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The Crystal and Molecular Structure of Potassium *N*,*N'*-Ethylenebis(acetylacetoniminato)-*trans*-diglycinatocobaltate(III) Hexahydrate

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The crystal structure of potassium *N*,*N'*-ethylenebis(acetylacetoniminato)-*trans*-diglycinatocobaltate(III) hexahydrate, $K[Co(C_{16}H_{26}O_6N_4).6H_2O]$, has been determined by heavy-atom methods and refined by three-dimensional least-squares techniques. The crystals are orthorhombic, space group $P2_12_12_1$, $Z=4$, with $a=14{\cdot}385$ (5), $b=18{\cdot}056$ (8) and $c=10{\cdot}037$ (6) Å. Intensity data for all unique reflections less than 56° in 2θ were collected on an automatic diffractometer using Mo $K\alpha$ radiation. The final R value for all 3525 data was 5·0%. The glycine residues are coordinated to the cobalt as unidentate ligands through the terminal amino groups. The Co–N(amino)–C^α bond angles are both near 120°. The cobalt ion lies in the plane of the bis(acetylacetoniminato)ethylenediamine chelate ring. The waters of hydration serve principally to form inter-molecular bonds between the carboxyl oxygens.

Introduction

Metal complexes of tetradentate Schiff bases such as bis(acetylacetoniminato)ethylenediamine (baen) have been widely studied as model molecules having properties similar to the cobalamines, such as vitamin B_{12}, and cobalt corrinoids in general. A review of the structural determinations of metal complexes with Schiff bases has been published (Calligaris, Nardin & Randaccio, 1971).

The cobalamines are labile for apical ligand substitution, which may be important in their functions as coenzymes for transmethylation reactions. Also metal complexes with Schiff bases are known to reversibly bind molecular oxygen as an apical ligand. In order to study the lability of the apical ligands of Co(III)–baen complexes Fuji (1972) synthesized a series of complexes of Co(III)–baen with two unidentate amino acids as apical ligands. Intermolecular exchange reactions of the anionic amino acid apical ligands were studied by n.m.r. Amino acids with unidentate coordination to metal ions are rare in the literature. Although some of these complexes have been reported (Fujita, Yasui & Shimura, 1965; Yasui, Hidaka & Shimura, 1966; Alexander & Busch, 1966) to our knowledge this is the first X-ray structural determination of a complex containing an amino acid as an unidentate ligand. We have therefore determined the structure of $K[Co(baen)gly_2].6H_2O$ to expand on the study of the unusual behavior of cobalt chelated with unsaturated cyclic ligands, to investigate the coordination of the labile apical ligands and to see the effect, if any, of unidentate coordination on the simplest amino acid, glycine.

Experimental

Synthesis of $K[Co(baen)gly_2].2H_2O$ has been reported by Fuji (1972). Recrystallization was from water–acetone. It was necessary to mount the crystal in a glass capillary to prevent decomposition of the crystals. The decomposition probably reflected a loss or gain of water of hydration. The space group was determined to be $P2_12_12_1$ on a G.E. XRD-5 diffractometer. 3525 data were collected with Mo $K\alpha$ radiation ($\lambda=0{\cdot}71069$ Å) on a Nonius CAD-4 automatic diffractometer. These were all unique reflections with 2θ less than 56°. These data were collected with θ–2θ scans in which the θ-scan range was between 0·80 and 0·92°. The maximum scan time was 180 s with $\frac{2}{3}$ of the time spent while scanning the peak and $\frac{1}{6}$ on each the left and right background. The least-squares cell dimensions were determined from averages of $+2\theta$ and -2θ values of 40 reflections measured at 25°C. The crystallographic data are shown in Table 1. There were 306 reflections which could not be distinguished from the background on the basis that the net count was less than $(1{\cdot}4)T^{1/2}$ (T=total count). These reflections were assigned intensities equal to $(0{\cdot}7)T^{1/2}$ for the purpose of least-squares refinement. Lorentz, polarization and absorption corrections were applied to the data. The program of Coppens, Leiserowitz & Rabinovich (1965) was used to make the absorption correction ($\mu=8{\cdot}83$ cm^{-1}), using 216 sampling points. The absorption coefficients varied between 0·768 and 0·864 as calculated by the Gaussian method of numerical integration. Each structure amplitude was assigned a weight given by $w_F=1/\sigma_F^2$ where the standard deviation. σ_F of the amplitude is given by $\sigma_F={}^1/_2\{[(\sigma)^2+(0{\cdot}05)P]^2/(\text{Lp})P\}^{1/2}$ in which: $\sigma=T^{1/2}V$, V=scan speed, $P=[\text{Pk}-2(R+L)]V$, Pk=peak count, R=right background count, L=left background count, Lp=Lorentz–polarization factor.

