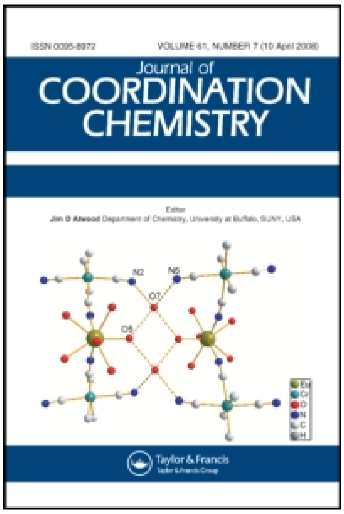

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CONFORMATIONS OF Co(III)(AMINOACIDATO) CHELATE RINGS. THE CONCEPT OF PSEUDOROTATION

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CONFORMATIONS OF Co(III)(AMINOACIDATO) CHELATE RINGS. THE CONCEPT OF PSEUDOROTATION

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The relationship between torsion angles in Co(III)(α-amino-acidato) five-membered rings and pseudorotational coordinates was established on the basis of experimental data. The pseudorotational parameters are useful for classification and demonstration of conformations in two dimensions. A mean geometry of the ring, correlations between structural parameters and factors influencing the geometry are discussed.

INTRODUCTION

The concept of pseudoration was introduced by Kilpatrick *et al.*,[1] for the description of the non-planarity of cyclopentane, (*1*),

$$z_i = (2/5)^{1/2}\cdot q\cdot \cos(\omega + 4\pi i/5), \quad i = 0, 1, 2, 3, 4 \tag{1}$$

where q is the amplitude of puckering, ω is the phase angle, and z_i is the height of atom i from the mean plane of the ring. This concept was later generalized by Cremer and Pople[2] for any monocyclic puckered ring. Altona[3-5] described pseudorotation in terms of torsion angles, an approach which is more convenient from the practical point of view as well as from the torsion energy insight. Altona's approach was theoretically generalized by Diez *et al.*,[6] to any puckered ring.

In this paper the pseudorotational concept was successfully applied to a classification and description of conformations of Co(III)(α-aminoacidato) chelate rings on the basis of a purely empirical analysis of experimental data. Description of conformations of this highly heterogenous systems is difficult due to lack of symmetry and the promulgation of arbitrary terms like "deformed envelope conformation". There is no compilation on the geometry of Co(III)(α-aminoacidato) complexes in the literature but the existence of the Cambridge Crystallographic Data Base[7] offers a unique chance to examine these systems. Older work on metal complexes of amino acids are based mainly on Cu(II) complexes.[8,9]

CALCULATIONS

Data

The Cambridge Crystallographic Data Base[7] was used for the data collection *via* the connectivity search program CONNSER. The search was originally for Co(III) complexes of α-aminoacids with uncoordinated side chains in order to avoid chelate rings with forced conformations (and far from an energy minimum). A list of the compounds used is given in Table I. Separately listed are data for glycine (Gly) complexes (14 chelate rings) and other amino-acid (Aa) complexes

TABLE I

A list of compounds with CCDB reference code, numbers for chelate rings used in Figures, compound name, and reference.

Co(Gly) complexes

AMGZCO, (1,3): Amineglycinato(1,4,7-triazacyclononane) cobalt(III) diiodide hydrate.
S. Sato *et al., Acta Cryst.* **B36**, 43 (1980).

COTRGL10, (10,13): (*SR*), (*RS*)-(triethylenetetramine)glycinatocobalt(III) chloride monohydrate.
D.A. Buckingham *et al., Inorg. Chem.* **14**, 1739 (1975).

GLAECO, (4,5): *Mer-cis(N)-cis(O)*-bis(glycinato)aminoethanolatocobalt(III) monohydrate.
H. Miyamae and Y. Saito, *Acta Cryst.*, **B34**, 937 (1978).

GLCOEN, (7): Glycinato(tris(2-aminoethyl)amine)cobalt(III) diperchlorate
Y. Mitsui *et al., J. Chem. Soc., Dalton Trans.*, 2095 (*1976*).

