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General relationship between ring structural and pseudorotational parameters of five-membered rings. Application to aminocarboxylato chelates in cobalt(III) complexes

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Abstract

A general relationship between the ring structural and the ring pseudorotational parameters for puckered five-membered rings is derived. The relationship enables direct calculation of the pseudorotational parameters from the known ring geometry.

The applicability of the derived relationship is demonstrated by classification of aminocarboxylato chelate rings in cobalt(III) complexes in terms of the pseudorotational coordinates. A strong preference of the aminocarboxylato chelate ring conformations having the Co–O–C–C torsional angle close to zero is observed.

INTRODUCTION

The empirical relationship between the endocyclic torsional angles and the pseudorotational coordinates of a pentagon, introduced by Kilpatrick et al. [1] and by Altona [2], allows an elegant classification of the ring conformations in terms of the pseudorotational coordinates [3]. This relationship was later derived by assuming infinitesimal displacement of a regular pentagon from planarity [4,5].

The relationship between the torsional angles ϕ_{k+i} and the pseudorotational coordinates (ring-puckering amplitude Φ and phase angle ω) of a pentagon, known as the pseudorotational formula

$$\phi_{k+i} = c_{k+i}\Phi_k \cos(\omega_k + \varepsilon_{k+i} + i\delta) \qquad i = 0, 1, 2, -2, -1 \qquad \delta = 144° \quad (1)$$

where k signifies the choice of an origin for counting the torsional angles, $k \in 1, 2, 3, 4, 5$; i counts the angles clockwise, $i = 1, 2$, and anticlockwise,

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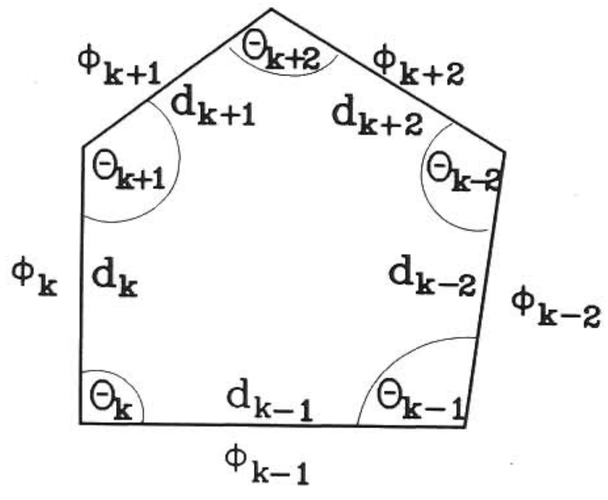


Scheme 1.

$i = -1, -2$, from the origin, $i = 0$ (see Scheme 1), requires that any three torsional angles in a pentagon are linearly related

$$\phi_{k+l} = a_{l,m,k}\phi_{k+m} + b_{l,m,k}\phi_k \qquad l \neq m \in 1, 2, -2, -1 \tag{2a}$$

where

$$a_{l,m,k} = \frac{c_{k+l}}{c_{k+m}} \cdot \frac{\sin(\varepsilon_{k+l} + l\delta)}{\sin(\varepsilon_{k+m} + m\delta)}$$

$$b_{l,m,k} = \frac{c_{k+l}}{c_k} \cdot \sin(\varepsilon_{k+l} + l\delta)\,[\cot(\varepsilon_{k+l} + l\delta) - \cot(\varepsilon_{k+m} + m\delta)] \tag{2b}$$

On writing eqn. (1) for $i = 0$ and $i = l$, the ring-puckering coordinate may be eliminated, giving

$$\tan\omega_k = \cot(\varepsilon_{k+l} + l\delta) - \frac{c_k/c_{k+l}}{\sin(\varepsilon_{k+l} + l\delta)} \cdot \frac{\phi_{k+l}}{\phi_k} \tag{2c}$$

Repetition of the same procedure for $i = 0$ and $i = m$ allows the elimination of the phase angle as well, which then gives eqns. (2a) and (2b).

To our knowledge, eqn. (2a) has not been proved, although it was introduced empirically by Pavelčik [6]. An important consequence of this eqn. is that among the c_{k+i} and ε_{k+i} parameters of the pseudorotational relationship, only six could be made mutually independent. This follows from eqns. (2a) and (2b) since only three linearly independent equations of the form eqn. (2a) may be constructed for five torsional angles. Consequently, only six independent coefficients $a_{l,m,k}$ and $b_{l,m,k}$ may be obtained.

Whether eqn. (2a) really exists in a pentagon is of crucial importance. If it exists, then it may be used for an exact transformation of the ring geometry parameters into the pseudorotational parameters.

Therefore we undertook the derivation of the relationship between three torsional angles in a pentagon in order to check to what extent it supports eqns. (1) and (2).

RELATIONSHIP BETWEEN RING STRUCTURAL AND PSEUDOROTATIONAL PARAMETERS

We derived the following relationship (see Appendix A) between three sequential torsional angles in a pentagon (Scheme 1) starting from the known bond distances (d_{k+i}) and valence angles (θ_{k+i}):

$$\sin\phi_{j+1}\cos\phi_j = A_j \sin\phi_{j-1} + (B_j^0 + \cos\theta_{j+1}\cos\phi_{j+1})\sin\phi_j \tag{3a}$$

where

$$A_j = -\frac{d_{j-2}\sin\theta_{j-1}}{d_{j+2}\sin\theta_{j+2}} \tag{3b}$$

$$B_j^0 = -\frac{\sin\theta_{j+1}(d_{j+1} - d_{j+2}\cos\theta_{j+2})}{d_{j+2}\sin\theta_{j+2}} \tag{3c}$$

When ring-puckering approaches zero, eqn. (3a) coincides with eqn. (2a). However, it is known that eqn. (1) works well for quite puckered rings. Therefore, eqn. (3a) has to be transformed further in order to establish a relationship between the torsional angles instead of the one between the sines of the torsional angles. For that purpose we applied the following approximation: $\sin\phi = (1/3)\phi(2 + \cos\phi)$, introducing in this way an inaccuracy which is below 0.1° for up to $\phi = 45°$. Thus, the inaccuracy is within the experimental error of the determination of the angle (the approximation is much superior to the usual one, i.e. $\sin\phi \approx \phi$, which for $\phi = 40°$ deviates by 4°). After rearrangement, eqn. (3a) transformed into

$$\phi_{j+1} = A_j\phi_{j-1} + B_j\phi_j \tag{4a}$$

where

$$B_j = B_j^0\frac{2 + \cos\phi_j}{2 + \cos\phi_{j-1}} + \left[\cos\theta_{j+1}\cos\phi_{j+1} + \frac{\dfrac{(2 + \cos\phi_{j-1})}{(2 + \cos\phi_{j+1})} - \cos\phi_j}{\sin\phi_j}\cdot\sin\phi_{j+1}\right]\cdot\frac{2 + \cos\phi_j}{2 + \cos\phi_{j+1}} \tag{4b}$$

Equation (4a) has the form of eqn. (2a) as desired. Namely, by linear combination of eqn. (3a) obtained for various j values, any three torsional angles in the pentagon may be related. We are aware, however, that for a complete analogy, the coefficients A_j and B_j have to be independent of the ring conformation. Considering eqn. (3b), it seems that A_j fulfills this requirement rather well, i.e. changes of bond lengths and valence angles are small in conformational changes. In addition, a strain introduced by

eventual enlargement of one bond length (d_{j-2}) may be partially compensated by diminishing adjacent valence angles (θ_{j-1}) or enlarging adjacent bond lengths (d_{j+2}). Hence, concerted changes keep A_j constant. For the other coefficient, B_j, the obtained eqn. (4b) is much more difficult to analyse. The critical part of the expression, the term in square brackets exhibits considerable resistance to change because of its analytical form in which the sines and cosines of the torsional angles mainly balance each other. However, we were not able to trace analytically the eventual overall constancy of B_j.

