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The Crystal Structure of Tetrakis(urea)cobalt(II) Nitrate

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The structure of tetrakis(urea)cobalt(II) nitrate, $[Co(H_2NCONH_2)_4](NO_3)_2$, has been determined from three-dimensional X-ray diffraction data using CoKα radiation. The pink crystals are monoclinic, space group $P2_1/c$, and have cell constants, a = 4.522(3)A, b = 17.69(1)A, c = 10.034(2) and β = 103.8(2)°. The cobalt atoms are found to be located at special positions. The measured density by flotation is 1.79 g/cc, while two molecules per unit cell give a calculated density of 1.80 g/cc. The intensities of 650 independent reflections above background, collected on film by the Weissenberg method, were estimated visually. The structure has been determined by three-dimensional Fourier methods and refined by full-matrix least squares to an unweighted conventional R-factor of 0.075. Co-ordination about the cobalt atom is octahedral with two oxygen bound urea molecules in the axial positions, and two urea molecules bound as bidentates through the oxygen and nitrogen forming bridges, along the a-axis, between cobalt atoms in adjacent unit cells. The nitrate groups are ionic. Structurally the compound is polymeric. Octahedral bond distances of interest are, Co–O(monodentate urea in axial position) 2.055(7)A, Co–O(bidentate urea) 2.100(9)A, Co–N(bidentate urea) 2.231(9)A. The octahedral angles, as well as bond angles and bond distances in the urea ligands are only slightly distorted. This compound exhibits for the first time a nonionic three atom bridging moiety with chemically different bonding terminals.

Introduction

Molecular urea can co-ordinate through either the oxygen or the nitrogen atoms[1–4]. Recently[5] a complex, $[Co(urea)_4](NO_3)_2$, was prepared in which the urea was postulated to be bound in the monodentate and the bidentate configuration. The evidence was based on infrared and visible spectra in addition to stoichiometric considerations. A single crystal X-ray analysis of the compound was undertaken in order to verify unequivocally this newly observed phenomenon of urea bidentation, and to establish the mode of urea bidentation be it chelating or bridging.

Experimental Section

Preparation

Tetrakis(urea)cobalt(II) nitrate prepared by solid-solid interaction was recrystallized from warm n-butanol by allowing the solvent to evaporate slowly in a dry atmosphere. Aggregates of pink needle-like crystals with melting point 114–5° C were obtained.
Anal. Calcd. for $Co(urea)_4(NO_3)_2$: Co, 13.93.
Found: Co, 13.98.

X-Ray

Lattice parameters were determined at room temperature using iron-filtered cobalt radiation from a rotation photograph about the *a*-axis and a Weissenberg photograph of the 0kl zone. Unit cell dimensions reported are obtained by extrapolation to a Bragg angle of 90°. The error is the standard deviation of the intercept. The monoclinic angle, β, was measured from a Weissenberg photograph of the h0l zone. The error reported is the standard deviation of the mean. Crystal data are collected in Table I.

Oscillation and equi-inclination Weissenberg photographs, 0kl–3kl, defined the space group uniquely as $P2_1/c$. There were no systematic absences in the general set hkl, however, reflections with k+l = 2n were

TABLE I. Crystallographic Data for $[Co(urea)_4](NO_3)_2$.

M.W. = 423.19	
Crystallographic system:	monoclinic
Space group:	$P2_1/c$
Unit cell parameters:	a = 4.522(3) Å
	b = 17.69(1) Å
	c = 10.034(2) Å
	β = 103.8(2)°
	V = 779.6 Å^3
	Z = 2
$d_{calcd.}$ = 1.80 g/cm^3	$\mu_{CoK\alpha}$ = 36 cm^{-1}
$d_{obs.}$ = 1.79 g/cm^3	λ = 1.7902 Å
F_{000} = 434	

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generally darker than reflections with $k+l = 2n+1$ indicating that the heavy atoms are located in special positions related by translation $b/2 + c/2$. Density measurement by flotation proved the presence of two molecules, $Co(urea)_4(NO_3)_2$, per unit cell and confirmed the location of the cobalt atoms at centers of inversion.

For the purpose of collection of intensity data, a crystal of dimensions $0.3 \times 0.1 \times 0.1$ mm ($a \times b \times c$) was employed. Equi-inclination Weissenberg levels, 0kl–3kl, were recorded using CoKα radiation and employing the multiple film technique in conjunction with different exposure time. The intensity of 650 out of 991 theoretically accessible reflections was estimated visually by comparison with a calibrated strip. The average intensities were then corrected for Lorentz, polarization, and cylindrical absorption effects[6]. The levels 0kl–3kl were then put on a common relative scala by intercorrelation with the levels h0l–h5l. The latter levels were recorded on film using a precession camera and zirconium-filered molybdenum radiation[7]. In order to double check the scale factors used in the intercorrelation of the levels 0kl–3kl, a separate scale factor was calculated for each level[8,9] at the last stage of the refinement. The scale factors thus obtained were in close agreement with the ones used in the structure determination.

