

(2) [2.340 (2) Å] but agrees well with that in *trans*-Pt(*P*<sup>*i*</sup>Pr<sub>3</sub>)<sub>2</sub>HCl (3) [2.287 (1) Å] (Robertson & Tucker, 1982). P–Pt–P angles in (1) and (3) also agree well [168.8 (2)° av. in (1), and 171.16 (3)° in (3)]. In contrast, the corresponding angle in (2) is symmetry constrained to 180°. Differences between (2) and (3) are attributable, in detail, to steric effects (Robertson & Tucker, 1982, 1983). The close similarity between the Pt–P distances and P–Pt–P angles in (1) and (3) reflects, primarily, the fact that the van der Waals thickness of an aromatic ring is approximately the same as the van der Waals diameter of a Cl atom. The Pt–C distance [av. 2.07 (2) Å] agrees well with that in the ( $\sigma$ -cyclohexyl)hydridobis(triphenylphosphine) analogue *trans*-Pt(PPh<sub>3</sub>)<sub>2</sub>H( $\sigma$ C<sub>6</sub>H<sub>9</sub>) [2.08 (1) Å] (Bilton & Robertson, 1982) but, reflecting both the differing steric requirements and differing  $\sigma$ -orbital radii of *sp*<sup>2</sup> *cf.* *sp*<sup>3</sup> hybridized donor C atoms, is appreciably shorter than that in *trans*-Pt(PPh<sub>3</sub>)<sub>2</sub>H(CH<sub>2</sub>CN) [2.15 (1) Å] (Ros, Michelin, Belluco, Zanotti, Del Pra & Bombieri, 1978). Other bond lengths and bond angles are insufficiently well determined to warrant discussion.

The ligating phenyl group in each molecule is approximately perpendicular to the Pt-coordination plane, as is required to avoid overcrowding in that plane. The conformational similarity of the right-hand sides of molecules 1 and 2 in Fig. 1 is self evident (even to the extent of the isopropyl-group disorder). The molecules differ principally in the orientation of the left-hand phosphine group. In molecule 1 the P–C bonds of the two phosphines are approximately eclipsed when viewed along the P–P vector whereas in molecule 2 they are approximately staggered. The present result supports our earlier contention (Bennett, Ho, Jeffery, McLaughlin & Robertson, 1982) that energy differences between eclipsed and staggered forms are small.

*Acta Cryst.* (1983). C39, 1357–1360

## Structure of the Pentahydrate of the Samarium(III) Perchlorate Complex with the Crown Polyether 1,4,7,10,13-Pentaoxacyclopentadecane, [Sm(C<sub>10</sub>H<sub>20</sub>O<sub>5</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>3+</sup> · 3ClO<sub>4</sub><sup>-</sup> · H<sub>2</sub>O

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(Received 6 September 1982; accepted 27 June 1983)

**Abstract.** *M<sub>r</sub>* = 979.30, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 16.150 (5), *b* = 14.898 (5), *c* = 21.055 (5) Å,  $\beta$  = 129.37 (3)°, *V* = 3916.27 Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.62 (3), *D<sub>x</sub>* = 1.66 Mg m<sup>-3</sup> (by flotation),  $\lambda$ (Mo *K* $\alpha$ ) = 0.71069 Å,  $\mu$ (Mo *K* $\alpha$ ) = 1.83 mm<sup>-1</sup>, *F*(000) = 1996, *T* = 296 (4) K, *R*(*F*) = 0.067 for 3540 observed reflec-

We thank Dr D. P. Arnold for supplying a sample of the title compound and the Computer Services Centres of the Australian National University and the University of Exeter for the use of their facilities.

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tions. The samarium(III) ion is found to be coordinated to nine oxygen atoms, five from one of the ether molecules and the remaining four from water molecules. The second ether molecule does not take part in coordination. Three of the water molecules link to the second ether ring by forming hydrogen bonds with the

oxygen atoms in it. The oxygen atom of the fourth coordinated water molecule forms hydrogen bonds with a perchlorate ion and the fifth water molecule.

