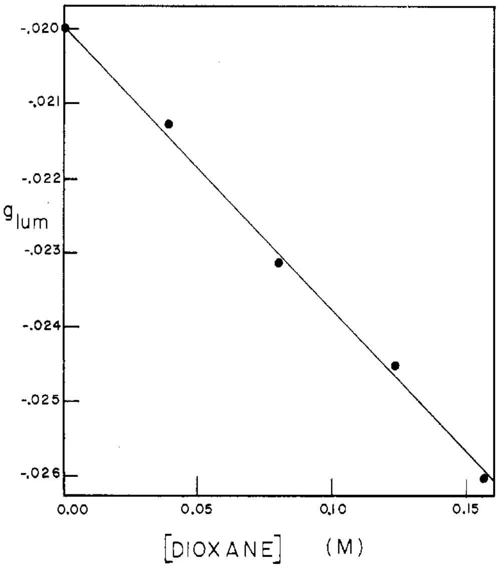


Figure 2. Enhancement of the luminescence dissymmetry factor in the $Tb(DPA)_3^{3-}$/Λ-$Cr(en)_3^{3+}$ system by the addition of dioxane.

found that g_{lum} = 0.020 when the CPL was induced by Λ-$Cr(en)_3^{3+}$ and g_{lum} = +0.022 when the CPL was induced by Δ-$Cr(en)_3^{3+}$.

For an understanding of the mechanism by which the optical activity was induced in the $Tb(DPA)_3^{3-}$ complex, a study was carried out in which the CPL of a $Tb(DPA)_3^{3-}$/Λ-$Cr(en)_3^{3-}$ solution was monitored during the addition of microliter amounts of neat dioxane. As may be seen in Figure 2 , the g_{lum} factor increases with added dioxane. This behavior with decreasing dielectric constant of the solvent is consistent with the existence of $Tb(DPA)_3^{3-}$/$Cr(en)_3^{3+}$ ion pairs. The decreased dielectric constant of the mixed solvent will lead to enhanced electrostatic attraction between the two complex ions. We therefore conclude that the Pfeiffer mechanism operational in the present system is one where optical activity is induced through the formation of an adduct species. Our work thus provides evidence that the associative mechanism[2] is operational in this Pfeiffer-active system.

It is of great interest to determine which isomer of the $Tb(DPA)_3^{3-}$ is favored by complexation with a particular enantiomer of $Cr(en)_3^{3+}$, since this would then permit one (hopefully) to assign absolute configurations of other Tb(III) complexes on the basis of CPL sign patterns. Such a possibility would be of great utility in the study of Tb(III)-substituted Ca-binding proteins, since the CPL associated with the Tb(III) emission in these proteins usually consists of one particular mirror image of a certain line shape.[9] Unfortunately, no CPL spectra of Tb(III) complexes having known absolute configurations have yet been reported, but it is possible to make certain predictions on the basis of existing information. In a recent study,[10] we have found that CPL can be induced in the emission spectrum of $Tb(DPA)_3^{3-}$ through outer-sphere coordination with L-ascorbic acid. TL and CPL spectra were obtained that were identical with those obtained in the present study when Λ-$Cr(en)_3^{3+}$ was used to induce the optical activity. One cannot assume that the L isomer of an added chiral agent will always enrich the L isomer of a racemic mixture in the course of a Pfeiffer-effect measurement.[3] Since our work represents the first investigation into Pfeiffer effects involving 9-coordinate complexes, we have no evidence to predict which enantiomer of $Tb(DPA)_3^{3-}$ ought to be enriched by a particular enantiomer of $Cr(en)_3^{3+}$. However, if one were to assume that the Λ isomer of $Cr(en)_3^{3+}$ enriches the system in the Λ isomer of $Tb(DPA)_3^{3-}$, the Tb(III) CPL spectrum having the major negative component at 543 nm would be due to the presence of the Λ isomer of $Tb(DPA)_3^{3-}$.

No evidence was obtained during the course of the present study to indicate that the added $Cr(en)_3^{3+}$ did anything to the $Tb(DPA)_3^{3-}$ complex except to coordinate in an outer-sphere fashion. The TL spectra of the Tb(III) ion were identical in $Tb(DPA)_3^{3-}$ and $Tb(DPA)_3^{3-}$/$Cr(en)_3^{3+}$, and we have reported this TL line shape before.[6,11] Some quenching of the Tb(III) TL intensity was noted after addition of the Cr(III) complex, but this quenching appears to be due to a combination of Tb(III)–Cr(III) energy transfer and an "inner-filter" effect of the Cr(III) complex absorbing some of the exciting light.

