Structures of the Complexes of $CdCl_2$ with the Aliphatic Triamines Bis(2-aminoethyl)amine, Bis(3-aminopropyl)amine, and 2-Aminoethyl-(3-aminopropyl)amine: Influence of Aliphatic Chain Length on Molecular Association

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Single-crystal *X*-ray analyses of the complexes obtained by reaction of $CdCl_2$ with the title amines, hereafter denoted by baa, bpa, and apa respectively, have shown different molecular conformations for the three compounds: Cd(baa)Cl_2 is polymeric while Cd(bpa)Cl_2 and Cd(apa)Cl_2 are dimeric with *cis* and *trans* configurations respectively. Co-ordination around cadmium is octahedral with one chlorine atom acting as a bridge, which is linear in the polymer and bent in the dimers. Nuclear magnetic resonance spectra are not indicative of the presence in solution of a multistructural model for the complexes.

SINGLE-CRYSTAL structural investigations have shown that most of the complexes of cadmium are octahedral [1] and that four- and five-co-ordination, limited to a few cases, are imposed either by the bulkiness of donor atoms [2-5] or by steric requirements of the ligands.[6]

Unhindered complexes of general formula CdL_xCl_2 (L = N or O) are always six-co-ordinate, their structures consisting of discrete octahedra for $x = 4$.[7] For $x = 2$ the co-ordination octahedra generally share two opposite edges, when the ligands are in the *trans* positions (linear arrangements),[8-11] and are skew when the occupation is in the *cis* positions; [12] for $x = 1$ the known structures are formed by cross-linked chains.[13-15] When $x = 3$ either dimeric or polymeric association of the octahedra are possible but, to our knowledge, no structural investigations of compounds having CdL_3Cl_2 stoicheiometry have appeared in the literature.

We have prepared the 1 : 1 adducts of $CdCl_2$ with the three chelating terdentate amines bis(2-aminoethyl)amine (baa), bis(3-aminopropyl)amine (bpa), and (2-aminoethyl)(3-aminopropyl)amine (apa). Their structures have been investigated by *X*-ray single-crystal analysis and by n.m.r. spectroscopy to ascertain which molecular associations are formed in order to satisfy six-co-ordination of the cadmium ion.

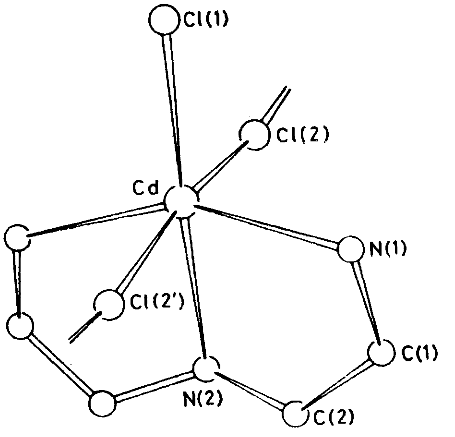


FIGURE 1 Perspective view of the structure of Cd(baa)Cl_2 with atom labelling

RESULTS AND DISCUSSION

As shown in Figures 1—3, different structures are present in the crystals of the three compounds: Cd(baa)Cl_2 consists of chains formed by octahedra which share apices occupied by chlorine atoms; Cd(bpa)Cl_2 consists of dimeric units having C_2 symmetry and a ' *cis* ' configuration, while centrosymmetric dimeric units with the usual ' *trans* ' configuration are present in Cd(apa)Cl_2.