One specific problem in the calculation of B_j starting from the bond lengths and valence angles is the calculation of the sines of the torsional angles. We derived the expression for the calculation of the cosines of the torsional angles from the bond lengths and valence angles of a pentagon (see Appendix B). From there, one may calculate the magnitudes, but not the signs of the torsional angles. Fortunately, in eqn. (4b), the sines of the two adjacent torsional angles appear. Adjacent torsions are of opposite signs unless either of them is relatively small. In that case, the term containing sines becomes very small and does not contribute significantly to B_j. Therefore, by assuming that adjacent torsions are of opposite signs, B_j may be calculated relatively accurately. The relevant expressions are

$$B_j = B_j^0 \frac{2 + \cos\phi_j}{2 + \cos\phi_{j-1}} + \left[\cos\theta_{j+1}\cos\phi_{j+1} - \frac{\dfrac{(2 + \cos\phi_{j-1})}{(2 + \cos\phi_{j+1})} - \cos\phi_j}{(1 - \cos^2\phi_j)^{1/2}} \cdot \sqrt{1 - \cos^2\phi_{j+1}} \right] \times \frac{2 + \cos\phi_j}{2 + \cos\phi_{j+1}} \tag{5a}$$

$$\cos\phi_j = (2d_{j+1}d_{j-1}\sin\theta_j\sin\theta_{j+1})^{-1} \cdot [d_{j-1}^2 + d_j^2 + d_{j+1}^2 - d_{j-2}^2 - d_{j+2}^2 - 2d_jd_{j-1}\cos\theta_j - 2d_{j+1}(d_j - d_{j-1}\cos\theta_j)\cos\theta_{j+1} + 2d_{j-2}d_{j+2}\cos\theta_{j-2}] \tag{5b}$$

This is a method of calculating B_j without relying on the torsional angles. However, if the torsional angles are known, then B_j may be calculated from eqn. (4a) as follows:

$$B_j = \frac{(\phi_{j+1} - A_j\phi_{j-1})}{\phi_j} \tag{6}$$

For the investigation of a correspondence between eqns. (2a) and (4a), we shall start with the case of an equilateral pentagon. It is well known that for an equilateral pentagon, the pseudorotational coefficients take

trivial values: $c_{k+i} = 1$ and $\varepsilon_{k+i} = 0$. Inserting these values in eqn. (2a) one obtains

$$a_{1,-1,k} = -1 \qquad b_{1,-1,k} = 2\cos\delta = -(1 + 5^{1/2})/2$$

When ring-puckering is zero, an equilaterial pentagon becomes an equiangular one as well [7]. Then, from eqns. (3b) and (4b) one obtains

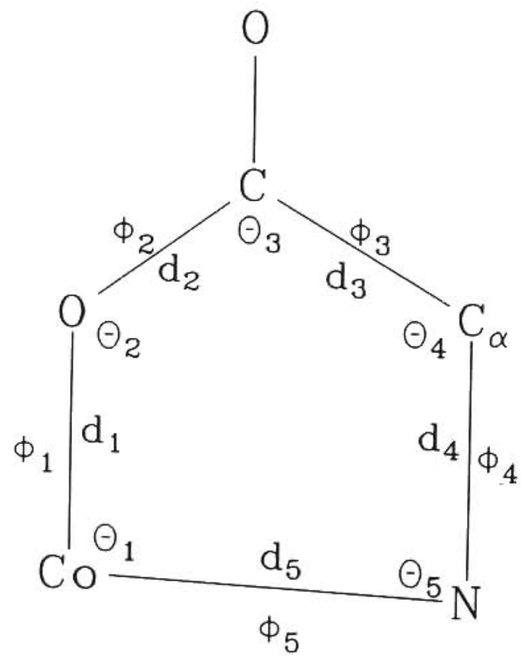
$$A_k = -1 \qquad B_k = 2\cos\theta - 1 = -(1 + 5^{1/2})/2$$

Therefore, the correspondence between eqns. (2a) and (4a) is complete in this limiting case.

When an equilateral pentagon becomes puckered, the valence angles become unequal. Then eqn. (3b) predicts that A_k has to be slightly different from -1, although the pseudorotational formula still requires that $a_{1,-1,k} = -1$. To keep $A_k = -1$, eqn. (3b) requires some inequality of the bond lengths as well. Thus, an inequality of bond angles of about 4° in highly puckered cyclopentane requires a bond length inequality of 0.02 Å. This difference of bond lengths is within the range of experimental error. Consequently, the experimental data on puckered cyclopentane can neither prove nor disprove the present theory. Therefore, the next consideration is very irregular pentagons.

Aminocarboxylato chelate rings in cobalt(III) complexes represent very irregular pentagons, with respect to both bond distances and valence angles (see Scheme 2), so they may be used for a rigorous test of the theory. For the present investigation, two hundred aminocarboxylato chelate ring conformations in cobalt(III) complexes were considered. The chelate ring geometries were taken from the Cambridge Crystallographic Database [8]. Various kinds of N- and C_α-substituted five-membered aminocarboxylato chelates, and glycinato chelates were considered. However, data have been taken only for the crystal structure analyses having $R \leqslant 0.06$. The typical geometry and ranges of the bond distances and the valence and torsional angles observed in the chelate rings considered are given in Scheme 2.

The system has been found to obey the pseudorotational relationship very well, since any three torsional angles are in a very good linear relationship, as required by eqn. (2a) (Fig. 1). For the test of theory we determined all $a_{-1,1,k}$ and $b_{-1,1,k}$ ($k = 1$–5) coefficients by regression analysis of experimental torsion angles according to eqn. (2a). Then we calculated A_j and B_j ($j = 1$–5) coefficients from the mean bond lengths and valence angles applying eqns. (3b) and (5). The comparison of the corresponding coefficients, which is presented in Table 1, strongly supports the equality of eqns. (2a) and (4a). We therefore conclude that the derived eqn. (4a) properly describes the pseudorotational relationship in five-membered ring



Average values

d_1 = 1.936 Å	θ_1 = 84.19°
d_2 = 1.284 Å	θ_2 = 115.02°
d_3 = 1.519 Å	θ_3 = 116.27°
d_4 = 1.487 Å	θ_4 = 109.59°
d_5 = 1.991 Å	θ_5 = 107.14°

Ranges

ϕ_1: 0-32°	d_1: 1.9-2.3 Å	θ_1: 72- 90°
ϕ_2: 0-24°	d_2: 1.2-1.3 Å	θ_2: 110-120°
ϕ_3: 0-42°	d_3: 1.4-1.6 Å	θ_3: 103-116°
ϕ_4: 0-55°	d_4: 1.4-1.6 Å	θ_4: 102-116°
ϕ_5: 0-47°	d_5: 1.8-2.3 Å	θ_5: 96-116°

Scheme 2.

