–O_2$ adducts and also significant changes in the CD spectra, even at the early stages of the reactions and particularly in the visible region. This is shown in Figure 10[16] for Co(sal-L-val) and in Figure 11 for Co(pdx-L-val). The amount of dioxygen absorbed by these solutions after ~8 h is about 0.2–0.3 mol of O_2 per cobalt.[27] The ESR signals completely disappear at any time of the oxygenations by bubbling nitrogen through the solutions at room temperature, while the CD spectra remain unaffected by this treatment.

The pyruvate complexes Co(pyv-L-his) and Co(pyv-L-hisOMe)Cl are inert to dioxygen either in the solid state or when dissolved in nonbasic solvents like methanol. However, while Co(pyv-L-hisOMe)Cl undergoes an easy oxygenation reaction in pyridine, as shown by the appearance of well-resolved ESR signals for the $Co–O_2$ species, solutions of Co(pyv-L-his) in the same solvent are completely unaffected by dioxygen. As expected, also $Co(pyc\text{-}L\text{-}his)ClO_4$ is unreactive to dioxygen.

Discussion

The spectral and magnetic properties of the present series of high-spin cobalt(II) complexes measured in the solid state are indicative of five- or six-coordinate structures. Since the geometries may be irregular, it is difficult to distinguish between these structural types from reflectance data[18,34] and room-temperature magnetic moments.[18,35] However, for Co(pyv-L-hisOMe)Cl and, partly, the red-violet form of Co(sal-L-his) the low-energy electronic absorptions are similar to those associated with five-coordinate cobalt(II)–imine complexes.[8a,36] Tetrahedral structures can be excluded on the basis of the electronic spectra of the complexes and seem actually precluded by the ligand systems described here. Dimeric or polymeric structures are likely to occur in the solid state to enable the cobalt(II) centers to fill the vacant coordination positions, e.g. via bridging donor groups that are part of the ligands of adjacent molecules. Support for this interpretation comes from the observation that within a given series of cobalt(II) complexes, e.g. Co(sal-L-aa) or Co(pdx-L-aa), the magnetic moments increase as the number of water molecules retained by the complexes increases (Table II). Most of these

(28) The oxygenations in dry pyridine or DMF were carried out on the base adducts of the complexes formed in situ under nitrogen immediately before the oxygenation run. To obtain the dry adducts, the cobalt complexes were dissolved in the minimum amount of freshly distilled solvent and the solution was evaporated to dryness under vacuum at room temperature.

(29) The oxygenations were carried out by stirring a suspension of ~100 mg of Co(sal-L-his) in 50 mL of methanol, with exposure to air for 4 days, or in dry pyridine, exposed to dry oxygen for 24 h. The products were filtered and dried under vacuum. The analytical data are in agreement with the formulations $[Co(sal\text{-}L\text{-}his)H_2O]_2O_2$ (Anal. Calcd for $Co_2C_{26}H_{26}N_6O_{10}$: C, 44.58; H, 3.74; N, 12.00. Found: C, 44.53; H, 3.86; N, 12.11.) and $[Co(sal\text{-}L\text{-}his)py]_2O_2$ (Anal. Calcd for $Co_2C_{36}H_{32}N_8O_8$: C, 52.56; H, 3.92; N, 13.62. Found: C, 51.90; H, 4.16; N, 13.05. The material is slightly hygroscopic.) for the products obtained in methanol and pyridine, respectively. The IR spectrum of $[Co(sal\text{-}L\text{-}his)H_2O]_2O_2$ is practically superimposable on that of $Co(sal\text{-}L\text{-}his)\cdot 2H_2O$, and that of $[Co(sal\text{-}L\text{-}his)py]_2O_2$ is also very similar except for the presence of a weak band at 840 cm^{-1} and a medium-intensity band at 700 cm^{-1} due to a pyridine vibration. The IR spectrum of the pyridine adduct $Co(sal\text{-}L\text{-}his)\cdot py$ is very complex, with apparent splitting of many of the bands observed for $Co(sal\text{-}L\text{-}his)\cdot 2H_2O$, and cannot be used for comparison purposes. The absorption and CD spectral data of freshly prepared DMF solutions of the peroxo complexes are as follows. For $[Co(sal\text{-}L\text{-}his)H_2O]_2O_2$, UV–vis λ_{max}, nm (ϵ, M^{-1}, cm^{-1}): 650 sh (200), 480 sh (330), 420 sh (1300), 395 (1600), 310 sh (3000). CD λ_{max}, nm ($\Delta\epsilon$): 625 (+2.09), 510 (+3.38), 425 (−3.73), 400 sh (−3.44), 316 (−1.43). For $[Co(sal\text{-}L\text{-}his)py]_2O_2$, UV–vis λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 620 sh (300), 480 sh (450), 420 sh (1400), 395 (1700), 310 sh (2750). CD λ_{max}, nm ($\Delta\epsilon$): 605 (+2.02), 490 (+3.12), 420 sh (−3.35), 395 (−3.95), 316 (−1.46). Magnetic susceptibility measurements at room temperature for the peroxo adducts correspond to an apparent μ_{eff} of ~ 1 μ_B. This residual paramagnetism may be due to small amounts of unreacted cobalt(II) complexes, since the oxygenations were carried out in heterogeneous media, or to some paramagnetic byproduct or impurity.

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(31) Pladziewicz, J. R.; Meyer, T. J.; Broomhead, J. A.; Taube, H. *Inorg. Chem.* **1973**, *12*, 639–643.

