

Models for Cobalt(II)-Substituted Zinc Metalloenzymes. 1. Comparison of the Crystal Structures of Complexes of the Type $[M(\text{RCOO})_2(\text{Im})_2]$ (Im = Imidazole; M = Co, Zn; R = CH₃, C₂H₅)

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The structures of 4-coordinate bis(acetato)bis(imidazole)cobalt(II) and -zinc(II) and the bis(propionato) analogues have been determined by X-ray diffraction on a CAD4 automatic diffractometer using Mo K α radiation and operating in a θ - 2θ scan mode. The four complexes $[\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_3\text{H}_4\text{N}_2)_2]$, $[\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_3\text{H}_4\text{N}_2)_2]$, $[\text{Co}(\text{C}_3\text{H}_5\text{O}_2)_2(\text{C}_3\text{H}_4\text{N}_2)_2]$, and $[\text{Zn}(\text{C}_3\text{H}_5\text{O}_2)_2(\text{C}_3\text{H}_4\text{N}_2)_2]$ crystallize in space groups $P\bar{1}$, $P\bar{1}$, $P2_1/c$, and $P\bar{1}$, respectively. They have the following respective unit cell constants: $a = 8.058$ (2), 8.065 (3), 7.971 (6), 7.841 (4) Å; $b = 11.245$ (1), 11.321 (2), 8.373 (1), 8.164 (2) Å; $c = 7.792$ (3), 7.736 (2), 23.703 (3), 12.392 (2) Å; $\alpha = 99.78$ (2), 99.81 (2), ..., 95.72(2)°; $\beta = 96.10$ (2), 96.31 (3), 98.32 (2), 96.55 (2)°; $\gamma = 92.66$ (2), 92.34 (2), ..., 94.47 (3)°. The respective Z values are 2, 2, 4, and 2. The structures were solved by heavy-atom methods and refined to final respective R values of 0.034, 0.036, 0.049, and 0.046. The first coordination spheres of the discrete complexes are distorted tetrahedra with bond angles centered on the metal ranging from 11° greater than to 15° less than the tetrahedral angle. The distortions appear to be independent of the metal. The metal-ligand bond distances are virtually identical for cobalt(II) and zinc(II). Implications of the results with regard to cobalt(II)-substituted zinc proteinases are discussed.

Introduction

Invaluable information concerning the chemical constitution and general stereochemistry of active metal ion sites is provided by crystallographic studies on metalloproteins. These structural results, which are of necessarily modest resolution, are the focus of attempts to synthesize structural and electronic mimics of these active sites in the form of model complexes.¹ Such models can then be subjected to high-resolution structural and other physical studies capable of elucidating details that cannot be determined from experiments on the macromolecular systems themselves. Particularly fruitful are parallel studies on metalloenzymes and on realistic models that, together, are capable of providing detailed information regarding the electronic and stereochemical structure of an active metal site.

Of particular interest here are crystallographic results on the zinc-requiring proteolytic enzymes carboxypeptidase A² and thermolysin.³ These studies have established that the active zinc site involves coordination by two imidazole moieties of histidine side chains, a carboxylate group from a glutamic acid residue, and a water molecule or hydroxide, which completes a highly distorted tetrahedral $[\text{ZnN}_2\text{O}_2]$ first coordination sphere. The study of the metal ion site of zinc metalloenzymes by physical techniques is hampered by the absence in the zinc(II) ion of suitable spectroscopic properties. A well-known approach to this problem is to substitute the open-shell, d^7 , cobalt(II) ion for zinc(II) ion at the active site.⁴ The cobalt(II)-substituted proteinases are active, attesting to the viability of the substitution, although no X-ray structure of the substituted proteolytic enzymes have been reported.

The spectroscopic parameters obtained from studies of various cobalt(II)-substituted proteins have generally been treated in a phenomenological fashion and used to monitor changes occurring at the active site as a function of changes in various biochemical parameters (pH, ionic strength, inhibitor binding, etc.). Owing to the dearth of realistic models for the active site in zinc proteinases or their cobalt analogues little in the way of a detailed interpretation of the spectroscopic

results has been offered. We have recently reported⁵ that 4-coordinate complexes of the type $[\text{Co}(\text{RCOO})_2(\text{Im})_2]$, where R = alkyl and Im is imidazole or a substituted imidazole, have visible absorption spectra and magnetic circular dichroism spectra remarkably similar to those of cobalt(II)-substituted carboxypeptidase A and thermolysin. This result suggests that the $[\text{CoN}_2\text{O}_2]$ coordination unit in these model complexes is a reasonably close mimic of the metal ion environment in these proteins.

