Inorg. Chem. **1987**, *26*, 3569-3576

Contribution from the Anorganisch-Chemisches Institut
der Universität Münster, D-4400 Münster, West Germany

Pentacoordinate Zinc Complexes of Imidazole Nitrogen Donors as Structural Models for the Active Site in Enzymes: Preparation and Crystal Structures of (μ-2,2′-Biimidazole)tetrakis(2,2′-biimidazole)dizinc(II) Tetraperchlorate Trihydrate and Bis(2,2′-biimidazole)(formato)zinc(II) Perchlorate

Christoph Kirchner and Bernt Krebs*

Received January 8, 1987

The preparation and molecular structures of the novel five-coordinate zinc–imidazole compounds $[Zn_2(\mu\text{-}H_2BiIm)(H_2BiIm)_4](ClO_4)_4 \cdot 3H_2O$ (**1**) and $[Zn(H_2BiIm)_2(HCO_2)]ClO_4$ (**2**) (H_2BiIm = 2,2′-biimidazole) as determined by single-crystal X-ray analysis are described. **1** was prepared from $Zn(ClO_4)_2 \cdot 6H_2O$ and H_2BiIm in aqueous solution. **2** is formed in a dioxane–water solution (1:1) containing $Zn(ClO_4)_2 \cdot 6H_2O$, H_2BiIm, and formic acid. **1** crystallizes in the orthorhombic space group $P2_12_12_1$, with $Z = 4$, $a = 19.743$ (6) Å, $b = 19.684$ (6) Å, $c = 12.034$ (3) Å, and $\rho_{calcd} = 1.78$ g cm^{-3}. Crystals of **2** are monoclinic, space group $P2_1/c$, with $Z = 4$, $a = 8.846$ (5) Å, $b = 26.921$ (16) Å, $c = 7.174$ (5) Å, $\beta = 90.35$ (6)°, and $\rho_{calcd} = 1.86$ g cm^{-3}. The structures were solved by direct methods and refined to conventional R factors of 0.053 and 0.048, respectively. Both complex cations have a distorted trigonal bipyramidal coordination geometry (tbp). Whereas in **1** both zinc atoms are exclusively coordinated by N atoms of the ligands, the central zinc atom in **2** is coordinated by an oxygen of a formato group and four nitrogen atoms of two bidentate biimidazole molecules. The apical bonds in the tbp of both complexes are Zn–N bonds with average distances of 2.219 Å for **1** and 2.203 Å for **2**. They are significantly longer than the bonds in the basal plane, which are on the average 2.025 Å for **1** and 2.037 Å for **2**. Molecular units in both structures are linked by three-dimensional hydrogen bond networks. The structures of the complexes are confirmed by vibrational and ^1H NMR spectroscopy and compared with related metal–biimidazole and metal–biimidazolate compounds. The metal environments of the complexes are relevant for the discussion of the active sites in zinc enzymes such as carboxypeptidase A; the importance of tbp five-coordinate intermediates for the catalytic action of zinc in enzymes is discussed.

Introduction

The imidazole moiety is of biochemical importance due to its presence in the side chain of histidine.[1] It has been found in more than 200 metalloenzymes as a zinc binding site. Some of these enzymes, such as carboxypeptidase A (CPA),[2] carbonic anhydrase (CA),[3] liver alcohol dehydrogenase (LADH),[4] and superoxide dismutase (SOD),[5] have been investigated most frequently in the past. The details of the reaction mechanisms at the metal centers, including the exact metal coordination, are only partially known in most of the cases, though the active sites of these enzymes have been the subjects of crystallographic investigation and a wide variety of spectroscopic studies. From some of these studies there was evidence for a pentacoordinate zinc center in the catalytic reaction intermediates (e.g. CPA,[6] CA,[7] or LADH[8]) or even in the native enzyme.[2] As these intermediates are often not accessible for structural studies, there is a need to investigate pentacoordinate zinc compounds with biomimetic ligands as synthetic analogues. They can mimic the biological unit concerning composition, ligand type, structure, and oxidation state. It should be stressed that, interestingly, the coordination number of 5 within a trigonal bipyramidal or square pyramidal ligand arrangement is more common in zinc chemistry than is generally known.[9] Examples of this class include compounds with simple unidentate ligands such as Cl^- in $Zn(C_{15}H_{11}N_3)Cl_2$, where the chelating ligand is terpyridyl,[10] or H_2O in $Zn(C_9H_8NO_3)_2(H_2O)_3 \cdot 3H_2O$, where the additional ligand is hippuric acid.[11] The water molecule is supposed to play an integral role in the catalytic mechanisms of most of the zinc enzymes (see below).

2,2′-Biimidazole can serve as an example for a biomimetic ligand. Interestingly enough, it occurs as the neutral bidentate molecule, H_2BiIm, as the monoanion, $HBiIm^-$, or as the dianion, $BiIm^{2-}$. The complexation by H_2BiIm to copper, nickel, cobalt, and ferrous iron was investigated, the complexes obtained being neutral and cationic.[12] Coordination compounds of univalent rhodium and iridium with the monoanion $HBiIm^-$ turned out to be monomeric square-planar species in which $HBiIm^-$ is bidentate. A binuclear rhodium compound with bridging $BiIm^{2-}$ was characterized by X-ray structure analysis, as well.[13] In $[Cu_2(Me_5dien)_2(BiIm)](BPh_4)_2$, where Me_5dien is 1,1,4,7,7-pentamethyldiethylenetriamine, the biimidazolate dianion bridges two Cu(II) centers.[14]

In the series of coordination compounds of transition-metal ions with neutral biimidazole the corresponding zinc compounds have not yet been prepared. The two complexes reported here are the first pentacoordinate zinc complexes containing neutral bidentate biimidazole as a bridging and nonbridging ligand. Octahedrally coordinated metal ions were found in the complexes of H_2BiIm with Fe(II), Fe(III), Co(II),[15] and Ni(II).[16] A corresponding

---

(1) Freeman, H. C. In *Inorganic Biochemistry*; Eichhorn, G. L., Ed.; Elsevier: Amsterdam, 1975.

(2) (a) Rees, D. C.; Lewis, M.; Lipscomb, W. N. *J. Mol. Biol.* **1983**, *168*, 367. (b) Rees, D. C.; Lewis, M.; Honzatko, R. B.; Lipscomb, W. N.; Hardman, K. D. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 3408. (c) Hardman, K. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1984**, *106*, 463.

(3) Kannan, K. K.; Liljas, A.; Waara, I.; Bergsten, P. C.; Lövgren, S.; Strandberg, B.; Bengtsson, U.; Carlbom, U.; Fridborg, K.; Järup, L.; Petef, M. *Cold Spring Harbor Symp. Quant. Biol.* **1971**, *36*, 221.

(4) Brändén, C.-I.; Jörnvall, H.; Eklund, H.; Furugren, B. In *The Enzymes*; Boyer, P. D., Ed.; Academic: New York, 1975; Vol. 11, p 104.

(5) Richardson, J. S.; Thomas, K. A.; Richardson, D. C. *Biochem. Biophys. Res. Commun.* **1975**, *63*, 986.

(6) (a) Kuo, L. C.; Makinen, M. W. *J. Biol. Chem.* **1982**, *257*, 24. (b) Christianson, D. W.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 7568.

(7) (a) Clementi, E.; Corongiu, G.; Jönsson, B.; Romano, S. *FEBS Lett.* **1979**, *100*, 313. (b) Hirose, J.; Kidani, Y. *Biochim. Biophys. Acta* **1980**, *622*, 71. (c) Dunn, M. F. *Struct. Bonding (Berlin)* **1975**, *23*, 61.

(8) Dworschak, R. T.; Plapp, B. V. *Biochemistry* **1977**, *16*, 111.

(9) Auf der Heyde, T. P. E.; Nassimbeni, L. R. *Acta Crystallogr., Sect. B: Struct. Sci.* **1984**, *B40*, 582. Recent references include: (a) Korp, J. D.; Bernal, I.; Merrill, C. L.; Wilson, L. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1951. (b) Smith, G.; O'Reilly, E. J.; Kennard, C. H. L.; Mak, T. C. W. *Inorg. Chem.* **1985**, *24*, 2321. (c) Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1985**, 2397. (d) Takahashi, K.; Nishida, Y.; Kida, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2628. (e) Castellano, E. E.; Oliva, G.; Zukerman-Schpector, J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 21. (f) Kai, Y.; Morita, M.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1631.

(10) Vlasse, M.; Rojo, T.; Beltran-Porter, D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 560.

(11) Grewe, H.; Udupa, M. R.; Krebs, B. *Inorg. Chim. Acta* **1982**, *63*, 119.

(12) Holmes, F.; Jones, K. M.; Torrible, E. G. *J. Chem. Soc.* **1961**, 4790.

(13) Kaiser, S. W.; Saillant, R. B.; Butler, W. M.; Rasmussen, P. G. *Inorg. Chem.* **1976**, *15*, 2681.

(14) Haddad, M. S.; Duesler, E. N.; Hendrickson, D. N. *Inorg. Chem.* **1979**, *18*, 141.

