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A Planar, Spin-Triplet Cobalt(III) Complex. The Crystal and Molecular Structure of the Tetrabutylammonium Salt of an Anionic Complex of a Quadridentate Ligand Derived from Biuret

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The crystal and molecular structure at 105 K has been determined by X-ray diffraction methods for tetrabutylammonium 1,3,5,8,10,12-hexaaza-2,4,9,11-tetraoxo-6,7-diphenyl-dodecanato(4−)cobaltate(III) monohydrate. The ligand is a condensation product between two molecules of biuret and (*R,S*)-1,2-diphenyl-1,2-ethanediamine. The complex anion is a planar, paramagnetic cobalt(III)-complex. The spin-triplet cobalt(III) ion is coordinated to the four deprotonated amido nitrogen atoms of the ligand. The compound crystallizes in the monoclinic space group *C2/c*. The unit cell dimensions are a=36.074(12) Å, b=8.019(3) Å, c=24.709(11) Å and β=93.60(3)°. The final least squares refinement has a unit weighted residual of 0.041. The four Co–N bonds have an average bond distance 1.837(3) Å which is less than the bond length (1.87–1.90 Å) for a cobalt(III)–amido nitrogen bond in a diamagnetic octahedral complex. The coordination geometry is nearly planar. The molecular dimensions of the two biuret fragments are identical, but one biuret is planar and coplanar with the coordination plane, while the other biuret moiety deviates from planarity and is twisted away from the coordination plane. This irregularity is rationalized in terms of different interactions between the two substituents on the ethylene bridge and the neighbouring oxygen atoms on the biuret units.

Relatively few four-coordinate d^6 systems have been structurally characterized in comparison with the large amount of structural data for six-coordinated d^6 systems. Most interest has focused on the planar iron(II) complexes which may throw light on the biologically important heme iron(II). Thus NMR studies have shown[1] that porphyrinatoiron(II) complexes have spin triplet ground states just as the phthalocyaninatoiron(II) complexes which have been studied by means of magnetic susceptibility,[2] Mössbauer spectroscopy,[3] magnetically induced circular dichroism,[4] and magnetic anisotropy.[5]

There are, however, conflicting reports on the detailed electronic structure of the ground states. In some cases the complexes have been postulated to have an electronic structure

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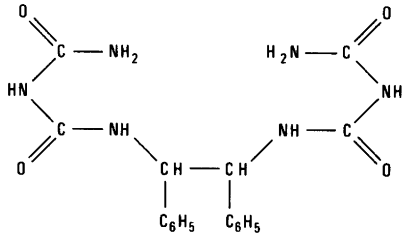
with an axis of symmetry perpendicular to the coordination plane[4,6] and in other studies such an arrangement has been refuted[5] or modified.[7] These discrepancies probably arise because iron(II) complexes of porphyrins and phthalocyanins are too complicated systems and because the present experimental data are inadequate. This investigation is part of a study of four-coordinate cobalt(III) complexes which are isoelectronic with the above-mentioned iron (II) complexes and therefore of direct relevance. The large volume of spectroscopic data for cobalt(III) complexes suggests that it may be easier to describe the electronic structure for a cobalt(III) complex of simple ligands than for the complicated iron(II) systems.

Four-coordinated, paramagnetic cobalt(III) complexes of biuret were discovered by Bour and Steggarda who found that the biuret dianion and related anions form complexes in which a high oxidation state of the metal atom is stabilized.[8] The coordination geometry is a planar arrangement achieved by coordination of four deprotonated amide nitrogen atoms.[9] Birker *et al.* prepared a number of cobalt(III), nickel(III) and copper(III) complexes and also determined the structure of some of these by X-ray diffraction methods.[10–13] Measurements of the magnetic susceptibility of cobalt(III) complexes of this type show that the ground state is indeed a spin triplet state as found for porphyrinatoiron(II) complexes.[11]

The compound studied here is derived from (*R,S*)-1,2-diphenyl-1,2-ethanediamine condensed with two molecules of nitrobiuret to form the protonated ligand, I:



Four-coordinated complexes derived from this and similar ligands may have structures closely analogous to complexes of ligands made by condensation of substituted 1,2-ethanediamines with two molecules of 2,4-pentanedione (acetylacetone, acacH). Complexes of the latter types of ligands with substituents on the bridging ethylene carbon atoms tend to have the substituents in axial positions in the puckered MNCCN ring.[13,14] In general, the equatorial position is energetically favoured in five-membered chelate rings as noticed by Corey and Bailar[15] but for these complexes an axial arrangement of the substituent on the bridge will minimize the steric repulsion between this substituent and the methyl group on the planar ring of the system. Based on this knowledge one can guess that the structure of complexes derived from 1,2-propanediamine and other substituted 1,2-ethanediamines condensed with two molecules of biuret is similar. The meso ligands derived from (*R,S*)-1,2-disubstituted-1,2-ethanediamine have necessarily one axial and one equatorial substituent on the MNCCN-ring if it adopts the normal puckered conformation. This must create a very strained situation and model considerations also indicate that there should be little space for a large equatorial substituent. The present investigation shows how the complex Co[*R,S*-stien(biuret)$_2$]$^-$ accommodates the strain and the results will form a stereochemical basis for spectroscopic work to be reported later.

EXPERIMENTAL

Preparations. The ligand: (*R,S*)-1,2-diphenyl-1,2-bis(biuret)=*R,S*-stien(biuretH_2)$_2$ was prepared according to the procedure given first by Weith[17] with slight modifications. 14.6 g *R,S*-1,2-diphenyl-1,2-ethanediamine[18] and 20.4 g nitrobiuret[19] (in the molar ratio 1:2) were suspended in 100 ml of water. 10 ml of pyridine (in excess) was added to prevent precipitation of an adduct between the amine and nitrobiuret. The mixture was heated to 70 °C and stirred. After approximately 2 h the gas production (N_2O) stopped. The reaction product was precipitated by cooling the mixture in an ice bath and isolated by filtration. The product was washed thoroughly first with water and then with 96 % ethanol and dried in air. The compound showed positive biuret reaction.[20]

The complex: Bu_4N[Co *R,S*-stien(biuret)$_2$]· H_2O. 1 g (2.6 mmol) *R,S*-stien(biuretH_2)$_2$ was dissolved in 10 ml 40 % tetraabutylammonium hydroxide (excess) and 50 ml 96 % ethanol. To this mixture a solution of 0.85 g (3.1 mmol) $Co(NH_3)_6Cl_3$ [21] in 10 ml water was added. The resulting brown mixture was heated with stirring for approx. 4 h at 60 °C and filtered while warm. The red filtrate was cooled in an ice bath and water was added until the first precipitate was formed. After prolonged cooling in the ice bath the solid product was isolated by filtration and recrystallized from ethanol.

Crystallographic examination. Crystals suitable for the X-ray diffraction work were obtained by dissolving the powder in ethanol to near saturation and slowly evaporating approximately half the solvent. The bright red crystals are elongated in the direction of the *b* axis. Preliminary Weissenberg and precession photographs showed that the crystals belong to the monoclinic system. A single crystal with the dimensions 0.1×0.2×0.5 mm^3 was selected for the collection of intensity data and for the determination of accurate unit cell parameters. These measurements were performed with an Enraf-Nonius CAD4 diffractometer using graphite monochromatized Mo$K\alpha$ radiation. The crystal was kept at 105 K during the experiments by means of an Enraf-Nonius gas-flow low-temperature device. Temperature variations recorded with a thermocouple were within 0.5 K.

The setting angles for 16 reflections were used in a refinement of the cell dimensions and the orientation matrix. The intensity data were collected by operating the diffractometer in the $\omega-2\theta$ scan mode. The scan width in ω was $1+0.35\tan\theta$. Scan range was increased by 25 % at both sides to define the background. The maximum scan time was 120 s. The intensities of three standard reflections were recorded after every 10 000 s. To check the orientation of the crystal the setting angles for three reflections were measured after every 100 reflections. These two types of measurements showed no significant variations during the data collection.

The intensities of the reflections with $\theta<27°$ in the octants *hkl* and $-hkl$ were recorded. The data were corrected for background, Lorentz and polarization effects and symmetry related reflections were averaged. The *R*-value between symmetry related reflections was 0.025. Of the 8599 independent reflections so obtained, 4347 satisfied the criterion $(|F|^2/\sigma(|F|^2)>2.0$ and were classified as observed. $\sigma(|F|^2)$ were calculated from counting statistics.

