Five-co-ordinated Copper(II) Complexes: a New Look at the Isomerization from Trigonal-bipyramidal to Square-pyramidal Geometry in Bis(bipyridyl)-(monodentate ligand)copper(II) and Related Complexes†

Oliviero Carugo *
Dipartimento di Medicina Preventiva, Occupazionale e di Comunità dell'Università di Pavia, via Boezio 24, I-27100 Pavia, Italy
Carla Bisi Castellani
Dipartimento di Chimica Generale dell'Università di Pavia, via Taramelli 12, I-27100 Pavia, Italy

A new method of analysis of the structures of the five-co-ordinated copper(II) complexes is proposed, in order to place them along an ideal pathway for the isomerization reaction from the trigonal-bipyramidal geometry to the square-pyramidal one. The reliability of the method, which takes into account all the possible Berry mechanisms, has been verified by correlating it with some structural parameters independent of its formulation. The method has also been applied to the analysis of the structures of $[Cu(bipy)_2X]$ and $[Cu(phen)_2X]$ complexes (bipy = 2,2'-bipyridine, phen = 1,10-phenanthroline, X = monodentate ligand).

The five-co-ordinated copper(II) complexes generally possess geometries intermediate between trigonal bipyramidal (t.b.) and square pyramidal (s.p.). The kind and the degree of distortion are very variable, owing to the plasticity of the Cu^{2+} cation.[1] While in the past considerable attention has been devoted to the analysis of the degree of distortion from t.b. to s.p. (or *vice versa*),[2–4] less work has been done on the problem of the kind of distortion (in the present paper, we use the expressions 'degree of distortion' to indicate how far a given structure is from the idealized regular t.b. one, and 'kind or type of distortion' to indicate towards what s.p. isomer a given structure is distorted). When a t.b. copper(II) complex is encountered its distortion towards the s.p. geometry is usually described by indicating which of the three equatorial donor atoms becomes apical in the idealized s.p., so limiting the analysis to the Berry mechanism.[5] This is probably not correct, because, owing to the plasticity of copper(II), any distortion from t.b. to s.p. is actually as a somewhat composite mix of these three different distortions, each implying as apical donor atom of the s.p. one of the three donor atoms of the equatorial plane of the t.b.

In this paper we present a simple technique to compare and to mix the three possible distortions from t.b. towards s.p. The results are plotted in a diagram, making possible an easy evaluation of the kind of distortion. The reliability of this method of analysis of the structural data is verified by correlating it with some structural parameters independent of its formulation. Structures belonging to the numerous family of $[Cu(bipy)_2X]$ and related complexes (bipy = 2,2'-bipyridine) are also analyzed with this technique.

Discussion

The five-co-ordinated copper(II) complexes containing two bidentate ligands, such as 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen), and a third monodentate ligand are generally found in a nearly regular t.b. geometry. The monodentate ligand and two nitrogen atoms (one for each bipy or phen molecule) are always in the equatorial plane and the other two nitrogen atoms in the axial positions (Figure 1). The t.b. chromophore is more or less distorted towards s.p. Three structural pathways for these distortions (related to the Berry mechanism) are generally considered (Figure 2), but the routes

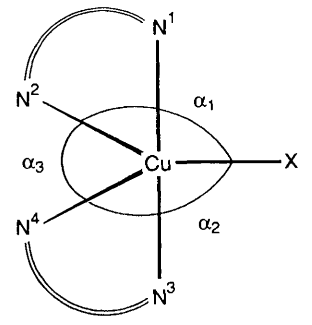

Figure 1. Angle notation and numbering scheme for $[Cu(bipy)_2X]$ and $[Cu(phen)_2X]$ complexes

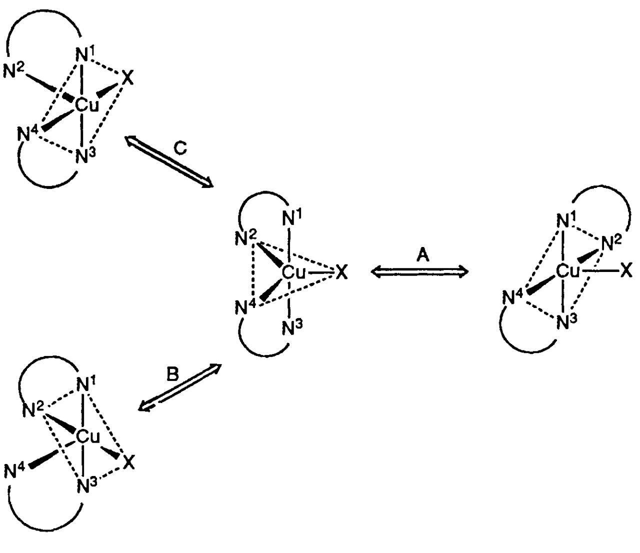

Figure 2. Structural pathways for the distortions of a t.b. complex like $[Cu(bipy)_2X]$ or $[Cu(phen)_2X]$ towards a s.p. one

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† *Non-S.I. unit employed:* cal = 4.184 J.

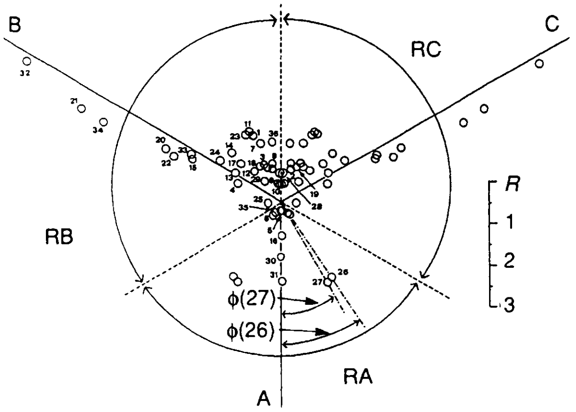

Figure 3. Plot combining the three possible distortions from t.b. to s.p. for complexes (**1**)—(**36**)

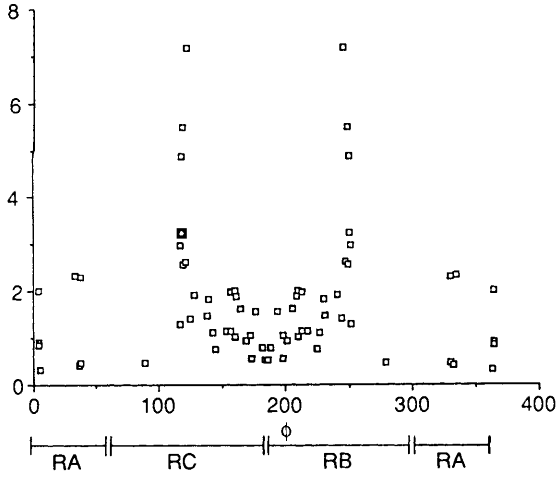

Figure 4. Two-dimensional version of the plot shown in Figure 3

B and C are equivalent, due to the equivalence of the two bipy (or phen) ligands.