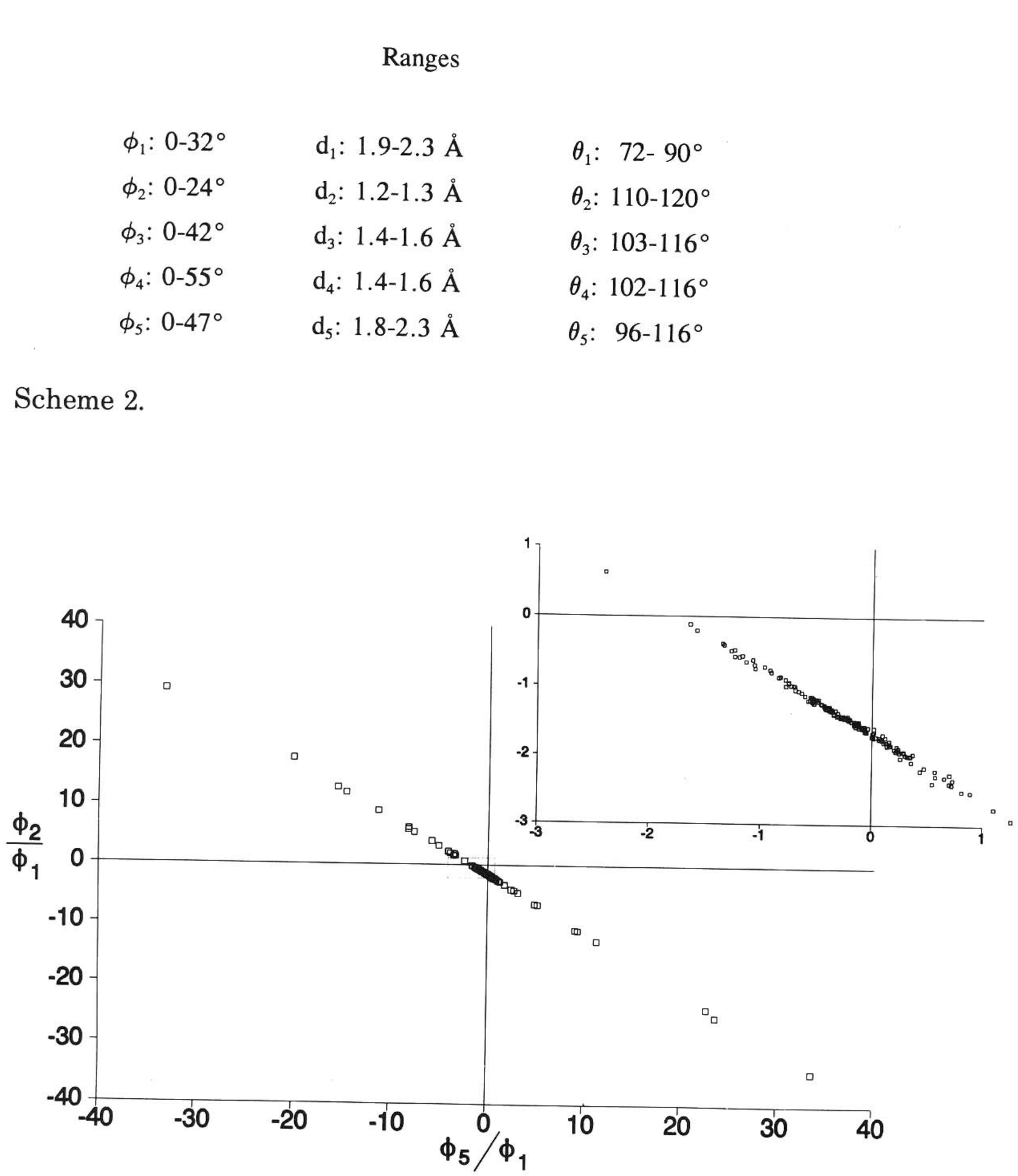


Fig. 1. Linear relationship between three sequential torsional angles for 200 aminocarboxylato five-membered chelate rings, according to eqn. (2a). Correlation coefficient of the displayed linear plot ($l = 1$, $m = -1$, $k = 1$) is 0.9998. For other relations investigated ($l = k + 1$, $m = k - 1$, $k = 2, 3, 4, 5$), correlation coefficients were close to 0.997. (The central area marked is enlarged in the upper right corner.)

TABLE 1

Comparison of the coefficients $a_{1,-1,k}$, $b_{1,-1,k}$ and A_k, B_k of the linear relationships between the three sequential torsional angles in the aminocarboxylato chelated rings. (The torsional angle numbering is given in Scheme 2.)

k	Coefficients from the torsional angles regression analysis (eqn. (2a))	Coefficients from the mean bond lengths and valence angles (eqns. (3b, 5a))	Coefficients from the bond lengths and valence angles (eqns. (3b, 4b)) of the single ring	Coefficients from the torsional angles (eqn. 6) of the single ring
	$a_{1,-1,k}$	A_k	A_k	
1	−1.05005	−1.04320	−1.02306	
2	−1.42437	−1.40320	−1.40895	
3	−0.92028	−0.92303	−0.92080	
4	−0.56934	−0.59718	−0.60262	
5	−1.21792	−1.22997	−1.25228	
	$b_{1,-1,k}$	B_k	B_k	B_k
1	−1.77862	−1.74329	−1.74890	−1.75687
2	−1.79002	−1.76871	−1.77513	−1.76943
3	−1.43188	−1.44429	−1.44939	−1.44540
4	−1.20800	−1.22252	−1.25616	−1.25660
5	−2.06380	−2.07950	−2.07567	−2.07462

conformations. At the same time, the empirical relationships eqns. (1) and (2) have established their theoretical buoyancy.

We consider the ability to predict the pseudorotational dynamics from a real ring conformation to be an important achievement. This is also illustrated in Table 1 by coefficients calculated from the structural parameters of a single ring. It may also be noted that values of B_j calculated from bond distances and valence angles (eqn. (5a)) and from torsional angles (eqn. (6)) do not differ significantly. Hence, the much simpler eqn. (6) may be used for calculation of B_j in a single ring.

CALCULATION OF THE PSEUDOROTATIONAL COORDINATES

The established equivalence of the coefficients of eqns. (2a) and (4a) allows calculation of the pseudorotational coordinates directly from a five-membered ring structure. By equating the corresponding coefficients, it follows that

$$A_k = \frac{c_{k+1}}{c_{k-1}} \cdot \frac{\sin(\varepsilon_{k+1} + \delta)}{\sin(\varepsilon_{k-1} - \delta)}$$

$$B_k = \frac{c_{k+1}}{c_k} \cdot \sin(\varepsilon_{k+1} + \delta)\,[\cot(\varepsilon_{k+1} + \delta) - \cot(\varepsilon_{k-1} - \delta)] \tag{7}$$

which in combination with eqns. (2c) and (1) gives

$$\tan\omega_k = \cot(\varepsilon_{k+1} + \delta) - \frac{1}{B_k} \cdot [\cot(\varepsilon_{k+1} + \delta) - \cot(\varepsilon_{k-1} - \delta)] \cdot \frac{\phi_{k+1}}{\phi_k}$$

$$= \cot(\varepsilon_{k-1} - \delta) - \frac{A_k}{B_k} \cdot [\cot(\varepsilon_{k+1} + \delta) - \cot(\varepsilon_{k-1} - \delta)] \cdot \frac{\phi_{k-1}}{\phi_k}$$

$$\Phi_k = \frac{\phi_k}{c_k} \cdot (1 + \tan^2\omega_k)^{1/2} \tag{8}$$

A direct relationship between ω_k and ϕ_k and the structural parameters is obscured here by the presence of three pseudorotational coefficients (ε_{k+1}, ε_{k-1} and c_k) out of the nine defined in eqn. (1). Since only six of these parameters are necessary, we shall put $\varepsilon_{k+1} = \varepsilon_{k-1} = 0$ and $c_k = 1$, to obtain

$$\tan\omega_k = \cot\delta\left(1 - \frac{2}{B_k} \cdot \frac{\phi_{k+1}}{\phi_k}\right)$$