Structure determination and refinement

The position of the cobalt ion was located by examination of the three Harker sections of a sharpened Patterson map. A superposition map calculated from

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Table 1. *Crystallographic data*

$K[Co(C_{16}H_{26}O_6N_4).6H_2O]$
F.W. 576·54
Systematic absences
$h00$, $h=2n+1$
$0k0$, $k=2n+1$
$00l$, $l=2n+1$
Space group :$P2_12_12_1$
$a=14·385$ (5) Å
$b=18·056$ (8)
$c=10·037$ (6)

$V=2606·97$ Å^3
$Z=4$
$D_c=1·469$ g cm^{-3}
$D_o=1·472$
(measured by flotation in CCl_4/benzene at 23 °C)
$F(000)=1216$

an unsharpened Patterson showed the location of the potassium ion. The cobalt and potassium positions were used in a structure-factor calculation and refined by block-diagonal least-squares calculations with isotropic temperature factors for five cycles to an $R=([\sum||F_o|-|F_c||/\sum|F_o|)$ of 0·36. The quantity minimized by least-squares was $\sum w_F(|F_o|-|F_c|)^2$. At this point a difference synthesis showed all atoms of the chelate ring and the cobalt coordination. These atoms were included in structure-factor least-squares calculations which refined to an R of 0·28. Another difference synthesis was calculated which yielded the remainder of the non-hydrogen atom positions including the oxygen atoms of six water molecules. All non-hydrogen atoms were given anisotropic temperature factors and included in several more cycles of least-squares refinement. The non-methyl hydrogen atoms of the cobalt complex were located from geometric considerations and a difference synthesis. Their positions and isotropic temperature factors were included in subsequent refinement. After convergence of the least-squares refinement at an R of 0·062, the methyl hydrogens and the hydrogen atoms of the water molecules were located. Again these hydrogens were given isotropic temperature factors and their parameters included in refinement. The molecule, although containing no asymmetric center, did appear to have an absolute conformation in the crystal form. In order to determine the absolute conformation, several hundred data were recollected using Cu $K\alpha$ radiation to maximize the anomalous dispersion effects. The $I(hkl)$ and $I(\bar{h}\bar{k}\bar{l})$ obtained in this manner were compared to corresponding pairs of $F_c^2(hkl)$ and $F_c^2(\bar{h}\bar{k}\bar{l})$ calculated by including the anomalous scattering factors of Co and K for Cu $K\alpha$ radiation in a structure-factor calculation using the refined parameters. It was determined that the structure had been refined in the correct absolute conformation. The anomalous dispersion corrections to the scattering factors of K and Co for Mo $K\alpha$ radiation were now included in the structure-factor refinement. Refinement continued until the shifts in

Table 2. *Atomic fractional coordinates and thermal parameters* (*all* × 10^4)