NDGACO, (11,14): Nitrodi(glycinato)amminecobalt(III) monohydrate.
P. Vasic *et al. Acta Cryst.*, **B32**, 91 (1976).

NGLACO, (8): Potassium trinitro(glycinato)amminecobalt(III) monohydrate.
R. Herak and B. Prelesnik, *Z. Anorg. Allg. Chem.*, **427**, 91 (1976).

TENCOG10, (2,6,12): (*RR*), (*RS*)-B(glycinato)(triethylenetetramine)cobalt(III) iodide hemihydrate.
D.A. Buckingham *et al., J. Am. Chem. Soc.*, **96**, 1713 (1974).

TRGLCO10, (2): Glycinato(tris(2-aminoethyl)amine)cobalt(III) chloride perchlorate.
Y. Mitsui *et al., J. Chem. Soc., Dalton Trans.*, 2095 (*1976*).

TRGLCP, (9): (RR), (SS)-(triethylenetetramine)glycinatocobalt(III) iodide trihydrate.
B.F. Anderson *et al., Inorg. Chem.* **16**, 3233 (1977).

Co(Aa) complexes

ALANCO, (17,19,21): *Mer*-tris(S-alaninato)cobalt(III) monohydrate.
R. Herak, B. Prelesnik and I. Krstanovic, *Acta Cryst.*, **B34**, 91 (1978).

ASPCOT, (22,25,29): *Fac*-delta-tris(S-asparaginato)cobalt(III) trihydrate.
M. Sekizaki, *Bull. Chem. Soc. Jpn.*, **52**, 403 (1979).

CYSENC10, (26): μ-Cysteinatobis(bis(ethylenediamine)cobalt(III)) perchlorate hexahydrate.
P.A. Tucker, *Acta Cryst.* **B35**, 71 (1979).

EALNCO, (18): S-Asparaginatobis(ethylenediamine)cobalt(III) iodide nitrate.
W.E. Keyes *et al., J. Am. Chem. Soc.*, **98**, 6939 (1976).

GLUCOE, (28): S-Glutamatobis(ethylenediamine)cobalt(III) perchlorate.
R.D. Gillard, N.C. Payne and G.B. Robertson, *J. Chem. Soc. A* 2579 (*1970*).

HHALCO, (20): (α-*N*-(*o*-Hydroxybenzyl)-S-histidinato)(S-alaninato)cobalt(III) dihydrate.
K.E. Voss, R.J. Angelici and R.A. Jacobson, *Inorg. Chem.*, **17**, 1922 (1978).

ILESCO, (15): S-Isoleucinato-(*N,N'*-ethylenebis(α-methylsalicylideneaminato))cobalt(III) sesquihydrate.
Y. Kushi *et al., Chem. comm.*, 266 (*1978*).

NARGCO, (16,24): Dinitrobis(S-arginine)cobalt(III) nitrate dihydrate.
W.H. Watson, *et al., Inorg. Chim. Acta*, **6**, 591 (1972).

NCOALA, (27): Silver(I) *cis*-dinitrobis(R-alaninato)cobaltate(III).
R. Herak *et al., Acta Cryst.*, **B30**, 229 (1974).

PAACCO, (23): S-Phenylalaninatobis(acetylacetonato)cobalt(III) chloroform solvate.
R. Fink, D. Revus and D. van der Helm, *Acta Cryst.*, **B33**, 1660 (1977).

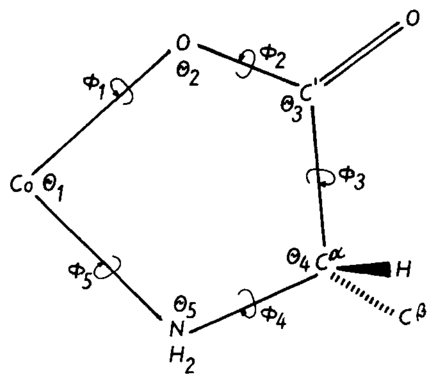

FIGURE 1 Co(III)(α-aminoacidato) chelate ring with numbering of torsion angles (ϕ_i) and bond angles (Θ_i).