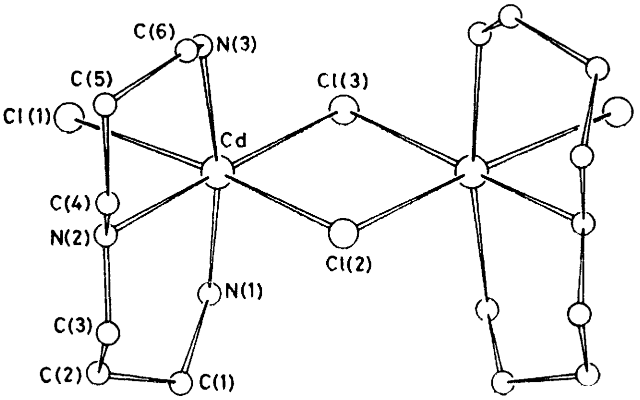
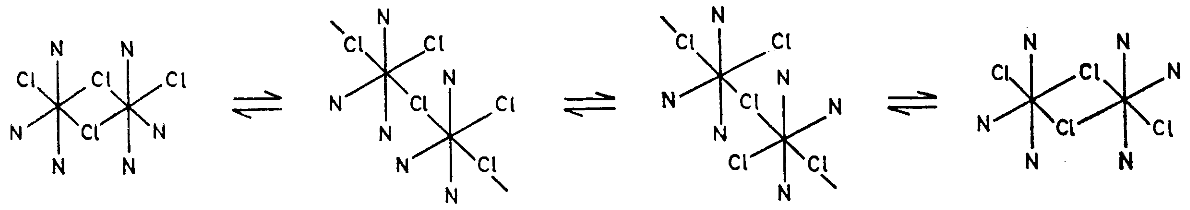


FIGURE 2 Perspective view of the molecular structure of Cd(bpa)Cl_2 with atom labelling

In the crystal structures there is no evidence of intramolecular interactions which could be responsible for the different association; moreover the different steric features of the amines do not influence their co-ordination mode, since the nitrogen atoms always lie on an equatorial plane of the octahedron and form close Cd–N bonds. It seemed reasonable, therefore, to suggest the presence in solution of an equilibrium between dimeric units and higher associations acting as intermediates in the *cis–trans* conversion, and to assume that crystallization would shift the balance to favour one of the possible structures shown below.



The consistency of this hypothesis was investigated by n.m.r. spectroscopy. A major difficulty arose due to the solubility of the compounds being negligible in apolar solvents and very low in others. Spectra at temperatures ranging from −60 to 40 °C were run for Cd(bpa)Cl_2 in a solution of CD_3OD and D_2O; the choice of this complex, as opposed to either of the other two, was dictated by its higher solubility. Figure 4 shows some typical spectra.

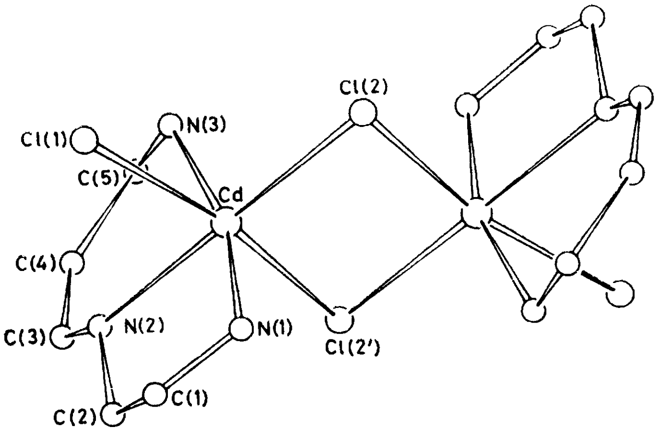


FIGURE 3 Perspective view of the molecular structure of Cd(apa)Cl_2 with atom labelling

The proton resonances were unambiguously assigned on the basis of shielding considerations and the measured area ratio. Hence the multiplet centred at *ca.* 2.7 p.p.m. was assigned to the four protons on the carbon atoms directly bonded to the N atoms whereas the two remaining methylenic protons were assigned to the multiplet at *ca.* 1.7 p.p.m.

The complexity of the absorption bands would have made it difficult to interpret any changes with temperature in terms of structural modifications, however the complete absence of spectral changes (frequency shifts and multiplicities) on both groups of resonances over the entire range of temperature indicated that no conformational change occurs in solution.

Changing the solvent from D_2O to CD_3OD or to $[^2H_6]$-dmso (dmso = dimethyl sulphoxide) did not alter the spectra, apart from irrelevant solvent shifts, thus, again confirming a retention of structure on changing the solvent polarity.

The relationship between structural behaviour and the polarity of the medium was also investigated for the Cd(baa)Cl_2 and Cd(apa)Cl_2 complexes but no evidence that conformational changes were taking place was observed. Figure 5 shows the ^1H n.m.r. spectra of Cd(apa)Cl_2 in two different solvents; the assignments parallel those of Cd(bpa)Cl_2.