Comparison of the g_{lum} values obtained during the course of the present study with earlier data (obtained in a study of mixed-ligand complexes formed between Tb(III), DPA, and L-malic acid[11]) provides strong evidence that we are dealing with configurational optical activity in the $Tb(DPA)_3^{3-}$/$Cr(en)_3^{3+}$ system. We believe that while lanthanide complexes may not be resolved through conventional techniques, the CD of these complexes may be studied via the Pfeiffer effect. Many studies have shown that the Pfeiffer CD of a particular complex is identical with that of resolved complex CD.[1] While it is difficult to place the data on an absolutely quantitative basis (one is never sure of the degree of resolution permitted by a Pfeiffer effect), it seems clear that line shapes and trends within the CPL data can be used to deduce stereochemical information for lanthanide complexes in the same manner that CD results have been used for transition metal complexes.

Acknowledgment. We thank Cindi Petrucci and Susan Thompson for performing the synthesis and resolution of the $Cr(en)_3^{3+}$ complex. This work was supported by the Research Corp. through Grant 8926 of the Cottrell Research Program.

Registry No. $Tb(DPA)_3^{3-}$, 38682-37-0; Λ-$Cr(en)_3^{3+}$, 41509-53-9; Δ-$Cr(en)_3^{3+}$, 51002-41-6.

---

(9) Brittain, H. G.; Richardson, F. S.; Martin, R. B. *J. Am. Chem. Soc.* **1976**, *98*, 8255.

(10) Madaras, J.; Brittain, H. G. *Inorg. Chim. Acta* **1980**, *42*, 109.

(11) Brittain, H. G. *Inorg. Chem.* **1980**, *19*, 2136.

Contribution from the Department of Chemistry,
The Pennsylvania State University,
University Park, Pennsylvania 16802

Crystal and Molecular Structure of Hexa(imidazolyl)cyclotriphosphazene

R. J. Ritchie, T. J. Fuller, and H. R. Allcock*

Received March 26, 1980

A knowledge of the structure and hydrolytic stability of cyclic and high polymeric aminophosphazenes is important for both fundamental mechanistic and biomedical reasons.[1–7] Imidazolyl-substituted phosphazenes are of particular interest because of their potential use as coordinative ligands for

---

(1) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.

(2) Allcock, H. R. "Phosphorus-Nitrogen Compounds"; Academic Press: New York, 1972; Chapters 5 and 7.

(3) Allcock, H. R.; Allen, R. W.; O'Brien, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 3984.

(4) Allen, R. W.; O'Brien, J. P.; Allcock, H. R. *J. Am. Chem. Soc.* **1977**, *99*, 3987.

(5) O'Brien, J. P.; Allen, R. W.; Allcock, H. R. *Inorg. Chem.* **1979**, *8*, 2230.

(6) Allcock, H. R.; Fuller, T. J.; Mack, D. P.; Matsumura, K.; Smeltz, K. M. *Macromolecules*, **1977**, *10*, 824.

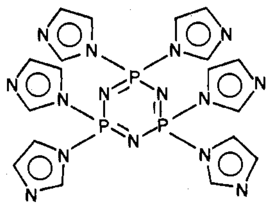
(7) Allcock, H. R.; Greigger, P. P.; Gardner, J. E.; Schmutz, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 606.

0020-1669/80/1319-3842$01.00/0 © 1980 American Chemical Society

Table I. Positional and Thermal Parameters for $N_3P_3(C_3N_2H_3)_6$ (I)

atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
P1	0.2780 (2)	0.8811 (2)	0.15628 (7)	2.89 (9)	2.54 (9)	2.14 (8)	−0.35 (9)	0.37 (7)	0.27 (8)
P2	0.0793 (2)	0.8240 (2)	0.12101 (7)	2.97 (9)	2.31 (9)	2.11 (8)	−0.52 (9)	0.79 (7)	0.07 (8)
P3	0.1811 (2)	0.9575 (2)	0.07109 (7)	3.22 (9)	2.47 (9)	2.23 (8)	−0.26 (9)	0.96 (7)	0.42 (8)
N1	0.1770 (5)	0.8166 (6)	0.1607 (2)	2.8 (3)	3.1 (3)	2.3 (3)	−0.7 (3)	0.5 (2)	0.4 (3)
N2	0.0761 (5)	0.9061 (5)	0.0785 (2)	3.0 (3)	2.8 (3)	2.3 (3)	−0.5 (3)	0.3 (2)	0.6 (3)
N3	0.2799 (5)	0.9393 (5)	0.1086 (2)	3.3 (3)	3.8 (4)	2.3 (3)	−1.1 (3)	0.2 (2)	1.2 (3)
N4	0.3024 (5)	0.9762 (6)	0.1978 (2)	4.6 (3)	3.0 (3)	3.3 (3)	−1.2 (3)	1.3 (3)	−0.9 (3)
N41	0.3229 (7)	1.0509 (7)	0.2678 (3)	8.2 (4)	8.5 (5)	4.5 (4)	−4.4 (4)	1.9 (4)	−3.1 (4)
N5	0.3781 (5)	0.7971 (5)	0.1700 (2)	3.4 (3)	2.8 (3)	3.3 (3)	0.0 (3)	1.1 (2)	0.3 (3)
N51	0.4801 (8)	0.6607 (8)	0.1912 (3)	7.5 (5)	7.6 (6)	6.6 (5)	2.0 (5)	0.2 (5)	0.8 (5)
N6	−0.0212 (4)	0.8544 (5)	0.1460 (2)	2.0 (3)	2.9 (3)	2.8 (3)	−0.4 (2)	0.7 (2)	−0.0 (3)
N61	−0.1075 (6)	0.8854 (7)	0.2007 (2)	4.7 (4)	7.4 (5)	3.8 (3)	0.9 (4)	2.4 (3)	0.0 (4)
N7	0.0492 (5)	0.7005 (5)	0.0985 (2)	2.9 (3)	2.4 (3)	2.8 (3)	−0.8 (3)	0.9 (2)	−0.5 (3)
N71	0.0316 (7)	0.5234 (6)	0.0947 (3)	7.5 (5)	2.8 (4)	7.6 (5)	−0.4 (4)	2.6 (4)	0.0 (4)
N8	0.2046 (5)	0.9217 (6)	0.0194 (2)	4.2 (3)	2.9 (3)	2.6 (3)	0.6 (3)	1.4 (2)	0.4 (3)
N81	0.2808 (6)	0.8565 (7)	−0.0345 (3)	8.1 (4)	5.5 (5)	5.1 (3)	−1.1 (4)	4.6 (3)	−1.0 (3)
N9	0.1547 (5)	1.0909 (5)	0.0616 (2)	4.7 (3)	1.6 (3)	3.6 (3)	0.1 (3)	1.8 (2)	0.9 (3)
N91	0.1773 (6)	1.2608 (6)	0.0426 (3)	6.1 (4)	2.6 (3)	5.5 (4)	−0.2 (3)	1.5 (3)	1.1 (3)
C1N4	0.3301 (15)	1.0803 (10)	0.1939 (5)	29 (2)	4.8 (6)	8.1 (7)	−8.2 (7)	7.8 (8)	−3.8 (5)
C2N4	0.3458 (12)	1.1223 (10)	0.2381 (4)	16 (1)	5.6 (6)	6.5 (7)	−3.5 (7)	1.3 (7)	−2.2 (6)
C3N4	0.3012 (11)	0.9621 (9)	0.2438 (4)	16.6 (9)	6.3 (6)	4.5 (5)	−5.6 (6)	5.1 (5)	−2.9 (5)
C1N5	0.4807 (8)	0.8252 (9)	0.1725 (5)	3.1 (4)	6.2 (6)	11.8 (8)	0.4 (5)	2.4 (5)	2.9 (6)
C2N5	0.5403 (7)	0.7461 (8)	0.1834 (3)	3.4 (4)	4.5 (5)	6.1 (5)	1.6 (4)	1.8 (4)	1.6 (4)
C3N5	0.3800 (8)	0.6916 (8)	0.1836 (4)	5.8 (5)	4.2 (5)	5.8 (5)	2.0 (4)	0.9 (4)	1.3 (5)
C1N6	−0.1206 (7)	0.8613 (9)	0.1255 (3)	2.8 (4)	7.5 (6)	3.3 (4)	0.5 (4)	0.6 (3)	−0.2 (4)
C2N6	−0.1751 (7)	0.8833 (9)	0.1589 (3)	4.1 (4)	6.6 (6)	3.7 (4)	0.3 (5)	1.1 (3)	0.2 (5)
C3N6	−0.0180 (7)	0.8704 (8)	0.1925 (3)	4.1 (4)	5.8 (5)	2.3 (3)	−0.0 (4)	1.3 (3)	−0.3 (4)
C1N7	−0.0087 (7)	0.6786 (8)	0.0556 (3)	3.5 (4)	5.1 (5)	5.1 (5)	−0.6 (4)	0.5 (4)	−1.8 (4)
C2N7	−0.0176 (8)	0.5664 (8)	0.0553 (4)	5.9 (5)	3.5 (5)	9.3 (6)	−1.7 (4)	3.6 (4)	−2.5 (5)
C3N7	0.0726 (7)	0.6030 (7)	0.1216 (3)	5.0 (4)	2.3 (4)	6.2 (5)	−0.3 (4)	2.7 (4)	0.2 (4)
C1N8	0.1396 (8)	0.9325 (9)	−0.0224 (3)	5.4 (5)	7.1 (6)	2.1 (4)	0.5 (5)	0.2 (4)	−0.7 (4)
C2N8	0.1857 (8)	0.8900 (9)	−0.0546 (3)	5.8 (5)	6.5 (6)	4.0 (5)	1.8 (5)	0.6 (4)	0.4 (5)
C3N8	0.2957 (7)	0.8739 (8)	0.0106 (4)	5.8 (5)	3.7 (5)	7.4 (5)	−1.5 (4)	4.1 (4)	−0.6 (5)
C1N9	0.0982 (8)	1.1535 (7)	0.0875 (3)	5.7 (5)	3.5 (5)	3.9 (4)	0.6 (4)	1.6 (4)	−1.0 (4)
C2N9	0.1138 (8)	1.2607 (8)	0.0745 (3)	5.6 (5)	3.5 (5)	4.5 (4)	0.2 (4)	1.4 (4)	−0.4 (4)
C3N9	0.2019 (7)	1.1607 (7)	0.0354 (3)	5.9 (5)	2.5 (4)	4.0 (4)	−0.6 (4)	1.8 (4)	1.5 (3)