During the crystallographic calculations use was made of the following computer programs: Data reduction programs of local origin,[22] MULTAN[23] and the XRAY SYSTEM[24] for the structure solution and refinement and ORTEP II for the illustrations.[25] The scattering factors used were those of Cromer and Mann[26] except for hydrogen where the values by Stewart *et al.* were employed.[27] The anomalous dispersion corrections added to the scattering factor of the cobalt atom were those reported by Cromer and Liberman.[28]

Crystal data. Tetrabutylammonium (6*R*,7*S*)-1,3,5,8,10,12-hexaaza-2,4,9,11-tetraoxo-6,7-diphenyldodecanato(4−) cobaltate(III), monohydrate; $CoC_{34}H_{54}N_7O_5$; M=698.9 g mol^{-1}; monoclinic; at 105 K: a=36.074(12) Å; b=8.019(3) Å; c=24.709(11) Å; β=93.60(3)°; V=7133 Å^3; D_c=1.30 g cm^{-3}; Z=8; $F(000)$=2992; μ(Mo$K\alpha$)=5.22 cm^{-1}. Systematically absent reflections: *hkl*: $h+k=2n+1$; *h0l*:$l=2n+1$. Spacegroup *C2/c* (No. 15); red crystals elongated along *b*.

Structure determination and refinement. The structure was solved by a combination of Patterson and direct methods. A standard MULTAN run showed the positions of the cobalt atom and the four coordinating nitrogen atoms. The position of the cobalt atom was in agreement with the coordinates deduced from the three-dimensional Patterson function.

After three successive structure factor and difference Fourier calculations the remaining non-hydrogen atoms in the structure were located. The structure was refined by the method of least squares, minimizing $\sum w(F_o-F_c)^2$.

A refinement of the scale factor, positional and anisotropic thermal parameters gave the conventional R-value 0.073. A difference Fourier map calculated at this stage of the refinement revealed the positions of all the hydrogen atoms in the structure. Due to the limited resolution of the data the parameters for the hydrogen atoms were not refined. The hydrogen atoms were introduced in idealized positions (C–H 1.00 Å) and they were given a common isotropic thermal parameter $U=0.03$ Å^{-2}. After the inclusion of the contribution from the hydrogen atoms the refinement converged at $R=0.055$. An analysis of the resulting difference density showed residual density close to two adjacent carbon atoms C63 and C64 in the tetrabutylammonium ion. These atoms both had large thermal parameters and unrealistic bond lengths. These findings suggested that the butyl chain containing these atoms was disordered. A refinement introducing four partly populated carbon atoms, two with a population parameter of 0.75 and two with one of 0.25 with isotropic temperature factors instead of the two fully populated anisotropic C63 and C64 resulted in an R-value of 0.050. A refinement of the population parameters with fixed thermal parameters for these atoms was also performed. For the two major positions C631 and C641 the population parameter was 0.80(2), the two minor sites, C632 and C642 had population parameter 0.2(1). To make this analysis chemically consistent the population parameters were fixed at 0.8 and 0.2 during the final refinement cycles, where anisotropic thermal parameters were introduced also for C631 and C641. This refinement resulted in unweighted and weighted residuals of 0.049 and 0.057, respectively. Weights following the expression $w^{-1}=\sigma(F_o)^2+0.0005F_o^2$ were used.

At this stage an examination of the intensity data showed that the reflections with $\theta>25°$ were of a poorer quality than the remaining data. As a consequence only the 3717 observed reflections with $\theta<25°$ were used in the final refinement. The 432 variables were the scale factor, positional and anisotropic thermal parameters for 47 non-hydrogen atoms and positional and isotropic thermal parameters for the two least populated atoms C632 and C642. The maximum shift of parameters in the final refinement was 0.13 σ and the largest peak in the difference density map, with a maximum of 0.4 e/Å^3, was found to be close to the cobalt atom. The final unweighted and weighted residuals were 0.041 and 0.046, respectively. The final positional parameters and equivalent isotropic temperature factors are given in Table 1. A list of observed and calculated structure amplitudes as well as anisotropic thermal parameters may be obtained from the authors upon request.

DISCUSSION AND DESCRIPTION OF THE STRUCTURE

The crystal structure is composed of discrete tetrabutylammonium ions, complex anions and water molecules. The bond lengths, bond angles and selected torsion angles are listed in Tables 2 and 3.