$$= -\cot\delta\left(1 + \frac{A_k}{B_k} \cdot \frac{\phi_{k-1}}{\phi_k}\right)$$

$$\Phi_k = \phi_k(1 + \tan^2\omega_k)^{1/2} \tag{9}$$

Hence, the pseudorotational coordinates may be calculated without know-

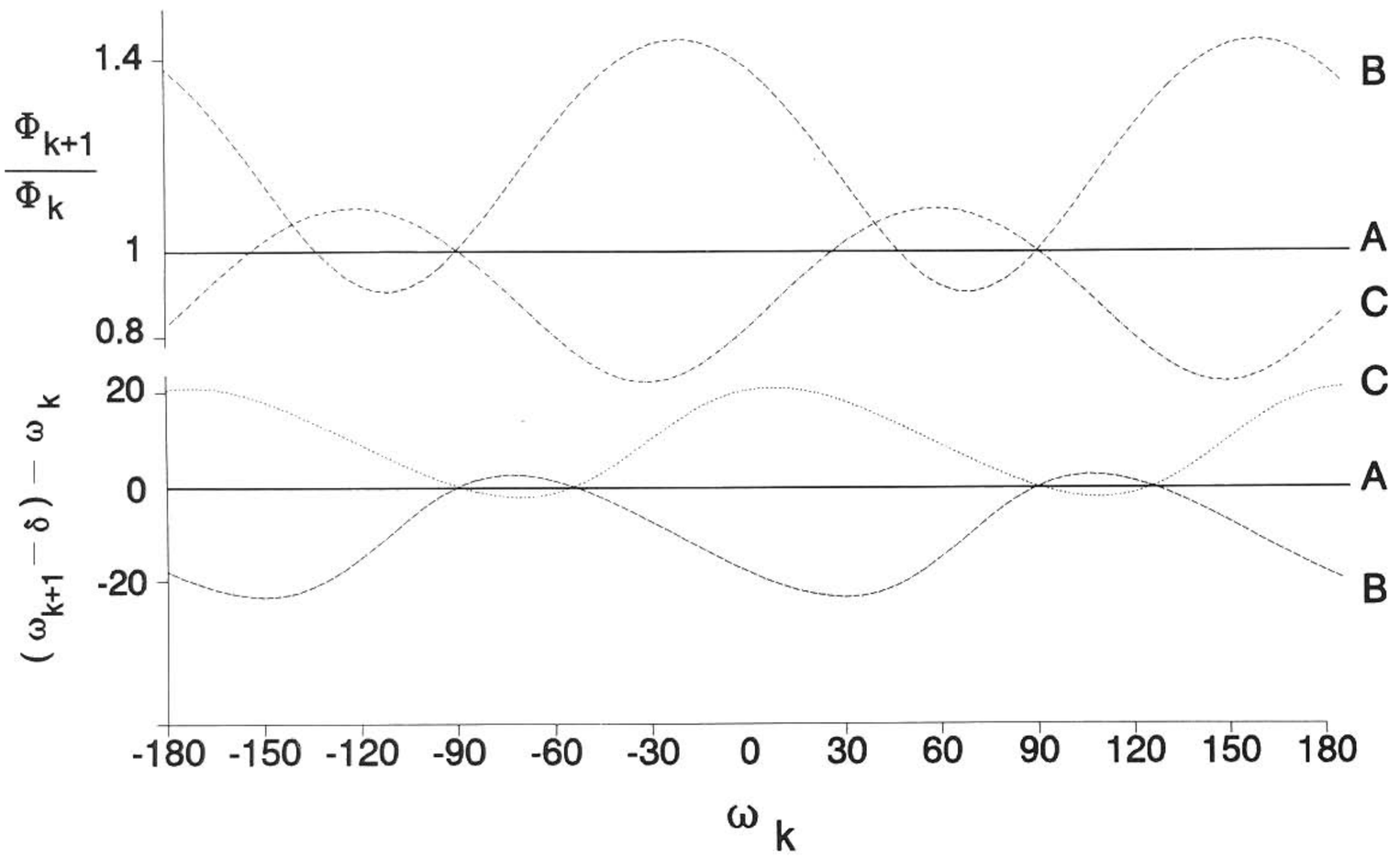


Fig. 2. Phase angle and puckering amplitude dependence on choice of an origin (ω_k or ω_{k+1}) for counting of torsional angles in a pentagon represented as functions of ω_k phase angle. (A) Equilateral, equiangular ($Q_k = -4/(1 + 5^{1/2})^2$) pentagon; (B) irregular ($Q_k = -0.5$) pentagon; (C) irregular ($Q_k = -0.3$) pentagon.

ledge of the pseudorotational coefficients ε_{k+i} and c_{k+i}. This is an important aspect in which the procedure devised here for the calculation differs from previous procedures, which required, as the first step, the determination of the pseudorotational coefficients ε_{k+i} and c_{k+i}. This was done by fitting eqn. (1) to a large set of ring conformations [9] or by calculation of the coefficients from an idealized geometry of a flat ring [4]. In the procedure presented here the first step is calculation of the pseudorotational coefficients A_j and B_j from a considered ring geometry. These coefficients contain the same information as the ε_{k+i} and c_{k+i} coefficients.

The question may be raised as to how representative the coefficients ω_k and Φ_k are for a ring. One would expect that classification of ring conformations in terms of the pseudorotational coordinates does not depend critically on the choice of an origin for measuring the torsional angles. this would be fulfilled if, between any ω_k and ω_{k+1} for a ring, there is a difference close to the step angle δ. To get an insight into this problem we derived the following relations from eqn. (9).

$$\omega_{k+1} - \delta = \arctan\left\{\cot\delta \cdot \left[1 + \frac{1 + \tan^2\delta}{4Q_k} \cdot (1 - \tan\omega_k \tan\delta)\right]\right\}$$

$$\frac{\Phi_{k+1}}{\Phi_k} = \frac{B_k}{2} \cdot (1 - \tan\omega_k \tan\delta) \cdot \left(\frac{1 + \tan^2\omega_{k+1}}{1 + \tan^2\omega_k}\right)^{1/2} \tag{10}$$

where $Q_k = A_{k+1}/B_k B_{k+1}$.

