The synthesis, crystal structures and infrared spectra of *bis*(2,2'-bipyridyl)mononitratozinc(II) hexafluorophosphate and *bis*(2,2'-bipyridyl)mononitratozinc(II) perchlorate: A comparison with existing [Zn(chelate)$_2$(OXO)][Y] and [Cu(chelate)$_2$(OXO)][Y] complexes of known crystal structure

Brian Murphy[a]; Brian J. Hathaway[a]

[a] Department of Chemistry, University College Cork, Republic of Ireland

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

THE SYNTHESIS, CRYSTAL STRUCTURES AND INFRARED SPECTRA OF *bis*(2,2′-BIPYRIDYL)MONONITRATOZINC(II) HEXAFLUOROPHOSPHATE AND *bis*(2,2′-BIPYRIDYL)MONONITRATOZINC(II) PERCHLORATE: A COMPARISON WITH EXISTING [Zn(CHELATE)₂(OXO)][Y] AND [Cu(CHELATE)₂(OXO)][Y] COMPLEXES OF KNOWN CRYSTAL STRUCTURE

BRIAN MURPHY* and BRIAN J. HATHAWAY†

Department of Chemistry, University College Cork, Republic of Ireland

In order to extend the number of [Zn(chelate)₂(OXO)][Y] complexes, with chelate = 2,2′bipyridyl, 1,10 phenanthroline and 2,2′-bipyridylamine and $(OXO)^- = (ONO)^-$, $(O_2NO)^-$, $(O_2CCH_3)^-$ and $(O_2CH)^-$, the crystal structures and infrared spectra of $[Zn(bipy)_2(O_2NO)][PF_6]$, (**9**) and $[Zn(bipy)_2(O_2NO)][ClO_4]$, (**10**) have been determined. Both zinc(II) complexes involve a slightly elongated *cis*-distorted ZnN_4O_2 chromophore. The slight elongation contrasts with the more significant compressed *cis*-distorted octahedral CuN_4O_2 chromophore of the corresponding copper(II) structures. The Zn–O bonds in (**9**) are 2.186(3) and 2.351(3) Å ($\Delta O = 0.165(3)$ Å), while the corresponding Zn–O(1) and Zn–O(2) bonds in (**10**) are 2.194(2) and 2.355(2) Å ($\Delta O = 0.161(2)$ Å), respectively. The mean Zn–O bond distance in (**9**) is 2.269(3) and 2.275(2) Å in (**10**). Although the significant *cis*-distortion of the Zn–O distances is comparable to the analogous Cu–O distances, the ΔO values are notably smaller. The thermal ellipsoids of (**9**) and (**10**), which are slightly asymmetric ($\Delta O \approx 0.16$ Å), are small and isotropic. Such differences reflect the spherical symmetry of the d^{10} zinc(II) configuration relative to the nonspherical symmetry of the d^9 copper(II) ion. The ZnN_4O_2 chromophores of (**9**) and (**10**) are similar, indicating the isomorphous and isostructural nature of the complexes. Both complexes have a common back-angle or magic angle of $\alpha_3 \approx 117°$, in contrast to the bipyam complexes where the back-angle is much less at $\approx 105°$, related to the conformation of the floppier bipyam chelate ligand.

Keywords: Zinc(II) complex; Nitrato coordination; Structural pathway; Ligand conformation

*Corresponding author. Present address: Department of Chemistry, Faculty of Science, United Arab Emirates University, PO Box 17551, Al Ain, United Arab Emirates. Tel.: +971-50-6630614. Fax: +971-3-7671291. E-mail: Murphy.Brian@uaeu.ac.ae

† Deceased.

INTRODUCTION

The number of $[Zn(chelate)_2(OXO)][Y]$ complexes of known crystal structure in the literature, with chelate = 2,2′bipyridyl, 1,10 phenanthroline and 2,2′-bipyridylamine and $(OXO)^- = (ONO)^-$, $(O_2NO)^-$, $(O_2CCH_3)^-$ and $(O_2CH)^-$ is relatively small, amounting at present to our knowledge to just five fully crystallographically characterized structures. Although the complexes $[Zn(phen)_2(O_2CCH_3)][ClO_4]$, (**1**), $[Zn(phen)_2$-$(O_2CCH_3)][ClO_4] \cdot 2H_2O$, (**2**) [1,2] and $[Zn(bipyam)_2(ONO)][NO_3]$, (**3**) [1,3] are known, their crystallographic data have not yet been published in full and hence the five complexes of known crystal structure are $[Zn(phen)_2(O_2CCH_3)][BF_4] \cdot 2H_2O$, (**4**) [4], $[Zn(bipyam)_2(ONO)][NO_2]$, (**5**) [1,3,5], $[Zn(bipyam)_2(O_2NO)][NO_3]$, (**6**) [6], $[Zn(bipy)_2(ONO)][NO_3]$, (**7**) [7,8] and $[Zn(bipy)_2(ONO)][ClO_4]$, (**8**) [9]. However, no zinc(II) bis-bipy nitrato complex is known. For this reason, the crystal structures of $[Zn(bipy)_2(O_2NO)][PF_6]$, (**9**) and $[Zn(bipy)_2(O_2NO)][ClO_4]$, (**10**) have been determined at room temperature and also to establish whether or not a structural pathway exists for the zinc(II) nitrato complexes, and to investigate the existence of preferred α_3 angles (magic angles) for such complexes [10,11].

EXPERIMENTAL

Preparation of [Zn(bipy)₂(O₂NO)][PF₆], (9)

Crystals of $[Zn(bipy)_2(O_2NO)][PF_6]$, (**9**) were prepared by the addition of 0.312 g (2.00 mmol) of bipy (in 6 mL acetonitrile) to a stoichiometric amount (0.595 g) of an aqueous solution (6 mL) of zinc(II) nitrate hexahydrate, $Zn(NO_3)_2 \cdot 6H_2O$. The solution was heated for a few minutes, before the addition of 0.368 g (2.00 mmol) of $K[PF_6]$. The clear mother liquor was filtered and allowed to stand for slow evaporation in the air. After 30 min, a crop of transparent, colorless crystals, with diamond-shaped crystal morphology and sharp edges formed in solution.

Anal. Calcd. for $C_{20}H_{16}N_5O_3ZnPF_6$(%); C, 41.08; H, 2.76; N, 11.98; Zn, 11.18. Found: C, 41.56; H, 2.72; N, 11.78; Zn, 11.67.

Preparation of [Zn(bipy)₂(O₂NO)][ClO₄], (10)

CAUTION: Perchlorates are explosive when ground.

0.936 g of bipy (5.99 mmol) was dissolved in 40 mL of a 3:1 solvent mixture of acetone and methanol. This solution was then added to 15 mL of an aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ (1.785 g, 6.000 mmol). After boiling for 5 min, 0.660 g (5.39 mmol) of $NaClO_4$ was added to the mixture and filtered. Two days later, the transparent mother liquor yielded a homogeneous batch of small, chunky, colorless, glass-like crystals. The crystals formed were subsequently determined to be the title compound $[Zn(bipy)_2(O_2NO)][ClO_4]$, (**10**).

Anal. Calcd. for $C_{20}H_{16}N_5O_7ZnCl$(%); C, 44.55; H, 2.99; N, 12.99; Zn, 12.13. Found: C, 44.16, H, 2.85; N, 12.60; Zn, 12.43.

Structure Determination and Refinement

The unit cell dimensions of (**9**) and (**10**) were determined and refined on an Enraf-Nonius CAD4 diffractometer, using graphite-monochromatized Mo-$K\alpha$ radiation ($\lambda = 0.71069$ Å). The data were collected at room temperature using an ω–2θ scan

mode. Reflections with $3.0 < \theta < 24°$ in one quadrant were collected. A constant scan speed of $7° \, min^{-1}$ was used with a variable scan width $(0.8 + 0.2\tan\theta)°$ and an acceptance criterion $I > 2.5\sigma(I)$. The intensity data were corrected for Lorentz and polarization effects, but not for absorption. Data reduction was carried out using the computer program XCAD [13].