This kind of description, although widely accepted, also on the basis of statistical factor analyses,[6] is probably too simplistic. Nothing prevents the t.b. structure from being distorted in a direction intermediate between the three routes A—C. Moreover, other reaction pathways might be present. For example, Auf der Heyde and Bürgi[7] recently reported that t.b. complexes of d^8 metals show, besides the Berry distortion towards s.p., two other reaction pathways: (*i*) lengthening of one axial bond with shortening of the other and concomitant umbrella-type distortion of the angles between the equatorial ligands and the two axial ones; (*ii*) simultaneous lengthening of the axial bonds and shortening of the equatorial ones or *vice versa*. We believe that, also limiting our attention to the Berry mechanism, a better description of the distortion from t.b. to s.p. can be achieved by the following simple method.

(*a*) Given a nearly t.b. structure, first we calculate the amounts of distortions through the routes A—C of Figure 2. This can be done by comparing the angles α_1, α_2, and α_3 of the structure under examination (see Figure 1) with the corresponding values of the three s.p. structures obtained after distortion through the three structural pathways. A typical formula for this purpose is equation (1) where D_j (j = A, B, or

$$D_j = [\Sigma\alpha(\text{theor.})]/[\Sigma|\alpha(\text{theor.}) - \alpha(\text{exptl.})|] \qquad (1)$$

C) is the amount of distortion, α(exptl.) is the experimental value for the angle α_i (i = 1—3), and α(theor.) is the theoretical value for the same angle in the s.p. idealized geometries. The values for the theoretical angles for a s.p. geometry depend probably on the *d*-orbital electronic configuration.[8–10] Thus, it is difficult to take into account their 'true value'. By general geometrical considerations, values of 150 and 105° have been proposed for the s.p. transbasal and apical–basal angles respectively (for example, for route A, $\alpha_3 = 150°$ and $\alpha_1 = \alpha_2 = 105°$).[2] However, these values do not seem suitable to describe a s.p. copper(II) complex with two bidentate and one monodentate ligands, where the transbasal angle (*i.e.* α_3 for the s.p. obtained after distortion through route A) is generally larger than 150°. In the present paper we prefer to consider them as follows: for distortion through route A, $\alpha_1 = \alpha_2 = 90°$ and $\alpha_3 = 180°$; route B, $\alpha_2 = \alpha_3 = 90°$ and $\alpha_1 = 180°$; route C, $\alpha_1 = \alpha_3 = 90°$ and $\alpha_2 = 180°$.

(*b*) Secondly, the three D_j so calculated are considered as vectorial components of a vector pointing at the origin, in the three-dimensional space defined by three coplanar axes at 120° (each indicating one of the three structural pathways A—C). The direction and the modulus of this distortion vector indicate respectively the type and the degree of distortion from t.b. to s.p. Thus, the end-point of the distortion vector can be considered as representative of the structure under examination. To summarize these results from a numerical point of view, the type of distortion can be seen as the parameter Φ, defined as the angle in degrees between the axis indicating the structural pathway A and the distortion vector; so, by simple trigonometric considerations,* it follows that the value of Φ is given by equation (2) {with $\delta = 90°$ if

$$\Phi = \arctan \frac{\{[D_A - (D_B + D_C)\cos 60°]}{[(D_B - D_C)\cos 30°]\}} + \delta \qquad (2)$$

$[(D_B - D_C)\cos 30°] < 0$ and 270° if $[(D_B - D_C)\cos 30°] \geqslant 0$} and the degree of distortion, R, is given by equation (3).

$$R = \{[D_A - (D_B + D_C)\cos 60°]^2 + [(D_B - D_C)\cos 30°]^2\}^{\frac{1}{2}} \qquad (3)$$

The accuracy of this description is not absolute, because it depends only on the angular deviations of the experimental structure from the idealized regular geometries [equation (1)], and consequently on the definition of the angular parameters of the idealized regular geometries. On the contrary, in order to establish the real distortion, it is essential to consider also the behaviour of the bond distances around the metal centre. However, at this stage, we are interested mainly in developing a new method of analysis of the five-co-ordinated copper(II) stereochemistry. Moreover, it is worthwhile pointing out that: (*i*) the reliability of the method used in equation (1) to evaluate the degree of distortion has already been discussed;[2,4] (*ii*) we think that the evaluation of the type of the distortion is not affected greatly by not having considered the bond distances around the copper(II) ion; in fact, the effects on the distortion due to the co-ordinative bonds tend to self-minimize in the geometrical construction described above.

Following this method and considering the $[Cu(bipy)_2X]$ and $[Cu(phen)_2X]$ complexes reported in Table 1, we obtain the plots of Figures 3 and 4. The complexes reported in Table 1 were selected on the bases of the following considerations.

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* The vectorial sum of the three vectors D_A, D_B, and D_C is obtained by summing their components in two-dimensional right-handed cartesian space defined by: (*i*) axis *y* coincident with the axis A of the three-dimensional space in Figure 3, and (*ii*) origin coincident with the origin of the three-dimensional space in Figure 3.