The tetrabutylammonium ion. The disorder of one of the chains (C61–C62–C63–C64) observed for the ion in this structural study arises from different populations (0.8 and 0.2) of two distinct conformations. The structure of the ion is highly irregular. Three chains are in the *anti* conformation which is normally considered to be the energetically favoured conformation. The disordered chain is found to adopt two different *gauche* conformations. The ORTEP drawing in Fig. 1 shows the two conformations.

The molecular dimensions do not differ significantly from those found in other structures containing this cation. The most frequently found conformation of the tetrabutylammonium ion has all the butyl chains in *anti* conformation resulting in the overall symmetry D_{2d} for the cation.[29] In structures where the ion contains butyl chains in both *anti* and *gauche* conformations, the latter often exhibits either orientational disorder or large thermal parameters. A good example of this correlation between conformation and crystallographic

Table 1. Positional parameters and equivalent isotropic temperature factors for the complex ion, the cation and for water (esd is given in parentheses in units of the last digit). Labelling corresponds to Fig. 2. The population of atoms marked *a* and *b* is 0.8 and 0.2, respectively. U_{eq} was calculated as $U_{eq}=\frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\bar{a}_i\bar{a}_j$.

	Atom	*x*	*y*	*z*	U_{eq}
The cation	N40	0.12435(8)	0.1494(4)	0.3710(1)	0.0184
	C41	0.09576(10)	0.0403(5)	0.3964(2)	0.0216
	C42	0.06368(11)	0.1346(5)	0.4189(2)	0.0286
	C43	0.03033(12)	0.0227(6)	0.4244(2)	0.0361
	C44	−0.00271(12)	0.1189(6)	0.4438(2)	0.0375
	C51	0.10629(11)	0.2558(5)	0.3253(2)	0.0235
	C52	0.08300(11)	0.1610(5)	0.2824(2)	0.0275
	C53	0.06722(15)	0.2812(6)	0.2393(2)	0.0526
	C54	0.04341(17)	0.1974(6)	0.1949(2)	0.0677
	C61	0.14106(11)	0.2659(5)	0.4145(2)	0.0239
	C62	0.16837(13)	0.3913(6)	0.3960(2)	0.0395
	C631[a]	0.18590(14)	0.4816(7)	0.4480(2)	0.0278
	C641[a]	0.22114(16)	0.3944(8)	0.4667(2)	0.0396
	C71	0.15388(10)	0.0389(5)	0.3473(2)	0.0222
	C72	0.18302(11)	−0.0314(5)	0.3875(2)	0.0256
	C73	0.21041(11)	−0.1420(5)	0.3591(2)	0.0286
	C74	0.24549(10)	−0.1754(6)	0.3955(2)	0.0301
	C632[b]	0.2079(5)	0.414(2)	0.4342(8)	0.0136
	C642[b]	0.1931(6)	0.524(3)	0.4793(10)	0.0321
The anion	Co	0.56937(1)	0.16949(6)	0.16309(2)	0.0147
	N1	0.61514(7)	0.1817(4)	0.2007(1)	0.0149
	N2	0.54519(8)	0.2360(4)	0.2226(1)	0.0175
	N3	0.59486(8)	0.1124(4)	0.1037(1)	0.0142
	N4	0.52408(8)	0.1468(4)	0.1260(1)	0.0189
	C1	0.62176(9)	0.1570(5)	0.2551(1)	0.0164
	O1	0.65135(7)	0.1055(3)	0.2764(1)	0.0205
	C2	0.55671(10)	0.2396(5)	0.2751(1)	0.0162
	O2	0.53671(7)	0.2782(3)	0.3122(1)	0.0190
	C3	0.58194(9)	0.0608(4)	0.0532(1)	0.0147
	O3	0.60215(6)	0.0300(3)	0.0160(1)	0.0178
	C4	0.51566(10)	0.0877(5)	0.0762(1)	0.0169
	O4	0.48292(7)	0.0694(3)	0.0578(1)	0.0228
	N5	0.59326(8)	0.1949(4)	0.2885(1)	0.0156
	N6	0.54383(8)	0.0419(4)	0.0443(1)	0.0167
	C5	0.64747(9)	0.1481(5)	0.1686(1)	0.0149
	C6	0.63407(9)	0.1627(5)	0.1076(1)	0.0159
	C7	0.68032(10)	0.2606(5)	0.1837(1)	0.0188
	C8	0.67548(11)	0.4295(5)	0.1944(2)	0.0230
	C9	0.70591(12)	0.5323(5)	0.2045(2)	0.0308
	C10	0.74154(12)	0.4682(7)	0.2039(2)	0.0387
	C11	0.74648(11)	0.3016(6)	0.1938(2)	0.0348
	C12	0.71616(10)	0.1984(5)	0.1839(2)	0.0248
	C13	0.63858(9)	0.3360(5)	0.0830(1)	0.0168
	C14	0.60996(11)	0.4519(5)	0.0797(2)	0.0276
	C15	0.61494(12)	0.6101(5)	0.0583(2)	0.0364
	C16	0.64855(13)	0.6543(6)	0.0393(2)	0.0386
	C17	0.67747(12)	0.5411(6)	0.0415(2)	0.0308
	C18	0.67233(10)	0.3815(5)	0.0630(1)	0.0226
The water oxygen	080	0.08988(7)	0.6239(3)	0.40856(10)	0.0248