The analysis of these relations is presented in Fig. 2. It can be seen that

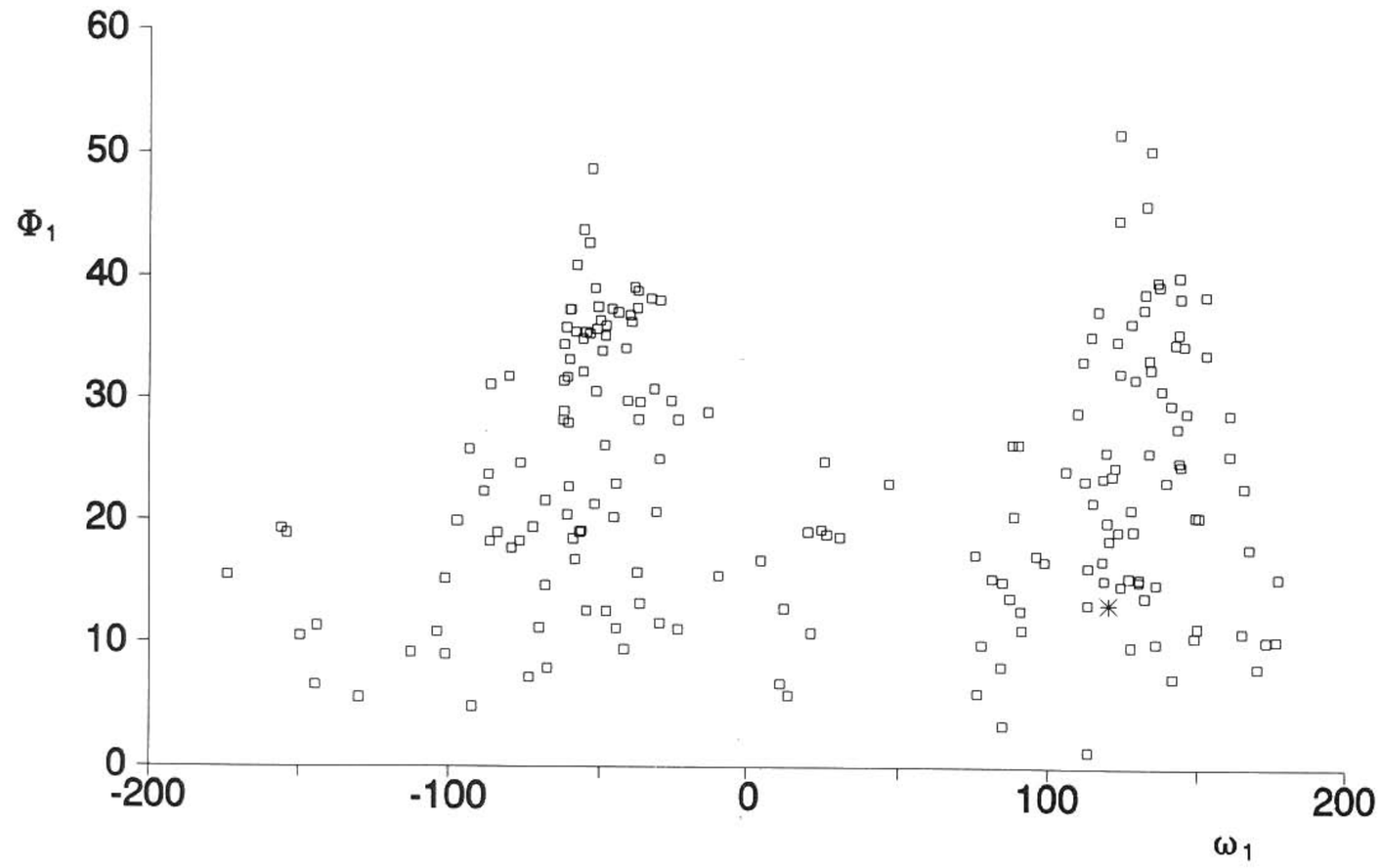


Fig. 3. Scattergram of pseudorotational coordinates, the ring puckering amplitude Φ_1 and phase angle ω_1 of 200 aminocarboxylato five-membered chelate ring conformtions in cobalt(III) complexes. (Characteristic ring, from which the coefficients in Table 1 were calculated, is marked by an asterisk (*).)

the choice of an origin only has no influence for a flat equilaterial pentagon ($Q_k = -4/(1 + 5^{1/2})^2$). In other cases the phase angle may be shifted appreciably. However, a shift as large as 18° is unlikely even for rings quite different from the equilateral, equiangular one. Hence, the classification of conformations according to the symmetry forms separated by 18° should be mainly independent of the origin. It is interesting that in the case of a neighboring torsion equal to zero ($\omega_k = -90°, -54°, 90°, 126°$), the phase angle remains unshifted for irregular pentagons.

In the classification of the considered aminocarboxylato chelate conformations, the observed influence of zero neighboring torsion has been taken into account. We assigned ϕ_k equal to ϕ_1, because the torsional angle ϕ_2 is mainly close to zero. Then the pseudorotational coordinates were calculated for 200 rings, applying eqn. (9).

We should point out that a degeneracy of the phase angle, introduced by the tangent function in eqn. (9), has been lifted in the following way:

$$\omega'_k = \arctan\left[\tan\delta\left(1 - \frac{2}{B_k} \cdot \frac{\phi_{k+1}}{\phi_k}\right)\right]$$

$$\omega_k = \frac{\omega'_k}{|\omega'_k|} \cdot \left(\frac{\phi_k}{|\phi_k|} - 1\right) \cdot 90° \qquad (11)$$

The obtained scattergram of conformational coordinates of the aminocarboxylato chelate rings in cobalt(III) complexes, which is presented in Fig. 3 will be discussed later.

TRANSFORMATION OF THE PSEUDOROTATIONAL COEFFICIENTS

The pseudorotational coefficients A_j and B_j may be transformed into the ε_{k+i} and c_{k+i} coefficients by applying eqn. (2a). This equation contains coefficients $a_{l,m,k}$ and $b_{l,m,k}$ of which only six are linearly independent, as previously stressed. The coefficients A_j, B_j and ε_{k+i}, c_{k+i} are connected through these. The six coefficients are defined by three equations of the form eqn. (2a). Without any loss of generality, we may select three equations which are obtained from eqn. (4a) by taking $j = k$, $k + 1$, $k + 2$. After writing down these equations

$$\phi_{k+1} = A_k\phi_{k-1} + B_k\phi_k$$

$$\phi_{k+2} = B_k\phi_{k+1} + A_k\phi_k$$

$$\phi_{k-2} = (A_{k+2} + B_{k+1}B_{k+2})\phi_{k+1} + A_{k+1}B_{k+2}\phi_k \tag{12}$$

and comparing them with the general eqn. (2a), the corresponding $a_{l,m,k}$ and $b_{l,m,k}$ coefficients are identified as

$$a_{1,-1,k} = A_k \qquad b_{1,-1,k} = B_k$$

$$a_{2,1,k} = B_{k+1} \qquad b_{2,1,k} = A_{k+1}$$

$$a_{-2,1,k} = A_{k+2} + B_{k+1}B_{k+2} \qquad b_{2,1,k} = A_{k+1}B_{k+2}$$

In combination with eqns. (2b) these give the six equations:

$$\frac{c_k}{c_{k+1}} = \frac{1}{B_k}\sin(\varepsilon_{k+1} + \delta)\,[\cot(\varepsilon_{k+1} + \delta) - \cot(\varepsilon_{k-1} - \delta)]$$

$$\frac{c_k}{c_{k+2}} = \frac{Q_k}{A_{k+1}} \cdot \sin(\varepsilon_{k+2} + 2\delta)\,[\cot(\varepsilon_{k+1} + \delta) - \cot(\varepsilon_{k-1} - \delta)]$$

$$\frac{c_k}{c_{k-2}} = \frac{R_k}{A_{k+1}B_{k+2}}\sin(\varepsilon_{k-2} - 2\delta)\,[\cot(\varepsilon_{k+1} + \delta) - \cot(\varepsilon_{k-1} - \delta)]$$

$$\frac{c_k}{c_{k-1}} = \frac{A_k}{B_k}\sin(\varepsilon_{k-1} - \delta)\,[\cot(\varepsilon_{k+1} + \delta) - \cot(\varepsilon_{k-1} - \delta)]$$

$$\cot(\varepsilon_{k+2} + 2\delta) = (Q_k + 1)\cot(\varepsilon_{k+1} + \delta) - Q_k\cot(\varepsilon_{k-1} - \delta)$$

$$\cot(\varepsilon_{k-2} - 2\delta) = (R_k + 1)\cot(\varepsilon_{k+1} + \delta) - R_k\cot(\varepsilon_{k-1} - \delta) \tag{13}$$

where

$$R_k = \frac{A_{k+1}B_{k+2}}{B_k(A_{k+2} + B_{k+1}B_{k+2})}$$

After applying the same choice of coefficients as before ($\varepsilon_{k+1} = \varepsilon_{k-1} = 0$, $c_k = 1$) one obtains