Solution and Refinement

The structure was determined by the heavy atom method. The positions of the cobalt atoms in the unit cell were taken to be at 0,0,0 and 0,1/2,1/2. An overall temperature factor of $4.0\ A^2$ was arbitrarily assigned to the structure. A three dimensional Fourier summation[8] phased on the cobalt atom alone showed the non-hydrogen light atoms which upon inclusion in the Fourier summation resulted in an unweighted residual of 0.34 if one scale factor and one overall temperature factor were employed. Assignment of individual isotropic thermal parameters, followed by six cycles of full matrix least squares refinement[10] of the coordinates, thermal parameters and overall scale factor reduced the unweighted residual to 0.16. Allowance of the anisotropic thermal motion of the atoms in the refinement reduced the unweighted residual to 0.075 and the weighted residual to 0.080. The maximum shift in the last cycle of refinement was less than

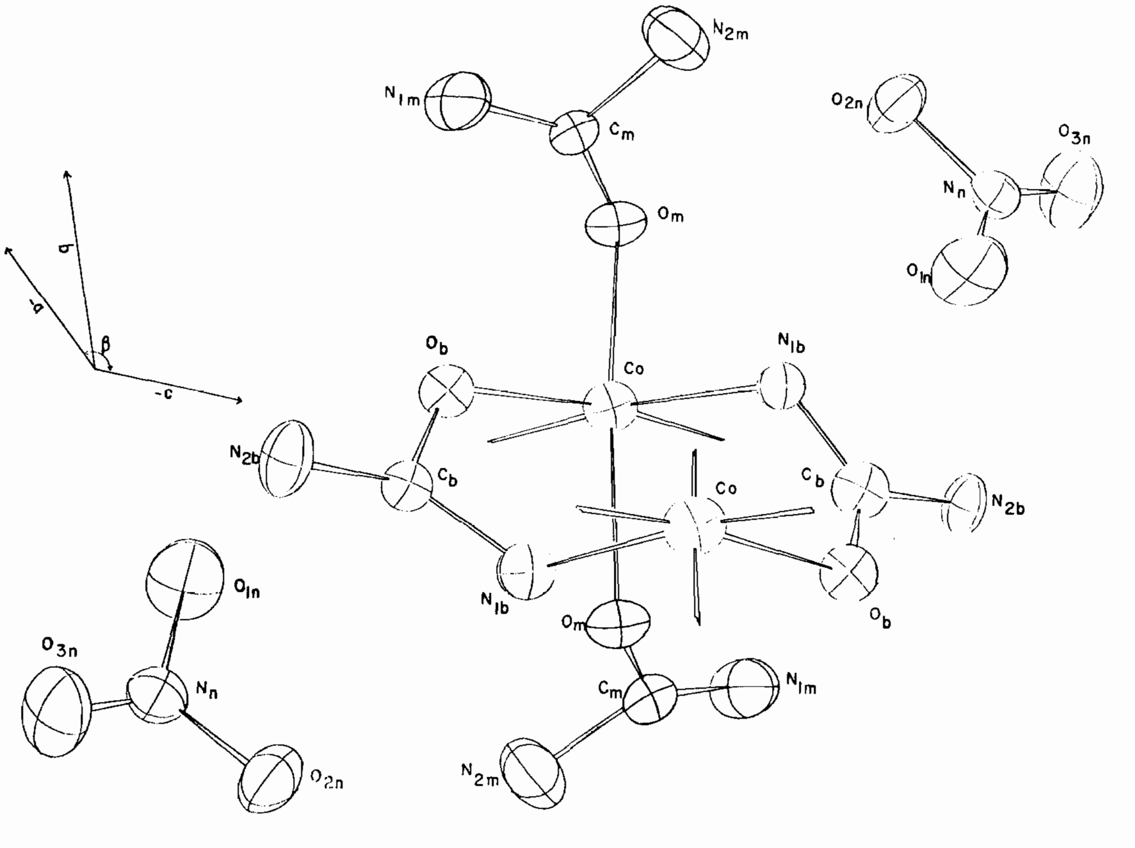

Figure 1. Three-dimensional view of the molecular unit.