The unit cell of $[Zn(bipy)_2(O_2NO)][PF_6]$, (**9**) was identified as triclinic, $P\bar{1}$, with two molecules in the unit cell. This choice was confirmed by the solution and successful refinement of the structure. The structure was solved by direct methods and subsequent partial structure expansion (SHELXS 86) and difference Fourier maps [14]. The positional and anisotropic thermal displacement parameters for the nonhydrogen atoms were refined with block-diagonal least-squares procedures minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ (initial $w = -0.000200$). It was also possible to locate the positions of the sixteen individual hydrogen atoms from the Fourier map. These were refined with isotropic temperature factors. Final refinement on F_o by full-matrix least-squares techniques resulted in convergence (maximum shift to e.s.d. $= 0.001$) at R-values of 0.0629 (R) and 0.0559 (R_w), respectively ($k = 4.8213$, $g = 0.005658$). A final difference Fourier synthesis revealed residual electron densities between $+0.58$ and $-1.01 \, \text{Å}^{-3}$.

The unit cell of $[Zn(bipy)_2(O_2NO)][ClO_4]$, (**10**) was also identified in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The positions of the Zn and Cl atoms were determined by direct methods. Subsequent iterative cycles of least-squares refinement and difference Fourier synthesis revealed all the nonhydrogen atoms. The positions of the hydrogen atoms were calculated geometrically, with a fixed C–H distance of 1.08 Å and floated on the associated carbon atom. The perchlorate anion was found to be disordered and characterized by a number of alternative oxygen positions, with partial site occupation factors. The disorder was modeled by allowing partial occupation of sites by the oxygen atoms. The site occupancy factors (s.o.f.) of the disordered group were then refined, accounting for the required total of four oxygen atoms. Table I(a) tabulates the respective s.o.f.'s. The final s.o.f. values were close to 0.5 (7 atoms having a half occupancy) and 0.25 (2 atoms having a quarter occupancy). The structure was refined by full-matrix least-squares with the function $\Sigma w(|F_o| - |F_c|)^2$ minimized. All nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter $0.07 \, \text{Å}^2$. The final R-values were 0.0666 (R) and 0.0628 (R_w), respectively ($k = 1.0000$; $g = 0.030056$). The maximum shift to estimated standard deviation in the final refinement cycle was 0.014 (0.228 for the oxygen atoms of the disordered perchlorate). A final difference map showed maximum and minimum residual electron densities of $+0.47$ and $-1.20 \, \text{Å}^{-3}$.

TABLE I   (a) Site occupation factors for the oxygen atoms of the perchlorate anion in (**10**)

Atom	Site occupation factor
O(4)	0.50
O(5)	0.50
O(6)	0.50
O(7)	0.50
O(8)	0.50
O(9)	0.25
O(10)	0.50
O(11)	0.25
O(12)	0.50

TABLE I   (b) Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for the nonhydrogen atoms of $[\text{Zn(bipy)}_2(\text{O}_2\text{NO})][\text{PF}_6]$, (**9**), with e.s.d.'s in parentheses. Equivalent isotropic U_{eq} is defined as one-third the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U_{eq}
Zn	0.05794(4)	0.14876(3)	0.78144(2)	0.0291(3)
N(1)	− 0.0288(4)	− 0.0389(3)	0.6672(2)	0.043(1)
C(1)	0.0143(5)	− 0.1473(3)	0.6725(3)	0.049(2)
C(2)	− 0.0536(6)	− 0.2672(4)	0.5963(3)	0.058(2)
C(3)	− 0.1690(6)	− 0.2761(4)	0.5107(3)	0.057(2)
C(4)	− 0.2131(5)	− 0.1629(4)	0.5039(3)	0.049(2)
C(5)	− 0.1422(4)	− 0.0466(3)	0.5836(2)	0.040(1)
C(6)	− 0.1821(4)	0.0786(3)	0.5836(2)	0.042(2)
C(7)	− 0.2908(5)	0.0885(4)	0.5013(3)	0.057(2)
C(8)	− 0.3209(5)	0.2075(5)	0.5066(3)	0.072(3)
C(9)	− 0.2448(6)	0.3143(5)	0.5934(4)	0.079(3)
C(10)	− 0.1375(5)	0.2992(4)	0.6723(3)	0.061(2)
N(2)	− 0.1047(4)	0.1830(3)	0.6680(2)	0.044(1)
N(3)	0.1382(3)	0.3338(2)	0.9008(2)	0.038(1)
C(11)	0.2458(4)	0.4415(3)	0.9011(3)	0.046(2)
C(12)	0.3124(4)	0.5517(3)	0.9868(3)	0.048(2)
C(13)	0.2763(5)	0.5492(3)	1.0772(3)	0.045(2)
C(14)	0.1681(4)	0.4374(3)	1.0768(2)	0.041(2)
C(15)	0.0980(4)	0.3327(3)	0.9876(2)	0.034(1)
C(16)	− 0.0281(4)	0.2134(3)	0.9801(2)	0.034(1)
C(17)	− 0.1094(4)	0.2062(3)	1.0585(2)	0.045(2)
C(18)	− 0.2299(5)	0.0910(3)	1.0437(3)	0.050(2)
C(19)	− 0.2641(4)	− 0.0111(3)	0.9545(3)	0.047(2)
C(20)	− 0.1815(4)	0.0026(3)	0.8792(2)	0.042(2)
N(4)	− 0.0657(3)	0.1123(2)	0.8915(2)	0.035(1)
N(5)	0.4081(3)	0.1354(2)	0.7804(2)	0.043(1)
O(1)	0.3110(4)	0.1834(3)	0.7296(2)	0.058(1)
O(2)	0.3334(4)	0.1000(3)	0.8408(2)	0.069(2)
O(3)	0.5608(4)	0.1266(4)	0.7679(3)	0.098(2)
P	0.44533(14)	0.63305(8)	0.72394(7)	0.0515(5)
F(1)	0.4602(5)	0.4921(2)	0.7176(2)	0.089(2)
F(2)	0.4804(5)	0.6782(3)	0.8427(2)	0.083(2)
F(3)	0.4275(6)	0.7744(3)	0.7335(3)	0.107(2)
F(4)	0.4023(7)	0.5876(3)	0.6067(2)	0.121(3)
F(5)	0.6599(5)	0.6745(4)	0.7367(3)	0.119(3)
F(6)	0.2319(4)	0.5904(4)	0.7177(4)	0.119(3)

All calculations were carried out on a VAX 6310 mainframe computer at University College Cork, using the SHELX 76 [14], SHELXS 86 [14], XANADU [15] and PUBTAB [16] computer programs. PLUTON-92 [17] was used for illustration of molecular structures. Crystal data and experimental details of the structure determination for both complexes are shown in Table II. The final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for the nonhydrogen atoms are given in Tables I(b) and (c) respectively. Table III(a) and (b) tabulate selected bond lengths and bond angles for both structures and Table IV(a) and (b) contain some mean plane data. Figure 1, gives the atomic numbering scheme and α_n notation normally used for such complexes. Figure 2(a) and (b) show the molecular structure of $[\text{Zn(bipy)}_2(\text{O}_2\text{NO})][\text{PF}_6]$, (**9**), and $[\text{Zn(bipy)}_2(\text{O}_2\text{NO})][\text{ClO}_4]$, (1°) along with the atomic numbering and α_n angle notation used. Figures 3(a) and (b) are illustrations of the unit cell contents of (**9**) and (**10**), respectively. Tables of displacement parameters and comprehensive lists of bond lengths and bond angles are available as supplementary material from the authors. CCDC (reference numbers 193561 and 193562) contains the supple-