(15 chelate rings). The type of chelate ring and the numbering scheme adopted is shown in Figure 1.

Pseudorotational parameters

A correlation was found among torsion angles within each chelate ring. Each torsion angle can be expressed as a linear combination of two others, (*2*),

$$\phi_i = a_{ij}\phi_j + a_{ik}\phi_k \qquad (2)$$

where a_{ij} are constants determined by least-squares analyses. Selected values and statistical characteristics are given in Table II.

The pseudorotational equations are defined as in (*3*), where

$$\phi_i = c_i\phi\cos(q + 144i + \varepsilon_i),\ i = 1, 2, 3, 4, 5 \qquad (3)$$

c_i and ε_i are empirical constants to be determined and are characteristic of a given type of the ring (*e.g.* for cyclopentane all $c_i = 1$ and $\varepsilon_i = 0$ and equation (*3*) is reduced to Altona's formula). The parameter ϕ is a puckering parameter and ω is a phase angle describing the various kinds of puckering for each individual ring (*e.g.* for the abovementioned cyclopentane $\omega = 0°$ represents twist (C_2) and 18° envelope (C_s) conformations). One pair of terms c_i, ε_i is trivial due to the definition of ϕ and ω. These equations can be linearized using the simple trigonometric formula (*4*).

$$\phi_i = c_i\cos(144i + \varepsilon_i) \cdot \phi\cos\omega - c_i\sin(144i + \varepsilon_i)\,\phi\sin\omega \qquad (4)$$

TABLE II
Coefficients of the equation $\phi_i = a_{i5}\phi_5 + a_{i1}\phi_1$, i=2,3,4 with esd's in parentheses, standard errors(s), correlation coefficients (R) and pseudorotational parameters (c_i, ε_i)[a].

i	a_{i5}	a_{i1}	s_i	R_i	ε_i	c_i
2	−1.022(10)	−1.739(17)	0.39°	0.999(10)	2.652°	1.0925
3	1.798(12)	1.668(23)	0.51°	0.998(11)	− 6.561°	1.0781
4	−1.662(11)	−0.801(20)	0.44°	0.999(9)	−11.087°	1.1177

[a] For meaning of symbols see text.

There is a one-to-one correspondence between equations (*2*) and (*4*) when the formal equations $\phi_j = 1.\phi_j + 0.\phi_k$ and $\phi_k = 0.\phi_j + 1.\phi_k$ are added. There are 6 empirical constants in equations (*2*) and 8 constants in equations (*4*) so that an infinite number of solutions can be found. We selected one solution by fixing $c_1 = c_5 = 1$ and $\varepsilon_1 = \varepsilon_5 = 0$ and this choice reflects a minor pseudosymmetry (in terms of bond lengths) of the ring. The other values of ε_i and c_i can be calculated from equations (*5a*) and (*5b*).

$$tg^{-1}(144i + \varepsilon_i) = \frac{a_{i5}}{a_{i1}.\sin(144)} + \frac{\cos(144)}{\sin(144)} \qquad (5a)$$

$$c_i = \frac{a_{i1}.\sin(144)}{\sin(144i + \varepsilon_i)} \qquad (5b)$$

Selection of one from an infinite number of solutions by arbitrarily fixing values of some c_i and ε_i terms is questionable and other choices are possible (*e.g.* the simplest one; $\phi_1 = \phi \cos\omega$, $\phi_2 = -\phi\sin\omega$), but they lead to large values of ε_i or c_i. Our choice gives values of c_i and ε_i not far from 1 or 0, respectively,, so that c_i and ε_i can be regarded as correction coefficients for non-equilateral pentagons. When coefficients c_i and ε_i are once determined (for numerical values see Table II) then the two parameters ϕ and ω are enough for calculation of all five torsion angles of the ring. ϕ and ω can be calculated simply, using only two experimental torsion angles, as in equations (*7a*) and (*7b*),

$$\phi\cos\omega = \phi_5 \qquad (7a)$$

$$\phi\sin\omega = (\phi_5.\cos 144 - \phi_1)\cdot\sin 144 \qquad (7b)$$

or more exactly by least-squares for $\phi\cos\omega$ and $\phi\sin\omega$ using linearized equations (*4*) for all five experimental torsion angles. This second approach was used in all the calculations presented here. Distributions of ω and ϕ are expressed, separately for Co(Gly) and Co(Aa) complexes, with help of conformational wheels in Figures 2 and 3, respectively.