0.01 σ. The function minimized was $\Sigma w(|F_o|-k|F_c|)^2$ where w is a weighting factor and k is a scale factor. The unweighted residual, R, is defined as $\Sigma(|F_o|-k|F_c|)/\Sigma|F_o|$, and the weighted residual, wR, as $[\Sigma w(|F_o|-k|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. The normal atomic scattering factors, f_o. were evaluated from Dirac-Slater wave functions by Cromer and Waber[10]. The scattering factors for the cobalt atom were corrected for real, $\Delta f'$, and immaginary, $\Delta f''$, dispersion as suggested by Cromer[11]. Empirical weighting schemes were attempted but all gave worse values of R and wR than simply weighting all observations equally. All observations were therefore given unit weight. Reflections were not excluded from refinement because of extinction effects. Unobserved planes were not included in the calculation of the residual.

The highest peak on the final difference-Fourier synthesis was equal to 1.5 e/A^3 and was located intermediate between cobalt atoms in adjacent unit cells and along the *a*-axis (1/2,0,0). The second highest peak was equal to 0.5 e/A^3. The positions of the hydrogen atoms were not apparent. Interatomic distances, bond angles and dihedral angles were calculated[12] without correction for thermal motion. Figure 1 is an ORTEP program plot of a three-dimensional view of the molecular unit[14] (Tables II to VI).

TABLE II. Observed and Calculated Structure Amplitudes (F_{000} = 434).