The temperature factor is expressed in the form exp $\{-(h^2b_{11}+k^2b_{22}+l^2b_{33}+hkb_{12}+hlb_{13}+klb_{23})\}$. Standard deviations for the last digit are in parentheses.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
K(1)	−264·4 (9)	2585·5 (6)	−2211·3 (11)	57·7 (6)	30·7 (3)	97·7 (11)	33·5 (10)	−36·5 (16)	−25·9 (9)
Co(1)	270·6 (3)	1051·2 (2)	383·6 (4)	22·4 (2)	12·0 (1)	42·6 (3)	−4·2 (4)	2·3 (6)	−0·5 (3)
O(1)	−783 (2)	1530 (1)	−390 (3)	23 (1)	18 (1)	64 (3)	2 (3)	1 (3)	2 (1)
C(2)	−1641 (3)	1401 (2)	−61 (4)	25 (2)	19 (1)	83 (5)	−25 (4)	−4 (4)	2 (2)
C(3)	−1926 (3)	938 (2)	949 (5)	26 (2)	27 (1)	102 (5)	−9 (4)	23 (5)	−6 (3)
C(4)	−1333 (3)	533 (2)	1797 (4)	44 (2)	17 (1)	88 (5)	−12 (4)	40 (6)	−17 (3)
N(5)	−433 (2)	521 (2)	1663 (3)	39 (2)	13 (1)	55 (3)	−4 (3)	15 (4)	−2 (2)
C(6)	158 (4)	144 (2)	2644 (5)	57 (3)	24 (1)	80 (4)	31 (4)	21 (6)	3 (3)
C(7)	1071 (4)	−31 (3)	2040 (5)	61 (3)	28 (2)	87 (5)	32 (5)	1 (7)	22(4)
N(8)	1326 (2)	557 (2)	1087 (3)	30 (2)	18 (1)	65 (3)	−11 (3)	−21 (4)	13 (2)
C(9)	2182 (3)	622 (2)	663 (4)	30 (2)	22 (1)	88 (5)	−32 (4)	−29 (5)	13 (2)
C(10)	2428 (2)	1128 (2)	−366 (5)	22 (2)	28 (1)	111 (5)	−20 (5)	23 (5)	−4 (3)
C(11)	1841 (3)	1560 (2)	−1085 (4)	28 (2)	18 (1)	73 (4)	−18 (4)	23 (5)	−8 (2)
O(12)	948 (2)	1606 (1)	−905 (3)	28 (1)	20 (1)	55 (2)	2 (2)	9 (3)	−3 (2)
C(13)	−2342 (3)	1821 (3)	−884 (5)	32 (2)	34 (2)	112 (6)	−2 (5)	−30 (6)	10 (3)
C(14)	−1796 (4)	118 (4)	2925 (7)	71 (4)	45 (2)	161 (8)	66 (8)	107 (10)	4 (5)
C(15)	2944 (3)	140 (3)	1222 (6)	39 (2)	37 (2)	147 (7)	−19 (6)	−56 (7)	38 (4)
C(16)	2192 (3)	2041 (3)	−2205 (5)	42 (2)	30 (2)	116 (6)	4 (5)	55 (6)	−16 (3)
N(17)	460 (2)	1894 (2)	1614 (3)	30 (2)	16 (1)	58 (3)	−12 (3)	−3 (4)	−2 (2)
C(18)	−294 (3)	2135 (2)	2499 (4)	31 (2)	22 (1)	84 (4)	−28 (4)	14 (6)	−6 (3)
C(19)	−112 (3)	2875 (2)	3210 (4)	41 (2)	20 (1)	62 (4)	−11 (4)	1 (5)	7 (3)
O(20)	486 (2)	3302 (2)	2743 (3)	56 (2)	19 (1)	73 (3)	−2 (3)	9 (4)	−20 (2)
O(21)	−583 (2)	2986 (2)	4226 (4)	61 (2)	29 (1)	116 (4)	−55 (3)	66 (5)	−14 (2)
N(22)	171 (2)	284 (2)	−999 (3)	31 (2)	16 (1)	56 (3)	−10 (3)	−4 (4)	−4 (2)
C(23)	−550 (3)	−286 (2)	−949 (5)	40 (2)	22 (1)	87 (5)	−31 (4)	11 (5)	−12 (3)
C(24)	−642 (3)	−723 (2)	−2242 (4)	30 (2)	19 (1)	78 (4)	−14 (4)	−9 (5)	6 (2)
O(25)	−991 (2)	−1359 (2)	−2136 (3)	47 (2)	21 (1)	96 (3)	−27 (3)	−2 (4)	−12 (2)
O(26)	−384 (3)	−437 (2)	−3312 (3)	67 (2)	25 (1)	76 (3)	−18 (3)	3 (5)	−10 (3)
O(27)	−1433 (3)	3873 (2)	−3912 (4)	65 (2)	43 (1)	169 (5)	−94 (5)	68 (6)	−28 (3)
O(28)	1616 (2)	1617 (2)	4214 (3)	55 (2)	34 (1)	108 (4)	−13 (4)	−9 (5)	4 (3)
O(29)	1781 (2)	3180 (2)	4797 (4)	44 (2)	41 (1)	107 (4)	−6 (4)	−10 (5)	18 (2)
O(30)	−1333 (2)	1914 (2)	−4278 (4)	47 (2)	42 (1)	122 (5)	16 (4)	2 (5)	3 (3)
O(31)	−36 (3)	3429 (2)	38 (3)	112 (3)	31 (1)	87 (4)	17 (3)	−17 (5)	−40 (3)
O(32)	168 (2)	1000 (2)	−4089 (4)	60 (2)	29 (1)	134 (4)	23 (4)	−9 (5)	0 (3)

all non-hydrogen parameters were less than $\frac{2}{3}\sigma$. The final R value for all 3525 data was 0·050. The 306 reflections with assigned intensities were only included in the least-squares refinement when $|F_c| > 2|F_o|$. With this condition 12 of these 306 reflections were included in the last cycle of least-squares refinement. A final difference Fourier synthesis showed peaks ranging from 0·89 e Å^{-3} to $-$0·66 e Å^{-3} located near the Co ion position. No other peaks greater than 0·35 e Å^{-3} occurred in the map. The average values of $w_f \Delta F^2$ were independent of F_o and $\sin\theta/\lambda$ validating the weighting scheme employed in the refinement.

The atomic scattering factors for Co^{3+}, K^+, O, C, N and the anomalous scattering factors for Co and K were taken from *International Tables for X-ray Crystallography* (1962). The scattering factors for the hydrogen atoms were from Stewart, Davidson & Simpson (1965). The final atomic parameters are given in Tables 2 and 3.*

Results

A stereo view of the structure of the anion and location of the cation of potassium *N,N′*-ethylenebis(acetylacetoniminato)-*trans*-diglycinatocobaltate(III) hexahydrate is shown in Fig. 1. The six water molecules of hydration are excluded here for clarity. The bond lengths and numbering scheme are shown in Fig. 2.