The present research represents part of a program designed to scrutinize these and related complexes in detail by using crystallographic, spectroscopic, and magnetic resonance techniques. In particular, the present paper presents the first detailed structural comparison between corresponding cobalt(II) and zinc(II) model complexes of biologically relevant ligands. Our aim was to determine to what extent the complexes of these two metal ions differ in their structural parameters. It is noteworthy that this comparison is made with use of monodentate ligands so that any metal-dependent preferences will be reflected. Chelate ring and other constraints on ligand juxtaposition such as may occur in macromolecular systems owing to the tertiary structure of the protein are absent in the present models.

Experimental Section

Crystal Preparation. The $[\text{M}(\text{OAc})_2(\text{Im})_2]$ and $[\text{M}(\text{pr})_2(\text{Im})_2]$ (M = Co, Zn; OAc = acetate, pr = propionate) complexes were prepared as described elsewhere.^{5,6} $[\text{Co}(\text{OAc})_2(\text{Im})_2]$ has a measured density of 1.52 (2) g/mL.⁷ Crystals were grown by slow evaporation of 95% ethanol solutions. Irregularly shaped red-purple (Co(II)) or colorless (Zn(II)) crystals with the approximate dimensions listed in Table I were chosen for data collection. These were mounted with epoxy glue on glass fibers coincident with the longest crystal dimension.

Data Collection and Reduction. Our current crystallographic protocol will be described rather completely here and will not be repeated in detail in subsequent papers. A given crystal was optically centered on an Enraf-Nonius four-circle CAD4 automated diffractometer controlled by a PDP8/a computer coupled to a PDP11/34 computer. A full rotation orientation photograph was taken with the polaroid cassette accessory, and 25 rather intense reflections were chosen and centered with use of manufacturer-supplied software.⁸ The

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(3) Matthews, B. W.; Weaver, L. H.; Kester, W. R. *J. Biol. Chem.* **1974**, *249*, 8030.
(4) Vallee, B. L.; Riordan, J. F.; Johansen, J. T.; Livingston, D. M. *Cold Spring Harbor Symp. Quant. Biol.* **1971**, *36*, 517.

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(6) Doby-Duclaux, A.; May, A. *Bull. Soc. Chim. Biol.* **1970**, *52*, 1447.
(7) Gadet, A. *Acta Crystallogr., Sect. B* **1974**, *B30*, 349.

Table I. Crystallographic Parameters and Refinement Data

	[Co(OAc) ₂ (Im) ₂]	[Zn(OAc) ₂ (Im) ₂]	[Co(pr) ₂ (Im) ₂]	[Zn(pr) ₂ (Im) ₂]
formula	CoO ₄ N ₄ C ₁₀ H ₁₄	ZnO ₄ N ₄ C ₁₀ H ₁₄	CoO ₄ N ₄ C ₁₂ H ₁₈	ZnO ₄ N ₄ C ₄ C ₁₂ H ₁₈
space group	P1	P1	P2 ₁ c	P1
Z	2	2	4	2
cryst size, mm	0.15 × 0.25 × 0.45	0.12 × 0.12 × 0.34	0.07 × 0.24 × 0.44	0.18 × 0.45 × 0.52
a, Å	8.058 (2)	8.065 (3)	7.971 (6)	7.841 (4)
b, Å	11.245 (1)	11.321 (2)	8.373 (1)	8.164 (2)
c, Å	7.792 (3)	7.736 (2)	23.703 (3)	12.392 (2)
α, deg	99.78 (2)	99.81 (2)		95.72 (2)
β, deg	96.10 (2)	96.31 (3)	98.32 (2)	96.55 (2)
γ, deg	92.66 (2)	92.34 (2)		94.47 (3)
V, Å ³	690.3 (5)	690.6 (7)	1565 (2)	781.0 (8)
d _{calcd} , g cm ⁻³	1.507	1.537	1.448	1.478
abs coeff (μ), cm ⁻¹	13.09	18.47	11.62	16.41
no. of variables	172	172	190	190
measd refl	4269	4296	5189	2975
refl > 2σ(I)	3414	2696	2490	2271
ρ	0.015	0.015	0.020	0.015
2θ _{max} , deg	40	40	40	40
A, deg	0.70	0.55	0.50	0.60
R	0.034	0.036	0.049	0.046
R _w	0.041	0.036	0.046	0.057
drift cor	0.914–1.058		0.958–1.069	

INDEX program was used to obtain an orientation matrix and unit cell parameters. Successive centerings and least-squares refinements of 2θ values found for the 25 precisely centered reflections gave the lattice constants listed in Table I for each of the four crystals. Program TRACER was used to determine the appropriateness of the unit cell initially chosen, and a transformation was applied in cases where the initial choice was unsatisfactory. A small test data set (axial and zero-layer reflections) was collected to determine the systematic absences, if any. The space groups thus chosen are given in Table I and are confirmed by the successful refinement of the structures. The number of formula units per unit cell, Z (Table I), was determined on the basis of the measured density of the cobalt acetate complex.