0020-1669/87/1326-3569$01.50/0 © 1987 American Chemical Society

Cu(II) compound contains square-planar N-coordinated H_2BiIm.[17] In $[Fe(H_2BiIm)_2Cl_2]Cl\cdot H_2O$, the iron(III) ion is coordinated octahedrally by four nitrogen and two chlorine atoms.[18] Complexes of Ru(II) with both 2,2′-bipyridine and 2,2′-biimidazole investigated by means of electrochemical methods contain octahedrally coordinated Ru(II) centers.[19,20] The reaction of sterically hindered rigid 4,4′,5,5′-tetramethyl-2,2′-biimidazole (Me_4H_2BiIm) with copper(II) and copper–zinc leads to two pentacoordinate metal complexes with square pyramidal coordination, $[Cu(Me_4H_2BiIm)_2(ONO_2)]NO_3$ and $[Zn_{0.9}Cu_{0.1}(Me_4H_2BiIm)_2(ONO_2)]NO_3$, which were characterized by X-ray structure and UV and ESR spectral analysis.[21] In the present investigation unsubstituted (and thus less sterically hindered) 2,2′-biimidazole is used as an example for a biomimetic ligand that combines the two imidazole donor functions in a system capable of forming strained chelate rings with the metal; the aim is to design complexes with trigonal-bipyramidal coordination of the zinc, which are catalytically more relevant than the square pyramidal ones[9] (see below).

Experimental Section

Chemicals. Dioxane was purified as described[22] and dried over sodium wire. Formic acid (100%, Merck) was used as purchased.

Elemental Analyses and Spectroscopy. Elemental analyses were performed by standard combustion techniques. Metal analyses were carried out with use of standard EDTA-titration techniques. NMR spectra were run at 20 °C on a Bruker WM-300 spectrometer (300 MHz) using tetramethylsilane (Me_4Si) as an internal standard. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 457 grating IR spectrophotometer. Far-infrared spectra were obtained from a Bruker IFS 113v instrument.

Preparation of $Zn(ClO_4)_2\cdot 6H_2O$. Zinc perchlorate hexahydrate was obtained as needle-shaped deliquescent crystals by slow evaporation of a solution of zinc oxide in 60% perchloric acid (Merck). Anal. Calcd for $Zn(ClO_4)_2\cdot 6H_2O$; Zn, 17.56. Found: Zn, 17.89.

Preparation of H_2BiIm. This was prepared by a modification of Debus' procedure.[12,23] In order to increase the yield, the purification procedure was modified as follows: the crude product was dissolved in dilute hydrochloric acid, the solution was stirred with charcoal, which was removed after 30 min, and the product was finally precipitated with dilute ammonia. This purification procedure was repeated twice, and then the product was recrystallized from boiling ethylene glycol. The cooled filtrate deposited needles, which were collected, washed with ice-cold water and acetone, and dried in air; yield 4.6 g (11%). Anal. Calcd for $C_6H_6N_4$: C, 53.72; H, 4.51; N, 41.77. Found: C, 53.01; H, 4.41; N, 40.89. ^1H NMR (1% solution in DMSO; 300 MHz; ppm): 7.24 (arom C–H), 3.43 (arom N–H). IR (KBr pellet; cm^{-1}): 3600–3300 w, br; 3150, 3080, 3000, 2900, 2810, 2640 w; 1740 w; 1670 m; 1548 s; 1430 m; 1410 s; 1339 m; 1220 s; 1142 w; 1120 sh; 1105 s; 940 s; 918 w; 885 s, br; 828 w; 765 m; 750 s; 738 sh; 690 s.

Preparation of $[Zn_2(\mu\text{-}H_2BiIm)(H_2BiIm)_4](ClO_4)_4\cdot 3H_2O$ (1). The ligand and zinc salt were reacted in a molar ratio of 1:3. Accordingly 0.3 g (2.24 mmol) of 2,2′-biimidazole was suspended in 100 mL of hot water. While the mixture was stirred, 2.5 g (6.72 mmol) of $Zn(ClO_4)_2\cdot 6H_2O$ was added, upon which the solution became clear. The mixture was then evaporated to a volume of 20 mL, from which slightly yellow crystals deposited upon standing at ambient temperature after 24 h. Anal. Calcd for $C_{30}H_{36}N_{20}Cl_4O_{19}Zn_2$: C, 28.75; H, 2.89; N, 22.35; Zn, 10.43. Found: C, 28.27; H, 2.88; N, 22.37; Zn, 10.89. ^1H NMR (ppm): 7.52, 7.38 (arom C–H); 3.21 (arom N–H). Far-IR (cm^{-1}): 273, 196 cm^{-1} (ν(Zn–N)). IR (KBr pellet; cm^{-1}): 3610–3500 m, br; 3240 s, br; 2936 w; 1720 w; 1621 m; 1525 s; 1429 s; 1381 m; 1338 w; 1317 w; 1170 s; 1100 s, br; 990 s; 934 s; 879 w; 846 w; 739 s; 675 s; 623 s; 502 m; 437 m.

Table I. Details of Data Collection and Structure Refinements for $[Zn_2(\mu\text{-}H_2BiIm)(H_2BiIm)_4](ClO_4)_4\cdot 3H_2O$ (**1**) and $[Zn(H_2BiIm)_2(HCO_2)]ClO_4$ (**2**)

	1	**2**
formula	$C_{30}H_{36}Cl_4Zn_2N_{20}O_{19}$	$C_{13}H_{13}ClZnN_8O_6$
fw	1253.30	478.12
cryst syst	orthorhombic	monoclinic
a, Å	19.743 (6)	8.846 (5)
b, Å	19.684 (6)	26.921 (16)
c, Å	12.034 (3)	7.174 (5)
β, deg		90.35 (6)
V, $Å^3$	4676.7	1708.4
Z	4	4
d_{calcd}, g cm^{-3}	1.78	1.86
space group	$P2_12_12_1$	$P2_1/c$
temp, K	140	140
cryst dimens, mm	0.16 × 0.20 × 0.20	0.25 × 0.15 × 0.10
radiation (graphite monochromatized)	Mo Kα	Mo Kα
μ(Mo Kα), cm^{-1}	13.9	16.9
scan mode	θ–2θ	ω
scan speed (intens dependent), deg min^{-1}	4–29	4–29
ratio bkgd/scan time	0.75	0.50
scan rang in θ, deg	2–27	2–27
index range	$+h,+k,+l$	$+h,+k,\pm l$
no. of indep reflcns measd	5677	3739
reflcns used (rejection criterion)	4394 ($I > 1.96\sigma(I)$)	2673 ($I > 1.96\sigma(I)$)
no. of variables	676	262
R_1, R_2, %	5.32, 4.34	4.78, 5.38

Preparation of $[Zn(H_2BiIm)_2(HCO_2)]ClO_4$ (2). The ligand (H_2BiIm) and zinc salt were reacted in a molar ratio of 5:2. A 0.60-g (4.48-mmol) sample of 2,2′-biimidazole was dissolved in 100 mL of a hot mixture of dioxane–water (1:1). By addition of 0.5 mL of formic acid, biimidazole was kept in solution, when the mixture cooled off to ambient temperature. Then 0.67 g (1.79 mmol) of $Zn(ClO_4)_2\cdot 6H_2O$ was added to the stirred solution. The formation of crystals, which were slightly yellow as well, was obtained by the method described above. Anal. Calcd for $C_{13}H_{13}N_8ClO_6Zn$: C, 32.66; H, 2.74; N, 23.44; Zn, 13.67. Found: C, 32.79; H, 2.82; N, 23.58; Zn, 13.90. ^1H NMR (ppm): 8.17 (formato H); 7.49, 7.31 (arom C–H); 3.40 (arom N–H). Far-IR (cm^{-1}): 337 (ν(Zn–O)); 259, 192 (ν(Zn–N)). IR (KBr pellet; cm^{-1}): 3350–3105 s, br; 2850 m; 2750 w; 1610 s; 1515 s; 1420 s; 1388 m; 1321 s; 1292 s; 1170 s; 1080 s, br; 989 m; 924 m; 853 m; 780 sh, 750 s; 678 s; 616 s; 486 s; 437 w; 428 m; 329 m.

Both complexes turned out to be air-stable; thus an inert-gas atmosphere during the preparations is not necessary.

Caution! The metal perchlorate and the solutions and complexes containing perchlorate were handled with care in regard to possible hazards by explosive decomposition.[24]

X-ray Data Collection and Reduction. X-ray diffraction data were collected with a Syntex $P2_1$ four-circle diffractometer (Mo Kα radiation, λ = 0.71069 Å). Selected crystals of **1** and **2** were fixed with a trace of silicone grease at the top of a glass fiber and cooled by a stream of nitrogen with use of a modified Syntex LT-1 low-temperature device. The unit cell dimensions with standard deviations were derived from a least-squares fit from the scattering angles of 18 (for **1**) and 22 (for **2**) centered reflections in the range 20° $\leq 2\theta \leq$ 30°. The experimental data of the measurements are given in Table I together with relevant details of the structure refinements. The intensities of a reference reflection remeasured every 99 scans exhibited only random fluctuations. The intensities of both data sets were empirically corrected for absorption (ψ-scan method) and for Lorentz and polarization effects (Lp). The range of absolute transmission factors was 0.64–0.69 for **1** and 0.72–0.80 for **2**. The variance of *I* was calculated as $\sigma^2(I) = S + (B_1 + B_2)(t_S/2t_B)^2$, where *S*, B_1, and B_2 are the scan and individual background counts and t_S and t_B are their counting times.