As expected, the glycines are seen to coordinate to the Co ion as unidentate, *trans* apical ligands. Coordination occurs through the amine N with the carboxyl group carrying a negative charge. The Co ion lies approximately in the plane of its tetradentate (baen) ligand as shown by various least-squares planes calculated through the chelated ring system (Table 4). The C(14) and C(15) methyl groups lie out of the planes through the respective chelate rings while both groups are displaced approximately the same amount out of the planes and in opposite directions. The bond lengths in the (baen) chelate ring are within three standard deviations of the average values reported in the review of Calligaris *et al.* (1971), with the exception of C(6)–C(7) distance (1·481 Å) which is slightly shorter than the average of 1·503 Å and much shorter than a normal C(sp^3)–C(sp^3) distance of 1·54 Å. In the structure of [CH_2=CHCo(baen)H_2O] (Brückner, Calligaris, Nardin

Table 3. *Hydrogen atom parameters* (*coordinates* × 10^3)

	x	y	z	B (Å)
H(C3)	−262 (3)	83 (2)	101 (4)	4 (1)
H(C6)1	16 (3)	55 (2)	341 (5)	5 (1)
H(C6)2	−17 (3)	−31 (3)	299 (5)	5 (1)
H(C7)1	159 (3)	−15 (3)	268 (5)	5 (1)
H(C7)2	99 (3)	−54 (3)	141 (5)	5 (1)
H(C10)	308 (3)	116 (2)	−54 (4)	4 (1)
H(C13)1	−227 (3)	175 (2)	−181 (4)	3 (1)
H(C13)2	−301 (4)	169 (3)	−52 (7)	8 (2)
H(C13)3	−220 (3)	236 (2)	−75 (4)	3 (1)
H(C14)1	−167 (4)	23 (4)	385 (8)	10 (2)
H(C14)2	−247 (5)	23 (4)	290 (7)	9 (2)
H(C14)3	−167 (4)	−36 (4)	283 (7)	9 (2)
H(C15)1	356 (4)	29 (3)	79 (6)	6 (1)
H(C15)2	294 (3)	11 (3)	228 (6)	6 (1)
H(C15)3	274 (5)	−45 (4)	107 (8)	10 (2)
H(C16)1	185 (4)	184 (4)	−295 (7)	10 (2)
H(C16)2	277 (4)	190 (3)	−244 (6)	7 (2)
H(C16)3	207 (3)	257 (3)	−200 (5)	4 (1)
H(N17)1	95 (3)	179 (2)	206 (4)	3 (1)
H(N17)2	60 (3)	224 (2)	84 (5)	4 (1)
H(C18)1	−83 (3)	218 (3)	204 (5)	5 (1)
H(C18)2	−29 (4)	168 (3)	328 (6)	9 (2)
H(N22)1	17 (3)	58 (2)	−162 (4)	3 (1)
H(N22)2	83 (3)	5 (2)	−101 (4)	3 (1)
H(C23)1	−45 (3)	−65 (2)	−22 (4)	4 (1)
H(C23)2	−112 (3)	−7 (3)	−86 (5)	5 (1)
H(O27)1	−125 (3)	368 (3)	−453 (5)	5 (1)
H(O27)2	−195 (4)	367 (4)	−393 (7)	9 (2)
H(O28)1	122 (3)	146 (3)	465 (5)	4 (1)
H(O28)2	173 (3)	201 (2)	448 (4)	3 (1)
H(O29)1	146 (4)	344 (3)	414 (6)	9 (2)
H(O29)2	153 (3)	333 (3)	560 (5)	6 (1)
H(O30)1	−129 (5)	237 (4)	−484 (8)	10 (2)
H(O30)2	−184 (3)	179 (3)	−454 (6)	5 (1)
H(O31)1	16 (3)	354 (2)	70 (5)	4 (1)
H(O31)2	14 (3)	381 (3)	−23 (5)	5 (1)
H(O32)1	0 (3)	59 (2)	−392 (5)	5 (1)
H(O32)2	−28 (4)	124 (3)	−438 (6)	8 (2)

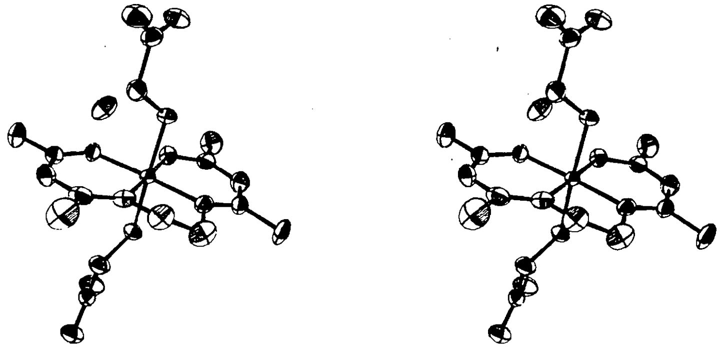

Fig. 1. Stereo view of the cation and anion (waters of hydration not shown) with 50% probability ellipsoids using the *ORTEP* program (Johnson, 1965).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30906 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

& Randaccio, 1968) the Co–O distances in the chelate ring are 1·913 and 1·930 Å (standard deviation 0·007 Å), and the Co–N distances are 1·888 and 1·892 Å (standard deviation 0·008 Å). These values are in good agreement with the Co–ligand distances in the baen chelate ring reported here.