TABLE I (c) Fractional atomic coordinates and isotropic displacement parameters ($\text{\AA}^2$) for the nonhydrogen atoms of [Zn(bipy)$_2$(O$_2$NO)][ClO$_4$], (9), with e.s.d.'s in parentheses. Equivalent isotropic U_{eq} is defined as one-third the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U_{eq}
Zn	0.44107(4)	0.85219(3)	0.22341(2)	0.0356(2)
N(1)	0.5275(3)	1.0452(2)	0.3332(2)	0.048(1)
C(1)	0.4822(3)	1.1581(2)	0.3291(2)	0.060(1)
C(2)	0.5515(3)	1.2832(3)	0.4026(2)	0.066(1)
C(3)	0.6674(3)	1.2896(3)	0.4849(2)	0.069(1)
C(4)	0.7109(3)	1.1740(3)	0.4916(2)	0.059(1)
C(5)	0.6392(3)	1.0512(2)	0.4130(2)	0.047(1)
C(6)	0.6772(3)	0.9215(2)	0.4132(2)	0.049(1)
C(7)	0.7854(3)	0.9108(3)	0.4942(2)	0.067(1)
C(8)	0.8188(3)	0.7851(3)	0.4866(2)	0.083(1)
C(9)	0.7441(3)	0.6745(3)	0.4011(2)	0.092(1)
C(10)	0.6337(3)	0.6943(2)	0.3266(2)	0.070(1)
N(2)	0.6019(2)	0.8131(2)	0.3316(2)	0.051(1)
N(3)	0.3574(2)	0.6640(2)	0.1055(2)	0.045(1)
C(11)	0.2499(3)	0.5511(2)	0.1064(2)	0.057(1)
C(12)	0.1794(3)	0.4405(2)	0.0207(2)	0.065(1)
C(13)	0.2150(3)	0.4451(2)	$-$0.0674(2)	0.059(1)
C(14)	0.3245(3)	0.5605(2)	$-$0.0699(2)	0.055(1)
C(15)	0.3966(3)	0.6664(2)	0.0184(2)	0.042(1)
C(16)	0.5247(3)	0.7882(2)	0.0235(2)	0.043(1)
C(17)	0.6032(3)	0.7972(2)	$-$0.0564(2)	0.058(1)
C(18)	0.7284(3)	0.9151(2)	$-$0.0433(2)	0.070(1)
C(19)	0.7713(3)	1.0164(2)	0.0466(2)	0.060(1)
C(20)	0.6887(3)	0.9991(2)	0.1232(2)	0.053(1)
N(4)	0.5685(2)	0.8906(2)	0.1127(2)	0.042(1)
N(5)	0.0907(2)	0.8676(2)	0.2287(2)	0.050(1)
O(1)	0.1874(3)	0.8191(2)	0.2802(2)	0.068(1)
O(2)	0.1664(3)	0.9028(2)	0.1669(2)	0.075(1)
O(3)	$-$0.0612(2)	0.8782(2)	0.2416(2)	0.101(1)
Cl	0.06487(17)	0.35814(10)	0.27894(8)	0.0769(3)
O(4)	0.0721(3)	0.2173(3)	0.2675(3)	0.098(1)
O(5)	0.2562(3)	0.4076(3)	0.2775(3)	0.097(1)
O(6)	$-$0.0221(3)	0.3442(3)	0.1884(3)	0.170(1)
O(7)	0.0243(3)	0.4240(3)	0.3718(3)	0.114(1)
O(8)	0.0458(3)	0.5014(3)	0.2901(3)	0.089(1)
O(9)	$-$0.1249(3)	0.3468(3)	0.2412(3)	0.214(1)
O(10)	$-$0.0086(3)	0.2551(3)	0.3101(3)	0.156(1)
O(11)	0.1290(3)	0.3866(3)	0.3718(3)	0.144(1)
O(12)	0.1224(3)	0.3098(3)	0.1914(3)	0.148(1)

mentary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

RESULTS

Description of the Crystal Structures of [Zn(bipy)$_2$(O$_2$NO)][PF$_6$], (9) and [Zn(bipy)$_2$(O$_2$NO)][ClO$_4$], (10)

Crystal Structure of [Zn(bipy)$_2$(O$_2$NO)][PF$_6$], (9)

The crystal structure of (9) represented in Figure 2(a) is built up of discrete [Zn(bipy)$_2$-(O$_2$NO)]$^+$ cations and hexafluorophosphate anions in the unit cell. The cation involves

TABLE II   Crystallographic and structure refinement data for (**9**) and (**10**)

	(*9*)	(*10*)
Stoichiometry	$C_{20}H_{16}N_5O_3ZnPF_6$	$C_{20}H_{16}N_5O_7ZnCl$
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (C_i^1, No. 2)	$P\bar{1}$ (C_i^1, No. 2)
a (Å)	7.5586(14)	7.5379(12)
b (Å)	11.2932(17)	10.8450(19)
c (Å)	14.4989(26)	14.5688(30)
α (°)	110.1774(149)	109.6932(183)
β (°)	98.7086(154)	96.5502(159)
γ (°)	99.1019(148)	99.2255(136)
V (Å³)	1118.37	1088.56
Z	2	2
D_c (g cm⁻³)	1.74	1.65
$F(000)$	584.0	544.0
μ (cm⁻¹)	12.12	12.66
No. of unique reflections used (N)	3466	3323
No. of varied parameters (P)	389	353
N/P	8.910	9.414
R	0.0629	0.0666
R_w	0.0559	0.0628
k	4.8213	1.0000
g	0.005658	0.030056
Maximum Δ/σ	0.001	0.014
Residual electron density (Å⁻³)	+ 0.58, − 1.01	+ 0.47, − 1.20
No. of anisotropic atoms	36	39

a six-coordinate *cis*-octahedral ZnN_4O_2 chromophore. The basic chromophore is formed by four nitrogen atoms, from two bidentate bipy ligands and two oxygen atoms from a coordinated nitrate group. Two of the nitrogens N(1) and N(3) comprise the axial bonds at distances 2.115(3) and 2.125(3) Å from the zinc ($\Delta N_{1,3} = 0.010(3)$ Å; Zn–$N_{MEAN/OUT} = 2.120(3)$ Å). The other inplane zinc–nitrogen bonds are approximately equal, but slightly shorter than the two out-of-plane bonds, Zn–N(2) = 2.084(3) Å and Zn–N(4) = 2.091(3) Å respectively, with $\Delta N_{2,4} = 0.007(3)$ Å and Zn–$N_{MEAN/IN} = 2.088(3)$ Å. The remaining two coordination sites of the chromophore are occupied by O(1) and O(2). The two *cis* zinc–oxygen bonds are clearly elongated with values Zn–O(1) = 2.186(3) Å and Zn–O(2) = 2.351(3) Å. The difference, ΔO, in these two bond distances is 0.165(3) Å. The average zinc–oxygen bond-distance is 2.269(3) Å. The axial bond Zn–N(3) (2.125(3) Å) is also longer than the equatorial Zn–N(4) bond (2.091(3) Å), giving an elongated, *cis*-distorted, ZnN_4O_2 chromophore, as opposed to the compressed nature of the corresponding copper(II) complexes [18]. Unlike the majority of the corresponding [Cu(chelate)₂(OXO)][Y] complexes, it is the short-bonded oxygen O(1), which lies *trans* to Zn–N(4) in (**9**). Within the N(2), N(4), Zn, O(1) plane of the ZnN_4O_2 chromophore, the angles also vary. α_1 is 94.4(1)°, α_2 is 147.5(1)° and α_3, the back-angle, is 117.9(1)°. The two bite angles, α_6 and α_7 of the bipy ligands are almost identical with values of 78.4(1) and 78.6(1)°, respectively. If the Zn, N(1)–N(4) mean plane data (Plane 8) of Table IV(a) is examined, it can be seen that N(2), N(3) and N(4) are all located below the zinc atom. N(1) is positioned

TABLE III Selected bond lengths (Å) and angles (°) for (9) and (10), with e.s.d.'s in parentheses

(a) Bond distances (Å)	(9)	(10)
Zn–N(1)	2.115(3)	2.106(2)
Zn–N(2)	2.084(3)	2.077(2)
Zn–N(3)	2.125(3)	2.119(2)
Zn–N(4)	2.091(3)	2.092(2)
Zn–O(1)	2.186(3)	2.194(2)
Zn–O(2)	2.351(3)	2.355(2)
ΔO	**0.165(3)**	**0.161(2)**
Zn–O$_{MEAN}$	**2.269(3)**	**2.275(2)**
N(5)–O(1)	1.269(4)	1.279(3)
N(5)–O(2)	1.252(4)	1.250(3)
N(5)–O(3)	1.209(4)	1.199(3)
N–O$_{MEAN}$	**1.243(4)**	**1.243(3)**
P–F(1)	1.585(3)	
P–F(2)	1.584(3)	
P–F(3)	1.584(3)	
P–F(4)	1.561(3)	
P–F(5)	1.578(4)	
P–F(6)	1.588(4)	
P–F$_{MEAN}$	**1.580(3)**	

Due to disorder in the [ClO$_4$]$^-$ anion, no chlorine–oxygen bond distances are included