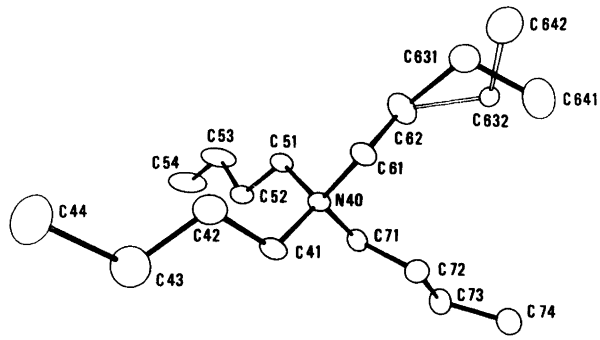


Fig. 1. The tetrabutylammonium ion. The two conformations of one of the butyl groups are shown in full (population 0.8) and in open (population 0.2)

Table 2. Bond distances (in Å) and bond angles (in degrees) in the complex anion.

Distances	Co–N1	1.846(3)	N1–C5	1.475(4)
	Co–N2	1.834(3)	N3–C6	1.468(4)
	Co–N3	1.838(3)	C5–C6	1.558(5)
	Co–N4	1.831(3)	C5–C7	1.517(5)
	N1–C1	1.365(4)	C6–C13	1.529(5)
	N2–C2	1.338(5)	C7–C8	1.393(6)
	N3–C3	1.368(4)	C8–C9	1.383(6)
	N4–C4	1.335(5)	C9–C10	1.385(6)
	C1–O1	1.231(4)	C10–C11	1.373(7)
	C2–O2	1.241(4)	C11–C12	1.381(6)
	C3–O3	1.233(4)	C12–C7	1.385(5)
	C4–O4	1.247(4)	C13–C14	1.387(5)
	C1–N5	1.392(5)	C14–C15	1.390(6)
	C2–N5	1.387(4)	C15–C16	1.373(7)
	C3–N6	1.387(4)	C16–C17	1.382(6)
	C4–N6	1.375(5)	C17–C18	1.401(6)
			C18–C13	1.391(5)
Angles	N1–Co–N2	92.1(1)	C5–N1–Co	115.6(2)
	N1–Co–N3	86.5(1)	C6–N3–Co	114.0(2)
	N2–Co–N4	88.6(1)	N1–C5–C6	107.4(2)
	N3–Co–N4	92.9(1)	N3–C6–C5	106.4(3)
	Co–N1–C1	125.7(2)	C6–C5–C7	112.5(3)
	Co–N2–C2	130.5(2)	C5–C6–C13	114.7(3)
	Co–N3–C3	130.1(2)	C7–C8–C9	120.4(4)
	Co–N4–C4	129.8(2)	C8–C9–C10	120.3(4)
	N1–C1–N5	117.6(3)	C9–C10–C11	119.6(4)
	N2–C2–N5	117.3(3)	C10–C11–C12	120.3(4)
	N3–C3–N6	117.0(3)	C11–C12–C7	120.9(4)
	N4–C4–N6	119.3(3)	C12–C7–C8	118.5(3)
	N1–C1–O1	124.3(3)	C13–C14–C15	121.4(4)
	N2–C2–O2	124.2(3)	C14–C15–C16	120.2(4)
	N3–C3–O3	123.8(3)	C15–C16–C17	119.8(4)
	N4–C4–O4	122.2(3)	C16–C17–C18	119.8(4)
	C1–N5–C2	129.9(3)	C17–C18–C13	120.9(4)
	C3–N6–C4	129.9(3)	C18–C13–C14	117.9(4)