H = 0			
K	L	FOBS	FCALC
2	0	65	75
4	0	21	17
6	0	93	98
8	0	36	35
10	0	37	34
12	0	22	18
16	0	8	7
18	0	15	17
1	1	56	55
2	1	21	19
3	1	61	66
4	1	11	12
5	1	70	72
6	1	24	24
7	1	8	4
8	1	34	28
9	1	45	41
10	1	18	17
11	1	39	34
12	1	20	19
13	1	13	12
14	1	11	9
17	1	25	23
19	1	16	18
0	2	66	68
1	2	48	49
2	2	13	9
3	2	10	13
4	2	41	39
5	2	61	56
8	2	56	55
9	2	14	15
10	2	22	20
11	2	8	7
12	2	19	17
13	2	27	25
14	2	23	21
17	2	7	8
19	2	17	16
1	3	31	31
2	3	20	18
3	3	4	1
4	3	16	16
5	3	9	9
6	3	9	8
7	3	15	13
8	3	14	13
9	3	39	37
10	3	21	18
11	3	39	35
13	3	13	12
14	3	5	6
17	3	14	14
0	4	14	17
1	4	31	25
2	4	17	18
3	4	43	39
4	4	16	17
6	4	32	31
7	4	22	22
8	4	49	46
10	4	33	30
11	4	9	9
12	4	33	29
14	4	22	18
16	4	12	11
17	4	8	9
19	4	15	17
1	5	62	61
2	5	19	18
3	5	34	31
5	5	11	11
6	5	25	23
7	5	38	36
9	5	47	41
10	5	20	19
11	5	29	29
13	5	15	15
15	5	12	9
16	5	9	9
17	5	9	9
0	6	70	66
2	6	42	39
4	6	38	32
6	6	39	36
7	6	18	18
10	6	19	17
12	6	12	9
13	6	11	10
14	6	11	10
15	6	7	5
16	6	9	10
1	7	30	27
2	7	33	30
3	7	9	9
4	7	9	8
7	7	14	14
9	7	14	13
10	7	8	7
11	7	8	9
12	7	7	7
14	7	5	4
2	8	25	23
3	8	11	12
4	8	6	4
8	8	19	18
9	8	10	15
10	8	14	14
12	8	8	8
1	9	14	13
2	9	16	15
3	9	19	17
4	9	15	13
5	9	12	10
6	9	13	11
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9	9	13	11
0	10	6	5
1	10	6	5
2	10	13	11
5	10	5	6
6	10	5	6
H = 1			
K	L	FOBS	FCALC
0	0	26	24
1	0	9	11
2	0	7	11
3	0	18	21
4	0	49	47
6	0	3	5
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10	0	36	39
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12	0	16	16
13	0	8	11
16	0	7	8
17	0	9	9
18	0	20	21
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2	1	28	24
5	1	49	51
6	1	32	31
7	1	38	39
8	1	26	24
9	1	6	9
10	1	23	23
11	1	12	10
12	1	8	7
13	1	22	26
14	1	8	9
15	1	13	14
17	1	15	18
19	1	14	17
0	2	79	81
1	2	44	39
2	2	46	46
3	2	9	11
4	2	15	16
5	2	17	16
6	2	9	11
8	2	29	31
10	2	37	39
11	2	15	15
12	2	28	32
14	2	11	13
16	2	12	14
18	2	23	28
1	3	51	47
2	3	57	57
3	3	65	66
4	3	19	20
5	3	24	26
6	3	28	29
7	3	35	37
9	3	24	26
10	3	19	18
12	3	13	14
13	3	14	16
16	3	10	10
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2	4	31	33
3	4	15	13
4	4	6	6
5	4	16	17
6	4	30	36
7	4	9	10
8	4	19	20
10	4	14	17
12	4	12	15
13	4	12	13
1	5	17	17
2	5	24	27
4	5	9	10
5	5	18	21
6	5	12	14
7	5	14	17
8	5	19	19
9	5	18	19
11	5	43	44
0	6	20	22
1	6	12	14
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8	6	25	28
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8	7	9	7
9	7	18	16
10	7	11	12
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1	8	7	7
2	8	13	12
5	8	8	9
6	8	10	10
7	8	4	4
8	8	10	11
11	8	7	9
1	9	14	14
2	9	6	8
3	9	20	23
7	9	6	7
8	9	4	10
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2	-1	31	34
3	-1	87	82
4	-1	72	69
5	-1	43	40
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15	-1	9	9
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6	-2	70	70
7	-2	25	24
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11	-2	5	5
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13	-2	11	13
15	-2	17	12
17	-2	9	9
1	-3	87	91
2	-3	84	81
3	-3	48	45
4	-3	42	36
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7	-3	53	55
8	-3	29	37
9	-3	55	58
10	-3	13	13
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12	-3	14	15
13	-3	29	31
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13	-5	7	7
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12	-6	7	8
14	-6	11	11
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1	-10	13	14
2	-10	6	6
3	-10	11	11
4	-10	4	6
5	-10	3	4
H = 2			
K	L	FOBS	FCALC
0	0	14	18
1	0	30	31
2	0	25	25
3	0	29	27
4	0	25	27
5	0	9	6
6	0	69	68
8	0	18	19
9	0	22	19
10	0	18	16
11	0	16	14
12	0	32	32
14	0	30	28
16	0	17	16
17	0	12	11
1	1	36	35
2	1	12	9
3	1	52	50
4	1	8	10
5	1	24	28
6	1	12	11
7	1	25	26
9	1	18	21
10	1	10	10
11	1	12	9
12	1	10	9
13	1	17	17
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1	2	20	17
2	2	46	47
4	2	42	42
5	2	15	16
6	2	31	30
7	2	44	41
8	2	25	23
9	2	17	18
11	2	10	9
12	2	14	14
14	2	11	10
1	3	48	44
2	3	8	7
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4	3	15	17
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4	4	34	31
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3	-1	16	17
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9	-1	35	36
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15	-1	17	17
16	-1	9	8
17	-1	19	21
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2	-2	18	19
3	-2	13	8
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6	-2	50	49
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16	-2	12	12
1	-3	23	22
2	-3	24	24
3	-3	26	25
5	-3	56	57
6	-3	5	5
8	-3	15	16
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11	-3	14	12
12	-3	17	16
13	-3	14	12
15	-3	12	11
16	-3	20	19
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0	-4	60	58
2	-4	44	43
4	-4	39	41
5	-4	37	35
6	-4	24	25
7	-4	18	13
8	-4	22	20
11	-4	14	12
12	-4	10	9
14	-4	17	16
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3	-5	63	70
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7	-5	26	27
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13	-5	23	21
14	-5	10	9
15	-5	17	16
0	-6	13	13
1	-6	11	10
2	-6	9	7
3	-6	19	17
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13	-7	17	19
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10	-8	5	5
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0	-10	14	14
1	-10	5	6
2	-10	20	23
4	-10	19	21
6	-10	16	17
H = 3			
K	L	FOBS	FCALC
0	0	18	16
2	0	38	39
3	0	12	9
4	0	49	49
6	0	37	37
8	0	28	26
10	0	15	11
11	0	14	9
14	0	23	24
12	0	21	21
13	0	14	11
1	1	23	23
3	1	29	30
5	1	35	37
6	1	9	7
7	1	34	33
9	1	21	19
11	1	28	26
13	1	25	23
15	1	9	10
1	2	19	18
4	2	16	16
5	2	18	20
6	2	35	41
8	2	12	13
9	2	8	10
12	2	20	17
14	2	14	17
3	3	14	11
4	3	15	12
5	3	15	13
11	3	21	22
6	4	35	37
8	4	10	7
9	4	10	10
1	-1	34	41
2	-1	23	24
3	-1	34	34
5	-1	50	49
6	-1	10	9
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2	-3	7	5
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5	-3	34	35
6	-3	17	15
7	-3	21	20
9	-3	12	10
12	-3	8	7
13	-3	26	28
15	-3	21	25
0	-4	25	25
2	-4	27	26
3	-4	25	24
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2	-6	17	16
4	-6	24	25
5	-6	8	8
6	-6	17	17
8	-6	25	26
1	-7	21	19
3	-7	31	31
5	-7	20	19
8	-7	17	17
9	-7	16	14
11	-7	8	7
0	-8	21	19
2	-8	18	16
4	-8	21	21
6	-8	18	18
7	-8	15	14
8	-8	9	8
9	-8	8	9
1	-9	10	10
2	-9	6	7
3	-9	16	18
5	-9	9	9
7	-9	6	8
2	-10	13	15