(b) Bond angles (°)	(9)	(10)[†]
N(2)–Zn–O(1) (α_1)	94.4(1)	94.8(1)
O(1)–Zn–N(4) (α_2)	147.5(1)	148.0(1)
N(2)–Zn–N(4) (α_3)	117.9(1)	117.0(1)
N(1)–Zn–O(1) (α_4)	90.9(1)	91.2(1)
O(1)–Zn–N(3) (α_5)	91.4(1)	91.2(1)
N(1)–Zn–N(2) (α_6)	78.4(1)	78.9(1)
N(3)–Zn–N(4) (α_7)	78.6(1)	78.6(1)
N(1)–Zn–N(3) (α_8)	177.2(1)	176.1(1)
N(1)–Zn–N(4) (α_9)	98.6(1)	97.7(1)
N(2)–Zn–N(3) (α_{10})	102.9(1)	104.0(1)
O(1)–N(5)–O(2)	115.2(3)	115.5(2)
O(1)–N(5)–O(3)	119.8(3)	120.5(3)
O(2)–N(5)–O(3)	125.1(3)	124.0(3)
O–N–O$_{MEAN}$	**120.0(3)**	**120.0(3)**

Bond distances for the [PF$_6$]$^-$ anion in (9):

F(1)–P–F(2)	88.8(2)	F(3)–P–F(5)	90.0(2)
F(1)–P–F(4)	91.4(2)	F(3)–P–F(6)	91.4(2)
F(1)–P–F(5)	91.0(2)	F(4)–P–F(5)	94.5(3)
F(1)–P–F(6)	87.5(2)	F(4)–P–F(6)	88.8(3)
F(2)–P–F(3)	89.6(2)	F(1)–P–F(3)	178.0(2)
F(2)–P–F(5)	87.8(2)	F(2)–P–F(4)	177.7(3)
F(2)–P–F(6)	88.9(2)	F(5)–P–F(6)	176.4(3)
F(3)–P–F(4)	90.2(2)	**F–P–F$_{MEAN}$**	**90.0(2), 177.4(3)**

[†] Since the ionic perchlorate in [Zn(bipy)$_2$(O$_2$NO)][ClO$_4$], (10) was refined as a disordered group, the respective O–Cl–O angles are not quoted here as our interest lies solely with the cation.

fractionally above the zinc, at *ca.* 0.07 Å. The sum of α_4 and α_5 is 182.3(1)°. This suggests the presence of a trigonal rather than a tetrahedral distortion. The α_8 angle, N(1)–Zn–N(3) is 177.2(1)°. The pyridine rings in each of the bipy ligands are reasonably coplanar (r.m.s.d's range from 0.0045 to 0.0142 Å). The carbon–carbon bond lengths vary from 1.359(5) to 1.492(5) Å (mean = 1.392(5) Å), and the carbon–nitrogen bonds vary from 1.338(4) to 1.355(5) Å (mean = 1.344(4) Å). The bond angles range from 115.4(3) to 123.3(3)°, with an average value equal to 119.8(3)°. The dihedral angles α_{11} and α_{12}, between the individual pyridine rings of the bipy ligands are 2.30 and

TABLE IV   (a) Equations of the least-squares planes for [9], in the form $lX + mY + nZ = p$, where X, Y and Z are a set of orthogonal axes. The deviations of the most relevant atoms from the planes are given in parentheses

	l	m	n	p
Plane 1: N(1), C(1)–C(5) (r.m.s.d.= 0.0045 Å) [C(1) 0.0053, C(4) 0.0071, C(5) −0.0049 Å]	6.4810	2.0784	− 8.9432	−6.2332
Plane 2: C(6)–C(10), N(2) (r.m.s.d.= 0.0046 Å) [C(6) −0.0057, C(8) 0.0055, C(9) −0.0049, N(2) 0.0063 Å]	6.5903	2.1081	− 8.5105	−5.9959
Plane 3: N(1), C(1)–C(10), N(2) (r.m.s.d. = 0.0199 Å) [N(1) 0.0214, C(1) 0.0299, C(3) -0.0259, C(7) 0.0238, C(8) 0.0284, C(10) –0.0251 Å]	6.5371	2.0944	− 8.7278	−6.1146
Plane 4: N(3), C(11)–C(15) (r.m.s.d. = 0.0142 Å) [C(11) 0.0167, C(12) −0.0203, C(15) −0.0176 Å]	6.6480	− 6.5142	2.7660	1.2336
Plane 5: C(16)–C(20), N(4) (r.m.s.d. = 0.0055 Å) [C(16) 0.0062, C(18) −0.0063, C(19) 0.0088 Å]	6.0200	− 6.9677	5.5111	0.7393
Plane 6: N(3), C(11)–C(20), N(4) (r.m.s.d.= 0.0964 Å) [C(11) -0.1186, C(14) 0.1560, C(17) −0.0974, C(18) −0.1358, N(4) 0.1203 Å]	6.3364	− 6.8416	4.2048	2.4443
Plane 7: N(5), O(1)–O(3) (r.m.s.d. = 0.0004 Å) [N(5) 0.0008 Å]	0.8683	7.5136	5.4523	5.6259
Plane 8: Zn, N(1)–N(4) (r.m.s.d. = 1.0068 Å) [Zn 0.8716, N(1) 0.9419, N(2) −0.1924, N(3) 0.7481, N(4) −0.2096 Å]	7.5389	− 2.5250	− 2.1941	−2.5250
Plane 9: Zn, N(2), N(4), O(1) (r.m.s.d. = 0.0215 Å) [Zn −0.0369 Å]	− 0.4496	9.3296	3.0658	3.7945

Dihedral angles (°) between normals to planes:

$$(1)–(2): \quad 2.30° \ (\alpha_{11})$$
$$(4)–(5): \quad 11.35° \ (\alpha_{12})$$
$$(3)–(6): \quad 62.00° \ (\alpha_{13})$$

where: α_{11} = the angle between the mean planes of the pyridine rings; α_{12} = the angle between the mean planes of the pyridine rings; α_{13} = the angle between the mean planes of the bipy ligands.

11.35°, respectively. θ, which is the angle of torsion, α_{13}, between the mean planes of the two bipy rings, is 62.00°.

   The coordinated nitrate $(O_2NO)^-$ has a significant spread of nitrogen–oxygen bond distances. The two coordinated oxygens O(1) and O(2) have considerably longer

TABLE IV   (b) Equations of the least-squares planes for (**10**), in the form $lX + mY + nZ = p$, where X, Y and Z are a set of orthogonal axes. The deviations of the most relevant atoms from the planes are given in parentheses

	l	m	n	p
Plane 1:	6.3089	1.9928	− 9.0488	2.3865
N(1), C(1)–C(5)				
(r.m.s.d. = 0.0092 Å)				
[N(1) 0.0094, C(1) −0.0145, C(4) −0.0109 Å]				
Plane 2:	6.4174	2.1572	− 8.5884	2.7713
C(6)–C(10), N(2)				
(r.m.s.d. = 0.0102 Å)				
[C(6) 0.0135, C(7) −0.0108, C(9) 0.0133, C(10) −0.0116 Å]				
Plane 3:	6.3845	1.9996	− 8.7905	2.5422
N(1), C(1)–C(10), N(2)				
(r.m.s.d. = 0.0264 Å)				
[C(1) −0.0409, C(3) 0.0349, C(7) −0.0510, C(9) 0.0305 Å]				
Plane 4:	6.6691	− 6.3574	2.5189	−1.5633
N(3), C(11)–C(15)				
(r.m.s.d. = 0.0108 Å)				
[C(12) 0.0111, C(14) −0.0120, C(15) 0.0178 Å]				
Plane 5:	6.0600	− 7.0716	5.0819	−2.2739
C(16)–C(20), N(4)				
(r.m.s.d. = 0.0049 Å)				
[C(17) 0.0050, C(20) 0.0077, N(4) −0.0062 Å]				
Plane 6:	6.3711	− 6.7880	3.8575	−1.8607
N(3), C(11)–C(20), N(4)				
(r.m.s.d. = 0.0912 Å)				
[C(11) 0.1223, C(12) 0.0930, C(14) −0.1462, C(18) 0.1222, N(4) −0.1280 Å]				
Plane 7:	0.9430	7.4395	5.3165	7.7594
N(5), O(1)–O(3)				
(r.m.s.d. = 0.0019 Å)				
[N(5) −0.0033 Å]				
Plane 8:	7.4970	− 2.5195	− 2.2537	1.5181
Zn, N(1)–N(4)				
(r.m.s.d. = 1.0213 Å)				
[Zn −0.8619, N(1) −0.9476, N(2) 0.1987, N(3) −0.7496, N(4) 0.2462 Å]				
Plane 9:	− 0.2611	8.9370	3.2345	8.1899
Zn, N(2), N(4), O(1)				
(r.m.s.d. = 0.0195 Å)				
[Zn 0.0336 Å]				

Dihedral angles (°) between normals to planes:
(1)–(2):	2.78°	(α_{11})
(4)–(5):	10.75°	(α_{12})
(3)–(6):	61.85°	(α_{13})