**Introduction.** The interaction of crown ethers with various metal ions has been successfully used in many organic syntheses. Moreover, these macrocycles also provide a facile route for the mutual separation of alkali and lanthanide metal ions. Only a few studies have been reported on the crystal structures of the lanthanide complexes of crown ethers. This work describes the preparation and structure determination of the crown ether 1,4,7,10,13-pentaoxacyclopentadecane complex of samarium(III).

**Experimental.** A solution of 10 mmol pentaoxacyclopentadecane (15-crown-5 polyether) in 35 ml acetonitrile was added dropwise to a hot solution (333 K) of 2.44 g Sm(ClO<sub>4</sub>)<sub>3</sub> in 30 mmol acetonitrile. Upon heating and stirring for 12 h, the solution was cooled down to room temperature or below, precipitation of the complex then occurred. The precipitate was filtered and washed with methylene chloride. The crude crystal was dissolved in an appropriate amount of the acetonitrile–diethyl ether mixture and put aside for recrystallization. The crystals thus grown are plate-like and semi-transparent and deteriorate in the air within a few hours.

Experimental data and structure solution parameters are summarized in Table 1. After correction for background, Lorentz, polarization, absorption, and

time-decay effects, 3540 independent reflections were used for structure solution and refinement. Positions of Sm, Cl, O and C located, hydrogen atoms found with a program in the PDP crystal-analysis package supplied by Professor Wang (Taiwan University), with the constraints: C–C–H and H–C–H 109.5°, C–H 1.08 Å, O–C–C, C–C–O and C–O–C calculated according to the coordinates obtained from the result of least-squares fitting; least-squares refinement of all coordinates, anisotropic for nonhydrogen atoms, isotropic for H atoms,  $R = 0.067$ ,  $\sum w(|F_o| - |F_c|)^2$  minimized,  $w = 1/\sigma_F^2$  (Stout & Jensen, 1972);  $\Delta_{av} = 0.2\sigma$ ,  $\Delta_{max} = 0.4\sigma$ .\*

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsional angles around the ether rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38688 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atomic coordinates ( $\times 10^4$ ) with their *e.s.d.*'s and  $B_{eq}$  values ( $\text{\AA}^2$ )

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B_{eq}$
Sm	1387.7 (4)	2799.6 (1)	4509.2 (2)	3.1
Cl(1)	1883 (3)	4928 (2)	2624 (2)	6.8
Cl(2)	1975 (2)	4625 (2)	7002 (2)	5.8
Cl(3)	2460 (2)	-1965 (2)	5107 (2)	4.9
O(11)	1707 (7)	5347 (6)	1956 (4)	9.3
O(12)	2748 (11)	4289 (6)	2987 (8)	13.3
O(13)	2325 (9)	5598 (7)	3241 (6)	12.0
O(14)	1147 (10)	4456 (10)	2525 (7)	17.3
O(21)	2203 (7)	4919 (5)	6502 (6)	9.3
O(22)	2491 (7)	3796 (6)	7352 (5)	9.4
O(23)	2227 (7)	5227 (7)	7590 (6)	11.3
O(24)	836 (6)	4464 (5)	6495 (6)	9.6
O(31)	1424 (6)	-1804 (9)	4569 (7)	15.5
O(32)	2637 (9)	-2231 (12)	4436 (6)	17.7
O(33)	2805 (8)	-2704 (5)	5537 (5)	9.1
O(34)	3155 (10)	-1275 (6)	5418 (7)	13.9
O(101)	1292 (6)	1416 (4)	5144 (4)	6.2
O(102)	633 (4)	2983 (4)	5241 (3)	5.2
O(103)	-605 (4)	2893 (3)	3640 (3)	4.9
O(104)	378 (5)	2788 (4)	2994 (3)	6.1
O(105)	1123 (6)	1316 (4)	3842 (4)	6.9
O(201)	5157 (7)	1045 (6)	6548 (6)	9.2
O(202)	4718 (6)	1881 (6)	7065 (5)	8.0
O(203)	4834 (5)	3526 (5)	6770 (4)	6.5
O(204)	4551 (6)	3592 (7)	5244 (5)	8.5
O(205)	4486 (6)	1697 (7)	5009 (5)	8.7
OW(1)	878 (5)	4371 (4)	4229 (3)	5.3
OW(2)	2656 (4)	3645 (4)	5756 (3)	4.9
OW(3)	2429 (5)	3385 (4)	4146 (4)	6.2
OW(4)	3164 (4)	2072 (3)	5358 (3)	5.1
OW(5)	2419 (6)	5563 (4)	4671 (5)	7.7
C(101)	892 (9)	1421 (8)	5570 (7)	7.4
C(102)	988 (12)	2309 (9)	5850 (7)	8.2
C(103)	-447 (7)	3264 (7)	4767 (6)	5.7
C(104)	-1140 (8)	2813 (8)	4005 (8)	7.8
C(105)	-1282 (6)	2767 (7)	2763 (5)	6.4
C(106)	-738 (8)	3140 (7)	2498 (5)	6.3
C(107)	395 (11)	1966 (8)	2600 (6)	8.5
C(108)	1042 (13)	1322 (9)	3136 (9)	10.5
C(109)	1471 (13)	551 (7)	4318 (9)	9.4
C(110)	1133 (7)	556 (6)	4783 (8)	8.4
C(201)	4728 (16)	570 (12)	6888 (13)	12.9
C(202)	4853 (14)	1132 (11)	7495 (10)	11.3
C(203)	4590 (13)	2643 (11)	7581 (7)	9.5
C(204)	5418 (10)	3116 (8)	7550 (6)	7.7
C(205)	5624 (8)	3853 (8)	6710 (8)	7.9
C(206)	5004 (9)	4248 (8)	5871 (10)	9.5
C(207)	5195 (11)	3171 (14)	5082 (10)	10.0
C(208)	4683 (14)	2348 (18)	4652 (12)	13.8
C(209)	5413 (10)	1216 (9)	5580 (9)	8.8
C(210)	5153 (14)	553 (10)	5941 (10)	12.7