Solutions and Refinements of the Structures. All calculations were performed with use of programs of the Syntex EXTL and SHELXTL program packages. In both cases the space groups could be unambiguously determined by their systematic absences to be $P2_12_12_1$ for **1** and $P2_1/c$ for **2**. Starting points for the solutions of both structures were provided by direct methods, resulting in the location of the zinc atoms. Repeated

---

(15) Abushamleh, A. S.; Goodwin, H. A. *Aust. J. Chem.* **1979**, *32*, 513.

(16) Mighell, A. D.; Reimann, C. W.; Mauer, F. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 60.

(17) Sakaguchi, U.; Addison, A. W. *J. Chem. Soc., Dalton Trans.* **1979**, 600.

(18) Dance, I. G.; Abushamleh, A. S.; Goodwin, H. A. *Inorg. Chim. Acta* **1980**, *43*, 217.

(19) Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 2660.

(20) Haga, M.-A. *Inorg. Chim. Acta* **1983**, *75*, 29.

(21) Bernarducci, E. E.; Bharadwaj, P. K.; Lalancette, R. A.; Krogh-Jespersen, K.; Potenza, J. A.; Schugar, H. J. *Inorg. Chem.* **1983**, *22*, 3911.

(22) Weissberger, A.; Proskauer, E. S.; Riddick, J. A.; Toops, E. E. In *Techniques of Organic Chemistry*; Interscience: New York, 1955; Vol. VII, p 371.

(23) Debus, H. *Justus Liebigs Ann. Chem.* **1859**, *107*, 199.

(24) Raymond, K. N. *Chem. Eng. News* **1983**, *61* (Dec 5), 4.

Table II. Positional Parameters with Standard Deviations and Equivalent Isotropic Temperature Factors for $[Zn_2(\mu\text{-}H_2BiIm)(H_2BiIm)_4](ClO_4)_4\cdot 3H_2O$

	x	y	z	U_{eq},[a] Å^2		x	y	z	U_{eq}, Å^2
Zn(1)	0.03797 (4)	0.30078 (4)	0.38546 (6)	234 (2)	C(5)	−0.0255 (4)	0.3899 (3)	0.1610 (6)	31 (2)
Zn(2)	0.30755 (4)	0.17229 (3)	0.41489 (6)	209 (2)	C(6)	−0.0718 (3)	0.3717 (3)	0.0845 (5)	28 (2)
N(1)	−0.0318 (3)	0.2261 (3)	0.3660 (4)	25 (2)	C(7)	0.0246 (4)	0.4513 (3)	0.4736 (6)	39 (3)
N(2)	−0.1146 (3)	0.1809 (3)	0.2695 (5)	30 (2)	C(8)	0.0424 (4)	0.4818 (4)	0.5698 (7)	57 (3)
N(3)	−0.0233 (3)	0.3424 (3)	0.2444 (4)	25 (2)	C(9)	0.0629 (3)	0.3745 (3)	0.5838 (5)	28 (2)
N(4)	−0.0986 (3)	0.3111 (3)	0.1180 (4)	29 (2)	C(10)	0.0832 (3)	0.3066 (3)	0.6185 (5)	28 (2)
N(5)	0.0373 (3)	0.3826 (3)	0.4842 (4)	30 (2)	C(11)	0.1023 (3)	0.2001 (3)	0.5995 (5)	28 (2)
N(6)	0.0674 (3)	0.4334 (3)	0.6372 (5)	51 (2)	C(12)	0.1220 (4)	0.2168 (4)	0.7046 (6)	39 (3)
N(7)	0.0792 (3)	0.2566 (3)	0.5454 (4)	24 (2)	C(13)	0.1511 (3)	0.3571 (3)	0.2446 (5)	27 (2)
N(8)	0.1091 (3)	0.2848 (3)	0.7160 (4)	33 (2)	C(14)	0.2099 (3)	0.3411 (3)	0.1921 (5)	26 (2)
N(9)	0.1255 (3)	0.3006 (3)	0.2997 (4)	20 (2)	C(15)	0.1682 (3)	0.2517 (3)	0.2760 (5)	17 (2)
N(10)	0.2196 (3)	0.2737 (3)	0.2104 (4)	20 (2)	C(16)	0.1635 (3)	0.1820 (3)	0.3178 (5)	16 (2)
N(11)	0.2119 (3)	0.1478 (3)	0.3679 (4)	19 (2)	C(17)	0.1839 (3)	0.0854 (3)	0.3921 (5)	23 (2)
N(12)	0.1069 (3)	0.1457 (2)	0.3108 (4)	22 (2)	C(18)	0.1192 (3)	0.0834 (3)	0.3576 (5)	25 (2)
N(13)	0.2881 (3)	0.2756 (3)	0.4743 (5)	32 (2)	C(19)	0.2469 (4)	0.3140 (4)	0.5370 (7)	42 (3)
N(14)	0.3046 (3)	0.3827 (3)	0.4346 (5)	45 (2)	C(20)	0.2559 (4)	0.3800 (4)	0.5136 (7)	50 (3)
N(15)	0.3751 (3)	0.2253 (3)	0.3209 (4)	29 (2)	C(21)	0.3240 (3)	0.3189 (3)	0.4125 (6)	31 (2)
N(16)	0.4200 (3)	0.3230 (3)	0.2769 (5)	51 (2)	C(22)	0.3720 (4)	0.2925 (3)	0.3380 (5)	31 (2)
N(17)	0.3473 (3)	0.0748 (3)	0.3577 (4)	24 (2)	C(23)	0.4268 (4)	0.2130 (4)	0.2490 (6)	40 (2)
N(18)	0.3752 (3)	−0.0284 (2)	0.4106 (4)	18 (2)	C(24)	0.4539 (4)	0.2732 (4)	0.2196 (6)	49 (3)
N(19)	0.3185 (3)	0.1228 (3)	0.5631 (4)	24 (2)	C(25)	0.3663 (3)	0.0381 (3)	0.2669 (6)	28 (2)
N(20)	0.3293 (3)	0.0255 (3)	0.6503 (4)	30 (2)	C(26)	0.3844 (4)	−0.0260 (3)	0.2985 (5)	31 (2)
C(1)	−0.0454 (3)	0.1632 (3)	0.4087 (5)	31 (2)	C(27)	0.3530 (3)	0.0324 (3)	0.4440 (5)	19 (2)
C(2)	−0.0971 (3)	0.1353 (3)	0.3488 (6)	31 (2)	C(28)	0.3360 (3)	0.0577 (3)	0.5515 (5)	18 (2)
C(3)	−0.0734 (3)	0.2351 (3)	0.2830 (5)	22 (2)	C(29)	0.2997 (3)	0.1304 (3)	0.6732 (5)	21 (2)
C(4)	−0.0679 (3)	0.2966 (3)	0.2153 (5)	23 (2)	C(30)	0.3063 (4)	0.0709 (3)	0.7259 (5)	28 (2)
Cl(1)	0.24908 (8)	0.87288 (8)	0.53141 (12)	214 (5)	O(9)	0.0357 (3)	0.0934 (2)	0.1093 (4)	42 (3)
Cl(2)	−0.03162 (10)	−0.00264 (9)	0.58649 (14)	407 (6)	O(10)	−0.0496 (3)	0.1613 (3)	0.0302 (4)	53 (2)
Cl(3)	0.02142 (9)	0.15540 (9)	0.05109 (13)	328 (6)	O(11)	0.0442 (3)	0.2124 (2)	0.1153 (4)	45 (2)
Cl(4)	0.23432 (11)	0.45641 (10)	0.80340 (19)	510 (7)	O(12)	0.0584 (3)	0.1543 (3)	−0.0522 (4)	42 (2)
O(1)	0.2025 (2)	0.8300 (2)	0.5917 (4)	31 (1)	O(13)	0.1998 (4)	0.3974 (3)	0.7656 (6)	86 (3)
O(2)	0.3096 (2)	0.8810 (2)	0.5966 (4)	28 (1)	O(14)	0.2079 (5)	0.5131 (4)	0.7498 (5)	138 (5)
O(3)	0.2661 (2)	0.8417 (2)	0.4269 (3)	32 (2)	O(15)	0.2276 (5)	0.4645 (4)	0.9199 (6)	118 (4)
O(4)	0.2181 (2)	0.9379 (2)	0.5120 (4)	30 (2)	O(16)	0.3008 (4)	0.4509 (5)	0.7805 (9)	158 (5)
O(5)	−0.0315 (3)	−0.0717 (2)	0.6239 (4)	53 (2)	O(w1)	0.2007 (3)	0.7035 (3)	0.4196 (5)	58 (2)
O(6)	0.0351 (3)	0.0169 (3)	0.5574 (5)	69 (2)	O(w2)	0.1359 (3)	0.3071 (3)	0.9447 (4)	72 (2)
O(7)	−0.0579 (4)	0.0377 (3)	0.6756 (5)	83 (3)	O(w3)[b]	0.1695 (6)	0.5937 (6)	0.5508 (11)	101 (5)
O(8)	−0.0735 (3)	0.0063 (3)	0.4912 (5)	71 (3)					

