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The Structures of Bis(2,2′-bipyridyl)mononitritocopper(II) Tetrafluoroborate Bis(2,2′-bipyridyl)mononitritozinc(II) Nitrate

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Abstract

The structures of bis(2,2′-bipyridyl)mononitritocopper(II) tetrafluoroborate $[Cu(C_{10}H_8N_2)_2(ONO)]BF_4$, $C_{20}H_{16}CuN_5O_2^+.BF_4^-$ (1), and bis(2,2′-bipyridyl)mononitritozinc(II) nitrate $[Zn(C_{10}H_8N_2)_2(ONO)]NO_3$, $C_{20}H_{16}N_5O_2Zn^+.NO_3^-$ (2), have been determined by X-ray analysis. Both complexes crystallize in the monoclinic space group $P2_1/n$ with, for (1), a = 10·839 (3), b = 12·367 (3), c = 16·219 (3) Å, β = 105·25 (5)°, U = 2097·5 Å^3, Z = 4, R = 0·0468 (R_w = 0·0566) for 2769 unique reflections and, for (2), a = 11·27 (5), b = 11·93 (5), c = 15·49 (6) Å, β = 101·2 (2)°, U = 2042·7 Å^3, Z = 4, R = 0·0953 (R_w = 0·1033) for 2083 unique reflections. Both complexes involve an MN_4O_2 chromophore but while (1) has a (4+1+1*)-type coordination involving a trigonal-bipyramidal stereochemistry with a square-pyramidal distortion with an elongation along one of the in-plane Cu—N directions and an off-the-axis sixth O ligand, (2) involves a *cis*-distorted ZnN_4O_2 chromophore stereochemistry. The two structures may be related by a linear combination of the components of the E mode of vibration of the parent trigonal-octahedral tris(chelate)metal(II) structure.

Introduction

The nitrite ion is unique in the stereochemistry of the $[Cu(bpy)_2(OXO)]Y$ complexes, where bpy = 2,2′-bipyridyl, in forming a *cis*-distorted octahedral CuN_4OO' chromophore in bis(2,2′-bipyridyl)mononitritocopper(II) nitrate (Proctor & Stephens, 1969). To obtain more information on this stereochemistry the crystal structure of $[Cu(bpy)_2(ONO)]BF_4$ (1) has been determined and to obtain information on the electronic properties (Proctor, Hathaway, Billing, Dudley & Nicholls, 1969; Hathaway, Proctor, Slade & Tomlinson, 1969) of the $[Cu(bpy)_2(ONO)]^+$ cation doped in the corresponding $[Zn(bpy)_2(ONO)]NO_3$ complex as a host lattice, the crystal structure of $[Zn(bpy)_2(ONO)]NO_3$ (2) has also been determined.

Experimental

Preparation

(1) was prepared by addition of an aqueous solution of excess $NaNO_2$ (0·05 mol in 20 ml) to a 1:1 aqueous alcohol solution (20 ml) (0·01 mol) of $Cu(bpy)_2(BF_4)$ (0·01 mol) (Hathaway, Proctor, Slade & Tomlinson, 1969). Single crystals were obtained by carrying out the preparation at a much higher dilution, 200 ml. (Composition: found: C = 46·76, H = 3·28, Cu = 12·08, N = 13·58%; $C_{20}H_{16}CuN_5O_2^+.BF_4^-$ requires: C = 47·21, H = 3·15, Cu = 12·50, N = 13·77%.)

Crystals of (2) were prepared as reported by Proctor, Hathaway, Billing, Dudley & Nicholls (1969) for the pure Cu^{II} complex with the stoichiometric amount of $Zn(NO_3)_2.6H_2O$. Large crystals were obtained if methanol rather than ethanol was used in the preparation. (Composition: found: C = 49·07, H = 3·52, N = 17·34, Zn = 13·29%; $C_{20}H_{16}N_5O_2Zn^+.NO_3^-$ requires: C = 49·44, H = 3·29, N = 17·30, Zn = 13·46%.)

Crystal data

The crystal and refinement data for (1) and (2) are summarized in the *Abstract* and in Table 1. For both complexes preliminary cell dimensions and space group were determined from precession photographs and for (1) refined on a Philips PW 1100 four-circle diffractometer. The intensities for (1) were collected on the diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. A θ–2θ scan mode was used and reflections with 3° < θ < 32° in one quadrant were examined. A constant scan speed of 0·05° s^{-1} was used with a variable scan width of (0·7 + 0·1 tan θ)°. With an acceptance criterion $I > 2{\cdot}50\sigma(I)$, 2769 reflections were retained. The data for (2) were collected photographically with five-film packs on an equi-inclination Weissenberg goniometer. The data (integrated reflections) were estimated visually and 2083 unique reflec-

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Table 1. *Additional crystal and refinement data*

	(1) $[Cu(bpy)_2(ONO)]BF_4$	(2) $[Zn(bpy)_2(ONO)]NO_3$
M_r	508·37	485·4
D_m(flotation) (Mg m^{-3})	1·65	1·58
D_c (Mg m^{-3})	1·611	1·577
Radiation	Mo *Kα*	Cu *Kα*
$F(000)$	1028·0	984·0
μ(mm^{-1})	1·059	1·916
Collection data	–	*hk*(0–9), *h*0*l**
Number of unique reflections	2769	2083
Number of anisotropic atoms	36	37
Number of varied parameters	330	300
$R\ (=\sum \Delta/\sum \lvert F_o \rvert)$	0·0468	0·0953
$R_w (=\sum w^{1/2}\Delta/\sum w^{1/2} \lvert F_o \rvert)$	0·0556	0·1033
k	1·000	1·9380
g	0·02002	0·006202
Maximum final shift/e.s.d.	0·05	0·02
Residual electron density (e Å^{-3})	0·319	0·745

* The data were actually collected on 0·1% copper-doped $[Zn(bpy)_2(ONO)]NO_3$, but in the structure determination the small percentage of copper was ignored.

tions retained. Lorentz and polarization corrections were applied but no corrections for absorption or extinction were made.

Both structures were solved by Patterson and Fourier techniques and refined by blocked-matrix least squares, with anisotropic temperature factors for all the non-hydrogen atoms. The positions of the H atoms were calculated geometrically with C—H = 1·08 Å and a fixed temperature factor of 0·07 Å^2 and floated on the adjacent C atoms. The refinements converged when the ratio of the maximum shift to e.s.d. was <0·05 for (1), and <0·02 for (2), with a weighting scheme, $w = k/[\sigma^2(F_o) + g(F_o)^2]$ (Table 1). Complex neutral scattering factors (Cromer & Liberman, 1970; Cromer & Waber, 1965) were used for the non-hydrogen atoms

Table 2. *Fractional atomic coordinates* (×10^4) *and* U_{eq} (Å^2 ×10^3)

$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$ for (1) and (2).