$$\varepsilon_{k+2} = \operatorname{arccot}[(1 - 2Q_k)\cot\delta] - 2\delta + 360°$$

$$\varepsilon_{k-2} = \operatorname{arccot}[(1 - 2R_k)\cot\delta] + 2\delta - 360°$$

$$c_{k+1} = \frac{B_k}{2\cos\delta}$$

$$c_{k+2} = B_k B_{k+1}[\tan^2\delta + (1 + 2Q_k)^2]^{1/2}$$

$$c_{k-2} = A_{k+1}\frac{B_{k+2}}{R_k}[\tan^2\delta + (1 + R_k)^2]^{1/2}$$

$$c_{k-1} = -\frac{B_k}{2A_k\cos\delta} \tag{14}$$

It has already been shown that the A_j and B_j coefficients are fairly constant over two hundred aminocarboxylato chelates. From eqns. (14), it is evident that the coefficients ε_{k+i} and c_{k+i} have to be constant as well. In order to illustrate this requirement, the coefficients for rings covering a whole range of conformations were calculated and are presented in Table 2. In addition, the coefficients calculated from A_j and B_j, which themselves have been obtained by regression analysis of the torsional angles, or from the mean bond lengths and valence angles, are presented. As can be seen, the coefficients are fairly constant; some deviation is observed for the extremely puckered ring.

REPRODUCTION OF TORSIONAL ANGLES

A classical test of the validity of the pseudorotational coefficients is the reproduction of the torsional angles by the pseudorotational formula (eqn. (1)). Our claim is that the coefficients ε_{k+i} and c_{k+i}, calculated from the A_j and B_j coefficients, which themselves are derived from the bond distances and valence angles of individual rings, could well be applied to all ring conformations.

However, the pseudorotational coefficients taken from one ring do not allow an exact reproduction of all the torsional angles in another ring. Therefore, the average values of the pseudorotational coordinates should be calculated in order to reproduce the torsional angles with equal accuracy. For that purpose the average phase angle is obtained as

$$\overline{\omega_k} = \tfrac{1}{4}(\omega_{k/k+1} + \omega_{k/k+2} + \omega_{k/k-2} + \omega_{k/k-1}) + \frac{\omega_{k/k+1}}{|\omega_{k/k+1}|}\left(\frac{\phi_k}{|\phi_k|} - 1\right)\cdot 90°$$

$$\omega_{k/k+i} = \arctan\left[\cot(\varepsilon_{k+i} + \delta) - \frac{c_k/c_{k+i}}{\sin(\varepsilon_{k+i} + \delta)}\cdot\frac{\phi_{k+i}}{\phi_k}\right] \tag{15}$$

TABLE 2

Pseudorotational coefficients, calculated from the structures of aminocarboxylato chelate rings of different conformations, compared with those calculated from the coefficients of torsional angles regression analysis for 200 aminocarboxylato chelate rings, and with those calculated from the mean bond lengths and valence angles of the same 200 rings. In the last column, the standard deviation of torsional angles reproduction (eqn. (17) is given for 1000 angles of the considered rings.

Origin of calculation	ω_1	Φ_1	ε_3	ε_4	c_1	c_2	c_1	c_3	c_4	σ
Structures of	−156.3	17.22	−12.38	−14.58	1	1.12054	1.22070	1.25151	1.04790	0.64
aminocarboxylato	−76.5	17.99	−10.89	−12.65	1	1.06000	1.12741	1.18996	1.06554	0.50
chelate rings	−65.6	13.56	−11.26	−11.81	1	1.06377	1.11986	1.20746	1.04070	0.41
of different	−46.1	18.96	−11.09	−13.35	1	1.07100	1.10892	1.16989	1.02120	0.40
conformations	4.5	5.82	−10.36	−12.52	1	1.0883	1.11817	1.19480	1.05010	0.44
	85.1	3.14	−11.00	−11.94	1	1.06914	1.13142	1.20489	1.03969	0.39
	113.7	12.01	−10.90	−11.65	1	1.08240	1.13417	1.21642	1.05800	0.43
	132.8	42.34	−17.94	−25.95	1	1.07141	1.00748	1.15940	1.03659	0.79
	134.1	12.45	−8.41	−13.12	1	1.09027	1.10928	1.19538	1.02020	0.56
	178.9	9.45	−13.83	−13.26	1	1.05309	1.12206	1.25502	1.06010	0.48
Regression of torsional angles			−9.76	10.59	1	1.09925	1.16863	1.20886	1.04685	0.39
Mean bond lengths and valence angles			−10.95	−12.33	1	1.07741	1.12863	1.19705	1.03280	0.38

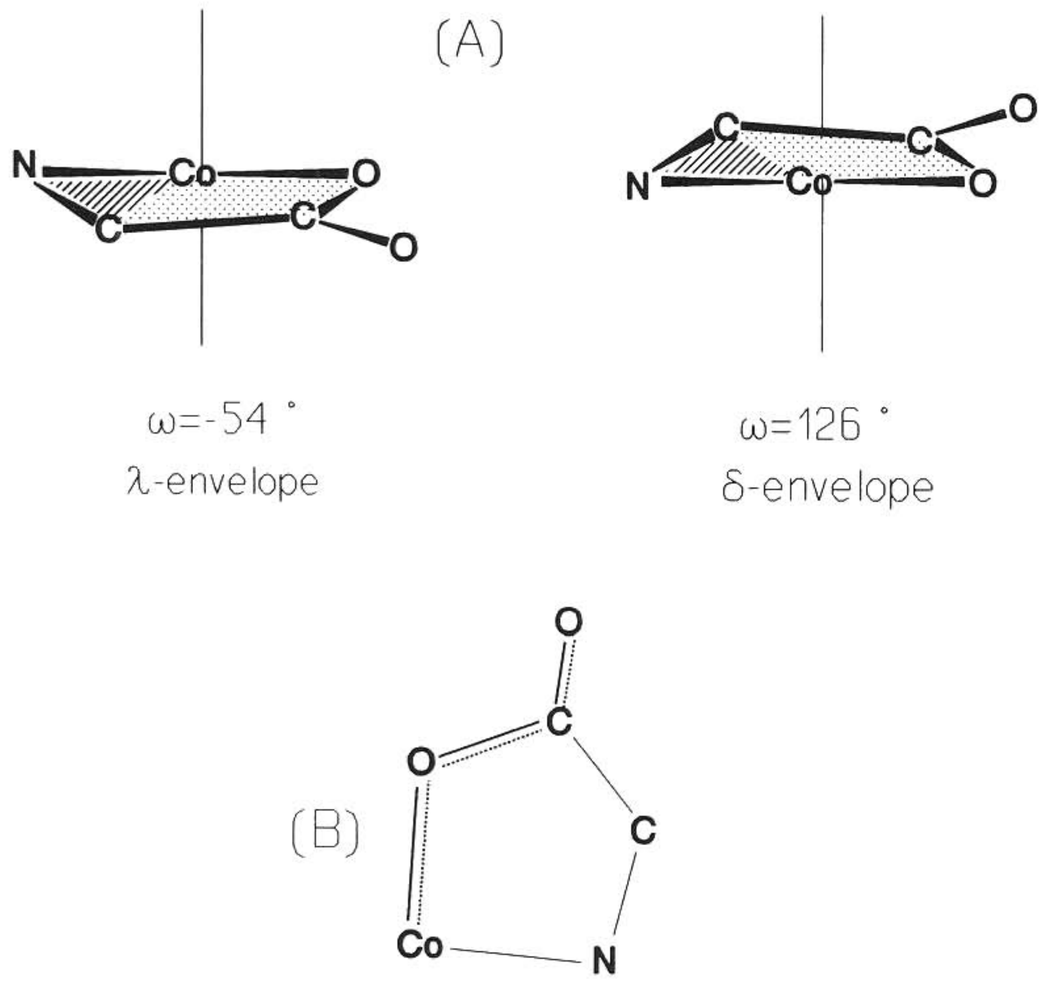


Fig. 4. Favored conformations of aminocarboxylato chelate rings in (A) cobalt(III) complexes could be explained by π-delocalization along (B) Co–O–C–O bonds.