Description of the Crystal Structures.—A view of the crystal structure of Cd(baa)Cl_2 along the *b* axis is shown in Figure 1. The Cd, Cl(1), Cl(2), and N(2) atoms lie on the mirror plane at 0.25 *b*; co-ordination around Cd is octahedral with Cl(1) and the amine nitrogen atoms in the basal plane; the apical positions are filled by Cl(2) atoms which are shared by adjacent octahedra giving rise to chains which run parallel to the *a* direction.

The crystal structure of Cd(bpa)Cl_2 consists of discrete dimeric units (Figure 2), having the bridging Cl(2) and Cl(3) atoms on the two-fold crystallographic axis; the molecule therefore has C_2 symmetry and a *cis* configuration.

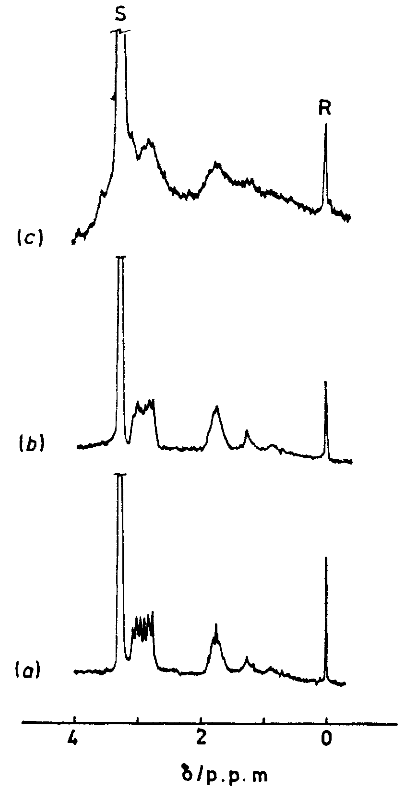


FIGURE 4 Temperature-dependent spectra of Cd(bpa)Cl_2 in CD_3OD: at 35 (*a*); 0 (*b*); and −40 °C (*c*). R and S indicate the reference dss and $[^2H_2]$methanol resonances

The crystal structure of Cd(apa)Cl_2 consists of discrete centrosymmetric dimers, formed by two octahedra which share the Cl(2)–Cl(2′) edge; the molecule has C_i symmetry and a *trans* configuration.

Bond distances and angles reported in Table 1 show that the main deviation of the three co-ordination polyhedra from the ideal octahedral geometry is due to the value of intrachelate N–Cd–N angles, which are *ca.* 75°.