	(1)				(2)			
	x	y	z	U_{eq}	x	y	z	U_{eq}
*X	2445 (1)	560 (1)	3645 (1)	59	2395 (1)	508 (1)	1253 (1)	51
N(1)	2035 (3)	580 (2)	4771 (2)	90	2696 (7)	519 (5)	−62 (4)	49
C(1)	2569 (4)	−48 (3)	5438 (2)	85	2041 (10)	−54 (7)	−762 (6)	52
C(2)	2192 (5)	−56 (4)	6184 (3)	83	2425 (10)	−152 (7)	−1555 (5)	71
C(3)	1187 (5)	617 (3)	6235 (3)	84	3510 (10)	312 (6)	−1634 (6)	76
C(4)	641 (4)	1286 (3)	5561 (3)	78	4175 (9)	872 (7)	−939 (6)	96
C(5)	1079 (4)	1254 (3)	4828 (2)	48	3742 (8)	1005 (6)	−162 (5)	65
C(6)	566 (3)	1939 (3)	4067 (2)	53	4359 (8)	1643 (6)	613 (6)	66
C(7)	−315 (4)	2759 (3)	4023 (3)	96	5304 (9)	2364 (7)	592 (7)	67
C(8)	−733 (5)	3345 (3)	3268 (3)	100	5816 (11)	2939 (8)	1340 (9)	57
C(9)	−257 (5)	3104 (4)	2592 (3)	93	5386 (10)	2791 (8)	2120 (8)	49
C(10)	624 (4)	2275 (3)	2676 (3)	76	4448 (9)	2059 (7)	2094 (7)	55
N(2)	1020 (3)	1701 (2)	3387 (2)	62	3932 (6)	1499 (5)	1365 (4)	44
N(3)	2820 (3)	563 (2)	2499 (2)	63	2112 (7)	565 (5)	2586 (4)	52
C(11)	2163 (4)	−12 (4)	1830 (2)	65	2712 (10)	−45 (8)	3272 (6)	88
C(12)	2543 (5)	−108 (4)	1079 (3)	86	2288 (12)	−148 (9)	4046 (6)	90
C(13)	3655 (5)	426 (3)	1037 (3)	101	1240 (11)	352 (8)	4118 (6)	78
C(14)	4320 (4)	1023 (3)	1715 (3)	103	613 (9)	1004 (7)	3434 (6)	69
C(15)	3889 (4)	1098 (3)	2448 (2)	72	1104 (8)	1096 (6)	2670 (5)	37
C(16)	4522 (3)	1749 (3)	3204 (2)	71	540 (8)	1805 (5)	1894 (5)	45
C(17)	5512 (4)	2461 (3)	3205 (3)	80	−363 (8)	2567 (6)	1921 (6)	73
C(18)	6000 (5)	3071 (4)	3945 (3)	80	−771 (9)	3237 (7)	1183 (7)	70
C(19)	5506 (5)	2960 (4)	4637 (3)	66	−284 (9)	3111 (7)	437 (6)	63
C(20)	4534 (4)	2223 (3)	4587 (3)	69	599 (9)	2314 (6)	460 (6)	63
N(4)	4056 (3)	1628 (3)	3890 (2)	59	990 (6)	1676 (5)	1152 (4)	47
N(5)	2658 (5)	−1643 (3)	3657 (2)	103	2095 (9)	−1684 (7)	1276 (5)	100
O(1)	3481 (4)	−908 (4)	3893 (2)	111	1256 (7)	−1026 (6)	1047 (5)	74
O(2)	1583 (4)	−1289 (3)	3403 (2)	107	3134 (6)	−1215 (5)	1453 (4)	86
B(1)	2289 (5)	−1062 (5)	8685 (3)	73				
F(4)	3248 (4)	−456 (4)	9173 (2)	83				
F(1)	2710 (4)	−1741 (4)	8137 (3)	158				
F(2)	1685 (6)	−1624 (5)	9138 (3)	132				
F(3)	1567 (8)	−346 (4)	8174 (4)	246				
F(1′)	1155 (12)	−795 (13)	8921 (11)	139				
F(2′)	2627 (27)	−1888 (16)	9030 (14)	493				
F(3′)	2191 (20)	−923 (17)	7946 (6)	72				
N(6)					2243 (7)	3842 (5)	8746 (4)	40
O(3)					2843 (6)	4688 (5)	8727 (5)	90
O(4)					1187 (8)	3937 (7)	8831 (5)	85
O(5)					2674 (9)	2966 (7)	8676 (9)	195

* X: Cu in (1) and Zn in (2).

and those for the heavy atoms were corrected for anomalous dispersion. All calculations were carried out with *SHELX* 76 (Sheldrick, 1976), *XANADU* (G. M. Sheldrick), *PLUTO* (W. D. S. Motherwell), and *XPUB* (R. Taylor), on an IBM 370/138 computer. The final non-hydrogen atomic coordinates are given in Table 2, the bond distances and angles in Table 3, and some mean planes in Table 4. Fig. 1 illustrates the local molecular structure and atom numbering.*

Discussion

Description of crystal structures

The structures of (1) and (2) consist of discrete $[M(\mathrm{bpy})_2(\mathrm{ONO})]^+$ cations and BF_4^- and NO_3^- anions, respectively. The unit cells of (2) and $[\mathrm{Cu(bpy)_2(ONO)]NO_3}$ (Proctor & Stephens, 1969) are isomorphous with unit-cell parameters which are as near equivalent as they can be for a $\mathrm{Zn^{II}}$ complex (d^{10}) and a $\mathrm{Cu^{II}}$ complex (d^9) (Table 5), with comparable packing of the $[M(\mathrm{bpy})_2(\mathrm{ONO})]^+$ cations and NO_3^- anions. Neither complex has any unusual features in the bond lengths or angles of the bpy ligands (Stephens, 1969). In (1) the BF_4^- ion showed evidence of disorder (Stynes & Ibers, 1971), which was best represented by two interpenetrating $\mathrm{BF_4}$ tetrahedra with the B and F(4) atoms common; the site-occupation factor was initially set at 0·5 but refined to 0·75 for F(1)–F(3) and was then fixed. There were no unusual features in either the bond lengths or angles of the nitrate ion (Addison, Logan, Wallwork & Garner, 1971) of (2). There was no evidence for semi-coordination (Proctor, Hathaway & Nicholls, 1968) of either the BF_4^- ion in (1) or the NO_3^- ion in (2) to the $M\mathrm{N_4O_2}$ chromophores.

The stereochemistry of the $[\mathrm{Cu(bpy)_2(ONO)}]^+$ cation of (1) is basically five-coordinate (Barclay,

Table 3. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

X = Cu in (1) and Zn in (2).

