

Models for Cobalt(II)-Substituted Zinc Metalloenzymes. 2. Comparison of the Crystal Structures of Complexes of the Type $[M(\text{RCOO})_2(2\text{-X-Im})_2]$ (Im = Imidazole; M = Co, Zn; R = CH₃, C₂H₅, C₃H₇; X = CH₃, C₂H₅). An Unusual Type of Linkage Isomerism

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The structures of four bis(alkanecarboxylato)bis(2-alkylimidazole)cobalt(II) and one zinc(II) analogue 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 five complexes $[\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{CH}_3\text{C}_3\text{N}_2\text{H}_3)_2]$, $[\text{Co}(\text{C}_3\text{H}_5\text{O}_2)_2(\text{CH}_3\text{C}_3\text{N}_2\text{H}_3)_2]$, $[\text{Co}(\text{C}_4\text{H}_7\text{O}_2)_2(\text{CH}_3\text{C}_3\text{N}_2\text{H}_3)_2]$, $[\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_2\text{H}_5\text{C}_3\text{N}_2\text{H}_3)_2]$, and $[\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_2\text{H}_5\text{C}_3\text{N}_2\text{H}_3)_2]$ crystallize in space groups $P2_12_12_1$, $P2_1/n$, $Pbna$, $P2_12_12_1$, and $P2_12_12_1$, respectively. They have the following respective unit cell constants: $a = 7.539$ (1), 8.406 (2), 13.295 (3), 8.805 (3), 8.767 (6) Å; $b = 7.704$ (2), 7.844 (7), 14.948 (2), 8.938 (5), 8.938 (4) Å; $c = 26.239$ (3), 26.414 (4), 9.810 (2), 23.574 (10), 23.703 (18) Å; $\beta = 93.95$ (2) $^\circ$ for the monoclinic ($P2_1/n$) structure; $Z = 4$ in every case. The structures were solved with heavy-atom methods and refined to final respective R values of 0.033, 0.057, 0.049, 0.056, and 0.062. The second, fourth, and fifth structures in the above list are 4-coordinate with monodentate coordination by the carboxylate ligands. The first and third complexes are 6-coordinate with the carboxylate ligands adopting a bidentate mode of coordination. The 6-coordinate complexes revert to 4-coordinate linkage isomers upon dissolution in ethanol, a result corroborated by visible and infrared absorption spectroscopy. The 4-coordinate cobalt(II) and zinc(II) complexes are extremely similar and display little stereochemical preference on the part of the metal.

This paper examines the structures of bis(alkanecarboxylato)bis(2-alkylimidazole)cobalt(II) complexes and the zinc(II) analogue of one of them. These complexes were studied for several reasons, some of them similar to those outlined in the Introduction of the preceding paper.¹ It was hoped that further insight into the comparative structural chemistry of zinc(II) and cobalt(II) complexes of biologically relevant ligands would be obtained. The 2-alkyl-substituted imidazole ligands were chosen because in our earlier study of the absorption and magnetic circular dichroism spectra of cobalt(II) complexes in this class, subtle differences between these and unsubstituted imidazole derivatives were noted.² The spectra of the 2-alkyl-substituted derivatives appeared to mimic those of cobalt(II)-substituted carboxypeptidase A somewhat more closely than the corresponding spectra of thermolysin. We wished to determine whether these spectral differences reflected a significant structural feature.

Finally, although all of the cobalt(II) complexes examined in this and the preceding paper have roughly the same red-purple color to the eye, an interesting observation was made regarding certain of the 2-alkylimidazole complexes. Comparison of the solution-state (ethanol) and the solid-state (Nujol mull) absorption spectra reveals that, while a strong band is observed in the visible region in both cases, in certain instances there is a significant shift to lower wavelength (~ 15 nm) of the solid-state absorption maximum with respect to its solution-state counterpart. In other cases the spectra in the two states were virtually superimposable with regard to the absorption envelope with only minor variations in the relative intensities of unresolved components. Interestingly, the complexes $[\text{Co}(\text{pr})_2(2\text{-Me-Im})_2]$ and $[\text{Co}(\text{bu})_2(2\text{-Me-Im})_2]$ exhibit the above mentioned shift to shorter wavelengths for the solid-state spectra (OAc = acetate, pr = propionate, bu = butyrate, 2-Me-Im = 2-methylimidazole, 2-Et-Im = 2-ethylimidazole). The present structural studies explain these observations and reveal a novel type of linkage isomerism.

Experimental Section

Crystals of the zinc(II) and cobalt(II) complexes were prepared as described in the preceding paper. Single-crystal automatic X-ray

diffractometry (Enraf-Nonius CAD4) data were taken, and the structures were solved and refined as described elsewhere,¹ with the exception that no attempt was made to locate the hydrogen atoms in the $[\text{Co}(\text{pr})_2(2\text{-Me-Im})_2]$ structure. The crystal data, data collection, and refinement parameters are set out in Table I.