Table 4. *Least-squares planes*

The equations of the planes are in the form $Ax+By+Cz=D$, where x, y, and z are fractional coordinates and D is the distance from the origin in Å.

Plane	A	B	C	D
1	1·569	13·606	6·507	1·681
2	0·947	13·766	6·462	1·746
3	1·931	13·265	6·675	1·707
4	1·625	13·490	6·575	1·705

	$\Delta(1)$		$\Delta(2)$
*Co(1)	0·041 Å	*Co(1)	−0·025 Å
*O(1)	0·024	*O(1)	0·034
*C(2)	−0·071	*C(2)	−0·011
*C(3)	−0·090	*C(3)	−0·024
*C(4)	0·004	*C(4)	0·022
*N(5)	0·042	*N(5)	0·004
*C(6)	0·260	C(13)	−0·033
*C(7)	−0·228	C(14)	0·137
*N(8)	−0·008		
*C(9)	−0·061		
*C(10)	−0·003		
*C(11)	0·025		
*O(12)	0·064		
K(1)	0·357		
C(13)	−0·146		
C(14)	0·101		
C(15)	−0·233		
C(16)	0·005		

	$\Delta(3)$		$\Delta(4)$
*Co(1)	−0·004 Å	*Co(1)	0·009 Å
*N(8)	0·013	*O(1)	−0·025
*C(9)	−0·018	*O(12)	0·020
*C(10)	0·014	*N(5)	0·020
*C(11)	−0·006	*N(8)	−0·024
*O(12)	0·002	C(6)	0·253
C(15)	−0·137	C(7)	−0·232
C(16)	−0·049		

* Atoms included in the least-squares plane calculation.

The conformation of the baen chelate ring is shown by the conformational angles of Table 5 or the deviations from the least-squares planes shown in Table 4. The six-membered acetylacetoniminato rings are planar while the ethylene carbon atoms C(6) and C(7) are symmetrically displaced above and below the coordination plane in a 'half-chair' conformation of the five-membered ring, putting the hydrogens on these carbon atoms in a *gauche* relationship. The baen ligand can also exist in a planar conformation in which both ethylene carbons lie on the same side and above or below the coordination plane (Calligaris *et al.*, 1972).

Several factors should be noted with respect to the apical glycine ligands. The Co–N bond lengths, Co–N(17) and Co–N(22), are between values reported for cobalt glycine and glycylglycine metal–amino distances ranging from 1·949 to 2·00 Å (Buckingham *et al.*, 1973; Gillard, McKenzie, Mason & Robertson, 1966; Hsu, 1971) and compare favorably with the Co–axial N distance in wet cyanocobalamin of 1·97 Å (Brink-Shoemaker, Cruickshank, Hodgkin, Kamper & Pilling, 1964). The N–C^{α} distances of 1·462 and 1·467 Å in this structure, however, are over four standard deviations shorter than the average value for amino acids of 1·487 Å as tabulated by Marsh & Donohue (1967) and the same average value is found for coordinated α-amino acids (Freeman, 1967).

Freeman (1973) states that the only geometrical requirement for coordination of amino acids through the terminal amino group is that the metal–N(amino)–

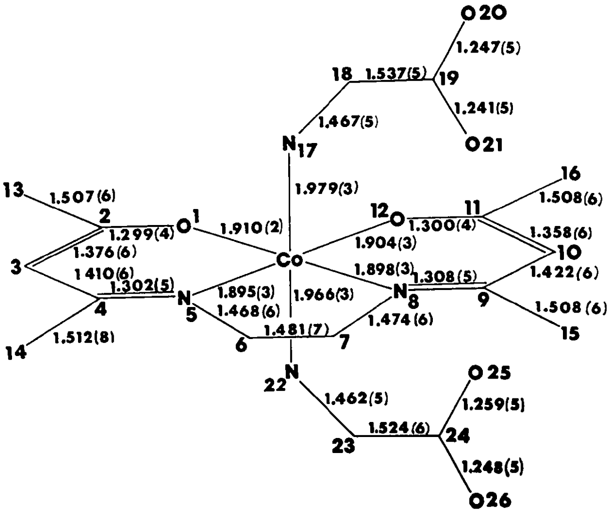

Fig. 2. Numbering scheme and bond distances in Å with the standard deviation of the last digit given in parentheses.