	(1)	(2)		(1)	(2)		(1)	(2)
N(1)–X	1·990 (5)	2·129 (9)	N(2)–C(6)	1·353 (6)	1·355 (13)	C(19)–C(18)	1·372 (9)	1·380 (16)
N(2)–X	2·052 (5)	2·076 (9)	C(8)–C(7)	1·392 (8)	1·373 (16)	C(20)–C(19)	1·379 (8)	1·372 (14)
N(3)–X	2·004 (5)	2·151 (9)	C(9)–C(8)	1·362 (9)	1·398 (20)	N(4)–C(20)	1·334 (6)	1·319 (11)
N(4)–X	2·142 (5)	2·092 (9)	C(10)–C(9)	1·383 (7)	1·366 (15)	N(5)–O(1)	1·261 (7)	1·227 (13)
O(1)–X	2·117 (6)	2·223 (9)	N(2)–C(10)	1·326 (6)	1·343 (12)	O(2)–N(5)	1·211 (7)	1·279 (13)
O(2)–X	2·462 (6)	2·217 (8)	C(11)–N(3)	1·336 (6)	1·355 (12)	F(1)–B(1)	1·384 (9)	
C(1)–N(1)	1·334 (6)	1·370 (11)	C(15)–N(3)	1·356 (6)	1·329 (12)	F(2)–B(1)	1·306 (10)	
C(5)–N(1)	1·352 (6)	1·349 (13)	C(12)–C(11)	1·390 (7)	1·380 (17)	F(3)–B(1)	1·320 (9)	
C(2)–C(1)	1·375 (7)	1·384 (15)	C(13)–C(12)	1·392 (8)	1·347 (18)	F(4)–B(1)	1·355 (8)	
C(3)–C(2)	1·391 (8)	1·369 (17)	C(14)–C(13)	1·363 (7)	1·391 (13)	F(1′)–B(1)	1·419 (17)	
C(4)–C(3)	1·375 (7)	1·361 (13)	C(15)–C(14)	1·390 (7)	1·405 (14)	F(2′)–B(1)	1·176 (22)	
C(5)–C(4)	1·392 (7)	1·393 (14)	C(16)–C(15)	1·476 (6)	1·506 (12)	F(3′)–B(1)	1·188 (13)	
C(6)–C(5)	1·480 (6)	1·476 (12)	C(17)–C(16)	1·388 (7)	1·371 (13)	O(3)–N(6)		1·218 (10)
C(7)–C(6)	1·382 (7)	1·374 (14)	N(4)–C(16)	1·346 (6)	1·352 (12)	O(4)–N(6)		1·228 (13)
			C(18)–C(17)	1·398 (8)	1·397 (14)	O(5)–N(6)		1·166 (12)

	(1)	(2)		(1)	(2)		(1)	(2)
N(2)–X–N(1)	80·8 (2)	77·9 (4)	C(6)–C(5)–C(4)	124·0 (4)	124·9 (9)	C(19)–C(18)–C(17)	120·5 (6)	120·1 (10)
N(3)–X–N(1)	178·6 (1)	177·8 (2)	C(7)–C(6)–C(5)	124·5 (5)	123·2 (10)	C(20)–C(19)–C(18)	118·3 (5)	117·3 (9)
N(3)–X–N(2)	97·8 (2)	100·3 (4)	N(2)–C(6)–C(5)	114·7 (4)	116·4 (8)	N(4)–C(20)–C(19)	122·3 (5)	123·2 (10)
N(4)–X–N(1)	101·0 (2)	100·6 (4)	N(2)–C(6)–C(7)	120·8 (5)	120·4 (9)	C(16)–N(4)–X	112·3 (3)	114·6 (6)
N(4)–X–N(2)	98·5 (2)	103·5 (3)	C(8)–C(7)–C(6)	119·2 (6)	119·6 (12)	C(20)–N(4)–X	127·8 (4)	125·0 (7)
N(4)–X–N(3)	79·4 (2)	78·4 (4)	C(9)–C(8)–C(7)	119·3 (5)	120·5 (11)	C(20)–N(4)–C(16)	119·5 (4)	120·3 (8)
O(1)–X–N(1)	94·1 (2)	93·6 (4)	C(10)–C(9)–C(8)	118·7 (5)	116·9 (11)	O(2)–N(5)–O(1)	112·5 (5)	113·8 (9)
O(1)–X–N(2)	164·1 (1)	158·4 (3)	N(2)–C(10)–C(9)	122·7 (5)	123·3 (11)	N(5)–O(1)–X	105·3 (4)	95·4 (7)
O(1)–X–N(3)	87·2 (2)	88·6 (4)	C(6)–N(2)–X	113·5 (3)	115·5 (6)	N(5)–O(2)–X	89·4 (4)	94·1 (6)
O(1)–X–N(4)	97·3 (2)	97·5 (4)	C(10)–N(2)–X	126·8 (4)	124·8 (8)	F(2)–B(1)–F(1)	109·7 (6)	
O(2)–X–N(1)	89·5 (2)	90·8 (3)	C(10)–N(2)–C(6)	119·3 (4)	119·5 (9)	F(3)–B(1)–F(1)	104·2 (6)	
O(2)–X–N(2)	111·9 (2)	103·4 (3)	C(11)–N(3)–X	123·9 (4)	126·3 (7)	F(1)–B(1)–F(4)	112·3 (6)	
O(2)–X–N(3)	90·9 (2)	91·0 (4)	C(15)–N(3)–X	116·3 (3)	113·5 (6)	F(3)–B(1)–F(2)	114·1 (7)	
O(2)–X–N(4)	149·2 (1)	152·4 (3)	C(15)–N(3)–C(11)	119·5 (5)	119·0 (9)	F(2)–B(1)–F(4)	112·8 (6)	
O(2)–X–O(1)	52·7 (2)	56·5 (4)	C(12)–C(11)–N(3)	122·7 (5)	121·7 (11)	F(3)–B(1)–F(4)	103·5 (56)	
C(1)–N(1)–X	125·7 (4)	126·3 (7)	C(13)–C(12)–C(11)	117·6 (5)	119·3 (10)	F(2′)–B(1)–F(1′)	104·9 (18)	
C(5)–N(1)–X	115·5 (3)	114·7 (6)	C(14)–C(13)–C(12)	119·9 (6)	120·6 (11)	F(3′)–B(1)–F(1′)	112·6 (14)	
C(5)–N(1)–C(1)	118·7 (5)	118·2 (8)	C(15)–C(14)–C(13)	120·1 (5)	117·4 (10)	F(3′)–B(1)–F(2′)	122·7 (17)	
C(2)–C(1)–N(1)	123·5 (5)	122·1 (10)	C(14)–C(15)–N(3)	120·3 (4)	122·0 (8)	F(1′)–B(1)–F(4)	107·4 (7)	
C(3)–C(2)–C(1)	117·8 (5)	118·9 (9)	C(16)–C(15)–N(3)	115·7 (4)	115·2 (8)	F(2′)–B(1)–F(4)	96·2 (12)	
C(4)–C(3)–C(2)	119·5 (6)	119·5 (10)	C(16)–C(15)–C(14)	124·0 (5)	122·8 (9)	F(3′)–B(1)–F(4)	111·1 (11)	
C(5)–C(4)–C(3)	119·3 (5)	120·5 (10)	C(17)–C(16)–C(15)	122·5 (5)	123·3 (9)	O(4)–N(6)–O(3)		118·7 (8)
C(4)–C(5)–N(1)	121·0 (4)	120·7 (8)	N(4)–C(16)–C(15)	115·6 (4)	116·4 (8)	O(5)–N(6)–O(3)		119·8 (10)
C(6)–C(5)–N(1)	115·0 (4)	114·3 (9)	N(4)–C(16)–C(17)	121·9 (4)	120·3 (8)	O(5)–N(6)–C(4)		121·5 (9)
			C(18)–C(17)–C(16)	117·5 (6)	118·9 (10)			