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor and is multiplied by 10^4 for zinc and chlorine and by 10^3 for nitrogen, carbon, and oxygen. [b] Refined occupancy 0.606.

least-squares refinements followed by difference Fourier syntheses revealed the positions of all non-hydrogen atoms in the unit cells. Anomalously low electron density and a high temperature factor for atom O(w3) in the structure of **1** indicated partial loss of crystal water at this site. Chemical and optical investigation of the crystals at room temperature showed that this was due to slow dehydration after the crystals were removed from the mother liquor and before they were cooled down for data collection. Hence, the site occupation factor of the oxygen atom was allowed to vary and refined to a final value of 0.61. Hydrogen atoms were added to the models at calculated positions with N–H bond lengths of 0.88 Å and C–H bond lengths of 0.96 Å.[25] A planar geometry was assumed for the aromatic N and C atoms as well as for C(13) of the formato group in **2**. The hydrogen atoms were fixed in subsequent refinement cycles at their idealized positions relative to the atom to which they are bonded with isotropic temperature factors, U(H), 1.2 times the equivalent isotropic U values of their bonded atoms. Additional full-matrix least-squares refinement cycles using anisotropic temperature factors for all non-hydrogen atoms converged to $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.053$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.043$ for **1** and $R_1 = 0.048$ and $R_2 = 0.054$ for **2**. The quantity minimized was $\sum w(|F_o| - |F_c|)^{1/2}$, w being defined as $w = [\sigma^2(F_o) + (0.0001F_o)^2]^{-1}$ with $\sigma(F_o) = \sigma(I)/(2F_oLp)$. Extinction corrections were not applied. Atomic scattering factors for spherical, neutral, free (all except H) or bonded (H) atoms as well as anomalous scattering contributions were taken from ref 26. For the final cycle the mean parameter shift was within 0.010σ for **1** and 0.004σ for **2**, respectively, where σ is the esd obtained from the inverse matrix. A final difference Fourier synthesis showed a general background of approximately ±0.5 e/Å^3 in the vicinity of the oxygen atoms of the perchlorate ions. The anomalous dispersion of Zn was used to determine the absolute configuration of **1** in the crystal investigated. In the final stage of the refinement the coordinates of all atoms were inverted, and the structure was refined for both enantiomers with the same complete structure factor set. The final R values ($R_1 = 0.058$, $R_2 = 0.047$) for the wrong enantiomeric form were significantly higher than those (Table I) for the correct one reported here.

Final fractional coordinates of non-hydrogen atoms with standard deviations and equivalent isotropic temperature factors are listed in Table II (for **1**) and Table III (for **2**). A librational analysis of rigid-body motion was performed for all perchlorates by using the method of Schomaker and Trueblood.[27]

Results and Discussion

Synthesis of the Complexes. It is interesting to note that in both complexes zinc prefers a stoichiometric composition of the reaction product that enables five-coordination of the metal, even if the ratio of the reactants is varied within certain limits. It is difficult to trace down the dominating factor of those that determine the nature of the complex and that include (a) the coordinational preference of the metal, (b) steric requirements of the chelating ligands (bite, interligand repulsion), (c) packing considerations in the crystal, and (d) influence of the external charge of the complex. An a priori prediction of the possible products would require a careful multivariant analysis of these factors, which has not been reported for zinc complexes in any case.

Crystal Structures. $[Zn_2(\mu\text{-}H_2BiIm)(H_2BiIm)_4](ClO_4)_4\cdot 3H_2O$ (1). The numbering scheme of the cation of **1** is shown in Figure 1. The crystal structure consists of dinuclear $[Zn_2(H_2BiIm)_5]^{4+}$ complexes, perchlorate ions, and water molecules linked by hy-

---

(25) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(26) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(27) Schomaker, V.; Trueblood, K. N. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *B24*, 63.

Table III. Positional Parameters with Standard Deviations and Equivalent Isotropic Temperature Factors for $[Zn(H_2BiIm)_2(HCO_2)]ClO_4$

	x	y	z	U_{eq},[a] Å^2		x	y	z	U_{eq}, Å^2
Zn(1)	0.01650 (7)	0.36336 (2)	−0.02400 (8)	161 (1)	C(11)	0.7288 (6)	0.2782 (2)	−0.0819 (7)	20 (1)
C(1)	0.2992 (6)	0.4449 (2)	0.0672 (7)	19 (1)	C(12)	0.7246 (6)	0.2284 (2)	−0.0519 (7)	20 (1)
C(2)	0.2984 (6)	0.4893 (2)	0.1602 (7)	21 (2)	C(13)	0.0883 (6)	0.3968 (2)	−0.4062 (7)	20 (1)
C(3)	0.0710 (5)	0.4586 (2)	0.1560 (7)	13 (1)	N(1)	0.1567 (5)	0.4254 (2)	0.0650 (6)	18 (1)
C(4)	0.9135 (6)	0.4469 (2)	0.1804 (7)	17 (1)	N(2)	0.1535 (5)	0.4971 (1)	0.2144 (6)	17 (1)
C(5)	0.7090 (6)	0.4041 (2)	0.1584 (8)	25 (2)	N(3)	0.8583 (5)	0.4056 (2)	0.1089 (6)	18 (1)
C(6)	0.6758 (6)	0.4451 (2)	0.2596 (8)	21 (2)	N(4)	0.8066 (5)	0.4723 (2)	0.2723 (6)	19 (1)
C(7)	0.3040 (6)	0.3058 (2)	0.1494 (7)	18 (1)	N(5)	0.1580 (5)	0.3100 (2)	0.0871 (6)	16 (1)
C(8)	0.3338 (6)	0.2568 (2)	0.1877 (7)	21 (1)	N(6)	0.2032 (5)	0.2312 (1)	0.1478 (6)	16 (1)
C(9)	0.1006 (5)	0.2639 (2)	0.0877 (7)	14 (1)	N(7)	0.8685 (5)	0.2963 (1)	−0.0335 (6)	16 (1)
C(10)	0.9476 (6)	0.2571 (2)	0.0256 (7)	17 (1)	N(8)	0.8633 (5)	0.2154 (2)	0.0147 (6)	19 (1)
Cl(1)	0.50412 (14)	0.38454 (4)	0.64326 (17)	203 (3)	O(4)	0.6661 (5)	0.3846 (2)	0.6627 (6)	33 (1)
O(1)	0.0575 (4)	0.3601 (1)	−0.2985 (5)	20 (1)	O(5)	0.4622 (4)	0.3609 (2)	0.4724 (5)	29 (1)
O(2)	0.0514 (4)	0.4402 (1)	−0.3817 (5)	22 (1)	O(6)	0.4379 (5)	0.3577 (2)	0.7966 (6)	34 (1)
O(3)	0.4482 (5)	0.4348 (1)	0.6434 (6)	30 (1)					

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor and multiplied by 10^4 for zinc and chlorine and by 10^3 for carbon, nitrogen, and oxygen.

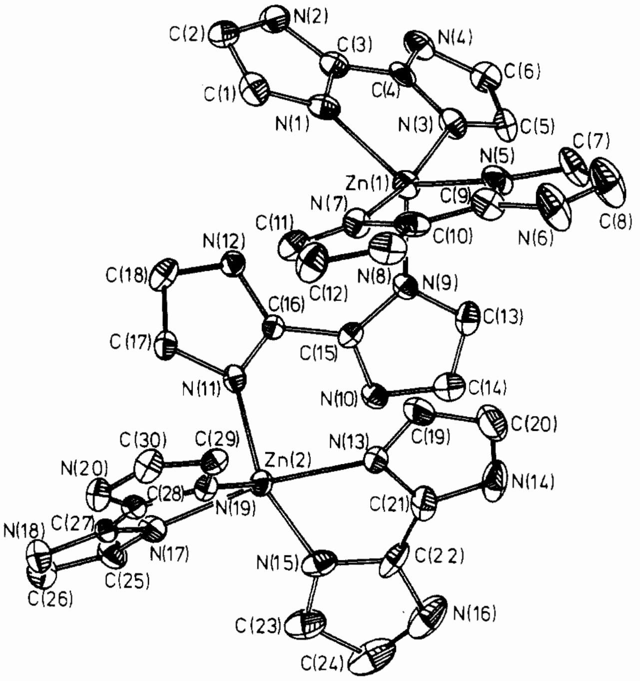


Figure 1. Ellipsoid plot of the $[Zn_2(H_2BiIm)_5]^{4+}$ cation structure of **1** showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are given for 50% probability.

drogen bonds. A stereoscopic projection of the unit cell is displayed in Figure 2. Selected bond distances and angles in the complex are listed in Table IV. Hydrogen bond information is given in Table V.