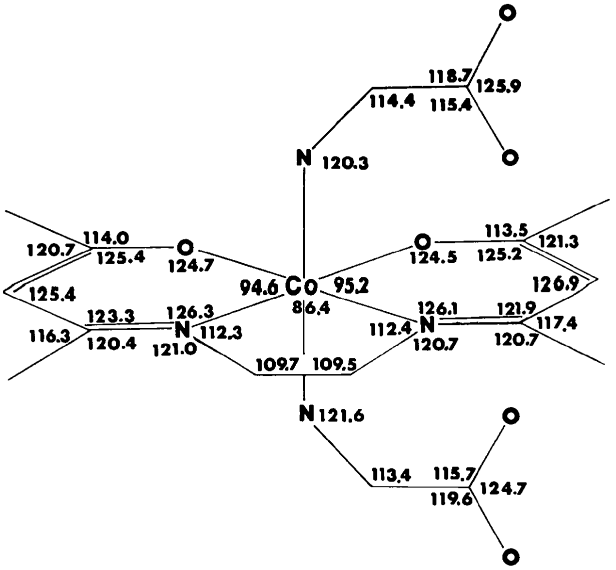

Fig. 3. Bond angles (°). Standard deviations between 0·1° and 0·4°.

C^{α} angle should be near the tetrahedral value of 109·5° (standard deviation 1° for amino acids). Both glycinato groups in this structure show expansion of this bond angle to near 120°. Some close intramolecular contacts between the hydrogen atoms on C(18) and C(23) with the baen chelate ring may necessitate this expansion of bond angles. H(C18)1 is 2·71 Å from O(1) and H(C18)2 is 2·65 Å from N(5). In a similar manner the distance from H(C23)1 to N(5) is 2·84 Å and H(C23)2 has contacts of 2·88, 2·82 and 2·90 Å with C(2), C(3), and C(4) respectively. Clearly a tetrahedral value for the Co-N(amino)-C^{α} bond would cause these atoms to be unacceptably close (shortening these distances by approximately 0·3 Å). A smaller expansion of the bond angles N(17)-C(18)-C(19) and N(22)-C(23)-C(24) from the average value of 110·5° (Freeman, 1967) is also seen. All other parameters of the glycinato ligand are consistent with accepted values. Bond angles are shown in Fig. 3. Standard deviations are between 0·1 and 0·4°.

The conformational angles are given in Table 5. The dihedral angles for the C^{α}–C(carboxyl) bonds are 20 and 24° which is in the range of values from 0–27° found for the various glycine modifications and peptides with terminal glycine residues whose structures are known (Marsh & Donohue, 1967).

The cobalt coordination is a distorted octahedron. The smallest angle of 83·8° is observed between O(1) and O(12). The greatest expansion is to 95·2° between N(8) and O(12). The angle between the apical ligands is not linear, but 173°. All the angles are listed in Table 6.

Table 5. *Conformational angles*

Co——O(1)—C(2)—C(3)	4°
O(1)—C(2)—C(3)—C(4)	1
C(2)—C(3)—C(4)—N(5)	−4
C(3)—C(4)—N(5)—Co	2
C(4)—N(5)—Co——O(1)	2
N(5)—Co——O(1)—C(2)	−5
Co——N(5)—C(6)—C(7)	−28
N(5)—C(6)—C(7)—N(8)	34
C(6)—C(7)—N(8)—Co	−26
C(7)—N(8)—Co——N(5)	9
N(8)—Co——N(5)—C(6)	11
Co——N(8)—C(9)—C(10)	4
N(8)—C(9)—C(10)-C(11)	−4
C(9)—C(10)-C(11)-O(12)	3
C(10)-C(11)-O(12)-Co	−2
C(11)-O(12)-Co——N(8)	1
O(12)-Co——N(8)—C(9)	−2
Co——N(17)-C(18)-C(19)	190
N(17)-C(18)-C(19)-O(20)	20
Co——N(22)-C(23)-C(24)	168
N(22)-C(23)-C(24)-O(26)	−24
C(18)-N(17)-Co——N(5)	−39
C(23)-N(22)-Co——N(5)	19

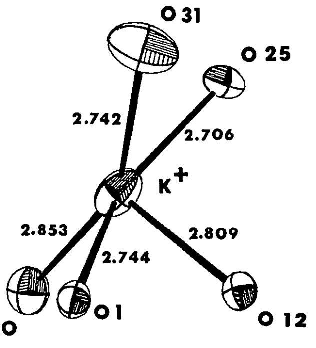

Fig. 4. Sphere of coordination of the potassium cation. Distances are given in Å.

Table 6. *Bond angles in cobalt coordination sphere*

Standard deviation for the last digit is given in parentheses.