(32) See for instance: Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1966**, *5*, 1514–1517.

(33) The oxygenation product of Co(pdx-L-his) was obtained from a stirred suspension of the complex in methanol after exposure to air for 4 days. The analytical data are in agreement with the formulation $[Co(pdx\text{-}L\text{-}his)(H_2O)_2]_2O_2$ for the product (Anal. Calcd for $Co_2C_{28}H_{36}N_8O_{14}$: C, 40.69; H, 4.39; N, 13.56. Found: C, 40.33; H, 3.88; N, 13.00.) Absorption and CD spectral data in DMF solution are as follows. UV–vis λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 600 sh (280), 440 sh (1000), 400 (1500), 325 sh (3000). CD λ_{max}, nm ($\Delta\epsilon$): 620 (+1.58), 495 (+1.68), 435 (−3.90), 400 sh (−2.00), 360 sh (−2.10). The IR spectrum is practically identical with that of $Co(pdx\text{-}L\text{-}his)\cdot 2H_2O$. Magnetic susceptibility measurement at room temperature gave an apparent μ_{eff} or ~1.6 μ_B.

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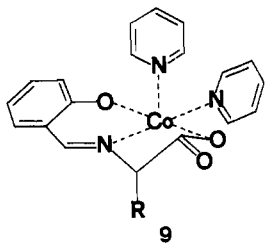
(35) See for instance: Konefal, E.; Loeb, S. J.; Stephan, D. W.; Willis, C. J. *Inorg. Chem.* **1984**, *23*, 538–545.

(36) (a) Boge, E. M.; Freyberg, D. P.; Kokot, E.; Mockler, G. M.; Sinn, E. *Inorg. Chem.* **1977**, *16*, 1655–1660. (b) Chen, Y.-Y.; Chu, D. E.; McKinney, B. D.; Willis, L. J.; Cummings, S. C. *Ibid.* **1981**, *20*, 1885–1892.

water molecules appear to be coordinated to the cobalt(II) centers and can effectively reduce or prevent polymerization in the solid state. The spectral oddities observed in solution for some of the complexes may be an indication that oligomeric structures are maintained in solutions of nonbasic solvents.

The light pink-orange colors and spectra of oxygen-free methanolic solutions of the cobalt(II) complexes are those typical of high-spin six-coordinate species. If octahedral symmetry labels are used for simplicity, the CD bands labeled I and II may be attributed to transitions to the split levels of the $^4T_{1g}(P)$ parentage and CD band III to the transition $^4A_{2g}(F)$,[37] while excitations to the parent $^4T_{2g}(F)$ occur beyond the long wavelength limit of the CD instrument. The broad CD activity above 600 nm probably results from contribution of spin-forbidden, dichroic transitions to the octahedral $^2T_{1g}(G)$ and $^2T_{2g}(G)$ parentages.[21,38] When the size of the solvent or other donor molecules like pyridine, DMF, or imidazole is relatively large it is likely that the complexes cannot achieve coordination numbers higher than five. This is indicated by the number of pyridine molecules found in the adducts that have been isolated in the solid state and by the CD spectra of the complexes recorded in pyridine or DMF solution. These invariably display imine CD bands of negative sign and, in particular, for the complexes derived from salicylaldehyde or pyridoxal indicate a λ conformation of the L-amino acid chelate ring and a pseudoaxial side chain.[2,3,8a] Therefore, when the complexes contain nonpolar side chains, one of the metal axial sites is not accessible to bulky donor molecules, as shown schematically by the pyridine adduct **9**. When the complexes are derived from histidine, there



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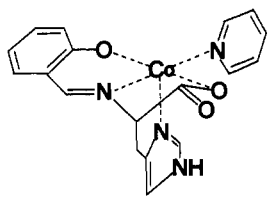
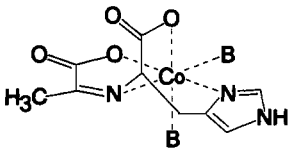
is apparently room only for a single bulky donor molecule, probably because the cobalt atom is displaced significantly from the equatorial plane toward the imidazole group, and the ligand assumes a reversed "umbrella shape" structure that hinders the approach to an additional, bulky axial ligand. This is suggested, besides the isolation of the monopyridine adduct **10**, by the sim-



10

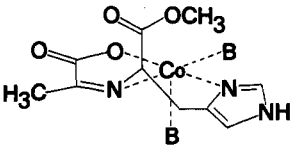
ilarity between the CD spectrum of Co(sal-L-ala) with excess imidazole (hence Co(sal-L-ala)·2im) and those of Co(sal-L-his) or Co(pdx-L-his).

In the pyruvate complexes of type **4** the histidine residues are bound histamine-like; as for the corresponding copper(II) complexes,[3a] this arrangement is revealed by CD spectra with an overall mirror-image relationship to those of the derivatives of amino acids with a nonpolar side chain of the same absolute configuration. Interestingly, while for the copper(II) complex Cu(pyv-L-his) an inversion of the CD spectrum in pyridine indicates that two base molecules occupy the axial positions and the histidine carboxylate group is noncoordinated,[3a] the CD spectrum of Co(pyv-L-his) remains unchanged in pyridine and shows that the carboxylate group is axially coordinated to cobalt(II); the structure of this complex is shown schematically by **11** (B stands for any donor molecule). For the methyl ester derivative Co(pyv-L-hisOMe)Cl



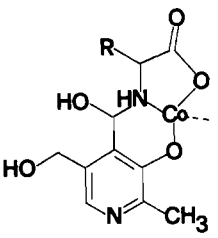
11

(**12**) the ester group is not coordinated, but its pseudoaxial disposition sterically hinders the access of bulky donor molecules to one of the axial sites.