TABLE 1

Bond distances and angles with standard deviations in parentheses

	$Cd(baa)Cl_2$	$Cd(bpa)Cl_2$	$Cd(apa)Cl_2$
(*a*) Distances (Å)			
Cd–Cl(1)	2.49(1)	2.76(1)	2.64(2)
Cd–Cl(2)	2.73(1)	2.67(1)	2.54(1)
Cd–Cl(2′)	2.83(1)		2.89(2)
Cd–Cl(3)		2.65(1)	
Cd–N(1)	2.33(1)	2.28(1)	2.31(3)
Cd–N(2)	2.40(2)	2.33(1)	2.40(2)
Cd–N(3)		2.27(1)	2.28(2)
N(1)–C(1)	1.47(2)	1.48(2)	1.52(3)
N(2)–C(2)	1.40(2)		1.52(4)
N(2)–C(3)		1.49(2)	1.39(3)
N(2)–C(4)		1.51(2)	
N(3)–C(5)			1.46(3)
N(3)–C(6)		1.51(2)	
C(1)–C(2)	1.50(2)	1.50(2)	1.46(3)
C(2)–C(3)		1.51(2)	
C(3)–C(4)			1.52(5)
C(4)–C(5)		1.54(2)	1.47(4)
C(5)–C(6)		1.52(2)	
(*b*) Angles (°)			
Cl(1)–Cd–Cl(2)	94.8(5)	172.7(1)	104.9(2)
Cl(1)–Cd–Cl(2)	95.8(5)		167.3(2)
Cl(1)–Cd–Cl(3)		98.5(2)	
Cl(2)–Cd–Cl(2′)	169.5(1)		87.4(3)
Cl(2)–Cd–Cl(3)		88.7(2)	
Cl(1)–Cd–N(1)	105.7(3)	85.3(3)	94.8(6)
Cl(1)–Cd–N(2)	177.9(3)	82.6(3)	84.3(5)
Cl(1)–Cd–N(3)		82.3(3)	87.3(6)
Cl(2)–Cd–N(1)	92.2(3)	94.8(3)	96.5(5)
Cl(2)–Cd–N(2)	83.1(6)	90.1(3)	169.5(6)
Cl(2)–Cd–N(3)		97.4(3)	97.8(5)
Cl(3)–Cd–N(1)		94.7(3)	
Cl(3)–Cd–N(2)		177.2(2)	
Cl(3)–Cd–N(3)		87.6(3)	
Cl(2′)–Cd–N(1)	84.9(3)		86.8(6)
Cl(2′)–Cd–N(2)	86.4(6)		83.8(5)
Cl(2′)–Cd–N(3)			87.9(6)
N(1)–Cd–N(1′)	147.8(3)		
N(1)–Cd–N(2)	74.5(3)	88.0(4)	77.5(8)
N(1)–Cd–N(3)		167.6(4)	164.4(7)
N(2)–Cd–N(3)		90.0(4)	87.4(7)
Cd–Cl(2)–Cd′	169.5(2)	90.7(3)	92.6(3)
Cd–Cl(3)–Cd′		91.8(3)	
Cd–N(1)–C(1)	111.1(9)	116.0(8)	107(2)
Cd–N(1)–C(2)	107.5(8)		107(1)
Cd–N(2)–C(3)		116.0(7)	122(2)
Cd–N(2)–C(4)		113.6(7)	
Cd–N(3)–C(5)			114(2)
Cd–N(3)–C(6)		120.9(8)	
C(2)–N(2)–C(2′)	122(1)		
C(3)–N(2)–C(4)		108(1)	
N(1)–C(1)–C(2)	111(1)	113(1)	115(2)
N(2)–C(2)–C(1)	114(1)		111(2)
N(2)–C(3)–C(2)		114(1)	
N(2)–C(3)–C(4)			110(2)
N(2)–C(4)–C(5)		111(1)	
N(3)–C(5)–C(4)			117(2)
N(3)–C(6)–C(5)		110(1)	
C(1)–C(2)–C(3)		118(1)	
C(3)–C(4)–C(5)			120(2)
C(4)–C(5)–C(6)		115(1)	

The Cd–Cl distances fall in a rather large range, with terminal bonds in bpa and apa derivatives having particularly high values; this fact is probably the consequence of intermolecular Cl · · · H–N hydrogen bonding, as suggested by the molecular packing which, on the other hand, does not show any other relevant contacts (Table 2).

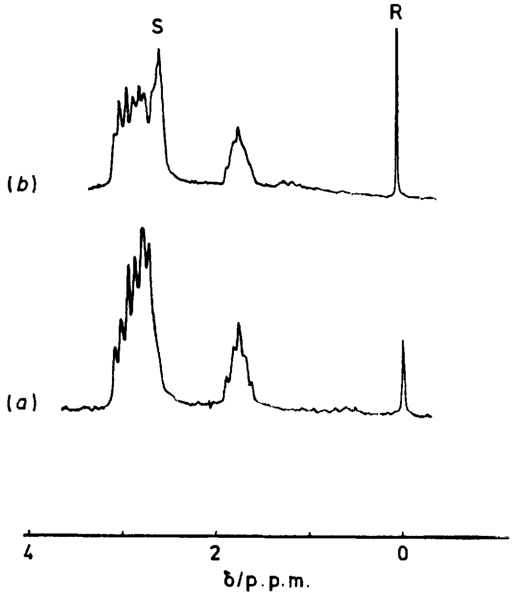


FIGURE 5 Solvent-dependent spectra of $Cd(apa)Cl_2$ in D_2O (*a*) and dmso–$CDCl_3$ (1 : 1 v/v) (*b*). R and S indicate the reference dss and [$^2H_4$]dmso resonances respectively

The Cd–N distances are in the range 2.28—2.35 Å, except Cd–N(2) distances in bpa and apa derivatives, which are close to 2.40 Å.

The geometries of the ligands are close to those found in other structures;[16] the five-membered chelate rings adopt the *gauche* unsymmetrical configuration and the six-membered rings the distorted chair one. Distances of carbon atoms from the pertinent N–Cd–N planes are given in Table 3.