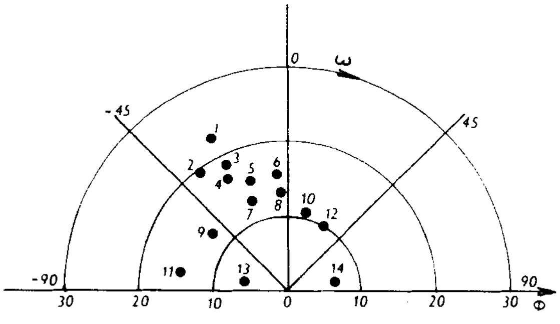

FIGURE 2 A conformational wheel for Co(III)(Gly) chelate rings. Only one half is necessary. Enantiomers have the phase angle advanced by 180°. Numbers of individual rings are given in Table I.

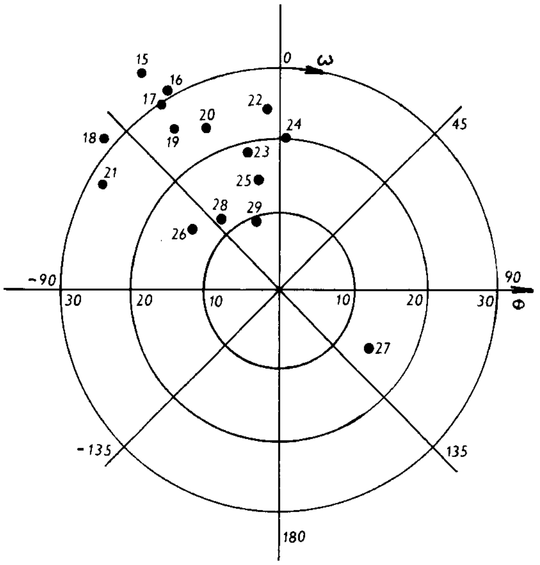

FIGURE 3 A conformational wheel for Co(III)(*S*-Aa) chelate rings. A point with $\phi = 14.3°$ and $\omega = 122.7°$ is the only pseudoaxial conformer. Numbers of individual rings are given in Table I.