12

Besides the electronic and CD bands associated with the imine chromophores, the spectra of the cobalt(II) complexes derived from salicylaldehyde and pyridoxal often display nonnegligible absorptions at 320–330 nm. These can be accounted for by chromophores containing sp^3-hybridized carbon atoms attached to the phenyl or pyridine rings of the ligands[39] but cannot be associated with the presence of ketimine species of type **8** at the equilibrium in solution. We attribute the 320–330-nm absorptions to carbinolamine species of type **13** and **14**. Carbinolamines are



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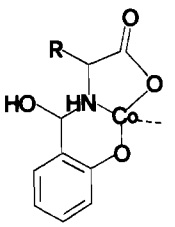
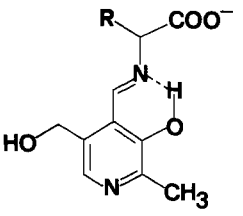


14

intermediates in the formation of Schiff bases,[25,40] and it is possible that some kind of stabilization of complexes of type **13** and **14**, or simply their low solubility, makes difficult the subsequent dehydration reaction to the corresponding imine complexes **1** and **2**. For the systems derived from pyridoxal, additional equilibria between the pyridine ring protonated (**7**) or nonprotonated (**1**) forms must be considered and we expect that different amounts of the two forms will be present in solutions of the complexes of types Co(pdx-L-aa) and Co(Hpdx-L-aa)Cl. Since these complexes behave as nonelectrolytes and, like the corresponding copper(II) complexes[3a] and the metal-free systems **15** and **16**,[41] display similar



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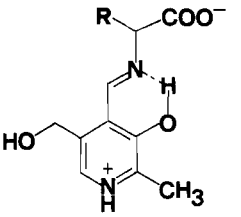


16

spectra it is difficult to establish the relative amounts of the two species **1** and **7** without detailed analysis. However, we can note

(37) In regular O_h symmetry the $^4T_{1g} \rightarrow {}^4A_{2g}$ transition is actually not dichroic, but components of this transition become magnetically allowed in fields of lower symmetry.
(38) Liehr, A. D. *J. Phys. Chem.* **1963**, *67*, 1314–1328.
(39) (a) Tobias, P. S.; Kallen, R. G. *J. Am. Chem. Soc.* **1975**, *97*, 6530–6539. (b) Korpela, T.; Mäkelä, M.; Lönnberg, H. *Arch. Biochem. Biophys.* **1981**, *212*, 581–588.
(40) (a) Cordes, E. H.; Jencks, W. P. *J. Am. Chem. Soc.* **1962**, *84*, 832–837. (b) Abbott, E. H.; Martell, A. E. *Ibid.* **1971**, *93*, 5852–5856. (c) Jo, B. H.; Nair, V.; Davis, L. *Ibid.* **1977**, *99*, 4467–4471.
(41) Metzler, C. M.; Cahill, A.; Metzler, D. E. *J. Am. Chem. Soc.* **1980**, *102*, 6075–6082.

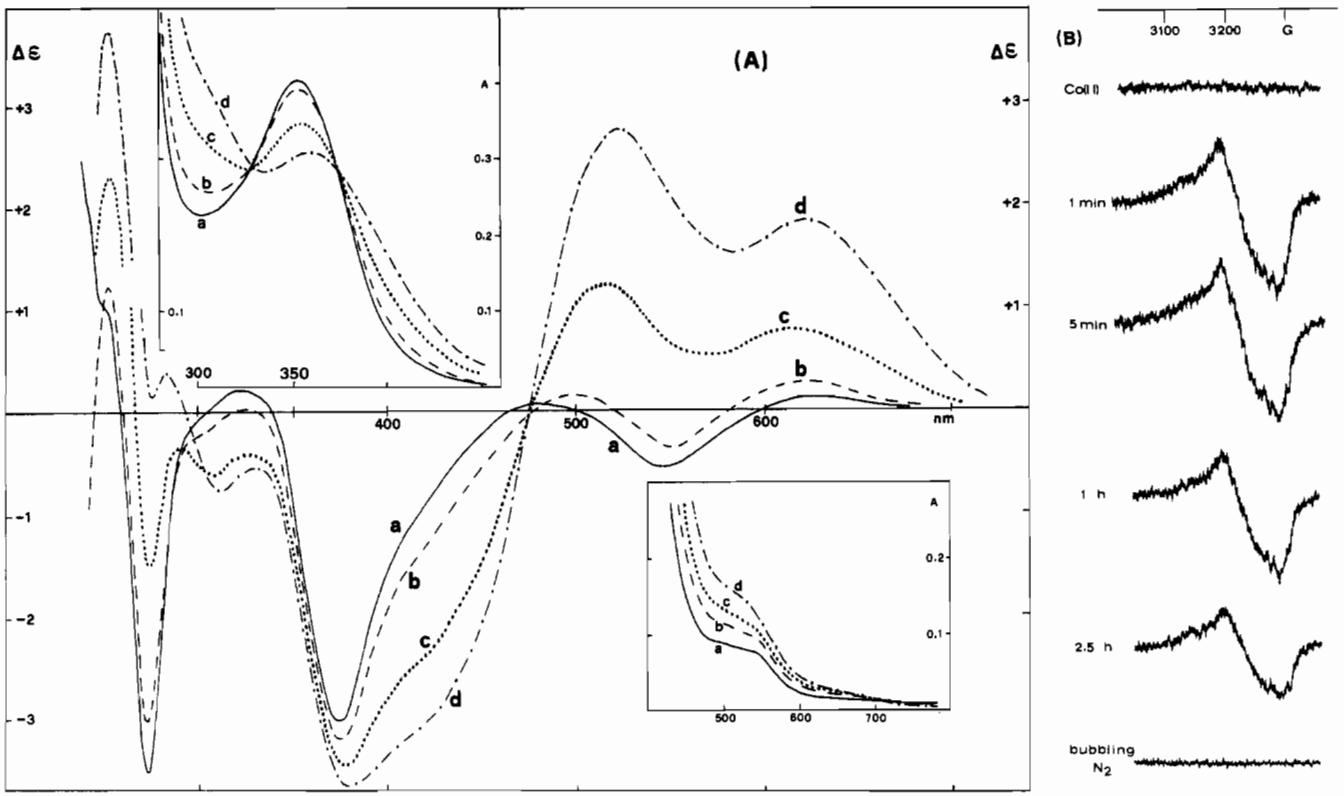
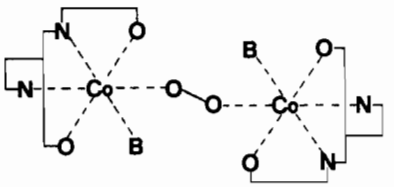