TABLE 2

Intermolecular Cl · · · N contacts (Å) less than 3.5 Å

(*a*) $Cd(apa)Cl_2$	
Cl(1) (x,y,z) · · · N(1) $(1 - x, \bar{y}, 1 - z)$	3.30
Cl(1) (x,y,z) · · · N(1) $(x, y, 1 + z)$	3.43
(*b*) $Cd(bpa)Cl_2$	
Cl(1) $(\bar{x},\bar{y},\bar{z})$ · · · N(1) (x,y,z)	3.40
Cl(1) $(\bar{x},\bar{y},\bar{z})$ · · · N(3) $(\bar{x}, y, \frac{1}{2} - z)$	3.41
Cl(2) (x,y,z) · · · N(3) $(\bar{x}, \bar{y}, 1 - z)$	3.45

EXPERIMENTAL

The compounds were prepared by dropwise addition of the ligands to a hot alcohol solution of $CdCl_2$, and were characterized by elemental analyses.

The proton magnetic resonance spectra were run on a Varian FT80A pulse spectrometer, equipped with a variable-temperature device, operating at a frequency of 80 MHz, and using 5-mm sample tubes. The solvents [$^2H_6$]dmso, CD_3OD, $CDCl_3$, and D_2O (Merck) were employed for heteronuclear field-frequency lock. The proton resonances were digitally computed from dss (sodium 4,4-dimethyl-4-silapentanesulphonate) used as internal standard.

Single crystals for *X*-ray analysis were obtained by evaporation of a methanol solution, containing a few drops of water. Preliminary cell dimensions were obtained from Weissenberg photographs and were refined together with orientation matrices by least-squares fit to values of θ, χ, and ϕ accurately measured on a Siemens AED diffractometer. Intensity data were collected by the θ—2θ scan technique, using zirconium-filtered Mo-K_α radiation ($\lambda = 0.710\,7$ Å); the stability of the entire assembly was monitored by measuring three reflections after every 200 reflections. The values of I and $\sigma(I)$ were corrected for Lorentz-polarization effects; no absorption or extinction corrections were applied. The structures were solved by conventional Patterson and Fourier techniques and refined by block-diagonal least-squares methods using reflections with $I \geqslant 2\sigma(I)$; the quantity minimized was $\Sigma\, w(\Delta F)^2$. Anisotropic temperature factors for cadmium and chlorine atoms, which were introduced in the final stage of refinement and checked by three-dimensional Fourier maps calculated with final parameters (Table 4), are given in Supplementary Publication No. SUP 22839 (21 pp.) together with observed and calculated structure factors.* Atomic scattering factors for Cd, Cl, N, and C were taken from ref. 17.

TABLE 3

Equations of molecular planes, referred to *a*, *b*, and *c* axes, with deviations of atoms (Å) from the planes given in square brackets

(*a*) Cd(baa)Cl_2
Plane: Cd, N(1), N(2)
$$5.514X - 0.669Y - 0.560Z = 0.935$$
[C(1) −0.19, C(2) 0.44]

(*b*) Cd(bpa)Cl_2
Plane 1: Cd, N(1), N(2)
$$-10.577X + 7.803Y + 5.334Z = 1.259$$
[C(1) 0.84, C(2) 0.422, C(3) 0.797]
Plane 2: Cd, N(2), N(3)
$$-8.342X + 7.689Y + 7.153Z = 1.689$$
[C(4) 0.71, C(5) 0.06, C(6) 0.60]

(*c*) Cd(apa)Cl_2
Plane 1: Cd, N(1), N(2)
$$2.581X - 2.051Y + 5.329Z = 1.628$$
[C(1) 0.37, C(2) −0.28]
Plane 2: Cd, N(2), N(3)
$$2.008X - 1.774Y + 5.622Z = 1.637$$
[C(3) −0.61, C(4) −0.18, C(5) −0.67]

Crystal Data.—(*a*) [Cd(baa)Cl_2], $C_4H_{13}CdCl_2N_3$, $M = 286.47$, Monoclinic, $a = 5.53(1)$, $b = 8.98(2)$, $c = 9.36(2)$ Å, $\beta = 91.9(2)°$, $U = 464.2$ Å^3, D_m (flotation) = 1.95 g cm^{-3}, $Z = 2$, $D_c = 2.05$ g cm^{-3}, $F(000) = 280$. Space group $P2_1/m$, (from structure analysis; systematic extinctions $0k0$, $k = 2n + 1$); $\mu = 27.3$ cm^{-1}. A total of 871 independent reflections were measured up to $2\theta < 50°$. The final R factor is 0.074 for the 800 refined reflections and 0.080 for the 871 measured ones.