Intensity data were collected at room temperature ($\lambda = 0.71073$ Å) with a graphite single-crystal monochromator (using Mo $K\alpha$ radiation (takeoff angle 2.8°). A θ - 2θ scan mode was used with 2θ ranging from $(A + 0.347 \tan \theta)^\circ$ below the calculated position of the $K\alpha_1$ reflection to $(A + 0.347 \tan \theta)^\circ$ above the calculated position of the $K\alpha_2$ reflection. The A values used are given in Table I. The scan rate was varied automatically from 1 to 5° min^{-1} , depending on the intensity of a reflection as determined by a preliminary brief scan. Background counts were measured with the detector stationary and positioned at the beginning and end of the scan each for one-fourth of the total scan time. Three standard reflections were measured after every 80 min of X-ray irradiation, and the same reflections were recentered automatically after every 200 reflections to check on crystal orientation and stability. The total numbers of unique reflections measured and their numbers with respect to the standard deviation in intensity, $\sigma(I)$, are indicated in Table I for each of the crystals.

Linear absorption coefficients for Mo $K\alpha$ radiation are given in Table I. ϕ scans indicated absorption problems were not severe, and no absorption corrections were applied. The data were processed by manufacturer-supplied software.⁸ The integrated intensity, I , was calculated according to the expression⁹ $I = [\text{SC} - 2(B_1 + B_2)]T_R$, where SC is the count accumulated during the scan, B_1 and B_2 are the background counts at each end of the scan, and T_R is the 2θ scan rate in degrees per minute. $\sigma(I)$ was calculated as follows: $\sigma(I) = T_R[\text{SC} + 4(B_1 + B_2) + (\rho I)^2]^{1/2}$, where the ρ values are indicated in Table I.

In two cases the standard reflections were used to rescale the data automatically to correct for drift due to changes in temperature, centering, etc. during data collection. The ranges of random long-term drift are indicated in Table I. The unique, normalized, integrated intensity set was processed to give F and E values. The polarization corrections were calculated under the assumption that the incident beam is polarized to some extent by the monochromator. The graphite

Table II. Positional Parameters and Their Estimated Standard Deviations for [Co(OAc)₂(Im)₂]

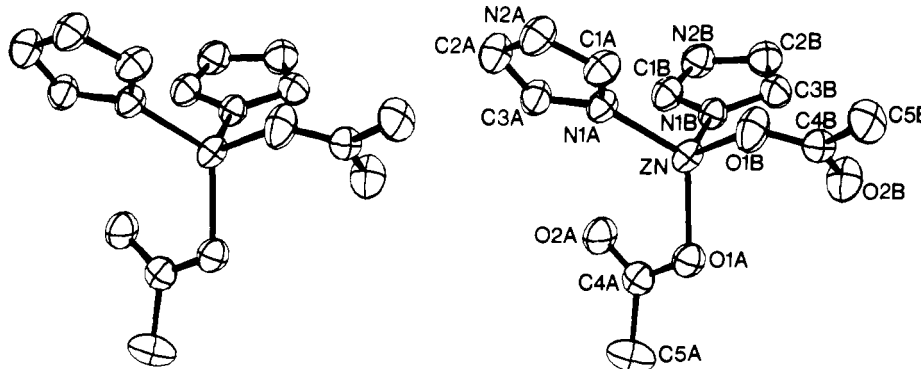
atom	x	y	z
Co	0.41629 (3)	0.24555 (2)	0.16154 (3)
O1A	0.3098 (2)	0.3495 (1)	0.3492 (2)
O1B	0.4301 (2)	0.0881 (1)	0.2369 (2)
O2A	0.4009 (2)	0.4676 (1)	0.1808 (2)
O2B	0.1569 (2)	0.0643 (1)	0.2319 (2)
N1A	0.6638 (2)	0.2695 (1)	0.1503 (2)
N1B	0.2968 (2)	0.2288 (1)	-0.0827 (2)
N2A	0.9262 (2)	0.2251 (2)	0.1671 (2)
N2B	0.2487 (2)	0.2565 (2)	-0.3531 (2)
C1A	0.7718 (3)	0.1918 (2)	0.1951 (3)
C2A	0.9187 (3)	0.3296 (2)	0.1010 (3)
C3A	0.7574 (2)	0.3563 (2)	0.0908 (3)
C4A	0.3269 (2)	0.4543 (2)	0.3075 (3)
C5A	0.2547 (4)	0.5570 (2)	0.4152 (4)
C1B	0.3358 (3)	0.2959 (2)	-0.1982 (3)
C2B	0.1480 (3)	0.1586 (2)	-0.3380 (3)
C3B	0.1783 (3)	0.1427 (2)	-0.1717 (3)
C4B	0.2984 (2)	0.0290 (2)	0.2561 (2)
C5B	0.3209 (3)	-0.0904 (2)	0.3138 (3)

crystal was assumed to be 50% perfect and 50% perfectly mosaic for this purpose.