and the average puckering amplitude as

$$\overline{\Phi_k} = \left[\frac{\sum_i \left(\frac{\phi_{k+i}}{c_{k+i}} \right)^2}{\sum_i \cos^2(\overline{\omega_k} + \varepsilon_{k+i} + \delta)} \right]^{1/2} \tag{16}$$

The torsional angles are then reproduced by the pseudorotational formula

$$\phi_{k+i} = c_{k+i} \overline{\Phi_k} \cos(\overline{\omega_k} + \varepsilon_{k+i} + i\delta) \tag{17}$$

For the considered set of aminocarboxylato chelate rings, the torsional angles were reproduced using the coefficients given in Table 2. Very good reproduction of the torsional angles was generally achieved (the standard deviation was approximately 0.4°, see Table 2). Especially important is the fact that the coefficients derived from one ring were appropriate for all of the 200 rings. Hence, we may conclude that our direct method of calculation of the pseudorotational parameters is relatively accurate.

AMINOCARBOXYLATO CHELATE RING CONFORMATIONS IN COBALT(III) COMPLEXES

The investigation of the conformations of aminocarboxylato chelate rings in cobalt(III) complexes has been our long-term interest [10]. It is generally believed that five-membered aminocarboxylato chelate rings do not possess favored conformations, i.e. conformational energy minima [11]. The classification of a small number of aminocarboxylato chelate ring

conformations in terms of the pseudorotational parameters [6] did not contradict this belief.

The scattergram (Fig. 3) of the aminocarboxylato chelate ring pseudorotational coordinates is very interesting in that it shows that this ring does possess favored conformations. The phase angle of pseudorotation (ω_1) is heavily centered around two values, $-54°$ and 126°. About 40% of the examined rings have a pseudorotational phase of $126 \pm 20°$, which corresponds to the δ-envelope conformation having the torsional angle around the O–C bond which is close to zero (see Fig. 4A). About 40% of the examined rings have a pseudorotational phase of $-54 \pm 20°$, which corresponds to the λ-envelope conformation having the torsional angle around the O–C bond which is also close to zero. For C_α-substituted aminocarboxylato chelate rings and for glycinato chelate rings, the pseudorotational phases are found almost exclusively in the above specified regions. This strong preference of the aminocarboxylato chelate ring conformations for a Co–O–C–C torsional angle close to zero was not clearly observed in the previous pseudorotational classification of a much smaller number of aminocarboxylato chelates [6]. However, such behavior could well be a consequence of π-delocalization of electrons along the Co–O–C–O bonds (Fig. 4B). This delocalization has been considered important in connection with the trans influence of an aminocarboxylato chelate carboxylato group on the shortening of the Co–NO_2 bond [12].

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APPENDIX A: SINES RULE FOR A PENTAGON

To the four planes containing the valence angles θ_{j-1}, θ_j, θ_{j+1} and θ_{j+2}, the corresponding perpendicular planes containing the torsional angles ϕ_{j-1},

ϕ_j and $-\phi_{j+1}$ are raised (Fig. A1). These three planes are constructed so that they possess a common point A, in which the bonds d_{j+2} and d_{j-2} are joined. From the planes containing the valence angles θ_j and θ_{j+1}, the vertical lines h_{j+1} and h_{j-1}, respectively, are raised to the point A, so that three rectangular triangles containing the torsional angles $-\phi_{j-1}$, $-\phi_j$ and ϕ_{j+1} are formed. For these triangles, the following trigonometric relationships hold:

$$h_j = l\tan(\phi_j)$$
$$h_{j+1} = d_{j+2}\sin(\theta_{j+2}) \cdot \sin(-\phi_{j+1})$$
$$h_{j-1} = d_{j-2}\sin(\theta_{j-1}) \cdot \sin(\phi_{j-1}) \qquad \text{(A1)}$$

where

$$l = \frac{d_{j+1} - d_{j+2}\cos(\theta_{j+2})}{\cos(\alpha)}\sin(\theta_{j+1} - \alpha)$$

$$tg\alpha = \frac{d_{j+2}\sin(\theta_{j+2})\cos(\phi_{j+1})}{d_{j+1} - d_{j+2}\cos(\theta_{j+2})} \qquad \text{(A2)}$$