Figure 6. (A) Circular dichroism spectra recorded during the air oxygenation of Co(sal-L-his) in methanol solution at room temperature: (a) –, before oxygenation; (b) - -, within 5–10 min of the reaction; (c) ···, after 1 h; (d) – · –, after 5 h. Concentration of the complex = 1.2×10^{-3} M; cell path = 0.1 cm. The inserts show the corresponding electronic spectra recorded in the ranges 300–500 and 500–800 nm with cell paths of 0.1 and 1.0 cm, respectively. (B) ESR spectra at −140 °C of frozen methanol solutions of Co(sal-L-his) taken at different times of the oxygenation (ν = 9.072 GHz). Conditions are the same as in part A.

that the complexes of type Co(pdx-L-aa) and Co(Hpdx-L-aa)Cl exhibit appreciably different reactivity: the compound Co(Hpdx-L-ala)Cl undergoes racemization more easily than Co(pdx-L-ala), while Co(Hpdx-L-his)Cl reacts with dioxygen at a slower rate than Co(pdx-L-his). Both these aspects of the reactivity of cobalt(II)–pyridoxal model systems can be accounted for by considering that the conjugated pyridine system acts as an electron sink more effectively when the ring nitrogen atom is protonated.[7]

The most interesting property of the present series of cobalt(II)–imine complexes of amino acids is their reactivity to molecular oxygen. The histidine complexes Co(sal-L-his), Co(pdx-L-his), and Co(Hpdx-L-his)Cl undergo oxygenation reactions in solution even in the absence of an added base. The 1:1 Co–O_2 adducts formed initially can be detected by ESR spectroscopy,[42] but are not accumulated in solution, since readily they form the 2:1, ESR-silent Co–O_2–Co adducts. The magnitude of the Cotton effects in the visible CD spectra of these binuclear μ-peroxo adducts is consistent with a cobalt(III) description for their metal centers. Since the site symmetry for these low-spin d^6 cobalt(III) centers is represented at best by C_{2v}, the visible CD bands near 430, 500, and 600 nm can be assigned to magnetically allowed transitions to the split $^1T_{1g}(O_h)$ levels of cobalt(III) ($^1A_2$, $^1B_1$, and $^1B_2$ in C_{2v}). For bridging peroxo groups two closely spaced LMCT transitions are expected in the range 300–400 nm, labeled $\pi_a^* \rightarrow d\sigma^*$ and $\pi_b^* \rightarrow d\sigma^*$ according to an established notation.[43] The higher energy transition, $\pi_a^* \rightarrow d\sigma^*$, corresponds to the absorption and CD bands observed between 300 and 330 nm in the spectra of the oxygenated solutions, while the other is comprised within the broad absorption and CD bands centered near 400 nm. It is likely that the site of oxygen attack to the cobalt(II)–histidine complexes (see e.g. **10**) is trans to the imidazole group; therefore two structural types, **17** or **18**, are possible for the μ-peroxo adducts. Of these, the symmetric arrangement **17** is preferable on the basis of the almost identical spectra in different solvents, since it implies less steric crowding when B is equal to pyridine or DMF. In undried, protic solvents one equatorial position of these complexes is occupied by water, and a second μ-hydroxo bridge cis to the dioxygen bridge may form.[44] These doubly bridged μ-peroxo, μ-hydroxo species are generally characterized by a LMCT band near 350 nm,[43] where the absorption spectra of the present μ-peroxo–Co–histidine complexes exhibit a trough; therefore, they are probably not important in neutral solution. However, their contribution may become nonnegligible at higher pH, since the spectra in methanol solution of the peroxo complexes show a significant increase of absorption near 350 nm on mild basification.



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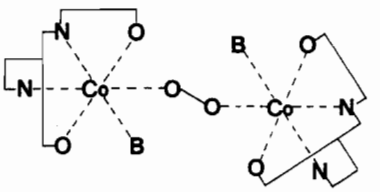

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(42) The small cobalt hyperfine splittings (10–20 G) and g values near 2.0 of the ESR signals are taken as evidence for 1:1 superoxocobalt(III) complexes.[11a,b] The eight-line pattern for $g_\parallel$ is sufficiently resolved in pyridine or DMF frozen-solution spectrum, though an accurate analysis of the ESR signals requires appropriate simulation and is beyond the scope of the present investigation.