Structure Solution and Refinement. The position of the metal atom in each case was determined from a sharpened, origin-removed Patterson map. The remaining non-hydrogen atoms were located with one or two Fourier syntheses. Hydrogen atoms were located at their calculated positions. In the case of methyl groups a tetrahedral model was used wherein the hydrogen atoms were placed at positions giving the closest agreement with peaks found in difference Fourier maps ($C-H = 0.97$ Å; $N-H = 0.87$ Å). All hydrogen atoms were assigned isotropic temperature parameters¹⁰ of $B = 5.0$ Å². The number of parameters including overall scale factor, positional parameters, and anisotropic thermal parameters¹⁰ varied in each case are listed in Table I. None of the parameters for the hydrogen atoms was varied. Neutral-atom scattering factors were those given by Cromer and Mann¹¹ and by Stewart et al.¹² for non-hydrogen and hydrogen atoms, respectively. Real and imaginary anomalous dispersion corrections to the atomic scattering factors were included.¹³ In the last cycle of least-squares refinement the maximum parameter shift was less

- (8) All programs used in data collection reduction and refinement are part of the "Enraf-Nonius Structure Determination Package"; Enraf-Nonius: Delft, The Netherlands, 1975, revised 1977.
 (9) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.
 (10) Isotropic thermal parameters are of the form $\exp[-B(\sin^2 \theta)/\lambda^2]$; anisotropic parameters are of the form $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$.

- (11) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.
 (12) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
 (13) "International Tables for X-Ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, U. K., 1968; Vol. III, Table 3.3.2C, pp 2115–2116.

Figure 1. Stereoview of $[\text{Zn}(\text{OAc})_2(\text{Im})_2]$.Table III. Positional Parameters and Their Estimated Standard Deviations for $[\text{Zn}(\text{OAc})_2(\text{Im})_2]$

atom	x	y	z
Zn	0.41615 (4)	0.23961 (3)	0.15401 (4)
O1A	0.3097 (2)	0.3459 (2)	0.3364 (2)
O1B	0.4268 (2)	0.0858 (2)	0.2370 (3)
O2A	0.4039 (2)	0.4754 (2)	0.1858 (2)
O2B	0.1540 (2)	0.0596 (2)	0.2245 (3)
N1A	0.6624 (2)	0.2648 (2)	0.1469 (3)
N1B	0.2952 (2)	0.2277 (2)	-0.0881 (2)
N2A	0.9235 (3)	0.2221 (2)	0.1652 (3)
N2B	0.2484 (3)	0.2563 (2)	-0.3605 (3)
C1A	0.7704 (3)	0.1873 (2)	0.1907 (4)
C2A	0.9152 (3)	0.3266 (3)	0.1007 (4)
C3A	0.7535 (3)	0.3530 (2)	0.0902 (4)
C4A	0.3279 (3)	0.4532 (2)	0.3055 (3)
C5A	0.2492 (5)	0.5496 (3)	0.4202 (5)
C1B	0.3363 (3)	0.2940 (2)	-0.2037 (3)
C2B	0.1452 (4)	0.1609 (3)	-0.3462 (4)
C3B	0.1738 (3)	0.1438 (2)	-0.1785 (3)
C4B	0.2958 (3)	0.0263 (2)	0.2543 (3)
C5B	0.3204 (4)	-0.0908 (3)	0.3176 (4)

Table IV. Positional Parameters and Their Estimated Standard Deviations for $[\text{Co}(\text{pr})_2(\text{Im})_2]$

atom	x	y	z
Co	0.83312 (6)	0.41800 (6)	0.12517 (2)
O1A	0.7774 (3)	0.4331 (3)	0.2047 (1)
O1B	0.6334 (3)	0.3331 (3)	0.0730 (1)
O2A	0.7481 (4)	0.1763 (3)	0.1908 (1)
O2B	0.8176 (3)	0.3946 (3)	0.0174 (1)
N1A	1.0642 (3)	0.3154 (3)	0.1285 (1)
N1B	0.8555 (4)	0.6585 (3)	0.1157 (1)
N2A	1.3248 (3)	0.2799 (4)	0.1112 (1)
N2B	0.8326 (4)	0.9108 (4)	0.1355 (1)
C1A	1.1761 (4)	0.3505 (4)	0.0942 (1)
C2A	1.3101 (5)	0.1954 (4)	0.1595 (2)
C3A	1.1482 (4)	0.2164 (4)	0.1698 (1)
C4A	0.7457 (5)	0.2932 (5)	0.2217 (1)
C5A	0.7005 (7)	0.2788 (5)	0.2805 (2)
C6A	0.6552 (8)	0.1245 (7)	0.2995 (2)
C1B	0.8057 (5)	0.7628 (5)	0.1524 (2)
C2B	0.9010 (6)	0.9038 (5)	0.0867 (2)
C3B	0.9149 (5)	0.7471 (4)	0.0744 (2)
C4B	0.6789 (5)	0.3392 (4)	0.0237 (1)
C5B	0.5570 (5)	0.2764 (6)	-0.0258 (2)
C6B	0.6218 (7)	0.1392 (7)	-0.0540 (2)