Results and Discussion

The crystal structures of the following five complexes have been determined: $[\text{Co}(\text{OAc})_2(2\text{-Me-Im})_2]$, $[\text{Co}(\text{pr})_2(2\text{-Me-Im})_2]$, $[\text{Co}(\text{bu})_2(2\text{-Me-Im})_2]$, $[\text{Co}(\text{OAc})_2(2\text{-Et-Im})_2]$, and $[\text{Zn}(\text{OAc})_2(2\text{-Et-Im})_2]$ (see introduction for abbreviations). The crystallographic and structure refinement parameters are set out in Table I. The final atomic positional parameters are given in Tables II-VI, respectively. Hydrogen atom parameters are listed in Tables A-D.³ The atom-labeling schemes are indicated in the stereoviews of Figures 1-4, respectively. The atom-labeling scheme for $[\text{Zn}(\text{OAc})_2(2\text{-Et-Im})_2]$ is identical with that of the cobalt(II) analogue. Selected bond distances and angles for all the complexes are presented in Table VII. Other bond distances and angles are given in Table F.³ Tables of the anisotropic thermal parameters for the complexes are given in Tables G-K,³ and the final observed and calculated structure factors are available³ also.

General Description of the Structures. The complexes all consist of discrete, monomeric, neutral coordination units (Figures 1-4). The most striking observation is that, while three of them exhibit 4-coordination similar to the complexes examined in the preceding paper,¹ two are 6-coordinate. This 6-coordination is achieved by having the carboxylate ligands coordinate in a bidentate rather than in a monodentate fashion. Both bidentate and monodentate coordination by carboxylate groups is well-known, but we are not aware of other examples of linkage isomerism of this type in complexes that contain virtually identical sets of ligands. This novel class of isomerism will be discussed further below.

The structural parameters (Table VII) of the imidazole and carboxylato ligands are unremarkable and require no discussion. The coordination is such that the central metal ion lies in or near the plane of these ligands.

4-Coordinate Complexes. Cobalt(II)-Zinc(II) Comparison. The complexes $[\text{Co}(\text{pr})_2(2\text{-Me-Im})_2]$ and $[\text{Co}(\text{OAc})_2(2\text{-Et-Im})_2]$ as well as the zinc analogue of the latter are 4-coordinate with monodentate coordination by the carboxylate ligands.

(1) Horrocks, W. D., Jr.; Ishley, J. N.; Whittle, R. R. *Inorg. Chem.*, preceding paper in this issue.

(2) Horrocks, W. D., Jr.; Ishley, J. N.; Holmquist, B.; Thompson, J. S. *J. Inorg. Biochem.* 1980, 12, 131.

(3) Supplementary material.

Table I. Crystallographic Parameters and Refinement Data

	[Co(OAc) ₂ (2-Me-Im) ₂]	[Co(pr) ₂ (2-Me-Im) ₂]	[Co(bu) ₂ (2-Me-Im) ₂]	[Co(OAc) ₂ (2-Et-Im) ₂]	[Zn(OAc) ₂ (2-Et-Im) ₂]
formula	CoO ₄ N ₄ C ₁₂ H ₁₈	CoO ₄ N ₄ C ₁₄ H ₂₂	CoO ₄ N ₄ C ₁₆ H ₂₆	CoO ₄ N ₄ C ₁₄ H ₂₂	ZnO ₄ N ₄ C ₁₄ H ₂₂
space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /n	Pbna	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
Z	4	4	4	4	4
crystal size, mm	0.21 × 0.21 × 0.40		0.35 × 0.37 × 0.39	0.37 × 0.60 × 0.65	0.33 × 0.35 × 0.36
a, Å	7.539 (1)	8.406 (2)	13.295 (3)	8.805 (3)	8.767 (6)
b, Å	7.704 (2)	7.844 (7)	14.948 (2)	8.938 (5)	8.938 (4)
c, Å	26.239 (3)	26.414 (4)	9.810 (2)	23.574 (10)	23.703 (18)
β, deg		93.95 (2)			
V, Å ³	1524 (1)	1738 (2)	1950 (1)	1855 (2)	1857 (4)
d _{calcd} , g cm ⁻³	1.487	1.412	1.354	1.322	1.344
abs coeff (μ), cm ⁻¹	11.93	10.53	9.44	9.86	13.86
no. of variables	244	208	114	208	208
measd refl	3051		4993	2699	2658
refl > 2σ(I)	2064	2641 (3σ(I))	2085	2243	1726
ρ	0.018	0.040	0.020	0.010	0.030
2θ _{max} , deg	40.0	40.0	40.0	57.0	56.52
A, deg	0.60	0.70	0.65	0.60	0.60
R	0.033	0.057	0.049	0.056	0.062
R _w	0.035	0.078	0.053	0.063	0.060
drift cor	0.954–1.065		0.950–1.063	0.962–1.013	0.982–1.011