Each zinc atom is coordinated by two biimidazole molecules and connected with the other zinc atom by a bridging neutral biimidazole. Four perchlorate ions are incorporated in the lattice and held by Coulomb forces and weak hydrogen bonds to three water molecules and imidazole N–H groups. The coordination geometry around both zinc atoms is best described as distorted trigonal bipyramidal with the zinc atoms exclusively N-coordinated. Distances and angles within the coordination sphere are

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $[Zn_2(\mu\text{-}H_2BiIm)(H_2BiIm)_4](ClO_4)_4\cdot 3H_2O$[a]

	Coordination Sphere		
Zn(1)–N(1)	2.027 (5)	Zn(2)–N(11)	2.029 (5)
Zn(1)–N(3)	2.240 (5)	Zn(2)–N(13)	2.189 (5)
Zn(1)–N(5)	2.002 (5)	Zn(2)–N(15)	2.036 (5)
Zn(1)–N(7)	2.265 (5)	Zn(2)–N(17)	2.184 (5)
Zn(1)–N(9)	2.013 (5)	Zn(2)–N(19)	2.044 (5)
N(1)–Zn(1)–N(3)	79.1 (2)	N(11)–Zn(2)–N(13)	98.5 (2)
N(1)–Zn(1)–N(5)	130.3 (2)	N(11)–Zn(2)–N(15)	125.1 (2)
N(1)–Zn(1)–N(7)	93.7 (2)	N(11)–Zn(2)–N(17)	92.2 (2)
N(1)–Zn(1)–N(9)	121.5 (2)	N(11)–Zn(2)–N(19)	103.2 (2)
N(3)–Zn(1)–N(5)	98.7 (2)	N(13)–Zn(2)–N(15)	79.7 (2)
N(3)–Zn(1)–N(7)	168.3 (2)	N(13)–Zn(2)–N(17)	169.0 (2)
N(3)–Zn(1)–N(9)	94.4 (2)	N(13)–Zn(2)–N(19)	100.1 (2)
N(5)–Zn(1)–N(7)	78.9 (2)	N(15)–Zn(2)–N(17)	92.3 (2)
N(5)–Zn(1)–N(9)	108.2 (2)	N(15)–Zn(2)–N(19)	131.4 (2)
N(7)–Zn(1)–N(9)	97.2 (2)	N(17)–Zn(2)–N(19)	79.5 (2)
Zn(1)–N(1)–C(3)	114.6 (4)	Zn(2)–N(11)–C(16)	133.0 (4)
Zn(1)–N(3)–C(4)	108.3 (4)	Zn(2)–N(13)–C(21)	108.5 (4)
Zn(1)–N(5)–C(9)	116.2 (4)	Zn(2)–N(15)–C(22)	113.0 (4)
Zn(1)–N(7)–C(10)	107.5 (4)	Zn(2)–N(17)–C(27)	109.5 (4)
Zn(1)–N(9)–C(15)	131.6 (4)	Zn(2)–N(19)–C(28)	113.2 (4)
Zn(1)–N(1)–C(1)	138.3 (4)	Zn(2)–N(11)–C(17)	121.7 (4)
Zn(1)–N(3)–C(5)	145.1 (4)	Zn(2)–N(13)–C(19)	144.4 (5)
Zn(1)–N(5)–C(7)	137.2 (5)	Zn(2)–N(15)–C(23)	138.9 (5)
Zn(1)–N(7)–C(11)	146.8 (4)	Zn(2)–N(17)–C(25)	144.8 (4)
Zn(1)–N(9)–C(13)	123.8 (4)	Zn(2)–N(19)–C(29)	139.1 (4)
	Ligand (Mean)		
type *a*	1.322	type *d*	1.351
type *b*	1.343	type *e*	1.371
type *c*	1.359	type *h*	1.442

[a] See Figure 3 for an explanation of ligand bond distance type.

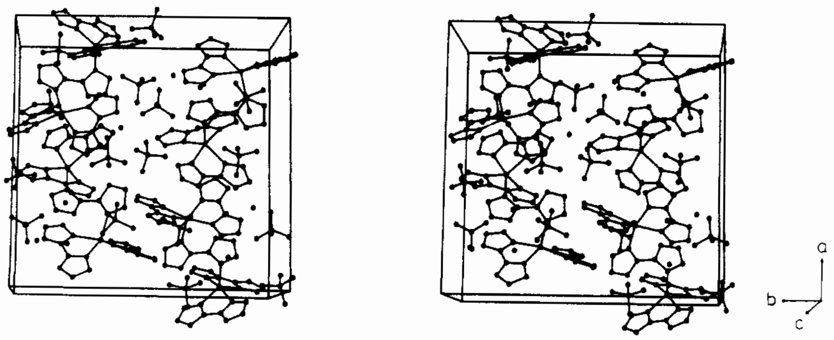


Figure 2. Stereoscopic drawing of the unit cell of **1**. Hydrogen atoms are omitted.

Table V. Hydrogen-Bonding Distances (Å) and Angles (deg) in $[Zn_2(\mu\text{-}H_2BiIm)(H_2BiIm)_4](ClO_4)_4 \cdot 3H_2O$[e]

bond type X–H···Y	X···Y	H···Y	∠X–H···Y
N(2)–H(N2)···O(w1)[a]	2.88	2.06	154
N(4)–H(N4)···O(w1)[a]	2.96	2.16	150
N(8)–H(N8)···O(w2)	2.84	2.07	149
N(16)–H(N16)···O(7)[b]	2.84	1.99	159
N(20)–H(N20)···O(2)[c]	2.99	2.23	137
O(w3)–H···O(10)[d]	2.88		
O(w1)–H···O(w3)	2.75		

[a] Symmetry operation $-x, -0.5 + y, 0.5 - z$. [b] Symmetry operation $0.5 + x, 0.5 - y, 1 - z$. [c] Symmetry operation $x, -1 + y, z$. [d] Symmetry operation $-x, 0.5 + y, 0.5 - z$. [e] Positions of hydrogen atoms bonded to nitrogen were calculated with d(N–H) set to 0.88 Å. Positions of hydrogen atoms of water molecules could not be calculated.

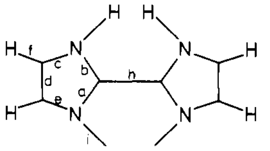


Figure 3. Bond indexation for the comparison of imidazole ring dimensions in 2,2′-biimidazole.

normal.[28] The apical Zn(1)–N(3) (2.240 (5) Å) and Zn(1)–N(7) (2.265 (5) Å) bonds are in the same range as the apical Zn(2)–N(13) (2.189 (5) Å) and Zn(2)–N(17) (2.184 (5) Å) ligations and are thus significantly longer than the average distance of 2.025 Å for the six basal Zn–N bonds. As shown in Table IV, the angles at the two zinc atoms agree better with a distorted trigonal bipyramidal (tbp) than with a square pyramidal (spy) geometry. The zinc atom Zn(1) (Zn(2)) is 0.006 Å (0.066 Å) under (above) the best plane defined by the basal nitrogen atoms N(1), N(5), and N(9) (N(11), N(15), and N(19)) of the tbp. Each imidazole ring is planar, with no atom deviating more than 0.010 Å from the best five-atom least-squares plane. The two rings of each nonbridging biimidazole ligand are slightly twisted around the C–C single bonds, forming dihedral angles between 4.3 and 9.2°. Consequently, individual ligand atoms are displaced by up to 0.10 Å from the least-squares planes of the biimidazoles. Steric requirements force the nearly planar imidazoles of the bridging biimidazole to form a dihedral angle of 49.8°, resulting in a deviation of up to 0.48 Å of the individual ligand atoms from the least-squares plane of that bridging ligand. The observed bond distances and angles within the imidazole moieties of the biimidazole ligands compare well with those reported for imidazole[29] and metal-coordinated imidazole.[30] However, the C–N bond length indicated as *a* in Figure 3 is significantly shortened compared with the C–N bond *b* to the protonated nitrogen. This fact does not agree with the observation of effective bond-length symmetry $a = b$ and $c = e$ by statistical comparison of imidazole ring dimensions in complexes of 2,2′-biimidazole and of the 2,2′-biimidazolate dianion.[18] Thus, the effects of metal coordination and hydrogen-bonded protonation at imidazole nitrogen atoms seem to have different consequences for the ring electronic structure in this case.

The four perchlorate groups show slightly distorted T_d symmetry. The largest deviation from the ideal angle of 109.5° is 2.4° at Cl(2). The librational analysis of rigid-body motion resulted in the bond lengths listed in Table XII (supplementary material) with corrections of up to 0.11 Å (e.g. for Cl(4)–O(16)).

$[Zn(H_2BiIm)_2(HCO_2)]ClO_4$ (2). The structure of **2** consists of discrete $[Zn(H_2BiIm)_2(HCO_2)]^+$ cations separated by perchlorate anions. The numbering scheme is shown in Figure 4.

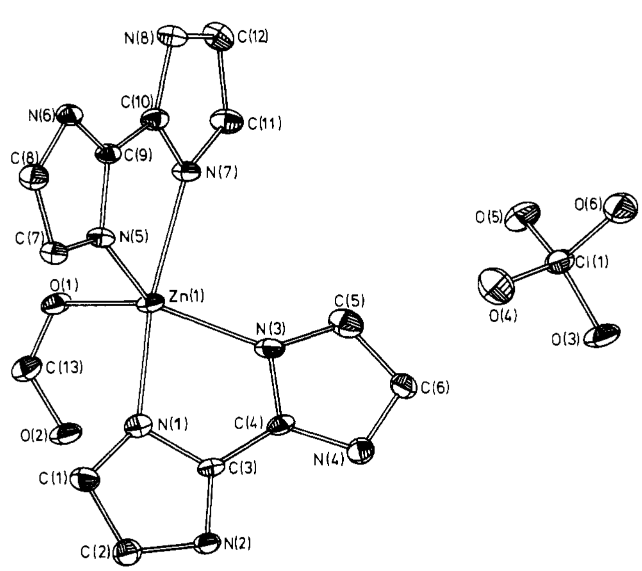


Figure 4. Molecular structure of **2** showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are given for 50% probability.