than 0.33 of a standard deviation. The final R values¹⁴ are listed in Table I. Final difference Fourier maps showed no peaks greater than $0.31 \text{ e } \text{Å}^{-3}$, with the largest usually located $\sim 1 \text{ Å}$ from the metal atom.

Results and Discussion

The crystal structures of the four complexes of the type $[\text{M}(\text{OAc})_2(\text{Im})_2]$ and $[\text{M}(\text{pr})_2(\text{Im})_2]$ where $\text{M} = \text{Co}$ or Zn have been determined. The crystallographic and structure

Table V. Positional Parameters and Their Estimated Standard Deviations for $[\text{Zn}(\text{pr})_2(\text{Im})_2]$

atom	x	y	z
Zn	0.16632 (8)	0.39618 (7)	0.25569 (5)
O1A	0.2378 (5)	0.3813 (4)	0.1099 (3)
O1B	0.3469 (4)	0.3077 (4)	0.3509 (3)
O2A	0.2478 (5)	0.1113 (4)	0.0834 (3)
O2B	0.1826 (5)	0.3888 (5)	0.4733 (3)
N1A	-0.0703 (5)	0.2856 (5)	0.2478 (3)
N1B	0.1612 (5)	0.6431 (4)	0.2732 (3)
N2A	-0.3403 (5)	0.2518 (5)	0.2734 (4)
N2B	0.1773 (6)	0.8942 (5)	0.2275 (4)
C1A	-0.1843 (7)	0.3252 (6)	0.3127 (4)
C2A	-0.3263 (7)	0.1601 (6)	0.1783 (5)
C3A	-0.1592 (7)	0.1799 (6)	0.1615 (4)
C4A	0.2605 (7)	0.2496 (6)	0.0525 (4)
C5A	0.3083 (11)	0.2667 (7)	-0.0593 (5)
C6A	0.2842 (13)	0.4184 (10)	-0.1046 (6)
C1B	0.2066 (7)	0.7371 (6)	0.1982 (4)
C2B	0.1130 (8)	0.9012 (6)	0.3241 (5)
C3B	0.1029 (7)	0.7450 (6)	0.3527 (4)
C4B	0.3090 (7)	0.3252 (6)	0.4495 (4)
C5B	0.4323 (9)	0.2583 (8)	0.5324 (5)
C6B	0.3682 (11)	0.1758 (11)	0.6125 (7)

Table VI. Selected Bond Distances (Å) and Angles (Deg)

	$\text{Co}(\text{OAc})_2\text{-(Im)}_2$	$\text{Zn}(\text{OAc})_2\text{-(Im)}_2$	$\text{Co}(\text{pr})_2\text{-(Im)}_2$	$\text{Zn}(\text{pr})_2\text{-(Im)}_2$
M-O1A	2.005 (1)	1.987 (1)	2.002 (2)	1.947 (2)
M-O1B	1.962 (1)	1.958 (1)	2.000 (2)	1.967 (2)
M-N1A	2.013 (1)	2.003 (2)	2.023 (2)	1.987 (2)
M-N1B	2.014 (1)	1.995 (2)	2.037 (2)	2.010 (2)
M-O2A	2.485 (1)	2.645 (2)	2.698 (2)	3.151 (2)
M-O2B	3.009 (1)	3.034 (2)	2.547 (2)	2.692 (2)
O1A-C4A	1.280 (2)	1.283 (2)	1.276 (3)	1.265 (4)
O1B-C4B	1.263 (2)	1.261 (2)	1.274 (3)	1.286 (4)
O2A-C4A	1.232 (2)	1.220 (2)	1.224 (3)	1.228 (3)
O2B-C4B	1.230 (2)	1.228 (2)	1.228 (3)	1.206 (4)
O1A-M-O1B	105.1 (1)	104.8 (1)	109.8 (1)	106.8 (1)
N1A-M-N1B	108.6 (1)	109.9 (1)	109.3 (1)	110.4 (1)
O1A-M-N1A	119.5 (1)	118.5 (1)	108.3 (1)	109.2 (1)
O1A-M-N1B	115.4 (1)	112.8 (1)	94.4 (1)	95.9 (1)
O1B-M-N1A	94.6 (1)	96.0 (1)	120.8 (1)	116.3 (1)
O1B-M-N1B	111.4 (1)	113.8 (1)	111.0 (1)	116.0 (1)
M-O1A-C4A	102.3 (1)	107.0 (1)	108.7 (2)	125.9 (2)
M-O1B-C4B	120.0 (1)	121.3 (1)	104.3 (2)	108.4 (2)
M-N1A-C1A	122.8 (1)	122.7 (1)	124.9 (2)	125.5 (2)
M-N1B-C1B	124.1 (1)	124.0 (1)	122.5 (2)	122.6 (2)
M-N1A-C3A	131.8 (1)	131.1 (1)	129.0 (2)	127.1 (2)
M-N1B-C3B	129.9 (1)	129.7 (1)	131.3 (2)	130.5 (2)