Table 1. Experimental data and structure refinement parameters

Crystal size (mm)	0.4 × 0.5 × 0.3
Diffractionmeter and data collection technique	$\omega$ -2 $\theta$ scan, four-circle diffractometer (Syntax PT) with Nb filter
Scan width (°)	2.0 + 0.7 tan $\theta$ ; starting 1° below $K\alpha_1$ and 1° above $K\alpha_2$
Number of reflections and $\theta$ range for measuring lattice parameters	15 reflections with $12 < 2\theta < 25^\circ$
Absorption correction applied	Experimental absorption correction based on $\psi$ scan (North, Phillips & Mathews, 1968)
Maximum value of (sin $\theta$ )/ $\lambda$	0.6497 Å <sup>-1</sup>
Range of $hkl$	0, 0, 20 to 19, 18, 24
Standard reflections and their intensity variation	Two check reflections, intensities show 10% decay after 134 h of irradiation
Number of reflections measured	17 836
Number of unique reflections	3 540
Criterion for recognizing unobserved reflections	$I < 3\sigma(I)$
Method used to solve structure	Patterson and Fourier methods
Maximum and minimum heights in final difference Fourier	0.31 and 0.11 e Å <sup>-3</sup>
Parameters refined	
Nonhydrogen atoms	(Coordinates and anisotropic temperature factors) 459
Hydrogen atoms	(Coordinates and isotropic temperature factors) 200
Extinction correction	Not applied
Atomic scattering factors, $f'$ and $f''$	International Tables for X-ray Crystallography (1968)
Number of reflections per parameter	5
R and $wR$	0.067 and 0.068

**Discussion.** The final atomic coordinates and interatomic distances are listed in Tables 2 and 3. The bond angles around the ring are in Table 4. A perspective view of the molecule with the atom numbering scheme is shown in Fig. 1, where the coordination and hydrogen-bond lengths are indicated. Fig. 2 shows a stereoview of the crystal packing. From the bond lengths listed in Table 3, the samarium atom seems to be nine coordinated by five oxygen atoms of the first ether ring and four oxygen atoms of the water molecules. Among these four water molecules, three form hydrogen bonds with the oxygens in the second ether ring, the other oxygen *OW*(1) forms a hydrogen bond with O(24) in the perchlorate ion 2 and the *OW*(5) of another water molecule which is not coordinated to the samarium. The average coordination length between samarium and the five oxygens in the first ether ring is 2.51 (1) Å and that between Sm and

Table 4. Bond angles ( $^{\circ}$ ) around the ether rings, the average e.s.d. is estimated to be around  $0.8^{\circ}$

*I* = 1 or 2 indicates first or second ether ring, respectively.