transition metals or as biodegradable carrier molecules for chemotherapeutic agents. The recent synthesis in our laboratory of the first of these derivatives, hexa(imidazolyl)cyclotriphosphazene (I), has revealed that, unlike most aminophosphazenes, this species is hydrolytically unstable.[8] An X-ray crystal structure determination has, therefore, been carried out for I in an attempt to identify any unusual structural features of this molecule.



I

Crystallographic Section

Collection and Reduction of X-ray Data. Compound I was synthesized by the interaction of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, with imidazole in tetrahydrofuran.[8] Recrystallization was effected from a solution in tetrahydrofuran.

A clear crystal of dimensions 0.25 × 0.20 × 0.25 mm was wedged into a glass capillary in an atmosphere of dry nitrogen. The capillary was mounted on a eucentric goniometer head which was transferred to an Enraf-Nonius CAD-4 diffractometer. The diffractometer was controlled by a PDP8/a computer and was fitted with a molybdenum X-ray tube ($\lambda(K\alpha) = 0.7107$ Å) and a graphite monochromator. Twenty-five reflections were located and centered with the use of the Enraf-Nonius program SEARCH. A least-squares refinement of the 2θ values for these 25 reflections gave a monoclinic cell with $a = 13.283$ (12) Å, $b = 12.331$ (8) Å, $c = 29.425$ (14) Å, $\beta = 101.89$ (9)°, $V = 4716.1$ Å^3, $d_m = 1.494$ g cm^{-3} (by flotation in aqueous potassium iodide solutions), $d_c = 1.514$ g cm^{-3}, $Z = 8$, and $M_r = 537.37$. The linear absorption coefficient is 3.0 cm^{-1} for molybdenum radiation.

Intensity data were collected over $-h00$ to hkl, using a θ–2θ scan mode for all reflections for which $0.01° \le 2\theta \le 60°$. The observed systematic absences hkl, $h + k \neq 2n$, and $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, were consistent with $C2/c$ or Cc as the space group.