refinement parameters are set out in Table I. The final atomic positional parameters for the complexes $[\text{Co}(\text{OAc})_2(\text{Im})_2]$, $[\text{Zn}(\text{OAc})_2(\text{Im})_2]$, $[\text{Co}(\text{pr})_2(\text{Im})_2]$, and $[\text{Zn}(\text{pr})_2(\text{Im})_2]$ are set out in Tables II–V, respectively. The hydrogen atom parameters are given in Tables A–D;¹⁵ the anisotropic thermal pa-

(14) $R = \sum F_o - F_c / \sum F_o$; $R_w = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$, $w = 1/\sigma(F_o)^2$.

(15) Supplementary material.

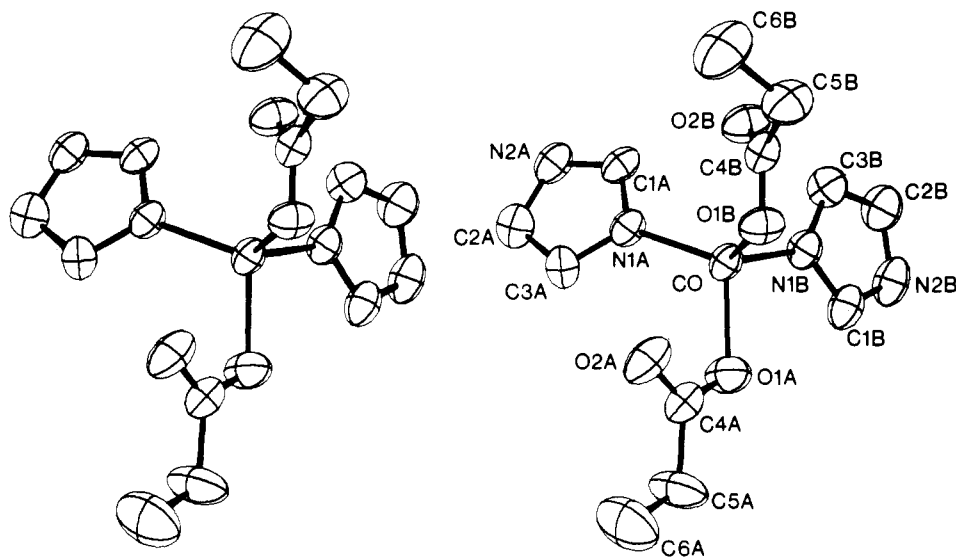


Figure 2. Stereoview of $[\text{Co}(\text{pr})_2(\text{Im})_2]$, space group $P2_1/c$.