(*b*) [{Cd(bpa)Cl_2}$_2$], $C_{12}H_{34}Cd_2Cl_4N_6$, $M = 629.12$, Monoclinic, $a = 17.42(3)$, $b = 11.08(2)$, $c = 12.01(3)$ Å, $\beta = 97.5(2)°$, $U = 2\,287.6$ Å^3, D_m (flotation) = 1.80 g cm^{-3}, $Z = 4$, $D_c = 1.824$ g cm^{-3}, $F(000) = 1\,248$. Space group $C2/c$ (from structure analysis; systematic absences: hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$); $\mu = 23.2$ cm^{-1}. A total of 1 363 independent intensities were measured up to $2\theta < 44°$. The final R factor is 0.059 for 1 182 refined reflections and 0.093 for 1 363 measured ones.

(*c*) [{Cd(apa)Cl_2}$_2$], $C_{10}H_{30}Cd_2Cl_4N_6$, $M = 601.0$, Monoclinic, $a = 9.33(2)$, $b = 17.48(3)$, $c = 7.06(3)$ Å, $\beta = 114.5(2)°$, $U = 1\,049.6$ Å^3, D_m (flotation) = 1.88 g cm^{-3}, $Z = 2$, $D_c = 1.90$ g cm^{-3}, $F(000) = 592$. Space group $P2_1/n$ (systematic extinctions $h0l$, $h + l = 2n + 1$, $0k0$, $k = 2n + 1$); $\mu = 25.2$ cm^{-1}. A total of 1 738 independent reflections were measured up to $2\theta < 50°$. The final R factor is 0.123 for the 1 380 refined reflections and 0.155 for the 1 738 measured ones. The higher R factor in this structure is a consequence of the poor quality of the crystals, whose diffraction photographs all exhibit satellite peaks around the maxima positions.

TABLE 4

Positional parameters ($\times 10^4$) with estimated standard deviations in parentheses

	x/a	*y/b*	*z/c*
(*a*) Cd(baa)Cl_2			
Cd	2 411(2)	2 500(0)	4 050(1)
Cl(1)	2 514(7)	2 500(0)	6 714(5)
Cl(2)	−2 514(6)	2 500(0)	3 778(5)
N(1)	2 646(18)	4 998(13)	3 376(11)
N(2)	2 150(25)	2 500(0)	1 483(15)
C(1)	2 166(26)	5 177(18)	1 826(15)
C(2)	3 071(25)	3 859(18)	1 018(14)
(*b*) Cd(bpa)Cl_2			
Cd(1)	773(0)	1 624(1)	1 517(1)
Cl(1)	1 676(2)	113(3)	405(3)
Cl(2)	0(0)	3 319(4)	2 500(0)
Cl(3)	0(0)	−40(4)	2 500(0)
N(1)	−53(6)	1 620(9)	−115(9)
N(2)	1 482(5)	3 118(9)	739(8)
N(3)	1 758(6)	1 373(10)	2 937(9)
C(1)	−230(8)	2 814(13)	−639(11)
C(2)	477(8)	3 447(13)	−943(12)
C(3)	1 022(8)	4 010(13)	−4(11)
C(4)	2 017(8)	3 816(13)	1 601(11)
C(5)	2 596(9)	2 963(15)	2 294(13)
C(6)	2 303(8)	2 395(15)	3 306(12)
(*c*) Cd(apa)Cl_2			
Cd	1 415(2)	517(1)	2 569(2)
Cl(1)	3 243(8)	526(4)	6 594(9)
Cl(2)	594(7)	−870(3)	1 717(8)
N(1)	3 476(24)	488(11)	1 559(35)
N(2)	2 137(22)	1 840(11)	2 729(30)
N(3)	−594(21)	893(11)	3 405(29)
C(1)	4 309(26)	1 255(14)	2 147(36)
C(2)	3 271(26)	1 917(15)	1 686(38)
C(3)	1 028(28)	2 423(15)	2 231(38)
C(4)	−49(32)	2 286(16)	3 330(43)
C(5)	−1 194(25)	1 656(13)	2 676(34)

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