Table VI. Selected Interatomic Distances (Å) and Angles (deg) for $[Zn(H_2BiIm)_2(HCO_2)]ClO_4$[a]

Coordination Sphere			
Zn(1)–N(1)	2.174 (4)	Zn(1)–N(7)	2.231 (4)
Zn(1)–N(3)	2.043 (4)	Zn(1)–O(1)	2.006 (3)
Zn(1)–N(5)	2.062 (4)		
Zn(1)···O(2)	3.311 (4)		
N(1)–Zn(1)–N(3)	80.0 (2)	N(3)–Zn(1)–N(7)	93.5 (2)
N(1)–Zn(1)–N(5)	94.4 (2)	N(3)–Zn(1)–O(1)	127.7 (2)
N(1)–Zn(1)–N(7)	164.7 (2)	N(5)–Zn(1)–N(7)	78.6 (1)
N(1)–Zn(1)–O(1)	102.5 (1)	N(5)–Zn(1)–O(1)	103.6 (1)
N(3)–Zn(1)–N(5)	128.5 (2)	N(7)–Zn(1)–O(1)	92.5 (1)
Zn(1)–N(1)–C(3)	109.4 (3)	Zn(1)–N(5)–C(9)	114.6 (3)
Zn(1)–N(3)–C(4)	113.5 (3)	Zn(1)–N(7)–C(10)	109.0 (3)
Zn(1)–N(1)–C(1)	145.5 (3)	Zn(1)–N(5)–C(7)	138.9 (3)
Zn(1)–N(3)–C(5)	140.3 (3)	Zn(1)–N(7)–C(11)	145.5 (3)
Ligands (Mean)			
type *a*	1.334	type *d*	1.361
type *b*	1.354	type *e*	1.369
type *c*	1.366	type *h*	1.438
C(13)–O(1)	1.287 (6)	C(13)–O(2)	1.226 (6)
Zn(1)–O(1)–C(13)	126.7 (3)	O(1)–C(13)–O(2)	125.9 (5)

[a] See Figure 3 for an explanation of bond distance type.

The zinc atom has a trigonal bipyramidal N_4O coordination by two neutral bidentate biimidazole molecules and one oxygen of the formato group. There is no binding contact to the second formato oxygen (Zn(1)···O(2) = 3.311 (4) Å). The Zn(1)–O(1) bond is the shortest of the zinc–ligand bonds at 2.006 (3) Å. Details of the coordination sphere around the zinc atom are given in Table VI together with selected bond distances and angles. The apical bonds are averaged to a value of 2.203 Å; the mean value for the basal ligation is 2.037 Å. In addition, the angles at the zinc atom are indicative of tbp symmetry. The zinc atom is 0.051 Å above the best plane defined by the basal O(1), N(3), and N(5) atoms of the tbp. Each imidazole ring is planar, with no atom deviating more than 0.004 Å from the five-atom least-squares plane. The two rings of each biimidazole ligand are slightly twisted around the C–C single bonds by up to 3.4°. Consequently, the individual ligand atoms are displaced by up to 0.04 Å from the least-squares planes of the biimidazoles. The best planes defined by the zinc atom and a biimidazole on one hand (plane 1) and the zinc atom and the second biimidazole on the other hand (plane 2) form a dihedral angle of 49.9°. This unexpectedly small value results from one bidentate biimidazole molecule bridging the apex

---

(28) (a) Glick, M. D.; Cohen, G. H.; Hoard, J. L. *J. Am. Chem. Soc.* **1967**, *89*, 1996. (b) Grewe, H. Ph.D. Thesis, Münster, 1983.

(29) Martinez-Carrera, S. *Acta Crystallogr.* **1966**, *20*, 783.

(30) (a) Lundberg, B. K. S. *Acta Crystallogr.* **1966**, *21*, 901. (b) Bear, C. A.; Duggan, K. A.; Freeman, H. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr., Cryst. Chem.* **1975**, *B31*, 2713. (c) Sandmark, C.; Bränden, C. I. *Acta Chem. Scand.* **1967**, *21*, 993.

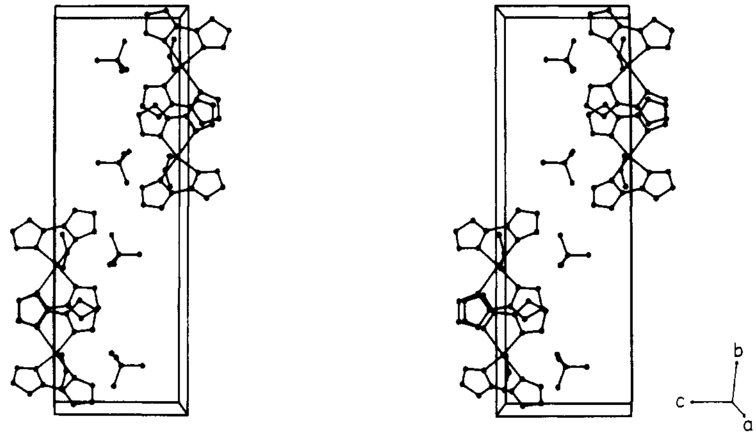


Figure 5. Stereoscopic view of the unit cell of **2**. Hydrogen atoms are omitted.

Table VII. Hydrogen-Bonding Distances (Å) and Angles (deg) in $[Zn_2(H_2BiIm)_2(HCO_2)]ClO_4$[c]

bond type X–H···Y	X···Y	H···Y	∠X–H···Y
N(2)–H(N2)···O(2)[a]	2.76	1.97	149
N(4)–H(N4)···O(2)[b]	2.78	2.00	148

[a] Symmetry operation x, $1 - y$, $-z$. [b] Symmetry operation $1 - x$, $1 - y$, $-z$. [c] Hydrogen positions were calculated with d(N–H) set to 0.88 Å.

and one edge of the basal triangle of the tbp via N(1) (apex) and N(3), while the second ligand bridges the other apex and another edge of the triangle via N(5) (apex) and N(7). The third edge of the triangle is occupied by O(1) of the formato group. Thus, the angle of the least-squares plane defined by the zinc atom and the formato moiety with plane 1 is 69.2° and with plane 2 is 94.4°.

The C–O distances of the formato ion indicate the delocalization of the π bond between the two C–O bonds. They are in the same range as were found in the formato–metal complexes *catena*-(μ-aqua)bis(benzimidazole)bis(formato)copper(II)[31] and bis(formamide)(formato)zinc(II) formate.[32] The interatomic distances in the two biimidazole molecles are listed for comparison in Table XIII (supplementary material). The bond length indicated as *a* (see Figure 3) of one biimidazole equals the distance *a* in the second ligand within the esd. The same applies to the interatomic distances *b*, *c*, *d*, and *e* in the imidazole moieties of the biimidazole ligands.

The symmetry of the perchlorate group is ideally tetrahedral (T_d) within the limits of error. A librational analysis was performed as well (see description of **1**), resulting in the corrected Cl–O bond lengths listed in Table XIII.

The cations and the perchlorate anions are held together by a network of hydrogen bonds. Detailed information is given in Table VII. Figure 5 shows a stereoscopic view of the unit cell without hydrogen atoms.

Five-Coordinate Zinc and Its Significance in Metalloenzymes. The two novel 2,2′-biimidazole–zinc compounds and their crystal structures are relevant additions to the small number of five-coordinate zinc complexes with nitrogen and oxygen donors that can be regarded as structural models for active sites in zinc enzymes. Besides some sterically overconstrained cases where the ligand atoms are part of a porphyrin or similar system excluding trigonal bipyramidal coordination,[33] and besides several catalytically less interesting halide complexes, not many structurally well characterized five-coordinate zinc compounds with biologically relevant ligands (including the ligand H_2O) have been reported (for a review up to 1983 see ref 9). Four typical examples with ligand-induced constrained geometries similar to those of the present compounds are $[Zn(dien)(bipyam)]^{2+}$ (dien = bis(2-aminoethyl)amine, bipyam = di-2-pyridylamine;[34] **3**), $[Zn(L\text{-}bisp)]^{2+}$ (L-bisp = 2,6-bis[1-((1-(carboxymethyl)-2-imidazol-4-ylethyl)imino)ethyl]pyridine;[35] **4**), and $[Zn(datau)]^{2+}$ (datau = 1,11-diamino-3,6,9-triazaundecane;[36] **5**), all three with tbp or approximate tbp ZnN_5 coordination geometry, and $[Zn(O_2COCH_3)(Me_4[14]aneN_4)]^-$ ($Me_4[14]aneN_4$ = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane;[37] **6**) with tbp ZnN_4O coordination. The details of the coordination polyhedra around Zn are remarkably similar in all cases. They are very close to tbp with the axial Zn–N bond lengths (average lengths (Å): **1**, 2.219; **2**, 2.203; **3**, 2.20; **4**, 2.195; **5**, 2.179; **6**, 2.229 Å) being significantly and uniformly longer than the basal Zn–N(O) ones (average lengths (Å): **1**, 2.025; **2**, 2.037; **3**, 2.09; **4**, 2.007; **5**, 2.063; **6**, 2.079 Å), with rather uniform N(ax)–Zn–N(ax) bond angles of 168.7 (**1**), 164.7 (**2**), 168.3 (**3**), 151.1 (**4**), 161.3 (**5**), and 166.2° (**6**) and with a planar arrangement of the ligand atoms in the base of the tbp (sums of the basal angles $\geq$359.6°, individual values dictated by steric requirements between 110.1 and 138.0°).