TABLE III. Fractional Atomic Coordinates and Isotropic Thermal Parameters.[1]

Atom	x/a	y/b	z/c	B
Co	0.0000	0.0000	0.0000	1.3
O_m	−0.1797(17)[2]	0.1055(04)	0.0147(08)	4.2
C_m	−0.0433(26)	0.1681(06)	0.0375(11)	4.9
N_{1m}	0.1288(27)	0.1852(06)	0.1675(11)	4.2
N_{2m}	−0.0752(29)	0.2206(07)	−0.0590(12)	5.5
O_b	0.3480(19)	0.0248(04)	0.1742(08)	2.1
C_b	0.3823(28)	−0.0039(07)	−0.2146(11)	2.9
N_{1b}	0.2466(21)	0.0505(05)	−0.1461(09)	2.5
N_{2b}	0.2001(24)	−0.0335(06)	−0.3333(10)	2.6
N_n	0.4562(25)	−0.1418(06)	0.4158(11)	3.8
O_{1n}	0.2262(24)	−0.1009(06)	0.3934(10)	5.4
O_{2n}	0.5180(22)	−0.1795(05)	0.3206(09)	4.0
O_{3n}	0.6275(23)	−0.1429(06)	0.5320(10)	7.3

[1] The form of the isotropic thermal parameter is exp–B (sin $\Theta/\lambda)^2$. The values reported for the isotropic thermal parameters are at R of 0.16.

[2] The quantities enclosed in brackets are the estimated standard deviations.

TABLE IV. Anisotropic Thermal Parameters[1] as Mean Square Amplitude.

Atom	$U_{11} \times 10^4$	$U_{22} \times 10^4$	$U_{33} \times 10^4$	$U_{13} \times 10^4$
Co	68(28)[2]	285(15)	362(15)	394(48)
O_m	166(55)	269(48)	520(56)	461(173)
C_m	145(82)	285(63)	372(71)	250(240)
N_{1m}	640(90)	444(63)	449(71)	−874(269)
N_{2m}	815(109)	507(79)	571(76)	413(317)
O_b	88(64)	427(48)	449(46)	394(173)
C_b	114(93)	349(63)	449(71)	634(259)
N_{1b}	217(72)	349(63)	423(61)	865(211)
N_{2b}	370(78)	539(63)	331(61)	− 96(221)
N_n	380(94)	365(63)	454(76)	548(279)
O_{1n}	561(84)	856(79)	709(71)	423(250)
O_{2n}	701(78)	555(63)	444(61)	461(231)
O_{3n}	568(79)	919(79)	469(66)	−653(240)

[1] The form of the anisotropic thermal parameter is exp–$[2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{13}hla^*c^*\cos\beta^*)]$. $U_{ij} = B_{ij}/8\pi^2$.

[2] The quantities enclosed in brackets are the estimated standard deviations.

TABLE V. Interatomic Distances (Å).

Co–O_m	2.055(7)[1]
Co–O_b	2.100(9)
Co–N_{1b}	2.231(9)
C_m–O_m	1.263(12)
C_m–N_{1m}	1.383(16)
C_m–N_{2m}	1.325(14)
C_b–O_b	1.246(13)
C_b–N_{1b}	1.419(14)
C_b–N_{2b}	1.368(14)
N_n–O_{1n}	1.242(13)
N_n–O_{2n}	1.251(15)
N_n–O_{3n}	1.236(16)
Co...N_n	4.883(12)
Co...C_m	3.011(11)
Co...C_b (N_{1b} side)	3.085(11)
Co...C_b (O_b side)	3.101(14)
N_{1m}...O_b	3.000(15)
N_{2b}...O_{1n}	3.019(16)

[1] The quantities enclosed in brackets are the estimated standard deviations.

TABLE VI. Bond Angles (°).