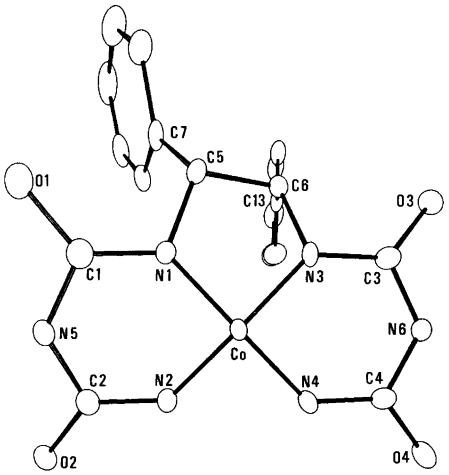


Fig. 2. An ORTEP drawing of the anion Co[*R*,*S*-stien(biuret)$_2$]. The phenyl group on C6 is the axial substituent and the phenyl group on C5 is an equatorial substituent on the puckered chelate ring N1CoN3C6C5.

disorder is found in the structure of tetrabutylammonium dicyanidocuprate(I).[30] This compound contains two crystallographically independent cations. One of these has all four butyl groups in *anti* conformations and normal molecular dimensions and thermal parameters are observed. The other ion contains two *anti* chains and two *gauche* chains and significant disorder is observed for the latter groups. Other examples of structures containing both ordered and disordered tetrabutylammonium ions confirming this generalization are found in Refs. 29–35. An ordered tetrabutylammonium ion containing both *anti* and *gauche* chains has been published but for this cation the overall symmetry is relatively high (C_{2v}).[36] Accordingly, it is not surprising that conformational disorder is observed in the present structure where the cation lacks symmetry.

The complex anion. The molecular dimensions of the anion are given in Table 2. The cobalt atom is surrounded by an approximately planar arrangement of the four coordinating nitrogen atoms. The molecule, as seen perpendicular to the coordination plane, is shown in Fig. 2 which also illustrates the labelling. The four Co–N bonds in this paramagnetic cobalt(III)-complex are much shorter ⟨Co–N⟩=1.837(3) Å than Co–N bonds in octahedrally coordinated diamagnetic cobalt(III)–amine complexes, which are typically 1.95–2.00 Å. The distance between low-spin Co(III) and amido-nitrogen should be shorter and it has been found to be in the range 1.87–1.89 Å as *e.g.* in the amidine complex $[Co(NH_2CH_2CH_2NC(NH_2)CH_2NH_2)\ (NH_2CH_2CH_2NH_2)Cl]^{2+}$.[37] The bite angles for the biuret fragments are slightly larger (92.5°) than the bite angle over the bridging diamine group, N1–Co–N3, 86.5°. This is in agreement with the results found in a similar complex of copper(III) and in the structures of the previously mentioned metal(II) complexes of ligands formed from condensation products between diamines and enones. The bond lengths and bond angles within the biuret moieties of the ligand agree well with those found in structures containing coordinated and uncoordinated deprotonated biuret[9,12,13,38] fragments. The only significant difference between biuret in this structure and related ones is that the two C–N bonds adjacent to the bridging ethylenediamine (C1–N1 and C3–N3) are significantly longer ⟨C–N⟩=1.367(4) Å than the similar bonds (C2–N2 and C4–N4) ⟨C–N⟩=1.337(4) Å. The latter value is identical to the C–N bond lengths found in other biuret structures. 1,2-Phenylenebis(biuretato)cuprate(III) is an example of another structure with a ligand

Table 3. Bond distances (in Å) and bond and torsion angles (in degrees) in the tetrabutylammonium ion.