N(5)–O bond lengths than the uncoordinated O(3). The N(5)–O(3) bond is 1.209(4) Å whereas the N(5)–O(1) and N(5)–O(2) bonds are 1.269(4) and 1.252(4) Å. The mean N–O bond length is 1.243(4) Å. The average O–N–O bond angle is 120.0(3)° and the nitrate is essentially planar (r.m.s.d. = 0.0004 Å). The hexafluorophosphate anion is regular octahedral, with normal bond lengths (mean = 1.580(3) Å) and bond angles (mean = 90.0(2) and 177.4(4)°).
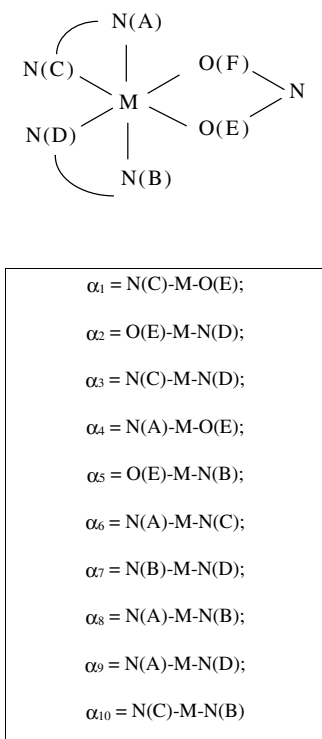
$\alpha_1 = N(C)\text{-}M\text{-}O(E);$

$\alpha_2 = O(E)\text{-}M\text{-}N(D);$

$\alpha_3 = N(C)\text{-}M\text{-}N(D);$

$\alpha_4 = N(A)\text{-}M\text{-}O(E);$

$\alpha_5 = O(E)\text{-}M\text{-}N(B);$

$\alpha_6 = N(A)\text{-}M\text{-}N(C);$

$\alpha_7 = N(B)\text{-}M\text{-}N(D);$

$\alpha_8 = N(A)\text{-}M\text{-}N(B);$

$\alpha_9 = N(A)\text{-}M\text{-}N(D);$

$\alpha_{10} = N(C)\text{-}M\text{-}N(B)$

FIGURE 1   Atomic numbering scheme used and α_n notation for the $[M(bipy)_2(OXO)][Y]$ complexes.
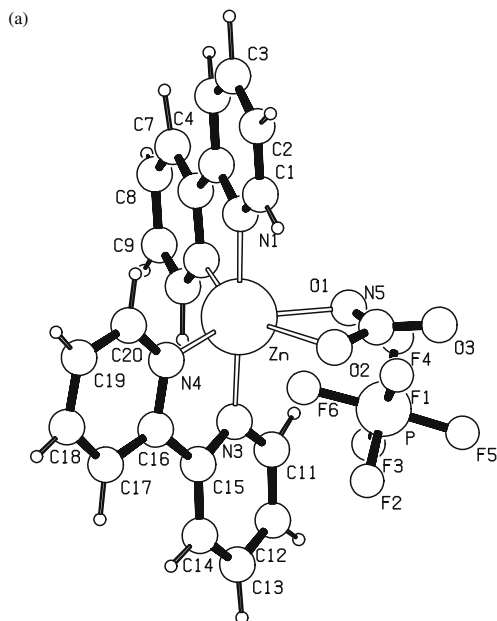
FIGURE 2 (a) Molecular structure of $[Zn(bipy)_2(O_2NO)][PF_6]$, (**9**). (b) Molecular structure of $[Zn(bipy)_2(O_2NO)][ClO_4]$, (**11**).

(b)
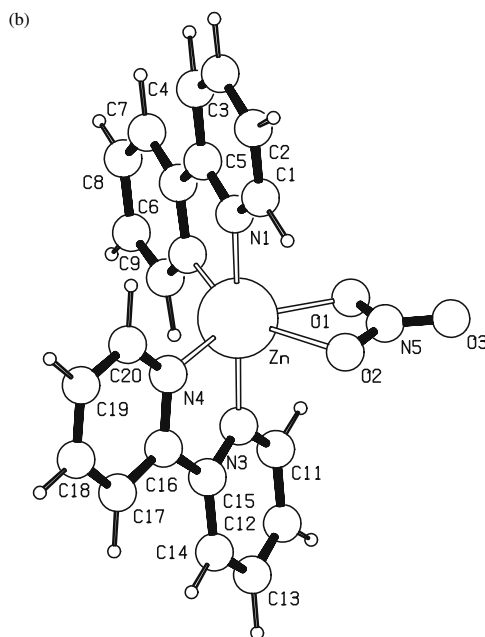
FIGURE 2   Continued.

(a)
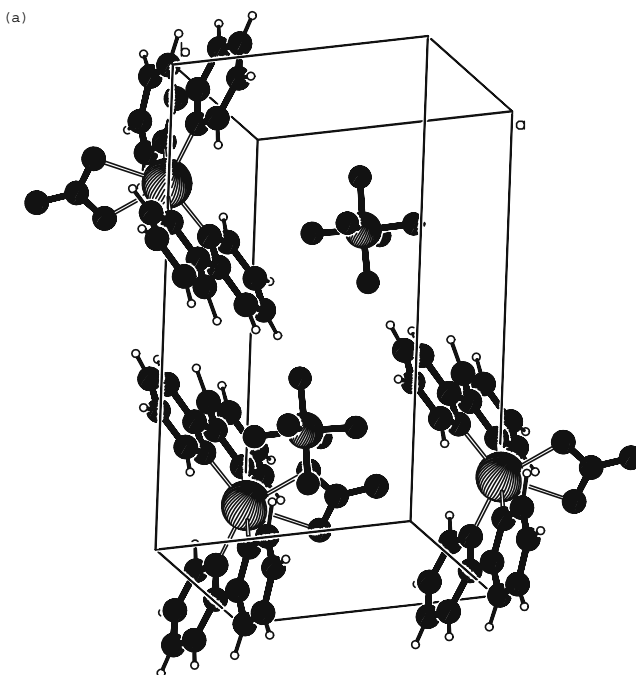
FIGURE 3   (a) Crystal packing of [Zn(bipy)$_2$(O$_2$NO)][PF$_6$], (**9**), showing the unit cell contents: (space group: $P\bar{1}$ 2 molecules in the unit cell). The [Zn(bipy)$_2$(O$_2$NO)]$^+$ cation in the next asymmetric unit is also shown. (b) Unit cell diagram of [Zn(bipy)$_2$(O$_2$NO)][ClO$_4$], (**10**), showing the crystal packing (space group: $P\bar{1}$ 2 molecules in the unit cell). (The two disordered perchlorate molecules are omitted for clarity.)

(b)
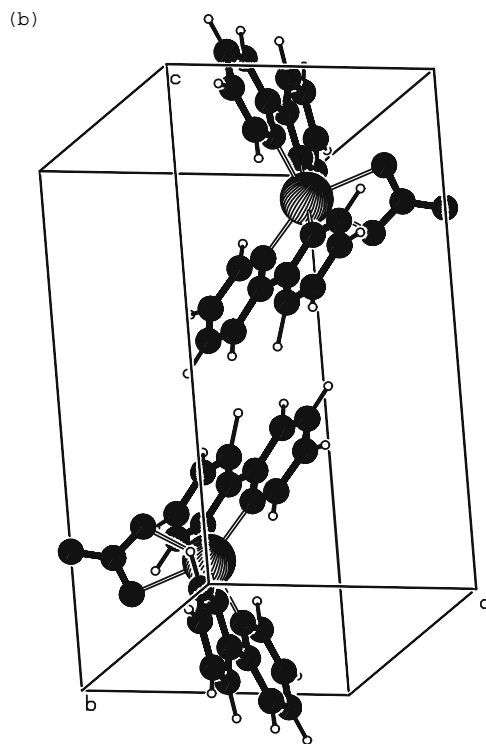
FIGURE 3   Continued.