Scan widths were determined by using the formula SW = $A + B^*$ tan θ, where A was estimated from the mosaic character of the crystal and B accounts for the increase in the width of the peak, due to $K\alpha_1$ and $K\alpha_2$ splitting. The values determined for A and B were 0.50 and 0.35, respectively. A 25% increase in scan angle on each side of the reflections was employed for the measurement of background intensities. The net intensities, I, were calculated with the formula I = CTS − 2(BGR + BGL) where CTS defines the total number of counts and BGR and BGL are the right and left background counts, respectively. Three check reflections were measured every hour. No significant change in the intensities of these check reflections occurred throughout the entire data collection process. All data were corrected for Lorentz and polarization effects. An absorption correction was not applied to the data. Of the total 9057 reflections measured, 2054 that had an intensity greater than $3\sigma(I)$ were used in the refinement.

Solution and Refinement of the Structure. The atomic scattering factors tabulated by Cromer and Waber[9] were used for all the atoms in this structure. The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F_o)^2$. The equations $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ express the residuals. The structure was solved by direct methods. Three phosphorus and two ring nitrogen atoms were located among the six highest peaks on the E map generated from the set of signs giving a combined figure of merit of 3.00 and a Karle R of 24.42. Successive difference Fourier calculations allowed the location of the remaining ring nitrogen atom, exocyclic nitrogen atoms and carbon atoms. Isotropic refinement lowered R_1 to 0.109. The hydrogen atoms

---

[8] Allcock, H. R.; Fuller, T. J., submitted for publication in *J. Am. Chem. Soc.*

[9] Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

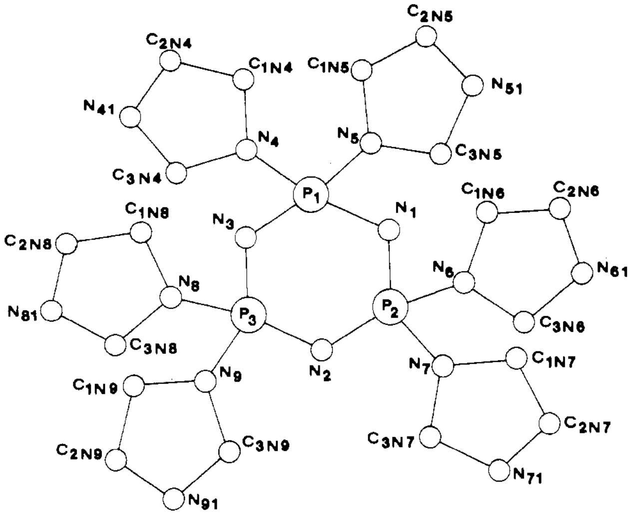


Figure 1. Atom designations for hexa(imidazolyl)cyclotriphosphazene (I).

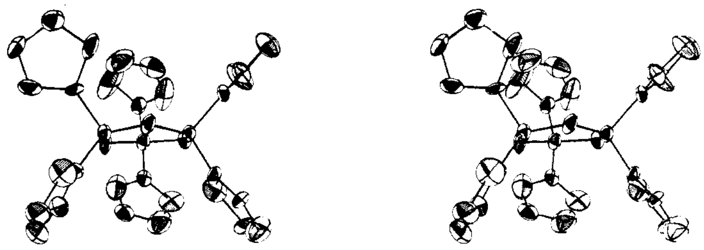


Figure 2. Stereoscopic view of hexa(imidazolyl)cyclotriphosphazene (I).

could not be located in this structure. A change of the thermal parameters to anisotropic, followed by three final cycles of refinement, gave $R_1 = 0.065$ and $R_2 = 0.086$.

The refined positional and anisotropic thermal parameters for all the atoms are given in Table I. A listing of the observed and calculated structure factor amplitudes for the 2054 reflections used in the refinement appearing in Table II are available as supplementary material.

Computations were carried out with the use of a PDP 11/34 computer and the Enraf-Nonius structure determination package.

Results and Discussion

General Structure of the Molecule. The phosphazene ring is planar. The largest deviation from a mean plane through P1, P2, P3, N1, N2, and N3 is 0.09 Å. The imidazole rings are also planar. The largest deviation from planarity for any of the imidazole rings is 0.03 Å. Five of the imidazole groups (those containing nitrogen atoms N4–N8) are arranged in such a way that the average dihedral angle between the imidazole rings and the phosphazene ring is 53.5°. The imidazole ring containing N9 has a 80.5° dihedral angle with the phosphazene ring. The perturbation of the dihedral angles between ring planes is almost certainly a result of crystal packing forces. The atom designations are shown in Figure 1. A stereoscopic view of the molecule is given in Figure 2. A tabulation of bond distances and bond angles is shown in Table III.