Table 1. Structural parameters (distances in Å, angles in °) for the complexes $[Cu(bipy)_2X]$ and $[Cu(phen)_2X]$

Formula	Cu-N^1	Cu-N^3	Cu-N^2	Cu-N^4	Cu-X	α_1	α_2	α_3	Ref.
(1) $[Cu(bipy)_2Cl]ClO_4$	1.993(4)	1.991(4)	2.076(3)	2.136(3)	2.263(3)	137.1(1)	126.4(2)	96.5(2)	*a*
(2) $[Cu(bipy)_2Cl]NO_3{\cdot}3H_2O$	1.989(6)	1.989(6)	2.089(6)	2.112(5)	2.308(3)	127.8(2)	123.4(2)	108.8(2)	*a*
(3) $[Cu(bipy)_2Cl]S_5O_6{\cdot}6H_2O$	1.992(6)	1.988(6)	2.092(6)	2.106(5)	2.292(4)	130.7(1)	122.0(2)	107.3(2)	*b*
(4) $[Cu(bipy)_2Cl][CuCl_2]_2$	1.985(5)	1.995(5)	2.063(5)	2.086(5)	2.356(5)	133.4(1)	111.1(1)	115.5(1)	*c*
(5) $[Cu(bipy)_2Cl]Cl{\cdot}6H_2O$	1.989(10)	1.970(10)	2.077(10)	2.087(11)	2.361(4)	118.7(3)	118.6(3)	122.8(4)	*d*
(6) $[Cu(bipy)_2Cl]PF_6{\cdot}H_2O$	1.996(6)	2.005(6)	2.105(6)	2.108(6)	2.344(2)	115.7(2)	120.5(2)	123.8(2)	*e*
(7) $[Cu(bipy)_2Br]BF_4$	1.996(7)	1.995(7)	2.068(8)	2.114(9)	2.419(3)	134.5(2)	126.2(3)	99.4(3)	*f*
(8) $[Cu(bipy)_2Br]Br$	1.978(6)	1.977(6)	2.085(7)	2.075(8)	2.429(2)	124.7(2)	128.6(2)	106.7(3)	*g*
(9) $[Cu(bipy)_2I]I$	2.03(4)	2.00(4)	2.10(4)	1.96(4)	2.70(4)	124	122	114	*i*
(10) $[Cu(bipy)_2I]ClO_4$	1.989(6)	1.987(6)	2.090(8)	2.100(7)	2.675(4)	122.9(2)	122.8(2)	114.3(3)	*f*
(11) $[Cu(bipy)_2(CN)]NO_3{\cdot}2H_2O$	1.996(4)	2.008(4)	2.088(4)	2.161(6)	1.974(5)	138.0(1)	126.5(2)	95.4(2)	*j*
(12) $[Cu(bipy)_2(NCS)]NCS^h$	1.967(10)	1.982(10)	2.108(9)	2.076(8)	1.969(9)	118.5(4)	131.4(4)	110.0(3)	*k*
(13) $[Cu(bipy)_2(NCS)]NCS^h$	2.007(9)	2.006(9)	2.126(10)	2.067(8)	1.951(14)	112.7(4)	134.8(4)	112.5(4)	*k*
(14) $[Cu(bipy)_2(NCS)]BF_4$	1.993(7)	1.980(7)	2.069(7)	2.120(6)	1.967(9)	137.9(2)	117.5(3)	104.6(3)	*l*
(15) $[Cu(bipy)_2(H_2O)]S_5O_6$	1.983(5)	1.973(6)	2.123(6)	2.024(6)	2.054(5)	104.9(2)	143.6(1)	111.4(3)	*b*
(16) $[Cu(bipy)_2(H_2O)]S_2O_6$	1.977(9)	1.977(9)	2.013(9)	2.013(9)	2.158(15)	115.1(3)	115.1(3)	129.8(5)	*m*
(17) $[Cu(tmbipy)_2(H_2O)][ClO_4]_2{\cdot}H_2O^{h,n}$	1.968(16)	1.974(16)	2.106(16)	2.211(18)	2.004(19)	135(1)	117(1)	108(1)	*q*
(18) $[Cu(tmbipy)_2(H_2O)][ClO_4]_2{\cdot}H_2O^{h,n}$	2.003(16)	2.029(17)	2.150(15)	2.142(17)	2.100(18)	131(1)	121(1)	108(1)	*q*
(19) $[Cu(bipy)_2(NH_3)]BF_4$	1.982(7)	1.958(7)	2.112(7)	2.070(7)	2.045(7)	122.3(3)	129.5(3)	108.2(3)	*r*
(20) $[Cu(bipy)_2(MeCO_2)]ClO_4{\cdot}H_2O$	1.971(5)	1.994(5)	2.056(5)	2.168(5)	2.031(5)	147.6(1)	100.7(2)	111.6(2)	*s*
(21) $[Cu(bipy)_2(MeCO_2)]BF_4$	1.995(6)	2.016(6)	2.033(5)	2.209(6)	1.980(4)	156.5(1)	92.3(2)	111.0(2)	*s*
(22) $[Cu(bipy)_2(HCO_2)]BF_4{\cdot}H_2O$	1.978(5)	2.001(5)	2.061(5)	2.158(5)	2.024(5)	146.1(1)	100.5(2)	113.2(2)	12
(23) $[Cu(bipy)_2(aasp)]EtOH{\cdot}4H_2O^o$	1.961(7)	1.958(7)	2.112(9)	2.094(6)	1.977(6)	125.0(3)	138.1(3)	96.7(3)	14
(24) $[Cu(bipy)_2(pydca)][Cu(pydca)]{\cdot}4H_2O^p$	1.985(3)	1.986(3)	2.115(3)	2.062(3)	2.029(3)	112.4(2)	138.9(2)	108.7(2)	15
(25) $[Cu(tmbipy)_2(ClO_4)]ClO_4$	1.979(5)	1.959(5)	2.052(6)	2.040(6)	2.491(6)	115.6(2)	123.8(2)	120.6(3)	*q*
(26) $[Cu(bipy)_2(NO_3)]NO_3{\cdot}H_2O$	1.99	2.01	2.07	2.04	2.30	91.9	127.7	140.4	*u*
(27) $[Cu(bipy)_2(S_2O_8)]{\cdot}H_2O$	1.972(4)	1.959(5)	2.039(4)	2.032(4)	2.367(4)	93.0(2)	126.0(2)	141.0(2)	17
(28) $[Cu(bipy)_2(tu)][ClO_4]_2{}^t$	1.974(7)	1.985(7)	2.097(7)	2.098(7)	2.369(4)	124.4(2)	125.1(2)	110.5(3)	*v*
(29) $[Cu(phen)_2Cl]ClO_4$	2.004(6)	1.986(6)	2.136(6)	2.077(6)	2.298(2)	119.0(2)	127.6(2)	113.4(2)	*w*
(30) $[Cu(phen)_2I]I{\cdot}S_8$	2.00(1)	2.00(1)	2.10(1)	2.10(1)	2.672(3)	125.3(3)	125.3(3)	97.0(4)	*x*
(31) $[Cu(phen)_2(H_2O)][NO_3]_2$	1.99(1)	1.99(1)	2.03(1)	2.03(1)	2.18(1)	110.0(4)	110.0(4)	139.6(4)	*y*
(32) $[Cu(phen)_2(MeCO_2)]BF_4$	2.010(2)	2.025(2)	2.062(2)	2.218(2)	1.996(2)	160.5(1)	95.7(1)	103.5(1)	13
(33) $[Cu(dmphen)_2(NO_3)]CCl_3CO_2{\cdot}CCl_3CO_2H^z$	2.03(1)	2.06(1)	2.07(1)	2.14(1)	2.15(4)	106(1)	144(1)	110(1)	*
(34) $[Cu(phen)_2(ONO)]BF_4$	1.999(4)	2.019(3)	2.049(3)	2.167(3)	2.072(4)	154.5(1)	93.2(1)	112.1(1)	†
(35) $[Cu(phen)_2(tu)][ClO_4]_2{\cdot}H_2O$	2.003(5)	1.983(5)	2.080(4)	2.087(4)	2.405(4)	120.2(1)	116.4(1)	123.2(1)	‡
(36) $[Cu(phen)_2(CN)]NO_3{\cdot}H_2O$	2.001(10)	2.014(10)	2.102(6)	2.123(6)	1.935(10)	132.4(3)	129.0(3)	98.6(2)	§