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* Lists of structure factors, anisotropic thermal parameters and H atom coordinates for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35904 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Equations of least-squares planes in the form $lX + mY + nZ = p$, where X, Y and Z are a set of orthogonal axes*

Deviations (Å) of relevant atoms from the planes are given in square brackets.

	l	m	n	p
(*a*) Complex (1) (e.s.d.'s 0·001–0·003 Å)				
Plane (1): N(1), C(1)–C(5) (r.m.s. deviation 0·0077)				
	0·6633	0·7181	0·2105	3·4409
[C(3) –0·0124, C(2) 0·0093, N(1) –0·0077]				
Plane (2): N(2), C(6)–C(10) (r.m.s. deviation 0·0038)				
	0·7454	0·6520	0·1387	2·8942
[N(2) –0·0060, C(10) 0·0039]				
Plane (3): N(1), C(1)–C(10), N(2) (r.m.s. deviation 0·0620)				
	0·7060	0·6862	0·1754	3·1919
[N(2) –0·0829, C(1) 0·0824, C(7) 0·0771]				
Plane (4): N(3), C(11)–C(15) (r.m.s. deviation 0·0058)				
	–0·5431	0·8059	–0·2358	–1·7975
[N(3) –0·0090, C(15) 0·0085]				
Plane (5): C(16)–C(20), N(4) (r.m.s. deviation 0·0054)				
	0·6714	–0·7168	0·1881	2·3678
[C(16) –0·0082, C(19) –0·0064]				
Plane (6): N(3), C(11)–C(20), N(4) (r.m.s. deviation 0·0795)				
	0·6075	–0·7662	0·2093	1·9907
[N(4) 0·1221, C(11) –0·1129, C(14) 0·1090]				
Plane (7): Cu, N(2), N(4), O(1) (r.m.s. deviation 0·0142)				
	0·0145	0·0486	0·9987	5·3028
[Cu –0·0239, N(2) 0·0107]				
Plane (8): N(1), N(2), N(3), O(1) (r.m.s. deviation 0·1334)				
	0·7699	0·6174	0·1618	3·0995
[N(1) 0·1401, N(2) –0·1376, N(3) 0·1265 O(1) –0·1290, Cu 0·1404]				
Plane (9): N(5), O(1), O(2)				
	–0·1140	–0·0537	0·9920	4·9245

Dihedral angles (°) between planes (e.s.d.'s 0·4–1·3°): 1–2, 7·31; 4–5, 9·37; 3–6, 93·45; 7–9, 9·4; 8–9, 87·7.

	l	m	n	p
(*b*) Complex (2) (e.s.d.'s 0·001–0·003 Å)				
Plane (1): N(1), C(1)–C(5) (r.m.s. deviation 0·0144)				
	–0·4764	0·8438	–0·2472	–0·7180
[C(5) 0·0233, C(4) –0·0177, C(2) 0·0144]				
Plane (2): C(4)–C(5), N(2) (r.m.s. deviation 0·0025)				
	0·6483	–0·7490	0·1364	1·6540
[N(2) 0·0043]				
Plane (3): N(1), C(1)–C(10), N(2) (r.m.s. deviation 0·1092)				
	–0·5683	0·7990	–0·1967	–1·1543
[C(4) –0·1705, C(8) 0·1439, C(1) 0·1407)]				
Plane (4): N(3), C(11)–C(15) (r.m.s. deviation 0·0114)				
	0·5205	0·8080	0·2761	2·7526
[C(15) 0·0144, C(12) 0·0136, N(3) –0·0142]				

Table 4 (*cont.*)

	l	m	n	p
Plane (5): C(16)–C(20), N(4) (r.m.s. deviation 0·0080)				
	0·6972	0·6846	0·2125	2·4748
[C(16) 0·0139, N(4) –0·0097]				
Plane (6): N(3), C(11)–C(20), N(4) (r.m.s. deviation 0·1087)				
	0·6106	0·7540	0·2421	2·7224
[N(4) –0·1669, C(18) 0·1533, C(11) 0·1513]				
Plane (7): N(1)–N(4) (r.m.s. deviation 0·6244)				
	0·0720	0·9974	0·0012	1·4623
[N(1) –0·6309, N(2) 0·6359, N(3) –0·6177, N(4) 0·6126, Zn –0·6655]				
Plane (8): N(1)–N(3), O(1) (r.m.s. deviation 0·1930)				
	0·7138	–0·6890	0·1256	1·8234
[N(1) –0·2088, N(2) 0·2047, N(3) –0·1761, O(1) 0·1803, Zn –0·1731]				
Plane (9): N(5), O(1), O(2)				
	–0·0923	0·1067	0·9900	1·0746
Plane (10): Zn, N(2), N(4), O(1) (r.m.s. deviation 0·0324)				
	0·0877	–0·0560	0·9946	1·5520
[Zn 0·0551, N(2) –0·0242, O(1) –0·0222]				

Dihedral angles (°) between planes (e.s.d.'s 0·4–1·3°): 1–2, 12·94; 4–5, 12·90; 3–6, 78·01; 9–10, 13·94.