O_b–Co–N_{1b} (about *a*-axis)	94.03(32)[1]
O_b–Co–N_{1b} (about *c*-axis)	85.97(32)
O_m–Co–O_b	88.89(31)
O_m–Co–N_{1b}	87.24(31)
Co–O_m–C_m	128.73(73)
Co–O_b–C_b	134.28(60)
Co–N_{1b}–C_b	113.54(56)
O_m–C_m–N_{2m}	121.36(108)
O_m–C_m–N_{1m}	120.14(102)
N_{2m}–C_m–N_{1m}	118.38(102)
N_{1b}–C_b–N_{2b}	116.21(106)
N_{1b}–C_b–O_b	122.54(104)
N_{2b}–C_b–O_b	121.24(106)
O_{1n}–N_n–O_{2n}	120.17(109)
O_{2n}—N_n–O_{3n}	120.51(111)
O_{3n}–N_n–O_{1n}	119.28(105)

[1] The quantities enclosed in brackets are the estimated standard deviations.

Discussion

The most interesting feature of the crystal structure is the bridging bidentation of two of the four urea molecules in the molecular unit thus forming with the cobalt atoms a polymeric chain made from eight membered rings. It can be seen from Figures 1, 2, and 3 that urea molecules form bridges along the *a*-axis joining adjacent cobalt atoms at the fractional co-ordinates 0,0,0 and adjacent cobalt atoms at the fractional coordinates 0,1/2,1/2. In this structure the bidentate urea is probably the only reported case of a three atom bridging structure with chemically different bonding sites which is not ionic.

The assignment of an oxygen and a nitrogen as the bonded terminals in bidentate urea rather than two nitrogen atoms was based on chemical grounds, electron density, and bond length considerations. In order to double check the bonding sites the O_b and N_{2b}

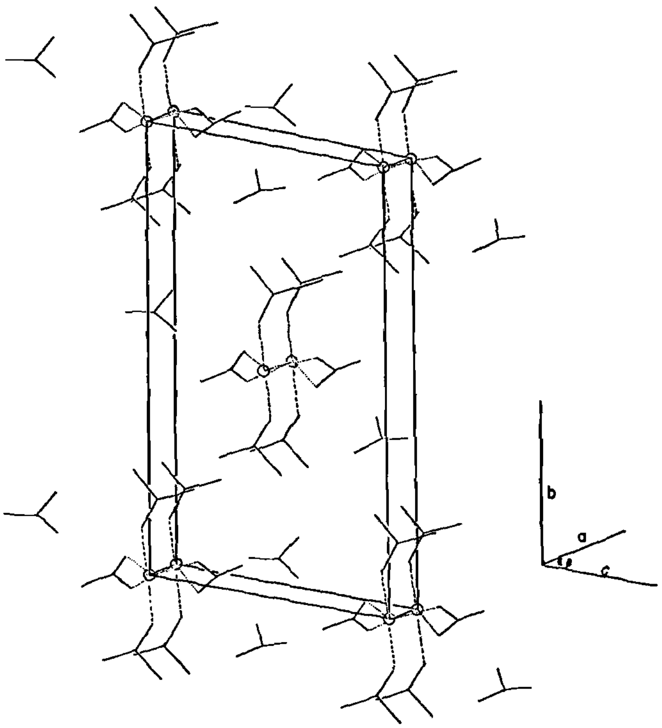

Figure 2. Packing diagram.