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(*a*) The bipy and phen ligands are quite similar with respect to their complexing properties, but first, their copper(II) complexes were analysed separately, to determine whether there are important differences between them (they have very different steric requirements: for example, the strict planarity of phen, which is not conserved in bipy, where the two pyridine rings can be twisted).

(*b*) We selected, as the fifth monodentate ligand X, either purely monodentate ligands or potentially bidentate ones, anionic or neutral, bulky or not severely bulky. This allowed the evaluation of the deformation of the $[Cu(chelate)_2]^{2+}$ moiety under very variable conditions, but, of course, a deeper analysis of the $[Cu(bipy)_2X]$ or $[Cu(phen)_2X]$ complexes is possible only within each specific class of X ligands. In this regard, it is worthy of note that only a few carboxylate and nitrito adducts of $[Cu(bipy)_2]^{2+}$ and $[Cu(phen)_2]^{2+}$ have been considered out of the known ones. The $[Cu(bipy)_2(OXO)]^+$ and $[Cu(phen)_2(OXO)]^+$ complexes (OXO = carboxylate or nitrite) are known to involve a fluxional (4 + 1 + 1*) stereochemistry and thus should not be included in a discussion of the static five-co-ordinate CuN_4X stereochemistry.[11] However, complexes (**22**) and (**32**) were observed to be 'near static extreme of the fluxional (4 + 1 + 1*) chromophore',[12,13] and, from the exhaustive analysis performed by Fitzgerald and Hathaway,[12] complexes (**20**), (**21**), and (**34**) are examples of quite extreme distortion towards five-co-ordination (see Figure 4 of ref. 12). Therefore, with reservation, compounds (**20**), (**21**), and (**34**) were included in the present analysis. Moreover, for complex (**23**), neither

Table 2. Distortion parameters for the complexes [Cu(bipy)$_2$X] and [Cu(phen)$_2$X], expressed as distortion degree (R) and type (Φ/°) calculated with equations (2) and (3)

	(1)	**(2)**	**(3)**	**(4)**	**(5)**	**(6)**	**(7)**	**(8)**	**(9)**
R	1.78	0.82	1.02	1.17	0.21	0.35	1.51	0.95	0.44
Φ	204.1	196.5	207.8	247.6	358.9	33.9	200.4	167.0	192.5
Φ^a	155.9	163.5	152.2	112.4	1.1	326.1	159.6	193.0	167.5
	(10)	**(11)**	**(12)**^{b}	**(13)**^{b}	**(14)**	**(15)**	**(16)**	**(17)**^{b}	**(18)**^{b}
R	0.41	1.88	1.00	1.31	1.70	2.45	0.81	1.36	1.02
Φ	180.7	205.2	137.9	120.3	225.4	115.4	0.0	226.8	212.0
Φ^a	179.3	154.8	222.1	239.7	134.6	244.6	360.0	133.2	148.0
	(19)	**(20)**	**(21)**	**(22)**	**(23)**	**(24)**	**(25)**	**(26)**	**(27)**
R	0.92	3.13	5.38	2.87	1.86	1.79	0.35	2.17	2.21
Φ	155.2	245.8	245.2	247.5	151.4	123.8	84.9	33.9	29.8
Φ^a	204.8	114.2	114.8	112.5	208.6	236.2	275.1	326.1	330.2
	(28)	**(29)**	**(30)**	**(31)**	**(32)**	**(33)**	**(34)**	**(35)**	**(36)**
R	0.67	0.65	1.37	1.90	7.06	2.50	4.75	0.29	1.46
Φ	176.9	139.5	0.0	0.0	241.5	117.2	246.1	328.0	188.6
Φ^a	183.1	220.5	360.0	360.0	118.5	242.8	113.9	32.0	171.4

^{a} Value obtained after permuting the labels of the two bipy or phen ligands (see text). ^{b} There are two independent complexes in the asymmetric unit.

structural nor e.s.r. data provide evidence for any fluxional behaviour,[14] and **(24)** is probably anomalous, with respect to the fluxionality, because of the steric constraint of the CO_2^- bonding group which is a part of a pyridine-2,6-dicarboxylate anion.[15] It is worthwhile noting that neither complex **(23)** nor **(24)** lies in the trend described in Figure 4 of ref. 12.

In each plot of Figures 3 and 4 one structure is actually represented by two points, symmetric with respect to axis A (in Figure 3) and to point $\Phi = 180°$ (in Figure 4). This is because the complex shown in Figure 1 is equivalent to that obtained by permuting the labels of N^1 and N^3, and of N^2 and N^4.[16] After this permutation, the distortion through route B is transformed into a distortion through route C. The values of Φ and R [equations (2) and (3)] are reported in Table 2. In Table 3 are reported the maximum, minimum, and mean values for R and the difference ΔR between its maximum and minimum values, for Φ intervals of 30°.