	<i>I</i> = 1	<i>I</i> = 2
O( <i>I</i> 1)—C( <i>I</i> 01)—C( <i>I</i> 02)	107.4	108.2
C( <i>I</i> 01)—C( <i>I</i> 02)—O( <i>I</i> 02)	114.0	90.8
C( <i>I</i> 02)—O( <i>I</i> 02)—C( <i>I</i> 03)	117.1	99.1
O( <i>I</i> 02)—C( <i>I</i> 03)—C( <i>I</i> 04)	113.5	79.4
C( <i>I</i> 03)—C( <i>I</i> 04)—O( <i>I</i> 03)	104.2	106.8
C( <i>I</i> 04)—O( <i>I</i> 03)—C( <i>I</i> 05)	115.8	105.8
O( <i>I</i> 03)—C( <i>I</i> 05)—C( <i>I</i> 06)	107.3	105.7
C( <i>I</i> 05)—C( <i>I</i> 06)—O( <i>I</i> 04)	111.2	113.2
C( <i>I</i> 06)—O( <i>I</i> 04)—C( <i>I</i> 07)	109.9	120.1
O( <i>I</i> 04)—C( <i>I</i> 07)—C( <i>I</i> 08)	113.6	108.1
C( <i>I</i> 07)—C( <i>I</i> 08)—O( <i>I</i> 05)	113.3	119.7
C( <i>I</i> 08)—O( <i>I</i> 05)—C( <i>I</i> 09)	119.6	109.9
O( <i>I</i> 05)—C( <i>I</i> 09)—C( <i>I</i> 10)	110.2	107.0
C( <i>I</i> 09)—C( <i>I</i> 10)—O( <i>I</i> 01)	111.0	105.7
C( <i>I</i> 10)—O( <i>I</i> 01)—C( <i>I</i> 01)	110.1	116.4

Table 3. Atomic distances (Å), approximate average e.s.d. is 0.01 Å

$\langle \rangle_i$  indicates the average atomic distance in the *I*th ether ring.