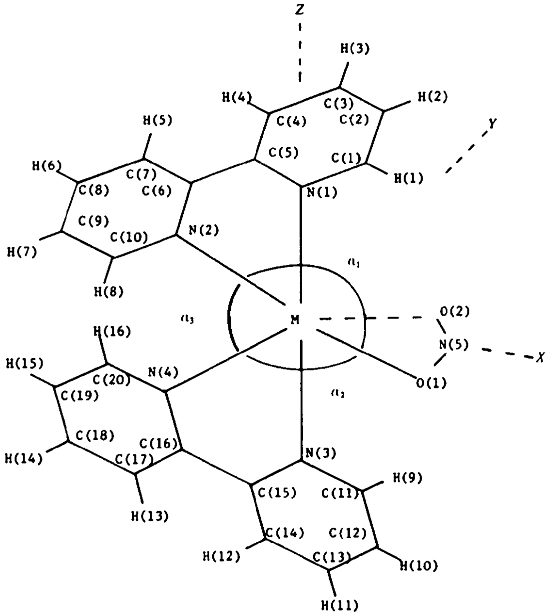

Fig. 1. The molecular structure of the $[Cu(bpy)_2(ONO)]^+$ cation and the atom numbering.

Table 5. *The unit-cell data for* (*a*) $[Zn(bpy)_2(ONO)]NO_3$ *and* (*b*) $[Cu(bpy)_2(ONO)]NO_3$ (*space group* $P2_1/n$)

	Zn	Cu
a (Å)	11·27 (5)	11·101
b (Å)	11·93 (5)	12·058
c (Å)	15·49 (5)	15·385
β (°)	101·2 (2)	99·17

Table 6. *The local molecular structures* (Å *and* °) *of sc*

	$[Cu(bpy)_2$-(ONO)]-BF_4	$[Zn(bpy)_2$-(ONO)]-NO_3	$[Cu(bpy)_2$-(ONO)]-NO_3	$[Cu(bipyam)_2$-(ONO)]-NO_2	$[Cu(bpy)_2$-$(CH_3CO_2)]$-BF_4	$[Cu(bpy)_2$-$(CH_3CO_2)]$-$ClO_4.H_2O$
	(1)	(2)	(3)	(4)	(5)	(6)
Reference	Present	Present	(*a*)	(*b*)	(*c*)	(*c*)
M—N(1)	1·990 (5)	2·129 (9)	1·980 (11)	2·008 (8)	1·995 (6)	1·971 (5)
M—N(2)	2·053 (5)	2·077 (9)	2·065 (10)	2·095 (9)	2·033 (5)	2·056 (5)
M—N(3)	2·005 (5)	2·151 (9)	2·006 (10)	2·008 (8)	2·016 (5)	1·994 (5)
M—N(4)	2·141 (5)	2·092 (9)	2·100 (10)	2·095 (9)	2·209 (6)	2·168 (5)
M—O(1)	2·117 (6)	2·217 (9)	2·238 (10)	2·074 (16)	1·980 (4)	2·031 (5)
M—O(2)	2·463 (6)	2·223 (8)	2·329 (10)	2·551 (26)	2·785 (5)	2·648 (5)
X—O(1)	1·261 (7)	1·227 (13)	1·234 (13)	1·262 (40)	1·270 (6)	1·238 (5)
X—O(2)	1·211 (7)	1·278 (13)	1·207 (13)	1·228 (40)	1·252 (7)	1·241 (5)
α_1	164·5	153·9	157·8	162·9	156·5	147·6
α_2	97·4	97·5	99·2	96·5	92·5	100·7
α_3	98·4	103·5	103·0	100·5	111·0	111·6
O(1)—*X*—O(2)	112·6	113·9	111·9	118·6	122·2	122·8
O(1)—*M*—O(2)	52·7	56·5	52·5	54·0	52·0	52·0
ΔN	0·088 (6)	0·015	0·035 (20)	0·0	0·176 (10)	0·112 (10)
ΔO	0·346 (8)	0·006	0·091 (20)	0·0	0·805 (10)	0·617 (10)

References: (*a*) Proctor & Stephens (1969); (*b*) Chen & Fackler (1980); Power & Hathaway (1980); (*c*) Hathaway, Ray, Kennedy,
(*f*) Simmons, Seff, Clifford & Hathaway (1980); (*g*) Walsh, Power & Hathaway

Hoskins & Kennard, 1963), but with the second O atom of the nitrite group occupying the sixth coordinate position at a distance >2·4 Å to give a (4+1+1*)-type coordination (Hathaway, 1973). The CuN_4O chromophore involves a very distorted stereochemistry intermediate between trigonal bipyramidal and square pyramidal, but still related to the more usual distorted trigonal-bipyramidal stereochemistry of the $[Cu(bpy)_2X]Y$ complexes (Barclay, Hoskins & Kennard, 1963; Stephens & Tucker, 1973; Kaiser, Brauer, Schroder, Taylor & Rasmussen, 1974; Harrison, Hathaway & Kennedy, 1979; Hathaway & Murphy, 1980), with the mean planes of the bpy ligands inclined at *ca* 120° to each other. The axial Cu—N(1) and Cu—N(3) distances are not significantly different, mean 1·999 Å, and the N(1)—Cu—N(3) angle is 178·6°. The mean in-plane Cu—N distance 2·097 Å is significantly longer than the mean out-of-plane Cu—N distance 1·997 Å by *ca* 0·1 Å as previously reported (Huq & Skapski, 1971) for the trigonal-bipyramidal Cu^{II} stereochemistry. Nevertheless, the in-plane Cu—N distances are significantly different with $\Delta N = \{[Cu—N(4)] - [Cu—N(2)]\} = 0·088$ Å. The in-plane Cu—O(1) distance of 2·117 Å is significantly longer than the normal short Cu—O distance (Hathaway & Hodgson, 1973) of *ca* 2·00 Å. This difference (0·11 Å) could also be associated with the increase of 0·1 Å for the in-plane Cu—*L* distance in the trigonal-bipyramidal stereochemistry (see later).

There are no unusual out-of-the-trigonal-plane angular distortions, values 90 ± 10°, but the in-plane angles do show divergences from the 120° of a regular trigonal-bipyramidal stereochemistry: the O(1)—Cu—N(2) angle is significantly >120° (164·5°), while the N(2)—Cu—N(4) and O(1)—Cu—N(4) angles, 98·4 and 97·4° respectively, are almost equal, but significantly <120° and together amount to a very substantial distortion of the trigonal plane. As the large O(1)—Cu—N(2) angle is opposite the elongated Cu—N(4) direction, it could be taken as the basal angle of a square-pyramidal stereochemistry with the Cu—N(4) direction the elongation direction, especially in view of the near equivalence of the O(1)—Cu—N(4) and N(2)—Cu—N(4) angles. Nevertheless, the square-pyramidal stereochemistry of (1) is not regular {as in $K[Cu(NH_3)_5](PF_6)_3$ (Duggan, Ray, Hathaway, Tomlinson, Brint & Pelin, 1979), which has almost equal basal angles of 166 ± 1°}, but has a clear trigonal distortion of the N(1), N(2), N(3), O(1) plane with N(1)—Cu—N(3) = 178·6° and O(1)—Cu—N(2) = 164·5°, which results in a large r.m.s.d. of 0·133 Å, compared to 0·0105 Å in the corresponding basal plane of $K[Cu(NH_3)_5](PF_6)_3$.