Table III. Bond Distances and Angles for $N_3P_3(C_3N_2H_3)_6$

Distances, Å			
C1N6–C2N6	1.361 (8)	P1–N4	1.677 (5)
C2N6–N61	1.366 (8)	P1–N5	1.669 (5)
N61–C3N6	1.276 (7)	P2–N1	1.560 (4)
C3N6–N6	1.374 (6)	P2–N2	1.603 (4)
N7–C1N7	1.365 (7)	P2–N6	1.693 (4)
C1N7–C2N7	1.388 (9)	P2–N7	1.675 (4)
C2N7–N71	1.319 (9)	P3–N2	1.586 (4)
N71–C3N7	1.307 (8)	P3–N3	1.548 (4)
C3N7–N7	1.384 (7)	P3–N8	1.673 (4)
N8–C1N8	1.357 (7)	P3–N9	1.693 (4)
C1N8–C2N8	1.337 (9)	N4–C1N4	1.346 (5)
C2N8–N81	1.346 (8)	C1N4–C2N4	1.373 (11)
N81–C3N8	1.320 (8)	C2N4–N41	1.320 (10)
C3N8–N8	1.419 (8)	N41–C3N4	1.302 (8)
N9–C1N9	1.406 (7)	C3N4–N4	1.367 (8)
C1N9–C2N9	1.403 (8)	N5–C1N5	1.394 (8)
C2N9–N91	1.385 (8)	C1N5–C2N5	1.256 (8)
N91–C3N9	1.306 (7)	C2N5–N51	1.368 (8)
C3N9–N9	1.388 (7)	N51–C3N5	1.357 (9)
P1–N1	1.587 (4)	C3N5–N5	1.359 (7)
P1–N3	1.581 (4)	N6–C1N6	1.337 (7)

Angles, Deg			
N1–P1–N3	117.92 (23)	C1N4–N4–C3N4	105.33 (61)
N1–P1–N4	109.18 (24)	P1–N5–C1N5	125.49 (47)
N1–P1–N5	108.31 (25)	P1–N5–C3N5	129.24 (48)
N3–P1–N4	107.06 (25)	C1N5–N5–C3N5	105.17 (56)
N3–P1–N5	109.92 (24)	P2–N6–C1N6	127.70 (40)
N4–P1–N5	103.49 (24)	P2–N6–C3N6	126.78 (40)
N1–P2–N2	120.41 (23)	C1N6–N6–C3N3	105.40 (47)
N1–P2–N6	107.24 (23)	P2–N7–C1N7	126.02 (44)
N1–P2–N7	109.57 (24)	P2–N7–C3N7	125.84 (42)
N2–P2–N6	107.57 (23)	C1N7–N7–C3N7	107.98 (51)
N2–P2–N7	107.48 (23)	P3–N8–C1N8	126.53 (44)
N6–P2–N7	103.25 (21)	P3–N8–C3N8	127.01 (46)
N2–P3–N3	118.96 (23)	C1N8–N8–C3N8	106.45 (54)
N2–P3–N8	110.73 (24)	P3–N9–C1N9	124.12 (40)
N2–P3–N9	104.56 (24)	P3–N9–C3N9	126.28 (43)
N3–P3–N8	108.64 (25)	C1N9–N9–C3N9	108.22 (48)
N3–P3–N9	112.06 (25)	N4–C1N4–C2N4	105.65 (81)
N8–P3–N9	100.27 (23)	C1N4–C2N4–N41	111.40 (75)
P1–N1–P2	119.73 (27)	C2N4–N41–C3N4	104.86 (63)
P2–N2–P3	118.44 (27)	N41–C3N4–N4	112.53 (67)
P1–N3–P3	122.20 (29)	N5–C1N5–C2N5	112.26 (65)
P1–N4–C1N4	128.27 (53)	C1N5–C2N5–N51	106.38 (61)
P1–N4–C3N4	126.37 (47)	C2N5–N51–C3N5	109.95 (62)
N51–C3N5–N5	106.12 (67)	N8–C1N8–C2N8	107.75 (61)
N6–C1N6–C2N6	108.01 (53)	C1N8–C2N8–N81	109.65 (61)
C1N6–C2N6–N61	107.84 (56)	C2N8–N81–C3N8	108.93 (61)
C2N6–N61–C3N6	106.90 (52)	N81–C3N8–N8	107.15 (66)
N61–C3N6–N6	111.77 (54)	N9–C1N9–C2N9	104.22 (54)
N7–C1N7–C2N7	103.50 (66)	C1N9–C2N9–N91	109.21 (56)
C1N7–C2N7–N71	111.69 (71)	C2N9–N91–C3N9	108.53 (53)
C2N7–N71–C3N7	107.42 (61)	N91–C3N9–N9	109.82 (56)
N71–C3N7–N7	109.41 (60)		