Before we consider the consequences of this kind of analysis on the [Cu(bipy)$_2$X] and [Cu(phen)$_2$X] complexes, some remarks should be made about the plot in Figure 3. Each of the three 120° axes indicates a distortion from t.b. to s.p. purely through one of the three structural pathways A, B, or C of Figure 2; however, we note that a structure equidistorted in two directions (for example B and C) and not distorted in the third one (A, in the example) appears as purely distorted in the reverse third direction (*i.e.*, it should be reported in the plot of Figure 3 as a point on the dotted extension of axis A at $\Phi = 180°$); however, it is possible to imagine that a 'negative' distortion in one direction is the same as two 'positive' and equal distortions in the other two directions. The intersection of the three 120° axes, *i.e.* the centre of the plot, indicates a regular t.b. geometry; *ab absurdo*, a hypothetical structure equidistorted in all the three routes A—C should be reported at the centre of the plot; however it is not difficult to imagine that such a structure could actually be seen as a compressed t.b. Eventually, the bisecting lines among each pair of the three 120° axes indicate a useful logical separation between the three routes of distortion A—C; so, in Figure 3, we can isolate three regions, RA, RB, and RC, where the representative points of the structures mainly distorted through the routes, A, B, and C are found. Likewise, in Figure 4, the space $\Phi = -60$ to $+60°$ represents the region RA, $\Phi = 60$—180° the region RC, and $\Phi = 180$—300° the region RB.

Moreover, in order to verify the substantial correctness of the parameter Φ, we correlated it with some structural parameters independent of its definition, and whose behaviour, ranging between t.b. and s.p., is quite well known. In this regard, it has to be remembered that we do not expect from these correlations a linear dependence between Φ and the structural parameters described below. In fact, the parameter Φ does not indicate the degree of distortion, only its type. On the contrary, the structural parameters described below are expected to agree qualitatively with the values of Φ indicating a certain type of distortion. Moreover, the correctness of the parameter Φ was verified only by considering the structural parameters of the complexes [Cu(bipy)$_2$X] with X = halide, pseudohalide, water, ammonia, nitrato, or thiourea. In this way we avoided as far as possible any misjudgement due to too large differences between the ligands.[17] However, the results achieved by considering all the compounds reported in Table 1 are quite analogous, thus supporting the validity of the present analysis.

First, we correlated Φ and a function BD, defined as in equation (4) where DA1 is the t.b. equatorial donor atom which

$$BD = d_{Cu-DA1} - (d_{Cu-DA2} + d_{Cu-DA3})/2 \qquad (4)$$

becomes apical in the s.p. isomer, DA2 and DA3 are the other two t.b. equatorial donor atoms which become basal in the s.p. isomer, and d_{Cu-DAi} are their distances from the copper(II) centre, corrected for the different covalent radii of the various donor atoms (in the present paper, we are concerned with nitrogen, chloride, bromide, iodide, and carbon, with covalent radii 0.70, 0.99, 1.14, 1.33, and 0.603 Å respectively).[18] It is well known that in a s.p. structure the distance between the copper(II) centre and the donor atom in the apical position is greater than the basal bond distances around Cu^{2+}.[1] The function defined by equation (4) is therefore of interest because it indicates the lengthening of the incipient s.p. apical bond (Cu-DA1), in moving from t.b. to s.p., with respect to the average of the other two t.b. equatorial copper–donor atom distances (d_{Cu-DA2} and d_{Cu-DA3}) which becomes s.p. basal after isomerization.

Table 3. Distortion degrees (R) of complexes [Cu(bipy)$_2$X] and [Cu(phen)$_2$X] from 0 to 360° for Φ intervals of 30°

$\Phi/°$	n^a	$R_{\text{min.}}{}^b$	$R_{\text{max.}}{}^b$	ΔR^c	$\bar{R}^b$
[Cu(bipy)$_2$X] (**1**)—(**28**)					
0—15	2	0.21	0.81	0.60	0.51
15—45	3	0.35	2.21	1.86	1.58
45—75	0	—	—	—	—
75—105	1	—	—	—	0.35
105—135	9	1.17	5.38	4.21	2.35
135—165	9	0.82	1.88	1.06	1.31
165—195	4	0.41	0.95	0.54	0.62
195—225	9	0.82	1.88	1.06	1.31
225—255	9	1.17	5.38	4.21	2.35
255—285	1	—	—	—	0.35
285—315	0	—	—	—	—
315—345	3	0.35	2.21	1.86	1.58
345—360	2	0.21	0.81	0.60	0.51
[Cu(phen)$_2$X] (**29**)—(**36**)					
0—15	2	1.37	1.90	0.53	1.64
15—45	1	—	—	—	0.29
45—75	0	—	—	—	—
75—105	0	—	—	—	—
105—135	3	2.50	7.06	4.56	4.77
135—165	1	—	—	—	0.65
165—195	1	—	—	—	1.46
195—225	1	—	—	—	0.65
225—255	3	2.50	7.06	4.56	4.77
255—285	0	—	—	—	—
285—315	0	—	—	—	—
315—345	1	—	—	—	0.29
345—360	2	1.37	1.90	0.53	1.64
[Cu(bipy)$_2$X] and [Cu(phen)$_2$X] (**1**)—(**36**)					
0—15	4	0.21	1.90	1.69	1.07
15—45	4	0.29	2.21	1.92	1.26
45—75	0	—	—	—	—
75—105	1	—	—	—	0.35
105—135	12	1.17	7.06	5.89	2.96
135—165	10	0.65	1.88	1.23	1.25
165—195	5	0.41	1.46	1.05	0.79
195—225	10	0.65	1.88	1.23	1.25
225—255	12	1.17	7.06	5.89	2.96
255—285	1	—	—	—	0.35
285—315	0	—	—	—	—
315—345	4	0.29	2.21	1.92	1.26
345—360	4	0.21	1.90	1.69	1.07

[a] Number of complexes with distortion type Φ included in the corresponding interval. [b] Minimum ($R_{\text{min.}}$), maximum ($R_{\text{max.}}$), and mean values ($\bar{R}$) of the distortion degrees of the complexes having distortion type Φ included in the corresponding Φ interval. [c] $\Delta R = R_{\text{max.}} - R_{\text{min.}}$.

In Figure 5(*a*), one can see that BD, defined with DA1 = X, DA2 = N^2, and DA3 = N^4, has high values for Φ approaching 0 or 360°, and lower values in the central part of the Φ axis. This is consistent with the previous statement that structures distorted through route A of Figure 2, *i.e.* towards a s.p. with atom X in apical position, have to be described by a parameter Φ = 0° or near 0°. Similarly, in Figure 5(*b*) we find that BD, defined with DA1 = N^2, DA2 = N^4, and DA3 = X, has the highest values for Φ near 120°, as expected for a t.b. distorted through route C. An analogous trend is observed in Figure 5(*c*), where BD defined with DA1 = N^4, DA2 = N^2, and DA3 = X has the highest values at Φ near 240°, as expected for a t.b. distorted through route B.