In (1) the Cu—N(4) elongation is restricted by the out-of-plane bite of the N(3)/N(4) bpy ligand, to a bite angle of 80 ± 1°, as in symmetrically coordinated bpy ligands (Harrison & Hathaway, 1978). It has been suggested (Anderson, 1972) that when the bpy ligand is coordinated to a Cu^{II} ion involved in significant elongation in one of the Cu—N bond distances the bite angle can decrease to *ca* 74° and the dihedral angle between the pyridine rings can increase up to 31·3°. In (1) the bite angles are 80·8 and 79·4° for the N(1)/N(2) and N(3)/N(4) bpy ligands, respectively, and the opper(II) *and zinc*(II) $[M(\mathrm{chelate})_2(\mathrm{O}X\mathrm{O})]Y$*-type complexes*

$[\mathrm{Cu(bipyam)}_2$- $(\mathrm{CH_3CO_2})]$- $\mathrm{NO_3}$	$[\mathrm{Cu(phen)}_2$- $(\mathrm{ONO})]$- $\mathrm{BF_4}$	$[\mathrm{Cu(phen)}_2$- $(\mathrm{CH_3CO_2})]$- $\mathrm{ClO_4}$	$[\mathrm{Cu(phen)}_2$- $(\mathrm{CH_3CO_2})]$- $\mathrm{BF_4.2H_2O}$	$[\mathrm{Zn(bipyam)}_2$- $(\mathrm{ONO})]$- $\mathrm{NO_2}$	$[\mathrm{Zn(bipyam)}_2$- $(\mathrm{ONO_2})]$- $\mathrm{NO_3}$	$[\mathrm{Cu_2(bpy)}_2$- $(\mathrm{pydca})]$.- $\mathrm{4H_2O}$	$[\mathrm{Cu(bipyam)}_2$- $(\mathrm{ONO})]$- $\mathrm{BF_4}$
(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
(*d*)	(*e*)	(*f*)	(*e*)	(*b*)	(*g*)	(*h*)	(*d*)
2·012 (5)	1·999 (4)	1·994 (4)	2·000 (4)	2·163	2·116	1·986	1·986
2·032 (6)	2·048 (4)	2·098 (4)	2·123 (4)	2·069	2·061	2·062	2·023
2·010 (5)	2·019 (3)	2·006 (4)	2·000 (4)	2·163	2·130	1·985	2·012
2·158 (6)	2·167 (3)	2·130 (4)	2·123 (4)	2·069	2·058	2·115	2·139
2·029 (6)	2·072 (3)	2·220 (4)	2·261 (5)	2·22	2·221	2·029	2·111
2·673 (6)	2·597 (3)	2·421 (5)	2·261 (5)	2·22	2·326	2·866	2·550
1·271 (9)	1·254 (6)	1·175 (6)	1·233	1·227	1·264	–	1·289
1·247 (9)	1·207 (7)	1·160 (6)	1·233	1·227	1·248	–	1·219
161·3	154·5	154·7	150·4	154·0	151·4	108·7	163·4
99·8	93·2	91·1	95·0	100·0	101·8	112·4	93·4
98·9	112·1	114·1	114·7	104·6	106·9	138·9	102·8
125·5	113·4	121·7	117·0	114·4	116·1	–	112·9
53·9	50·7	52·1	55·4	55·4	55·8	–	5
0·126 (12)	0·119	0·032 (8)	0·0	0·0	0·003	0·053	0·116
0·644 (12)	0·525	0·201 (10)	0·0	0·0	0·005	0·837	0·439

’Brien & Murphy (1980); (*d*) Kasempimolporn, Tyagi & Hathaway (1980); (*e*) Simmons, Lundeen, Payne, Seff & Hathaway (1980);
1981); (*h*) Nardin, Randaccio, Bonomo & Pizzarelli (1980).

dihedral angles 7·28 and 9·36°, respectively, both less than the 11° previously (Anderson, 1972) reported for coordinated bpy ligands, which suggests that the bpy ligands in (1) are not strained by elongation of the Cu—N bond distance.

The nitrite group (Sutton, 1959, 1965) of (1) has no unusual bond lengths or angles, and the plane of the O(1)N(5)O(2) group is reasonably coplanar (9·4°) with the Cu,N(2),N(4),O(1) plane. Due to the O(1)—Cu—O(2) bite angle of 52·7°, O(2) lies well off the perpendicular to the N(1),N(2),N(3),O(1) plane by 30·1° [a direction to which the Cu—N(4) bond makes an angle of 11·0° in the Cu,N(1),N(3),N(4) plane] and at a distance of 2·46 Å, sufficiently close to the Cu atom to be involved in significant off-the-axis coordination (Hathaway, 1973). The mean N—O distance, 1·24 Å, of the nitrite group is not significantly different (Sutton, 1959, 1965) from the 1·236 Å for the free nitrite ion, but the O(1)—N—O(2) angle of 112·6° is significantly smaller than the 115·4° of the free ion. There is a significant difference between the two N—O distances, 1·261 (7) and 1·211 (7) Å, consistent with the presence of more single-bond character (Addison, Logan, Wallwork & Garner, 1971) in the N(5)—O(1) distance, and with the shorter bonding of O(1) to the Cu atom. Consequently, the asymmetric bonding role of the chelate nitrito group in (1) is reflected in the asymmetry of the N—O distances of the nitrite group, and implies that, despite the relative shortness of the Cu—O(2) distance of 2·463 Å, the bonding at this distance will be less than the bonding of Cu—O(1) at 2·117 Å. This situation contrasts with that in the bonding of acetate (Hathaway, Ray, Kennedy, O'Brien & Murphy, 1980) and formate (Fitzgerald & Hathaway, 1980) ligands in these $[\mathrm{Cu(bpy)}_2(\mathrm{O}X\mathrm{O})]Y$-type complexes.