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

atom	x	y	z
Co	0.13015 (5)	0.10282 (5)	0.12139 (1)
O1A	0.2676 (3)	0.2363 (3)	0.17818 (7)
O2A	0.3940 (3)	0.2547 (3)	0.10374 (8)
O1B	0.1871 (3)	-0.0513 (3)	0.05700 (8)
O2B	0.2962 (3)	-0.1387 (3)	0.12937 (8)
N1A	-0.0135 (3)	0.3076 (3)	0.09135 (9)
N2A	-0.1698 (3)	0.4754 (4)	0.04149 (10)
N1B	-0.0691 (3)	-0.0095 (3)	0.16345 (8)
N2B	-0.2180 (3)	-0.1391 (4)	0.22385 (9)
C1A	-0.1197 (4)	0.3126 (4)	0.0511 (1)
C2A	-0.0940 (5)	0.5812 (4)	0.0775 (1)
C3A	0.0010 (4)	0.4777 (4)	0.1074 (1)
C7A	-0.1778 (5)	0.1618 (4)	0.0205 (1)
C1B	-0.0575 (4)	-0.0932 (4)	0.2076 (1)
C2B	-0.3395 (4)	-0.0847 (5)	0.1888 (1)
C3B	-0.2479 (4)	-0.0044 (5)	0.1522 (1)
C7B	0.1071 (4)	-0.1265 (5)	0.2370 (1)
C4A	0.3909 (4)	0.2954 (4)	0.1492 (1)
C5A	0.5264 (5)	0.4128 (6)	0.1711 (1)
C4B	0.2871 (4)	-0.1527 (4)	0.0823 (1)
C5B	0.3958 (6)	-0.2835 (5)	0.0556 (2)

Table III. Positional Parameters and Their Estimated Standard Deviations for [Co(pr)₂(2-Me-Im)₂]

atom	x	y	z
Co	-0.0013 (1)	0.1710 (1)	0.12227 (4)
O1A	-0.1077 (6)	0.3316 (8)	0.1672 (2)
O1B	-0.0277 (6)	0.2633 (7)	0.0531 (2)
O2A	-0.0162 (7)	0.1411 (8)	0.2210 (2)
O2B	-0.2889 (7)	0.2838 (8)	0.0535 (2)
N1A	0.2362 (7)	0.2163 (8)	0.1362 (2)
N1B	-0.0761 (7)	-0.0721 (8)	0.1146 (2)
N2A	0.4858 (8)	0.2715 (9)	0.1236 (3)
N2B	-0.1205 (8)	-0.3450 (9)	0.1261 (3)
C1A	0.3497 (9)	0.201 (1)	0.1037 (3)
C2A	0.4592 (11)	0.339 (1)	0.1712 (3)
C3A	0.3026 (10)	0.302 (1)	0.1784 (3)
C4A	-0.0826 (9)	0.275 (1)	0.2123 (3)
C5A	-0.1459 (13)	0.384 (2)	0.2555 (4)
C6A	-0.0625 (16)	0.367 (2)	0.3043 (5)
C7A	0.3343 (12)	0.121 (1)	0.0529 (4)
C1B	-0.0301 (9)	-0.209 (1)	0.1405 (3)
C2B	-0.2318 (10)	-0.290 (1)	0.0876 (3)
C3B	-0.2037 (10)	-0.119 (1)	0.0806 (3)
C4B	-0.1649 (9)	0.295 (1)	0.0319 (3)
C5B	-0.1663 (10)	0.347 (1)	-0.0239 (3)
C6B	-0.3323 (12)	0.376 (1)	-0.0489 (4)
C7B	0.1042 (11)	-0.219 (1)	0.1808 (4)

These complexes represent further models for the distorted tetrahedral active metal site of certain proteolytic enzymes.