N(5)-Co-N(8)	86·4 (1)	N(8)—Co-O(12)	95·2 (1)
N(5)-Co-N(17)	92·3 (1)	N(17)-Co-N(22)	173·0 (1)
N(5)-Co-N(22)	94·8 (1)	N(17)-Co-O(1)	98·8 (1)
N(5)-Co-O(1)	94·6 (1)	N(17)-Co-O(12)	87·1 (1)
N(5)-Co-O(12)	178·3 (1)	N(22)-Co-O(1)	88·5 (1)
N(8)-Co-N(17)	91·1 (1)	N(22)-Co-O(12)	85·9 (1)
N(8)-Co-N(22)	89·4 (1)	O(1)—Co-O(12)	83·8 (1)
N(8)-Co-O(1)	177·8 (1)		

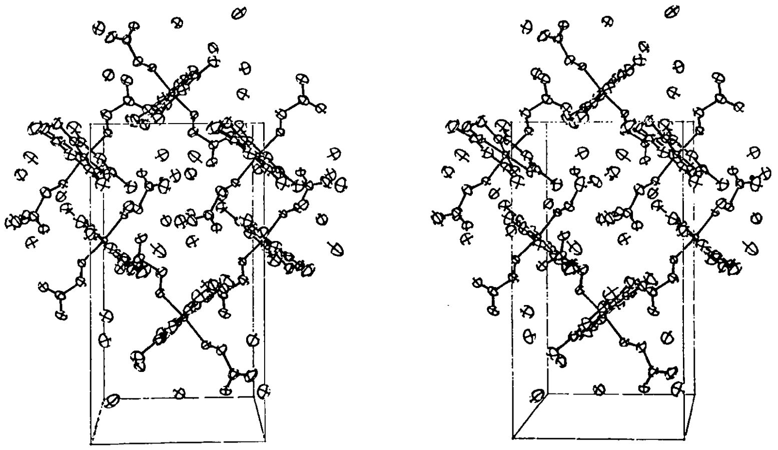

Fig. 5. Packing drawing showing hydrogen bonding scheme. View is down the *a* axis.

The potassium ion is at a distance of 3·879 Å from the cobalt ion and is surrounded by five oxygen atoms. Two water molecules O(30) and O(31), the negatively charged O(1) and O(12) and the carboxyl oxygen O(25) make up the potassium sphere of closest contact shown in Fig. 4.

The six water molecules of hydration serve the function of forming intermolecular hydrogen-bonding networks between the cobalt chelate anions and potassium cations. All hydrogen atoms of the water molecules are involved in hydrogen bonds. The carboxyl oxygens are involved in this network as acceptors of water hydrogens, with O(25) being in close contact with the potassium ion. The carboxyl oxygens are connected intermolecularly by spirals of hydrogen bonds around screw axes in primarily the x and y directions. The water molecules O(29) and O(31) directly bridge carboxyl oxygens O(20) and O(25) $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ and O(26) $(-x, \frac{1}{2}+y, -\frac{1}{2}-z)$. The hydrogen bonding and packing viewed down the a axis are shown in Fig. 5. The H-bond distances are shown in Table 7.

Table 7. *Hydrogen bonding*

Donor (X)	Acceptor (Y)	Hydrogen (H)	X–H$\cdots Y$	H$\cdots Y$	$X\cdots Y$
O(27)	O(21*a*)	H(O27)1	163·5°	2·009 Å	2·749 Å
O(27)	O(28*b*)	H(O27)2	165·9	2·149	2·959
O(28)	O(32*c*)	H(O28)1	180·0	2·142	2·912
O(28)	O(29)	H(O28)2	164·5	2·130	2·892
O(29)	O(20)	H(O29)1	141·1	1·994	2·787
O(29)	O(25*d*)	H(O29)2	180·0	1·810	2·738
O(30)	O(21*a*)	H(O30)1	148·3	1·771	2·676
O(30)	O(29*b*)	H(O30)2	158·6	1·995	2·767
O(31)	O(20)	H(O31)1	151·3	2·145	2·826
O(31)	O(26*e*)	H(O31)2	153·1	2·025	2·749
O(32)	O(26)	H(O32)1	173·2	2·032	2·822
O(32)	O(30)	H(O32)2	156·2	1·947	2·725

(*a*) $x, \quad y, z-1$
(*b*) $-\frac{1}{2}+x, \frac{1}{2}-y, \quad -z$
(*c*) $x, \quad y, z+1$
(*d*) $-x, 1\frac{1}{2}+y, \quad \frac{1}{2}-z$
(*e*) $-x, \quad \frac{1}{2}+y, -\frac{1}{2}-z$

The thermal parameters for all non-hydrogen atoms appear reasonable and low enough that little effect should be seen in the bond distances. The hydrogen atom distances vary between 0·75 Å and 1·12 Å.