If the structures of these and other (also of partially S-coordinated) four-, five-, and six-coordinate zinc complexes are reviewed, an unusual variability and coordinational flexibility[9,38] of this metal center are evident. It has been shown[2c,7c,39] from mechanistic considerations and experiments, from spectroscopic investigations of cobalt(II) analogues and cobalt(II)-doped derivatives, and from structural correlation analysis[9] as well that this behavior is a prerequisite for the unusually efficient and kinetically rapid action of this metal in enzymatic catalysis. Most of the known Zn-catalyzed enzymatic reactions involve nucleophilic substitutions or nucleophilic attack with subsequent activation of one of the ligands at the metal sites,[40] and five-coordinate tbp zinc–ligand bonding in the "entatic state" plays a key role in the

---

(31) Bukowska-Strzyzewska, M.; Tosik, A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 203.

(32) Fortier, S.; Creber, K. A. M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 1763.

(33) (a) Kobayashi, T.; Ashida, T.; Uyeda, N.; Suito, E.; Kakudo, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2095. (b) Spaulding, L. D.; Eller, P. G.; Bertrand, J. A.; Felton, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 982. (c) Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 3761. (d) Cullen, D. L.; Meyer, E. F., Jr. *Acta Crystallogr., Sect. B: Struct. Crystallogr., Cryst. Chem.* **1976**, *B32*, 2259. (e) Kuila, D.; Lavallee, D. K.; Schauer, C. K.; Anderson, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 448.

(34) Ray, N.; Hathaway, B. *J. Chem. Soc., Dalton Trans.* **1980**, 1105.

(35) Casella, L.; Silver, M. E.; Ibers, J. A. *Inorg. Chem.* **1984**, *23*, 1409.

(36) Harrison, P. G.; Begley, M. J.; Kikabhai, T.; Killer, F. *J. Chem. Soc., Dalton Trans.* **1986**, 929.

(37) Kato, M.; Ito, T. *Inorg. Chem.* **1985**, *24*, 509.

(38) (a) Williams, R. J. P. *Pure Appl. Chem.* **1982**, *54*, 1889. (b) Prince, R. H.; Woolley, P. R. *Angew. Chem.* **1972**, *84*, 461; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 408.

(39) (a) Makinen, M. W.; Kuo, L. C.; Yim, M. B.; Maret, W.; Wells, G. B. *J. Mol. Catal.* **1984**, *23*, 179. (b) Dickinson, L. C.; Chien, J. C. W. *J. Am. Chem. Soc.* **1983**, *105*, 6481. (c) Lipscomb, W. N. *Colloq. Ges. Biol. Chem.* **1981**, 17. (d) Prince, R. H. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 349.

(40) (a) Vallee, B. L.; Galdes, A.; Auld, D. S.; Riordan, J. F. In *Metal Ions in Biology*; Spiro, T. G., Ed.; Wiley: New York, 1983; Vol. 5, pp 25–75. (b) Vallee, B. L. In *Zinc Enzymes*; Bertini, I., Luchinat, C., Maret, W., Zeppezauer, M., Eds.; Birkhäuser: Boston, 1986; p 4 ff. (c) Galdes, A.; Vallee, B. L. In *Metal Ions in Biological Systems*; Sigel, H., Ed.; Marcel Dekker: New York, 1983; Vol. 15, p 1 ff. (d) Williams, R. J. P. *J. Mol. Catal.* **1985**, *30*, 1.

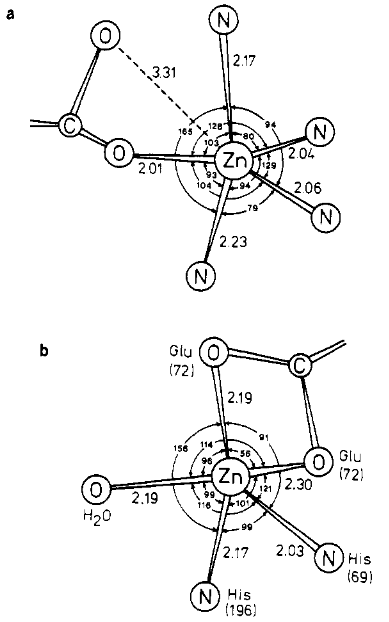


Figure 6. Schematic drawing of (a) the metal ion environment in **2** and (b) the configuration around the Zn(II) center in the active site of CPA.[2]

stereochemistry and dynamics of these reactions.[6,41] The more weakly bonded axial tbp positions are assumed as the sites of the nucleophile and the leaving (or activated) group. The tbp geometry may be present already in the native enzyme structure, as is the case for CPA,[2] or it may represent a transient state in the course of the substitution at tetrahedral centers, as postulated e.g. for LADH and CA.[42]

In accordance with the results from the investigation of the dynamic stereochemistry at five-coordinate zinc centers by structure correlation analysis[9] it can be suggested that the ZnN_5 and ZnN_4O stereochemistries found in **1** and **2** are close models for the geometry of the relevant tbp intermediate in the catalytic reaction path. An interesting comparison can be made with the active site of CPA, in which, as the only zinc enzyme yet, five-coordination has been identified in the most recent 1.54-Å resolution structure analysis.[2] In Figure 6a a schematic drawing of the metal environment of **2** is depicted. Figure 6b shows the configuration around the zinc(II) center in the active site of CPA based on the high-resolution X-ray structure analysis. In CPA the coordination is similar to that of **2** and can also be described as a (strongly distorted) trigonal bipyramid; however, in contrast to the case for **2** the carboxylate ligand (of glutamate-72) is bidentate chelating, and besides two imidazoles (of histidine-69 and -196) one water molecule completes the coordination sphere.

In the two alternative mechanisms put forward in the literature for the hydrolytic action of CPA,[43] namely (a) the direct nucleophilic attack of a water or OH^- at the scissile carbonyl carbon of the substrate, the nucleophile being activated by the γ-carboxylate of glutamate-270 and the zinc ("general base mechanism"), or (b) the attack of the γ-carboxylate of glutamate-270 at the substrate carbonyl carbon, yielding a mixed-anhydride intermediate to be hydrolyzed to the final products ("mixed-anhydride mechanism"), zinc plays an active role in polarizing the substrate carbonyl group and activating a coordinate water molecule. In each case a reaction intermediate must be assumed with coordination number 5 at the active site and most probably with a tbp geometry similar to those at the zinc in **1** and **2**.

In a comparison of the unidentate coordination of the carboxylate to the zinc in **2** to the asymmetric bidentate ligation in the structure of CPA (Figure 6), **2** may serve as a model for the probable modification of the zinc coordination sphere in CPA upon addition of a substrate carbonyl to the metal center. It can be proposed that the reaction path to a kinetically more inert six-coordinate complex is avoided in favor of a still five-coordinated reaction intermediate. This is achieved, with a pseudorotative rearrangement in the coordination sphere,[9] by a concerted nucleophilic addition of the substrate and simultaneous change of the carboxylate from bidentate to unidentate.

Spectroscopic and Solubility Properties. The IR spectra of the solids (KBr pellets) show a broad absorption band at 3500–3050 cm^{-1}, which is assigned to the ν(N–H) stretching vibrations. Their shift to higher energies compared to the position in the free ligand is indicative of their coordination as bidentate chelating ligands. Several absorption bands in the spectra of the complexes are basically identical with those assigned to the free ligands. Both spectra reveal the ν_3 and ν_4 absorption bands of the perchlorate anion, whereas the ν_1 and ν_2 fundamentals are not observed (cf. ref 44). The ν_3 absorption at 1120–1010 cm^{-1} for **1** and **2** is a broad and split band because of hydrogen bridging via $O-H\cdots OClO_3$ and $N-H\cdots OClO_3$ (see Tables V and VII), which implies a distortion of T_d toward C_{3v} symmetry.[45] The strong and sharp band at 620 cm^{-1} is assigned to ν_4. Waters of hydration in **1** show their H–O–H bending mode at 1621 cm^{-1}. The coordination of the formato moiety to the zinc atom in **2** is proved by the shifts of the stretching vibrations ν_{as} and ν_s of the carboxyl group relative to their locations in the free ligand. The asymmetric bond distribution in the coordinated group[46] shifts ν_{as}(OCO) to higher energy at 1610 cm^{-1} and lowers the frequency of ν_s(OCO) to 1420 cm^{-1}. The difference $\nu_{as}(OCO) - \nu_s(OCO) = 190\ cm^{-1}$ is indicative of a unidentate carboxyl moiety, in contrast to a chelating one, where the two absorption bands appear closer to each other.[46] The far-IR spectra (Figures 7 and 8, supplementary material) show a number of bands that do not appear in the spectrum of the free ligand and are thus assigned to fundamental skeletal modes of the tbp unit (D_{3h}).[47] Absorptions pertaining to Zn–N and Zn–O stretching vibrations can be assigned as follows: bands at 273 and 196 cm^{-1} in the spectrum of complex **1** are attributed to Zn–N stretching modes, corresponding to two bands at 259 and 192 cm^{-1} (ν(Zn–N)) in the spectrum of complex **2**. The absorption band at 337 cm^{-1} in this spectrum is assigned to the ν(Zn–O) vibration. This is in good agreement with the observations of da Silveira et al.[48] and of our group.[11]