Table IV. Positional Parameters and Their Estimated Standard Deviations for [Co(bu)₂(2-Me-Im)₂]

atom	x	y	z
Co	0.14000 (3)	0.2500 (0)	0.0000 (0)
O1	0.1795 (1)	0.3599 (1)	0.1300 (2)
O2	0.2623 (1)	0.3436 (1)	-0.0593 (2)
N1	0.0388 (2)	0.1777 (1)	0.1163 (2)
N2	-0.0845 (2)	0.1383 (2)	0.2528 (3)
C1	-0.0341 (2)	0.2070 (2)	0.1979 (3)
C2	-0.0430 (2)	0.0611 (2)	0.2045 (3)
C3	0.0324 (2)	0.0854 (2)	0.1216 (3)
C4	0.2473 (2)	0.3855 (2)	0.0496 (3)
C5	0.3070 (2)	0.4683 (2)	0.0820 (3)
C6	0.2829 (3)	0.5454 (2)	-0.0099 (4)
C7	0.3458 (4)	0.6274 (2)	0.0187 (5)
C8	-0.0590 (3)	0.3022 (2)	0.2251 (4)

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

atom	x	y	z
Co	0.2511 (1)	0.00833 (8)	0.12526 (3)
O1A	0.4093 (5)	-0.0169 (5)	0.1836 (2)
O1B	0.2888 (5)	-0.1544 (5)	0.0707 (2)
O2A	0.2847 (5)	0.1616 (5)	0.2277 (2)
O2B	0.4959 (5)	-0.0256 (5)	0.0509 (2)
N1A	0.2225 (6)	0.2135 (5)	0.0890 (2)
N2A	0.1613 (6)	0.3990 (6)	0.0330 (2)
N1B	0.0380 (6)	-0.0518 (6)	0.1506 (2)
N2B	-0.1561 (6)	-0.1608 (7)	0.1904 (2)
C1A	0.1631 (7)	0.2504 (7)	0.0398 (2)
C2A	0.2202 (8)	0.4598 (7)	0.0806 (3)
C3A	0.2608 (8)	0.3468 (7)	0.1147 (2)
C7A	0.1073 (9)	0.1432 (8)	-0.0046 (3)
C8A	0.1890 (11)	0.1526 (11)	-0.0603 (3)
C1B	-0.0040 (8)	-0.1499 (7)	0.1896 (3)
C3B	-0.0956 (7)	-0.0023 (8)	0.1257 (3)
C2B	-0.2140 (7)	-0.0691 (8)	0.1505 (3)
C7B	0.0977 (9)	-0.2337 (9)	0.2280 (3)
C8B	0.1055 (11)	-0.1702 (13)	0.2861 (4)
C4A	0.3896 (7)	0.0694 (8)	0.2259 (3)
C5A	0.4991 (9)	0.0564 (10)	0.2756 (3)
C4B	0.4104 (8)	-0.1334 (7)	0.0428 (3)
C5B	0.4440 (12)	-0.2421 (12)	-0.0041 (5)

We wished to determine whether alkyl substituents in the 2-position of the imidazole ligands caused marked structural changes when these compounds were compared to the unsubstituted derivatives examined in the preceding paper. No dramatic structural consequence is apparent. The M–O and M–N (M = Co, Zn) bond distances (Table VII) are comparable to those of the unsubstituted derivatives. The O–M–O bond angles appear normal and are all quite near the ideal

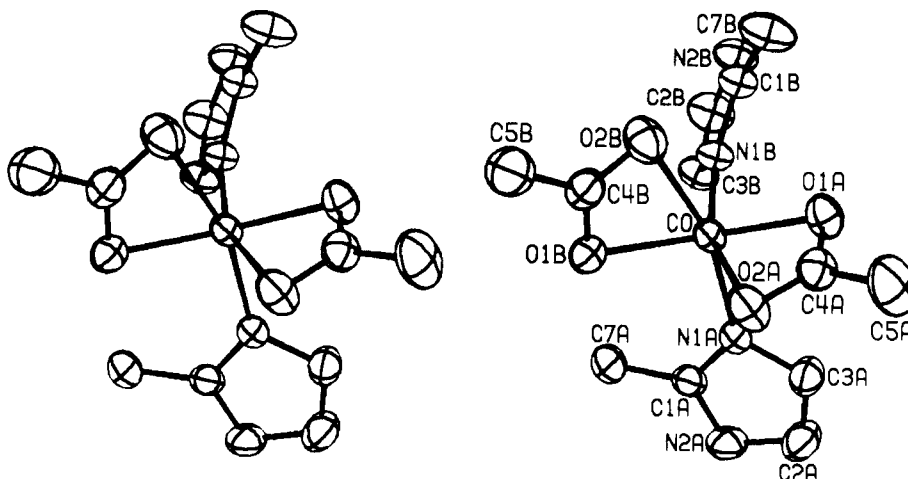


Figure 1. Stereoview of $[\text{Co}(\text{OAc})_2(2\text{-Me-Im})_2]$.