C(101)—C(102)	1.42	C(201)—C(202)	1.43
C(103)—C(104)	1.41	C(203)—C(204)	1.55
C(105)—C(106)	1.42	C(205)—C(206)	1.49
C(107)—C(108)	1.34	C(207)—C(208)	1.43
C(109)—C(110)	1.40	C(209)—C(210)	1.46
$\langle C-C \rangle_1$	1.40	$\langle C-C \rangle_2$	1.47
O(101)—O(102)	2.63	O(201)—O(202)	2.05
O(102)—O(103)	2.61	O(202)—O(203)	2.56
O(103)—O(104)	2.67	O(203)—O(204)	2.95
O(104)—O(105)	2.59	O(204)—O(205)	2.86
O(105)—O(101)	2.58	O(205)—O(201)	2.86
$\langle O-O \rangle_1$	2.62	$\langle O-O \rangle_2$	2.66
C(101)—O(101)	1.40	C(201)—O(201)	1.46
C(102)—O(102)	1.43	C(202)—O(202)	1.36
C(103)—O(102)	1.42	C(203)—O(202)	1.67
C(104)—O(103)	1.48	C(204)—O(203)	1.41
C(105)—O(103)	1.44	C(205)—O(203)	1.44
C(106)—O(104)	1.49	C(206)—O(204)	1.42
C(107)—O(104)	1.49	C(207)—O(204)	1.43
C(108)—O(105)	1.41	C(208)—O(205)	1.38
C(109)—O(105)	1.38	C(209)—O(205)	1.38
C(110)—O(101)	1.43	C(210)—O(201)	1.47
$\langle C-O \rangle_1$	1.44	$\langle C-O \rangle_2$	1.44
Sm—O <i>W</i> (5)	4.37	Cl(2)—O(21)	1.39
Sm—Cl(1)	5.50	Cl(2)—O(22)	1.41
Sm—Cl(2)	5.45	Cl(2)—O(23)	1.37
Sm—Cl(3)	7.22	Cl(2)—O(24)	1.45
Cl(1)—O(11)	1.39	Cl(3)—O(31)	1.29
Cl(1)—O(12)	1.45	Cl(3)—O(32)	1.48
Cl(1)—O(13)	1.42	Cl(3)—O(33)	1.40
Cl(1)—O(14)	1.28	Cl(3)—O(34)	1.35
Sm—O(101)	2.53	O <i>W</i> (1)—O <i>W</i> (2)	2.84
Sm—O(102)	2.53	O <i>W</i> (1)—O <i>W</i> (3)	3.00
Sm—O(103)	2.50	O <i>W</i> (2)—O(4)	2.78
Sm—O(104)	2.48	O <i>W</i> (2)—O(102)	2.89
Sm—O(105)	2.50	O <i>W</i> (2)—O(21)	2.84
Sm—O <i>W</i> (1)	2.43	O <i>W</i> (3)—O <i>W</i> (4)	2.81
Sm—O <i>W</i> (2)	2.43	O <i>W</i> (3)—O(12)	3.10
Sm—O <i>W</i> (3)	2.39	O <i>W</i> (3)—O(14)	3.09
Sm—O <i>W</i> (4)	2.47	O <i>W</i> (4)—O(101)	2.93
O <i>W</i> (1)—O <i>W</i> (5)	2.70	O <i>W</i> (4)—O(105)	3.00
O <i>W</i> (1)—O(103)	2.89	O <i>W</i> (4)—O(201)	2.96

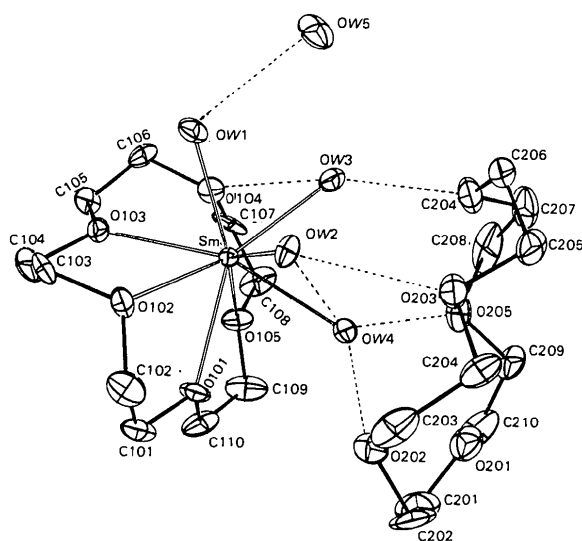


Fig. 1. ORTEP drawing (Johnson, 1976) of the molecule with numbering scheme. The coordination bonds are indicated by open lines, interatomic bonds by heavy lines, hydrogen bonds by dashed lines. *OW*'s are oxygens of water molecules.

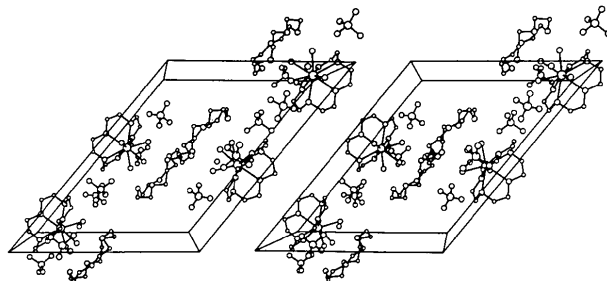


Fig. 2. Stereoview of the packing of molecules in a unit cell, view down the *b* axis. Origin: lower right corner, *a* axis to the left, *b* axis towards the reader, *c* axis upward.

oxygens of the water molecules is 2.43 (2) Å. The average O–O distance in the first ring is 2.62 (2) Å, whereas in the second ring it is 2.66 (4) Å. This is indicative of the coordination of the first ring to the samarium. The present Sm–O distance agrees fairly well with the average value found in the Sm(ClO<sub>4</sub>)<sub>3</sub><sup>-</sup> (dibenzo-18-crown-6) complex, where the Sm–O distances range from 2.36 (1) to 2.59 (1) Å with an average value of 2.51 (1) Å and Sm is ten coordinated (Ciampolini, Nardi, Cini, Mangani & Orioli, 1979). The perchlorate ions are disordered, as can be seen from the fact that the bond lengths between chlorine and oxygens in the ions are not equal.