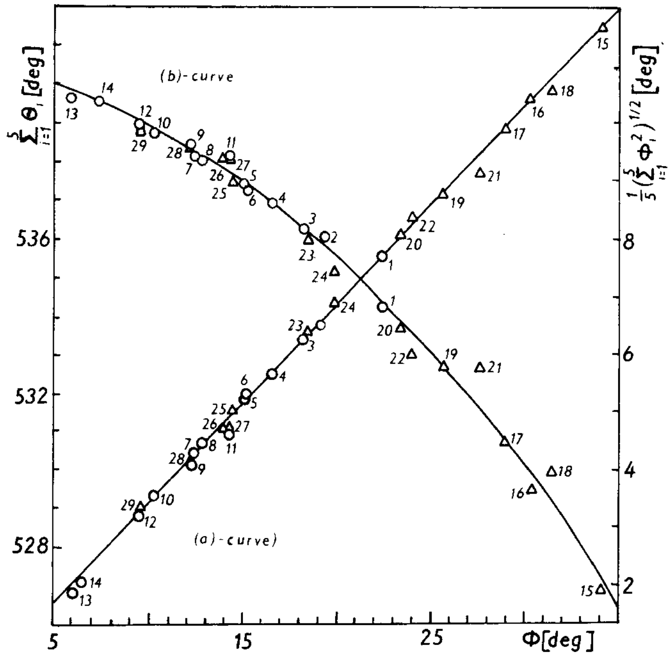

FIGURE 4 a) Scattergram of $\phi' = 1/5[\Sigma\phi_j^2]^{1/2}$ against the ring puckering parameter ϕ. The least-squares equation is $\phi' = C\cdot\phi$ with $C=0.3417(12)$. The correlation coefficient is $R=0.999(9)$, the standard error is 0.12°; b) Scattergram of the sum of valence angles against the puckering parameter ϕ. The least-squares equation is $\Sigma\Theta_i = C1+C2\cdot\sin^2(\phi/2)$ with $C1 = 540.05(11)$ and $C2 = -149.1(3.0)$. The correlation coefficient is 0.995(19) and the standard error is 0.362. Co(Gly) complexes are marked by a circle, Co(Aa) complexes by a triangle. Numbers of individual rings are given in Table I.

Puckering of the ring can be described indirectly by a sum of bond angles (Θ_i) from published data (Fig. 4). Various function forms were tried to fit the experimental curve and the best fit was found for equation (*8*).

$$\sum_{i=1}^{5} \Theta_i = C1 + C2 \cdot \sin^2(\phi/2) \qquad (8)$$

For numerical values of empirical constants C1 and C2 see Fig. 4. The term of ϕ obtained in this way has not only a mathematical but also a physical meaning as a ring puckering parameter.

DISCUSSION

The extended concept of pseudorotation has been shown to be useful for the description of conformations of Co(Aa) chelate rings in spite of the fact that no real pseudorotation in the ring is expected. The torsion angles in the ring are reproduced with a standard error, $\left[\sum_{i=1}^{5}(\phi^o_i - \phi^c_i)^2/(5\text{-}2)\right]^{1/2}$, of about 0.3°, a value which is fully comparable with esd's obtainable from X-ray structural analysis.

The pseudorotational equations with coefficients presented in Table II were tested on 51 Co(Aa) rings not used in parameterization, including 26 chelate rings of α-aminoacids with chelated side chain and 25 chelate rings of *N*-substituted aminoacids (mainly glycine) in multidentate ligands of the EDTA type. The mean standard error was larger (0.4°) but the agreement is still excellent. The largest disagreement (standard error 1.3°) was found in a highly strained complex of the tridentate ligand 2,3-diaminopropionic acid.[10] Two parameter description of the conformation seems to be very convenient for graphical representation, as shown in Figures 2 and 3.

The similar function to equation (*8*), shown in (*9*),

$$\sum_{i=1}^{5} \Theta_i = C1 + C2 \cdot \sin^2(\phi'/2) \qquad (9)$$

where $\phi' = 1/5\left[\sum_{i=1}^{5}\phi^2_i\right]^{1/2}$, has a correlation coefficient of 0.996(12), and a standard error of 0.20° for C1 = 540.03(6)° and C2 = −1255(13)°. Both equations (*8*) and (*9*) give by extrapolation the sum of bond angles 540° for the planar ring.

The mean geometry data for the Co(Gly) and Co(Aa) complexes in Tables III and IV show that bond lengths are equal within standard deviation. The bond angles for the Co(Aa) complexes are all smaller than corresponding bond angles in Co(Gly) complexes but the changes are within standard deviations; the only exception is $C'\text{-}C^{\alpha}\text{-}N$ bond angle but the environment of C^{α} is different.

Differences in bond angles in the carboxyl groups $[\Delta\Theta = \Theta(C^{\alpha}\text{-}C'{=}O) - \Theta(C^{\alpha}\text{-}C'\text{-}O)]$ seem to be correlated (Figure 5) with differences in bond lengths $[\Delta d = d(C'\text{-}O)\text{-}d(C'{=}O)]$ in the same way as in a free carboxyl group.[11] It is difficult to estimate errors associated with Δd and $\Delta\Theta$ on the basis of CCDB only, but errors in Δd (roughly estimated as 0.04 Å) are of the same order as Δd values themselves. More accurate data are necessary for a detailed analysis. Nevertheless, this effect may be of some importance, because it shows a mechanism of influencing ring geometry (and conformation) by external coordination or hydrogen bonding (electronic effect) in addition to expected conformational dependences by external steric effects. For a