(43) (a) Lever, A. B. P.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 348–355. (b) Reference 34, pp 285–296.

(44) Martell, A. E. *Acc. Chem. Res.* **1982**, *15*, 155–162.

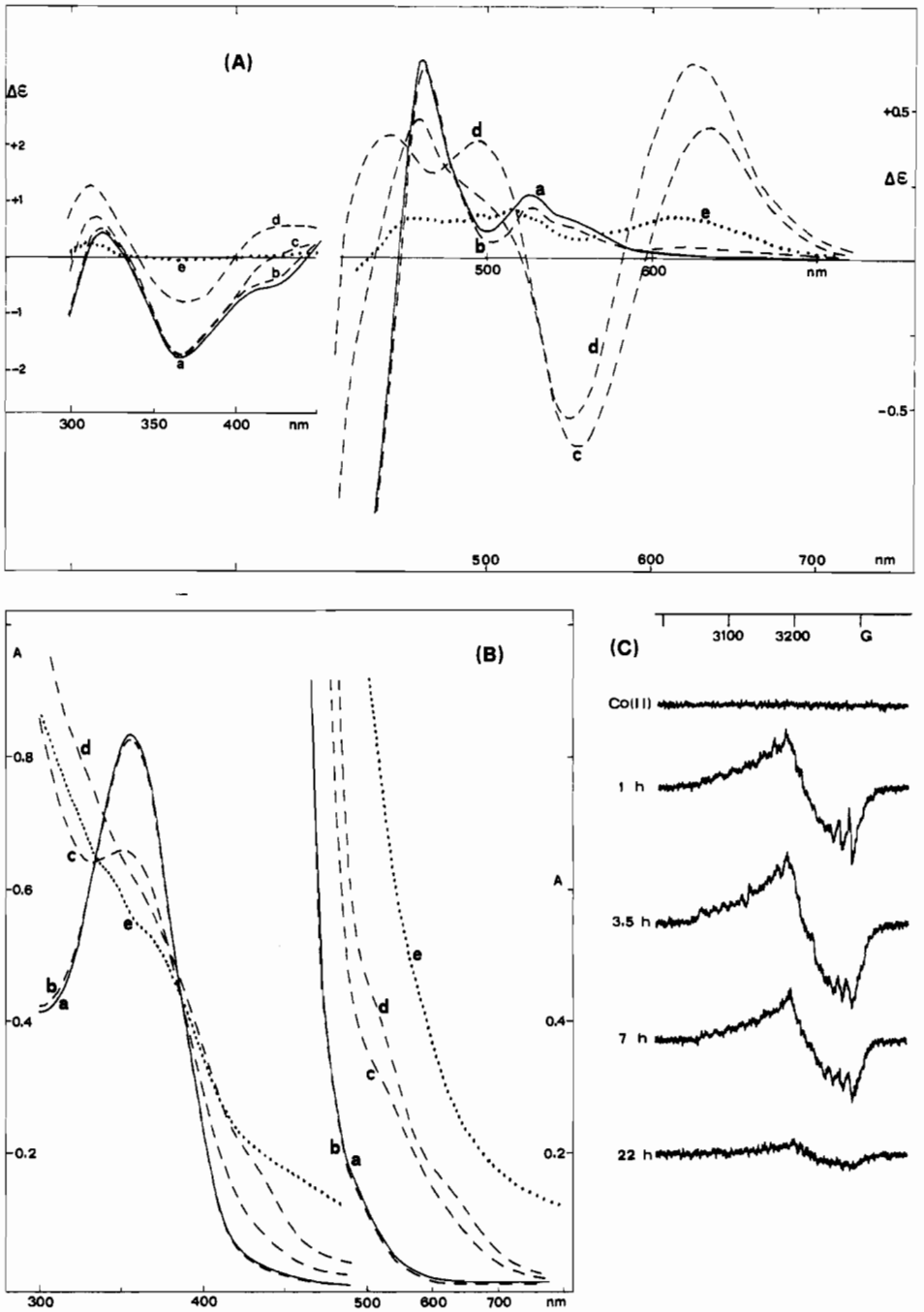

Figure 8. (A) Circular dichroism spectra recorded during the oxygenation (1 atm) of Co(sal-L-val) in dry pyridine at room temperature: (a) –, before oxygenation; (b, c, d) - -, after 3.5, 7, and 24 h of the reaction, respectively; (e) ···, after degassing and refluxing of solution d under a nitrogen stream for ~30 min. Concentration of the complex = 1.6×10^{-3} M. The spectrum in the range 300–450 nm was recorded with a 0.1-cm cell, that in the range 450–800 nm with a 1-cm cell. (B) Electronic structure of solutions a–e described in part A. (C) ESR spectra at −140 °C of frozen pyridine solutions of Co(sal-L-val) at different times of the oxygenation (ν = 9.079 GHz). Conditions are the same as in part A.

It is important to emphasize that the ready oxygenation reactions undergone by the histidine complexes derived from salicylaldehyde or pyridoxal is determined essentially by the presence of an axially coordinated imidazole group, i.e. by the glycine-like mode of binding of the histidine residues. When the histidine residue binds histamine-like, as in the pyruvate complex Co(pyv-L-his) (**11**) no dioxygen adduct is formed because the coordination position trans to the imidazole group is occupied by the carboxylate oxygen of the pyruvic residue. These results may be of some importance for the understanding of the oxygenation behavior of simple cobalt(II) complexes of histidine or histidine-containing peptides,[5,12,13,45] where many isomers can exist in solution but not all of them are likely to form dioxygen adducts.