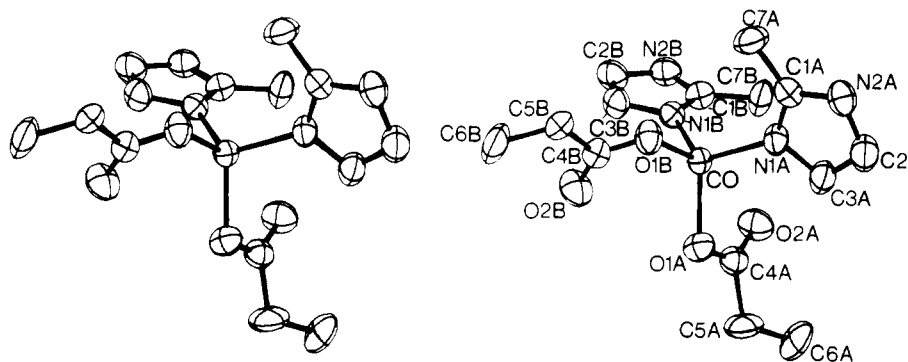


Figure 2. Stereoview of $[\text{Co}(\text{pr})_2(2\text{-Me-Im})_2]$.

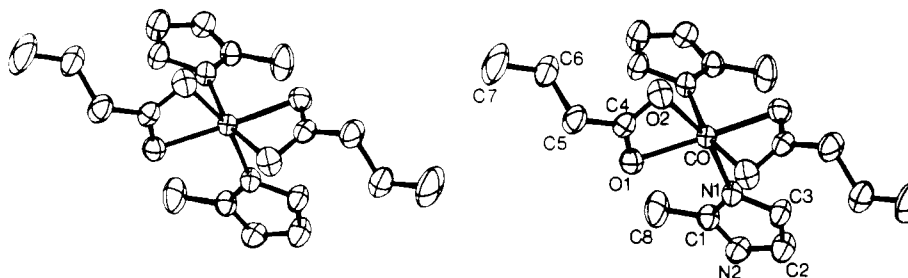


Figure 3. Stereoview of $[\text{Co}(\text{bu})_2(2\text{-Me-Im})_2]$.

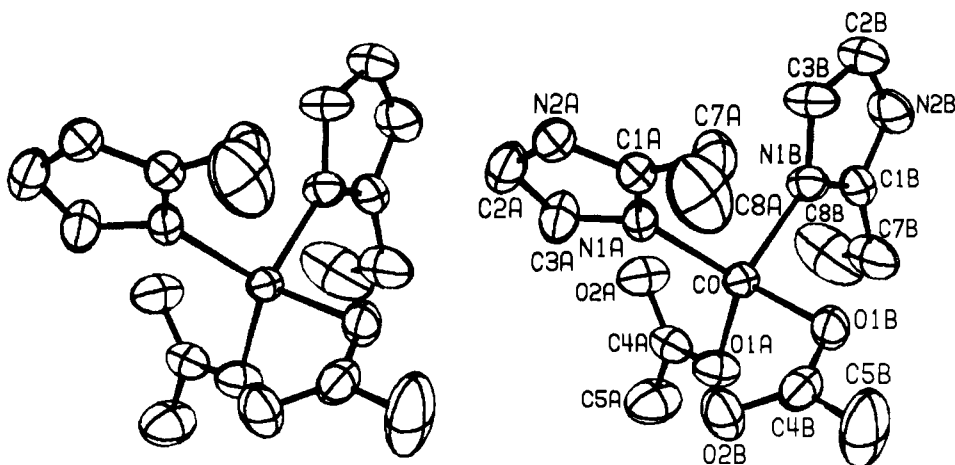


Figure 4. Stereoview of $[\text{Co}(\text{OAc})_2(2\text{-Et-Im})_2]$.

tetrahedral angle (109.5°). In $[\text{Co}(\text{pr})_2(2\text{-Me-Im})_2]$ the N–Co–N angle has expanded to 118.6° ; however, for $[\text{Co}(\text{OAc})_2(2\text{-Et-Im})_2]$ it is 104.6° , suggesting that the expansion in the former case is not due to the substituent in the 2-

position of the imidazole. It would appear that the observed distortions from idealized C_{2v} symmetry for the first coordination sphere are due to crystal-packing forces as was the case in the unsubstituted imidazole complexes.¹ As noted in the

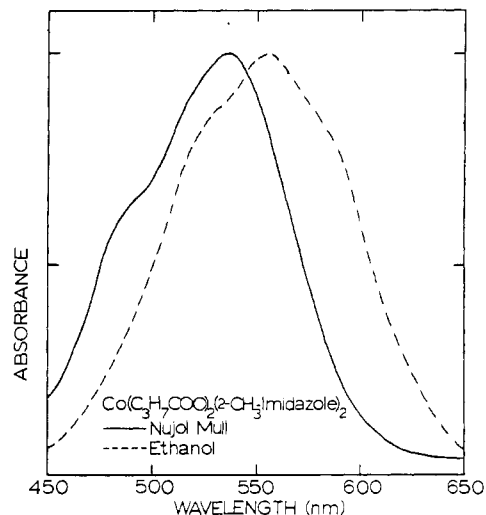
Table VI. Positional Parameters and Their Estimated Standard Deviations for $[\text{Zn}(\text{OAc})_2(2\text{-Et-Im})_2]$