TABLE III

Mean values of bond lengths (d) and bond angles (Θ) of Co(III)(Gly) chelate rings (n=14)

Bond lengths, Å				
Bond	<d>	σ_{n-1}	d_{min}	d_{max}
Co-O	1.911	0.017	1.891	1.953
Co-N	1.952	0.046	1.818	2.012
C'-O	1.292	0.025	1.252	1.365
C'=O	1.229	0.015	1.207	1.260
C'-C$^{\alpha}$	1.508	0.027	1.457	1.559
C$^{\alpha}$-N	1.480	0.010	1.464	1.500

Bond angles,°				
Angle	<Θ>	σ_{n-1}	Θ_{min}	Θ_{max}
N-Co-O	85.70	1.45	84.39	89.90
Co-O-C'	115.28	1.80	111.10	117.91
O-C'=O	122.44	1.54	119.19	123.88
O-C'-C$^{\alpha}$	116.77	1.76	114.42	120.95
O=C'-C$^{\alpha}$	120.61	1.91	117.79	126.16
C'-C$^{\alpha}$-N	110.37	1.52	107.52	112.92
Co-N-C$^{\alpha}$	109.62	1.05	108.06	111.09
ΣΘ	537.78	1.45	534.27	539.70

TABLE IV

Mean values of bond lengths (d) and bond angles (Θ) of Co(III)(Aa) chelate ring (n=15).

Bond lengths, Å				
Bond	<d>	σ_{n-1}	d_{min}	d_{max}
Co-O	1.898	0.018	1.863	1.936
Co-N	1.949	0.021	1.920	1.993
C'-O	1.289	0.023	1.233	1.323
C'=O	1.238	0.021	1.201	1.272
C'-C$^{\alpha}$	1.516	0.031	1.444	1.576
C$^{\alpha}$-C^{B}	1.537	0.024	1.511	1.574
C$^{\alpha}$-N	1.487	0.028	1.457	1.576

Bond angles,°				
Angle	<Θ>	σ_{n-1}	Θ_{min}	Θ_{max}
N-Co-O	85.39	0.90	83.02	86.77
Co-O-C'	115.14	1.11	113.49	117.04
O-C'=O	122.37	1.77	118.35	124.67
O-C'-C$^{\alpha}$	116.59	1.74	113.09	118.49
O=C'-C$^{\alpha}$	120.89	1.99	118.09	125.21
C'-C$^{\alpha}$-C^{B}	112.80	2.47	107.20	115.89
C'-C$^{\alpha}$-N	108.10	1.53	104.85	111.38
C$^{\beta}$-C$^{\alpha}$-N	112.52	2.07	107.89	115.01
Co-N-C$^{\alpha}$	108.87	1.64	106.35	112.33
ΣΘ	534.09	3.77	526.85	538.93

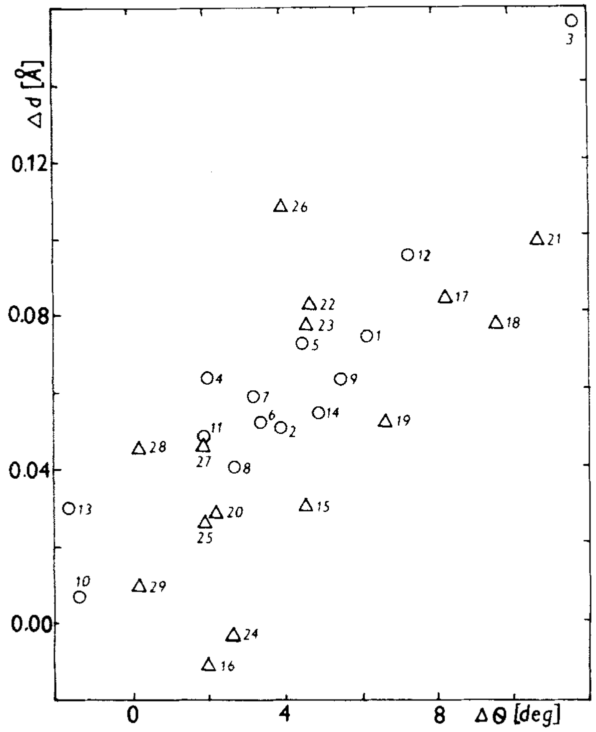

FIGURE 5 Scattergram of $\Delta d = d(C'\text{-}O)\text{-}d(C'{=}O)$ against $\Delta\Theta = \Theta(C^{\alpha}\text{-}C'{=}O)\text{-}\Theta(C^{\alpha}\text{-}C'\text{-}O)$. Numbers of individual rings are given in Table I.