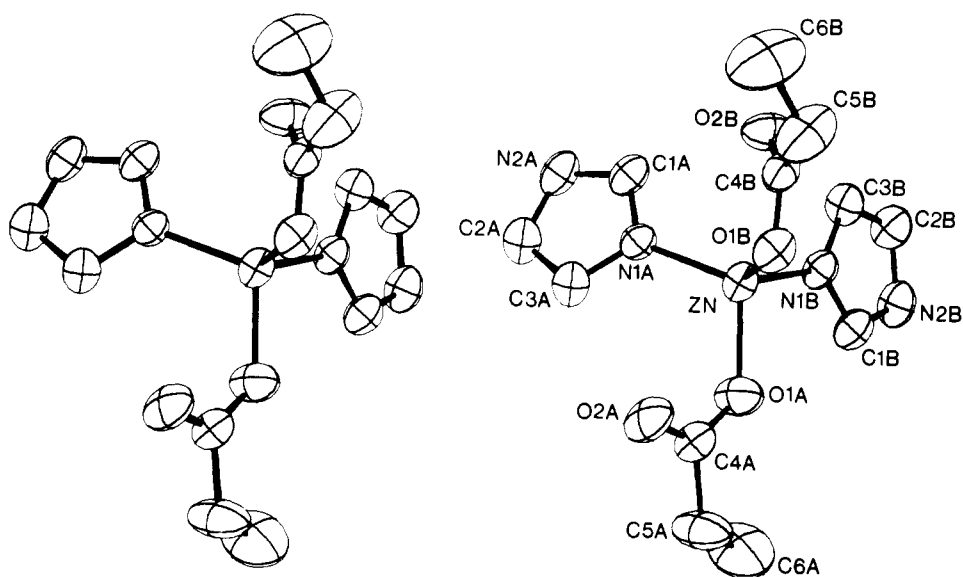


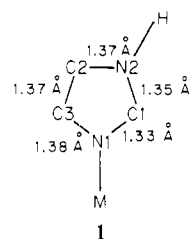
Figure 3. Stereoview of $[\text{Zn}(\text{pr})_2(\text{Im})_2]$, space group $P\bar{1}$.

parameters for the complexes are given in Tables E-H;¹⁵ a listing of the final observed and calculated structure factors is also available.¹⁵ The atom-labeling scheme for the isomorphous ($P\bar{1}$) and isotructural $[\text{M}(\text{OAc})_2(\text{Im})_2]$ ($\text{M} = \text{Co}, \text{Zn}$) complexes are indicated in the stereoview of the zinc complex shown in Figure 1. The atom-labeling scheme for the propionate complexes, which are not isomorphous, is indicated in the stereoviews of Figures 2 and 3. Selected bond distances and angles for the four complexes are presented in Table VI. All other bond lengths and angles are given in Table J.¹⁵

General Description. The structures all consist of discrete, monomeric, 4-coordinate $[\text{M}(\text{RCOO})_2(\text{Im})_2]$ coordination units, which are neutral overall. The first coordination spheres are all best described as being distorted tetrahedra (vide infra). The carboxylate ligands each bond in a monodentate fashion with $\text{M}-\text{O}-\text{C}$ angles ranging from 102 to 126° . The distances from the metal ion to the nonbonded carboxylate oxygen atoms range from 2.49 to 3.15 \AA , all beyond normal bonding distance. In each case the metal atom lies approximately in the plane of the carboxylate moiety with the greatest deviation being 0.12 \AA . The carboxylate ligands are unremarkable, with the average distance from the carboxylate carbon to the oxygen atom bonded to the metal ($\text{O1}-\text{C4} = 1.28 \text{ \AA}$) being slightly longer than the average distance to the unbonded carboxylate

oxygen ($\text{O2}-\text{C4} = 1.23 \text{ \AA}$), owing to the greater double-bond character in the latter case.

The average bond lengths for the eight independently determined imidazole ligands are indicated in structure 1. These



are in excellent agreement with the parameters reported for the structure of imidazole itself determined at -150°C .¹⁶ The imidazole ligands are quite accurately planar, with no atom deviating from a least-squares plane through the five atoms by as much as 0.01 \AA . The imidazole ligands coordinate so that the metal ion lies in or near the plane of the cyclic ligand, the largest deviation being 0.36 \AA in the case of $[\text{Zn}(\text{pr})_2(\text{Im})_2]$. Thus the carboxylate and imidazole ligands themselves

(16) Martinez-Canera, S. *Acta Crystallogr.* 1966, 20, 783.

and their modes of coordination appear to be entirely normal.

Structural Comparison between the Cobalt(II) and Zinc(II) Complexes. A principal aim of the present work is to assess the intrinsic similarities and differences between analogous cobalt(II) and zinc(II) complexes involving biologically relevant ligands. The two metals differ in atomic number by 3 units. Cobalt(II) with the $[\text{Ar}]3d^7$ electronic configuration is potentially susceptible to ligand field stabilization of certain ligand arrangements, although this effect is expected to be small in a pseudotetrahedral complex. Zinc(II), on the other hand, having the $[\text{Ar}]3d^{10}$ configuration is incapable of exhibiting ligand field stabilization effects of any kind. Unlike the situation when cobalt(II) replaces zinc(II) at the metal ion binding site of a protein, the present comparisons are made between complexes devoid of constraints on ligand disposition imposed by the architecture of the protein. With monodentate ligands only the stereochemical preference of the metal ion, interligand repulsive forces, and crystal-packing energetics determine the stereochemistry of the complex.

The ionic radius of 4-coordinate cobalt(II) is given as 0.58 Å while that of zinc(II) is listed as 0.60 Å in a recent compilation.¹⁷ In contrast, the structures of the two pairs of complexes of interest here show the Zn–O and Zn–N bond lengths to be the same as, or slightly shorter than, the corresponding Co–O and Co–N bond distances. The differences, however, are very small and of marginal significance when compared to experimental error. Our finding that the corresponding bond distances for the two metals are so similar is certainly consistent with the fact that cobalt(II) readily substitutes for zinc(II) in several enzymes with retention of biological activity.