The structure of (1) is clearly different from the symmetrical elongated rhombic-octahedral (4+2) chromophore in $[\mathrm{Cu(bpy)_2(S_3O_6)}]$ (Ferrari, Fava & Pelizzi, 1977) and $[\mathrm{Cu(bpy)_2(S_4O_6)}]$ (Harrison & Hathaway, 1978) and the unsymmetrical rhombic-octahedral (4+1+1*) chromophore of $[\mathrm{Cu(bpy)_2(ClO_4)_2}]$ (Nakai, 1971). There is some similarity to the *cis*-distorted rhombic-octahedral stereochemistries of Table 6, namely (3), (4) and (10), but in which the nitrito group is more symmetrically coordinated with two Cu—O distances of 2·22–2·33 Å, all of which are clearly elongated compared with the short Cu—O of 2·117 Å in (1). There is a closer similarity to the remaining $\mathrm{Cu^{II}}$ structures of Table 6, all of which have a (4+1+1*)-type coordination of the $\mathrm{CuN_4O_2}$ chromophore with the second O atom involved in a bonding direction off the approximate Cu—N(4) axis, but with significant differences in the trigonal in-plane bonding distances of {[Cu—N(4)] − [Cu—N(2)]} and {[Cu—O(2)] − [Cu—O(1)]}. If these differences, ΔN and ΔO (Table 6), are plotted against each other (Fig. 2) a significant correlation is observed; the greater ΔN, the greater the value of ΔO. This also implies that the greater the Cu—N(4) distance the greater will be the Cu—O(2) distance and suggests that even for the large Cu—O(2) distances of *ca* 2·8 Å, O(2) must still be involved in weak off-the-axis bonding and that the $\mathrm{O}X\mathrm{O}^-$ anions of Table 6 are involved in a

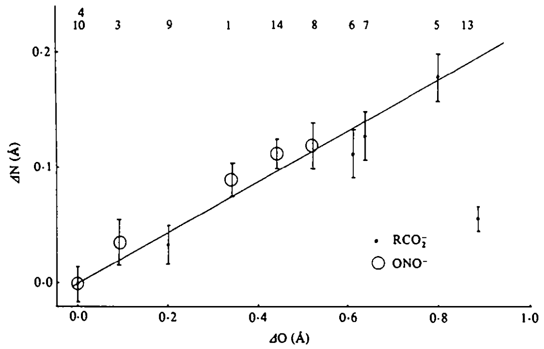

Fig. 2. Correlation of the ΔN {[Cu–N(4)]–[Cu–N(2)]} and ΔO {[Cu–O(2)]–[Cu–O(1)]} distances (Å).

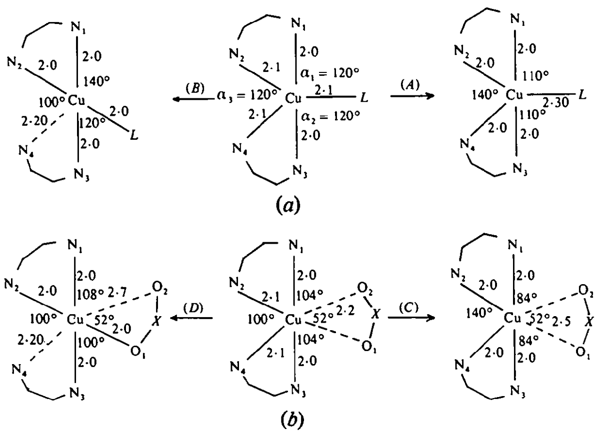

Fig. 3. The alternative routes for distortion towards square-pyramidal of (a) a trigonal-bipyramidal $[Cu(bpy)_2L]Y$ system and (b) a cis-distorted octahedral $[Cu(bpy)_2(ONO)]Y$ system.

synergic bidentate function, with the bonding in the Cu–N(4) direction.

It has already been suggested (Harrison & Hathaway, 1980) that the sense of distortion of the regular trigonal-bipyramidal stereochemistry of a $[Cu(bpy)_2L]Y$ system (Fig. 3a) can take the two alternative routes (A) and (B), related by the mechanistic pathway of the Berry (1960) twist, both of which result in a square-pyramidal distortion but with elongation in two different directions, due to the presence of non-equivalent ligands, namely, the Cu–L and Cu–N(4) directions. These differences have been illustrated for a series of cation distortion isomers (Ray, Hulett, Sheahan & Hathaway, 1978), where L = Cl (Elliott, Hathaway & Slade, 1966; Kennedy, Ray, Sheahan, Power & Hathaway, 1980) and L = H_2O (Harrison, Hathaway & Kennedy, 1979; Harrison & Hathaway, 1979). Comparable modes of distortion of the $[Cu(bpy)_2(OXO)]Y$ system can also be suggested (Fig. 3b), involving the two alternative modes of distortion (C) and (D), which nicely describe the range of structural situations observed in Table 6, from symmetrical *cis*-distorted octahedral to a (4+1+1*)-type distortion (D), involving a very asymmetrically bonded OXO^- anion plus a long Cu–N(4) distance. In this respect the OXO^- anion may be considered to occupy a single coordinate position in the five-coordinate $[Cu(bpy)_2L]Y$ system as was suggested previously (Proctor, Hathaway, Billing, Dudley & Nicholls, 1969), but there are advantages in considering these $[Cu(bpy)_2(OXO)]^+$ systems as genuinely six-coordinate and based upon a parent tris(chelate)-copper(II) complex, whose E-type mode of vibration is illustrated in Fig. 4. Mode (IB) accounts for the elongation of a *cis*-distorted bis(chelate)$_2$-(OXO)copper(II) complex (Fig. 3b) as in (4) and (10) (Table 6), while mode (IIB) accounts for the extreme square-pyramidal distortion (D) (Fig. 3b), involving very asymmetric coordination of one chelate OXO group along with elongation of the *trans* N(4) atom of the bpy ligand and as illustrated in (5) and (13) (Table 6). In general, the pure extreme modes (IB) and (IIB) do not occur separately, but as a linear combination of modes (IB) and (IIB), so that intermediate degrees of distortion occur determined by packing factors and resulting in a range of observed distortions, (1), (3), (6)–(9) and (14) (Table 6), which illustrates the plasticity effect (Gazo *et al.*, 1976) in the stereochemistry of the Cu^{II} ion and which relate (1) and (3) as cation distortion isomers of the $[Cu(bpy)_2(ONO)]^+$ cation.

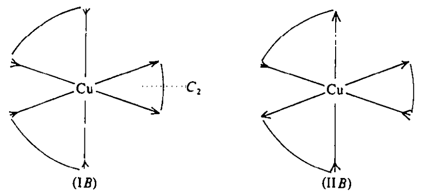

Fig. 4. The two components of the E-type mode of vibration of a regular tris(chelate)metal(II) complex.

The (4+1+1*)-type coordination of the $[Cu(bpy)_2(OXO)]^+$ system has been observed previously (Nardin, Randaccio, Bonomo & Rizzarelli, 1980) in one of the two Cu geometries of $[Cu_2(bpy)_2(pydca)_2].4H_2O$ (13) (see Table 6 for structural data; pydca = 2,6-pyridinedicarboxylate). The CuN_4O_2 geometry is closely comparable to that of (6) (Table 6), but with the Cu–O(2) distance, 2·866 Å, significantly longer: if the ΔN and ΔO values of (13), 0·053 and 0·837 Å, are plotted in Fig. 2 the point for (13) lies clearly away from the observed correlation. The reason for this lies in the geometric factor introduced in the OXO group which forms part of a 2,6-pyridinedicarboxylate anion and is constrained by the geometry of this ligand to bond with a much longer Cu–O(2) distance than observed in the majority of complexes of Table 6 whose OXO groups involve no such constraints.