Crystal Structure of [Zn(bipy)₂(O₂NO)][ClO₄], (10)

The crystal structure of (**10**) consists of a $[Zn(bipy)_2(O_2NO)]^+$ cation and a $[ClO_4]^-$ counterion. The ZnN_4O_2 chromophore is six-coordinate, with a *cis*-distortion of the two oxygens, O(1) and O(2) of the coordinated nitrate, and two out-of-plane Zn–N bonds, Zn–N(1) and Zn–N(3), respectively, at distances 2.106(2) and 2.119(2) Å from the zinc atom ($\Delta N_{1,3} = 0.013(2)$ Å; $Zn-N_{MEAN/OUT} = 2.113(2)$ Å). The two oxygens, O(1) and O(2), occupy the *cis*-octahedral positions of the coordination sphere. The two inplane nitrogens N(2) and N(4) are greater than 2.0 Å, but are slightly shorter than the axial bonds: Zn–N(2) = 2.077(2) Å; Zn–N(4) = 2.092(2) Å ($\Delta N_{2,4} = 0.015(2)$ Å; $Zn-N_{MEAN/OUT} = 2.085(2)$ Å). This means that (**10**) (like (**9**)), has a slight elongation of the axial Zn–N distances. The coordinated nitrate is also bidentate, with one short bond to oxygen, O(1) at 2.194(2) Å from the zinc and one long bond O(2), at 2.355(2) Å. This difference, $\Delta O = 0.161(2)$ Å, between the two Zn–O bonds suggests an asymmetric six-coordinate $(4 + 1 + 1^*)$ stereochemistry, involving a bidentate coordinated nitrate anion. The average zinc–oxygen bond distance is 2.275(2) Å. The three angles α_1, α_2 and α_3 have values 94.8(1), 148.0(1) and 117.0(1)°, respectively. The stereochemistry of (**10**) is *cis*-distorted octahedral with a slight square-pyramidal distortion towards a trigonal bipyramidal stereochemistry. Like (**9**), Table IV(b) suggests a trigonal distortion is present for the basic chromophore. N(2), N(3) and N(4) are all located above the zinc, whereas N(1) is centered marginally below *ca.*

0.09 Å. Additionally, such a distortion is evident from the value of $\alpha_4 + \alpha_5$. The sum of these two angles is 182.4(1)°, notably greater than the linear value of 180.0°.

The pyridine rings of the bipy ligands are near planar (the r.m.s.d.'s range from 0.0049 to 0.0108 Å), and the bond lengths and bond angles are normal for such a complex [19]. The carbon–carbon bond lengths vary from 1.357(5) to 1.480(4) Å (average = 1.397(4) Å) and the carbon–nitrogen bond distances from 1.316(3) to 1.360(3) Å (mean = 1.341(3) Å)°. Furthermore, the bond angles vary from 115.6(2) to 123.6(2)°, with an average value 119.8(2)°. The angles of twist between the pyridine rings, α_{11} and α_{12} are 2.78 and 10.75°, respectively. Between the mean planes of the bipy ligands, the dihedral angle α_{13} is 61.85°.

The nitrate has a marked spread in the N–O bond distances. These vary from 1.199(3) Å for N(5)–O(3), to 1.279(3) Å for the N(5)–O(1) bond. The corresponding N(5)–O distance for the long oxygen bond O(2) is slightly shorter than the N(5)–O(1) bond, at a value of 1.250(3) Å. The nitrate is essentially trigonal planar; however, with an average O–N–O bond angle of 120.0(3)° and a r.m.s.d. of just 0.0019 Å.

As mentioned previously, the perchlorate anion is undergoing considerable positional disorder, with the four oxygen atoms proportionally populated over nine potential alternative sites, as shown in Table I(a). On the basis of this, no reference will be made here to the description of the anion.

Infrared Spectra of [Zn(bipy)$_2$(O$_2$NO)][PF$_6$], (9) and [Zn(bipy)$_2$(O$_2$NO)][ClO$_4$], (10)

Infrared spectra were recorded on a Perkin Elmer 682 Spectrometer, using a KBr disc, over the range 625–4000 cm^{-1}. The infrared spectra of (9) and (10) were found to be virtually indistinguishable, apart from the difference in peaks due to the counterions in each case. The spectra of both complexes are dominated by a well-split coordinated nitrate at 1278 and 1451 cm^{-1}. The extent of this separation, 173 cm^{-1}, is reflected by a virtual window, in the normally masked ionic nitrate region. The fact that the peak for the nitrate is exactly the same in both spectra, serves as a potential *marker for a bidentate nitrate* [24–26]. The only means of distinguishing the two spectra in question are the peaks due to the two anions. The ionic bands differentiate the two spectra, showing that they are different. The spectrum of (9) has a broad relatively strong band resulting from the hexafluorophosphate ion at 830 cm^{-1}. The spectrum of (10) shows an intense absorption due to the perchlorate centered at 1070 cm^{-1}.
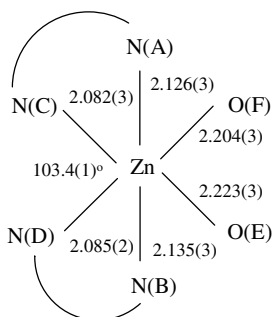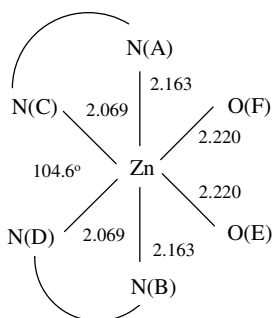
DISCUSSION

In contrast to the nonspherical symmetry of the copper(II) ion with d^9 configuration, the zinc(II) ion is spherically symmetrical, with a d^{10} electron configuration. Regular tetrahedral and octahedral stereochemistries do exist for Zn(II), as exemplified by the complexes [Zn(CN)$_4$]$^{2-}$, (14) and [Zn(NH$_3$)$_6$]$^{2+}$, (15) [20]. However, like the corresponding [Cu(chelate)$_2$(OXO)][Y] complexes, the ZnN$_4$O$_2$ chromophore in [Zn(chelate)$_2$(OXO)][Y] structures involves a *cis* rather than a *trans* structure. Although the ZnN$_4$O$_2$ chromophore involves a *cis*-distortion, there is a clear elongation of the Zn–N(1) and Zn–N(3) bonds along the *z*-direction, unlike the corresponding compressed CuN$_4$O$_2$ chromophore in copper(II) complexes [7]. Table V gives a summary of the main bond angle and bond length data for some of the complexes of

TABLE V Selected bond lengths and bond angles for some [M(bipy)$_2$(OXO)][Y] complexes; (OXO)$^-$ = (ONO)$^-$ and (O$_2$NO)$^-$ where M = Cu(II) and Zn(II)

(OXO)$^-$ [Y]$^-$	(7) Zn(II) (ONO)$^-$ [NO$_3$]$^-$	(8) Zn(II) (ONO)$^-$ [ClO$_4$]$^-$	(9) Zn(II) (O$_2$NO)$^-$ [PF$_6$]$^-$	(10) Zn(II) (O$_2$NO)$^-$ [ClO$_4$]$^-$	(11) Cu(II) (O$_2$NO)$^-$ [PF$_6$]$^-$	(12) Cu(II) (O$_2$NO)$^-$ [ClO$_4$]$^-$
M–N(A)/Å	2.126(3)	2.129(4)	2.115(3)	2.106(2)	1.986(3)	1.9897(28)
M–N(B)/Å	2.135(3)	2.135(4)	2.125(3)	2.119(2)	1.978(3)	1.9975(29)
M–N(C)/Å	2.082(3)	2.090(4)	2.084(3)	2.077(2)	2.037(2)	2.0582(28)
M–N(D)/Å	2.085(3)	2.085(4)	2.091(3)	2.092(2)	2.105(2)	2.0518(29)
M–O(E)/Å	2.223(3)	2.197(5)	2.351(3)	2.355(2)	2.732(3)	2.3448(40)
M–O(F)/Å	2.204(3)	2.216(5)	2.186(3)	2.194(2)	2.144(3)	2.6600(40)
ΔO/Å	0.019(3)	0.019(5)	0.165(3)	0.161(2)	0.594(3)	0.3152(40)
M–O$_{mean}$/Å	2.214(3)	2.207(5)	2.269(3)	2.275(2)	2.441(3)	2.5024(40)
α_1/°	152.4(1)	150.33(18)	94.4(1)	94.8(1)	141.4(1)	132.1(1)
α_2/°	98.2(1)	108.98(17)	147.5(1)	148.0(1)	92.6(1)	91.8(1)
α_3/°	103.4(1)	99.73(18)	117.9(1)	117.0(1)	126.0(1)	136.0(2)