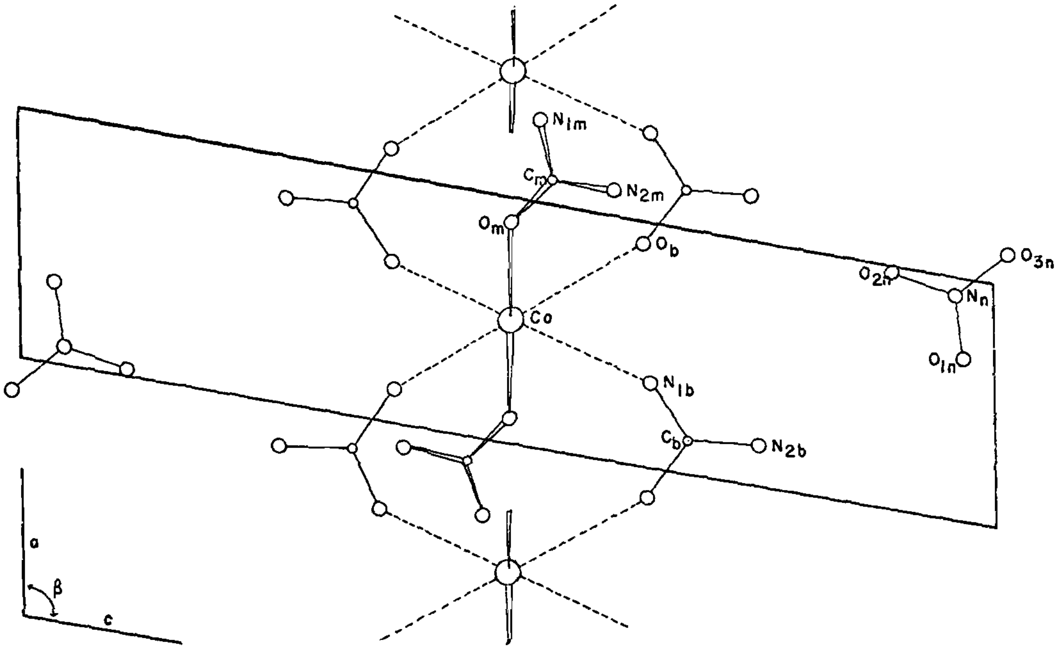

Figure 3. Schematic representation of the structure; m, monodentate urea; b: bidentate urea; n: nitrate ion.

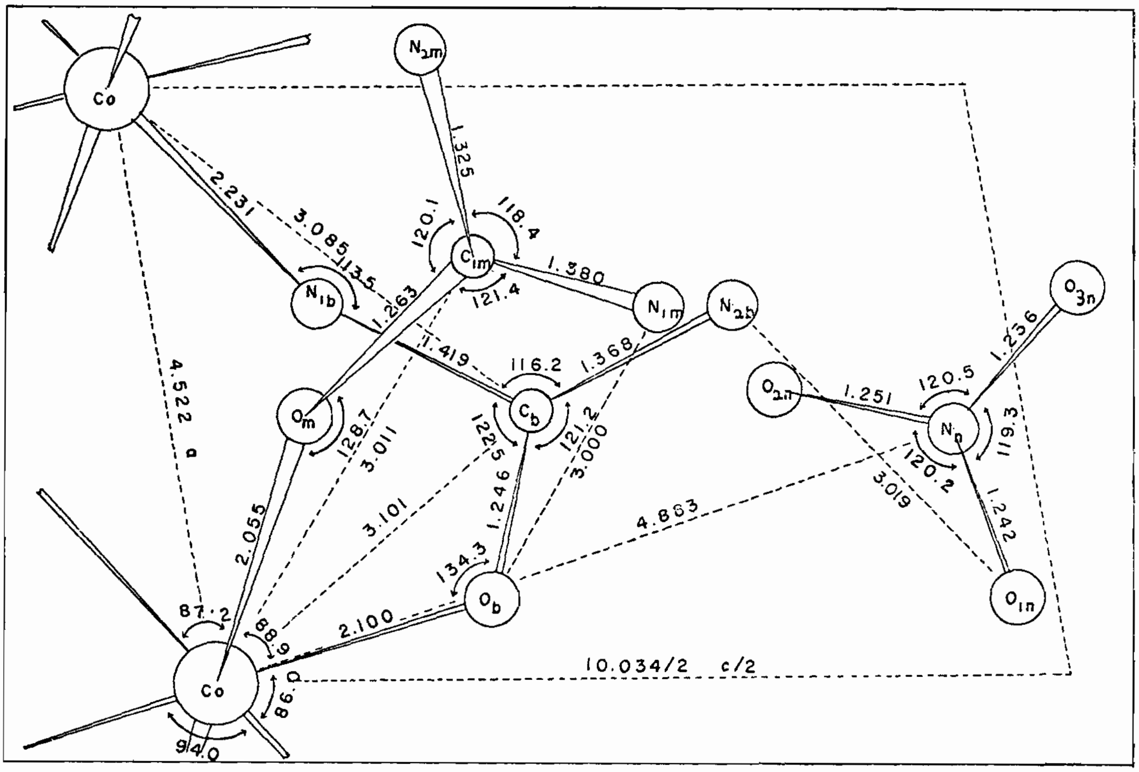

Figure 4. Interatomic distances (Å) and bond angles (degree).

atoms were interchanged and all the varying parameters refined. The R-factor increased by 0.6%. Perhaps more important, is a six fold increase in some of the anisotropic thermal parameters which took place, as well as an increase in their standard deviations. The significant difference in bond length between Co–O_b (2.100A) and Co–N_{1b} (2.231A) is additional evidence that one of the bonding sites in the bidentate urea is the oxygen while the other is a nitrogen.