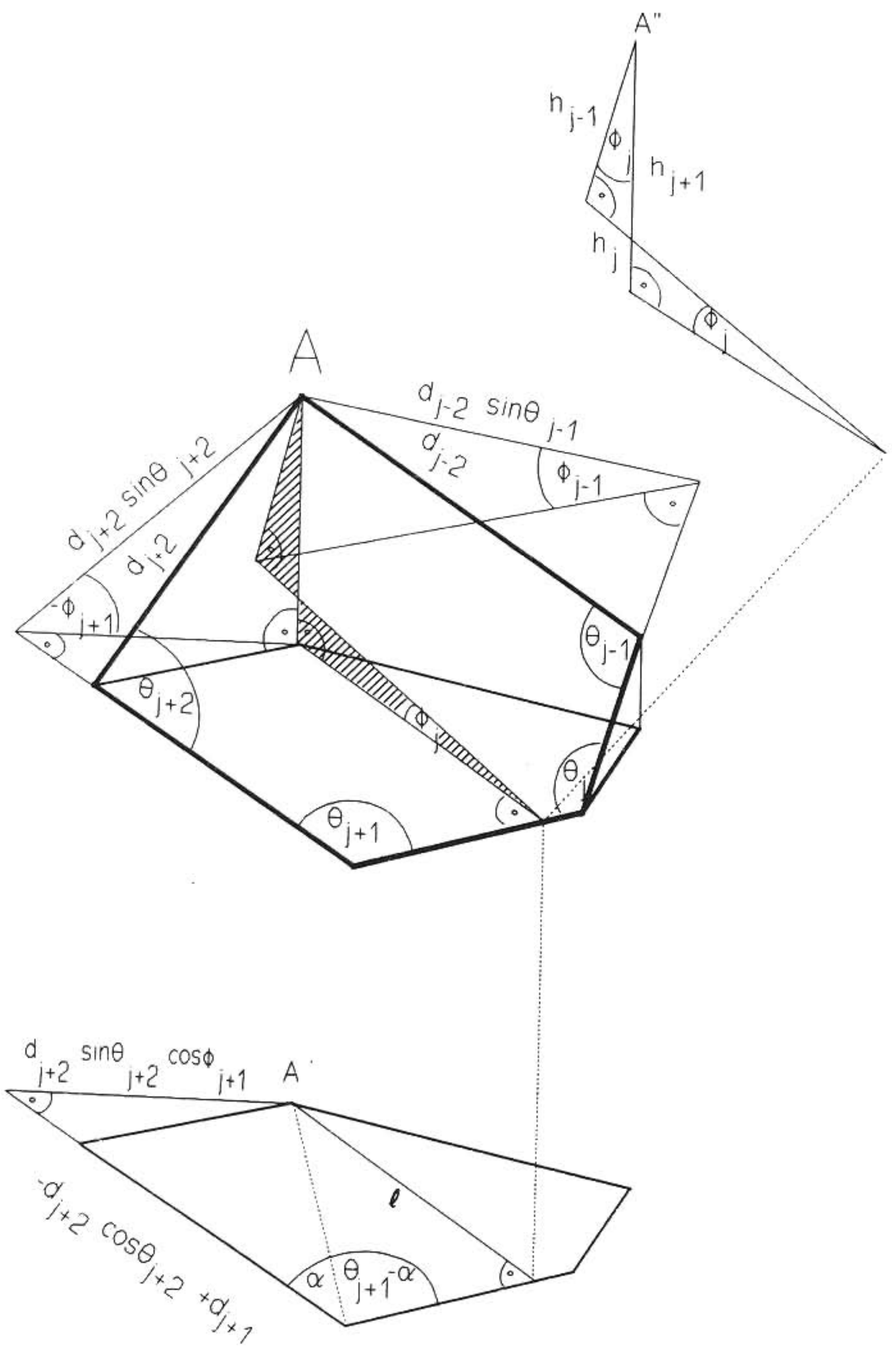

Fig. A1. Geometry of an irregular, puckered pentagon. Four planes, containing valence angles θ_{j-1}, θ_j, θ_{j+1}, θ_{j+2}, and corresponding perpendicular planes containing torsional angles ϕ_{j-1}, ϕ_j, $-\phi_{j+1}$ are drawn. Trigonometry on which calculations are based is presented in two projections.

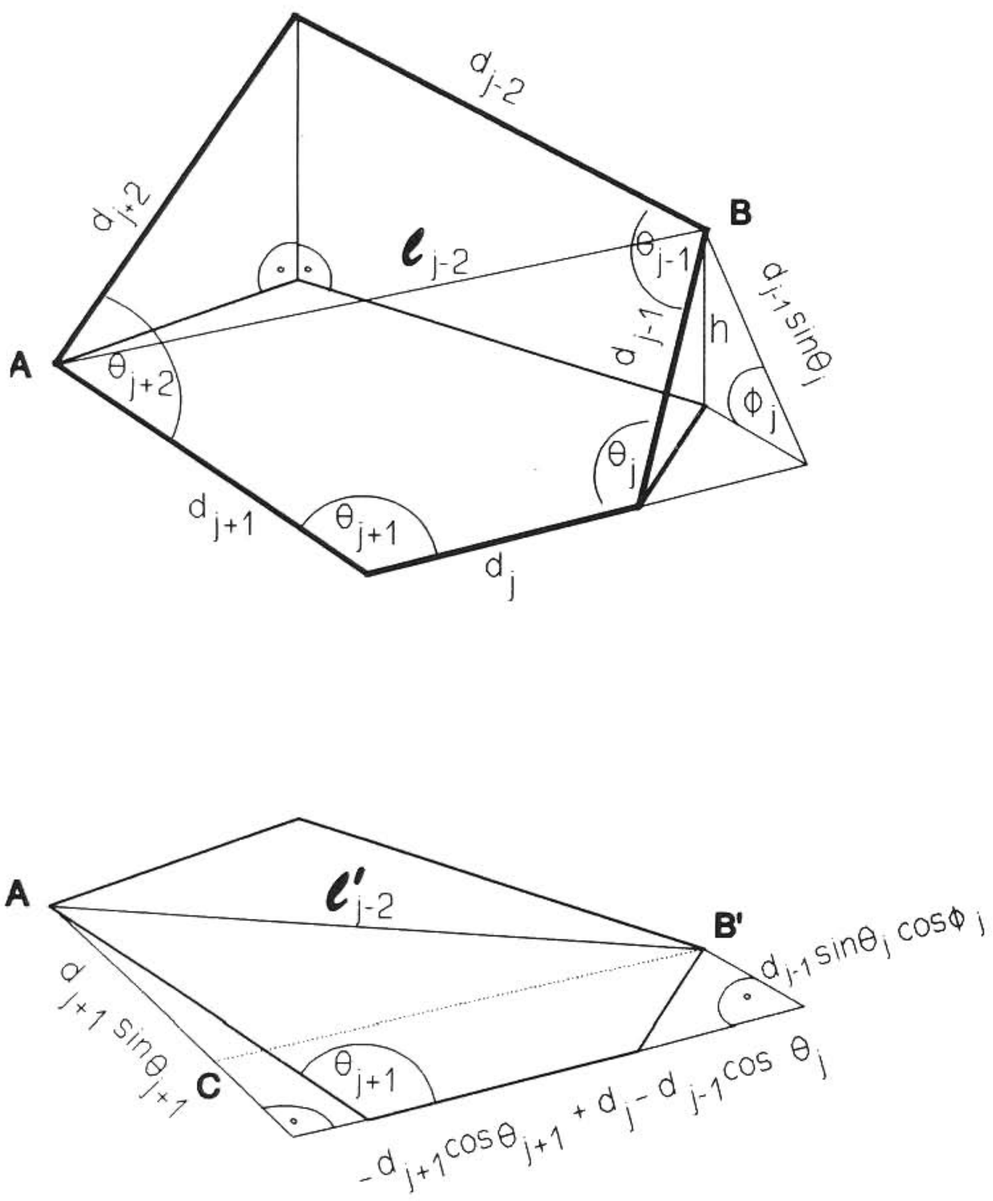

Fig. B1. Geometry of an irregular, puckered pentagon. Diagonal line is projected on to the plane containing valence angle θ_{j+1} and two triangles are formed, ABB' and $AB'C$.

From the two perpendicular rectangular triangles (shaded triangles in Fig. A1), the general relationship follows:

$$h_{j-1} = (h_{j+1} - h_j)\cos(\phi_j) \tag{A3}$$

which in combination with eqn. (A1) gives directly the relationship between the sines of the torsional angles stated in eqn. (3).

APPENDIX B: COSINE RULE FOR THE TORSIONAL ANGLES IN A PENTAGON

In a pentagon, a diagonal line l_{j-2} is constructed so as to close a triangle containing the valence angle θ_{j-2} and the bonds d_{j+2} and d_{j-2} (Fig. B1). The cosine rule for this triangle gives

$$l_{j-2}^2 = d_{j+2}^2 + d_{j-2}^2 - 2d_{j+2}d_{j-2}\cos\theta_{j-2} \tag{B1}$$

The pentagon is then projected on to the plane containing the valence angle θ_{j+1}. Between the diagonal line l_{j-2} and its projection, the following relation is established (triangle ABB'):

$$l_{j-2}^2 = h^2 + l_{j-2}'^2 \tag{B2}$$

Now, h may be calculated from the triangle containing the torsional angle ϕ_j:

$$h = d_{j-1}\sin\theta_j\sin\phi_j \tag{B3}$$

while l'_{j-2} may be calculated from the triangle AB′C constructed on the projected pentagon:

$$l'^2_{j-2} = (d_j - d_{j+1}\cos\theta_{j+1} - d_{j-1}\cos\theta_j)^2 + (d_{j+1}\sin\theta_{j+1} - d_{j-1}\sin\theta_j\cos\phi_j)^2 \tag{B4}$$

By eliminating l_{j-2}, l'_{j-2}, and h from eqns. (B1)–(B4), one obtains the expression for $\cos\phi_j$ given in eqn. (5b). That expression may also be put in the form

$$\cos\phi_j = \frac{l_j^2 + l_{j+1}^2 - l_{j-2}^2 - d_j^2}{2d_{j+1}d_{j-1}\sin\theta_j\sin\theta_{j+1}} + \cot\theta_j\cot\theta_{j+1}$$

$$l_r^2 = d_r^2 + d_{r+1}^2 - 2d_r d_{r+1}\cos\theta_r \quad r = j, j+1, j-2 \tag{B5}$$