Discussion

Several interesting factors are observed in relation to the rapid intermolecular exchange of apical amino acid ligands observed in solution by Fuji for this type of molecule. The Co–apical N distances do not show significant lengthening when compared to other structures containing Co–N ligands. A sufficient number of accurate structures of similar compounds does not exist to make any statement concerning small changes in these bond lengths. It appears however, that the weakness of this apical coordination bond, reflected in its lability in solution, may be observed in the Co–N(amino)–C^α bond angles observed to be near 120°. If normal tetrahedral sp^3 hybridization is assumed (and as previously stated all other metal-terminal amino–C^α bond angles have been found to be near 109·5°), the effect would be less efficient overlap of the nitrogen and cobalt orbitals. The reason for this bond-angle expansion may be due to either or both; steric crowding of the C^α carbons and the *trans*-effect of the opposite apical nitrogen (Costa & Mestroni, 1968; Firth, Hill, Pratt, Thorp & Williams, 1970). Five-coordinate complexes of baen chelates are easily isolated and have been characterized (Brückner *et al.*, 1968). Therefore, owing to the low energy of a five-coordinate intermediate, the rate of replacement reactions is fast. Since the *trans*-effect and probably stability of the five-coordinate intermediate is increased by increasing the electron donating ability of the apical ligand one would expect nitrogen to have an even larger effect than the alkyl ligands previously studied (Hill, Morallee & Pellizer, 1969).

The shortening of the N–C^α bond when compared to previous structures although small is an unexpected effect of the coordination of the amino acid and may be related to the lability of the apical ligands.

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Glycylglycinatocopper(II) Dihydrate*

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Glycylglycinatocopper(II) dihydrate, $[(O_3N_2C_4H_6)Cu].2H_2O$, crystallizes in the monoclinic system, systematic absences hkl, $h+k=2n+1$ and $h0l$, $l(h)=2n+1$ consistent with the space groups Cc and $C2/c$, with $a=12{\cdot}488$ (5), $b=9{\cdot}245$ (6), $c=13{\cdot}360$ (5) Å, $\beta=97{\cdot}68$ (3)°, $V=1528{\cdot}60$ Å^3, $Z=8$, $D_m=2{\cdot}00$ (1), $D_c=1{\cdot}996$ g cm^{-3}, $\mu(\text{Mo } K\alpha)=29{\cdot}6$ cm^{-1}. Intensities for 2229 independent reflections were collected by counter methods. The structure was solved by standard heavy-atom methods ($C2/c$) and refined by full-matrix least-squares calculations, based on F, to a final R value of 0·038. The final weighted R value and goodness-of-fit are 0·045 and 1·8, respectively. The coordination sphere about the copper atom is square pyramidal with the tridentate glycylglycine dianion and one water molecule, Cu–O distance 1·946 (1) Å, completing an approximate square plane and the second water molecule, Cu–O distance 2·383 (1) Å, occupying an apical position. The crystal contains an extensive array of hydrogen bonds and a weak dimerization of the complexes about centers of symmetry.

Introduction

We have recently initiated a systematic study of several complexes obtained by the reaction of glycylglycinatocopper(II) with substituted and unsubstituted purines and pyrimidines (Kistenmacher, Szalda & Marzilli, 1975). Our interest in these systems stems primarily from an attempt to understand clearly the role played by interligand interactions (*i.e.* interactions between two or more ligands in the coordination sphere of a metal complex) in determining the preferential site for complexation to multi-site ligands (Marzilli, Kistenmacher, Darcy, Szalda & Beer, 1974). In particular, we are interested in multi-site ligands (*e.g.* purines and pyrimidines) where electronic effects play only a small role in binding-site selectivity.

As an aid in the interpretation of these binding site studies, we wished to examine in detail a complex of glycylglycinatocopper(II) where no interligand interactions were present. An obvious choice for such a study is the complex of glycylglycinatocopper(II) with water. Prior to the present work, structural data on glycylglycinatocopper(II) trihydrate appeared (Hermodsson & Strandberg, 1957; Strandberg, Lindqvist & Rosenstein, 1961; Freeman, 1967). However, until very recently structural parameters based on accurate data were unavailable (Freeman, 1974). We have been able, by a slight modification of a synthetic route to the monohydrate (Manyak, Murphy & Martell, 1955), to obtain crystals of glycylglycinatocopper(II) as the dihydrate.

Experimental

The preparation of glycylglycinatocopper(II) followed essentially from the method of Manyak *et al.* (1955). 2·4 g of $Cu(NO_3)_2.3H_2O$ (0·01 mole) was dissolved in water and converted to copper hydroxide by the addition of 50 ml of 1*N* NaOH. The precipitate was thoroughly washed with water. A suspension of the hydroxide was treated with 1·32 g of glycylglycine (0·01 moles). The deep-blue solution was then filtered and allowed to evaporate slowly. After several days, deep-blue crystals of the dihydrate formed.

Crystals of the dihydrate are monoclinic prisms with [101] as the prism axis. Preliminary photographs indicated a monoclinic lattice with systematic absences hkl, $h+k=2n+1$; $h0l$, $l(h)=2n+1$ consistent with the space groups Cc and $C2/c$. Unit-cell dimensions and their associated standard deviations were obtained

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