Another structural parameter independent of the definition of the function Φ derives from the observation that the t.b. copper(II) complexes are generally compressed, *i.e.* the equatorial bond distances around the metal centre are greater than the axial ones, while in s.p. copper(II) complexes the four basal co-ordinative bond distances are generally equivalent. Since, in moving from t.b. to s.p. (see Figure 2), the two axial and two equatorial bonds around Cu^{2+} (in the t.b. isomer) are transformed into the four basal co-ordinative bonds (in the s.p. isomer), we expect that the more the t.b. structure is distorted towards s.p. the less pronounced is the difference between its axial and equatorial (incipient s.p. basal) co-ordinative bond lengths. In order to correlate this difference with the parameter Φ, we used two functions defined as in equations (5) and (6),

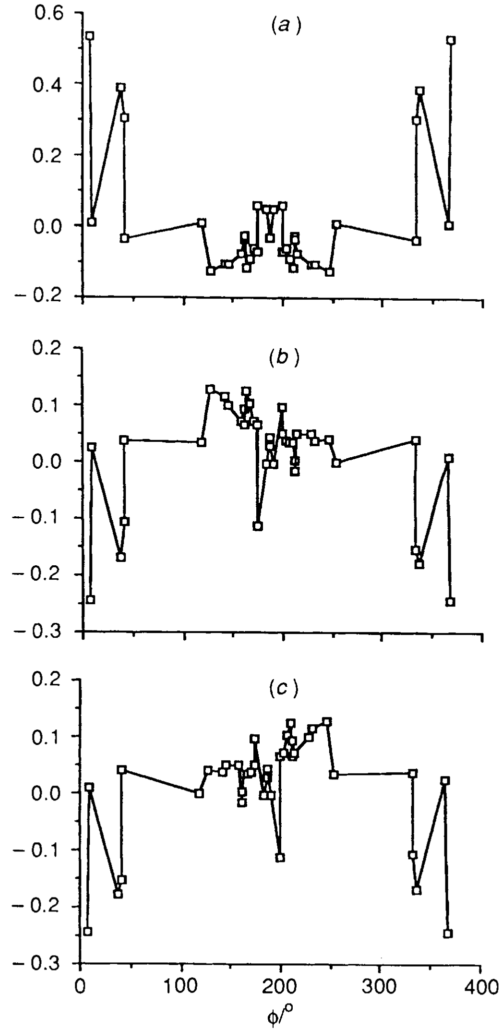

Figure 5. Correlation between the parameter Φ and the distortion function BD [see equation (4) in the text]

$$\sigma = (1/4)[(d_{\text{Cu-N1}} - d)^2 + (d_{\text{Cu-N3}} - d)^2 + \Sigma(d_{\text{Cu-DA}i} - d)^2]^{\frac{1}{2}} \quad (5)$$

$$\text{AE} = (1/2)(d_{\text{Cu-N1}} + d_{\text{Cu-N3}}) - (1/2)(\Sigma d_{\text{Cu-DA}i}) \quad (6)$$

where $d_{\text{Cu-N1}}$ and $d_{\text{Cu-N3}}$ are the bond distances between Cu and N^1 and N^3 respectively (*i.e.* the t.b. axial co-ordinative bond distances), DA*i* are the two t.b. equatorial donor atoms which become basal in the s.p. isomer, $d_{\text{Cu-DA}i}$ are their distances from the copper(II) centre, and d is defined as in equation (7). The

$$d = (1/4)[d_{\text{Cu-N1}} + d_{\text{Cu-N3}} + \Sigma(d_{\text{Cu-DA}i})] \quad (7)$$

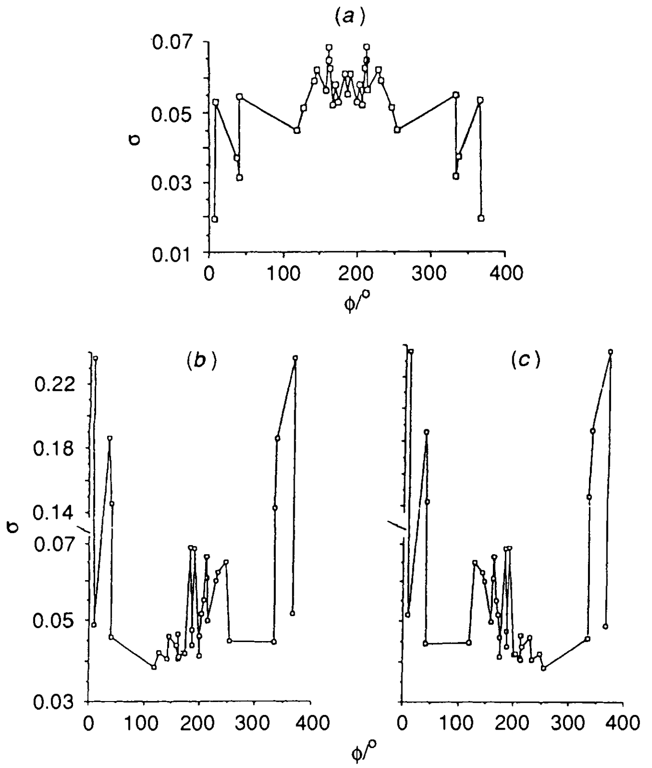

Figure 6. Correlation between the parameter Φ and the distortion function σ [see equation (5) in the text]