The $[Zn(bpy)_2(ONO)]^+$ cation of (2) involves a six-coordinate *cis*-octahedral ZnN_4O_2 chromophore with the two Zn—O bonds clearly elongated, mean 2·22 Å, and significantly longer than the four Zn—N distances, mean 2·11 Å (Table 6). The individual bpy ligands are unsymmetrically coordinated with the Zn—N distances significantly different, but the corresponding Zn—N bonds of the two bpy ligands are not significantly different, mean 2·08 and 2·15 Å, such that the *cis*-distorted ZnN_4O_2 chromophore has an approximate C_2 axis of symmetry bisecting the O(1)—Zn—O(2) and N(2)—Zn—N(4) angles.

The two long Zn—N bonds are nearly collinear [N(1)—Zn—N(3) = 177·8, N(2)—Zn—N(4) = 103·5, O(1)—Zn—O(2) = 56·5°], and the overall chromophore stereochemistry of (2) is best described as *cis*-distorted octahedral. This differs from the stereochemistry of the CuN_4O_2 chromophore of (3) in that the Zn—N distances in the N(1)—Zn—N(3) direction are significantly longer than the in-plane Zn—N(2) and Zn—N(4) distances (Table 6). The relative elongation of the N(1)—Zn—N(3) direction of the ZnN_4O_2 chromophore of (2) is typical of other *cis*-distorted rhombic-octahedral Zn^{II} complexes containing a ZnN_4O_2 chromophore, *e.g.* $[Zn(bipyam)_2(ONO)]NO_3$ (11) and $[Zn(bipyam)_2(ONO_2)]NO_3$ (12) (Walsh, Power & Hathaway, 1981) (Table 6). In (2) the nitrito group is almost symmetrically coordinated as neither the Zn—O distances, 2·217 (8) and 2·223 (9) Å, nor the N—O distances, 1·278 and 1·227 Å, are significantly different, although there is no crystallographic C_2 symmetry present.

Probably the most significant feature of the structure of the ZnN_4O_2 chromophore of (2) is its similarity to that of the CuN_4O_2 chromophore in (3) (Table 6), especially the *cis* distortion, which in Cu^{II} could originate in the non-spherical symmetry of the Cu^{II} ion with a d^9 configuration. In the Zn^{II} chromophore the distortion cannot originate from this source as the Zn^{II} ion with a d^{10} configuration has spherical symmetry. Consequently, the cause of the Zn distortion must originate from the normal modes of vibration of a parent tris(chelate)zinc(II) complex, Fig. 4(I*B*). In the $[Zn(chelate)_2(ONO)]Y$ complex the C_2 distortion of mode (I*B*) is enhanced by the presence of a non-equivalent ONO chelate ligand which determines the ground-state structure of the ZnN_4O_2 chromophore with bond-length distortions of 0·1–0·2 Å. As this magnitude of distortion in the Zn^{II} chromophore is only slightly less than that of 0·1–0·3 Å in the Cu^{II} chromophore it lends added support to the earlier suggestion (Proctor, Hathaway, Billing, Dudley & Nicholls, 1969) that the *cis* distortion of the CuN_4O_2 chromophore in (3) also arises from a linear combination of the *E* modes of vibration of the parent tris(chelate)copper(II) complex, Fig. 4 (I*B*, II*B*). The observed differences in the Cu and Zn *M*—N(1) and *M*—N(2) bond distances of *ca* 0·1 Å can then be rationalized in terms of the non-spherical symmetry of the Cu^{II} ion, d^9 configuration (oblate ellipsoid), and the spherical symmetry of the Zn^{II} ion, d^{10} configuration (Hathaway & Billing, 1970).

The pyridine rings in each of the bpy ligands are reasonably coplanar (Table 4) with dihedral angles of 12·94 and 12·90° for the N(1)/N(2) and N(3)/N(4) ligands respectively, a difference that is consistent with the near bonding equivalence of the two bpy ligands and with the small differences in the Zn—N bonding distances.

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Bis(1,2-diaminoethan)-1,6-diiodoplatin(IV) Diiodid Dihydrat, 1,6-$[Pt(en)_2I_2]I_2.2H_2O$

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Abstract

$[Pt(C_2H_8N_2)_2I_2]I_2.2H_2O$, $C_4H_{16}I_2N_4Pt^{2+}.2I^-.2H_2O$, is triclinic, $P\bar{1}$, with $a = 7{\cdot}151\ (5)$, $b = 7{\cdot}729\ (5)$, $c = 8{\cdot}331\ (7)$ Å, $\alpha = 111{\cdot}80\ (8)$, $\beta = 96{\cdot}28\ (7)$, $\gamma = 98{\cdot}09\ (6)°$, $V = 426{\cdot}1$ Å^3, $D_c = 3{\cdot}36$ Mg m^{-3}, $Z = 1$. The compound may be prepared in solution by oxidative addition of I_2 to $[Pt(en)_2]I_2$. The structure has been solved by Patterson and Fourier methods from diffractometer data and refined by full-matrix least squares to $R = 0{\cdot}034$ for 1452 independent reflections. The structure can be interpreted in terms of nearly tetragonal bipyramidal complexes $[Pt(en)_2I_2]^{2+}$ and I^- ions. The I^- ions are at a rather short distance (3·905 Å) from the coordinated I atoms and the $I\cdots I$ groups are perpendicular to the $[Pt(en)_2]$ moiety to give linear units $I\cdots I—Pt—I\cdots I$. These small units are arranged nearly in the $[1\bar{1}1]$ direction. The slightly disordered water molecules fill cages in this arrangement.

Einleitung

Bei unseren systematischen chemischen und strukturellen Untersuchungen an Polyiodiden komplexer Kationen (Tebbe, 1977, 1978) konnten wir einen Verbindungstyp $[M(en)_2I_6]$ näher charakterisieren (bisher mit $M = Ni^{2+}$, Pd^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}; en = 1,2-Diaminoethan), dessen einzelne Vertreter strukturverwandt sind, sich aus einer einfachen hexagonalen Säulenpackung herleiten lassen und bedingt durch die unterschiedlichen geometrischen und zusätzlichen koordinativen Eigenschaften der Komplexe $[M(en)_2]^{2+}$ geordnete Triiodid-$(\cdots I—I—I\cdots)_\infty$ und gestreckte oder gewinkelte Iod-Iodid-Ketten $(\cdots I—I\cdots I\cdots)_\infty$ in verschiedenen Varianten enthalten (Düker, Freckmann,

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