Distances	N40–C41	1.518(5)	C53–C54	1.508(7)
	N40–C51	1.528(5)	C61–C62	1.499(6)
	N40–C61	1.520(5)	C62–C631	1.573(7)
	N40–C71	1.530(5)	C631–C641	1.498(8)
	C41–C42	1.516(6)	C62–C632	1.67(2)
	C42–C43	1.514(6)	C632–C642	1.55(3)
	C43–C44	1.522(6)	C71–C72	1.510(5)
	C51–C52	1.515(5)	C72–C73	1.531(6)
	C52–C53	1.522(6)	C73–C74	1.530(5)
Angles	C41–N40–C51	111.0(3)	C51–C52–C53	109.8(3)
	C41–N40–C61	108.1(3)	C52–C53–C54	113.5(4)
	C41–N40–C71	109.4(3)	N40–C61–C62	115.9(3)
	C51–N40–C61	108.1(3)	C61–C62–C631	107.4(4)
	C51–N40–C71	108.4(3)	C62–C631–C641	109.0(4)
	C61–N40–C71	111.8(3)	C61–C62–C632	117.0(7)
	N40–C41–C42	114.7(3)	C62–C632–C642	98(1)
	C41–C42–C43	111.5(3)	N40–C71–C72	115.9(3)
	C42–C43–C44	111.8(4)	C71–C72–C73	110.9(3)
	N40–C51–C52	115.4(3)	C72–C73–C74	111.4(3)
Torsion angles	C41–C42–C43–C44	−176.6(3)	N40–C71–C72–C73	178.9(3)
	C51–C52–C53–C54	−179.7(4)	C41–N40–C51–C52	−52.4(4)
	C61–C62–C631–C641	93.6(5)	C41–N40–C61–C62	−176.3(3)
	C61–C62–C632–C642	−79.2(1)	C41–N40–C71–C72	−78.5(4)
	C71–C72–C73–C74	164.6(3)	C51–N40–C41–C42	−57.4(4)
	N40–C41–C42–C43	159.2(3)	C51–N40–C61–C62	−56.1(4)
	N40–C51–C52–C53	−179.2(3)	C51–N40–C71–C72	160.4(3)
	N40–C61–C62–C631	−172.7(3)	C61–N40–C71–C72	41.3(4)
	N40–C61–C62–C632	−133.8(8)	C71–N40–C61–C62	63.2(4)

formed by condensation with biuret. The average metal-nitrogen distance is longer in the copper(III) complex (1.86 Å) than in the cobalt(III) complex [1.837(3) Å] and this could indicate that the former complex has more electron density in an antibonding σ^* orbital (d_{z^2}). Unfortunately, the precision of the structure determination of the copper(III) complex does not make it possible to conclude if condensation has caused elongation of two of the C–N bonds.[13]

Another view of the anion showing the stereochemistry is given in Fig. 3. Deviations from planarity have been analyzed by calculating least-squares planes. One biuret moiety is nearly planar (maximum deviation: 0.08 Å), but the other is distorted from planar geometry (maximum deviation: 0.144 Å). This lack of symmetry in the ligand is also apparent from the angles between the least-squares planes of each biuret moiety and the coordination plane formed by cobalt and the four nitrogen atoms. The "planar" biuret group forms an angle of 5.4° with the coordination plane. This is interpreted as a small tetrahedral distortion observed for the nearly planar coordination geometry. The magnitude of the angles is as expected from comparisons with structures of the abovementioned "planar" complexes.[15] In contrast, the biuret group which is not planar has an angle of 20.2° with the coordination plane.

The ethylene bridge adopts an distorted *gauche* conformation with one carbon atom, C6, 0.505 Å above the coordination plane, and the other, C5, nearly in the plane (0.009 Å). The

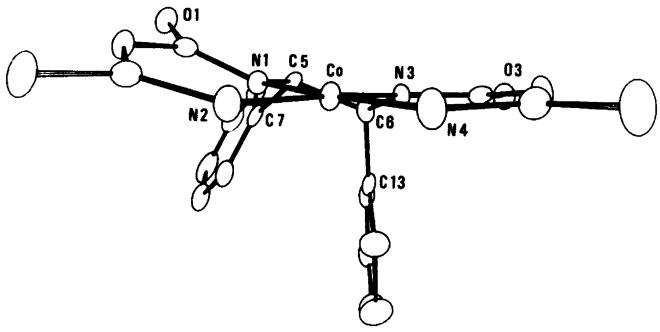


Fig. 3. An ORTEP drawing along the pseudo C_2 axis of Co[*R*,*S*-stien(biuret)$_2$] showing how the equatorial phenyl group on C5 and the oxygen atom of the adjacent biuret group avoid contact.

dihedral angle defined by N1–C5–C6–N3 is −30.5°. In an idealized *gauche* conformation, the carbon atoms will be situated symmetrically above and below the coordination plane with a dihedral angle of 60°.