Bonding within the Phosphazene Ring. The various phosphorus–nitrogen bond distances within the phosphazene ring are similar to each other. The average P–N bond length, 1.577 Å, is comparable to phosphorus–nitrogen bond distances reported for other symmetrically substituted cyclotriphosphazenes. For example, hexachlorocyclotriphosphazene, $(NPCl_2)_3$, has an average P–N bond distance of 1.581 Å.[10] In hexafluorocyclotriphosphazene, $(NPF_2)_3$, the value is 1.57 Å,[11] and in octakis(dimethylamino)cyclotetraphosphazene, $[NP(N(CH_3)_2)_2]_4$, the average P–N bond distance is 1.58 Å.[12] If delocalization of electron density occurs between the imidazole substituent and the phosphazene ring of I, it has no observable influence on the bond lengths within the phosphazene ring. The endocyclic skeletal bond angles were found to vary little from 120°. The endocyclic N–P–N bond angles averaged to 119.1° and the P–N–P angles to 120.1°. These angles are comparable to those reported elsewhere for other related compounds.[10,13]

Bonding of the Imidazole Groups to the Phosphazene Ring. The exocyclic phosphorus–nitrogen bond lengths average 1.68 Å in this structure. This suggests that these bonds have more single-bond character than those within the phosphazene ring.

---

(10) Bullen, G. J. *J. Chem. Soc. A* **1971**, 1450.

(11) Dougill, M. W. *J. Chem. Soc.* **1961**, 5471.

(12) Bullen, G. J. *J. Chem. Soc.* **1962**, 3193.

(13) Ahmed, F. R.; Singh, P.; Barnes, W. H. *Acta Crystallogr., Sect. B* **1969**, *B25*, 316.

This value is reminiscent of a number of other exocyclic phosphorus–nitrogen bond lengths that have been reported.[12,14-16] For example, octakis(dimethylamino)cyclotetraphosphazene, $[NP(N(CH_3)_2)_2]_4$, has an average exocyclic P–N bond length of 1.69 Å.[12] From this structural consideration alone, a difference cannot be detected between (alkylamino)-, (arylamino)-, or imidazolylcyclophosphazenes that would explain the enhanced ease of hydrolysis of the latter species.

Bonding within the Imidazole Rings. The imidazole groups in I are aromatic in character. The average bond distance within each imidazole group is 1.353 Å. This bond length value provides a clue to the hydrolytic instability of I. The amino nitrogen (bound to phosphorus) lone-pair electrons can be delocalized into the phosphazene ring in (alkylamino)- or (arylamino)phosphazenes. However, in I, the lone pairs are delocalized into the aromatic π system of the imidazole substituents. Hence, these lone-pair electrons cannot enhance the electron density on the skeletal phosphorus or nitrogen atoms in a way that would inhibit (nucleophilic) hydrolysis reactions. This also suggests that the second nitrogen atom within the imidazole group may constitute an alternative site for protonation. This, in turn, could assist in the hydrolysis process by stabilizing the imidazole substituent as a leaving group.

Bond Angles at Phosphorus. The geometry around the phosphorus atoms in I provides a second explanation for the ease of hydrolysis of this compound. Although the exocyclic N–P–N bond angle (102.34° average) is comparable to those in related phosphazenes,[10,12,16] the planarity of both the phosphazene and imidazole rings exposes the phosphorus atoms to nucleophilic attack. Moreover, the presence of a five-membered ring as a substituent further reduces the shielding power of the side group.

Acknowledgment. This work was supported by the Public Health Service through Grant No. 5R01HL11418-09.

Registry No. I, 74868-58-9.

Supplementary Material Available: Table II, a listing of the observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

---

[14] Mani, N. V.; Wagner, A. J. *J. Chem. Soc., Chem. Commun.* **1968**, 658.