discussion of the influence of hydrogen bonding on the geometry of the free carboxyl group see reference 12.

Conformations of the Co(Gly) ring can be found (Fig. 2) over a full range of ω, but the most populated area is around $\omega = -21°$ (or 159° for the enantiomer) and the mean ϕ value is 13.6°. C^{α} substitution leads to an important restriction on possible values of ω (Fig. 3); only one quarter of the wheel is occupied when (*S*)-aminoacids are considered. The only exception is NCOALA (change of absolute configuration was taken in account) with a pseudoaxial methyl substituent. In all other cases the substituents were pseudo-equatorial. This is in contradiction with Gollogly's calculations[13] which indicate that the axial and equatorial possitions are of approximately equal energy. The Co(Aa) rings are in general more puckered than Co(Gly) rings with a mean value of $\phi = 21.9°$ and $\omega = -30.9°$. The most common conformations can be described as *N*-envelope ($\omega = -20.7°$), C^{α}-envelope ($\omega = -54°$) or one intermediate between them.

There is an important correlation between the Co-N-C^{α}-C' torsion angle and the ring puckering parameter ϕ (Fig. 6) which reflects the energetics of the ring. Energy barriers around metal-ligand bonds are negligible, the C'-C^{α} barrier is less than 2 kJ mol^{-1}. The barrier around C'-O is uncertain but due to partial double bond character and the partial sp^2 hybridization of the oxygen atom the minimum is expected near the zero value of the Co-O-C'-C^{α} torsion angle. Rotation around the N-C^{α} bond (barrier *ca* 8 kJ mol^{-1} in organic amines) is the only torsion for which ring puckering leads to a significant lowering of torsion energy and this is the reason for abovementioned correlation. The Co-N-C^{α}-C' torsion angle is usually the largest in the ring and is responsible for values of the ring puckering parameter.

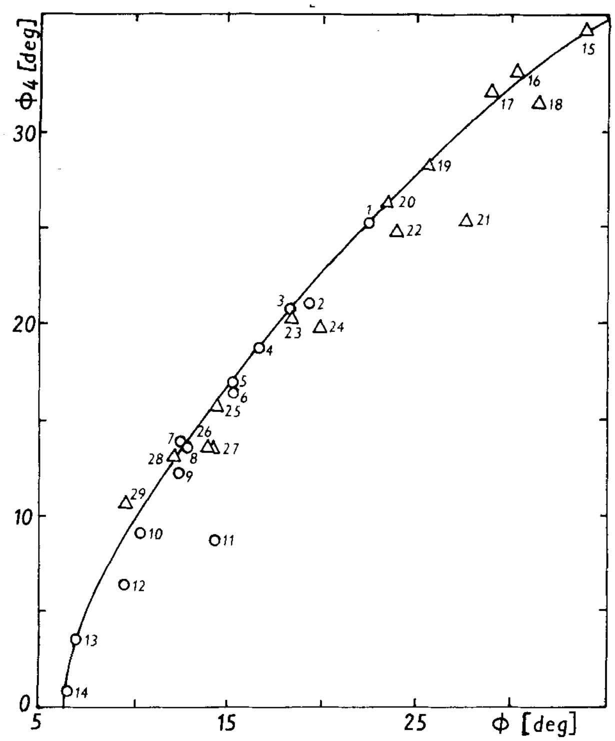

FIGURE 6 Scattergram of the ϕ(Co-N-C$^\alpha$-C') torsion angle against the ring puckering parameter ϕ. Numbers of individual rings are given in Table I.

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