The cobalt(II)–imine complexes of type **1** and **2** derived from amino acids with a nonpolar side chain and the pyruvate complex Co(pyv-L-hisOMe)Cl undergo oxygenation reactions when a coordinating base is present in solution. Since the base adducts of the cobalt(II) complexes derived from salicylaldehyde or pyridoxal have the structure shown schematically by **9**, it is likely that the site of oxygen attack is the axial coordination position trans to the added base. The formation of superoxo Co–O_2 adducts is evidenced by ESR spectroscopy,[42] and the evolution of these species depends on many factors: the type of carbonyl compound forming the imine ligand, the size of the amino acid side chain, the nature of the base added, and, likely, the temperature and oxygen pressure. Since we were interested mainly in the qualitative aspects of the reactivity of the cobalt(II)–pyridoxal model systems, we routinely followed the oxygenations at room temperature and 1

(45) (a) Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 385–426. (b) Gillard, R. D.; Spencer, A. *J. Chem. Soc., Dalton Trans.* **1972**, 902–907. (c) Harris, W. R.; Martell, A. E. *J. Am. Chem. Soc.* **1977**, *99*, 6746–6750.

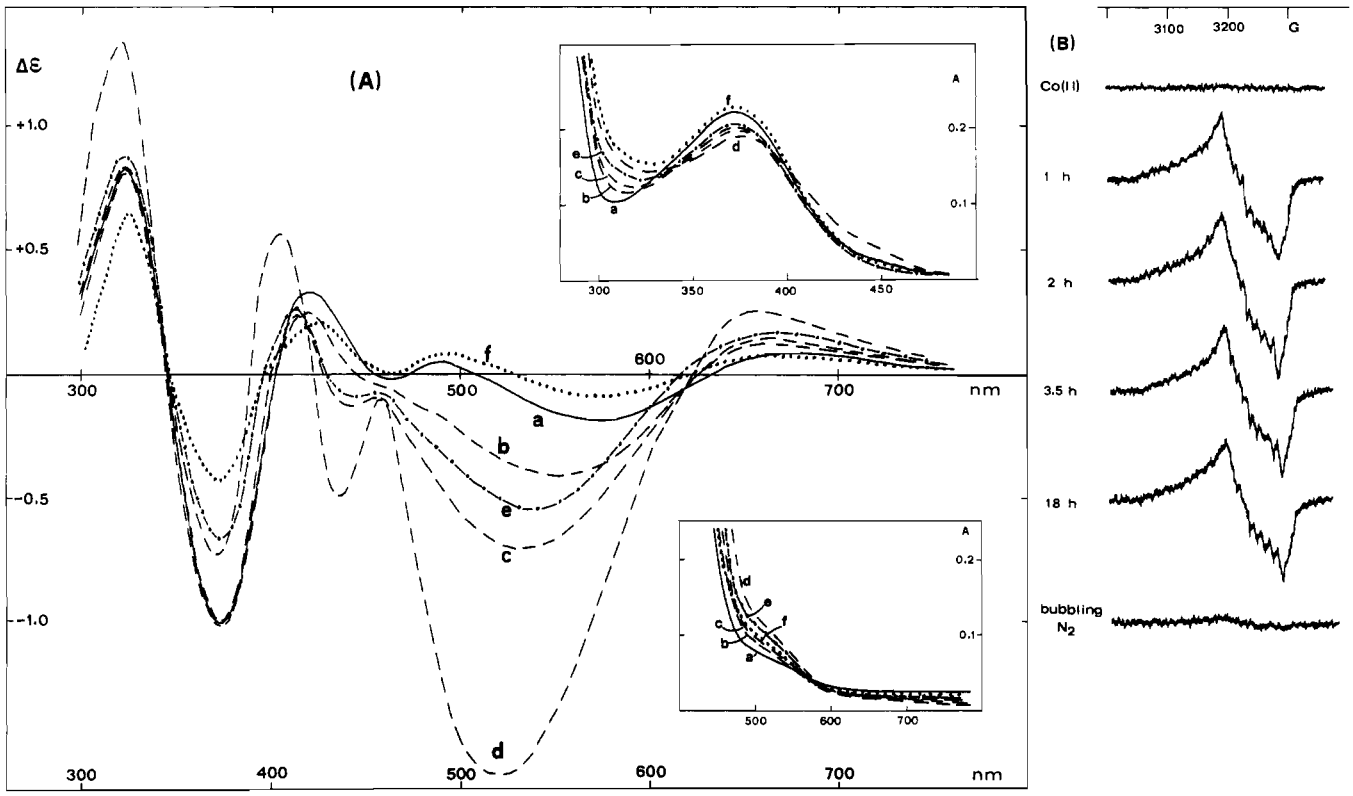

Figure 11. (A) Circular dichroism spectra recorded during the oxygenation (1 atm) of Co(pdx-L-val) in dry DMF at room temperature: (a) –, before oxygenation; (b, c, d) --, after 1, 3.5, and 18 h of the reaction, respectively; (e) –·–, after degassing and refluxing of solution d under a nitrogen stream for ~15 min; (f) ···, after refluxing of solution e for ~3 h under a nitrogen stream. Concentration of the complex = 6.5×10^{-4} M; cell path = 1.0 cm. The inserts show the corresponding electronic spectra in the range 300–500 nm (0.1-cm cell) and 500–800 nm (1.0-cm cell). (B) ESR spectra at −140 °C of frozen DMF solutions of Co(pdx-L-val) at various times of the oxygenation (ν = 9.080 GHz). Conditions are the same as in part A.