[15] Wagner, A. J.; Vos, A. *Acta Crystallogr., Sect. B* **1968**, *B24*, 1423; **1971**, *B27*, 51.

[16] Bullen, G. J.; Mallinson, P. R. *J. Chem. Soc., Chem. Commun.* **1969**, 691.

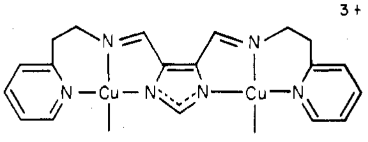
Contribution from the Department of Chemistry,
Columbia University, New York, New York 10027

An Asymmetric Imidazolate-Bridged Dicopper(II) Complex

Robert N. Katz, Gary Kolks, and Stephen J. Lippard*

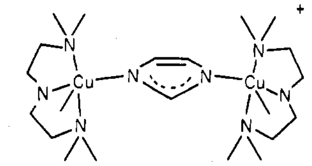
Received May 29, 1980

The discovery[1] of an imidazolate-bridged copper(II)–zinc(II) center in bovine erythrocyte superoxide dismutase and the postulated existence of a histidine-bridged copper(II)–iron(III) unit in cytochrome *c* oxidase[2] have stimulated recent interest in the imidazolate ion (im) as a bridging ligand. In particular, a variety of imidazolate-bridged dicopper(II) complexes has been synthesized and characterized.[3-8] In all cases, for example, **1**[3] and **2**,[5] the $Cu_2(im)^{3+}$ ion was part of a symmetric complex where, except for weakly coordinating anions or solvent molecules,[3b] the two copper coordination spheres were identical.



Cu_2bpim^{3+}

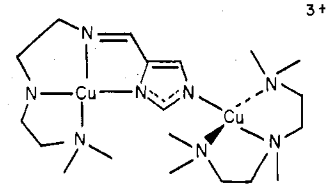
1



$[(TMDT)_2Cu_2(im)(ClO_4)_2]^+$

2

The magnetic exchange coupling constants in the imidazolate-bridged dicopper(II) complexes fall into two categories.[4-8] When the bridging imidazolate ion is part of the chelating ligand and therefore constrained to lie in the copper coordination plane, as for compounds containing the Cu_2bpim^{3+} unit (**1**), the value of J is ~ -85 cm^{-1}. Complexes such as **2**, where the bridging ligand is an independent unit that can rotate out of the principal copper coordination plane, have J values that lie in the range -15 to -40 cm^{-1}, vary smoothly with the pK_a of the bridging ligand,[4b] and are usually ~ -30 cm^{-1}. It was therefore of interest to learn how the spin-exchange interaction in asymmetric **3**, which may be viewed as a hybrid of **1** and **2**, would relate to that of its symmetric analogues. The present note reports the synthesis and magnetic exchange properties of **3** and also describes the



$Cu_2(deim)(PMDT)^{3+}$

3

---

[1] (a) Richardson, J. S.; Thomas, K. A.; Rubin, B. H.; Richardson, D. C. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 1349–1353. (b) Beem, K. M.; Richardson, D. C.; Rajagopalan, K. V. *Biochemistry* **1977**, *16*, 1930–1936.

[2] Palmer, G.; Babcock, G. T.; Vickery, L. E. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 2206–2210.

[3] (a) Kolks, G.; Frihart, C. R.; Rabinowitz, H. N.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 5720–5721. (b) Dewan, J. C.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 2079–2082.

[4] (a) Kolks, G.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 5804–5806. (b) Kolks, G.; Lippard, S. J., to be submitted for publication.

[5] (a) O'Young, C.-L.; Dewan, J. C.; Lilienthal, H. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1978**, *100*, 7291–7300. (b) Coughlin, P. K.; Dewan, J. C.; Lippard, S. J.; Watanabe, E.-i.; Lehn, J.-M. *Ibid.* **1979**, *101*, 265–266.

[6] (a) Haddad, M. S.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 2622–2630. (b) Haddad, M. S.; Duesler, E. N.; Hendrickson, D. N. *Ibid.* **1979**, *18*, 141–148.

[7] Mori, W.; Nakahara, A.; Nakao, Y. *Inorg. Chim. Acta* **1979**, *37*, L507–L508.

[8] Hendricks, H. M. J.; Reedjik, J. *Inorg. Chim. Acta* **1979**, *37*, L509–L510.

0020-1669/80/1319-3845$01.00/0