atom	x	y	z
Zn	0.2498 (1)	0.00887 (8)	0.12456 (4)
O1A	0.4040 (5)	-0.0123 (6)	0.1829 (2)
O2A	0.2845 (7)	0.1632 (7)	0.2296 (2)
O1B	0.2939 (6)	-0.1551 (5)	0.0711 (2)
O2B	0.5006 (6)	-0.0247 (6)	0.0491 (2)
N1A	0.2228 (7)	0.2125 (6)	0.0899 (2)
N2A	0.1652 (7)	0.3976 (7)	0.0343 (3)
N1B	0.0366 (7)	-0.0536 (7)	0.1484 (3)
N2B	-0.1570 (8)	-0.1636 (8)	0.1880 (3)
C1A	0.1654 (8)	0.2511 (8)	0.0405 (3)
C2A	0.2251 (9)	0.4596 (8)	0.0826 (3)
C3A	0.2641 (9)	0.3468 (8)	0.1159 (3)
C1B	-0.0034 (9)	-0.1532 (9)	0.1861 (3)
C2B	-0.2160 (9)	-0.0719 (10)	0.1489 (3)
C3B	-0.0973 (8)	-0.0024 (9)	0.1240 (3)
C4A	0.3884 (9)	0.0679 (10)	0.2259 (3)
C5A	0.5012 (11)	0.0522 (13)	0.2725 (4)
C4B	0.4138 (10)	-0.1324 (8)	0.0411 (3)
C5B	0.4482 (13)	-0.2441 (14)	-0.0031 (6)
C7A	0.1081 (10)	0.1426 (9)	-0.0033 (4)
C8A	0.1902 (11)	0.1519 (10)	-0.0587 (4)
C7B	0.0986 (11)	-0.2379 (11)	0.2238 (4)
C8B	0.1067 (14)	-0.1843 (15)	0.2822 (5)

previous paper the Zn-O and Zn-N bond distances are virtually identical with the corresponding Co-O and Co-N distances in the $[\text{M}(\text{OAc})_2(2\text{-Et-Im})_2]$ complexes.

A description of the $[\text{Co}(\text{pr})_2(2\text{-Me-Im})_2]$ structure as pseudo-5-coordinate as discussed in the previous paper¹ is also possible. In this case the fifth "bond" (Co-O2A) distance of 2.630 Å is somewhat longer than the corresponding bond length (2.485 Å) in $[\text{Co}(\text{OAc})_2(\text{Im})_2]$. The Co-O2B distance of 3.054 Å is clearly out of bonding range. In the other 4-coordinate cobalt(II) structure, $[\text{Co}(\text{OAc})_2(2\text{-Et-Im})_2]$, the Co-O2A and Co-O2B distances are virtually identical (2.79 Å) and outside of any reasonable bonding distance.

6-Coordinate Complexes. Isomerism upon Dissolution. The crystal structures of the homologous series of these complexes, $[\text{Co}(\text{RCOO})_2(2\text{-Me-Im})_2]$, show that for R = CH₃ and C₂H₅ the complexes crystallize as 6-coordinate structures, while for

**Figure 5.** Visible absorption spectra of $[\text{Co}(\text{bu})_2(2\text{-Me-Im})_2]$ in the solid state (Nujol mull) and solution (ethanol).

R = C₂H₅ a 4-coordinate structure results. These findings suggest that there is very little free energy difference between the 4- and 6-coordinate structures. Presumably minor changes in crystal-packing forces as the carboxylate alkyl chain length is varied account for the variability in coordination number in the crystalline state.

The 6-coordinate complexes revert to 4-coordinate structures upon dissolution in ethanol. Figure 5 shows the visible absorption spectra of $[\text{Co}(\text{bu})_2(2\text{-Me-Im})_2]$ in the crystalline state (Nujol mull) and in an ethanolic solution. The shift in the band position to lower energy upon dissolution is clearly evident. In contrast, the solution-state and solid-state spectra (not shown) are virtually identical for complexes which are 4-coordinate in the solid state. This isomerization process is also corroborated by infrared evidence. The symmetric and antisymmetric C-O stretching frequencies of the carboxylate moiety are separated by about 190 cm⁻¹ in the known 4-coordinate complexes both in the solid state and in solution. In the crystalline 6-coordinate complexes this separation decreases

Table VII. Selected Interatomic Distances (Å) and Angles (Deg)