atm oxygen pressure. In these conditions the concentration of $Co–O_2$ species remains low, and all the prominent changes observed in the optical and CD spectra of the oxygenated solutions can be ascribed to the formation of ESR-silent, binuclear μ-peroxo adducts and, eventually, to some irreversibly oxidized cobalt(III) compounds. In general, the dimerization of the $Co–O_2$ adducts is relativley slow in pyridine but much faster in DMF solution. Also, the rate of dimerization in pyridine depends markedly on the size of the amino acid side chain, since we have found that, for both Co(sal-L-aa) and Co(pdx-L-aa) systems under oxygenation, the reaction time after which the intensity of the ESR signal begins to decrease and the optical and CD spectra show some significant changes increases in the order ala << val < phe. For the valine and phenylalanine complexes the formation of μ-peroxo dimers in (dilute) pyridine solutions is negligible within several hours of exposure to dioxygen, and under these conditions their oxygenation behavior appears fully reversible. On the other hand, the easy dimerization of the $Co–O_2$ adducts in DMF may be related to incomplete formation of bis(dimethylformamide) adducts of the cobalt(II) complexes according to the equilibria (B = DMF):

$$Co(L) + B \rightleftharpoons Co(L)(B) \quad (1)$$

$$Co(L)(B) + B \rightleftharpoons Co(L)(B)_2 \quad (2)$$

Dimerization of the $Co(L)(B)_2(O_2)$ adducts probably involves the less sterically hindered complexes Co(L)(B), rather than $Co(L)(B)_2$.

In conclusion, we have investigated several aspects of the chemistry of cobalt(II)–pyridoxal model systems. A number of representative complexes derived from salicylaldehyde, pyridoxal, and pyruvic acid have been prepared and characterized. A few adducts with donor bases have been isolated to establish the coordination number of the metal centers, but the most interesting adducts are those formed by the cobalt(II) complexes with molecular oxygen. Both monomeric, $Co–O_2$, and dimeric, $Co–O_2–Co$, adducts are formed, but in some cases the presence of a bulky side chain on the amino acid residue can virtually stop the dimerization of the 1:1 adducts and provide a reversible oxygenation behavior at room temperature. Combined ESR and optical/CD experiments are very useful to follow the oxygenation reactions since they give complementary information on the evolution of the 1:1 and 2:1 dioxygen adducts, respectively. Preliminary experiments show that these dioxygen adducts can perform oxidation reactions of organic substrates and that individual types of cobalt(II) complexes can serve as appropriate reagents for different substrates or different reaction media. Thus, for instance, while Co(sal-L-his) catalyzes the oxidation of 3,5-di-*tert*-butylcatechol by O_2,[46] the complexes containing nonpolar amino acid side chains do not perform this oxidation unless a base is added. By contrast, while Co(sal-L-ala) catalyzes the oxidation of benzylamine by O_2,[47] Co(sal-L-his) is totally inert in this reaction, possibly because this amine can form a stable bis adduct of the complex and prevent the buildup of $Co–O_2$ adduct. It is indeed surprising that in spite of the broad interest in the chemistry of pyridoxal model systems their reactivity to dioxygen was never reported before. Dioxygen adducts of pyridoxal complexes have been only proposed as intermediates in the oxidation of amines by O_2 catalyzed by pyridoxal and metal ions[48] and may have biological significance, since some copper-containing amine oxidases require an additional carbonyl compound identified as pyridoxal phosphate for activity[49] (but see ref 50 for a critical review).

(46) The reactions were carried out in dimethyl sulfoxide with [Co]/[catechol] = 10^{-2} and were followed through the characteristic absorption of 3,5-di-*tert*-butylquinone at 400 nm.
(47) The reactions were performed in boiling ethanol with [Co]/[amine] = 5/100. A product identified as *N*-benzylidenebenzylamine was detected by gas chromatography in 5–10% yield after a few hours.
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Acknowledgment. This work was supported by the Italian CNR. We thank M. S. Frazoni for measuring the magnetic susceptibility of the cobalt(II) complexes.

Registry No. **9** (R = CH_3), 101200-39-9; **9** (R = $CH(CH_3)_2$), 101200-40-2; **10**, 101200-41-3; Co(pdx-L-phe), 101200-35-5; Co(pyv-L-his), 101200-38-8; Co(sal-L-ala)·dab, 101200-42-4; $[Co(sal\text{-}L\text{-}his)H_2O]_2O_2$, 101200-43-5; $[Co(sal\text{-}L\text{-}his)py]_2O_2$, 101200-44-6; $[Co(pdx\text{-}L\text{-}his)(H_2O)_2]_2O_2$, 101226-94-2; sal, 90-02-8; L-ala, 56-41-7; L-val, 72-18-4; L-phe, 63-91-2; L-his, 71-00-1; HpdxCl, 65-22-5; pdx, 66-72-8; pyv, 127-17-3; L-hisOMe·2HCl, 7389-87-9; pdm, 85-87-0; phg, 611-73-4; O_2, 7782-44-7; 2-formylpyridine, 1121-60-4.