[M(chelate)$_2$(OXO)][Y] series with M = Zn(II) and Cu(II). Both (9) and (10) involve this slightly elongated *cis*-distorted ZnN$_4$O$_2$ chromophore, with axial zinc–nitrogen bonds of 2.115(3) Å for Zn–N(1) and 2.125(3) Å for Zn–N(3) in (9) and 2.106(2) Å and 2.119(2) Å in (10), as shown in Table III(a). The slight elongation contrasts with the more significant compressed *cis*-distorted octahedral CuN$_4$O$_2$ chromophore of the corresponding copper(II) complexes. [Cu(bipy)$_2$(O$_2$NO)][PF$_6$], (11) has Cu–N(1) and Cu–N(3) bonds of 1.970(3) and 1.988(3) Å, respectively [11]. Likewise, the axial bonds in [Cu(bipy)$_2$(O$_2$NO)][ClO$_4$], (12) are 1.9897(28) and 1.9975(29) Å [12]. The significant elongated *cis*-distortion of the zinc–oxygen distances in (9) and (10) are comparable to the corresponding copper–oxygen distances. Nonetheless, the differences in the zinc–oxygen bonds are considerably less than the corresponding ΔO values in the copper(II) complexes. The ΔO's for (9) and (10) are 0.165(3) and 0.161(2) Å. Even though this amounts to an asymmetric distortion of the zinc–oxygen bonds, the extent of the distortion is not as marked as that seen in [Cu(bipy)$_2$(O$_2$NO)][PF$_6$], (11) and [Cu(bipy)$_2$(O$_2$NO)][ClO$_4$], (12), where the asymmetry is much greater with ΔO = 0.3152(40) Å in (12) and ΔO = 0.594(3) Å in (11). If one examines the differences between the ZnN$_4$O$_2$ chromophore in [Zn(bipy)$_2$(O$_2$NO)][PF$_6$], (9) and [Zn(bipy)$_2$-(O$_2$NO)][ClO$_4$], (10), it can be seen that the two structures are virtually identical. Both complexes have a six-coordinate *cis*-octahedral ZnN$_4$O$_2$ chromophore with slightly elongated Zn–N(1) and Zn–N(3) axial bonds, ≈ 2.11 Å. The ΔO values are also comparable ≈ 0.16 Å. However, of particular interest is the value of the back-angle α_3, which is ≈ 117° for both complexes. Furthermore, considering the near proximity of the unit cell parameters (as tabulated in Table II), it can be stated that (9) and (10) are not just isomorphous but also isostructural, which is remarkable considering the differences between the two anions involved i.e. a hexafluorophosphate anion in (9) and a perchlorate anion in (10).

There are, however, some questions that remain unanswered. The differences between (9) and (10) and the corresponding copper(II) complexes raises the question of the possibility of the [Zn(chelate)$_2$(OXO)][Y] series of complexes having temperature variable or fluxional behavior [8] as reflected by the individual anisotropic temperature factors and the related direction of the thermal ellipsoids. Of particular interest are the thermal ellipsoids for the oxygen atoms of the coordinated nitrate. In

(a) [Zn(bipy)₂(ONO)][NO₃], **(7)**

(ΔO = 0.019(3) Å)
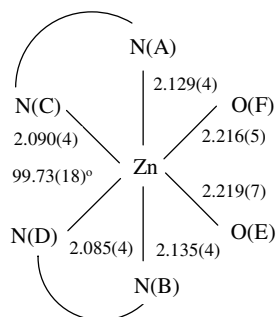
(b) [Zn(bipy)₂(ONO)][ClO₄], **(8)**

(ΔO = 0.019(5) Å)
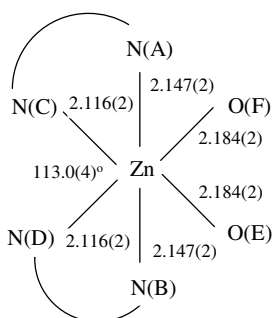
(c) [Zn(phen)₂(O₂CCH₃)][BF₄]

.2H₂O, **(4) (ΔO = 0.000 Å)**
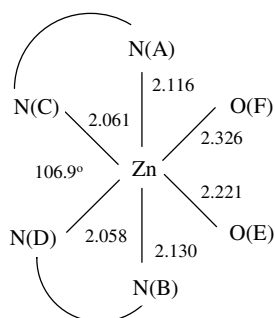
(d) [Zn(bipyam)₂(O₂NO)][NO₃], **(6)**

(ΔO = 0.105 Å)

(e) [Zn(bipyam)₂(ONO)][NO₂], **(5)**

(ΔO = 0.000 Å)

FIGURE 4 Local molecular structures of the five [Zn(chelate)₂(OXO)[Y] complexes of known crystal structure.

Zn-O(1) = 2.186(3) Å

Zn-O(2) = 2.351(3) Å

ΔO = 0.165(3) Å

[Zn(bipy)$_2$(O$_2$NO)][PF$_6$], **(a)**

Cu-O(1) = 2.144(3) Å

Cu-O(2) = 2.738(0) Å

ΔO = 0.594(3) Å

[Cu(bipy)$_2$(O$_2$NO)][PF$_6$], **(11)**

Zn-O(1) = 2.194(2) Å

Zn-O(2) = 2.355(2) Å

ΔO = 0.161(2) Å

[Zn(bipy)$_2$(O$_2$NO)][ClO$_4$], **(10)**

Cu-O(1) = 2.210(4) Å

Cu-O(2) = 2.210(4) Å

ΔO = 0.00 Å: C_2-axis

[Cu(bipyam)$_2$(ONO)][Cl], **(13)**
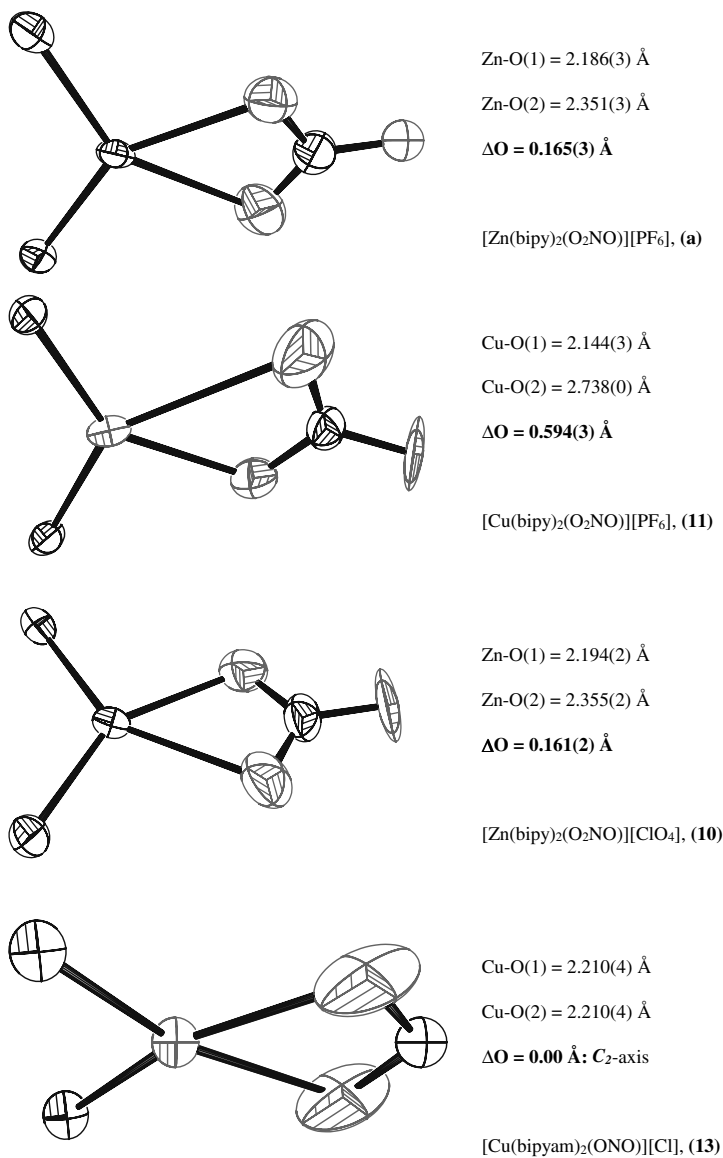
FIGURE 5   ORTEP diagrams of the equatorial inplane atoms in **(9)**, **(10)**, **(11)** and **(13)** [11].