	$\text{Co}(\text{OAc})_2(2\text{-Me-Im})_2$	$\text{Co}(\text{pr})_2(2\text{-Me-Im})_2$	$\text{Co}(\text{bu})_2(2\text{-Me-Im})_2$	$\text{Co}(\text{OAc})_2(2\text{-Et-Im})_2$	$\text{Zn}(\text{OAc})_2(2\text{-Et-Im})_2$
M-O1A	2.086 (2)	1.986 (2)	2.145 (2)	1.970 (2)	1.944 (4)
M-O1B	2.109 (2)	1.963 (2)		1.970 (2)	1.976 (4)
M-N1A	2.069 (3)	2.037 (3)	2.069 (1)	2.039 (2)	2.010 (4)
M-N1B	2.055 (3)	2.014 (3)		2.041 (3)	2.031 (5)
M-O2A	2.354 (2)	2.630 (2)	2.222 (1)	2.793 (2)	2.862 (5)
M-O2B	2.253 (2)	3.054 (2)		2.794 (4)	2.850 (4)
O1A-C4A	1.284 (3)	1.275 (4)	1.257 (1)	1.273 (4)	1.253 (7)
O1B-C4B	1.271 (3)	1.271 (4)		1.270 (4)	1.286 (7)
O2A-C4A	1.234 (3)	1.206 (4)	1.255 (1)	1.238 (4)	1.250 (8)
O2B-C4B	1.243 (3)	1.226 (4)		1.238 (4)	1.241 (7)
O1A-M-O1B	138.5 (1)	107.2 (1)	151.6 (1)	104.6 (1)	104.4 (2)
N1A-M-N1B	98.2 (1)	118.6 (1)	98.8 (1)	104.2 (1)	104.7 (2)
O1A-M-N1A	99.01 (1)	105.0 (1)	103.4 (1)	118.9 (1)	117.4 (2)
O1A-M-N1B	100.8 (1)	120.7 (1)	95.0 (1)	114.6 (1)	114.5 (2)
O1B-M-N1A	103.3 (1)	98.6 (1)		114.3 (1)	115.6 (2)
O1B-M-N1B	110.0 (1)	104.0 (1)		98.7 (1)	98.9 (2)
O1A-M-O2A	58.4 (1)		59.6 (1)		
O1B-M-O2B	59.7 (1)				
O2A-M-N1A	89.3 (1)		161.6 (1)		
O2A-M-N1B	158.9 (1)		90.2 (1)		
O2A-M-O1B	87.2 (1)		98.4 (1)		
O2A-M-O2B	87.7 (1)		86.0 (1)		
O2B-M-N1A	162.9 (1)				
O2B-M-N1B	90.5 (1)				
O2B-M-O1A	93.7 (1)				
M-O1A-C4A	94.4 (1)	106.7 (2)	92.1 (1)	112.4 (2)	116.6 (4)
M-O1B-C4B	92.8 (2)	121.5 (2)		111.7 (2)	113.4 (4)
M-O2A-C4A	85.4 (1)		88.5 (1)		
M-O2B-C4B	87.0 (2)				

to about 100 cm⁻¹, diagnostic of bidentate coordination by the carboxylate groups.⁴ When the 6-coordinate complexes are dissolved in alcohol, this separation goes up to about 190 cm⁻¹, indicative of monodentate coordination by the carboxylate moieties in solution.

The 6-coordinate structures are best described as having highly distorted octahedral coordination polyhedra. The principal distortion occurs because of the small bite size of the bidentate carboxylate ligands, the two Co-O bonds of which subtend angles of about 60° at the cobalt atom. The structure of [Co(OAc)₂(2-Me-Im)₂] (Figure 1) might best be described as having an equatorial plane consisting of O1A, N1B, O1B, and O2A with axial ligation by O2B and N1B. Note that the O2B-Co-N1A angle (161.6°) deviates considerably from the 180° angle of idealized octahedral geometry. The coordination polyhedron for [Co(bu)₂(2-Me-Im)₂] is quite similar (Figure 3), although the structures are not isomorphous and in this case the cobalt atom lies on a special position of C₂ symmetry. A description of the 6-coordinate structures in terms of a pseudotetrahedral model is unsatisfactory. The positions of the two liganding imidazole nitrogen atoms and the centers of the bites of the two carboxylate ligands form an extremely poor tetrahedron.

The expected increase in the effective ionic radius upon increasing the coordination number from 4 to 6 is observed. The effect is slight for the Co-N bonds, which increase an average of only 0.03 Å on going to the higher coordination number. The effect is much more pronounced, however, for the carboxylate coordination in which the two carboxylate

oxygen atoms are not bonded equally. In the 6-coordinate structures the shorter of the C-O bonds average 2.11 Å while the longer set average 2.28 Å. These distances are to be compared with an average value of 1.97 Å for the Co-O bonds in the 4-coordinate structures, which involved monodentate coordination. In the 4-coordinate structures the nonbonded Co-O distances range from 2.63 to 3.05 Å. It is perhaps significant that in the 6-coordinate structures the longer of the two Co-O bonds is in each case trans to an imidazole ligand, while the shorter Co-O bond is trans to another Co-O bond.