The configuration about the cobalt is octahedral with slight distortions as can be seen from Table VI. The axial oxygen-cobalt bond length (2.055A) and the equatorial oxygen-cobalt bond length (2.100A) agree well with published data for this kind of bond (2.06–2.12A)[14]. However, the nitrogen-cobalt bond length (2.321A) is significantly longer than that found in cobalt amines and nitryls (1.97–2.03A)[15,16]. This is expected since bonding through the oxygen in bidentate urea makes the nitrogen terminals more positive and hence leads to a longer and weaker nitrogen–cobalt bond. The hygroscopic nature of the complex confirms the weakness of the Co–N_{1b} bond as two water molecules will easily replace the nitrogen atoms at the cobalt's octahedral bonding sites. The resulting dihydrated complex, $[Co(urea)_4(H_2O)_2](NO_3)_2$, will have an oxygen co-ordination sphere as confirmed by its visible spectrum[5].

The monodentate and bidentate urea molecules are planar. The distance[17] of the central carbon atom in urea molecule from the mean plane passing through the oxygen and the two nitrogen atoms is 0.02(2)A in the monodentate urea, and 0.004(5)A in the bidentate urea. The following is a table of bond lengths and angles in free urea[18,19] and those in monodentate and bidentate urea:

	Free Urea	Monodentate Urea	Bidentate Urea
C–O	1.262A	1.263A	1.246A
C–N_1	1.335A	1.383A	1.419A
C–N_2	1.335A	1.325A	1.368A
N_1–C–N_2	118.0°	118.4°	116.2°
N_1–C–O	121.0°	120.1°	122.5°
N_2–C–O	121.0°	121.4°	121.2°

In the monodentate urea, there is no substantial change in carbon–oxygen bond length as compared to the carbonyl bond length in free urea. The difference in bond length between the two carbon–nitrogen bonds may be explained by hydrogen bonding between one of the nitrogen atoms, N_{1m}, and the oxygen atom in the bidentate urea which are 3.000A apart. Hydrogen bonding in crystalline urea is documented with an N–H...O distance of 3.035A[18]. The differences in bond angles as compared to those in free urea are minor.

The bidentate urea molecule is, generally speaking, more electron deficient than free or monodentate urea since it shares its electrons with two cobalt cations. As a result of this electron deficiency, the bond distances are in general longer than in free or monodentate urea. As expected[4], the carbon-co-ordinated nitrogen bond distance (1.419A) is longer than in cases where nitrogen is not co-ordinated (1.368A). This variation in bond lengths has been previously suggested by observing frequency shifts in the infrared spectra[4,5]. No significant differences in internal bond angles exist between bidentate urea and free urea. However, the angle of entry of the carbonyl oxygen of the bidentate urea (134.2°) is more obtuse than that formed with monodentate urea (128.7°). In addition, the angle of entry of the nitrogen atom in the bidentate urea (113.6°) is more obtuse than similar angles (105°) formed in cobalt ethylenediamine complexes[16].

The nitrate groups are ionic and are located at distance of 4.883A from the closest cobalt atom. Hydrogen bonding probably exists between the nitrate oxygen O_{1n} and the unbonded nitrogen atom in the bidentate urea, N_{2b}, which are 3.019A apart. The average nitrogen–oxygen bond length is 1.243A as compared to 1.218A for sodium nitrate[20], 1.203A for $[Co(thiourea)_4](NO_3)_2$[21], and 1.24A for methylguanidine nitrate[22]. The dihedral angle between the plane of the nitrate ion and the plane of the bidentate urea on the same side of the cobalt atom is 0.96° (Table VII). This coplanarity may be explained by packing considerations.

The thermal vibrations of the atoms (Table IV) are anisotropic and are consistent with a chain like structure. The anisotropic thermal parameter (U_{ij}) of the vibration along the *a*-axis for the cobalt atom is $68 \times 10^{-4} A^2$ as compared with $280 \times 10^{-4} A^2$ along the *b*-axis, and $362 \times 10^{-4} A^2$ along the *c*-axis. It is expected that vibration along the chain axis should be smaller than in a perpendicular direction.

TABLE VII. Dihedral Angles Between Planes Each Defined by Three Atoms.

First Plane	Second Plane	Degree
$Co–O_b–N_{1b}$	$O_{1n}–O_{2n}–O_{3n}$	112.56(47)[1]
$Co–O_b–N_{1b}$	$O_m–N_{1m}–N_{2m}$	40.37(43)
$Co–O_b–N_{1b}$	$N_{1b}–N_{2b}–O_b$	113.52(43)
$N_{1b}–N_{2b}–O_b$	$O_{1n}–O_{2n}–O_{3n}$	.96(63)

[1] The quantities enclosed in brackets are the estimated standard deviations.

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