One half section of the molecule containing the planar biuret fragment has the expected geometry of a planar four-coordinate complex with a bridging ethylene group but the other half shows great deviatins from the ideal conformation. The drawing in Fig. 3 shows clearly that the half of the molecule containing the axial phenyl group attached to C6 is planar. It is obvious that the way the biuret group is twisted has the effect of alleviating steric repulsions between the equatorial phenyl group and the oxygen atom of the biuret. The shortest distance is observed between O1 and C7, 2.86 Å, while the equivalent distance from O3 to a carbon atom on the axial phenyl group O3–C13 is 3.20 Å.

In order to asses if some of the structural irregularity of the ligand could be due to intermolecular interactions, the packing in the crystal was examined. The water molecule of

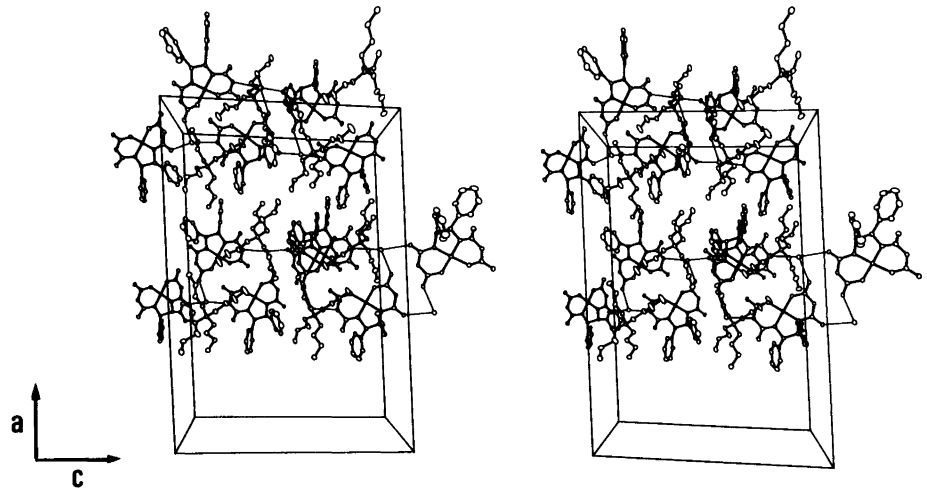


Fig. 4. A stereo pair showing how bands of anions are kept together by a hydrogen bond network while contacts between the bands are provided through interactions between phenyl groups and tetrabutylammonium ions.

crystallization is involved hydrogen bonding to three different complex anions resulting in a hydrogen-bond pattern as illustrated in the stereo pair shown in Fig. 4. The distances of the hydrogen bonds are: O80–O4 ($\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z$)=2.837(4) Å, O80–N5 ($x-\frac{1}{2},\frac{1}{2}+y,z$)= 3.030(4) Å, O80–O3 ($x-\frac{1}{2},\frac{1}{2}-y,\frac{1}{2}+z$)=2.935(4) Å. The bands of hydrogen bonded complex anions are held together by weak interactions between the phenyl groups and butyl groups from the cation. The shortest distance between two carbon atoms is 3.60 Å. This distance corresponds to the sum of the van der Waals radii. Thus it seems unlikely that the packing would cause the distortions observed in the anion. It is concluded that intramolecular interaction between the substituent on the planar chelate ring and a substituent on the puckered bridging chelate ring determines the structure of the complex. In this case the result is a highly distorted structure. In a structure containing two axial substituents on the ethylene bridge as in Co[*R,R*-stien(biuret)$_2$] we would expect a weak tetrahedral distortion of the coordination plane and both biuret fragments to be planar.

The drawing of the crystal packing shows that the coordination plane is nearly parallel to the *ac* plane. The angle between the two planes is 16.5°. The absorption causing the red colour of the crystal in solution has a maximum near 500 nm. Under a polarizing microsope the colour (absorption) is most intense when the electric vector is perpendicular to the *b* axis. We can therefore conclude that this light absorption is polarized perpendicular to the *b* axis and thus essentially takes place in the coordination plane.

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