A comparison of the angular distortions in ligand disposition in the first coordination spheres between cobalt(II) and zinc(II) complexes is of interest. Deviations from ideal T_d bond angles are to be expected for 4-coordinate complexes involving two types of monodentate ligand. The highest symmetry, considering the metal and four ligand atoms only, is C_{2v} . The actual bond angles about the metal (Table VI) reveal that, while some of the angles are quite near the tetrahedral angle (109.5°), there are significant deviations in many cases. These deviations do not preserve even C_{2v} symmetry (in which the O–M–O and N–M–N would differ but all O–M–N angles would be identical). In fact the greatest deviations from tetrahedral angles are found for O–M–N angles, which range from 94.4 to 120.8° for the four complexes. In contrast, none of the O–M–O or N–M–N angles deviate by more than 5° from 109.5°. For the isomorphous $[\text{M}(\text{OAc})_2(\text{Im})_2]$ pair it is not surprising that the corresponding bond angles are virtually identical for the two metals, with the largest discrepancy being 2.4°. In this situation crystal-packing and interligand forces will be potentially the same for the two complexes. Since the $[\text{M}(\text{pr})_2(\text{Im})_2]$ pair crystallize in different space groups, the above mentioned forces need not be identical in the two crystals. This is reflected in deviations of up to 5° between corresponding bond angles in the two molecules. In the case of the isomorphous $[\text{M}(\text{OAc})_2(\text{Im})_2]$ complexes the

largest and smallest O–M–N angles span opposite edges of the distorted tetrahedron while for the $[\text{M}(\text{pr})_2(\text{Im})_2]$ pair the largest and smallest angles span adjacent sides of the coordination polyhedron. These subtle distortional differences have a profound effect on the EPR spectra of the cobalt(II)-doped zinc(II) complexes.⁵ Distortion from idealized T_d symmetry do not appear to be systematically greater for either the cobalt(II) or zinc(II) complexes.

A reviewer suggested that the structure of $[\text{Co}(\text{OAc})_2(\text{Im})_2]$ provides evidence for the incipient formation of a fifth bond to cobalt(II). The Co–O2A distance of 2.485 Å is significantly shorter than the corresponding distance (2.645 Å) in the isomorphous zinc complex. If this is a valid description of the structure, then the acetate ligand acts as a bidentate ligand and the coordination polyhedron is best described as a distorted trigonal bipyramid with O2A and O1B occupying apical positions while N1A, N1B, and O1A occupy equatorial positions. The Co atom is displaced from the equatorial plane by 0.45 Å in the direction of O1B. The O1B–Co–O2A angle is 160° compared to the ideal 180°. The angles subtended at the Co atom by the bonds in the “equatorial plane” (ideally 120°) range from 109 to 120°. Regardless of one’s view of the “best” description of this structure, the results attest to the flexibility of cobalt(II) in adjusting its coordination environment. This flexibility is further demonstrated in the following paper,¹⁸ where it is shown that 4- and 6-coordinate cobalt(II) structures of this type differ only marginally in energy.

Taken all together our findings show, for monodentate 4-coordination at least, that cobalt(II) and zinc(II) complexes of the same ligands are structurally very similar and that the two ions possess virtually identical radii. Angular distortions from idealized T_d symmetry of the atoms in the first coordination sphere of up to 11° greater than and 15° less than the tetrahedral angle are observed and are similar for both metals. The fact that the distortions occur for both cobalt(II) and zinc(II) complexes rules out ligand field stabilization as a cause in the former case. The variability in the various bond angles suggests that neither metal shows marked stereochemical preference, although, as discussed above, cobalt(II) may exhibit a greater tendency to achieve a higher coordination number than does zinc(II). Further discussion will be deferred to the following paper¹⁸ in which the structures of analogous complexes formed from imidazole ligands with alkyl substituents in the 2-position are examined.

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Registry No. $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_3\text{H}_4\text{N}_2)_2$, 32627-42-2; $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_3\text{H}_4\text{N}_2)_2$, 74194-01-7; $\text{Co}(\text{C}_3\text{H}_5\text{O}_2)_2(\text{C}_3\text{H}_4\text{N}_2)_2$, 74194-04-0; $\text{Zn}(\text{C}_3\text{H}_5\text{O}_2)_2(\text{C}_3\text{H}_4\text{N}_2)_2$, 74194-05-1.

Supplementary Material Available: Listings of H atom positional parameters, thermal parameters, bond distances and angles (Tables A–H), positional and thermal parameters, and structure factor amplitudes (61 pages). Ordering information is given on any current masthead page.

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