In summary, the present structural studies have uncovered a novel type of linkage isomerism. Our results suggest that the free energy difference between 4- and 6-coordinate structures of this type is extremely small and that the actual structure adopted will depend upon crystal-packing forces. In solution it appears that 4-coordination is favored. Further evidence is presented regarding the great similarity and general lack of stereochemical preference for 4-coordinate complexes of both cobalt(II) and zinc(II), which are intended to mimic the active-site geometry of certain metalloenzymes.

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Registry No. Co(C₂H₃O₂)₂(CH₃C₃N₂H₃)₂, 74194-12-0; Co(C₃H₅O₂)₂(CH₃C₃N₂H₃)₂, 82281-51-4; Co(C₄H₇O₂)₂(CH₃C₃N₂H₃)₂, 82281-52-5; Co(C₂H₃O₂)₂(C₂H₅C₃N₂H₃)₂, 82265-73-4.

Supplementary Material Available: Listings of H atom positional parameters, bond distances and angles, thermal parameters (Tables A-K), positional and thermal parameters, and structure factor amplitudes (63 pages). Ordering information is given on any current masthead page.

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Comparison of the Molecular Structures of Five-Coordinate Copper(II) and Zinc(II) Complexes of 2,6-Diacetylpyridine Dioxime¹

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X-ray diffraction studies of Cu(DAPDH₂)Cl₂·2H₂O and Zn(DAPDH₂)Cl₂·H₂O, where DAPDH₂ is 2,6-diacetylpyridine dioxime, were performed to determine the molecular configurations of these five-coordinate complexes. In both compounds DAPDH₂ behaves as a tridentate ligand. For Cu(DAPDH₂)Cl₂ the metal coordination geometry resembles a distorted square pyramid with C_s-m symmetry, whereas for Zn(DAPDH₂)Cl₂ it can be viewed roughly as a distorted trigonal bipyramid with C_{2v}-mm2 symmetry. The susceptibility of Cu(DAPDH₂)Cl₂ to second-order Jahn-Teller distortions is reflected by the ca. 0.24-Å difference in the apical and basal Cu-Cl bonds of 2.463 (1) and 2.220 (1) Å, respectively. A comparison of the M-N(oxime) and M-N(py) bond lengths reveals that these bonds are ca. 0.13 and 0.20 Å longer in Zn(DAPDH₂)Cl₂ than the respective bonds in Cu(DAPDH₂)Cl₂. In contrast, the basal Cu-Cl bond distance in Cu(DAPDH₂)Cl₂ is comparable in magnitude to the Zn-Cl distances in Zn(DAPDH₂)Cl₂. These results suggest that the directional orientation of the available metal orbitals with respect to the dioxime's N donor orbitals leads to poorer angular overlap in the five-coordinate Zn complex. Cu(DAPDH₂)Cl₂·2H₂O crystallizes in the centrosymmetric triclinic space group P $\bar{1}$ with refined lattice parameters of a = 7.992 (2) Å, b = 10.282 (3) Å, c = 10.462 (3) Å, α = 105.15 (2)°, β = 107.05 (2)°, γ = 106.43 (2)°, V = 730.7 (4) Å³, and Z = 2, whereas Zn(DAPDH₂)Cl₂·H₂O crystallizes in the centrosymmetric monoclinic space group P2₁/n with a = 10.104 (3) Å, b = 14.505 (4) Å, c = 9.768 (2) Å, β = 103.90 (2)°, V = 1394.5 (6) Å³, and Z = 4. Full-matrix least-squares refinement (based on F_o²) of diffractometry data with F_o² > σ(F_o²) converged to final discrepancy indices of R(F_o) = 0.026, R(F_o²) = 0.038, and σ₁ = 1.53 for Cu(DAPDH₂)Cl₂·2H₂O and R(F_o) = 0.035, R(F_o²) = 0.049, and σ₁ = 1.61 for Zn(DAPDH₂)Cl₂·H₂O.

Introduction

Structural studies have been performed on a wide variety of transition-metal oxime complexes to examine the possible metal-coordination modes associated with oxime ligands and

their subsequent influence upon the geometry of the metal complex.³ In particular, a systematic investigation of the coordination chemistry of 2,6-diacetylpyridine dioxime, DAPDH₂, with Cu(II) has led to the isolation and characterization of a monomeric species, Cu(DAPDH₂)Cl₂, and the tetrafluoroborate salt of the binuclear copper cation, [Cu-

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