A structure determination on the lanthanum complex of the same ligand was also performed, which gave rise to an identical structure except for the replacement of

samarium by a lanthanum atom. The report will be published elsewhere.

Thanks are due to NSC of Taiwan for financial support.

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*Acta Cryst.* (1983). **C39**, 1360–1367

## Pseudo-Jahn–Teller Complexes: The Structures of Nitritobis(1,10-phenanthroline)copper(II) Tetrafluoroborate (I), [Cu(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)]BF<sub>4</sub>, and Acetatobis(1,10-phenanthroline)copper(II) Tetrafluoroborate Dihydrate (II), [Cu(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)]BF<sub>4</sub> · 2H<sub>2</sub>O

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(Received 5 April 1982; accepted 4 May 1983)

**Abstract.** (I):  $M_r = 556.8$ , triclinic,  $P\bar{1}$ ,  $a = 10.442$  (4),  $b = 16.022$  (3),  $c = 7.408$  (2) Å,  $\alpha = 93.13$  (2),  $\beta = 101.86$  (2),  $\gamma = 110.13$  (2)°,  $V = 1128.2$  (5) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.62$  (1),  $D_x = 1.639$  Mg m<sup>-3</sup>,  $F(000) = 562$ ,  $\mu(\text{Mo } K\alpha) = 1.03$  mm<sup>-1</sup>. (II):  $M_r = 605.8$ , monoclinic,  $P2/c$ ,  $a = 9.639$  (2),  $b = 8.237$  (2),  $c = 17.575$  (4) Å,  $\beta = 108.66$  (2)°,  $V = 1322.1$  (5) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.53$  (1),  $D_x = 1.522$  Mg m<sup>-3</sup>,  $F(000) = 618$ ,  $\mu(\text{Mo } K\alpha) = 0.86$  mm<sup>-1</sup>. The crystal structures of [Cu(phen)<sub>2</sub>(ONO)]BF<sub>4</sub> (I) and [Cu(phen)<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)]BF<sub>4</sub> · 2H<sub>2</sub>O (II) (phen = 1,10-phenanthroline) have been determined at room temperature by single-crystal X-ray diffraction techniques using counter methods and Mo  $K\alpha$  radiation ( $\lambda$   $K\alpha_1 = 0.70930$  Å;  $\lambda$   $K\alpha_2 = 0.71359$  Å). The structures have

been refined by full-matrix least-squares procedures using 3266 (3 $\sigma$ ) and 1834 (2 $\sigma$ ) unique and significant reflections to the final weighted  $R$  indices of 0.059 and 0.056 respectively. In (I), the nitrito group coordinates asymmetrically to Cu<sup>II</sup> and the [Cu(phen)<sub>2</sub>(ONO)]<sup>+</sup> cation has a stereochemistry intermediate between five- and six-coordinate. In contrast, the acetato group in (II) appears to coordinate symmetrically to Cu<sup>II</sup>; however, it has unusually large thermal motion which suggests that the [Cu(phen)<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)]<sup>+</sup> cation is either statically or dynamically disordered with respect to its twofold axis. ESR results for (II) indicate that the disorder is dynamic with the complex interconverting, through a form with  $C_2$  symmetry, between two stereochemically equivalent asymmetric forms. The distortional behavior of (I), (II), and other [Cu(phen or bpy)<sub>2</sub>(OXO)]Y complexes (OXO<sup>-</sup> = CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>, HCO<sub>2</sub><sup>-</sup>, and NO<sub>2</sub><sup>-</sup>) is rationalized in terms of a pseudo-Jahn–Teller formalism.

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