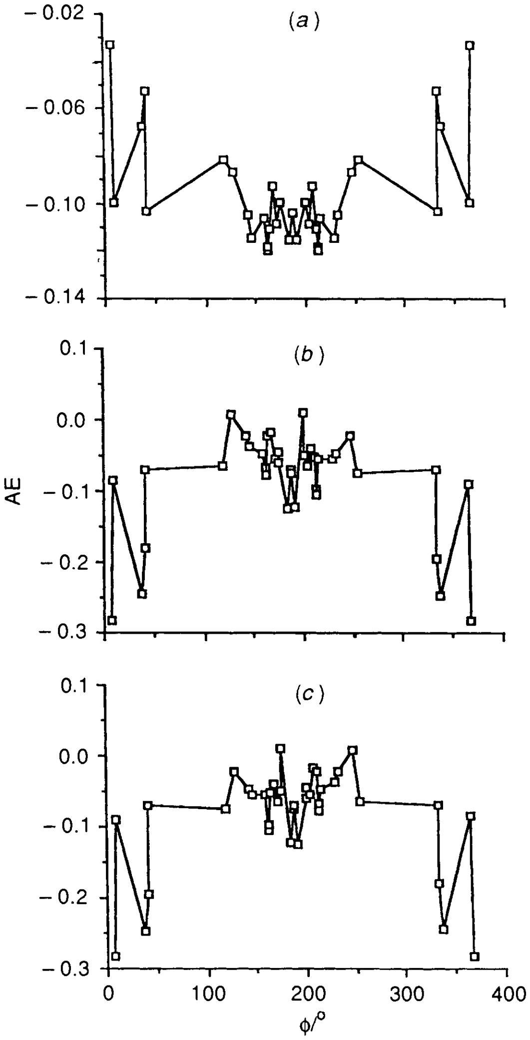

Figure 7. Correlation between the parameter Φ and the distortion function AE [see equation (6) in the text]

function σ, defined by equation (5), is simply the average standard deviation of the four t.b. co-ordinative bond distances, which are transformed into s.p. basal ones, with respect to their mean, and we expect it to decrease on going from t.b. to s.p. The function AE, defined by equation (6), is the difference between the average of the t.b. axial bond distances and the average of the t.b. equatorial ones (incipient s.p. basal), and it is expected to range from lower values (<0) for low distortions to higher values for high distortions from t.b. to s.p.

The expected trends are actually observed. In Figure 6(*a*), the σ function, defined with DA*i* = N^2 and N^4, has low values for Φ approaching 0 and 360°; this implies that distortions towards s.p. with the donor atom X in apical position have to be described by parameters Φ near 0°. In Figure 6(*b*) and 6(*c*), the σ functions, defined with DA*i* = N^4 and X, and DA*i* = N^2 and X respectively, have low values for Φ near 120 and near 240° respectively, implying that distortions towards s.p.s with apical donor atoms N^2 and N^4 are characterized by parameters Φ near 120 and 240° respectively. Moreover, the function AE, defined with DA*i* = N^2 and N^4 [see Figure 7(*a*)], has high values for Φ near 0 and 360°, as expected for a distortion towards a s.p. with the X donor atom in apical position. Finally, the functions AE defined with DA*i* = X and N^4, and DA*i* = X and N^2 respectively [see Figure 7(*b*) and 7(*c*)], have high values for Φ near 120 and 240° respectively, as expected for distortions towards s.p.s with donor atoms N^2 and N^4 in apical position.

Having constructed the distortion plots of Figures 3 and 4, and demonstrated the reliability of the parameter Φ, we can now examine in some detail the consequences of this kind of analysis on the [Cu(bipy)$_2$X] and [Cu(phen)$_2$X] complexes.

(*i*) No systematic differences between bipy and phen can be evidentiated. The data concerning the [Cu(phen)$_2$X] complexes (**29**)—(**36**) are less numerous than those concerning the [Cu(bipy)$_2$X] ones. However, they are represented in the plots of Figures 3 and 4 as the [Cu(bipy)$_2$X] complexes, *i.e.* by parameters Φ well distributed between 0 and 360° and very changeable degrees of distortion. This feature is evident also from the data reported in Table 3, where it is possible to see that the Φ regions around 0, 120, and 240° are the most populated both for [Cu(bipy)$_2$X] and [Cu(phen)$_2$X] complexes; moreover, the dependence of $\bar{R}$ and ΔR on Φ is similar for both types of compounds, and no apparent relation exists between the values of $\bar{R}$ and ΔR of [Cu(bipy)$_2$X] and [Cu(phen)$_2$X] complexes. Therefore, the higher rigidity of phen with respect to bipy does not seem to determine a substantial difference between [Cu(bipy)$_2$X] and [Cu(phen)$_2$X] complexes.

(*ii*) The most evident feature of the plots of Figures 3 and 4 is the asymmetric distribution of points between the three regions RA, RB, and RC. Only 13 points out of 70 lie in the first one which indicates a distortion from t.b. to s.p. through the route A. Moreover, from the data reported in Table 3, it is seen that both $\bar{R}$ and ΔR are greater in the Φ regions around 120 and 240° than around 0 or 360°, *i.e.* the distortion vector moduli and their variabilities are larger along the axes B and C than along A (see Figure 3). Therefore we can conclude that the nearly t.b. [Cu(bipy)$_2$X] and [Cu(phen)$_2$X] complexes do not easily distort towards s.p. through route A, but they do through routes B or C (or, better, in a direction intermediate between the axes B and C; see below), with a nitrogen atom in s.p. apical position. This is in accord with the hypothesis that the Cu(bipy)$_2$ and

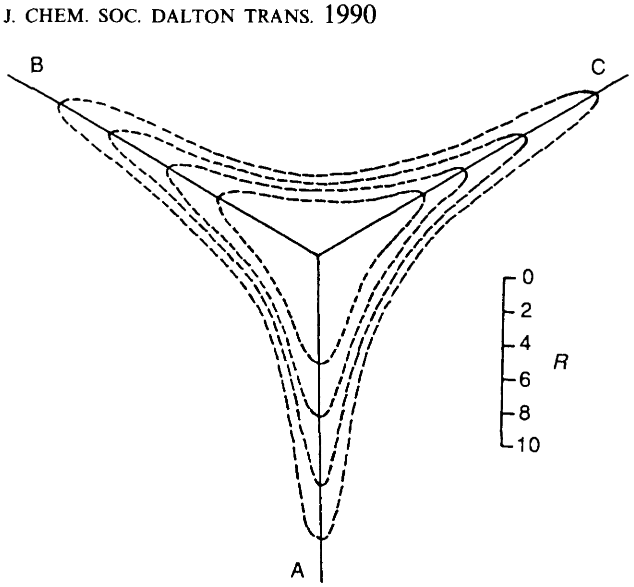

Figure 8. Projection of the potential-energy surface onto the plot shown in Figure 3. Energy levels, calculated with equation (8) by using the parameters reported by Giglio,[23] are drawn at 0.1 kcal mol^{-1}

Cu(phen)$_2$ chromophores cannot be square planar because of the steric hindrance between the hydrogen atoms near to the nitrogen atoms in each pyridinic ring.[19] Furthermore, this trend is emphasized when these hydrogen atoms are substituted by methyl groups, see complexes (**17**), (**18**), (**25**), and (**33**).