TABLE VI α_3 angles for the [Zn(chelate)$_2$(OXO)][Y] series of complexes

Complex	$\alpha_3/°$
[Zn(bipy)$_2$(O$_2$NO)][PF$_6$], **(9)**	117.9(1)
[Zn(bipy)$_2$(O$_2$NO)][ClO$_4$], **(10)**	117.0(1)
[Zn(bipy)$_2$(ONO)][NO$_3$], **(7)**	103.4(1)
[Zn(bipy)$_2$(ONO)][ClO$_4$], **(8)**	99.73(4)
[Zn(phen)$_2$(O$_2$CCH$_3$)][BF$_4$] · 2H$_2$O, **(4)**	113.0(4)
[Zn(bipyam)$_2$(O$_2$NO)][NO$_3$], **(6)**	106.9(4)
[Zn(bipyam)$_2$(ONO)][NO$_2$], **(5)**	104.6(4)

the [Cu(chelate)$_2$(OXO)][Y] complexes, the ellipsoids are small and nearly isotropic for very asymmetric complexes, such as [Cu(bipy)$_2$(O$_2$NO)][PF$_6$], (**11**) (ΔO $= 0.594(3)$ Å). In contrast, the thermal ellipsoids are large and very anisotropic for symmetric complexes such as [Cu(bipyam)$_2$(ONO)][Cl], (**13**) (C_2) (Fig. 5, ORTEP diagrams [13]). In 1987, Simmons and coworkers [8] claimed that the ellipsoids represent the super-positions of two asymmetric structures with relative contributions ranging from 1 : 1 for the symmetric structures (i.e. those with average C_2 symmetries) to approximately 1 : 0 for the very asymmetric complexes. In addition, this interpretation is further supported by the large and very anisotropic oxygen ellipsoids in [Cu(phen)$_2$-(O$_2$CCH$_3$)][BF$_4$]$\cdot$2H$_2$O, (**14**), which is reported as disordered about a crystallographic C_2-axis [22,23] and the small and nearly isotropic oxygen ellipsoids of the isostructural but ordered [Zn(phen)$_2$(O$_2$CCH$_3$)][BF$_4$]$\cdot$2H$_2$O, (**4**) complex, which has static C_2 symmetry [8]. These differences reflect the spherical symmetry of the d^{10} zinc(II) configuration, relative to the nonspherical symmetrical d^9 configuration of copper(II).

If one then considers the seven complexes of known crystal structure, (**4**)–(**10**) inclusive, of the [Zn(chelate)$_2$(OXO)][Y] complexes, and the additional complexes, (**1**)–(**3**), it can be seen that three of the total number of complexes involve acetate as the oxoanion and phen as the chelate ligand. The molecular structures of the five zinc(II) complexes (**4**)–(**8**), are represented in Figure 4. Two of the structures, (**4**) and (**5**), lie on a crystallographic C_2-axis of symmetry. The back-angle, α_3 in (**4**) is 113.0(4)°. In contrast, to the three bipyam complexes, [Zn(bipyam)$_2$(ONO)][NO$_2$], (**5**) [1,3,5] (also on a C_2) has a lower α_3 angle, equal to 104.6(4)°. The complex, [Zn(bipyam)$_2$(O$_2$NO)][NO$_3$], (**6**) [6], ($\alpha_3 = 106.9(4)°$), is slightly asymmetric associated with the two zinc–oxygen bonds, Zn–O(1) $= 2.326(10)$ Å and Zn–O(2) $= 2.221(9)$ Å (ΔO $= 0.105(9)$ Å). This then begs the question that within the [Zn(chelate)$_2$(OXO)][Y] series there is supporting evidence for the occurrence of preferred α_3 angles i.e. magic angles. One of the interesting features of the [Zn(chelate)$_2$(OXO)][Y] series of complexes is the variation in the back-angle α_3. Table VI gives the α_3 angles of some zinc(II) complexes of known crystal structure solved to date, including (**9**) and (**10**), described in this article. What is noticeable from the table is that the two bipyam complexes have low α_3 values: 104.6(4)° in (**5**); 106.9(4)° in (**6**), whereas the analogous one phen and five bipy structures have angles in both high and low α_3 clusters. This is observed if one compares [Zn(bipy)$_2$-(ONO)][NO$_3$], (**7**) ($\alpha_3 = 103.4(1)°$) with (**9**) and (**10**) ($\alpha_3 = 117.9(1)$ and 117.0(1)°, respectively). This suggests that the difference in discrete angles may be related to the conformation of the chelating ligand involved.

Furthermore, it still remains to be seen whether or not a structural pathway [21] exists for the [Zn(bipy)$_2$(O$_2$NO)][Y] series of complexes. As stated already, the two complexes (**9**) and (**10**) are essentially isostructural, suggesting any difference between the two complexes is too small to indicate a comparable zinc(II) structural pathway. Nevertheless, considering the disproportionate number of [Zn(chelate)$_2$(OXO)][Y] structures, even this interpretation is tentative and must await more structural data.

Acknowledgments

References

[1] C.J. Simmons, *New J. Chem.* **17**, 77 (1993).

[2] C.J. Simmons and H. Stratemeier, unpublished results.

[3] C.J. Simmons, unpublished results.

[4] W. Fitzgerald, B.J. Hathaway and C.J. Simmons, *J. Chem. Soc., Dalton Trans.* **141** (1985).

[5] P.C. Power, PhD Thesis, National University of Ireland, University College Cork (1975).

[6] B.A. Coppins, PhD Thesis, National University of Ireland, University College Cork (1978).

[7] A. Walsh, B. Walsh, B. Murphy and B.J. Hathaway, *Acta. Crystallogr., Sect. B*, **37**,1512 (1981).

[8] C.J. Simmons, B.J. Hathaway, K. Amornjarusiri, B.D. Santarsiero and A. Clearfield, *J. Am. Chem. Soc.*, **109**, 1947 (1987).

[9] D. Cunningham, PhD Thesis, National University of Ireland, University College Cork (1992).

[10] B. Murphy, M. Aljabri, M. Light and M.B. Hursthouse, paper submitted to *J. Chem. Crystallography* (in press).

[11] B. Murphy, PhD Thesis, National University of Ireland, University College Cork (1994).

[12] I.I. Mathews, N. Vijayashree, A.G. Samuelson and H.Manohar, unpublished results.

[13] P. McCardle, XCAD, programme for data reduction of CAD4 output, National University of Ireland, Galway, 1990; ORTEX, Fortran thermal ellipsoid plot programme for the illustration of crystal structures (interactive version of ORTEP), National University of Ireland, Galway (1989).

[14] G.M. Sheldrick, SHELX 76, programme for crystal structure determination, University of Cambridge, UK, 1976; G.M. Sheldrick, SHELXS 86, programme for crystal structure solutions, University of Göttingen, Germany (1986).

[15] P. Roberts and G.M. Sheldrick, XANADU, programme for the calculation of crystallographic data, University of Cambridge, UK (1979).

[16] K. Hendrick, PUBTAB, Programme to prepare and print crystallographic tables for publication, University of North London, UK (1980).

[17] A.L. Spek, PLUTON92, programme for the illustration of molecular structures, University of Utrecht, Netherlands, 1982; *Acta Crystallogr., Sect. A*, **46**, C-34 (1990).

[18] B.J. Hathaway, In: G. Wilkinson, R.D. Gillard and J.A. McCleverty (Eds.), *Comprehensive Coordination Chemistry, the Synthesis, Reactions, Properties and Applications of Coordination Compounds*, Vol. 5 (Pergamon, Oxford), pp. 553–774 (1987).

[19] M. Liu and S.K. Arona, *Acta Crystallogr., Sect. C* **49**, 372 (1993).

[20] K.M. Mackay and R.A. Mackay, *Introduction to Modern Inorganic Chemistry*, 2nd Edn., Ch. 14, p. 228 (Prentice Hall, London, 1989).

[21] C. O'Sullivan, G. Murphy, B. Murphy and B. Hathaway, *J. Chem. Soc., Dalton Trans.* 1835 (1999).

[22] F. Clifford, E. Counihan, W. Fitzgerald, K. Seff, C.J. Simmons, S. Tyagi and B.J. Hathaway, *J. Chem. Soc., Chem. Commun.* 196 (1982).

[23] C.J. Simmons, K. Seff, F. Clifford and B.J. Hathaway, *Acta Crystallogr., Sect. C* **39**, 1360 (1983).

[24] Y. Ihara, Y. Fukuda and K. Sore, *Inorg. Chem.* **26**, 3745 (1987).

[25] A.B.P. Lever, E. Mantovani and B.S. Ramaswanry, *Can. J. Chem.* **49**, 1957 (1971).

[26] D. Gomez de Anderez, A.K. Mukherjee, S. Koner and N.R. Chaudhuri, *Polyhedron* **10**, 2225 (1991).