Supplementary Material Available: Listings of elemental analyses (Table I), complete IR data (Table III), electronic and CD spectral data in pyridine of the cobalt(II) complexes (Table V), and absorption and CD spectral data for various systems formed in situ in solution (Table VI) and electronic and CD spectra of Co(sal-L-ala) and various adducts (Figure 1), Co(sal-L-his) and Co(pdx-L-his) (Figure 2), and Co(pdx-L-val) (Figure 3) in various solvents, absorption spectra of the ternary system pyridoxamine–pyruvic acid–cobalt(II) (1:1:1) at various times (Figure 4), CD spectra of Co(pyv-L-his), Co(pyv-L-hisOMe)Cl, and the ternary system pyruvic acid–L-valine–cobalt(II) (1:1:1) (Figure 5), and absorption, CD, and frozen-solution ESR spectra recorded at various times of the oxygenation of Co(pdx-L-his) in DMF (Figure 7), Co(pdx-L-val) in pyridine (Figure 9), and Co(sal-L-val) in DMF (Figure 10) (18 pages). Ordering information is given on any current masthead page.

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Structures, ^1H NMR Spectra, and Ligand-Exchange Properties of Costa-Type Organocobalt B_{12} Models with P-Donor Ligands

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Received November 4, 1985

The first extensive series with L = P-donor ligands of the organocobalt B_{12} model $[LCo((DO)(DOH)pn)CH_3]X$ has been prepared and characterized by ^1H NMR spectroscopy, by L ligand dissociation rates, and by X-ray crystallography. Assignment of the CH_3 ^1H NMR signals by chemical shift alone is not possible since 1D NOE experiments demonstrate that the order of shifts is dependent on L. However, the 5-bond ^{31}P–^1H coupling constant is smaller for the oxime CH_3 than for the Schiff base CH_3. The relative dissociation rates of 10 different L ligands is ca. a factor of 2 greater than those of the analogous cobaloxime complexes. The dissociation rate increases by 10^4 across the series $P(OMe)_2Ph < P(OEt)Ph_2 < PEtPh_2 < P(OMe)_3 < P(4\text{-}Me_2NPh)_3 < PViPh_2 < P\text{-}i\text{-}PrPh_2 < PCyPh_2 < PEtCNPh_2 < PPh_3$ (Vi = vinyl). The three-dimensional structures of $[LCo((DO)(DOH)pn)CH_3]PF_6$, L = $P(OMe)_3$ (I) and L = PPh_3 (II), were determined. Crystallographic details follow. For I: $C_{15}H_{31}CoF_6N_4O_5P$, $C2/c$, a = 21.978 (4) Å, b = 8.331 (1) Å, c = 27.713 (4) Å, d(calcd) = 1.54 g cm^{-3}, Z = 8, R = 0.055 for 2893 independent reflections. For II: $C_{30}H_{37}CoF_6N_4O_2P$, $Pbca$, a = 17.115 (6) Å, b = 25.424 (3) Å, c = 14.866 (2) Å, d(calcd) = 1.48 g cm^{-3}, Z = 8, R = 0.051 for 3294 independent reflections. These are the first two P-donor ligand complexes characterized by X-ray methods in the $[LCo((DO)(DOH)pn)R]X$ class of B_{12} models. Only minor differences are found between the structures of I and II and the analogous cobaloximes (except, of course, for differences that arise from the different equatorial ligands). It can be concluded that the two different types of model do not differ greatly in the Co(III) states except for somewhat greater sensitivity to L bulk of L leaving rates of $[LCo((DO)(DOH)pn)CH_3]^+$. Combined with the well-established greater ease of reduction to Co(II) in the Costa system, these differences suggest that the Costa-type system is superior to the cobaloximes as B_{12} models.

Introduction

Organocobalt B_{12} model compounds have been the subject of much recent interest.[1-6] In particular, factors that influence Co–C bond stability in such compounds provide valuable insight into the avenues available for coenzyme B_{12}-dependent enzymes to promote Co-C bond homolysis—an important step in the catalytic process.[1,6]

The longstanding hypothesis and most widely accepted explanation for the enzymic process falls under the umbrella term "mechanochemical trigger". In general, it is felt that an enzyme-induced conformational change in the coenzyme leads to a conformation with a greatly weakened Co–C bond.[1] The subsequent more facile Co–C bond homolysis generates a deoxyadenosyl radical, which in turn promotes radical rearrangement reactions characteristic of B_{12}-dependent processes.[6]

Two different types of conformational change have been postulated as possibly being responsible for Co–C bond weakening. Both possibilities are made credible by comparison of Co–C bond dissociation energies (BDE's) to structure.

First, the longer held and more widely accepted explanation for the "trigger" mechanism involves direct steric interaction between the corrin ring and the deoxyadenosyl moiety.[1,7,8] More specifically, the amide side chains of the corrin are believed to interact with the enzyme.[7] A conformational change in the enzyme could increase steric interactions involving the adenosyl moiety—weakening and perhaps breaking the Co–C bond. In addition to evidence that conformational changes do take place in enzymic systems, studies on models provide support for this mechanism. For example, Halpern and co-workers have demonstrated weak Co–C bonds in complexes of the type $LCo(DH)_2CHMePh$, when L = bulky phosphine ligands.[9] (DH = monoanion of dimethylglyoxime and these compounds are collectively known as cobaloximes.) In turn, we have demonstrated by crystallographic and NMR methods that such bulky phosphine ligands distort the $Co(DH)_2$ moiety toward R.[10,11] Taken together, this evidence demonstrates the feasibility of promoting Co–C bond

[†] Emory University.
[‡] Universita di Trieste.

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