In the ^1H NMR spectra metal coordination to biimidazole results in downfield chemical shifts of the ring protons (see Experimental Section). This is in accordance with a lowering of electron density in the ring system.[49] All spectra show a signal for the N–H protons whose intensity and width is solvent- and concentration-dependent. Bridging H_2BiIm in **1** cannot be distinguished from bidentate chelating H_2BiIm. Intermolecular proton exchange causes the coalescence of the C–H resonances in the spectrum of the free ligand. This signal is split into two peaks in the spectra of the complexes, thus indicating coordination at the imidazole nitrogen atom. The signal in the spectrum of complex **2** at 8.17 ppm is assigned to the proton of the formic acid moiety.[50]

---

(41) (a) Suigimoto, T.; Kaiser, E. T. *J. Am. Chem. Soc.* **1979**, *101*, 3946. (b) Sander, M. E.; Witzel, H. *Biochem. Biophys. Res. Commun.* **1985**, *132*, 681.

(42) (a) Zeppezauer, M.; Andersson, I.; Dietrich, H.; Gerber, M.; Maret, W.; Schneider, G.; Schneider-Bernlöhr, H. *J. Mol. Catal.* **1984**, *23*, 377. (b) Makinen, M. W.; Maret, W.; Yim, M. B. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 2584. (c) Pocker, Y.; Deits, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 3949; **1982**, *104*, 2424.

(43) (a) Lipscomb, W. N. *Acc. Chem. Res.* **1982**, *15*, 232. (b) Lipscomb, W. N. *Annu. Rev. Biochem.* **1983**, *52*, 17. (c) Vallee, B. L.; Galdes, A. *Adv. Enzymol.* **1984**, *56*, 283.

(44) Reedijk, J. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1451.

(45) Uson, R.; Gimeno, J.; Oro, L. A.; Valderrama, M.; Sariego, R.; Martinez, E. *Transition Met. Chem.* (*Weinheim, Ger.*) **1981**, *6*, 103.

(46) Nakamato, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1978.

(47) Weidlein, J.; Müller, U.; Dehnicke, K. *Schwingungsfrequenzen I*; Thieme Verlag: Stuttgart, 1981.

(48) Da Silveira, A.; Marques, M. A.; Marques, N. M. *Mol. Phys.* **1965**, *9*, 271.

(49) Carlson, R. H.; Brown, T. L. *Inorg. Chem.* **1966**, *5*, 268.

(50) Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der Organischen Chemie*; Thieme Verlag: Stuttgart, 1979.

Both complexes are insoluble in water and nonpolar solvents. Compound **1** is soluble in methanol, ethanol, and acetone and compound **2** in a mixture of dioxane-water only. Decomposition of both is observed in DMF and DMSO.

Acknowledgment. Financial support from the Fonds der Chemischen Industrie is gratefully acknowledged. We also thank M. Dartmann for technical assistance. This work has been funded by the German Federal Minister for Research and Technology (BMFT) under Contract No. 05339GAB/3.

Supplementary Material Available: Lists of anisotropic thermal parameters (Table VIII for **1** and Table X for **2**), fractional atomic coordinates for hydrogen atoms (Table IX for **1** and Table XI for **2**), and additional interatomic distances and angles (Table XII for **1** and Table XIII for **2**) and the far-IR spectra of **1** and **2** (Figures 7 and 8) (15 pages); lists of observed and calculated structure factors (Table XIV for **1** and Table XV for **2**) (40 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Missouri, Columbia, Missouri 65211

Effect of Ring Size on Properties of Technetium Amine Oxime Complexes. X-ray Structures of $TcO_2Pent(AO)_2$, Which Contains an Unusual Eight-Membered Chelate Ring, and of $TcOEn(AO)_2$

Silvia Jurisson,* Karl Aston,[†] C. Kay Fair,[‡] Elmer O. Schlemper, Paul R. Sharp, and David E. Troutner

Received January 14, 1987

A series of neutral technetium(V) complexes have been synthesized ($TcO(AO)_2$, $TcOEn(AO)_2$, $TcO_2Bn(AO)_2$, and $TcO_2Pent(AO)_2$) in which the length of the hydrocarbon backbone of the amine oxime ligand is varied to effect chemical changes in the resultant complexes. $Pn(AO)_2$, 3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime, is the prototype for these ligands. In this series of technetium(V) complexes in which the overall ring size is varied, both monooxo and *trans*-dioxo cores are observed, and an unusual eight-member chelate ring with the technetium(V) center is found with $TcO_2Pent(AO)_2$. $TcO_2Pent(AO)_2\cdot CHCl_3$, $TcCl_6O_4N_4C_{17}H_{33}$, crystallizes in the triclinic system, space group $P\bar{1}$, with a = 1.418 (2) Å, b = 13.940 (7) Å, c = 18.992 (10) Å, α = 69.29 (4)°, β = 90.00 (3)°, γ = 83.69 (3)°, and Z = 4. $TcOEn(AO)_2$, $TcO_3N_4C_{12}H_{23}$, crystallizes in the orthorhombic system, space group *Pbca*, with a = 11.581 (2) Å, b = 12.596 (4) Å, c = 21.155 (3) Å, and Z = 8.

Introduction

The technetium-99m complex of $Pn(AO)_2$, 3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime (Table I), has been shown to be neutral, lipophilic, and able to cross the intact blood brain barrier.[1,2] Recently, we reported the synthesis and characterization of a number of technetium-99-oxo-tetradentate amine oxime complexes in which the substituents on the $Pn(AO)_2$ backbone had been varied.[3] Of these, *dl*-^{99m}TcOHM-PAO has been shown to be an effective cerebral blood flow agent.[4-6]

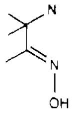
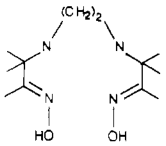
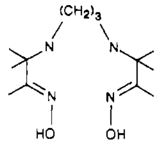
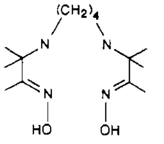
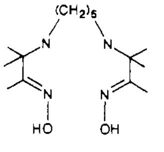
We have been interested for some time in technetium complexes of amine oxime ligands in which the lengths of the hydrocarbon backbones, rather than the substituents on the backbones, are varied to probe the effect(s) on the chemistry of the resultant complexes. The amine oxime ligands of interest are shown in Table I. The amine oxime is varied monotonically from AO, which has no amine-amine hydrocarbon backbone and thus is a bidentate ligand, to $Pent(AO)_2$, which has a five-carbon backbone and forms an unusual eight-member chelate ring on coordination to the Tc(V) center. This series allows the overall macrocyclic ring size about the technetium to be varied from the 13-member $En(AO)_2$ to the 16-member $Pent(AO)_2$ and includes the open-ended member AO.

With these technetium(V) amine oxime complexes we observe both five-coordinate monooxo technetium(V) species (as in $TcOPn(AO)_2$) and six-coordinate *trans*-dioxo technetium(V) species. The syntheses and characterization of $Pent(AO)_2$ and the technetium-99 complexes with these amine oxime ligands are reported.

Experimental Section

General Data. Syntheses were performed with technetium-99, a low-energy (0.292 MeV) β-particle emitter with a half-life of 2.12 × 10^5 years. When handled in milligram quantities, ^{99}Tc does not present a serious health hazard since common laboratory materials provide adequate shielding. Bremsstrahlung is not a significant problem due to the low energy of the β-particle emission, but normal radiation safety procedures must be used at all times to prevent contamination.

Table I. Ligand Nomenclature

ligand	acronym	name
$-CH_2CH_2-$	En	ethylene
$-CH_2CH_2CH_2-$	Pn	propylene
$-CH_2CH_2CH_2CH_2-$	Bn	butylene
$-CH_2CH_2CH_2CH_2CH_2-$	Pent	pentyl
	AO	3-amino-3-methyl-2-butanone oxime or amine oxime
	$En(AO)_2$	3,3,8,8-tetramethyl-4,7-diazadecane-2,9-dione dioxime
	$Pn(AO)_2$	3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime
	$Bn(AO)_2$	3,3,10,10-tetramethyl-4,9-diazadodecane-2,11-dione dioxime
	$Pent(AO)_2$	3,3,11,11-tetramethyl-4,10-diazatridecane-2,12-dione dioxime

---

* To whom correspondence should be addressed. Current address: E. R. Squibb, P.O. Box 191, New Brunswick, NJ 08903.

[†] Current address: 9907 Gilbrook, Rock Hill, MO 63119.

[‡] Current address: Enraf-Nonius, Bohemia, NY 11716.

(1) Troutner, D. E.; Volkert, W. A.; Hoffman, T. J.; Holmes, R. A. *Int. J. Appl. Radiat. Isot.* **1984**, *35*, 467.

0020-1669/87/1326-3576$01.50/0