(*iii*) The point distribution in Figure 3 is near Y-shaped (although the vertical segment is smaller than the other two), and in Figure 4 we have sharp maxima at Φ near 120 and 240°, and smaller ones at Φ near 0 and 360°. The distortion vector moduli are smaller in the zones between the 120° axes than in the directions of the axes. This is, of course, a consequence of the way in which these plots were constructed. However, in order to reach a deeper understanding of this feature, we mapped the plot of Figure 3 with the potential energy of its points, calculated considering the van der Waals attractive and repulsive interactions between the five donor atoms (all taken as equivalent nitrogen atoms at 2.00 Å from the metal centre) using equation (8) where r_{ij} is the non-bonding distance between the

$$V = \Sigma\Sigma A \exp(-Br_{ij})r_{ij}^{-D} - Cr_{ij}^{-6} \qquad (8)$$

two donor atoms i and j. Using this equation, we disregarded the Coulombic interaction energies, but it is presumed that in this case their contribution does not determine the relative stability of the different isomers.[20–22] The coefficients of equation (8) were taken from Giglio[23] (A = 387 000.0, B = 0.0, C = 354.0, and D = 12; if r is expressed in Å, V is in kcal mol^{-1}) and from Gavezzotti and Simonetta[24] (A = 42 000.0, B = 3.78, C = 259.0, D = 0). Moreover, by fixing the attractive coefficients, we derived the repulsive parameter (by minimizing the complete function at a distance corresponding to the sum of the van der Waals radii) for values of the van der Waals radii in the range 1.50—1.80 Å, and for coefficient D varying between 8 and 15, in order to have a more or less 'hard' description of the potentials. Under all these different conditions we obtained qualitatively similar results (see Figure 8).

There is an energy minimum in the centre of the plot, corresponding to a regular t.b. structure, and the energy increases with the distortion towards s.p., but the slope of this increase is smaller along the axes than between them. This explains why the degrees of distortion through the structural pathways identified by the axes are higher than those relative to distortions in other directions. The shape of the potential-energy map in Figure 8 does not account for the asymmetric distribution of points described under point (*ii*), and which should imply a less easy distortion along axis A than along B and C. This is probably a consequence of the fact that we calculated the potential-energy surface for the simple case of five equivalent unidentate ligands. The reason why this procedure was adopted is that a potential-energy surface calculated with a more accurate model, *i.e.* Cu(bidentate ligand)$_2$(monodentate ligand), would be very influenced by the choice of the chelate ring geometry.[22] Since in the complexes examined here some variability within the geometries of the chelate rings is present, the design of an appropriate model would be quite difficult.

(*iv*) While there are three complexes purely distorted through route A, (**16**), (**30**), and (**31**), no cases of distortions purely through routes B and C are presently known. This may be a consequence of the symmetry of these complexes, which can accommodate a C_2 along the Cu–X bond only. In other words, the equivalence of the two bipy or phen ligands makes very unlikely a distortion from t.b. to s.p. purely through route C or B. This is also the reason why most of the points of Figure 3 are in the part of the regions RC and RB limited by the axes B and C; *i.e.* the most likely distortion from t.b. to s.p. in [Cu(bipy)$_2$X] and [Cu(phen)$_2$X] complexes is through a structural pathway intermediate between the routes B and C.

(*v*) There is no systematic influence on the type and degree of distortion from the non-co-ordinated anions. The most frequently encountered (BF_4^-, NO_3^-, ClO_4^-, *etc.*) are present in complexes showing quite variable degrees of distortion and quite randomly distributed parameters Φ.

(*vi*) An analysis of the stereochemical effects, on the [Cu(bipy)$_2$X] and [Cu(phen)$_2$X] complexes, due to the X donor atom (or, more precisely, due to the monodentate ligand having X as donor atom), shows some systematic features. While for X = Cl^- [complexes (**1**)—(**6**) and (**29**)] or H_2O [(**15**)—(**18**) and (**31**)] the degrees and the types of distortion are quite randomly distributed, for X = Br^- [(**7**) and (**8**)] or I^- [(**9**) and (**10**)] only the parts of the regions RB and RC limited by the axes B and C are populated [with the exception of compound (**30**), where, however, a co-crystallized sulphur molecule could greatly affect the copper(II) stereochemistry]. This may be considered as the effect of the increasing size of the donor atom X, which implies of course lengthening of the Cu–X bond distances. However, while the van der Waals radii increase linearly with the covalent radii, the non-bonding contacts between X and N^2, and between X and N^4, do not increase linearly with the lengthening of the covalent radius of X, because the angles α_1 and α_2 are smaller than 180°. Thus, by increasing the size of the donor atom X, we observe a greater compression of the bonds Cu–N^2 and Cu–N^4, which implies a reduction of the angle α_3 and an increase of α_1 and α_2. This causes a distortion of the idealized regular t.b. towards a s.p. through a structural pathway intermediate between the routes B and C.

Another interesting observation is that when X = carboxylate (aspartate, acetate, formate, pyridine-2,6-dicarboxylate), the complexes are distinctly distorted through routes B and C [(**20**)—(**24**) and (**32**)]. Although the [Cu(chelate)$_2$(carboxylate)] complexes have been demonstrated to involve a fluxional (4 + 1 + 1*) stereochemistry, the examples included in the present analysis can be considered quite static extremes of this type of chromophore. In this (4 + 1 + 1*) stereochemistry the metal is co-ordinated by the four nitrogen atoms of the bipy or phen ligands, and the two oxygen atoms of the carboxylic ligand, one near (average 2.02 Å) and the other one far (average 2.76 Å) from the copper(II) ion. Since the angle between the plane of the carboxylic group and t.b. equatorial plane is generally small (1—13°), the second semico-ordinated oxygen atom actually causes a compression of the Cu–N^2 (or Cu–N^4) bond, implying a considerable enlargement of the α_1 (or the α_2) angle, and a smaller one of the α_3 angle. Thus, the steric requirements of the carboxylic ligand imply a distortion of the idealized regular t.b. complex towards a s.p. one through the structural pathway B or C. The same interpretation is probably valid for X = ONO [complex (**34**)], although we have only one example of a complex containing this ligand.

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